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# Description and genetic modelling of the Outokumpu-type rock assemblage and associated sulphide deposits

Final technical report for GEOMEX J.V., Workpackage "Geology"



Geological Survey of Finland, Kuopio Unit, PO Box 1237, FI-71211

# KUMPU

## Petri Peltonen & Hannu Huhma

Geological Survey of Finland, Espoo Unit, PO Box 96, FI-02150

Transform fault

Seawater convection

hot mantle & gabbro intrusions









### GTK report M 10.4 /2006/ 1

## DESCRIPTION AND GENETIC MODELLING OF THE OUTOKUMPU-TYPE ROCK ASSEMBLAGE AND ASSOCIATED SULPHIDE DEPOSITS

by Asko Kontinen<sup>1</sup> Petri Peltonen<sup>2</sup> Hannu Huhma<sup>2</sup>

Prepared for Geomex A Joint Venture between Outokumpu Mining Oy and the Geological Survey of Finland

> Joint Venture Manager Urpo Kuronen<sup>3</sup>

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<sup>1</sup> Geological Survey of Finland, Kuopio Unit, Neulaniemenkatu 5, 71200 Kuopio

<sup>2</sup> Geological Survey of Finland, Espoo Unit, Betonimiehenkuja 4, 02150 Espoo

<sup>3</sup> Polar Mining Oy, Kummunkatu 34, 83500 Outokumpu

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#### A. Kontinen

Geological Survey of Finland, Kuopio Unit, PO Box 1237, FIN-71211

#### P. Peltonen & H. Huhma

Geological Survey of Finland, Espoo Unit, PO Box 96, FIN-02150

#### ABSTRACT

The acronym GEOMEX refers to a five-year joint venture project between the Geological Survey of Finland and Outokumpu Mining Oy, established in late 1998 to conduct Cu-Ni-Zn-Au exploration in the classical Outokumpu mining area. A modelling sub-project was commenced within the main project in the spring 1999, with an ultimate goal to develop an updated Outokumpu ore model. The subsequent work included, apart from reviewing of the existing reports, publications and databases, also a review of a large number of drill cores, and a study of trace element and Pb isotope geochemistry of the Outokumpu type ores and their typical wall rocks. This report documents the research results and the revised Outokumpu model, which was first time presented in a brief summary report in the spring 2001. The new "GEOMEX Outokumpu model" is abstracted below.

The Upper Kaleva metaturbidites in the basal parts of the Jormua – Outokumpu thrust belt in eastern Finland enclose numerous variable-size fault-bound ultramafic-mafic massifs, comprising mainly residual mantle peridotites now altered to serpentinized metaperidotites and metaserpentinites. The serpentinite bodies are commonly enveloped by thin selvages of chromian and weakly Ni sulphide disseminated carbonate-skarn-quartz rocks, which are hosting numerous tattered, subeconomic Ni-sulphide mineralizations, and in the Outokumpu area, a dozen massive-semimassive, polymetallic Cu-Co-Zn-Ni-Ag±Au sulphide deposits.

The available geological, isotope and geochemical evidence attest to an origin of the ore hosting mafic-ultramafic massifs as ophiolitic fragments from the embryonic ocean basin that was opened west of the present Karelian craton following its break-up ca. 1.97 Ga ago. Pb isotope evidence of an unradiogenic, mantle-like metal source, and 1.95 Ga age of the Outokumpu-Vuonos Cu-Co-Zn ores provide strong indication of that they would represent oceanic sulphides obducted with the host ophiolite fragments. The carbonate-skarn-quartz rocks have previously interpreted as cogenetic chemical sediments, but strong evidence are provided of that these rocks in fact formed by marginal carbonate-silica alteration of the adjacent peridotite bodies, concurrent or immediately after their ca. 1.90 Ga obduction.

However, simple ocean floor sulphide deposit models poorly explain many distinct features of the Outokumpu ores, as e.g. their constantly high Ni. To provide a model that addresses most of the Outokumpu characteristics, it is proposed that the ores would represent syntectonic mixing of the obducted, ca. 1.95 Ga Cu "proto-sulphides" with the ca. 1.90 Ga Ni sulphides in the serpentinite fringing carbonate-skarn-quartz rocks. And, further that the mixing process comprised a pervasive syntectonic remobilization of the Cu proto-sulphides that started already in the ophiolite obduction stage, and extended throughout the subsequent regional tectonism.

The process seems to have involved: (1) pervasive, liquid-state remobilization of the Cu protosulphides; (2) their redeposition at quartz rock – black schist interfaces at the margins of the ultramafic bodies, and at the end; (3) a mixed state remobilization of the reprecipitated sulphides in fault-controlled quartz-sulphide lodes. Introduction of the Ni component probably occurred principally during the earliest stages of the remobilization, probably by fluid assisted diffusion from any Ni-mineralized metasomatites that occurred along the remobilization paths. Subsequent peak-metamorphic recrystallization upgraded the deposits by coarsening the grainsizes and simplifying the mineral intergrowth fabrics.

The above briefed GEOMEX ore model provides a reasonable explanation of the mantlelike Pb and apparent 1.95 Ga age of the Outokumpu ores, versus their present strictly structurally controlled occurrence in host rock assemblages that are practically speaking devoid of syngenetic volcanic rocks and seafloor hydrothermal sediments. The model also explains the uniquely high Ni content of the Outokumpu-type sulphides (for hydrothermal sulphides) and recognizes the metasomatic peridotite origin of the usually associated carbonate-skarn-quartz rocks. The highly elongated ore shapes and lack of volcanic rocks and hydrothermal sediments in the ore associations, and the dominantly peridotitic composition of the host bodies suggest the Cu proto-sulphides formed in fissure zones of a largely ultramafic oceanic crust.

For exploration in eastern Finland the new model has a clear message: Outokumpu type Cu sulphide ores can be found only in close association with the ophiolitic ultramafic-mafic massifs in the allochthonous parts of the Proterozoic cover. Despite the ultimate origin of the ore bodies as oceanic hydrothermal accumulations, because of their inferred inhalative origin and extensive remobilization, any of the common sea-floor sulphide deposit models will be of little help in exploration. Although the new model yields a much improved understanding of the genesis of Outokumpu type ores and especially their host rocks; it will not change the traditional view of that the best method to explore these deposits consists of reasonably dense drilling at the very margins of such, preferably large, serpentinite bodies that show thick carbonate-skarn-quartz rock selvages.

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#### 1. Introduction

A joint-venture project called GEOMEX was established in December 1998 between the Geological Survey of Finland and Outokumpu Mining Oy. The aim of the project was to conduct geological modelling and exploration for especially the Outokumpu type Cu-Co-Zn sulphides within the traditional Outokumpu mining district of eastern Finland. A geology-modelling subproject was established under the main project in early 1999. The objectives of the sub-project were to review the existing data and models of the Outokumpu assemblage and ores, and to conduct new research where considered necessary and conceivable within the allocated resources. The aimed main delivery of the sub-project was to provide an ore model to test in the upcoming exploration.

A. Kontinen and Dr. P. Peltonen from GTK were commissioned as the principal researchers in the sub-project. Choosing these people was mainly because of their then fresh familiarity of the Outokumpu problematics, for part of the first author in the just-before-closed Kainuu-Outokumpu project, operative in years 1992-2000 in the Kuopio unit of the GTK. This paper is a final report of the work and results of the modelling sub-project. To provide access also for foreign readers without Finnish skills, the report has been written in English. However, the text is delivered without any professional language correction, mainly representing penning of the first author; therefore, our deepest apologies to all those readers who will suffer from the undoubtedly in many ways awkward and erroneous language usage.

#### 2. About the objectives of the subproject research and structure of the report

Although there are a truckload of published research of the Outokumpu assemblage and sulphide deposits, it must be said that as most of it predates the mid-1980s, large parts of it has been outdated by the recent years rapid developments in science concepts and technical means of study. Therefore, when the GEOMEX project was started, need for considerable new basic research was recognized, but in several areas difficult to conduct within the relatively limited research resources allocated for the project. Within the available resources, three main new research efforts were considered reasonable: (1) A review of representative core from all the known Outokumpu deposits and their immediate wall-rock associations (usually poorly exposed); to clarify the nature of the host rock assemblages and sulphide host rock relationships; (2) A trace element study of all the known Outokumpu deposits in North Karelia, to provide a consistent geochemical reference data set of their main sulphide and host rock types; (3) A Pb-isotope study of mainly the Outokumpu and Kylylahti deposits, to complement the Pb-isotope data of Outokumpu sulphides that already existed in GTK at the time of the GEOMEX project start.

The extensive drill core review was considered necessary because the since 1950s universally adopted interpretation of the carbonate-skarn-quartz rocks in the Outokumpu ore assemblage as chemical sediments at seafloor hydrothermal vents (e.g. Borchert, 1954; Huhma, 1976; Mäkelä, 1974; Peltola, 1978; Koistinen, 1981; Park, 1988; 1990) had been recently questioned by a reinterpretation of these rocks to carbonated-silicified peridotites (e.g. Auclair et al., 1993; Kontinen, 1998). Noting the fundamental importance of a valid interpretation of the carbonate-skarn-quartz rocks for modelling of the Outokumpu system, it was clearly in a top priority for the modelling subproject to revisit the question of their origin. Another important aspect related to the carbonate-skarn-quartz rocks, and that was considered important to review at the core boxes, was their contact relationships with the ore bodies for all those deposits for which drill core still was available.

The geochemical survey of the massive-semimassive sulphides was chosen a focal topic in the new research, simply because the lack of published modern trace element data from the Outokumpu sulphides and their typical host rocks, and the readiness of the GTK laboratories to deliver the analytical services. An opportunity to collect samples from mafic rocks observed in serpentinites during the core review process was utilized, and a set of representative sample of them was also analysed for major and trace elements. For comparison purposes also a few outcrop samples from the "epicontinental amphibolites" such as e.g. at Heinävesi and Riihilahti were collected and chemically analyzed. The idea behind analysing of the mafic rocks was to get constraints for interpreting of the tectonic origin of the host serpentinite bodies.

More than 35 000 m of drill core became reviewed (or primarily logged) by the modelling team, mainly by the first author. What comes to the inspection of the ore host rock relationships, underground mine or open pit observations would of coarse have been superior compared to the now conducted drill core review. This, however, was an unattainable option as there is currently no underground access to any Outokumpu-type deposit in North Karelia.

The following section is a direct citation form the preface by R.V. Kirkham to the book "Mineral Deposit Modelling" (Kirkham and al., 1993).

"A mineral deposit model can be viewed as "systematically arranged information describing the essential attributes (properties) of a class of mineral deposits" and may be empirical (descriptive) or theoretical (genetic) (Cox et al., 1986). It includes such things as: geological features, economic commodities, grade and tonnage characteristics, geological setting, genesis, ore controls, geophysical and geochemical characteristics, aspects that are useful in exploration, economic features and environmental characteristics."

Much along the lines of the above view of ore deposit modelling, the first part in this report is descriptive, including a short description of the regional geological setting, and brief summary descriptions for all the presently known Oku type deposits in North Karelia, and for comparison also for a few major but unsuccessful prospects. The second part comprises a review of the geological, geochemical and other data and constraints available for genetic modelling of the Outokumpu assemblage and sulphide deposits, including as a new contribution our own study of their trace element geochemistry. The third part comprises reviews for possible deposit analogues elsewhere in the world, for the previous Outokumpu model proposals, and after a discussion of the critical constraints, presents an updated Outokumpu ore model. The fourth, short part is about the exploration implications of the new model proposal and gives some suggestions for further study.

The ore model proposal the sub-project finally ended up was briefly outlined in a "summary report" of March 2001. The present report provides but a more detailed documentation of the new "GEOMEX Outokumpu model", also a full-blown documentation of the data basis and interpretations that we applied in formulation of the new model. Though this report is written much like a research paper, being e.g. briefly referenced, we want to stress that it was foremost written as to a technical report of the work and results of the modelling sub-project, not as to a formal scientific paper. Several research papers based on the study effort behind this report are under works in GTK.

This report was composed on the basis of several separate Outokumpu essays, which shows in that it is somewhat inconsistent and in parts repetitive for its content. We hope readers can cope with this and jump over those sections they find merely refresher courses.

#### 3. Study area, targets and sampling

Study area considered in this report comprises the map sheets 4221, 4222, 4223, 4224, 4311 and 4313 of the 1:100 000 scale Geological Map of Finland, covering a large part of the Outokumpu thrust belt in the western part of the North Karelia Schist Belt (NKSB), eastern Finland (Fig. 1). In addition, some Outokumpu type prospects from the Savonranta area in map sheets 4212 and 4214, and the Vehkalahti and Viitaniemi occurrences of Lower Kaleva metavolcanic rocks in the map sheet 3333 were briefly visited and sampled for geochemical study. For comparative purposes, some published / unpublished data by GTK for Outokumpu type rocks in the Kainuu Schist Belt (KSB), as e.g. for Jormua ophiolite complex, have been used.



Fig. 1. Location of the Geomex study area shown on a simplified geological map of Finland (Geological Survey of Finland, GTK). The inset lists the included 1:100 000 scale sheets of the Geological Map of Finland.

A considerable part of the field work/sampling and drill core logging/sampling, petrographical study and geochemical analysing, on which this report is based, was carried out already before the start of the GEOMEX joint venture project. This work was done in the Kainuu-Outokumpu project, which was operative in the Kuopio regional office of GTK in the years 1982-2000. Material of Kontinen (1987), Peltonen et al. (1996, 1998) and Säntti et al. (in press) of the Outokumpu-Jormua belt ultramafic-mafic rocks was available and became used where appropriate.

The major and trace element data produced during the GEOMEX project are stored in the GEOMEX data package, while the previous GTK data appears only in the diagrams (or in the referred publications). The isotope data, which are mostly previous GTK material, is documented only in the diagrams, major part of this data will be published in subsequent, peer-reviewed papers. All the Outokumpu data used here can be located in the GEOMEX data package.

#### 4. Analytical methods

#### 4.1. Major and trace element analyses

This report utilizes several sets of data collected by two organizations (Outokumpu Mining, GTK) over tens of years both *before and during* the GEOMEX, using variable sample preparation and analytical procedures, methods and equipment. However, the emphasis is on the samples analysed during the GEOMEX project, and the preceding Kainuu-Outokumpu project of GTK, for the reason that these samples were tested for the most extensive set of elements, and were all analysed by the same methods at the Geological Survey of Finland (GTK) laboratories in Espoo. The analytical methods applied in the modelling sub-project are shortly described below.

Samples, mostly taken from representative drill cores and selected to be devoid of secondary features, such as fracture-fillings and weathering related alteration etc., were first crushed by a Mn-steel jaw-crusher, and then splits of the chippings pulverized, in tungstencarbide bowl for X-ray fluorescence (XRF) analyses, and in carbon steel bowl, known to be free of elements other that Fe and Mn, for analyses by the other methods (ICP-AES, ICP-MS, GFAAS).

Major elements and Ba, Cr, Ga, Mo, Ni, Pb, Rb, Sn, Sr, V, Zn and Zr were determined from pressed pellets by XRF by using a Philips PW 1480 sequential wavelength dispersive spectrometer (GTK lab procedure 175X). Cobalt, Cu, Ni, Pb, and Zn were determined, but by XRF, also by inductively coupled plasma atomic emission spectrometry (ICP-AES) after partial dissolution of the pulps in hot aqua regia (GTK lab procedure 511P). Ag, As, Cd and Pb were determined from the same solutions by graphite furnace atomic absorption spectrofotometry (GFAAS, GTK lab procedure 511U). Gold, Te, Bi, Sb, Se were determined by GFAAS after leaching of usually 5gr samples in aqua regia and co-precipitation with mercury (GTK lab procedure 512U).

Rare earth elements, Y, Sc, U, Th, Zr, Hf, Nb, and Ta were determined using inductively coupled mass spectrometry (GTK lab procedure 308M; Rautiainen et al., 1996). The sample powders were dissolved in Teflon dishes in a mixture of hydrofluoric and perchloric acids. After evaporation and redissolution in nitric acid, to ensure total decomposition, the solutions were first filtered and the ashed filters fused with lithium metaborate and sodium perborate. The fused beds were then dissolved in nitric acid and the solutions combined with the filtrated solutions. The finish was by the ICP-MS.

Sulphur and total carbon were determined by automatic Leco SC-32 combustion analyser (GTK lab procedures 810L and 811L).

#### 4.2. Isotope determinations

Representative samples from several of the Outokumpu-type deposits and their immediate host rocks were analysed during this study for their Pb, Sm-Nd and Rb-Sr isotopic composition in the Isotope Laboratory of GTK at Espoo. However, a large part of the isotope geochemical data dealth with in this report is data produced in GTK already before the GEOMEX project. Most of the isotope analytical work during GEOMEX and before was supervised by the third author.

Lead isotope ratios were determined using the standard procedures of the Isotope Laboratory, described in detail e.g. by Mänttäri (1995). In brief the method was as follows. The sulphide concentrates for Pb isotope determinations were washed with dilute HCI in an ultrasonic bath and dissolved in 1:1 HCI–HNO<sub>3</sub> acid mixture. For whole rock analyses 150-200 mg of sample powder was dissolved in HF-HNO<sub>3</sub> using Savillex screw-cap Teflon beakers or Teflon bombs for 48h. After evaporation, the samples were redissolved into 1 N HBr. Lead was extracted using anion-exchange chromatography, and lead purification was completed with anodic electrodeposition, or in some cases by repeating the chromatographic separation. For some samples lead concentration was determined from separate dissolution using <sup>206</sup>Pb tracer and isotope dilution method. Lead was loaded on a Re-filament with a phosphoric acid – silica gel mixture and measured using a VG SECTOR 54 mass spectrometer. The measured lead isotope ratios were corrected for mass fractionation according to the analysed ratios of SRM 981 standard (0.11 % per a.m.u.). The average measured Pb blank was 1.2 ng.

The analytical methods of Sm-Nd isotope determinations also followed the standard procedures of the Isotope Laboratory as described e.g. in Peltonen et al. (1996). In brief the procedure was as follows. For Sm-Nd, as well as Rb-Sr isotope analyses, the sample powders were dissolved in Savillex screw-cap Teflon beakers. The chemical separations were done by standard chemical procedures and concentrations measured by isotope dilution using a VG SECTOR 54 mass-spectrometer. The estimated error for <sup>147</sup>Sm/<sup>144</sup>Nd was 0.4%. <sup>143</sup>Nd/<sup>144</sup>Nd ratio was normalized to <sup>146</sup>Nd/<sup>144</sup>Nd=0.7219, and <sup>87</sup>Sr/<sup>86</sup>Sr to <sup>86</sup>Sr/<sup>88</sup>Sr=0.1194. The average value for La Jolla standard was <sup>143</sup>Nd/<sup>144</sup>Nd = 0.511851 ± 6 (std, n=15), and for SRM987 <sup>87</sup>Sr/<sup>86</sup>Sr=0.710251 ± 10 (std, n=10). The average error expressed as  $\epsilon_{Nd}$  was ca. 0.5 units. The  $\epsilon_{Nd}$  is calculated according to DePaolo (1981). The  $\epsilon_{Sr}$  has been calculated using reference values of <sup>87</sup> Rb/ <sup>86</sup>Sr = 0.0816 and <sup>87</sup> Sr/<sup>86</sup> Sr=0.7045. The average concentrations in blanks measured during the analyses were: 30 pg for Sm, 100 pg for Nd, 40 pg for Rb and 200 pg for Sr.

#### 5. Outokumpu rock assemblage and its geological setting

With the exception of one deposit (Riihilahti), all the presently known Outokumpu-type sulphide deposits are found in association with a distinct rock assemblage consisting of carbonate, skarn, and quartz rocks ("quartzites"), characteristically in thin fringes to serpentinite bodies enclosed in black schist horizons in thick sequences of monotonously sandy metaturbidites or mica schists in the basal part of the so called Outokumpu Allochton (Koistinen,

1981; Gaal and Parkkinen, 1993; section 5.2). The serpentinite-carbonate-skarn-quartz rock assemblage is widely known as the Outokumpu assemblage (or Outokumpu association). Correctly interpreting the nature and formation history of this rock assemblage is clearly one of

the prerequisites for any relevant modelling of the Outokumpu-type sulphide deposits. The Outokumpu assemblage being that focal concept, we start by clarifying the historical definitions and considerations related to the term, and how it will used by us in this report.

#### 5.1. The term "Outokumpu assemblage" clarified

Gaál et al (1975) stated: "A characteristic feature in the vicinity of Outokumpu is the regular occurrence of quartzites, skarns and carbonate rocks around serpentinite bodies. This whole rock group is called the Outokumpu association in the present paper. The complete sequence of the enveloping rocks from serpentinite core outwards is: carbonate bearing serpentinite - carbonate - rock - tremolite skarn - diopside skarn - quartzite. The outer zone adjacent to the surrounding mica schist is commonly occupied by black schist."

This appears to be the first published definition of the Outokumpu association. In recent literature, the term "Outokumpu assemblage" is often used instead of the "Outokumpu association" (e.g. Park, 1988, 1992), and so also in this report. Importantly, the term "Outokumpu assemblage" is in this report used without any stratigraphic or genetic meaning, just as a handy name for the carbonate-skarn-quartz rocks so common in association with the serpentinite massifs in the NKSB.

Gaál et al. (1975) considered that the origin of the carbonate and quartz rocks in the Outokumpu assemblage was closely related with serpentinization of the ultrabasic rocks they usually surround. Probably inspired by previous modelling by Marttila (1972), they thought that "during serpentinization first SiO<sub>2</sub> then MgO were released in altering fluids and became precipitated around the margins of the ultrabasic masses on the bottom of a geosynclinal sea, and that as a result a shell was formed around the bodies in the outer portion of quartzitic, and in the inner portion of dolomitic composition".

Since the paper of Borchert (1954), the carbonate rocks and quartz rocks of in the Outokumpu assemblage have usually been interpreted to chemical sediments on the sea floor; the carbonate rocks as chemical dolostones (e.g. Koistinen, 1981; Park, 1988, 1992; Karhu, 1993) and quartz rocks as exhalative silica precipitates (e.g. Huhma and Huhma, 1979, Huhma, 1976; Koistinen, 1981; Park, 1988). More recently, however, Auclair et al. (1993) and Kontinen (1998) have proposed that the dolomites and quartz rocks in fact do represent dolomitized and silicified mantle peridotites, respectively.

Reflecting the since middle 1970s canonized interpretation of the carbonate and quartz rocks of the Outokumpu assemblage as chemogenic metasediments, in most of the research papers of recent years, the term Outokumpu assemblage has been associated with stratigraphic meaning (e.g. Koistinen, 1981; Park, 1988, 1992). Koistinen (1981) established based on a restoration of the undeformed condition of that what he believed to represent complexly deformed, mostly sedimentary strata in Outokumpu and Vuonos, the following stratigraphy for the Outokumpu assemblage:

Top Mica schist: thickness unknown. Black schist: 20 cm-several metres. Carbonaceceous quartzite: few centimetres to several metres-Keretti; few centimetres-Vuonos. Ore Carbonaceous quartzite: few centimetres to over 1 m; absent in parts; low-grade mineralization in parts. Quartzite with layers of skarn: possibly 20 m maximum. Serpentinite: about 200 m quartzite with skarn: metres to few tens of metres black schist ------ major tectonic break

Mica schist: thickness unknown

#### Base

Koistinen (1981) interpreted the Outokumpu rock assemblage of serpentinites, gabbros, pillow basalts (recognising the possible presence of pillow basalts elsewhere in the Outokumpu assemblage, though obviously not in Outokumpu and Vuonos), cherts and black schists as an ophiolite assemblage comprising mantle peridotites, mafic magmatic rocks and sea floor sedimentary rocks. It must be noted, however, that there is a certain conflict in the Koistinen's (1981) interpretation of the Outokumpu–Vuonos serpentinites to mantle comprising ophiolites, and how he presents the Outokumpu-Vuonos stratigraphy in the above column (copied 1:1 from Koistinen,1981). Namely, to make an ophiolite interpretation of the serpentinites sensible, he should have been putting a major tectonic break at least below, if not necessarily also above, the Outokumpu-Vuonos serpentinite layer.

Also Park (1988, 1990, 1992) has provided detailed interpretations of the stratigraphy in the Outokumpu assemblage (cf. Fig. 6, section 6.2.2.). Like Koistinen (1981), he also saw the carbonate and quartz rocks as conformal layers of chemical sediments in the Upper Kaleva assemblage, but interpreted the serpentinites to represent dunite sills of komatiitic affinity, sills that emplaced in the carbonate-chert horizon in the Outokumpu assemblage concurrent of its deposition.

Koistinen (1981) defined the Outokumpu and Vuonos ore bodies strata bound and stratiform. He assumed that the ores likewise the associated carbonate-quartz rocks deposited onto a serpentinitic seafloor, and that the Co-Ni parallel zones of the Outokumpu and Vuonos deposits represented stockworks/ feeder systems developed in uplow feeder chanells once beneath the carbonates-cherts and the ores (cf. Fig. 21 in Koistinen, 1981). As a comment must be said, however, that if the carbonate-quartz rocks in the Outokumpu assemblage are taken as carbonated-silicified serpentinites (primarily mantle peridotites) as proposed by Auclair et al. (1993) and Kontinen (1998), and which view is supported by many new evidence in this report, the concept of Outokumpu-Vuonos ores as stratabound-stratiform deposits loses much of its meaningfulness.

#### 5.2. North Karelia Schist Belt (NKSB)

Outokumpu mining camp is located within the Palaeoproterozoic North Karelia Schist Belt (NKSB), which rests on a late Archaean gneissic-granitoid basement east of the junction of the Neoarchaean-Palaeoproterozoic Karelian Craton and the 1.93-1.80 Ga Palaeoproterozoic Svecofennian island arc complex in southern Finland (Figs. 1-2; for reviews of the regional geology see e.g. Gaál and Gorbatschev, 1987; Korsman et al., 1999). The NKSB comprises mainly metasedimentary rocks, which for the older part, the 2.5-2.0 Ga Sariola-Jatuli strata, are autochthonous, shallow-water deposits on the Archaean basement, and for the younger part, the 2.0-<1.92 Ga Kaleva strata, partly parautochthonous, partly allochthonous, deeper water deposits, the latter being thrust, apparently from the "west", onto the Archaean basement complex. The allochthonus parts of the Upper Kaleva are in this report reffered collectively with the term Outokumpu Allochton.

The basement substructure consists mainly of granulite gneisses retrograded to amphibolite facies during the Svecofennian orogeny. The basement and NKSB are in the west



Fig. 2. Geological map of the Jormua-Outokumpu thrust belt showing distribution of the included serpentinite/ophiolite massifs. The Geomex study area is outlined by a box. The regional E-W peakmetamorphic zoning in NKSB is depicted by reaction isograds for core parts of the larger (>100 m) ultramafic bodies. The map is modified after Säntti et al. (in press).

intruded by1.87-1.85 Ga syn to late kinematic, largely infracrustally sourced granite plutons and batholiths (Huhma, 1986), traditionally considered to represent two distinct suites: 1) the ca. 1.87 Ga Heinävesi (or Kermajärvi) suite of diorites-quartz diorites-granodiorites, and 2) the slightly younger ca. 1.86 Ga Maarianvaara suite of diorites-quartz diorites-granodiorites-granodiorites-granites (Huhma, 1975, 1976; Huhma, 1986; Koistinen, 1993). Of these two suites, at least the Heinävesi-type plutons are spatially, and probably also in time and genesis, closely associated with the migmatite facies of the Kaleva metagreywackes, but so that they nevertheless post-date and cross-cut the leucosome-veining in the migmatites (Koistinen, 1993).

The Kaleva assemblage in the Outokumpu area consists of two main tectonostratigraphic units. The lower, probably mainly autochthonous-parautochthonous unit, "Lower Kaleva", comprises mainly metaturbiditic greywackes with thin intercalations of low-Ti tholeiitic metabasalts and black schists in its top part. The upper, at least for its major part allochthonous unit, "Upper Kaleva", consists of deep marine metaturbiditic greywackes with intercalations of black schists and lenses of dominantly serpentinized metaperidotite especially in its apparent basal part.

Single zircon U-Pb age data for detrital zircons indicate deposition of the Upper Kaleva metaturbidites at Outokumpu-Vuonos subsequent to ca. 1.92 Ga (Claesson et al., 1993). Exact timing of the thrusting of the allochthonous part of the Upper Kaleva, or the Outokumpu Allochthon, onto the Karelian Craton is not known, but it can be reasoned to have occurred about 1.90 Ga ago, certainly somewhere between 1.92 Ga and 1.87 Ga (cf. Koistinen, 1981).

The thrusting or obduction of the Outokumpu Allochthon preceded the apparently strikeslip type docking of the of the Svecofennian island arc complex to the margin of the Karelian Craton. In association of the early obduction and subsequent Svecofennian strike-slip tectonic processes, the NKSB and Outokumpu Allochthon became progressively polydeformed and metamorphosed. The thermal peak was attained in a relatively late stage of the orogenesis in the low amphibolite (in the east) to upper amphibolite facies (in the west) temperatures and pressures of 2-4 kb (Koistinen, 1981; Korsman et al., 1999).

A tectonostratigraphically correlative allochthonous package to the Outokumpu Allochton is found in the middle part of the Kainuu Schist Belt, hosting there the 1.95 Ga Jormua Ophiolite Complex (Kontinen, 1987; Peltonen et al., 1996; Peltonen et al., 1998). The Outokumpu and Jormua allochthons comprise as a whole an over 200 km long chain of mantle and ophiolite fragments, whose distribution is related to the early thrusting, and which are further modified by the subsequent Svecofennian multistage deformation and amphibolite facies metamorphism (Koistinen, 1981; Kontinen, 1987; cf. Fig. 2). The most complete and best-preserved member in the included chain of the ophiolite fragments, in terms of the ophiolite concept, is the 1.95 Ga Jormua complex in the middle part of the Kainuu Schist Belt (Kontinen, 1987; Peltonen et al., 1996, 1998). The 1.97 Ga Outokumpu "ophiolite complex" (Vuollo and Piirainen, 1989) in the NKSB is highly dismembered, and in fact represents hundreds of individual fragments of mainly ultramafic rocks distributed over an area of more than 5000 km<sup>2</sup> (Fig. 2).

#### 5.3. Major tectonostratigraphic units in the NKSB

Traditionally three main stratigraphic units have been distinguished in North Karelia: (1) the gneissic-granitic Archaean basement, (2) the littoral to shallow marine quartzitic Sariola-Jatuli and (3) the deeper marine "sandy-clayey" Kaleva sequences (cf. Figs. 2-3). Before availability of isotope data for the metasediments in Jatuli and Kaleva, these units were considered facies in a geosynclinal basin: Jatuli was interpreted as nearshore, the more eastern and lower parts of Kaleva (in the Höytiäinen belt) somewhat deeper water miogeoclinal deposits and the more western and upper parts of the Kaleva (in the Outokumpu area) eugeosynclinal flysch strata (e.g. Huhma, 1976). In these scenarios the Outokumpu serpentinites were interpreted as initial magmatic intrusions in an early, pre-flysch stage of the



Fig. 3. Major serpentinite containing "nappe" structures in the NKSB. These are termed to Outokumpu, Enonsalo, Kaavi, Miihkali, Rikkavesi, Savonranta and Vehkalahti structures. In addition, there occur serpentinites in narrow tectonic zones at Täilahti and Puiroonmäki in the west and at Rautavaara in the north. Some of the Lower Kaleva lithoassemblage units that are discussed in the text are indicated by number symbols: 1=Valkeasuo-Kalliojärvi, 2=Tohmajärvi Complex and Hammaslahti lithoassemblage, 3=Kuhnusta, 4=Haavanpää-Ruvaslahti, 5=Kinahmo, 6=Mulo, 7=Sotkuma, 8=Liperinsalo, 9=Oravisalo. The units 1-5 constitute the "Höytiäinen basin".Note that some of the units here included in the autochton-parautochthon, as e.g. 5 and 6, may actually be allochthonous. Also, e.g the Kaavi structure is more complex than can be presented in the scale of the map, comprising also obvious Lower Kaleva type units.

eugeosynclinal furrow (e.g. Väyrynen, 1954; Huhma, 1976).

No modern studies on the tectonostratigraphy, litostratigraphy, palaeosedimentology or petrology-petrogeochemistry of the Kaleva assemblage, and that would systematically cover the whole NKSB, have been carried out so far. This also means we do not have any uniform, formal tectonostratigraphic or litostratigraphic division and related nomenclature that would cover the entire NKSB. We above applied the more or less traditional tectonostratigraphic division in the Archaean basement, Sariola-Jatuli tectofacies, and Lower and Upper Kaleva tectofacies. In the following sections brief summary descriptions of these units are given, based on the existing literature data, and a few scattered field observations by the first author. It should be emphasized that much new systematic fieldwork must be done before any systematically updated view of the tectonostratigraphy in NKSB can be presented. Especially urgent such work would be for the Kaavi structure, i.e. within the area between Rikkavesi and Losomäki, since this area seems to preserve several stratigraphic units, which may be missing from other parts from the NKSB, but which have been mapped and studied just in a reconnaissance level, and mostly for their lithology only.

#### 5.3.1. Archaean basement complex

The Archaean basement below the northern part of the NKSB is most likely similar to the crust exposed further north in the lisalmi Complex, thus probably comprising mainly 3.2-2.7 Ga banded mafic-tonalitic-felsic gneisses in the W (lisalmi zone) and about 2.75-2.70 Ga metasedimentary-volcanic-granitic gneisses (Rautavaara zone) in the E (Paavola, 1988; Paavola, 1999; Mänttäri and Hölttä, 2002). The gneisses of the lisalmi complex were metamorphosed in high amphibolite to granulite facies conditions first 3.1Ga (lisalmi zone) and then again 2.7-2.63 Ga ago (lisalmi and Rautavaara zones), to be retrograded during the Svecofennian orogenesis variably to amphibolite facies (e.g. Kontinen et al., 1992; Mänttäri and Hölttä, 2002). Noting the broadly E-W structural trending in the Archaean basement in the Ilomantsi-Lieksa area E of the NKSB, one may assume that the middle and southern parts of the NKSB would overlay bedrock similar to the Lieksa and Ilomantsi areas, respectively. This should mean that the middle part of the NKSB would be underlain by banded migmatite gneisses intruded by large ca. 2.73 Ga pyroxene-bearing (partly charnockitic) diorite-tonalite and k-feldspar megacrystic granodiorite-granite plutons, while further in the south the basement would comprise ca. 2.75-2.70 Ga old amphibolite grade volcanic-sedimentary schists and tonalite-granodiorite-granite plutons (cf. e.g. Sorjonen-Ward, 1993; Halla, 2002).

#### 5.3.2. Sariola and Jatuli tectofacies

Best examples of the Sariola and Jatuli strata within NKSB occur E of the GEOMEX study area, in and west of the Koli hill range (Kohonen and Marmo, 1992), but extensive occurrences are present also in the Petonvaara area, though there in a more tectonized, more pervasively folded-schistose form (Fig. 3). Combined the Sariola-Jatuli tectofacies represent cratonic, fluvial-shallow marine deposition between ca. 2.5 and 2.1 Ga when the Eastern Finland basement complex obviously was part of a large, stable, and largely peneplanized continental block known as the Karelian craton. Well-washed, arkosic to supermature orthoquartzitic sands are the dominant content in this cratonic-epicratonic strata (Kohonen and Marmo, 1992). Shale interbeds, now transformed to sericite-muscovite-phlogopite schists make <10%. The sequence is topped by a thin unit of ca. 2.1 Ga dolomites, metabasites (lavas and tuffs) and metawackes (mica schists). Layered mafic sills are common, especially in basal parts of the Jatuli sequence as well as in the Archaean basement immediately below. The basement complex abounds in dolerite dykes, which together with the sills record at least three main episodes of continental flood-basalt-type, mantle-derived mafic magmatism: Areally very extensive (shield-wide), layered wherlite-gabbro-leucogabbro sills ("Karjalites") emplaced at ca. 2.2 Ga, Fe-tholeiitic dolerite dykes at ca. 2.1 Ga, and Mg-tholeiitic dolerite dykes and sills at ca. 1.97 Ga (Vuollo et al., 1995). From other parts of eastern Finland and Russian Karelia there are evidence for 2.4 Ga layered intrusions and related norite dykes and a ca. 2.3 Ga

shield-wide tholeiite dyke swarm. Up to this, there occur, along the Karelia-Scecofennia margin, ca. 2.06 Ga layered gabbros and tholeiitic to alkaline basalts (e.g. at Siilinjärvi and Otanmäki).

There are considerable variations from place to place in the thickness and apparent "completeness" of the Sariola-Jatuli sequence. On overall trend seems to be a thinning to the west, where usually only the very uppermost parts of the Jatuli sequence (if any) are seen to occur. Furthermore, it appears that in the west, along the "craton margin" the deposition of the Lower Kaleva was preceded by an uplift of the basement and related, in places complete, erosional removal of any remains of the older cover. Thus over most of the study area the preservation of the Sariola-Jatuli is patchy, and the total thickness of the preserved formations relatively minor.

#### 5.3.3. Lower Kaleva tectofacies

The lower autochthonous-parautochthonous units in the Kaleva in the NKSB, which are here informally called "Lower Kaleva" following the practise introduced by Kontinen (1987) for rocks of similar tectonic-stratigraphic character in the Kainuu Schist Belt, comprise variably metagreywackes, arkosic wackes, wacke conglomerates, quartz wackes, black schists, and locally also thin metabasite intercalations. Unfortunately, due to the outdated nature of quite many of the presently available geological maps and especially lithostratigraphical data for the NKSB, the areal distribution and tectonic-stratigraphic division of the included Lower Kaleva are currently only tentatively known.

The "Höytiäinen belt", appearing for its northwesternmost part in the eastern part of the GEOMEX study area (Fig. 3), represents the most extensive and best studied occurrence of Lower Kaleva type lithofacies in North Karelia (e.g. Huhma, 1975; Gaál et al., 1975; Ward, 1987; Kohonen, 1995). Though traditionally considered a coherent package of ca. 2.1 Ga (upper Jatulian), mainly turbidite-type psammitic-phyllitic, locally conglomeratic metasediments (e.g. Koistinen, 1981; Huhma, 1976; Ward, 1987), more recent investigations indicate the Höytiäinen belt would in fact represent tectonostratigraphically a rather complex package in which some units actually do correlate with the Lower Kaleva in Kainuu, and some probably are allochthonous and of Upper Kaleva affinity (Kohonen, 1995).

The second largest exposure of the Lower Kaleva type lithofacies in the GEOMEX study area is found in the Kaavi structure, where nappe slices of quartzitic-arkosic wackes and interbedded black schists tectonically interdigitate in an imbricate fashion with upper Kalevian greywacke metaturbidites and black schists, serpentinites, and slivers of Archaean basement and their Jatuli/Kaleva cover (Huhma, 1975; Koistinen, 1981; Park and Doody, 1990). Another more extensive occurrence of obvious Lower Kaleva type strata is found in the Viitaniemi-Virvujärvi area (e.g. at Punamäki) to the west of Juankoski, where a narrow, several km long stripe of quartzitic to arkosic wackes, black schists and intercalated metavolcanic rocks is rimming the Archaean lisalmi basement complex (Äikäs, 2000). Notably, there occur metal-rich (Ni, Cu, Zn, V) black schists among the Viitaniemi-Virvujävi black schists (Äikäs, 1996), very similar to the Talvivaara metal-rich black schists in the KSB (cf. Loukola-Ruskeeniemi and Heino, 1996; Loukola-Ruskeeniemi, 1999).

A further example of obvious Lower Kaleva strata occurs at Riihilahti, 15 km W of Outokumpu. The Riihilahti assemblage comprises a sequence of arkosic wackes and greywackes topped by a unit of amphibolitic and skarnoid metabasites and metal-anomalous (Ni, Cu, V, Zn) black schists (Vesanto, 1980). The skarn occurrences on map sheets 4222 and 4311 by Huhma (1971) indicate together with low-altitude air borne geophysical data that the Riihilahti type "Lower Kaleva" may extent, fringing thinly the entire western limb of the Salmijärvi structure, from Riihilahti to Miihkali area in the north.

Also the amphibolite-intercalated metagreywackes of the "epicontinental" Kaleva surrounding the domal basement windows in Juojärvi-Heinävesi area (Huhma, 1975; Koistinen, 1993) may possibly represent Lower Kaleva, or alternatively parautochthonous Upper Kaleva. The comparable amphibolite intercalated, metaturbiditic, partly conglomeratic arkosic wacke units fringing the Sotkuma and Oravisalo basement domes, and as well as those included in

the domal Liperinsalo structure (Laiti, 1985) also probably belong to the Lower Kaleva. Published maps and lithological data from the Savonranta area south of the GEOMEX study area indicate that thin slivers of quartz wacke intercalated Lower Kaleva may be present also there (cf. Lavikainen, 1985).

The formative tectonic setting(s) of the sedimentary units of the NKSB, which we here included in the Lower Kaleva, is currently known only tentatively. Based on studies in the Kainuu area, it has been proposed that Lower Kaleva represents deposition in rift-basins in earliest stages of the 1.95 Ga break-up of the Karelian supercontinent (e.g. Peltonen et al., 1996; 1998). The apparent very thinness of the Lower Kaleva sequences, as well as the thickness and relatively unreworked nature of the Archaean crust below the KSB and NKSB, indicate that the actual break-up of the Karelian continent must have taken place far away ("in the west") from the present Svecofennia-Archaean boundary line (cf. Kontinen 2002).

#### 5.3.4. Upper Kaleva tectofacies

The term Upper Kaleva was introduced by Kontinen (1987). He associated the deposition the Upper Kaleva turbidites in the KSB with post-rift thermal relaxation and related subsidence of the passive margin basin generated by the inferred 1.95 Ga break-up of the Karelian Craton. Subsequently Kontinen and Sorjonen-Ward (1991) found that the Upper Kaleva metaturbidites in the KSB are in their lithotype characters and chemical composition identical with the "eugeosynclinal" or "flysch" metaturbidites in the Outokumpu area, an inference that was soon strengthened by evidence of similar age distributions of detrital zircons in these metawackes in North Karelia and Kainuu (Claesson et al., 1993). Later on, Kohonen (1995) introduced the more neutral term "Western Kaleva" to replace the "Upper Kaleva". We will, however, use the "Upper Kaleva" in this report. Some of the reasons for this practice come out along with the discussion of the stratigraphical relationships of the facies of Kaleva in Liperinsalo and Suhmura areas.

The usage of the term "Upper" was no problem in Kontinen's (1987) original definition of the "Upper Kaleva", as he assumed that it included only strata that had been deposited directly on the underlying Lower Kaleva type units. However, it has become clear subsequently that, both in Kainuu and North Karelia, large parts of the Upper Kaleva must be in allochthonous units that have been thrust to their present locations from formative positions located for an unknown distance to "the west" of the present Svecofennia-Archaean boundary line (Peltonen et al., 1996; Peltonen et al., 1998; Kontinen, 2002). However, there exists both in North Karelia and Kainuu also such lithotypically and isotopically Uppr Kaleva type metagraywacke units that actually may be autochthonous/parautochthonous. Examples of such units include, e.g. the Kuhnusta (deep self?) sequence of monotonous metaturbidites (LA5 of Kohonen, 1995) in the core of the Höytiäinen "miogeosynclinal furrow", and the tempestitic muddy sands-silts of the Jalka-aho Formation at the western margin of the KSB. The Upper Kaleva satus of the Kuhnusta wackes is evident from their Outokumpu-type detrital zircon age population with abundant 1.92-1.98 Ga grains (GTK, unpublished data). The Jalka-aho strata were originally interpreted as a representative of Jatulian storm-dominated self-deposition (Kangas, 1985; Laajoki, 1991), but subsequently these sediments have been shown to exhibit clear Upper Kaleva type Sm-Nd isotope signature (Kontinen et al., 1996).

Kontinen and Sorjonen-Ward (1991) have proposed that the Upper Kaleva in KSB and NKSB would represent sediments of a major continental margin to ocean floor (slope-rise) turbidite fan system, something comparable to the present enormous Ganges-Brahmabutra-Indian Ocean river-delta-marine turbitite fan system. A deposition in front of the margin of the Karelian craton subsequent to its ca. 1.95 Ga break-up has been supported also by Kontinen et al. (1996,1998). Lahtinen (2000) has presented a different interpretation, proposing that the Upper Kaleva represents deposition in a fore-arc basin that subsided in front of an immature island arc (now part of the Primitive Arc Compex of Central Finland) colliding to the Karelian craton in an early stage of the Svecofennian orogenesis, and that the main sediment sources were in low-K bimodal rocks in the primitive arc and the Karelian Craton. Tectonic mixing of fragments from ocean flooring mantle among the Upper Kaleva turbidites before their obduction onto the craton margin is what is required to explain the tectonic mantle fragments (serpentinites) in the basal parts of the Outokumpu Allochton. Starting from the passive margin interpretation of Upper Kaleva, we envision that such mixing may have taken place in transform fault zones developed within the more distal parts of the inferred craton flanking vast turbidite fan comples, and assuming, in addition, that the distal parts of the basin were floored by a largely peridotitic, i.e. "Liguria/Calicia-type", oceanic crust. The transform fault associated mixing may have taken place already before, and unrelated to the obduction, or in its early stages, but in both cases so that the transform fault zone(s) eventually were translated into thrust fault/detachment zone(s) that initiated the obduction of the Outokumpu allochton.

#### 5.4. Distribution of the Outokumpu assemblage within the NKSB

Looking at the geological maps of the NKSB one gets easily the impression that the serpentinite containing structural units would contain black schists and serpentinites about only in their basal parts, and that the thickness of the serpentinite containing basal units would be relatively minor, discounting tectonic repetition, perhaps only a few hundreds of metres in maximum. In contrary, the units above the basal black schist-serpentinite horizon seem to comprise several km thick sequences of largely sandy turbidites with just infrequent, thin black schist intercalations with no associated serpentinite bodies.

It is clear that the serpentinite bodies in the basal black schist–serpentinite horizon must have been tectonically emplaced and distributed among the enclosing metasediments, probably already before, but at least no later than during the initial preD1-thrusting of the Outokumpu Allochthon onto the craton margin (cf. Koistinen, 1981). Subsequent phases of fault imbrication were locally an important redistributing/modifying process, but without significant impact on the regional distribution of the bodies, nor the average size of the serpentinite fragments.

Scrutiny of the published geological maps shows that there are several, at least in the present erosional surface unconnected structural units within the NKSB, and that contain serpentinites and related metasomatic rocks of the Outokumpu assemblage in their apparent basal parts; the largest of these "nappe structures" are the Outokumpu, Enonsalo, Kaavi and Miihkali structures (Fig. 3). It should be noted that, we in this report denote with Outokumpu Allochthon all the allochtnous units in the NKSB, but with Outokumpu structure only the "Outokumpu Nappe Complex" around Viinijärvi (cf. Fig. 1 in Gaál and Parkkinen, 1993). In addition, there are serpentinites in the area east of Juojärvi and SE of Rikkavesi, in an irregular bow-like chain extending from Maljasalmi via Varislahti to Lietukka. Small bodies are present also SW of Rikkavesi in the Ohtaansalmi-Paakkila area. We associate these occurrences in one unit, and name it to Rikkavesi structure. Outside GEOMEX area ultramafic bodies are present in in the Vehkalahti structure in Juankoski (Äikäs, 2000), and in the Savonranta structure west of Orivesi. One small sliver of Outokumpu assemblage is known from Puiroonmäki, Kangasniemi, there at the western margin of the large Heinävesi complex of 1.87 Ga granitoids and migmatite grade upper-Kaleva metaturbidites. In addition, one small Outokumpu-type ultramafic body has been recently found under the Täilahti bay of the Lake Kallavesi some 25 km to the S of Kuopio, indicating a small klippe of allochthonous Upper Kaleva in this area. In the north a narrow zone of fault-controlled serpentinite lenses runs from Losomäki via Rautavaara up to the KSB.

Tectonostratigraphic correlation of the obove outlined structural units remains an open question since any systematic structural-tectonostratigraphic study to cover the entire study area has not yet been realized. One possibility is that all the outlined units would represent a single multiply folded and imbricated thrust sheet (Outokumpu Allochton) that once covered the whole NKSB area. However, there are significant differences in lithological and petrochemical characteristics e.g. between the Kaavi and Outokumpu ultramafic-mafic rock assemblages that suggest, though do not necessarily require, that at least two superposed major thrust sheets would be present. These differences include, for example, that mantle peridotites in the Kaavi

mafic-ultramafic bodies appear significantly less depleted than they are in Outokumpu bodies, and that there are significantly more mafic rocks in association with the Kaavi bodies. In addition, the relatively rare mafic rocks of the Outokumpu assemblage appear somewhat more varied for their lithotypes than the apparently quite monotonously low-Ti tholeiitic metabasites in the Kaavi structure. Importantly, the mafic-ultramafic bodies in the Miihkali structure show clearly more similarity to the Kaavi than Outokumpu bodies.

If the Kaavi and Outokumpu thrust structures would really represent two separate sheets, what would then be their tectonostratigraphic relationship? In Miihkali area, west of Saramäki, there are serpentinite bodies apparently below the main Miihkali nappe. In geophysical maps the black schist strata associated with these serpentinite bodies can be traced around and east of the oval Miihkali structure until to Huutokoski where again serpentinites are met, in this case with similar gabbros than in the Kylylahti and Horsmanaho massifs in the Outokumpu structure. This might be an indication of that the Outokumpu nappe would locate structurally below the above inferred Miihkali-Kaavi sheet, although it must be said that this is really pure speculation. The Huutokoski and Horsmanaho gabbros have been dated at ca. 1.97-1.96 Ga (U-Pb, zircon); unfortunately we do not yet have age data for Miihkali and Kaavi gabbros.

Comparing the ultramafic-mafic bodies in the migmatite grade structures Enonsalo, Rikkavesi and Savonranta with those in the Outokumpu,Miihkali and Kaavi structures is difficult as the serpnetinite bodies in the migmatite environments usually are rather small, and have suffered from complex metasomatic-metamorphic modification. The Puiroonmäki occurrence of Outokumpu-type ultramafic rocks at the western margin of the Heinävesi complex is tectonostratigrapically important as it provides a hint of that the voluminous monotonous metagreywackes of the Heinävesi complex would be part of the allochthonous Upper Kaleva and perhaps correlative with the thick piles of monotonous metagreywackes capping the basal black schist–serpentinite horizon and forming the core of the synclinal Outokumpu structure. This correlation is supported by the close chemical similarity of the metagreywackes in the Heinävesi complex with the metagreywackes of the Outokumpu structure (Lahtinen, 2000).

#### 5.5. Tectonic-metamorphic evolution of the NKSB

#### 5.5.1. Tectonic-structural evolution

The Svecofennian structural evolution of the NKSB, as well as the Outokumpu assemblage and related ores was studied intensively during the 1980s (e.g. Koistinen, 1981; Park, 1983; Park and Bowes, 1983; Park et al., 1984; Park, 1988; Ward and Kohonen, 1989; Park and Doody, 1991; Koistinen, 1993), preceded by the important work of Gaál et al. (1975). The major achievement in these studies was the establishment of the polyphase nature of the regional structural evolution and documentation of the related structural sequence. Another major result was reinforcement of the allochthonous character of large units of the NKSB, a situation that had been recognized already during 1920s (e.g. Frosterus and Wilkman, 1920; Wegman, 1928, 1929; Väyrynen, 1954).

About five Svecofennian structural events or deformation stages/phases that resulted in at least locally important strain, rotation or displacement effects, have been recognised in the rocks of the NKSB (see e.g. Koistinen, 1981; Ward and Kohonen, 1989; Koistinen, 1993). A summation of the structural evolution of the NKSB, as it is currently understood, is given below, based mainly on the works of Koistinen (1981,1993) from the Outokumpu–Heinävesi area with some modifications from Ward and Kohonen (1998). We note that Park (1988) and Park and Doody (1990), who worked mainly in the Kaavi area, give a somewhat different view.

Main sages of the structural evolution of the NKSB (generalized with slight modification from Koistinen, 1981, 1993; and Ward and Kohonen, 1988):

#### Event Main structural process / rock fabric

**pre-D1** Emplacement of the Outokumpu nappe by thin-skinned thrusting / Bedding

parallel differentiation layering and quartz veins.

- **D1-D2** Recumbent folding and eventually thrusting along axial-plane parallel faults / Tight to isoclinal folds (F1) refolded to asymmetrical (F2) folds, development of the regionally prominent schistosity (S2) and intersection mineral lineation (L2). D2 culminated to extensive imbricate faulting and stacking of the D1-D2 deformed nappes, involving local basement slices and many mylonitic thrusts.
- D2c Development of NW trending wrench fault zones with usually dextral folds / Widespread weak NW-trending cleavage and crenulation.
- D3 Development of open, asymmetrical folds / Axial planar cleavage, crenulations. Temperature peak of regional metamorphism occurred late in D3.
- **D4-D5** Open, upright folds / Weak cleavages, weak to locally prominent lineations.

This structural sequence has usually been interpreted as a result of a continuum process under a sustained NNE-SSW orogenic (Svecofennian) compression, involving NNE-ENE directed thrusting (preD1 to D2) as a first stage, and NW directed shearing (D2<sub>C</sub>-D5) reorienting the preD1 to D2 structures as a second stage (e.g. Ward and Kohonen, 1989). The first stage is usually considered to have been linked with the presumably ca. 1.90±0.01 Ga docking of the Svecofennian island arc complex to the margin of the Karelian Craton, and the second stage to the subsequent, about 1.88-86 Ga dextral strike-slip faulting and associated granitoid emplacement episode along the Svecofennia-Karelia boundary (e.g. Ward and Kohonen, 1988).

Importantly, Koistinen (1981) saw that the Outokumpu and Vuonos ores and their host rocks would record the whole structural sequence from the pre-D1 to D5. For example, the distinct ruler-shapes of the Vuonos and Outokumpu ore bodies were interpreted by him as a cumulative result of F1 isoclinal folding and L1 elongation, reshaping the ore bodies from originally oval-shaped thin plates into long, narrow ribbons parallel to the L1 and F1 fold hinges. Koistinen (1981) further inferred that D1 was associated with considerable mobilization, preferentially in those parts of the originally pyritic ore that became metamorphically pyrrhotitised, and in a late stage of D1 widespread growth of pyrite porphyroblasts in the pyrrhotitic ore parts. According Koistinen (1981), D2 resulted in localised development of tight, asymmetrical, in maximum tens of metres size F2 folds, preferentially in D1 mobilised ore parts, while deformations from D3 further on had only little impact on the shapes and distribution of the ore bodies.

Like many other workers earlier and later on, Koistinen (1981) considered that the compositional banding in the pyritic ore parts of the Keretti ore, present "at scales of several cm to greater than 1 m", would represent  $S_0$  "sedimentary layering". We note, however, that the banding is defined just by variation in quartz to sulphide ratio and/or variation in sulphide species ratios from band to band, and that besides this banding there are no other possible indications of sedimentary origin such as e.g. clear hydrothermalite (chert or other) or clayey interbeds. Thus we are inclined to believe that the banding in the pyritic ores would in fact represent tectonic-metamorphic segregation/banding analogous to the ubiquitous banding in their peridotite-derived metabirbiritic wall rocks, in which the banding simply cannot be of sedimentary origin. Reservations about the sedimentary nature of the ore banding have been expressed also before. Gaál et al. (1975) formulate their suspicion as follows: "In the structural analysis primary stratification in the ore cannot be verified... On the structural basis the layering could be interpreted as either metamorphic segregation parallel to S<sub>1a</sub> or relics of stratification plus S<sub>1a</sub>."

#### 5.5.2. Metamorphic evolution

Koistinen (1981) inferred that the pre-D1 thrusting of the Outokumpu Allochton commenced in relatively low-temperature, sub-biotite grade (re pelites) conditions, while the actual regional metamorphic temperature elevation started in early stages of the main D1stage, which ended up in biotite-grade thermal conditions. During D2 garnet-grade (metapelite) thermal conditions were reached. The regional temperature progression culminated in a late static phase of D3 at about 550 °C (T for Outokumpu). Treloar et al. (1981) refined the estimate of the peak conditions in Outokumpu to 600±50 °C at pressures of 3.5±1 kb, based on an assessment of compositions of coexisting mineral phases of cordierite-amphibole rocks in Outokumpu.

It should be noted that though metamorphic temperature peaking over the entire area is a relatively late event, high temperatures in the western part of the study area were attained already relatively early as is evidenced by the D2 partial melting of the Kalevian mica gneisses (cf. Park, 1988; Park and Doody, 1990). In the Heinävesi area the D2 migmatization must have been taken place already before the ca. 1.87 Ga emplacement of the Heinävesi quartz diorites-granodiorites, which however seem spatially and possibly also genetically somehow related to the migmatization in the enclosing wackes (Koistinen, 1993). Scattered preservation of apparently early kyanite and its replacement by sillimanite in some Outokumpu metapelites suggest that the T-P evolution indeed was clockwise from higher P/lowerT (pre-D1/D1) to lowerP/higerT at the peak (late D3), quite as one would expect for such a thrust belt as the NKSB is currently understood.

Refractory ultramafic rocks such as in the Outokumpu assemblage keep reactive over an exceptionally wide temperature range of progressive metamorphism. Therefore mineral assemblages of ultramatic rocks also in the Outokumpu area faithfully record the regional variation of the peak-metamorphic temperatures. Based on a study of relict fabrics and mineral assemblages in serpentinites from Outokumpu and Kaavi areas, Park (1983) proposed a thermal climax (600–680 °C) during D2. A recent comprehensive study of the North Karelia-Kainuu ultramafics has found the peak-metamorphic assemblages frequently "static", which rather supports the view of Koistinen (1981) of a late D3 timing of the thermal peaking. The absolute timing of the peak is difficult but it probably was somewhere around 1.86 Ga and the emplacement of the 1957±8 Ma Maarianvaara granite. On the other hand, it is known by K-Ar and Ar-Ar mineral dating (e.g. Kontinen et al., 1992; Kontinen, 2002) that Svecofennian metamorphic temperatures in eastern Finland did not fall below 500 °C before ca. 1.81 Ga. Adding to this that the start of melting/migmatization of the veined gneisses in the western part of the study area occurred already before 1.87 Ga, i.e. before the emplacement of the circa 1.87 Ga Heinävesi-type granitoids; a fairly long residence (>50 Ma at least) of the NKSB in amphibolite facies temperatures is clearly indicated.

According to Säntti et al. (in press) peak mineral assemblages in the Outokumpu area metaultramafic rocks define four distinct zones recording an increase in regional metamorphic temperatures from east to west (Fig. 2):

East	A=antigorite zone:	Antigorite±olivine±tremolite	500-550 °C
	B= talc zone:	Olivine+talc	550-660 °C
	C=antophyllite zone:	Olivine+anthophyllite±cummingtonite±talc	660-700 °C
West	D=enstatite zone:	Olivine+enstatite±anthophyllite±MgAI-spinel	700-770 °C

Tremolite may occur in all the four zones, being usually more plentiful at the body margins and next to mafic inclusions. Talc-carbonate rocks frequently flank serpentinite bodies in zone A, and occur interfingered with olivine-talc carbonate rocks also in the easternmost parts of zone B. The given temperatures estimations are based on reaction temperatures indicated by the characteristic mineral assemblages and olivine-spinel thermometry. It has to be noted that the olivines, enstatites and anthophyllites are usually heavily altered to retrograde low-T serpentine (lizardite-chrysotile), and that hence prograde mineral assemblages in Outokumpu metaperidotites are rarely preserved fresh. Nevertheless, owing to the static nature of the retrogressive replacement, the peak assemblages are generally still pseudomorphically well preserved and easy to determine under the polarizing microscope.

It is important to note that temperatures for the reactions that produce the diagnostic mineral assemblages in zones A to D are all strongly dependent on the mole fraction of  $CO_2$  (=XCO<sub>2</sub>) in the metamorphic intragranular fluid (e.g. Johannes, 1969; Trommsdorff and Conolly, 1990; Will et al., 1990). Therefore the isograds separating the zones in Fig. 2 are based on mineral assemblages observed in the core parts of the bigger ultramafic bodies, where XCO<sub>2</sub> likely remained low, owing to the nature of the surrounding ultramafic material as an effective  $CO_2$  buffer. Due to variation in XCO<sub>2</sub> in the metamorphic fluid, assemblages typical for the zones C and D may appear already in the zone B massifs, however. This is the case for small bodies and the boundaries of larger ones. In fact, large bodies in zone B typically show a mineral assemblage zoning from olivine + talc in the core parts via olivine + anthophyllite to olivine + enstatite and olivine + enstatite + carbonate next to the carbonate, skarn and quartz rocks at their margins. Such metamorphic zoning is well developed e.g. in the relatively large Outokumpu body.

Metasedimentary rocks in the Kaleva assemblage, being mostly relatively immature quartz intermediate greywackes, rarely have mineral assemblages that would be useful in determining metamorphic pT conditions. In a comparison with the recently published metamorphic map of the Raahe-Ladoga Zone (Korsman and Glebovitsky, 1999), it is found that zones A and B of Säntti et al. (in press) approximately correspond to Garnet + Staurolite + Andalusite, zone C to Sillimanite + K-feldspar, and zone D to Garnet + Cordierite + K-feldspar + Biotite metapelite zone. It is to be noted that both the ultramafite and pelite based zones are sharply discordant with the regional structural pattern. This is a fact that fits well with the evidence of the late "static" culmination of the metamorphism from microstructures in both the metasedimentary and metaultramafic rocks (e.g. Koistinen, 1981; Treloar et al., 1981; Halden and Bowes, 1984; Säntti et al., in press).

## 6. Petrography and geochemistry of the Outokumpu assemblage and Kaleva formations

#### 6.1. Lower Kaleva

As we pointed earlier, large parts of the NKSB lack modern systematic lithostratigrapic, petrologic or geochemical study. In the case of the Lower Kaleva a positive exception is the "Höytiäinen basin", which has been recently investigated for its sedimentary geology by Ward (1987) and Kohonen (1995) and for lithogeochemistry by Lahtinen (2001). A small reconnaissance study of field setting and geochemistry of some supposedly Lower Kalevian metabasite units in the GEOMEX study area was undertaken during this work. This was done in hope of getting some more insight in the formative tectonic setting of the Lower Kaleva, and by that to the general tectonic evolution of the "craton margin" and NKSB. But for most, the following brief review of the Lower Kaleva is largely based on what one can put together from the available publications and some old notes of the first author.

#### 6.1.1. Metasediments

#### Höytiäinen belt

Höytiäinen belt (or basin) comprises the Lower Kaleva type metaturbidites between the Kiihtelysvaara and Koli quartzite ranges in the east, and the Suhmura thrust in the west. The northern part of the belt is included in the GEOMEX study area. Based on published studies (Huhma, 1975; Gaál et al., 1975; Ward 1987; Kohonen, 1995), our own sporadic field

observations and interpretations of geophysical maps, the belt in its N part seems to comprise five broadly N-S running main units, that are here informally named to: 1) Valkeasuo-Kalliojärvi (easternmost), 2) Tohmajärvi-Hammaslahti, 3) Kuhnusta and 4) Haavanpää-Ruvaslahti, and 5) Kinahmo units (westernmost) (Fig. 3). Traditionally all these units have been lumped together and considered representing a contiguous sequence of autochthonous strata significantly older (in some views ca. 2.1 Ga) than the metasediments in the Outokumpu Allochthon and Upper Kaleva (e.g. Koistinen, 1987; Ward, 1987). Is now known, however, that at least the Kuhnusta and Kinahmo rocks are in fact of Upper Kaleva affinity (GTK, unpublished data). This observation and the inadequately known nature of the unit contacts raise the possibility that the Höytiäinen belt may in fact comprise, but several distinct lithofacies, also their considerable tectonic stacking.

As an important detail, it has to be noted that there are minor conglomerate occurrences along the eastern contact of Höytiäinen belt, between it and the underlying Jatuli quartzites of the Kiihtelysvaara-Koli range (Nykänen, 1971; Pekkarinen, 1979; Pekkarinen and Lukkarinen, 1991, Kohonen, 1995). In some views these conglomerates have been interpreted to a basal unit of the Höytiäinen belt. However, mostly the conglomerates seem to immediately underlie W-dipping faults that probably represent a major detachment below the entire Höytiäinen package.

Summarizing, rather than a continuous in-situ sedimentary sequence, the Höytiäinen belt seems to represent an at least somewhat tectonically displaced package of possibly both allochthonous and parautochtonous thrust slices. The details remain to be better resolved in future studies, however. We provide below short descriptions about the here distinguished main lithotectonic units.

#### Valkeasuo-Kalliojärvi lithoassemblage

In the northern part of the Höytiäinen belt the L1 to LA 4 lithofacies assemblages of Kohonen (1995), here included in the Valkeasuo-Kalliojärvi lithoassemblage, represent obvious Lower Kaleva. The relative immaturity of the material prevents correlation with the underlying supermature Jatuli, while the arkosic wacke to guartz wacke and partly arenitic nature of the mainly turbidite sands, forming the main component in the LA1-LA4 package, is a typical character of Lower Kaleva in Kainuu. Additional typical Lower Kaleva characters of the LA1-LA4 include the rare, local intraformational polymictic conglomerates with granitoid (supposedly Archaean), quartzite and carbonate rock (supposedly mainly Jatulian) and mica schist phyllite fragments (supposedly intraformational). The clast-portfolio in the conglomerates indicates the source of the included material was the Archaean basement and its Jatuli cover E of the belt. The Archaean bulk zircon in these sediments (GTK, unpublished data) is also a feature suggesting they would be part of the Lower Kaleva tectofacies. In S-part of the Höytiäinen belt, the schists between Rekivaara (east of the Hammaslahti mine) and the Kiihtelysvaara guartzite range correlate with the LA1-LA4 package. A notable feature of the LA1-LA4 schists is their low sulphide and graphite content reflected in their overall low magnetic susceptibility and electrical conductivity. In Kainuu this is a distinct character of the lowermost strata in the Lower Kaleva tectofacies.

Lahtinen (2000) distinguishes four main "chemotypes" among the wackes-wacke pelites of the Höytiäinen belt but without any bound to the stratigraphy of the belt. Of these chemotypes, at least the wackes of the high Cr and low-Cr groups H1 and H3, respectively, are present within the Valkeasuo-Kalliojärvi unit (based on unpublished data of GTK/A. Kontinen and data in Glumoff, 1987). Both the H1 and H3 are lower in Ba, Na, Ca and Sr and higher in Rb and K than the typical Upper Kaleva sediments and thus represent clearly more weathered materials. The H1 type wackes are variably enriched over the average Upper Kaleva sand (WK1 of Lahtinen, 2000) in Co, Cr, Fe, Mg, Ni, Sc and V, which indicates a higher component of basaltic rocks in the source. No trends towards Archaean komatiite-basalt type sources are obvious in H1 element trends, instead the only moderately negative  $\varepsilon_{Nd}$ (1950Ma) of most of the H1 wackes (Huhma, 1987) suggest the basaltic component was Proterozoic, and possibly in sills and basalts in the Sariola-Jatuli cover of the Karelian craton. Some of the H3 type wackes

show features like low Sc/Yb and high Zr/Yb indicating relatively more Archaean basement type TTG-granite-granodiorite and/or recycled Sariola-Jatuli sediment component in the source of these wackes. LA1-LA4 considered together, clear source-related variations over short stratigraphic intervals are present, indicating relatively minor scale and tectonical instability of the depositional system, at least compared to Upper Kaleva in which such bed-to-bed source variation more or less completely lacks.

#### Tohmajärvi complex and Hammaslahti lithoassemblage

The 2.1 Ga Tohmajärvi complex in the S-part of the Höytiäinen belt is composed mainly of mafic dolerite sills, mafic tuffs and minor carbonate rocks (Nykänen, 1971; Nykänen et al., 1994), and that unconformally underlie the polymictic Kirkkoniemi conglomerate and Akkala quartz wackes fringing the complex in the S. The Kirkkoniemi conglomerate and Akkala wackes are here considered the lowermost unit of the overlying Hammaslahti lithoassemblage. Towards N from Tohmajärvi the dominant rocks in this unit are coarse-grained arkosic and lithic wackes and conglomerates with frequent pyritic black schist and occasional clastic carbonate-rich and mafic wacke interbeds. The mafic wackes probably represent erosion from the Tohmajärvi complex while the abundant quartzite and carbonate clasts in the conglomerates and sands indicate that the Jatuli carbonate-quartzite platform was an important source of material in the carbonate-rich wackes. Typical of the coarse quartz-feldspar wackes, plentiful in this lithofacies, is dark-coloured coarse quartz clasts that sometimes have a distinct blue hue. This suggests Archaean granulites-charnockites, as those in the Koitere area 70 km to the NE of Hammaslahti, were also an important source of the coarse quartz-feldspar-granitoid detritus.

The clast sortiment of the psefites-psammites indicate a post-"marine Jatuli", probably "Lower Kaleva" status for the Hammaslahti lithofacies. We note that an alternative opinion of these rocks as sediments related to a 2.1 Ga rifting of the Jatuli platform is currently in favour (e.g. Ward, 1987; Kohonen, 1995). The critical question is whether the mafic wackes in the Hammaslahti lithoassemblage would represent epiclastic mafic wackes eroded from the 2.1 Ga Tohmajärvi Complex subsequent of its volcanic formation, as we believe, or would these wackes instead represent redeposition concurrent with the volcanic built-up of the complex. A fact to consider here is that 1.98-1.97 Ga tholeiite dykes and sills common in the underlying Jatuli sequences and Archaean basement (Pekkarinen and Lukkarinen, 1991; Vuollo et al., 1992) are not found dissecting the Hammaslahti lithofacies or any other metasediments within the Höytiäinen belt. This strongly supports younger than 1.97 Ga age and hence Lower Kaleva status for the Hammaslahti strata.

It is here worth to note that the tholeiitic metabasites of the Tohmajärvi Complex are TiO<sub>2</sub> intermediate (average TiO<sub>2</sub> = 1.32 wt.%), relatively Fe-rich (av. Fe<sub>2</sub>O<sub>3</sub>T = 14.78 wt.%) and poor in Cr (av. Cr = 127 ppm) and Ni (av. Ni = 80 ppm) and that they thus clearly differ from the low-Ti, high-Cr tholeiites typical of Lower Kaleva type assemblages as e.g. at Riihilahti (cf. Nykänen et al., 1994; chapter 6.1.2.). The Tohmajärvi volcanic rocks also show positive  $\varepsilon_{Nd}$ (2100 Ma) of +-2.6 (Huhma, 1986), indicating a mantle source with a long pre-eruption LREE depletion history, whereas the low-Ti tholeiites in the Lower Kaleva sequences show significantly lower  $\varepsilon_{Nd}$ (1950Ma) of ca. ±0 (section 9.3.3.).

A low-grade Cu-Zn ore locating within the Tohmajärvi-Hammaslahti sequence was mined at Hammaslahti (Lähdekorpi) in years 1973-1986. The deposit (7 million tons of mined ore with 1.2 wt.% Cu) consisted of several lens-form bodies of mainly breccia-type±disseminated sulphides that had en echelon like distribution in a N-S shear zone within a unit of coarse, arkosic to quartz wackes of the Hammaslahti lithofacies (Hyvärinen et al., 1977). Compared to Outokumpu the Hammaslahti sulphides were distinctly low in Co (<50-450 ppm) and Ni (<80 ppm) although similarly low in Pb (20-120 ppm). There is a difference also in Pb isotope compositions of ore galenas; Pb in Hammaslahti galenas is more radiogenic and also yields an higher model age (ca.2250 Ma, Stacey and Kramers) than galenas in the Outokumpu ore (ca. 2100 Ma) (Hyvärinen et al., 1977; Vaasjoki, 1981). The most recent interpretations of Hammaslahti deposit propose that it was a SEDEX or Beshhi type massive sulphide concentration formed in a magmatically active rift environment, apparently concurrent with the built-up of the 2.1 Ga Tohmajärvi mafic complex (e.g. Ward, 1987). However, in an earlier view a syntectonic, shear-zone controlled origin for the ore has been proposed (e.g. Hyvärinen et al., 1977), and which perhaps still is the hypothesis that is most consistent with the available evidence. Especially if the dominant ore-formation stage alteration really showed up, as it appears from the available descriptions of the deposit, as silicification and chloritization of metamorphic plagioclase and amphiboles (tremolite). Furthermore, as we inferred above, the host strata very likely post-date the ca. 2.1 Ga Tohmajärvi mafic rocks, being most probably younger than ca. 1.97 Ga in age.

#### Kuhnusta lithoassemblage

We refer with this unit to the "monotonites" inside the Kuhnusta "syncline", which correspond to the LA5 as distinguished by Kohonen (1995). The Kuhnusta assemblage consists of monotonous, thickly bedded sandy turbidites that lithotypically closely resemble sandy turbidites in the Outokumpu structure, but which generally show a somewhat finer average grain-size. The match of the Kuhnusta wackes with the Outokumpu wackes is close also in terms of major element composition (Kohonen, 1995) and similar age distribution of detrital zircons (GTK, unpublished data). Kohonen (1995) considered that the LA5 sediments had a conformable relationship with the LA4 turbidites in the underlying Valkeasuo-Kalliojärvi lithofacies. We believe a thrust contact here a more likely situation – yet considering that the Kuhnusta, like the Haavanpää-Ruvaslahti turbidites (below) likely are parautochthonous, i.e. far less tectonically relocated strata than the Upper Kaleva turbidites in the Outokumpu Allochthon.

#### Haavanpää-Ruvaslahti lithoassemblage

There runs an apparently continuous, ca. 80 km long, for most part 4-6 km wide zone of often sulphidic-graphitic, usually fine-grained turbidite type sediments from S of Haavanpää E of the Hammaslahti to N of Ruvaslahti at the W margin of the Höytiäinen Lake. The unit shows up on geophysical maps as a distinct electrically conductive but relatively nonmagnetic unit. The included turbidites show considerable variation in terms of grain size and bed thickness but the dominant litofacies seems to be thinly bedded to laminar turbidites in which the thicker beds often show nicely preserved normal grading from sand to silt-clay (Huhma, 1975). The geophysical properties indicate that the abundant sulphide would be exclusively pyrite+hexagonal pyrrhotite. Distinctly sulphide-banded-laminar variants are exposed e.g. at Sorppankangas E of the Kinahmo village. There are no isotopic data available to confirm, but we consider it most likely that also these turbidites would represent time and source-wise Lower Kaleva. Evidence to support Lower Kaleva correlation include that the mica schistsphyllites at Ruvaslahti and Haavanpää show high Mg, Cr and Ni contents (Glumoff, 1987) pointing to correlation with the facies of relatively Cr-rich, dominantly Achaean sourced wackes in the Valkeasuo-Kalliojärvi assemblage. An alternative, though in our view a less likely possibility is that the Haavanpää-Ruvaslahti sediments would correlate with the Kuhnusta wackes, as a finer-grained, more distal facies, and that the source was partly in the ophiolites of the Outokumpu Allochthon. In that case the Kuhnusta-Haavanpää-Ruvaslahti turbidites could represent foredeep deposition in front of the obducting Outokumpu nappe complex. Whether of these two alternatives is the more correct one remains to be resolved in future studies.

#### Kinahmo lithoassemblage

There occurs an about 1 km wide slice of monotonously sandy turbidites along the western margin of the Höytiäinen belt, in between the Sotkuma basement window and the above described Haavanpää-Ruvaslahti type turbidites, being well exposed e.g. in the Kinahmo area. Like the monotonites in the Kuhnusta unit, these rocks, constituting our Kinahmo unit, show lithotypically and chemically clear Upper Kaleva affinities. Lahtinen (2000) includes these rocks in his Upper Kaleva like H4 chemotype of Höytiäinen metasediments.

The Sotkuma, Liperinsalo and Oravinsalo "domes", cropping out from beneath the apparently quite flat-lying Upper Kaleva type "monotonite" greywacke east of the Outokumpu structure, are covered by or composed of strata that may represent the Lower Kaleva tectofacies. Though in past considered e.g. Sariolan in age (e.g. Luukkonen and Lukkarinen, 1986), in recent views these "domes" and related metasediments have been interpreted in terms of Kalevian rift tectonism and sedimentation, to represent either local uplifted-tilted-eroded blocks of basement and their psephitic-sandy cover, or alternatively from west thrust allochthonous-parautochtonous slice(s) of rifted basement and rift sediments.

The Sotkuma basement "dome" (10x 20 km) is surrounded by a narrow, discontinuous stripe of weathering breccia and/or satrolite grading upwards to mostly calc-silicate bearing conglomerates and feldspathic quartzites (Huhma, 1975, Gaál et al., 1975), and which are overlain by black and mica schists of probable Upper Kaleva affinity. It is worth to note here that the satrolites do not contain alumina-rich silicates or have particularly aluminous bulk compositions (cf. Table 1 in Gaál et al., 1975), so that these rocks seem not to represent residuals of advanced chemical weathering similar to that recorded by the Sariola metasediments at the N margin of the nearby Kontiolahti dome. Somewhat surprisingly, the satrolites are reported to have massive, nonfoliated textures (Gaál et al., 1975). Diopside and tremolite occur in the matrix or in skarn layers both in the conglomerates and part of the quartzites. The presence of abundant scapolite in part of the calc-silicate quartzites may imply they originally contained evaporite intercalations. Where more pure the guartzites are graphitebearing and bluish grey in colour as is typical for many metaturbiditic quartzites in the Lower Kaleva, both in North Karelia and Kainuu. At Pölhönniemi locality the guartzites intercalate with graphite-bearing quartz-feldspar-biotite schists, in which the metamorphic biotite is largely retrograded to chlorite. The contact between the quartities and the overlying Kaleva metasediments is considered abrupt but sedimentary (Gaál et al., 1975).

The Liperinsalo "dome", ca. 20 km to the south of the Sotkuma "dome", is in its map-shape an oval-form body (5x10 km) composed of cobble to small-pebble conglomerates and coarse arkosic quartzites fringed thinly by a unit of black schists and amphibolites (cf. Laiti, 1985). The conglomerates and coarse arkosic wackes comprise mainly Archaean granitoids and Jatuli quartzites but also intraformational wackes as phenoclasts/rip ups and are intercalated with micaceous, locally garnet-bearing metagreywackes-phyllites. These are features that make them very similar with some conglomerates and sandy wackes in the Lower Kaleva in Kainuu. We note also that the association of black schist with amphibolite is known also elsewhere in the possibly correlative Lower Kaleva units like e.g. in Virvujärvi-Viitaniemi and Riihilahti. Whether the amphibolites at Liperinsalo would also be of the low-Ti tholeiite character, as the metabasites in these possibly correlative units, is not known. The massive, medium to coarsegrained, blastodiabasic textures of the Liperinsalo amphibolites suggest they would represent mainly sills in the metasediments.

The Oravinsalo "dome", circa 5 km to the S of the Liperinsalo dome, consists of a small (3x5 km), oval-shaped, E-S-directed body of Archaean gneisses associated with metabasite (sill?), some conglomerate and arkosic sands (Lavikainen, 1985; Ward, 1987). Ward (1987) provides evidence of deposition of the surrounding Upper Kaleva metawackes directly on the Archaean gneisses, with just a thin layer of conglomerate-like rock and coarse arkosic wacke in between. It should be noted that the small domal occurrence of polymictic conglomerates and basement gneiss at Suhmura about 25 km to the NE of Oravinsalo may represent a correlative unit, as also there the conglomerates occur basal to, and grade to the surrounding/overlying Upper Kaleva type metagreywackes (Ward, 1987). The stratigraphic correlation of the thick units of black tremolite rich metacarbonates at Mulo NNW of Suhmura is not well known although they seem to be intercalated in Upper Kaleva type monotonitic wackes.

To draw together, in spite of their traditional correlation with Jatuli (e.g., Huhma, Gaál et al., 1975) or even with Sariola (Luukkonen and Lukkarinen, 1986), the above review suggests that the Sotkuma, Liperinsalo and Oravinsalo metasediments would in fact more probably

represent, similarly as the comparable metasediments around the Juojärvi cupolas (below), some facies of the Lower Kaleva. Importantly, the strata in all these occurrences locate immediately below clear Upper Kaleva monotonites into which they seem to abruptly grade; therefore in a sense talking about Lower Kaleva is here particularly correct.

An important question remains, however. That is, whether the "Pyhäselkä bock", comprising the Sotkuma, Suhmura, Liperi and Oravisalo units and overlying Upper Kaleva monotonites, would represent an in situ development, or rather a from "west" transported imbricate thrust sliver? Deep-water turbiditic sediments like the Upper Kaleva monotonites, on a very thick, tectonically relatively undisturbed continental crust, such as that which seems to underlie the Pyhäselkä block, sounds an unlikely primary condition. Therefore we are inclined to believe that the Pyhäselkä block most likely represents an allochthonous unit detached and transported from an outer thinned part of the Kaleva stage margin of the Karelian Craton. We note that this interpretation would also provide an explanation to the lack of the Mulo type lithofacies from elsewhere in the NKSB – other slices of the Pyhäselkä type simply have not been preserved in the now deeply eroded thrust belt. Would the nappe slice interpretation be correct, then the ongoing seismic soundings (FIRE3 of GTK) should reveal a shallow-angle detachment plane(s) below the Pyhäselkä block. With the publication of the results of the recent FIRE3 deep seismic sounding of GTK, we will hopefully see whether this was the case or not.

#### Petronvaarat-Juuka area

In both these areas areally relatively extensive units of uppermost Jatulian quartzites dolomites, skarns, tuffites and mica schists do occur, being unconformally overlain by thin units of metasediments of possible Lower Kaleva status. The suspect Lower Kaleva rocks comprise e.g. polymictic conglomerates, garnet-staurolite mica schists etc. The conglomerates probably correlate with the conglomerates-breccias occurring at the interface of Lower Kaleva (eastern Kaleva) and Jatuli along the western margin of the Koli quartzite range (cf. Kohonen, 1995). Probably most of these conglomerates, if not all, are related with the earliest stages of the foundering of the upper Jatulian carbonate-platform and start of the break-up of the Karelian Craton some 2.1 -2.0 Ga ago.

#### Kaavi-Juankoski area

In the Kaavi-Juankoski area possible Lower Kaleva units are met in the Kaavi structure and west of Juankoski in the Viitaniemi-Virvujärvi zone.

The Kaavi structure comprises an imbricate pile of thrust slices of upper Kalevian metawackes, black schists and serpentinite, intercalated with slices of the Archaean basement and units of arkosic to orthoquartzitic sands, carbonate-skarn rocks, amphibolites, black schists and heterolithic wacke-wacke pelitic metasediments (Huhma, 1975). Traditionally the quartzites, dolomites-skarns and black schists have been correlated with the uppermost Jatulian (marine Jatulian) dolomites and tuffites in the Petronvaara and Juuka areas the E of the Kaavi structure. However, as at least part of the quartzite-carbonate usnits seem to occur as intercalations in the heterolithic assemblage comprising mica schists intercalated with graphitic quartz wackes and turbiditic quartzites, a correlation of the whole bunch with Lower Kaleva seems on serious alternative. Or, it could even be speculated that these rocks would represent post-1.95 Ga "Upper Kaleva" self deposition. Though the latter alternative may sound a bit far-fetched, we recall that also in Kainuu there occur micaceous shallow-marine wacke units, as e.g. the Jalka-aho Formation, that have been considered, based on field evidence, a shallow self sequence of the uppermost Jatuli (e.g. Laajoki, 1991), but which nevertheless isotopically correlate rather with the monotonites of Upper Kaleva (Kontinen et al., 1996).

In the Viitaniemi (Punamäki)-Virvujärvi zone, ca. 10-15 km to the NE of Juankoski, consists of quartzites, quartz wackes, black schists and amphibolites as a narrow stripe between the Iisalmi basement complex in the west and Upper Kalevian metawackes of the NKSB in the east

(cf. Äikäs, 2000). Part of the black schists in the Viitaniemi-Virvujärvi rock assemblage are quartz wacke intercalated and highly metal (Ni, Cu, Zn, V) anomalous with Ni contents up to 3000 ppm and more (Äikäs, 1996), which makes them very similar with the Talvivaara black schists in the upper part of Lower Kaleva in the sourthern part of the Kainuu schist belt.

#### Riihilahti-Varislahti area.

Circa 15 km to the west of Outokumpu at Riihilahti a small Outokumpu-type Cumineralization occurs in a rock assemblage that bears many similarities with the with the rock assemblage in the Viitaniemi (Punamäki)-Virvujärvi zone tackled above, and some to that in the Liperinsalo "dome". Alhough for its exposed area relatively small (1x1.5 km), diamond drilling data indicates the Riihilahti formation comprises a several hundreds of metres thick sequence of metagreywackes with intercalations of arkosic to quartz wackes in its basal and amphibolites and highly graphitic and sulphidic black schists in its top part. Similar to the black schists of the Viitaniemi (Punamäki)-Virvujärvi zone, the Riihilahti black schists are partly strongly metal anomalous, showing Ni, Cu, Zn and V contents akin to the Talvivaara metal-rich black schists in Kainuu. Though the nature of the lower contact of the Riihilahti package is not well known, it seems likely that the quartzose sedimants in its basal part would rest directly on an Archaean basement similar to that exposed immediately to the NW of Riihilahti at Varislahti (Vesanto, 1980).

Geophysical map images suggest that there would be more strata similar to the Riihilahti assemblage under the Lake Juojärvi immediately to the N of the Juojärvi basement dome and in the area west of Varislahti and Ohtaansalmi, and that the Riihilahti type assemblage could be in the SE traced as a zone of positive magnetic and electromagnetic anomalies along the E-shore of the Lake Juojärvi down to the isle Muuraissaaret, where a very strong positive magnetic and electromagnetic anomaly occurs, related to amphibolites, skarnoid rocks and black schists resembling those in Riihilahti. A few samples by GEOMEX from the amphibolites and skarnoid rocks of Muuraissaaret yielded also similar chemical compositions with the corresponding rocks in Riihilahti. In the NE from Riihilahti, a zone of skarnoid rocks and black schist occurrences of appears to run from Varislahti, in a position immediately below the Outokumpu Allochthon, via via Litukka and Saarivaata as far as to west of Miihkali, where thin layers in mica schists of skarnoid metabasites and metal-anomalous (Ni, Cu, Zn, V) black schists of the Lower Kaleva affinity have been intersected by exploration drilling.

#### The epicontinental sequences around the Juojärvi basement "cupolas"

The basement "cupolas" of the Juojärvi area, representing either in situ basement domes or windows of thrust slices, are surrounded by thin, from metres to some hundreds of metres thick, discontinuous layers of conglomerate and arkosic to feldsphatic quartzite overlain by a 0-200m thick layer with amphibolites and diopside+amhibole+ plagioclase±carbonate "skarns" (Huhma, 1975; Koistinen, 1993). We have noted that many of these "skarns" actually do represent calc-silicate altered metabasites while true carbonate rock-derived or carbonate rocks seem rare. Black schists and mica schists intercalate with the "skarns", and the whole association seems to grade into the overlying mica schists (metagreywackes). The strata around Juojärvi cupolas have traditionally been interpreted to "epicontinental", so-called marine Jatulian strata. In the lack of detrital zircon and Sm-Nd isotope data, this correlation must be considered debatable, however. Most importantly, there seems to be no discordance or tectonic break between the "epicontinental" sediments immediately covering the cupolas and the overlying thicker piles of metagreywackes. As the latter metasediments unlikely are "marine Jatulian", we consider also the underlying heterolithic assemblages rather correlate with either Lower or Upper Kaleva.

As an important aspect of the Kaleva in Heinävesi area, the cupola surrounding metagreywackes host in the area to the SW of Juojärvi, between Papinniemi and Karvio, thin but many kilometres long bands of amphibolite attached locally with minor conglomerates and

quartzites. These amphibolite layers have been considered tectonic slivers correlatable with the nearby cupola-fringing "epicontinental" amphibolites (e.g. Koistinen, 1993). There are, however, differences in the chemical compositions of the Papinniemi-Karvio amphibolites and basement cupola fringing amphibolites, that will be clarified below, and which make their direct correlation, if not unfeasible, at least debatable.

#### Synthesis

The Lower Kaleva in Kainuu has been interpreted to record the 2.0-1.95 Ga break-up of the Karelian craton. Starting from this interpretation, the relatively minor area and volume of the Lower Kaleva type lithofacies is an enigmatic feature. It may be explained, however, by assuming a combination of sediment-starved nature of the break-up and a much later tectonic removal of the more outer and more thinned parts of the rifted margin (Kontinen 2002). The tectonic removal could most naturally be addressed to strike-slip tectonics within the craton margin (passive margin), a most likely scenario if the 1.9 Ga docking of the Svecofennia to the Karelian craton was seriously oblique. In North Karelia any thicker volumes of possible 2.0-1.95 Ga syn break-up strata are found only in the parautochthonous Höytiäinen belt, which, however, comprises also Upper Kaleva type strata, but which is possibly representing autochthonous-parautochtonous strata of the inferred passive margin stage.

The Talvivaara type metal-rich black schists in the Lower Kaleva provide an important time marker as their deposition seems to only slightly precede the start of the Upper Kaleva type deposition and as they seem to have been deposited across the entire rifted margin. The presence of low-Ti tholeiites in their association in North Karelia (below) provides currently the only a clue to their timing. The obviously cogenetic and coeval metabasites in the "ophiolite" fragments in the Outokumpu Allochthon have been dated to ca. 1.96 Ga old (section 9.3.1.). However, if this date is taken as a proxy of the timing of the latest stage in the Lower Kaleva deposition, and if the deposition of the Upper Kaleva started just after 1.92 Ga as the presently available detrital zircon ages suggest, a considerable period of 40 Ma of nondeposition is indicated. We predict that this apparent cap will considerably narrow with more data from the various parautochthonous Upper Kaleva units.

Important in the context of this report is the rarity of evidence of either voluminous carbonate-rich or evaporite beds in the Lower Kaleva, and for the evaporites also in the older Jatuli-Sariola strata. There is thus little to suggest that these strata would have had a significant impact on either the  $CO_2$  or chlorine budget and metal complexing capacity of the Svecofennian regional fluids.

#### 6.1.2. Mafic rocks

#### Metabasites in the Lower Kaleva sequences

Metabasites at least in two main horizons appear to be present in the autochthonous to parautochtonous units below the Outokumpu Allochthon:

*LKB1 metabasites:* Examples of the lower horizon metabasites include e.g. amphibolites (sills, lava sheets, tuffs/tuffites) in the thin quartzite-dolomite-black schist successions in the Kaavi structure (e.g. at Tahasniemi-Retunen) and in the thin conglomerate-quartzite-dolomite-skarn fringes around the Juojärvi domes and in the immediately overlying mica schists (e.g. at Ranta-Kosula). These occurrences have been traditionally correlated with the "marine Jatulian". However, as we pointed above, the stratigraphy and timing of these units are yet poorly constrained and some aspects in the geology of the occurrences suggests rather Lower Kaleva, and in some cases (Tahasniemi-Retunen, Riihijärvi) perhaps even Upper Kaleva (shallow self) status. Geochemically the LKB1 metabasites seem to vary from medium Ti to relatively high Ti type tholeiites.

LKB2 metabasites: Examples of the upper horizon metabasites include e.g. amphibolites

in the quartz wacke-mica schist-black schist sequences in Riihilahti and Viitaniemi (Punamäki)-Virvujärvi and skarnoid metabasites in mica schists in the Heinävesi and Savonranta areas. Skarnoid metabasites intercalated in mica and black schists to the west of the Miihkali serpentinite complex and running from there towards Ohtaansalmi are further examples.

The LKB2 basites are associated with a correlation issue of crucial importance for tectonic interpretations of the Outokumpu Allochton. This issue stems from the close chemical similarity of the LKB2 metabasites to the supposedly extrusive basites in association with serpentinites in the Losomäki area, especially if the latter metabasites are taken to extrusives of a dismembered ophiolite assemblage (e.g. Koistinen, 1981; Vuollo and Piirainen, 1989). The problem is difficult as in Losomäki there occurs metabasites not only juxtaposed to or inside the serpentinites but also as intercalations in the local mica and black schists, as do compositionally very similar basites in the Lower Kaleva sequences of Viitaniemi-Virvujärvi and Riihilahti. Though this situation as such is by no means an obstacle to interpreting the Losomäki basalts as a part of an ophiolite assemblage, it is nevertheless a serious alternative to consider that at least part of the Losomäki metabasites would after all belong to the parautochthonous Lower Kaleva assemblage, and that their present close association with serpentinites would be only due to tectonic juxtaposition.

#### Type occurrences, field and geochemistry aspects

#### LKB1: Kaavi, Retunen and Riihijärvi

Several metres up to several tens of metres thick diopside-amphibolite intercalations occur in association of a thin sequence of quartzite, metacarbonate – calc-silicate metasediments and black schist in mica schists/gneisses in the are between Tahasniemi and Retunen ca. 3 km to the E of the Luikonlahti. Similar occurrences of thin diopside-amphibolite intercalations in mica schists are present also in the gneisses to the NE of Retunen-Tahasniemi between Lakes Retuisjärvi and Suuri-Kortteinen and further in the NE around Lake Riihijärvi. Unfortunately, a large component of late granite is present in this area hampering proper understanding of the stratigraphical relationships. It has been traditionally thought that these metabasites would represent either basic sills and/or volcanic intercalations in strata representing uppermost part of the Jatuli sequence ("Marine-Jatuli"), now in tectonic slivers detached from the basementcover interface. However, noting the biotite-rich, immature nature of the associated/intercalated mica schists/gneisses, more likely these metabasites, as in the case of Ranta-Kosula amphibolites in Heinävesi, do represent basaltic magmatism coeval with deposition of some facies of the Lower Kaleva, or maybe are correlative with the 2.06 Ga metabasites in the Siilinjärvi area. And, as we speculated above, it even is not excluded that the Tahasniemi-Riihijärvi metabasites would be younger than 1.95 Ga, and do in fact represent together with their host guartzite-dolomite-black schist-mica schists a previously unrecognised, either allochthonous or parautochthonous shallow water facies of the Upper Kaleva akin to the Jalkaaho Formation in Kainuu (cf. Laajoki, 1991; Kontinen et al., 1996).

The Retunen amphibolites are moderately to fairly magnesian (MgO=5.71-9.63 wt.%), medium-Ti (TiO<sub>2</sub> =0.92-1.45 wt.%) tholeiites. A relatively evolved, fractionated nature of these basites is evident in the light of their relatively low Mg# (44-66), Ni (81-119 ppm), Cr (81-119 ppm) and quite high Zr abundances (145-237 ppm). The three amphibolite samples analysed here from Retunen show all clear enrichment in LREE and MREE over HREE, with La<sub>N</sub>/Yb<sub>N</sub>=2.6-9.4 and Gd<sub>N</sub>/Yb<sub>N</sub>=1.4-2.4. The Retunen amphibolites resemble here the Ranta-Kosula LKB1 amphibolite from Heinävesi (below) and the presumably 2.2-2.1 Ga T1 tholeiite dykes from the Koli area (cf. Vuollo et al., 1992). The distinct negative Nb and Ti anomalies in the mantle normalised trace element patterns of the Ranta-Kosula amphibolite and Koli T1 dykes are not obvious in the Retunen amphibolites, however.

Metabasites in an apparently similar lithological assemblage than in Retunen are found abundant at Riihijärvi some 12 km to the N of Luikonlahti. The Riihijärvi metabasites are like those at Retunen fairly magnesian (MgO=7.21-7.75 wt.%) and of medium-Ti character (0.99-1.64 wt.% TiO<sub>2</sub>), but are significantly lower in Zr (49-75 ppm) and show nearly flat mantle-

normalised REE patterns with  $La_N/Yb_N=1.0-1.4$  and  $Gd_N/Yb_N=1.2-1.3$ . These are features the Riihijärvi amphibolites share e.g. with the  $1.965\pm0.01$  Ga T2 tholeiite dykes in the Koli area and the ca. 1.96 Ga E-MORB metalavas in the Jormua ophiolite complex (cf. Vuollo et al., 1992; Peltonen et al., 1996). This suggests that also the Riihijärvi basites were about 1.96 Ga in age and related to the inferred 1.98-1.95 Ga break-up of the Karelian Craton. However, more work in the field and labs with the Retunen and Riihijärvi occurrences must be done before the true tectonostratigraphic status of these rocks can be determined.

#### LKB2: Punamäki and Virvujärvi

In Punamäki-Virvujärvi area west of Juankoski there occur amphibolite intercalations in a Lower Kaleva type black schist-quartz wacke-greywacke (mica schist) sequence fringing and overlying (overthrust onto?) the Archaean lisalmi basement complex in the west. Correlation with the Lower Kaleva units in the Kainuu schist belt is strongly supported by the fact that part of the black schists at Punamäki are similarly high in Cu-Ni-Zn-V content and also quartz-wacke interbedded as the Talvivaara black schists in Sotkamo.

The metabasites in the Viitaniemi (Punamäki) and Virvujärvi occurrences are usually pervasively highly strained and do not preserve primary textures or structures, though an origin as pillow lava has tentatively been proposed for one particular amphibolite occurrence (O. Äikäs, pers. comm.). In the opinion of the first author of this report, nothing really conclusive evidence of autoclastic origin is visible either in this particular occurrence. Many of the Viitaniemi-Virvujärvi metabasites display pervasively metamorphosed (calc-silicate) carbonate-type alteration and have been previously mapped as skarns. In terms of the less mobile trace elements the "skarns" and associated more pure amphibolites are very similar, however, and both are clearly of metabasaltic origin being high in the distinctly basaltic elements like Sc (42.4-51.9 ppm), for example.

Surprisingly, the Viitaniemi and Virvujärvi metabasites show systematically the Losomäki type low-Ti, high-Mg basalt character - in spite of that they represent unquestioned intercalations (probable interbeds) in an obvious Lower Kaleva type metasedimentary assemblage! Accordingly, these metabasites are relatively high in MgO (6.29-10.20 wt.%), Cr (457-509 ppm) ppm and Ni (147-182 ppm), and very low in TiO<sub>2</sub> (0.30- 0.47 wt.%), Zr (16-21 ppm) and Y (16-19 ppm). Further Losomäki type characters of these metabasites include their low REE abundance level (Sm<sub>N</sub>=1.7-2.4) and depletion in both LREE and MREE with respect to HREE (La<sub>N</sub>/Yb<sub>N</sub>=0.21-0.54; Gd<sub>N</sub>/Yb<sub>N</sub>=0.51-0.65). And as for the Losomäki lavas, also in the case of the Viitaniemi and Virvujärvi metabasites, a positive rather than negative Nb anomaly are seen in their mantle normalized trace element profiles and values of their Nb<sub>N</sub>/La<sub>N</sub> ratios between 1.02 and 1.77. However, secondary mobility of LREE can be suspected on the basis of the relatively variable La<sub>N</sub>/Sm<sub>N</sub> between 0.53 and 1.11.

#### LKB1: Heinävesi, Ranta-Kosula

Thin layers of highly strained amphibolite and garnet-amphibolite are found in association with the conglomerates, quartzites, carbonate-skarn rocks and mica schists immediately covering the basement cupolas in the Juojärvi area. Most of these amphibolites probably are derived from sills intruded in the basement-cover interface but some may represent also lavas and/or tuffs. One sample from the latter lithotype from Ranta-Kosula was sampled and chemically analysed for this study.

The investigated Ranta-Kosula amphibolite (15-EPI-00) is relatively high in MgO (8.10 wt.%), intermediate in TiO<sub>2</sub> (1.09 wt.%) and REE (Sm<sub>N</sub>=49), shows strong enrichment in LREE (La<sub>N</sub>/Yb<sub>N</sub>=18.1) and has significantly fractionated HREE [(Gd/Yb)<sub>N</sub>=4.7]. The analysed sample is notably rich in P<sub>2</sub>O<sub>5</sub> (0.91 wt.%) and Zr (209 ppm). Very steep negative Nb and Ti anomalies are present in mantle-normalized trace element pattern, which may indicate heavy contamination by upper crustal material. Importantly, the Ranta-Kosula sample is very low in K<sub>2</sub>O (0.17 wt.%) and Rb (2 ppm) implying that it unlikely represents a mixed volcanic-epiclastic

tuffite. Thus the crustal contamination most probably is of pre-emplacement origin. The high Zr/Nb (24) and Zr/Yb (76) ratios of the Ranta-Kosula basite point to that the contaminant was in the presently underlying Archaean crust, which in eastern Finland has distinctly high average Zr/Nb and Zr/Yb (cf. Lahtinen, 2001). This interpretation is consistent with the low  $\epsilon_{Nd}$ (1950Ma) of -9.1 obtained for the Ranta-Kosula sample during this study.

#### LKB1(?): Heinävesi, NE of Karvio

A ca. 8 km long, narrow (mostly <400 m wide) thrust slice (?) of metabasites in Kalevian metagreywackes and black schists occurs with minor quartzite running from Karvio towards the NE (Koistinen 1993a, 1993b). Two amphibolitic samples from these metabasites, which usually show variably heavy calc-silicate type alteration were analysed here.

The two samples show moderate MgO (6.52-7.14 wt.%), TiO<sub>2</sub> (0.57-0.72 wt.%) and Zr (34-114 ppm) and flat mantle-normalised MREE (Gd<sub>N</sub>/Yb<sub>N</sub>=0.84-1.06) but are both clearly enriched in LREE (La<sub>N</sub>/Sm<sub>N</sub>=1.49-2.95). The one sample with higher LREE enrichment (3-EPI-00) shows mantle-normalized deep negative Nb, and TiO<sub>2</sub> anomalies while the other one (4-EPI-00) with less LREE enrichment has rather a positive Nb anomaly and is also depleted in Zr. This difference suggests the 3-EPI-00 would record pronounced crustal contamination akin to the above-discussed Ranta-Kosula sample 15-EPI-00, or then significant secondary element mobility. It is worth to note that Koistinen (1993, Table 3, sample 21) reports chemical data (XRF, GTK) for one skarnoid metabasite sample from Karvio. That this sample is much higher in TiO<sub>2</sub> (2.10 wt.%) and Zr (154 ppm) compared to the samples of this study, suggests that the Karvio amphibolites were of considerable petrogenetic variation.

Traditionally the amphibolites immediately fringing the margins of the Juojärvi basement "cupolas" have been correlated with the basite intercalations in the structurally (sratigraphically?) overlying metagreywackes, such as the amphibolites at Karvio, Papinniemi and Riihilahti, so that the latter would represent tectonic slices of the cupola fringes. While the Karvio metabasites somehow comply with this scenario, the drastic difference in trace element geochemistry and Sm-Nd isotopes between the Ranta-Kosula-Karvio and Papinniemi-Riihilahti metabasites (below) militate against their generation in a common magmatectonic setting and hence also their stratigraphic correlation.

#### LKB2: Heinävesi, Papinniemi-Lepikkomäki

About 3.5 km to the SE of the Karvio metabasite, between Lepikkomäki and Papinniemi, another narrow (mostly <300m) stripe of amphibolite and minor guartzite can be traced for ca. 10 km in metagreywacke-derived mica schists. Based on four analysed samples, these amphibolites have a distinct Losomäki type low-Ti, high-Mg basalt character. Accordingly, the amphibolites are high in MgO (8.96-11.60 wt.%), Cr (309-503 ppm) and Ni (120-151 ppm), and distinctly low in TiO<sub>2</sub> (0.28-0.38 wt.%), Zr (14-20 ppm) and Y (12-16 ppm). Also in term of mantle-normalised trace element patterns to the Losomäki metabasites is close; with the slight difference that the Lepikkomäki-Papinniemi amphibolites are a bit more depleted in MREE (Gd<sub>N</sub>/Yb<sub>N</sub>=0.48-0.54) compared to the Losomäki metabasites (Gd<sub>N</sub>/Yb<sub>N</sub>=0.74-1.03). In this respect, as overall the Papinniemi-Lepikkomäki amphibolites are very similar with the Punamäki-Virvujärvi and Riihilahti amphibolites (above). However, in a difference to Punamäki-Virvujärvi and Riihilahti assemblages, metal anomalous black schists are not known to accompany the Papinniemi-Lepikkomäki amphibolites. A point worth of note is that, for its NE part the Papinniemi amphibolite stripe is locally juxtaposed to serpentinites of the Outokumpu assemblage. However, this merely seems to be a tectonically introduced coincidence rather than an indication of genetical consanguinity.

#### LKB2: Outokumpu, Riihilahti

There are at least two types of LKB2 metabasites within the Riihilahti prospect. The one of these, called here as **RMB1**, comprises amphibolites and skarnoid-altered amphibolites of the Losomäki type low-Ti, depleted tholeiite composition, occurring with intercalations of Lower Kaleva-type metawackes in the upper part of the Riihilahti sequence. The other type, **RMB2**, includes major part the rocks reported as peridotites (in drill-core reports of Outokumpu Mining), hornblendites and garnet-cummingtonite rocks from within the Cu-mineralized domain of Riihilahti, there closely associated (intercalated) with the RMB1 type low-Ti amphibolites. The RMB2 metabasites differ from the RMB1 by their much higher TiO<sub>2</sub> (mostly >2 wt.%) and Zr (151-291 ppm).

#### RMB1: low-Ti amphibolites and tremolite-diopside skarns

The low-Ti RMB1 amphibolites at Riihilahti occur similarly as the Viitaniemi and Virvujärvi metabasites (above) as intercalations in an obvious Lower Kaleva metasedimentary sequence comprising but metagreywacke schists/gneisses also arkosic and quartzitic metawackes and highly Cu-Ni-Zn-V-anomalous (Talvivaara type) black schists. Being low in TiO<sub>2</sub> (0.39-0.45 wt.%), Zr (20-28 ppm) and Y (16-17 ppm) and high in MgO (7.06-12.00 wt.%), Cr (631-858 ppm) and Ni (214-233 ppm), the Riihilahti low-Ti amphibolites show remarkable compositional similarity to the serpentinite associated ("ophiolitic") low-Ti tholeiite basalts at Losomäki. As a minor difference compared to the Losomäki metabasites, the Riihilahti metabasites, like those from Viitaniemi-Virvujärvi and Lepikkomäki-Papinniemi as well, show slightly higher La<sub>N</sub>/Sm<sub>N</sub> (1.30-1.92) and lower Gd<sub>N</sub>/Yb<sub>N</sub> (0.67-0.84).

In Outokumpu prospect reports the principal host rock of the Riihilahti Cu-sulphides is named to tremolite-diopside skarn. The high Sc, V, Cr and Ni of the bulk of these "skarns" imply, however, that rather than carbonate-rich metasediments, most these rocks do in fact represent pervasively carbonated and then peak-metamorphically decarbonised "skarnoid" metabasaltic rocks similar to those common in association with amphibolites of e.g. Luikonlahti, Vehkalahti and Punamäki-Virvujärvi. The concentrations of more immobile trace elements (Ti, Zr and transition metals) in the "tremolite-diopside skarns being comparable with those in the low-Ti RMB1 amphibolites in the Riihilahti rock assemblage, we conclude that of the Cu-sulphide hosting "skarns" were derived from the RMB1 type low-Ti tholeiites. We note that calc-silicate altered metabasites, though not Cu-mineralized, are present also outside of the Riihilahti ore environment proper, e.g. in the large outcrops of low-Ti amphibolite E of the Riihilahti farmhouse at Pellavasniemi.

## RMB2: "peridotites" and garnet-cummingtonite rocks in association of the Riihilahti mineralization

The "peridotites" (variably spinel-olivine-amphibole-clinopyroxene-bearing chlorite-rich rocks) and garnet-amphibole (garnet-hornblende-cummingtonite) rocks in the Riihilahti ore environment form a problematic group of pervasively altered and metamorphosed rocks. Merkle (1982) interpreted the "peridotites" to mafic hydrothermally altered metaintrusive and metavolcanic rocks and the garnet-amphibole rocks mostly hydrothermally altered metasedimentary rocks. We in one stage interpreted part of the garnet-amphiboles to some variety of sedimentary iron formations, largely inspired by their high overall total iron content (Fe<sub>2</sub>O<sub>3</sub>t usually >20 wt.%) and sporadic high enrichments of magnetite, apatite and graphite, recalling that interbands with high P and/or C are common in the silicate iron formations (garnet-grunerite/cummingtonite) in the Lower Kaleva of Kainuu. However, the high Al<sub>2</sub>O<sub>3</sub> (usually 9.00-19.00 wt.%), TiO<sub>2</sub>, Sc and V abundances (below) even in the most Fe-rich Riihilahti "peridotites" and garnet-cummingtonite rocks actually do not support their origin as Fe-rich chemical metasediments but rather as altered basaltic rocks.

Nine of the eleven samples of the "peridotites" and garnet-cummingtonite rocks analysed for this study from Riihilahti have relatively high  $TiO_2$  (2.02-3.22 wt.%), Zr (151-249 ppm) and Nb (10-16 ppm). Two samples deviate by showing much lower  $TiO_2$  (0.48-0.68 wt.%) and Nb

(4.5-4.8 ppm), despite of the similarly high Zr (280-291 ppm). We will discuss the geochemistry of the usual high  $TiO_2$  stuff first, and then briefly the nature of the two deviating samples.

Relatively high Sc (30-58 ppm) and V (387-711 ppm) but low Cr (39-127 ppm) together with the high TiO<sub>2</sub> and Zr suggest an evolved basaltic protolith for the main part of the RMB2 type rocks. All the analysed samples coming from the sulphide-mineralised rock regime surrounding the Riihilahti "Cu-ore" proper, Ni shows high variation (30-711 ppm) and clear secondary enrichment in part of the samples. One of the most intriguing features in the RMB2 geochemistry is, that, though the "peridotites" and garnet-amphibole rocks are about similar in terms of their Nb, Zr, Ti, Sc and V abundances, the former are significantly higher in REE (Sm<sub>N</sub>=24.9-47.0) than the latter (Sm<sub>N</sub>=10.4-23.0). This is reflected in as very deep negative Nb, Ti, and Zr anomalies in the mantle normalized REE profiles of the "peridotites", much deeper than seen for the garnet-amphibolites (Fig. 4). We will comment the significance of this difference after first investigating the major element geochemistry of both these rock types.

The major element compositions of both the garnet-cummingtonite rocks and "peridotites" are typical of basaltic rocks in some stage affected by intense chlorite alteration. Accordingly, compared to typical unaltered basalt, the alkali element, CaO and SiO<sub>2</sub> concentrations are in these rocks very low, while MgO and especially total Fe are distinctly high. The much lower SiO<sub>2</sub> (23.9-28.3 wt.%) in the "peridotites" than in the garnet-amphibole rocks (43.2-47.9 wt.%) indicates the "peridotites" had suffered more intense chloritization. Importantly, the similar and relatively high Nb, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub> and Zr in bulk of both the "peridotites" and garnet-cummingtonite rocks imply they had a common protolith, which probably was a relatively evolved alkaline, Ti-Fe rich basalt. If this is true, then the much higher REE abundances in the "peridotites" must derive from secondary hydrothermal addition of REE, concurrent or subsequent to the inferred chlorite alteration. We demonstrate later in this report that most of the "ore" samples from the Riihilahti Cu-mineralization also show similar secondary hydrothermal REE enrichment.

As said above, two of the 11 samples collected us to represent the RMB2 turned out to be distinctly low in TiO<sub>2</sub>. Notably, these two samples are low also in Sc (20-28 ppm). Noting in addition that Th abundances in these two samples are much higher (12-16 ppm) than in the normal high TiO<sub>2</sub> RMB2 samples (0.89-3.97 ppm); we propose these samples would in fact represent pervasively altered, metasomatised wacke intercalations in the RMB2 sequence.

The genesis and alteration history of the "peridotites" and garnet-amphibole rocks at Riihilahti Cu-mineralization is clearly a complex, and, because of the high-T (upper amphibolite facies) peakmetamorphic overprint, difficult issue to study, remaining here largely unresolved. Proper understanding of the origin and alteration of these rocks would need more detailed sampling than was done for this study, including also of the correlative parts of the Riihilahti rock assemblage from outside the mineralized/heavily altered zone. Nevertheless, the combination of high Sc, V, Nb, Ti, Zr and P in bulk of the "peridotites" and garnet-amphibole rocks strongly suggests their derivation from, a probably alkaline, basaltic/gabbroic protolith. The high iron (partly as metallic iron!) and graphitic carbon abundances at the margins of the "peridotite" bodies (see Merkle, 1982) are an indication of that the chloritic alteration, or the subsequent metamorphism, was related with production of highly reducing fluids and development of local zones with steep redox gradients.

The inferred strong secondary REE (largely LREE) enrichment of the rocks hosting the Riihilahti Cu-mineralization, and the mineralised rocks themselves is an intriguing feature. Recalling that that similarly highly REE enriched rocks with similarly very steep negative Nb, Ti and Eu anomalies characterize also the metabasites in the "stringer" zones of the Outokumpu and Kylylahti deposits (cf. section 6.3.), it seems not too far-fetched to speculate that in all these cases the apparent REE mobility was concurrent and genetically linked with the hydrothermal processes responsible of the Co-Cu mineralization.

#### 6.2. Upper Kaleva metasedimentary assemblage

The following review of the Upper Kaleva metasediments is focused on the metaturbidites of the Outokumpu Allochton. However, much of the below should apply also to the suspect


Fig. 4. Mantle-normalized extended REE patterns of representative samples from the Riihilahti metachloritites ("peridotites"), garnet-cummingtonite rocks and low-Ti (LOTI) amphibolites. Note the enrichment in REE, especially in LREE, in the metachloritites.

parautochthonous counterparts as met around the Oravisalo-Liperi-Sotkuma or Heinävesi-Juojärvi basement domes or windows, for example. One interesting, and within NKSB unique aspect related to the parautochthonous (?) Upper Kaleva of the Oravisalo-Liperi-Sotkuma (Pyhäselkä) block is the spectacular Mulo type metacarbonate (tremolite±carbonate) rock along its eastern margin. Though often included in the Höytiäinen belt and considered "marine Jatulian" these metacarbonates actually seem to be intercalated by Upper Kaleva type wacke sediments and tectonostratigraphically be part of the Pyhäselkä block or slice. We note here that Mulo type metacarbonates occur also in Kainuu, e.g. immediately N of the Ristijärvi village, there within an undoubted Upper Kaleva lithoassemblage (unpubl. observations by A. Kontinen). Though the Mulo metacarbonates clearly are an important issue for understanding the depositional environment of the parautochtonous Kaleva, they are yet too sparsely documented for their stratigraphy and geochemistry to facilitate any palaeobasin analysis. We note that an origin of the Mulo metacarbonates as chemogenic sediments, perhaps partly evaporites, have been proposed by Ward (1987).

### 6.2.1. Greywackes and wacke pelites

As we pointed out above, the single most important sedimentological character of the Upper Kaleva is its remarkable monotonity, both in terms of modal/chemical composition and sedimentary lithofacies. At least 75% of the preserved total volume of the Upper Kaleva type strata in the NKSB consist of medium to fine-grained, mineralogically simple biotite + quartz + plagioclase schists (mica schists), which seem to derive mainly from immature mediumgrained, guartz-intermediate muddy sands deposited usually in 10 to120 cm thick tabular turbidite beds (Fig. 5). The bases of the mostly only weakly graded sand beds are usually sharp but rarely show grooving. In many outcrops the dominant lithotype is thus more ore less massive tabular sandy beds that rarely show higher Bouma units or fine-sediment interbeds. Furthermore, the wacke pelite interbeds, also in such lithofacies where they are relatively common, are usually relatively thin, often just 2-20 cm thick. Notably, also the interbedded metapelites are chemically immature, which is reflected in that they rarely contain aluminous porphyroblasts, not even there where the grade is definitely sufficiently high for their appearance, as e.g. in the terrane to the SW of Outokumpu. Where such porphyroblasts are present they are restricted largely to garnet±staurolite, while kyanite-sillimanite-andalusite are relatively rare.

No distinct local or regional trends in sedimentary features, such as e.g. for grain size or bed thickness, appear to be present – or at least have not been documented so far. It is important to note that coarse sands are rare, and conglomerates of any sort are apparently completely lacking. Therefore, and on the basis of their consistently mostly medium to thickly bedded, sand-dominated nature, it appears that the Upper Kaleva "monotonites" would >90% represent mid-fan parts of a very large-scale, and obviously deep-water turbidite fan complex, most probably one built up by relatively high density flows on an abyssal basin plain.

Geochemistry of the Upper Kaleva wackes has been recently studied by Glumoff (1987), Kontinen and Sorjonen-Ward (1991), Kohonen (1995) and Lahtinen (2000). A short summary and discussion of the results of these studies is introduced below.

The chemical data in above sources indicates that the Upper Kaleva wacke sands and shales show very homogenously relatively low CIA values mostly below 55 [CIA=chemical index of alteration=Al2O3/(Al2O3+CaO\*+Na2O+K2O), molar abundances]. Such low CIA values are consistent with the very rarity of alumina rich porphyroblasts in these metawackes, suggesting also just a low proportion of residual clays (kaolinite, illite) in the protolith wackes – wacke shales (Lahtinen, 2000). Compared to average early Proterozoic arc-related greywacke, the Upper Kaleva wackes consist of clearly mechanically more mature and evolved detritus, however. This is seen in the very tight plotting of both the sand and pelite samples along the "epiclastic sedimentary base line" in SiO<sub>2</sub> vs.  $Al_2O_3$  variation diagram, and moderately advanced differentiation in terms of the relatively large difference in  $Al_2O_3$  between the sands (11-15 wt.%) and shales (16-20 wt.%). That the compositional variation and hydraulic



Fig. 5. Photographs of sand-dominated Upper Kaleva metaturbidites forming the main lithological component in the Jormua-Outokumpu thrust belt. (A) A thickly to very thickly bedded metaturbidite from Pajukorpi, Paltamo. (B) A thickly to very thickly bedded metaturbidite at Karnukka 3 km SW of Polvijärvi.

sorting (Kontinen and Sorjonen-Ward, 1991; Lahtinen, 2000) is one expression of their high mechanical maturity.

As said above, the Upper Kaleva sands are systematically quartz intermediate with  $SiO_2$  for the majority being between 68 and 74 wt.%, while the intercalated wacke pelites show  $SiO_2$  mostly between 53 and 65 wt.%. The obvious cap in the  $SiO_2$  distribution (and  $Al_2O_3$  as well) reflects effective separation of sand-size quartz and feldspar from fine silt and clay in the course of the turbidite mass-flows. Lithic fragments in these mechanically evolved and reworked psammites probably were rare. In the fine sediment dominated layers a variable component from hemipelagic rain seems present, but there are absolutely no observations of chert or carbonate intercalations, for example. Horizons with abundant metacalcareous concretions of several types are relatively common, however.

Lahtinen (2000) argued that the graphite in the thick, solely psammitic bedsets in Upper Kaleva would be after carbonaceous matter recycled from contemporaneous nearshore, shallow water deposits. He saw evidence of this in the relatively low S/C ratios and low U and V in the graphite-bearing psammites, these features possibly pointing to fresh water or brackish water environments, and hence to likely deposition of the organic component initially near deltaic estuaries of large fresh water rivers. We agree with Lahtinen (2000) that the presence of carbonaceous material in the Upper Kaleva psammites is for large part by mixing from earlier carbonaceous sediments, but do not know any easy way to tell whether the material was cannibalised from intraformational black shale layers, or indeed ultimately derived and transported (partly/totally?) from possible black shales in the giant river estuarine-deltaic "middle-stores" that anyway must have existed to facilitate the remarkable compositional homogeneity of the Upper Kaleva psammites.

What comes to the redox conditions during the Kaleva deposition, it may be that effectively anoxic conditions prevailed only during the intervals of deposition of the thicker black schist intercalations. More probably, however, the usually low S/C ratios of the psammites do reflect oxygenated nature of the waters in the inferred estuarine-deltaic middle store environments and/or rapid piling up of the turbidites preventing significant sea-floor bacterial sulphate reduction. Moreover, from our experience S/C ratios from low-S samples based on XRF and Leco data (as in Lahtinen, 2000) are fairly unreliable, largely because of the high uncertainty of S determinations by either Leco or XRF for samples with less than ca. 0.1 wt.% S.

Wacke sand and shale samples comprising >0.1 wt.% S yield an average Se/S x  $10^6$  ratio of ca. 100, which is close to the estimated average of the post-Archaean upper continental crust (Taylor and McLennan, 1985). This suggests low component of hydrothermally, or in organic matter introduced sulphur-selenium. In comparison, the associated C-S-rich black schists usually have significantly higher Se/S x  $10^6$ , reflecting at least partly the tendency of Se, one of the essential nutrients, to be enriched in organic matter.

Sm-Nd isotope and detrital zircon age data define two likely major sources for the Upper Kaleva sands: 1) 2.80–2.65Ga late Archaean gneisses-granitoids, and 2) 1.92–1.98 Ga juveline early Proterozoic felsic-intermediate plutonic rocks (Huhma, 1987; Claesson et al., 1993). We note that there are some features in the geochemistry, such as the relatively high Ti/Zr that suggest a significant contribution also from a plateaux-basalt type source.

Being of mixed cratonic Archaean – juveline Proterozoic provenance, compared to average early Proterozoic, arc-related, volcanogenic greywacke (Condie, 1993), the Upper Kaleva sands are significantly lower in Al, Ba, Co, Cr, Fe, Sr and Ni, and to a lesser degree in LREE, while they are clearly enriched in Hf, HREE, Th, V and Zr. The strong effect of grain-size sorting is reflected in that the more shaly type interbeds are strongly enriched over the sands in Al, Cr, Fe, K, Mg, Nb, Ni, Rb, Sc, Ti, and V, that is, in elements that in rock weathering end up into the clay fraction. Despite the effective hydraulic sorting, the shales still remain notably high in Hf and Zr.

The dominantly coarse grain size and well-developed growth zoning typical of the 1.98-1.92 Ga zircons suggest that these zircons originated in deep-seated, slowly cooled plutons in a relatively thick crust. Therefore, unlike Lahtinen (2000), who proposed that the dominant Proterozoic component was form low-K, felsic–basaltic rocks of a primitive volcanic arc, we believe that the Proterozoic source featured, if an arc was involved, rather a mature, probably continental arc.

Referring to Lahtinen (1994) and Kohonen (1995), Lahtinen (2000) proposed that the deposition of Upper Kaleva was in a foredeep basin developed between an obliquely colliding primitive arc (the middle Finland primitive arc of Svecofennides) and the Karelian craton margin, and that the source of the ultimately arc-derived 1.98-1.92 Ga detritus was either from an accretionary prism within the collision zone or a more distal orogenic source. We think, however, that sediments deposited in such a tectonically active environment would be more varied in terms of their sources, intercalated rock types, bed-thicknesses, grain-sizes etc., and comprise a greater proportion of debris-flow and sediment-slide type deposits than what we see for the Upper Kaleva. We further argue that a to large delta middle-storing material carried by a large-continent giant river system was a necessary prerequisite for the extreme compositional homogeneity of the Upper Kaleva material – a truly remarkable feature noting the extremity of the two main sources, one an Archaean craton and the other in a juveline 1.98-1.92 Ga plutonic crustal domain.

It is to be noted also that the Upper Kaleva comprises, but obvious continental rise, also shallower, obviously deep self-type units, both in North Karelia and Kainuu, examples of them being e.g. the Kuhnusta (LA5) and Jalka-aho formations (Kohonen, 1995; Kontinen et al., 1996). In summary, we find a passive-margin type setting, as proposed by Kontinen and Sorjonen-Ward (1991), the most likely palaeotectonic scenario. A possible modern analogy for the Upper Kaleva palaeobasin might be provided by the thickly (10-25 km) turbidite-covered, 3000 km long and 1000 km wide Bengal Bay, receiving turbidite flows from the large estuarine-deltaic depositories at the mouths of the Ganges and Brahmabutra rivers, the deltas middle-storing materials eroded and transported from the mightly Himalayas and lesser degree Indian shield (e.g. Curray, 1994).

The actual source of the 2.0-1.92 Ga isotopically juveline plutonic component in the Upper Kaleva metasediments remains enigmatic, as no suitable source seems to exist within the frames of the Fennoscandian shield (cf. Vaasjoki et al., 2003). One option is that the source was in some of the voluminous 2.0-1.92 Ga plutonic-volcanic arcs now found as part of the Ukrainian Shield (Claesson et al., 2001, and references therein). The obvious enrichment of the Upper Kaleva wackes in plateaux-type basaltic material may reflect the high abundance of dolerite dyke swarms and related basalt sills/floods in/on the Early Proterozoic shields at 2.0-1.9 Ga.

Finally, on most diagrams for chemical discrimination of tectonic setting of sand deposition, the Kaleva sands plot as sands of mature continental arc environments. It must be noted, however that, for many reasons, these diagrams is only of speculative value. As a warning example: modern sands from the Argentinean costal turbidites would in such diagrams also plot as continental-arc related sands, in spite of that they actually rest on the passive margin to the South Atlantic Ocean. The closeness of the Andean arc, relatively short transport and relatively cool climate together yield the continental arc chemical signature for the Argentinean sands. When dealing with Precambrian, there is an additional concern about that the sand discrimination criteria based on modern/Phanerozoic examples may not be straightforwardly applicable at all. This because of the considerable secular change in several of the important factors, such as in the nature of vegetation cover on continents, and composition of Earth's atmosphere and hydrosphere.

### 6.2.2. Black schists

## Black schists and the Outokumpu assemblage, stratigrapical aspects

The Outokumpu rock assemblage has traditionally been understood as a specific layer of metasedimentary black schists, carbonate rocks and quartz rocks (metachert, quartzite) in the basal part of the "flysch" facies of Kaleva, enclosing serpentinite lenses that represent either igneous intercalations or "cold" tectonic blocks (cf. e.g. Väyrynen, 1939; Peltola, 1960;

Koistinen, 1981; Park, 1988, 1992; Loukola-Ruskeeniemi, 1999). Impressed by the high sulphide and metal enriched contents of the black schists, many workers have proposed a syngenetic, synsedimentary relationship of the Outokumpu type sulphide ores and the black schists in their host associations (e.g. Peltola, 1978; Koistinen, 1981; Park, 1988, 1992; Loukola-Ruskeeniemi and Heino, 1996; Loukola-Ruskeeniemi, 1999).

Based on detailed structural studies around Outokumpu and Vuonos ores Koistinen (1981) presented the following model for the stratigraphy of the Outokumpu assemblage:

Top Mica schist: thickness unknown. Black schist: 20 cm-several metres. Carbonaceceous quartzite: few centimetres to several metres-Keretti; few centimetres-Vuonos. Ore Carbonaceous quartzite: few centimetres to over 1 m; absent in parts; low-grade mineralization in parts. Quartzite with layers of skarn: possibly 20 m maximum. Serpentinite: about 200 m Quartzite with skarn: metres to few tens of metres Black schist ------- major tectonic break Mica schist: thickness unknown Base

Koistinen (1981) inferred that the serpentinites in the Outokumpu sequence originally formed "a one (discontinuous) unit whose maximum thickness may have been 100-200 m". He (1981) further stated that "apart from variations in thickness, this succession has been found to be consistent in the case of both Vuonos and Keretti ore bodies", and "the original ore layer must have been strata-bound and largely contained within (and towards the top) of carbonaceous quartzite. In places its top is against black schist or even intercalated within it in parts of the north western margin of the Keretti ore body."

The relationship of the black schists and serpentinites in the Outokumpu rock association is a key guestion to understanding the tectonic environment of the black schist deposition and serpentinite emplacement as well. Koistinen (1981) interpreted the Outokumpu-Vuonos serpentinities to fragments of mantle peridotites representing "remnants of an ocean floor". We agree to this interpretation but, as we pointed out already earlier, interpretation of the serpentinities to mantle fragments would be reasonable only if a fundamental tectonic break is assumed in the stratigraphic sequence (at least) immediately below the serpentinite-bearing horizon. This must be assumed because mantle fragments cannot emplace among metasediments by any other means but as tectonically emplaced solid bodies. A model that would imply least modification to the stratigraphic model of Koistinen (1981) would presume emplacement of the serpentinites as large olistholithic blocks that were sliding in the basin explicitly during the major black schist deposition event(s). The very rarity of typical melange or olisthostrome features in the Outokumpu black schists, and in the Upper Kaleva overall, render the synsedimentary gravitational emplacement of the serpentinite massifs less plausible, however. The emplacement mechanism and tectonic environment of the mantle blocks among the black schists and the deposition of latter remains a great enigma. We speculated above that the black schists represented a specific layer in the presumably abyssal Upper Kaleva turbidites in which serpentinites were mixed by post-depositional transfrom fault tectonic processes.

Park (1988, 1992) has proposed a quite different model from that of Koistinen (1981) for the origin and stratigraphy of the Outokumpu assemblage. Namely, he interpreted the Outokumpu serpentinites to saxonitic-dunitic sills in the Outokumpu assemblage, which he considered a metasedimentary unit of black schists; carbonate rocks and cherts (Fig. 6).



Fig. 6. Schematic internal stratigraphy of the Outokumpu assemblage in the Outokumpu area as presented by Park (1988).

The evidence of Park (1988, 1992) for the magmatic sill emplacement of the Outokumpu peridotites was based on interpretation of the olivine-carbonate rocks (Papunen, 1987; Säntti, 1996; Säntti et al., in press) in the Outokumpu assemblage to hornfelses of carbonate rocks along contacts of a hot-intruded sill. However, as we will show below (cf. chapters 7.1. and 7.4.), the metasomatic carbonate rocks in the Outokumpu assemblage do not represent sedimentary carbonate rocks but altered peridotites, and the Outokumpu serpentinites not magmatic saxonites (harzburgites)-dunites but residual mantle peridotites.

Most importantly, the ubiquitous presence of typical Upper Kaleva greywackes as intercalations in the Outokumpu type sulphidic black shales (OBS) at Outokumpu, Kylylahti and elsewhere (Peltola, 1960; 1968; this study), are an incontestable evidence of that their deposition was specifically an Upper Kaleva event. Chemical and isotope chemical evidence, which we will present below, confirm the Upper Kaleva nature of the terrigenic component in the OBS. This is a very important constraint considering the often-proposed correlation of the OBS with the Talvivaara-type metal-rich black schists in Kainuu (e.g. Mäkelä, 1981; Loukola-Ruskeeniemi and Heino, 1996; Loukola-Ruskeeniemi, 1999), which however show a clear affinity to the Lower Kaleva (below).

### Lithofacies of the Outokumpu black schists

Since the pioneering work by Peltola (1960) no comprehensive study of the black schist lithofacies in the Outokumpu area has been introduced. Peltola (op cit.) divided the black schists in three main types: 1) argillaceous, 2) calcareous, and 3) arenaceous blacks schists. Argillaceous in this division was used for micaceous black schists "resembling clayey sediments in composition", calcareous for amphibole-rich (tremolite-actinolite) black schists, and arenaceous for quartz-rich black schists. We note that Peltola (1960) considered the graphite-richest Outokumpu-type quartz rocks as a subtype of his arenaceous black schists. Loukola-Ruskeeniemi (1991, 1999) considered all Outokumpu-Kainuu schists containing >1 wt.% graphitic C as a black schists, and divided them based on Ca content into two groups:

"Ca-poor" black schists with  $\leq$  3.13 % Ca, and "Ca-rich" black schists with  $\geq$  3.13% Ca. In the latter group she recognised two main subtypes, tremolite-rich black schists and black calc-silicate (tremolite±diopside) rocks. In drill core reports of Outokumpu Mining various blacks schist types, as for instance, "sulphidic black schists", "skarn black schists", "black tremolite skarns" etc. are commonly recognised, but because of inconsistencies in the classification and naming practices, these data are difficult to apply in lithofacies mapping, either in local or regional scale.

Our observations during this study suggest that more detailed lithofacies classification and mapping of the black schists of the NKSB than those in Peltola (1960) and Loukola-Ruskeeniemi (1991; 1999) would be possible and desirable. In local and regional scale, there clearly are several distinct lithofacies among the OBS differing in terms of such features as sulphide-lamination (Fig. 7), P-C-rich bands (Fig. 7), metacarbonate intercalations, coarse wacke intercalations, or dominant sulphide species (pyrite-pyrrhotite), metal-enrichment pattern etc. We recognize that a better understanding of the OBS lithofacies could be very useful in terms of constraining not only the tectonic environment of the OBS deposition, but also the emplacement environment and mechanisms of the associated mafic-ultramafic massifs. However, any approach to systematic classification and mapping of the OBS for their lithofacies would clearly have been out of the resources available for the research within the GEOMEX, and was therefore not even attempted.



Fig. 7. Scanned images of relatively "lowly" metamorphosed and strained sulphide rich black schists of the Outokumpu area. (Left) Pyrite rich black, schistose metamud, Oku-779/384, Kylylahti. (Middle) Pyritic black metamud with thin, dark, P-C rich bands, Oku-794B/554.05, Kylylahti. (Right) Pyrite laminar metamud with quartz breccia veins, Oku-864/112.50, Kylylahti. The slabs are 30 mm wide, except the left sample 40 mm.

### Previous study

Owing to the generally close spatial association of the Outokumpu type ores with heavily sulphidic black schists, the OBS, especially their geochemistry, have been subjected to relatively many studies (e.g. Peltola, 1960, Loukola-Ruskeeniemi, 1991; Loukola-Ruskeeniemi; 1999). In the discussion and conclusion chapters most of these studies have ended up to models of cogenetic origin for the Outokumpu type ores and the OBS, but frequently with relatively little hard evidence of such a relationship in the data chapters. Instead, lead isotope studies have yielded strong contrary evidence (M. Vaasjoki, in Haapala et al., 1986, p. 64). The most recent model in which syngenesis of the Outokumpu type ores and black schists has been proposed, is by Loukola-Ruskeeniemi (1999). In this model the Outokumpu ores are considered to represent deposition from the same hydrothermal fluids that propelled the metals in the neighbouring black schists, but in a later stage of the hydrothermal system, below an impermeability cap of previously deposited thick layers of metal- and sulphide-enriched black schists. Loukola-Ruskeeniemi (1999) further proposed that the serpentinites in the Outokumpu association would represent tectonic intrusions, which emplaced subsequent to the black schist and ore deposition events, and that therefore the association of the ores with the serpentinites was entirely fortuitous. Statistically taken this proposal sounds odds, however, as all but one of the presently known 11 Oku-type Co-Co-Zn mineralizations are found in close association with Outokumpu-type serpentinite and/or metasomatic carbonate-skarn-guartz rocks, and not a single one confined exclusively to black schists. The one deviating deposit, the small stringertype mineralization at Riihilahti, sits in altered mafic magmatic rocks and wackes, showing actually fewer tie-ups with black schists than some of the 10 serpentinite-flanking deposits.

However, concentrations of most metals in Outokumpu black schists are highly elevated if compared to average metal concentrations in the Earth's upper continental crust or in greywackes and shales (Table 1). Adding to this the wide areal distribution and considerable thickness of the black schists horizons in North Karelia, they are seen to form a huge reservoir of all the metals that occur in the Outokumpu type ores. Therefore, any serious investigation of the genesis of the Outokumpu ore type simply must evaluate the possible connection of the metal enrichments in the ore and usually associated black schists. Moreover, even if found unrelated to the ore formation, proper understanding of the nature and causes of the metal enrichment in the black schists would anyhow help us to constrain better, more relevant Outokumpu models.

As said above, within the GEOMEX research only limited resources could be directed to the study of the OBS, and hence only a few representative black schist samples became analysed during the GEOMEX. But there are about 3000 whole rock XRF analyses of the OBS in the databases of the Outokumpu Mining, mostly from drill core from inside and close to the mineralised environments at Outokumpu, Perttilahti and Kylylahti. One could assume that this large number of data, especially as they are mostly for ore-prone prospects, should easily reveal if there was any type of syngenetic connection between the metal enrichments in the black schists and the ores.

Applying the Outokumpu XRF data has its problems, however. First, the data has been acquired during a long period of time using varying analytical apparatus and procedures, which means considerable secular variation in analytical calibrations and other quality aspects. Second, just a relatively restricted number of trace elements were included in the Outokumpu XRF. Although these facts seriously limit the usefulness of the Outokumpu XRF data, the metals important in Outokumpu ores are most included, and there are complementary data available from the GTK and literature sources to broaden the analysis and discussion.

#### Study material

The XRF data provided to GEOMEX by Outokumpu Company for the GEOMEX study area comprise 3065 whole rock analyses for rocks sampled as black schists. Most of these samples were analysed also by AAS for base metals. In order to study this data, it was first retrieved from the tables holding the Outokumpu XRF and AAS data into a single large MS-Excel sheet. After removing data for the Riihilahti prospect, the remaining data were found to come >95% from unambiguous monotonite related black schists, with a heavy bias to the so-called Outokumpu belt, most samples representing the Perttilahti and Kylylahti prospects.

The resultant sample set was then screened for obvious miss-classified (serpentinites, mica schists, skarns, quartz rocks, etc.) or otherwise problematic samples, as e.g. samples reported with totals greatly exceeding 100 wt.%, samples with data for one or two elements only, etc. As a further screening measure, all samples with either MgO or CaO abundances over 20 wt.% were rejected, to exclude obvious carbonate-skarnoid rocks. Samples with particularly high Cr ( $Cr_2O_3 > 0.2$  wt.%) became also rejected because most of those samples were found to come from black schists at serpentinite contacts, and their high Cr contents thus likely to reflect strong secondary, metasomatic interaction with the juxtaposed serpentinites. In addition, samples with

over 1 wt.% Cu were also rejected as such samples were noticed to come exclusively from black schist layers inside or next to Cu ore bodies, which have been observed to record rather secondary "ore influence" than primary metal concentrations and ratios (cf. Huhma and Huhma, 1970). The high Cu threshold used means that samples recording some lesser secondary ore influence probably still remain among the accepted samples.

The above screening procedure resulted in a set of 2957 black schist samples all analysed for major elements (XRF) and most for a varying set of trace elements (XRF+AAS). The total length of core included in the 2957 samples is 8535 metres. Assuming an average core diameter of 30 mm, half split core, and average rock density of 2.75 kg/dm<sup>3</sup>, the 2957 samples had a total weight of about 33200 kg.

The average sample length is rather high, 2.89 m (range: 0.10–15.20 m). This means, considering the turbiditic, interbedded sand-silt-mud nature of the Outokumpu area black schists that only a small proportion of the 2957 samples is likely to represent clean black muds, much less clean black shales. Instead most of the samples probably do represent muddy carbonaceous (now graphitic) sands with a varying proportion of carbonaceous, black mud to shale interbeds. It has to be noted, also, that there undoubtedly was variation in what was classified to black schist among the many geologists that were logging/sampling the core. The usual criteria to consider a rock as black schist appear to have been its black or dark grey rock colour, taken as an indication of an elevated graphite and sulphide content, and its assumed primarily fine grain size. Unfortunately, only a few (<200) of the ca. 3000 samples have been analysed for graphitic carbon (or carbon overall). That few data that is available suggest that most of the 2957 samples accepted here as black schists would contain over 2 wt.% graphite-bound carbon.

It must be noted, also, that the dataset comprises analytical data from a period of several tens of years, implying that various types of crushers and pans have been used in sample preparation, likewise varying analytical equipment, standardisation and calibrations in the chemical analysing. Scrutiny of the data using scatter plots shows that there are features in element-element distributions that clearly stem from secular variations in the analytical procedures and calibrations, and which make application of statistical methods difficult. References to element-element correlations in the following text are based partly on calculated Pearsson correlation coefficients, and partly on visual estimation from graphical element-element plots.

In spite of the many sources of uncertainty, the whole sample set yields for most of the

Table 1. Chemical composition of Outokumpu, Talvivaara and Bazhenov black schists and shale										
	Outokumpu		0054				Talvivaara		Bazhenov	1 (0 <b>T</b> 9
	OKU dataset		GSF-	L-R <sup>ou</sup>	L-R <sup>oo</sup>	L-R°°	L-R&H	KL-R&H	G&Z°	V&I°
	n	median	median	median	median	median	median		average	av. black5
			11-0	Ca<3.13%	Ca>3.13%	all	INI≤0.1%	INI20.1%		snale
SiO2	2957	52 30	47 75	51 18	47 86	48 95	45 82	43.38	55 67	
TiO2	2957	0.51	0.60	0.38	0.58	0.52	0.36	0.34	0.53	0.33
AI2O3	2957	12,10	11,25	11,70	11,32	11,48	11,97	10,76	11,19	13,23
Fe2O3t	2957	11,12	15,25	14,78	10,13	12,17	12,93	15,61	4,93	2,86
MnO	2957	0,05	0,05	0,05	0,06	0,06	0,31	0,31	0,03	0,02
MgO	2957	6,05	4,34	3,47	6,78	4,10	2,80	2,97	1,33	1,16
CaO	2957	4,22	3,66	2,29	6,63	4,48	1,62	1,93	2,21	2,10
Na2O	2957	1,14	1,13	1,42	1,36	1,37	0,63	0,36	1,28	0,94
K2O	2957	2,65	2,74	2,67	2,11	2,49	3,43	3,70	2,18	2,41
P2O5	2957	0,14	0,12	0,13	0,15	0,14	0,14	0,18	0,25	
S	2299	7,36	8,25	7,10	5,00	6,00	8,90	10,40	2,83	
Ctot	143	6,09	8,54	7,40	7,00	7,20	7,70	7,80	8,00	3,20
Co	2024	22	26	25	20	20	50	170	22	10
Cr	2924	(270)	1/2	105	30 115	110	140	1/0	23	10
	2342	300	278	280	340	328	610	1200	136	70
Ni	2369	390	270 454	380	380	380	380	2270	192	50
Sc	2000	000	16 7	15	16	15	15	20	16.4	10
V	49	490	592	540	655	563	740	675	461	150
Zn	2369	1610	1830	1460	1500	1495	2370	5340	659	<300
Ва	2943	(530)	351	350	320	338	330	230	320	300
Hf			2,8							
Nb			7,3						7,3	
Rb	49	50	89						90	
Sr	2943	120	77	80	140	110	70	60	248	200
Th	49	(12)	6,5	8,5	8	8	8	6	6,3	
U	49	18	15,2	16,5	24	17	16	20	35,7	
Zr	2943	110	118	105	105	105	100	85	148	70
Y	49	30	30	25	35	33	20	25	24	30
la	49	20	21.1				35	30	27	30
Ce	49	40	39.1	50	48	50	38	18	53	00
Pr			5.32							
Nd			20,6							
Sm			4,51						6,3	
Eu			0,97						1,34	
Gd			4,88							
Tb			0,76						0,89	
Dy			4,36							
Ho			0,90							
Er T			2,66							
Im			0,41						0.00	
YD			2,75						3,23	
Lu			0,43							
Aa	894	3.9	<1	<1	<1	<1	1	1	1.2	<1
As	2554	100	81				•	•	45	
(daa) uA			2.1			3.8*	18	9	4.2	
Cd			12,8				15	15	14	
Мо			89	50	55	55	60	50	123	10
Pb	2369	30	36	<14	<9	<14	38	55	16	20
Pd (ppb)			23,9			14.1*	30	20		
Sb			0,76						6,9	
Se	7	15	9,4	<1	<1	<1	18	22	27	
Cu/Zn		0.10	0 15	0.10	0.00	0.00	0.26	0.00	0.01	
Co/Ni		0,19	0,10	0,19 0.00	0,23 0 08	0,22 0 08	0,20 0.13	0,22	0,∠1 0.12	
00/14		0,00	0,00	0,03	0,00	0,00	0,10	0,07	0,12	

Major elements in wt%, trace elements in ppm except Au and Pd in pp

Fe2O3t = total iron as Fe2O3, Ctot = total carbor

Analyses by XRF and AAS (Ag, Co) in Outokumpu Mining (values in parentheses of suspect accurac

<sup>4</sup> Analyses by XRF, GFAAS (Ag, Pb, Sb, Se) and ICP-MS (Au, Co, Cr, Hf, Nb, PGE, REE, Th, U) in GTK

<sup>34</sup> Median of medians for low-Ca black schists P9-P17 in Table 3 in Loukola-Ruskeeniemi (199

" Median of medians for high-Ca black schists P9-P17 in Table 4 in Loukola-Ruskeeniemi (1999

\*\* Median of medians for blacks schists P9-P17 in Tables 3 and 4 in Loukola-Ruskeeniemi (1999

\*a Median of "barren" (Ni<0.1%) black schists, Tables 3 and 5 in Loukola-Ruskeeniemi and Heino (199

" Median of Ni-rich (Ni>0.1%) black schists, Tables 3 and 5 in Loukola-Ruskeeniemi and Heino (1990

<sup>3</sup> Average of Bazhenov black shales, Table 5 in Gavshin and Zakharov (199

<sup>°</sup> Average black shale, Table 1 in Vine and Tourtelot (1970

analysed elements average and median compositions that are reasonably close to those reported by Peltola (1960), and what can be calculated on the basis of the data in K. Loukola-Ruskeeniemi (1999) (cf. Table 1). To complement the relatively restricted spectra of elements routinely analysed by Outokumpu, analytical data for REE and some other trace elements available from GTK and from Loukola-Ruskeeniemi (1999) has been utilised in the following discussion.

### Geochemistry of the characteristic elements in the OBS

Compared to average Upper Kaleva metagreywacke (WK1, Lahtinen, 2000) but also average (Phanerozoic) black shale (Vine and Tourtelot, 1970), the OBS are strongly enriched in C, S and most metals as e.g. Ag, Au, As, Co, Cu, Mo, Ni, V, Se, Zn, U (cf. Tables 1, 3). Metal enrichment in black shales is generally addressed to preconcentration from "normal" seawater in the contained planktonic organisms (by their mediation or absorption on their dead bodies), absorption onto clay particles, co-precipitation with sulphides under anoxic conditions or post depositional anoxic diagenetic processes. In some rare occurrences also metalliferous hydrothermal fluids may have been of importance (e.g. Pasava et al., 1996; Steiner et al., 2001). For some highly Ni-PGE-enriched black shales input from major meteoritic impacts has been proposed. In the following sections we will try to characterize the nature of the clastic component and the source of metal enrichment in the OBS.

In the following discussion we start from the premise that the OBS would have preserved their primary syngenetic-diagenetic geochemistry relatively unmodified. The real effect of the amphibolite facies metamorphism is difficult to know, however, since no comprehensive studies on the metamorphic element mobility in the OBS or comparable sulphidic black schists have been published. Nevertheless, we believe that reasonable deductions of the nature of the clastic material and also metal enrichment in the OBS can be made.

### Major elements

Major element distribution in black muds/shales is controlled mainly by mineralogy in the clastic silicate component and hydraulic sorting. So that from major elements Si, Na and Ca are dominantly in quartz and feldspars (sand and silt fractions), whereas Al, Fe, Mg, K and Ti have a greater affinity to sheet silicates (clay minerals, chlorites and micas). Part of the Ca and Mg may locate in clastic and/or chemically precipitated carbonates. In addition, variable amounts of diagenetic silica, carbonatic concretions (Mg and Ca) and syngenetic-diagenetic sulphides (Fe and S) may be present.

The relatively high SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and Na<sub>2</sub>O abundances in the average OBS composition indicate presence of a relatively abundant, feldspar-quartz-rich clastic component. Notably, elements with low solubility in most geological waters (like ocean and weathering waters) are present in the OBS in the same ratios as in the Upper Kaleva wacke-shale composite WK2 by Lahtinen (2000). Cr/Th, Sc/Th, TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios (Table 2), for example, indicate that the clastic component in the OBS would have about the WK2 composition (and possibly also source). This allows us to use the WK2 as a proxy of the clastic component in the OBS.

The significant positive correlation of Na<sub>2</sub>O with Zr in the OBS indicates control of Na<sub>2</sub>O Table 2. Ratios of immobile elements in average OBS and WK2.

	OBS	WK2	
Cr/Th	13,75	14,78	
Sc/Th	2,00	2,21	
TiO2/Al2O3	0,04	0,05	

mainly by feldspar. Na<sub>2</sub>O and Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> vary greatly from <0.2 to 2.8 wt.%, and <0.02 and 0.2, respectively, but without clear correlation with Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>. Thus variation in Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> seems to reflect rather variation in the feldspar/quartz ratio in the clastic input than variation in

framework/sheet silicate ratio by sedimentary sorting. The OBS have median Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio of 0.09, which is intermediate between the 0.18 in the Upper Kaleva wacke pelites (WK2) and about 0.06 in average shales. This indicates a significantly more weathered source for the OBS than for the bulk of the Upper Kaleva wackes. K<sub>2</sub>O in OBS correlates positively with Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> ratio and hence was clearly associated with the sheet silicate dominated clay fraction (probably mostly illite). The average K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio in OBS is about the same 4.5 than in the Upper Kaleva wackes and also in the average upper crust.

Ca, Mg and Fe in the OBS are all present in relatively high abundances. Element/Al<sub>2</sub>O<sub>3</sub> ratios suggest total flux of all these three elements significantly over that what was present in the WK2 type clastic flux. The excess Ca, and Mg may have been introduced as clastic carbonate, by syngenetic chemical precipitation of carbonate, or diagenetic addition of carbonate (recycling). Constraining of the nature Ca, Mg enrichment in the TBS is difficult due to the extensive low amphibolite recrystallization that renders petrographic study largely pointless. Loukola-Ruskeeniemi (1999) has proposed that the increased Mg and Ca in OBS partly reflect metasomatic addition from the nearby serpentinites. This phenomena is certainly of local importance but cannot explain the universal Mg and Ca enrichment in the OBS. Overall the OBS show a positive correlation of CaO/Al<sub>2</sub>O<sub>3</sub> ratio with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, which trend is displayed also by the occasional metacarbonate intercalations in the OBS and could indicate periodical mass-flows enriched in carbonate and quartz clasts, or alternatively, diagenetic silicification of carbonate interbeds. It may be of importance that under pervasively anoxic conditions generation of HCO<sub>3-</sub> by sulphate reduction prevents carbonate dissolution. Therefore, the relatively high CaO and MgO in the OBS could reflect both higher flux of clastic carbonate and better preservation of carbonate compared to Upper Kaleva wackes, which according (Lahtinen, 2000) have deposited under relatively oxygenated conditions.

Much of the geochemistry of Fe in the OBS is related to syngenetic and diagenetic sulphide precipitation. Thus geochemistry of Fe will be discussed further together S in a later section.

## <u>Carbon</u>

There is little doubt about that graphitic carbon in Precambrian black shales is usually after degraded organic tissues (Schidlowski, 2001). The content of organic matter in black shales (originally sapropelic muds) reflects primary organic production, sedimentation rate (dilution by clastic material), and perhaps most critically, preservation during diagenesis and subsequent burial-metamorphism. Reducing conditions during deposition and diagenesis combined with slow sedimentation rates are factors that commonly are thought to enhance preservation. Organic productivity and oxygen depletion during deposition are likely to be linked phenomena, since high productivity would rapidly deplete oxygen in the basinal waters. High organic production requires high flux of nutrients that might be expected to require sufficient basinal circulation and water exchange; the latter requirement meaning that black shale intervals are not necessarily indicative of long-standing slack-water periods.

The median  $C_{tot}$  content of 7.4 wt.% (mostly graphite) in the OBS is significantly higher than in most Phanerozoic black shales (median  $C_{org}$  3.2 wt.%, Vine and Tourtelot, 1970) but comparable to that of many oil-source Phanerozoic black shales such as the Kimmeridge Clay (4.4 wt.% TOC on average, but up to >30 wt.% in most organic rich layers) in the North Sea area and Bazhenov black shale (8 wt.% TOC on average) in Western Siberia (e.g. Wignall, 1994; Gavshin and Zakharov, 1996; Tribovillard et al., 2004). In the following discussion we will compare the OBS mostly with the Bazhenov black shale, which is geochemically in many respects remarkably similar with the OBS, and for which a covering, high quality geochemical data set is available (Gavshin and Zakharov, 1996).

The Volgian (Jurassic) Bazhenov shale covers an area of more than 1 million km<sup>2</sup> and has an average thickness of 25-30 m. The Bazhenov Sea, in which the shale deposited, was a relatively deep (up to 500 m), wide  $(2.2 \times 10^6 \text{ km}^2)$  epicontinental sea that was connected to the world major ocean system by two relatively shallow straits. Regional climatical conditions during the black shale deposition were mostly semi-humid, subtropical. Significantly, there are no evidence for the Bazhenov basin about magmatism and related hydrothermal activity (or any other type of hydrothermal activity) that was contemporaneous with the black shale deposition.

### Sulphur and Selenium

The OBS contain 7.4 wt.% sulphur on average. This is considerably more than in most Phanerozoic black shales (cf. Vine and Tourtelot, 1970), including also the Bazhenov black shale that contains only 2.83 wt.% S on average (Table 1). Average S/C (total C) and S/Fe ratios of the OBS are high 1.18 and 0.91, respectively, based on the data in the Oku data set. Data by Loukola-Ruskeeniemi (1999) yields a somewhat lower median S/C value of 0.83. It is worth to note that a large part of the OBS have S/Fe close to the stoichiometric pyrite S/Fe ratio of 1.15. Such high sulphur content denotes that most of the Fe in the OBS has to locate in the sulphide phase, which in most of the samples must comprise dominantly pyrite (FeS<sub>2</sub>) as there usually is too little Fe to allow presence of any significant pyrrhotite (FeS<sub>1-x</sub>). The high partitioning of Fe in the iron sulphides is reflected in that the dominant mica species is frequently colourless phlogopite instead of brown biotite as in the adjacent relatively sulphide poor mica schists/gneisses. This indicates very high degree of pyritisation (DOP) in the protolith black muds, causing that the precursor clay minerals for the metamorphic biotites in the black schists became impoverished in Fe. The ratio Fe in pyrite/total Fe, which can be used as an estimation of minimum value of degree of pyritisation (DOP) (cf. Meyer and Robb, 1996), has in the OBS an average value of 0.79. About 40 % of the analysed OBS samples have Fe in pyrite/total Fe above 0.9; values >0.75 are usually considered an indication of persistently anoxic conditions during deposition and burial (Raiswell et al, 1988).

It can be calculated, based on the total Fe and S contents, and assuming the same Fe/Al for the clastic component as in the WK2, that in average only about 60 % of the S now present in the OBS could have been fixed by pyritisation of the iron in the clastic component. Clearly, large amounts of some "excess iron" to enable pyrite formation must have been introduced, either as soluted iron (Fe<sup>2+</sup>), hydroxides fixed on detrital particles, or in form of sea water carried Fe-oxyhydroxide particles, which iron then became sulphidized by reactions with H<sub>2</sub>S in anoxic bottom waters and sediments. Permanent anoxia during depositon was a likely situation based on the obvious high degree of pyritisation, the high S/C<sub>org</sub> ratio and systematically low Mn concentration in the OBS. Sulphur (sulphate) content in normal sea water (9 ppm) is relatively high, and should not have been a limiting factor provided sedimentation rates were low. It is here assumed that by 1.9 Ga the sulphate concentration in seawater was about the same as presently (Grotzinger and Kasting, 1993).

It may not be far-fetched to correlate the OBS in terms of the possible source of the excess Fe with the Proterozoic banded iron formations (BIF), that register high influx of Fe<sup>2+</sup>, related either to continental weathering under atmospheric conditions that still were relatively unoxidising, or influx of iron from deep hydrothermal sources, in oceans that still seem to have been largely anoxic, at least for their bottom parts. Nd isotope, and REE distribution evidence of the BIF suggest that their Fe was mainly from hydrothermal sources, probably by black smoker type venting at oceanic spreading ridges (e.g. Derry and Jacobsen, 1990; Bau et al., 1977). This is supported by the positive  $\varepsilon_{Nd}(t)$  values typical of the Archaean and Palaeoproterozoic BIF, indicating ocean crust as source of the metal enrichment (Derry and Jacobsen, 1990; Bau et al., 1997). In a contrast, the  $\varepsilon_{Nd}(1900Ma)$  values in the OBS average to negative –3. Therefore and as the  $\varepsilon_{Nd}$  values in OBS are rather lower than higher than  $\varepsilon$ Nd values in the OBS seems very unlikely.

Selenium is a rare non-metallic element that due to its chalcophile nature is generally located in sulphides. It is commonly found concentrated in high-temperature volcanic, magmatic or hydrothermal massive-sulphide ores, in which galena and chalcopyrite are the common host sulphides. Se/Sx10<sup>6</sup> ratio in seawater is about 0.15, whereas in hydrothermal fluids and ores this ratio is typically much higher, ranging anything between 100 and 100 000. Black shales and sapropelic muds commonly show strongly elevated Se and Se/S, probably

reflecting nature of Se as an essential trace nutrient and its relative immobility in reducing environments. In Bazhenov black shales the average Se concentration is 27 ppm with a corresponding average Se/S x 10<sup>6</sup> ratio of 950, for example.

Se concentration in OBS varies considerably, typically between 2 and 50 ppm (Peltola 1960, this study). Peltola (1960) reports an average of 20 ppm Se for 17 samples from the Outokumpu region. A median concentration for 8 samples analysed in GTK from Outokumpu, Vuonos and Kylylahti is 9.4 ppm. Data from Peltola (1960) indicates an average Se/S x  $10^6$  ratio of 374 for the OBS. The 8 black schist samples analysed in GTK yield a median Se/S x  $10^6$  ratio of 107, which is close to the median Se/S x  $10^6$  ratio of 112 in the enclosing Upper Kaleva metawackes (mica schists) and that of 87 in the average of upper crust. For comparison, Outokumpu ore has, for an ore body often considered consisting of seafloor hydrothermal sulphides, a curiously low median Se/S x  $10^6$  ratio of only 57.

#### <u>Manganese</u>

In contrast to the high Fe content, manganese content in Oku black shales is frequently distinctly low. Median Mn concentration is just 0.05 wt.%, and even local Mn enrichments are very uncommon (maximum MnO = 0.24 wt.%). Mn and Fe are redox sensitive elements that are under reducing conditions mobile, showing a tendency to concentrate into the bottom waters under restricted circulation. Thus the systematically low Mn concentrations in OBS could be taken as a strong indication of permanent anoxia but open circulation in their basin of deposition. The fractionation of Mn from Fe probably reflects the high solubility of Mn sulphides under reducing conditions and relatively low affinity of Mn to pyrite.

The OBS have Fe/Mn ratio that is 236 on average. In post Archaean shales the Fe/Mn ratio is 53, and in the average upper crust 61 (Taylor and McLennan, 1985). Hydrothermal sulphides at modern oceanic spreading ridge axis have Fe/Mn ratios typically in the range of 1000-2000, whereas metalliferous sediments distal to the axis zones, at flanks of mid-ocean ridges, exhibit much lower Fe/Mn ratios typically near 3.5 (German, et al., 1999, and references). For comparison, average Fe/Mn ratio in oceanic abyssal clays is ca. 10 (Taylor and McLennan, 1985).

The systematically low Mn in the OBS attest to a complete absence in the Outokumpu assemblage of metalliferous, Fe+Mn±Co±Ni rich sediments typical for large domains of modern oxygenated ocean bottoms or distal to many ancient seafloor VMS.

# **Phosphorous**

The median and average P concentrations in the OBS expressed as  $P_2O_5$  are relatively low 0.135 and 0.21 wt.%, respectively. These values are on par with the average  $P_2O_5$ concentration of 0.21 wt.% in the WK2 (Lahtinen, 2000). Significantly, however, there are 95 samples in the 2957 sample dataset that have exceptionally high  $P_2O_5$  in the range of 0.5-1.0 wt.%, and 97 samples that exhibit even higher values up to 3.8 wt.%  $P_2O_5$ . If these ca. 200  $P_2O_5$  enriched samples are excluded, the average  $P_2O_5$  concentration of the OBS is just 0.14 wt.%. The high  $P_2O_5$  sample population is characterized by high  $P_2O_5/Al_2O_3$  ratios between 0.03 and 0.8 compared to low  $P_2O_5/Al_2O_3$  ratios between 0.008 and 0.03 in the main OBS population.

We checked some of the particularly  $P_2O_5$  rich black schist intervals in the drill core Oku-770 from Kylylahti. These core intervals were frequently found to contain thin (<1-10cm) folded and boudinaged layers of black, distinctly fine-grained and obviously very graphite-rich material (Fig. 7). One sample from such layer (from Kylylahti) was chemically analysed. It turned out to contain ca. 47 wt.% total carbon (mostly in graphite) and 11 wt.%  $P_2O_5$ . Noting the usually lengthy 2-3 m drill core samples used in Outokumpu assaying, occasional thin carbon and phosphorous-rich layers may be a more common feature in the OBS than the existing  $P_2O_5$ data suggests.

We note that in Kylylahti the P-rich black schists appear especially common in the black

schists nearest to the Cu-Co mineralised zone. This raises question of their relation to Cu-Co mineralization, especially as there are scattered P enrichments (apatite) also inside of the Oku alteration assemblage, particularly in the "disseminated" ore zone. Maybe the P enrichments in the disseminated zone are related to syntectonic P mobility from the black schist regime? However, positive  $\epsilon$ Nd (1900Ma) between +2 and -1 in the mineralised P-rich skarn rocks are against source of the P from the black schists, which show, the P-rich black schists included, negative  $\epsilon$ Nd (1900Ma) typically in the range between -2 and -4. It should also be noted that the P-enriched black schists do not show any tendency to metal enrichment over that typical of the "normal" OBS.

The P-rich samples ( $P_2O_5>0.5$  wt.%) aside, the main population of OBS seems to exhibit weak but significant positive correlation of  $P_2O_5/Al_2O_3$  with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and also with TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, which suggests that P in the "normal" OBS would be mainly in the siliclastic phase. Calculations based on  $P_2O_5/Al_2O_3$  ratios in the OBS and WK2 also indicate that most of the P in the low-P OBS was introduced in the WK2 type clastic flux. Thus, it seems likely that deposition of the P-C-rich thin interbeds in part of the OBS were related with some sporadic, exceptional processes that did not operate continuously during the OBS deposition. One possibility is that these layers record episodes of sudden mass-mortality of pelagic sea organisms.

## Chromium, Scandium, Niobium, Thorium, Yttrium and Zirconium

These are all elements that show low solubility in most geological waters, including weathering solutions, sea water and hydrothermal fluids, and which are thus among the least mobile elements in common rock alteration processes.

Our calculations below indicate that Cr, Sc and Th concentrations in OBS are fully contained in the assumed WK2 type clastic phase (cf. Table 3). On the other hand, Zr and Hf in the OBS are depleted by some 20-25 % relative to the WK2. This difference most probably reflects sorting effects, which are possible as Zr and Hf in silicalstic metasediments are for large part located in the heavy mineral zircon, whereas Cr, Sc and Th tend to reside mainly in the relatively less dense sheet silicates of the clay fraction. Also Y and Nb are present in excess over the concentrations that one would expect if these elements were introduced only within the WK2 type clastic influx. The numbers are 60 % for Y and 40 % for Nb. The slightly superchondritic average Y/Ho ratio of 33 in the OBS may indicate oxygenated nature of at least the surface waters in the basin of OBS deposition (cf. Bau and Dulski, 1999). On the other hand, also the WK2 show a similar average Y/Ho ratio of 33.5. It is worth to note that the OBS and WK2 show similar low average Nb/La of 0.34, much below the chondritic Nb/La ratio of about 1.

Importantly, in spite of their close association with serpentinites, there is no evidence in their geochemistry of pronounced ultramafic component in their source. For example, the median ratios Sc/Th (=2.0) and Cr/Th (= 13.8) in the OBS, which should elevate by ultramafic-mafic contribution, are in fact lower than in the WK2 (Sc/Th=2.2; Cr/Th=14.8). This is in accordance with the absence of any type of synsedimentary mafic or ultramafic rock intercalations in the OBS and WK2.

## Molybdenum, Vanadium and Uranium

Vanadium and molybdenum belong to those elements that most commonly are highly enriched in black shales. The OBS are no exception but their median Mo and V concentrations of 55 ppm and 563 ppm, respectively, both greatly exceed the average concentrations of these metals in the upper continental crust, 1.5 ppm for Mo and 60 ppm for V. Median U content of the OBS is 17 ppm, again a considerably higher value than the 2 to 3 ppm of U that is typical of the upper continental crust or the enclosing Upper Kaleva wackes (cf. Table 3)

In oxygenated seawater V is present as dissolved vanadate (V<sup>5+</sup>) but is reduced to vanadyl

ion (V<sup>4+</sup>) under anoxic conditions. Vanadyl ion has a high tendency to be adsorbed on particles, and hence V<sup>4+</sup> is readily scavenged by organic and inorganic particles settling in seawater. Unlike solubility of V, that of Ni is not particularly redox sensitive, though under very anoxic conditions an availability of H<sub>2</sub>S may cause nickel sulphide formation. The ratio V/(V+Ni) in black shales has been proposed as a measure of basinal redox conditions. Data in Outokumpu database suggests that V/(V+Ni) in Outokumpu black schists would typically be about 0.55, which is a barely high enough value to indicate euxinic conditions (cf. Wignall, 1994, Fig. 4.3.). V/(V+Ni) based on the V and Ni data for OBS in Peltola (1960) and Loukola-Ruskeeniemi (1999) are 0.61 and 0.60, respectively. In comparison, the Bazhenov black shale has a slightly higher average V/(V+Ni) of 0.71.

Molybdenum is one of the most abundant metals in modern ocean water with an average concentration of 11 ppb (Taylor and McLennan, 1985). Mo precipitates in black shales probably principally absorbed onto humic substances (Brumsack, 1989; Coveney et al., 1991), although under anoxic conditions it may co-precipitate also with polymorphs of FeS (Huerta-Diaz and Morse, 1992).

Importantly, none of the elements Mo, V or U can be considered a typical "hydrothermal element". In black shales Mo, V and U, like many other metals, usually correlate positively with organic carbon (Vine and Tourtelot, 1970). However, concentrations in living marine organisms (plankton) are far too low to account the enrichment. Instead the positive correlation with carbon results in from that remains of dead planktonic organisms scavenge metals during their settling through anoxic bottom water columns, and under low rate of sedimentation, also at the water-bottom interfaces. In addition, adsorption of metals also to clay-organic particles tends to occur. Under euxinic conditions these two metal enrichment processes may occur with coprecipitation of syngenetic sulphides. Further anoxic processes during early diagenesis facilitate fixation of the organic-associated metals to sulphides and possible other anoxic phases.

Uranium and Th in normal shales are present in the clay mineral and accessory heavy mineral fractions, and usually these rocks have U/Th ratios close to the crustal average of 0.33 (Taylor and McLennan, 1985). Under anoxic conditions significant U is precipitated as an authigenic component, however, and therefore black shales usually have U/Th much over the crustal average. Permanent anoxia is required for U fixation since in oxic waters and at the redox boundary U is highly soluble (Langmuir, 1978). Thus authigenic U concentrations, Ua=Utotal-Th/3, provide a potential indicator of palaeo-oxygen levels. Ua in excess of 10 ppm are common in black shales that have deposited in anoxic-euxinic conditions. Most of the Ua in black shales probably co-precipitates with humic organic matter and/or francolite (Wignall, 1994). Ua in the OBS is typically 13-21 ppm based on the median compositions in Table 1.

The strongly elevated V, U (Ua) and Mo concentrations, and high V/AI, U/AI, Mo/AI and high U/Th ratios in the OBS provide a clear signature of organic-related metal enrichment. V and U enrichments in the OBS are on par with those in the Bazhenov black shales, whereas that of Mo is significantly lower.

## Cobalt, Copper, Nickel and Zinc

Median Cu, Ni and Zn concentrations in the OBS are 300 ppm, 390 ppm and 1610 ppm, respectively, based on the large Outokumpu XRF dataset. These are very high values compared to the average upper crust values: 25 ppm for Cu, 20 ppm for Ni and 71 ppm for Zn (Taylor and McLennan, 1985). What is important in the Outokumpu context, the Co in the OBS is far less enriched, however. The median concentration of Co in the OBS is only 33 ppm, and thus not so much higher than the average upper crustal Cu content of 10 ppm. Noting that Cu, Ni and Zn are the main metals also in the Outokumpu type sulphides, it is often proposed that the metal enrichment in the OBS and Outokumpu-type sulphide deposits were syngenetic and hydrothermal in both cases (e.g. Mäkelä, 1981; Loukola-Ruskeeniemi et al., 1991; Loukola-

Ruskeeniemi and Heino, 1996; Loukola-Ruskeeniemi, 1999). This is certainly a tempting idea considering the huge amounts of metals and sulphur present in the black schists, and the often close spatial association of the sulphide deposits with the OBS. Noticing the very different Pb isotope compositions of the OBS and the ore sulphides (M. Vaasjoki, p. 64 in Haapala et al., 1986; section 9.3.2.), a common origin of the Outokumpu type ores and the OBS metal enrichment is a very improbable case, however. We will below present also trace element evidence that strongly attests to unrelated origins of metal enrichments in the OBS and the sulphide ores. Nevertheless, it would be interesting to evaluate to what extent, if any, hydrothermal flux was an important metal contributor to the OBS.

We demonstrated above that most metals in the OBS are present in concentrations that greatly exceed their concentrations in common wacke sands or shales (Table 3). It is therefore obvious that their metal enrichment was largely by other mechanisms than in the clastic flux. The relatively high AI, Si and alkaline element concentrations in the OBS nevertheless imply presence of a significant amount of clastic (terrigenous) component and thus a certain amount of clastic-bound metals. To quantify the metal abundances in the clastic input, and further, the metal content in excess of the clastic-bound abundances, we will start from the premise that the clastic component in OBS would have similar chemistry and element/AI ratios with the pelitic WK2 of Lahtinen (2000). The excess element concentrations were then calculated based on:

Excess concentration of element A in OBS = concentration of element A in OBS – (concentration of element A in WK2 \* concentration of AI in OBS / concentration of AI in WK2),

and element enrichement factors based on:

Element enrichment factor of element A = concentration of element A in OBS / (concentration of element A in WK2 \* concentration of AI in OBS / concentration of AI in WK2),

in which:

concentration of element A in WK2 \* concentration of AI in OBS / concentration of AI in WK2 = concentration of element A in the clastic component of the OBS

For comparison, the same calculations were done also for the Bazhenov oil shale, using the average shale composition (PAAS) presented by Taylor and McLennan (1985) as estimation of the clastic component. The results of the calculations show that the base metals in the OBS are enriched 2-200 times over the abundances present in the clastic phase, and that excess metal enrichment pattern in OBS is remarkably similar with that in the Bazhenov oil shale (Table 3).

Table 3. Composition of Outokumpu and Bazhenov black shales compared with average crust, shale, greywacke and W								
and nonclastic element enrichments and enrichment factors for median Outokumpu BS and Bazhenov E								

and noncla	Clastic element enrichments		Bazhenov	Av. UC	Av. shale	Av.arevw.	WK2	WK2 Outokumpu BS			ວວ Bazhenov BS	
	OKU'ª,GTK	,L-R'`	G&Z <sup>2</sup>	T&McL <sup>3</sup>	T&McL <sup>35</sup>	Wedep. <sup>↑</sup>	Lahtinen	Median enric	hmen	Average enri	chmen	
	dataset	median	average	average	average	average	average	% / ppm	factor	% / ppm	factor	
SiO2	OKU	52,30	55,67	66,00	62,80	69,1	63,23	2,68	1,1	18,49	1,5	
TiO2	OKU	0,51	0,53	0,50	1,00	0,72	0,83	-0,14	0,8	-0,06	0,9	
AI2O3	OKU	12,10	11,19	15,20	18,90	13,5	15,42	0,00	1,0	0,00	1,0	
Fe2O3t	OKU	11,12	4,93	5,01	6,50	5,9	7,38	5,33	1,9	1,08	1,3	
MnO	OKU	0,05	0,03	0,08	0,11	0,10	0,08	-0,01	0,8	-0,04	0,4	
MgO	OKU	6,05	1,33	2,20	2,20	2,30	3,23	3,52	2,4	0,03	1,0	
CaO	OKU	4,22	2,21	4,20	1,30	2,60	2,36	2,37	2,3	1,44	2,9	
Na2O	OKU	1,14	1,28	3,90	1,20	3,00	2,84	-1,09	0,5	0,57	1,8	
K2O	OKU	2,65	2,18	3,40	3,70	2,00	3,36	0,01	1,0	-0,01	1,0	
P2O5	OKU	0,14	0,25		0,16	0,13	0,16	0,01	1,1	0,16	2,6	
S	OKU	7,36	2,83				0,06	7,31	156,3			
Ctot	OKU	6,09	8,00				0,07	6,04	110,9			
Co	OKU	33	23	10	23	15	21,3	16	2,0	9	1,7	
Cr	L-R	110	80	35	110	88	137	2	1,0	15	1,2	
Cu	OKU	300	136	25	50	24	32	275	11,9	106	4,6	
Ni	OKU	390	192	20	55	24	65,3	339	7,6	159	5,9	
Sc	L-R	16	16	11	16	16	20,5	0	1,0	7	1,7	
V	L-R	563	461	60	150	98	164	434	4,4	372	5,2	
Zn	OKU	1610	659	71	85	76	115	1520	17,8	609	13,1	
Ва	L-R	338	320	550	650	426	613	-143	0,7	-65	0,8	
Hf	GTK	2,8		5,8	5	3,5	4,46	-0,7	0,8			
Nb	GTK	7,3	7,3	25	19	8,4	11,2	-1,5	0,8	-3,9	0,6	
Rb	OKU	50	90	112	160	72	117	-42	0,5	-5	1,0	
Sr	OKU	120	248	350	200	201	223	-55	0,7	130	2,1	
Th	L-R	8	6,3	10.7	14.6	9.0	9.27	0,7	1,1	-2,3	0,7	
U	L-R	17	35,7	2,8	3,1	2,00	2,00	15,4	10,8	33,9	19,5	
Zr	OKU	110	148	190	210	302	203	-49	0,7	24	1,2	
Y	L-R	33	24	22	27	26	26,5	12	1,6	8	1,5	
La	GTK	21,1	27	30	38	34	33,2	-5,0	0,8	4,5	1,2	
Ce	GIK	39,1	53	64	80	58	65,4	-12,2	0,8	5,6	1,1	
Pr	GIK	5,32		7,1	8,9	6,1	8,02	-1,0	0,8			
Nd	GIK	20,6		26	32	25	28,9	-2,1	0,9			
Sm	GIK	4,51	6,3	4,5	5,6	4,6	5,55	0,2	1,0	3,0	1,9	
Eu	GIK	0,97	1,34	0,88	1,1	1,2	1,15	0,1	1,1	0,7	2,1	
Gd	GIK	4,88	0.00	3,8	4,7	4	5,04	0,9	1,2	0.4	0.0	
	GIK	0,76	0,89	0,64	0,77	0,63	0,75	0,2	1,3	0,4	2,0	
Dy	GIK	4,36		3,5	4,4	3,4	4,12	1,1	1,3			
HO F=	GIK	0,90		0,80	1,00	0,78	0,79	0,3	1,5			
Er	GIK	2,66		2,3	2,9	2,2	2,31	0,8	1,5			
I M	GIK	0,41	2.02	0,33	0,4	0.4	0,32	0,2	1,0	1.0	1.0	
YD	GIK	2,75	3,23	2,2	2,8	2,1	2,19	1,0	1,6	1,6	1,9	
LU	GIK	0,43		0,32	0,43	0,37	0,32	0,2	1,7			
Ag	OKU	3,9	1,2	0,05			0,061	3,9	81,5	1,2	40,5	
As	OKU	100	45	1,5			0,63	100	202,3	45	50,7	
Au (ppb)	L-R	3,8	4,2	1,8		4,8	0,4	3,5	12,1	4,2	3,9	
Cd	GTK	12,8	14	0,098				13	166,4	14	241,3	
Мо	L-R	55	123	1,5	1			54	46,7	122	207,7	
Pb	OKU	30	16	20	20	14,2		14	1,9	4	1,4	
Pd (ppb)	L-R	14,1		0,5		0,4	0,39	13,8	46,1			
Sb	GTK	0,76	6,9	0,2			0,021	0,7	46,1	6,8	58,3	
Se	GTK	9,4	27	0,05			0,15	9,3	79,9	27,0	912,1	
Cu/Zn		0,19	0.21	0.35	0,59	0.32	0,28	0,18		0,17		
Co/Ni		0,08	0.12	0.50	0,42	0.63	0.33	0.05		0.06		
		- ,	-, -	- ,	-, -	- ,	-,	- ,		-,		

Major elements in wt%, trace elements in ppm except Au in pp

Fe2O3t = total iron as Fe2O3, Ctot = total carbor

" Analyses by XRF and AAS (Ag, Co) in Outokumpu Mining (values in parentheses of suspect accurac

<sup>17</sup> Analyses by XRF, GFAAS (Ag, Pb, Sb, Se) and ICP-MS (Au, Co, Cr, Hf, Nb, PGE, REE, Th, U) in GTK <sup>17</sup> Median of medians for low-Ca & high-Ca black schists P9-P17 in Tables 3 and 4 in Loukola-Ruskeeniemi (199

<sup>4</sup> Average of Bazhenov black shales, Table 5 in Gavshin and Zakharov (199 <sup>34</sup> Average upper continental crust, Table 2.15 in Taylor and McLennan (198

"Average post-Archaean shale (PAAS), Table 2.9 in Taylor and McLennan (198

\*Average greywacke, Table 3 in Wedepohl (1995

Average upper Kalevian wacke shale, Table 1 in Lahtinen (2000

-0

Our calculations indicate that the amounts of excess Ni, Cu and Zn in the OBS are typically very high, whereas only relatively little excess Co is usually present. This results in that Co/Ni ratios calculated for the excess (i.e. in the possible hydrothermal) metal component are significantly lower than the Co/Ni ratios based on the total metal concentrations! This does not favour hydrothermal origin for the excess base metal content in the OBS, since due to the very low Ni abundances and relative immobility of Ni compared to Co in ore-forming hydrothermal fluids, any hydrothermal addition should rather increase than decrease the Co/Ni, and also the Cu/Ni and Zn/Ni ratios.

In the large Outokumpu XRF dataset, Ni exhibits significant positive correlation with S and to some extent also with As, whereas Cu, Zn and Co seem to be distributed independently of sulphur and As. This discrepancy between Ni and the other base metals is especially clear if the calculated excess abundances are considered. It appears that Cu and Zn were introduced mainly by organic scavenging, whereas at least part of the Ni and As probably co-precipitated with syngenetic sulphide.

Many studies of black shales demonstrate good correlations of base metal abundances with organic carbon content. In the Oku dataset relatively few samples (n=123) have been analysed for carbon, and moreover, those data that exist, is for total carbon only. This does not enable analysis of metal versus organic carbon correlations in the OBS. Loukola-Ruskeeniemi (1999) has found that metal/organic carbon correlations in the OBS are generally relatively poor. We are inclined to believe that the poor metal-carbon correlations more probably reflect secondary mobilisation of both organic carbon and metals (sulphides) than syngenetic processes. One would expect such secondary mobilization in association of hydrocarbon-rich fluid production during thermal maturation of the organic matter during the early burial of the OBS. In the case of presumably relatively impermeable Upper Kaleva wackes/black muds such mobilization may not have been very effective or spatially extensive, but perhaps still enough to blur the S/C and metal/C correlations. Redeposition effects during sedimentation and tectonic-metamorphic mobilisation of sulphides are other probable reasons for the poor S/C and metal/C correlations in the OBS.

### Silver, gold and platinum group elements (PGE)

Median Ag concentration in the OBS is 3.9 ppm based on the Oku dataset (n=908). This may be a bit two high value since the data by GTK and in Loukola-Ruskeeniemi (1999) suggest median concentration below 1 ppb. Only few high quality, high precision Au and PGE data is currently available for the OBS. Six samples analysed in the course of this study in GTK by ICP-MS (714M) from Outokumpu and Vuonos have Au concentrations in the range of <1 to 25 ppb. Loukola-Ruskeeniemi (1999) reports a median concentration of Au of 3.8 ppb for the OBS. The six samples from Outokumpu and Vuonos analysed by ICP-MS (714M) in GTK have Ir concentrations between <1 and 0.48 ppb, Pt concentrations between 4.04 and 13.6 ppb, and Pd concentrations between 12.4 and 35.7 ppb. Loukola-Ruskeeniemi (1999) reports median concentrations in the OBS of 0.1, 6.4, and 14.1 ppb for Ir, Pt and Pd, respectively.

Ag and Au are both elements that usually are slightly enriched in the more carbon-rich black shales. Average Ag concentration in the Bazhenov black shale is 1.2 ppm and that of Au 4.2 ppb, for example. These values yield an Ag/Au ratio of 286. The available data indicates that Ag/Au ratios in OBS would usually have values between 20 and 100. In comparison, the Outokumpu ore has a low average Ag/Au ratio of only 11.25, based on the reported average Ag and Au concentrations in the ore, 9 ppm and 0.8 ppm, respectively (Papunen, 1987).

In contrast to Au, concentrations of the Platinum-group PGE elements, especially those of Pd, appear to be significantly higher in the OBS than in the Outokumpu and Vuonos ores. Loukola-Ruskeeniemi reports a median Pd content of 14.1 ppb for the OBS, while the Outokumpu ore has an average Pd concentration of just 4.04 ppb, based on 24 representative samples analysed by ICP-MS (714M) in GTK.

## Arsenic, Antimony

Arsenic and Sb are both elements that commonly occur concentrated in black shales and sapropels, though there are considerable variations in the degree of enrichment. Compared to average black shales, and even many oil source black shales, the median As concentration (100 ppm, Oku dataset) in the OBS is rather high, while that of Sb (0.76 ppm, GTK dataset) is on the low side. Concentration of As is somewhat higher in the OBS than in the Bazhenov oil shale, whereas that of Sb is significantly lower (Table 3). It must be noted, however, that due to the low number of analysed samples (n=8), the median Sb reported here for the OBS is quite uncertain.

The sources of As and Sb, and enrichment processes in black shales are not well known. However, both these elements are present in moderately high relative concentrations in seawater (As 1.7 ppb, Sb 0.15 ppb, Taylor and McLennan, 1985). It is worth to note, also, that As and Sb are naturally volatile elements present in elevated concentrations in volcanic fumaroles and in fluids discharged at seafloor hydrothermal vents. Therefore strongly elevated As and Sb in black shales is a potential signature of increased hydrothermal input.

Plotted against sulphur, it is seen that the OBS divide in distinct high As and low As groups. In the high As group concentration of As ranges between 80 ppm and 500 ppm and there is a good positive correlation of As with S. In the low As group the As concentration level is below 50 ppm and As has no clear correlation with S. Surprisingly As in either groups shows hardly any correlation with other metals, only a weak positive correlation with Ni is apparent for the high As group. Due to its affinity to sulphur it seems probable that As in the high-As OBS co-precipitated with syngenetic sulphide.

### Rare-earth elements (REE)

Rare-earth elements in black shales are controlled by the contained clastic component, organic fraction and possible carbonate/phosphate and hydrothermal additions. The WK2 should provide a good basis for estimation of also the proportion of the clastic-bound REE component in the OBS. We have 8 samples from the OBS analysed for the complete set of the REE. Shale-normalised plots reveal that all of these eight samples are systematically enriched in HREE and depleted in LREE relative to WK2, and have more pronounced negative Ce anomalies than WK2 (Fig. 8). Therefore, there clearly was also some other flux(es) of the REE than that in the WK2 type clastic component.

To calculate the amounts of this "excess REE", we used the same procedure than we applied above for the trace metals. However, because REE/AI ratios in WK2 used as such turned out to yield negative excess LREE abundances for several of the included samples, we had to apply the REE/AI ratios of WK2 reduced by 25%. This adjustment yields positive values for all REE, and facilitates shale-normalised plotting. Need for the adjustment in REE/AI ratio in the assumed clastic component is not surprising noting that REE in metasediments associate less well with AI compared to trace metals. Note in addition that the uncertainty concerns the absolute abundances not the shapes of the REE profiles.

Shale-normalised the calculated excess REE components in the nine OBS samples all show profiles that closely resemble that of normal ocean water, showing the HREE enrichment over MREE and distinctive negative Ce anomaly that is a particular characteristic of ocean water (Fig. 9). The highest REE abundances encountered are present in the organic carbonand phosphorous-rich, alumina-poor (clastic matter poor) black schist sample (Oku-770/568.60) from Kylylahti. This sample has shale-normalised REE pattern particularly similar to that of modern ocean water. In summary, the chemical features of the OBS strongly suggest that a significant part of the REE in the OBS was derived from seawater and precipitated as phosphate complexes or adsorbed on oxyhydroxide or organic C particles.

The negative Ce anomalies in the REE patterns for the OBS are of special interest with respect to the redox state in the 1.9 Ga "Kaleva Ocean". Namely, though most REE in modern ocean waters occur in the relatively soluble 3+ oxidation state, Ce may occur either as 3+ or 4+ depending on redox conditions. In modern oxic oceans, Ce<sup>4+</sup> is preferentially precipitated with either Fe-oxyhydroxide or organic carbon particles, or by carbonate or phosphate

complexation, thus producing a negative Ce anomaly in REE patterns of oxygenated seawater. In a completely anoxic ocean the Ce<sup>3+</sup> cation should be stable and no Ce anomaly produced. It should be noted, however, that since REE has only a short residence time in seawater, Ce anomalies do not necessarily reflect global oceanic redox state, but waters in restricted subbasins with limited exchange with the major ocean system may have REE patterns of their own. Nevertheless, the negative Ce anomalies in the REE patterns of the OBS provide strong evidence of presence of large volumes of oxygenated seawater in the "Kaleva Ocean". This implies, combined with the evidence for euxinic bottom water conditions, that most probably the deposition of the OBS took place under a thick stratified water column, in which the surface parts were oxygenated and the bottom parts effectively anoxic.



Fig. 8. PAAS-normalized REE patterns for representative samples of the OBS and their metacarbonate intercalations (OKU-788/365.1-365.5) and P-C rich bands (Oku-770/568.60). For comparison patterns for WK2, ocean water and average mid-ocean ridge black smoker fluid are also shown. Compared to WK2 the OBS are enriched in HREE and depleted in LREE. Note that the OBS patterns all show a slight negative Ce anomalies but no Eu anomalies. PAAS=Post-Archaean average Australian shale (Taylor and McLennan, 1985).



Fig. 9. PAAS-normalized REE patterns for the calculated excess, non-clastic REE in the representative samples of OBS. Note that the patterns for the OBS are now highly reminiscent of Ocean water patterns with negative Ce anomalies and HREE enriched over MREE and LREE. PAAS=Post-Archaean average Australian shale (Taylor and McLennan, 1985).

## The Talvivaara black schists in Kainuu – correlation with the OBS

Talvivaara black schist (TBS) in the Kainuu area are often correlated with the Outokumpu black schists (OBS), if not strictly lithostratigraphically, at least in terms of coeval sedimentation in a common overall tectonic setting (e.g. Mäkelä, 1981; Loukola-Ruskeeniemi and Heino, 1996). Correlation of the OBS and TBS is problematic, however. First, in the Talvivaara area the black schists are intercalated and underlain by quartz wackes (Fig. 10) and aluminous garnet±staurolite bearing metapelites that entirely lack in the Outokumpu black schist association, but which are a "diagnostic" character of the Lower Kaleva" in Kainuu. Secondly, tentative studies of detrital zircons in the associated wackes indicate that clastic material in the OBS would be for large part from Palaeoproterozoic (2.0-1.92 Ga) sources (Claesson et al., 1993), whereas the TBS seem to contain dominantly recycled Archaean material (only Archaean detrital zircons, GTK/Huhma and Kontinen, unpublished data). Also Sm-Nd isotope data suggest a dominantly Archaean provenance for the Talvivaara wackes (GTK, Huhma and Kontinen, unpublished data), whereas an abundant early Proterozoic, juvenile component in the Upper Kaleva wackes in the Outokumpu area (Huhma, 1987). These are not surprising evidence since the Talvivaara black schists are clearly part of the local parautochthon.

Importantly, Talvivaara-type black schists with diagnostically high Ni concentrations (>0.2 %) and quartz wacke – arkosic wacke intercalations are present also in North Karelia, in Juankoski (Punamäki-Viitaniemi), Losomäki and Riihilahti, for example. However, like the Talvivaara black schists also these metal rich black schist seem a part of the parautochthon below the Outokumpu Allochthon. And thus not something one could correlate with the ores within the allochthonous Upper Kaleva.



Fig. 10. Photograph of a ca. 12 cm thick quartz wacke interbed in metal and sulphide rich black mud at Talvivaara in Sotkamo. The photo was taken before removing of the rocks in the photo by the Talvivaara Project Ltd for large-scale testing of bio-heapleaching of the sulphides.

The TBS yield a median Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio of 0.046, which is a significantly lower value compared to the average Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio of 0.10 in the OBS. The somewhat lower median Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio of 0.034 in the Ni-richest TBS (>0.1wt.% Ni) has been considered as an evidence of syndepositional hydrothermal alteration (Loukola-Ruskeeniemi and Heino, 1996). Noting the presence of mature quartz wacke and garnet-bearing pelite intercalations especially in the Ni-richest TBS, a more plausible explanation is that the low Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios in the TBS reflect simply a relatively high degree of weathering of the provenance, and that the degree of weathering was even more intense during the periods of increased metal accumulation in the black schists.

The TBS are for most par sandy muds that, in addition to phlogopitic mica and plagioclase, often comprise abundant sand-size, well-rounded quartz, most probably derived from the Jatuli type cover quartzites underlying the Talvivaara strata. This, together with the available Sm-Nd isotope data, indicates that the clastic material in the TBS would represent a mixture of Archaean material recycled from Jatulian deposits and directly derived from the Archaean basement. Unfortunately, there are currently no chemical data available from the quartz wackes and sandy mud intercalations in the TBS, so the clastic component in the TBS cannot be chemically modelled.

The clear differences in the lithological-sedimentological association, isotope geochemistry, provenance, and tectonostratigraphic setting between the TBS and OBS render any such ore models that involve stratigraphic correlation of the TBS with OBS as an essential element strongly suspected. It is important to notice, however, that there nevertheless are only

minor differences between the TBS and OBS in terms of their average metal ratios and enrichment profiles (cf. Table 1; Fig. 11). This implies that although these two black schists formations deposited in different environments and probably also in different times, the processes producing metal enrichment were the same and probably related to some universal character of the Palaeoproterozoic oceans.

Importantly, the several test pits excavated in the in the TBS at the Talvivaara prospect by Outokumpu Mining reveal that black shales are there by far not the main lithologic component, not even in the most Cu-Ni-Zn enriched horizon, but instead the main lithologies are metamorphic equivalents of muddy quartzose sands and sandy muds. Considering the abundance of muddy sands, one may ask what was the role of secondary late diagenetic-early metamorphic mobilisation and redistribution of the metals (sulphides) in creating the most metal-enriched horizon at Talvivaara? Maybe the metal-enrichment in the Ni-richest TBS was related to late diagenetic-burial metamorphic mobilisation of metals by sulphide-bearing fluids, which may have been produced by H<sub>2</sub>S released in conjunction of decomposition of the buried metal-enriched organic matter (cf. Ohmoto and Goldhaber, 1997). H<sub>2</sub>S generation and related metal mobility may have occurred also during the early metamorphism by interaction of the early metamorphic fluids with the kerogen, or trapped/migrated liquid/gaseous hydrocarbons, which had by all likelihood generated when the TBS thermally passed the "oil window". The more permeable sandy horizons may have provided pathways to the metal-bearing fluids, and the less permeable black mud horizons seals under which such fluids concentrated metals. The final metal fixation may have taken place preferentially in the more organic rich muddy layers, which would easily mislead the observer from noticing the importance of the late diageneticearly metamorphic metal mobility. Unfortunately, no study of the metal distribution between the sands and muds in Talvivaara has yet been performed.

In the light of above discussion, the lack of Talvivaara-type high metal enrichments in the OBS could perhaps reflect the relative scarcity of more permeable (quartz rich) sand intercalations in the Outokumpu black schists, curtailing potential to significant post-depositional mobility of hydrocarbons and metals.

Small positive Eu anomalies in shale-normalized (NASC) REE profiles of the TBS have been considered as an evidence of hydrothermal origin of the REE (and the base metal flux), and deposition of the TBS in a basin associated with seafloor spreading (Loukola-Ruskeeniemi, 1995; Loukola-Ruskeeniemi and Heino, 1996). However, it is more probable that the Eu anomalies in TBS are in fact associated with the clastic component, which as dominantly Archaean material is likely to yield small positive Eu anomalies if normalized by the NASC or PAAS compositions (representing Post-Archaean shales, cf. Taylor and McLennan, 1985). And, of coarse, the stratigraphical position of TBS in the Lower Kaleva on a rifted Archaean crust completely precludes the possibility of deposition in close proximity to any oceanic spreading centres.

In one notable difference, manganese concentrations in the TBS are in average higher than in the OBS (Table 1), and distinctly Mn-enriched black shale intervals and also Mn-enriched metacarbonate rock (black tremolite±diopside "skarn") layers are present (Loukola-Ruskeeniemi and Heino, 1996). Loukola-Ruskeeniemi (1995) and (Loukola-Ruskeeniemi and Heino, 1996) have interpreted that the Mn rich metacarbonate layers (black "skarns") would represent hydrothermal products. However, it is not uncommon in geologic record to have Mn-carbonate rocks as interbeds in black shales, and generally this situation is found to reflect fluctuations or lateral basinal variations in syndepositional redox conditions rather than fluctuations in supply or source of Mn. We note also that the strong LREE depletion and minor Eu and Ce anomalies in the shale-normalised REE profiles of the TBS are characters of normal seawater rather than high temperature hydrothermal fluids.

It must be recognized here, also, that the fallouts of the Mn-Fe rich particulate material at modern seafloor hydrothermal vents deposit mainly REE scavenged from normal seawater (e.g. Bau and Dulski, 1999). Only in precipitates very close (<100m) to the vents a high temperature hydrothermal component can be discerned in the REE budget and profiles of the falling particulates. This means that in modern oxic oceans the sulphide and oxyhydroxide deposits at the vents act as very effective REE sinks and REE flux from the spreading center

vents to oceans is negligible. In the Precambrian oceans, which may have been completely anoxic or permanently stratified with a lower anoxic layer and upper oxic layer, a significant hydrothermal REE flux in the ocean bottom waters may have been possible. Nothing in the REE geochemistry of the TBS or OBS indicates significant hydrothermal contribution, however.

Loukola-Ruskeeniemi and Heino (1996) report alabandite (Mn sulphide) from the metacarbonate rocks (black calc-silicate rocks) at Talvivaara, and name its presence as a possible evidence for hydrothermal Mn flux. However, due to the high solubility of Mn sulphide, it is only rarely present in unmetamorphosed black shales. Only under very reducing conditions some Mn may become accommodated as trace component in pyrite. Hence it is doubtful if the coarse-grained alabandite in the TBS would be of primary syngenetic origin. Exolution from manganeous pyrite in a retrogressive stage of the regional metamorphic history is a more probable origin for the Talvivaara alabandite.

# Origin of the metal enrichment in the OBS

Possible sources for metal enrichment in black schists include: seawater, marine organisms, digenetic recycling, riverine input, eolian input and hydrothermal input. There is considerable variation in black shale metal enrichment patterns between different black shale strata, and it can be demonstrated that these variations partly reflect variation in the metal sources and partly conditions during deposition (rate of deposition, redox and pH conditions, degree of water circulation etc).

In the case of OBS, it is practically speaking impossible to quantify the relative contributions of the various possible metal sources, as most of the required parameters like Palaeoproterozoic sea water composition, composition of river waters, level of free oxygen in atmosphere, basin water volumes, magnitude of exchange between various water reservoirs etc. are at best only inaccurately known. Nevertheless, some deductions of the relative importance of the sources are possible, and those we will be attempted below.

In the light of the overall relatively high metal concentrations of the OBS, metal enrichment just by internal diagenetic leaching and redeposition seems unlikely. Neither is there any evidence for particularly metal poor horizons in the enclosing sandy metaturbidites, and that could represent horizons wherefrom metals had been leached and removed in the black shale horizons. An input from some more far-sited leached metasedimentary source, no more present in the geological record, cannot be excluded, however, but seems unlikely. The depletion of OBS in Zr speaks against importance of wind-blown component. Considering the relatively low volumes of total water in the world rivers, and the low element abundances in the river waters, it is unlikely that, even under conditions of strongly enhanced on land weathering, that direct riverine influx would have been important to the very metal-enriched OBS. Thus, we are left with two possible metal sources: either hydrothermal or seawater.

Metal concentrations in seawater are very low, but because of the very large volume of the oceans, they anyway form an immense reservoir of metals. Phanerozoic metal-enriched black shales in such as the Jurassic Bazhenov oil shale in western Siberia (e.g. Gavshin and Zakharov, 1996), Pennsylvanian Mecca shales in central U.S.A (e.g. Coveney et al., 1991), or Lower Cambrian shales in southeast China (e.g. Mao et al., 2002) etc., provide strong evidence of that high metal enrichments in black shales can be derived from normal seawater by no involvement of proximal high temperature hydrothermal input. If there was a hydrothermal component for instance in the metal budget of the intracratonic Bazhenov black shale, it must have been by a long-distance (>> 1000 km) transport from the world major ocean system (Gavshin and Zakharov, 1996). The very similar metal enrichment patterns of OBS and Bazhenov shales (Fig. 11) provide strong evidence of that the metal enrichment processes were similar, and related primarily to scavenging of metals from chemically more or less normal sea water by dead organic material and co-precipitation of sulphides (cf. Gavshin and Zakharov, 1996).



Fig. 11. Upper crust-normalised metal patterns for median Outokumpu black schists (Table 1) and average Bazhenov black shales (Gavshin and Zakharov, 1996). Pattern for the more shaly Upper Kaleva mica schists WK2 (Lahtinen, 2000) is shown for comparison. Normalisation values from Taylor and McLennan (1985).

When evaluating metal sources of marine sediments, it is important to note that Co concentration in seawater is typically about two orders lower than that of Ni, whereas Co in most ore forming hydrothermal fluids is strongly enriched over Ni. Thus metal ratio plots that involve Ni and Co should provide a powerful tool for investigation of the seawater versus hydrothermal source of the metal enrichment. A clear trend in metal ratios towards seawater composition and away from the regime of common hydrothermal sulphides is seen in the Co/Cu versus Co/Ni diagram, for example (Fig. 12). Further, a contribution of metals in dead microorganisms is obvious in diagrams that integrate Zn (Fig. 13), which is the most abundant transitional metal (175 ppm in average) in marine microorganisms. The plotting of the OBS in these diagrams is strikingly similar with the Bazhenov shale.



Fig. 12. Co/Ni versus Co/Cu diagram for Outokumpu black schists. For comparison distributions of upper Kaleva metagraywackes and Jurassic Bazhenov black shales, likewise average compositions of Primitive mantle, N-MORB, upper crust and modern seawater are also shown. In addition, average ratios for Outokumpu ore and several major volcanic associated massive sulphide deposits are indicated. Note the trend of Outokumpu black shales from upper Kaleva (upper crust) compositions towards the seawater – not towards compositions of the Outokumpu or other plotted major massive sulphides. Instead, the Bazhenov metal-rich oil shales are in this diagram remarkably similar with the Outokumpu black schists. Note also how the Outokumpu ore deviates considerably from the other massive sulphides by its lower Co/Ni and especially higher Co/Cu.

However, although the general metal enrichment pattern of the OBS is remarkably similar with that of some of the more metal-rich Phanerozoic black shales, the abundances of Cu, Ni and Zn in the OBS are two to three-fold higher. Actually very few Phanerozoic black shales show similarly high metal enrichments than the OBS, yet the metal-richest TBS. Therefore it seems likely that some special, and perhaps just infrequently occurring conditions in world ocean system were required to produce the high Cu, Ni, Zn abundances in these Palaeoproterozoic black muds.



Fig. 13. Cu/Zn versus Co/Ni diagram for Outokumpu black schists. Comparative data as in Fig. 12. The biophile character of Zn in black shale deposition shows up in this diagram; both the Outokumpu and Bazhenov black shales trend towards compositions between modern Ocean water and marine organisms. Note that also in this diagram the trend of Outokumpu black shales is from upper Kaleva (upper crust) compositions towards the seawater – not towards compositions of the Outokumpu or the orther plotted major massive sulphide deposits.

The simplest explanation for the high metal concentrations in the OBS and TBS would be higher influx and concentrations of metals in the Proterozoic 2.00-1.90 Ga oceans. Condie et al. (2001) have provided evidence of a worldwide maximum in black shale abundance and black shale/normal shale ratio at 2.00-1.90 Ga. They connect this maximum with an inferred superplume event in Earths mantle at 1.90 Ga (Condie, 1998; Isley and Abbot, 1999), and propose it to reflect: 1) increased organic productivity in world oceans due to the superplume effects like increased flux of CO<sub>2</sub>, nutrients (increased weathering due to increased greenhouse effect) and increased hydrothermal activity; and 2) enhanced preservation of organic material by superplume related expanded anoxity in world oceans and world-wide marine transgressions onto the continental shelves. We note that the superplume-related increased hydrothermal activity very likely promoted increased flux of sulphur (SO<sub>2</sub>) and Fe (Fe<sup>2+</sup>) in world oceans, causing increased oceanic pH and dissolution of metals, which combined with the enhanced continental weathering rates may have resulted in "abnormally" high metal concentrations in ocean waters. Thus the superplume effects at 1.90 Ga seem to provide a feasible explanation for the distinctly high metal contents in the OBS and TBS black shales. If the superplume effects indeed were the factor behind the metal enrichment, 1.90 Ga metal-rich black shales/schists should be a worldwide phenomena.

In summary, we conclude that the metal flux in the OBS was mainly from ocean water by scavenging of the metals by organic matter and syngenetic precipitation of sulphides in a permanently anoxic depositional environment. REE evidence from the OBS indicates that the water column in the depositional basin was stratified so that only the bottom part was effectively anoxic. The very high S, C and trace metal abundances in the OBS indicate high organic productivity, relatively unrestricted water exchange with major oceans, low sedimentary rate, relatively vigorous circulation in the depositional basin, and attest for enhanced sulphur and metal concentrations in the 1.9 Ga oceans, which possibly were related to the inferred 1.9 Ga world-wide superplume event in the Earth's mantle.

In the above discussion we tactically assumed that the organic matter in these black schists would represent material that was ultimately accumulated from hemipelagic rain between periodical turbidite deposition events. However, considering the turbidite like nature of bulk of both the OBS and TBS, it is very much possible that their organic content is to a large degree resedimented material transported from extra-basinal sources by down slope turbidity currents. A detailed analysis of this possibility is difficult since any studies to address the petrography and paleosedimentology of the black schists either in the Outokumpu or Talvivaara areas have not yet performed. The common presence of finely laminated sulphidic lithofacies in the OBS suggests that at least parts of the OBS were in-situ sediments. Moreover, we believe that even in the case that the OBS represented mostly in mass flows redeposited material, much of the original chemical character of the primary organic rich metasediments was preserved more or less unchanged in the derivative sands and muds. Nevertheless we have here an issue that must be addressed in the future studies of the OBS and TBS.

# Tectonic setting of the OBS deposition

Basinal setting and depositional conditions favourable to black mud deposition appear to have existed mainly in the earliest phase of the Upper Kaleva deposition, and to have recurred only in minor scale during the later stages of the turbidite accumulation. The frequent association of the OBS with tectonically emplaced serpentinite bodies is an intriguing aspect of the Outokumpu Allochthon. One reason to this linkage is certainly due to the rheological properties of the serpentinites and the black schists. Remember the old saying: "Black shales are the sleeve and serpentinites the ball bearing of orogeny".

However, the spatial association of serpentinites and black schists appears in this case a too tight feature to be addressed by simple "we like each other during deformation" effect, but some more fundamental reason to the association must exist. One possible scenario would be, as we discussed in the beginning of this chapter, that the initial emplacement of the ophiolite fragments among the black muds occurred during their sedimentation, by down-slope gravity sliding as large, solid blocks or "olistoliths". Within frames of the currently popular tectonic models for the Svecofennia-Kaleva transition, the OBS might have been deposited about 1.90 Ga ago in a marginal basin developed on sinking margin of the Karelian Craton, the sinking of the margin reflecting the 1.90 Ga collision of the 1.93-1.91 Ga Svecofennian primitive arc complex from "west" against the craton margin (cf. e.g. Kohonen, 1995; Korsman et al., 1999; Lahtinen 2000). Mass-wastes of "olistholithic" oceanic lithosphere fragments in the enclosing marginal basin may easily be envisioned, from an accretionary complex developed at the eastern margin of the convergent arc and above the underthrust, westerly subducting oceanic crust. Deposition of black muds in the enclosing basin could have been operational during and subsequent the mass wastes of the ophiolite fragments, further enhancing the intimate association of the black shales and serpentinites. Capped thickly by sandy turbidites from the accretionary complex and thrust onto the thinned continental margin, the marginal basin fill could then be imagined to have provided an especially favourable environment for large scale gravity or load pressure driven systems of fluid flow, and associated low-temperature marginal alteration of the black mud enclosed serpentinites to listwaenite-birbirite.

If the formative setting of the Outokumpu black schists and serpentinites was as it is outlined above, it was in many respects analogous to the fore-arc basin setting of the Quebec Appalachian ophiolite fragments that also occur closely associated with thick black shale deposits and show local listwaenite-birbirite alteration. However, in the Appalachian case there are compelling evidence of an melange complex (e.g. St Daniel Melange) and lots of interbedded tuff and resedimented tuff layers derived from the converging arc within the fill of the marginal basin (e.g. Laurent, 1974). Similar evidence of nearness of any for-arc accretionary prism or an active arc is completely missing in the Kaleva association, however. In fact, the complete lack of evidence for synchronous arc magmatic activity or subduction complex in the Kaleva rock record, and the very homogenous, extremely well mixed nature of the Upper Kaleva are aspects that seriously undermine the creditability of the popular arc-continent collision models for the Upper Kaleva deposition (cf. Kohonen, 1995; Lahtinen, 2000).

Noting this difficulty, Kontinen and Ward (1991), inspired by Barbey et al. (1984), proposed that the Upper Kaleva would represent slope-rise turbidites to the ca. 2.0 Ga broken-up Karelian craton, with derivation of the sedimented material from the coevally exhuming Kola-Lappidic (Belomorian) orogen. We note that an alternative source of the Upper Kaleva could have been in the 1.9-2.0 Ga Palaeoproterozoic plutono-volcanic arcs and Archaean crust now buried below the Russian platform in Belorussia and Ukraina (cf. e.g. Bogdanova et al., 1994; Bogdanova, et al., 1996; Claesson et al., 1993).

The interpretation of passive margin setting for the Kaleva deposition finds support in the apparently total magmatic quiescence along the craton margin in the age period of from 1.95 to 1.88 Ga, i.e. in the period when the Svecofennian arcs were magmatically active and Kaleva was depositing. The first magmatic episode since 1.95 Ga appears to be the emplacement of the Juurusvesi tonalite, slightly postdating the early migmatism in the local Kaleva-type metasediments. Unfortunately the crystallization age of the Juurusvesi tonalite is currently known only by a rather imprecise zircon age of 1879+-32 Ma (GTK/unpublished data). The granitoid intrusions in the Kaleva assemblage in the area to the SW of Outokumpu yield fairly precise zircon ages close to 1870 Ma (Huhma, 1986). The only known possible example of 1.95-1.88 Ga magmatic activity along the craton margin is the Lapinlahti gabbro to the south of lisalmi, which has yielded a relatively imprecise zircon age of 1895±15 Ma (Paavola, 1988).

One of the few serious arguments against Upper Kaleva as a passive margin depository is the immaturity of its sediments. However, the lack of extensive sediment maturation typical of orthodox passive margin deposits could be explained by short, rapid transport and lack of onland vegetation during Precambrian. Large rivers comparable to the present Ganges and Brahmabutra may have collected the material eroding from the source areas to large continental marginal deltas that periodically failed, producing massive mass-flows in to the flanking Kaleva Ocean. The preserved part of the Kaleva probably represent relatively distal parts of the craton flanking turbidite fans, which seem to have deposited, similarly to the present Bengal Bay fans, on an oceanic substratum, now represented by the ophiolite fragments at the base of the Kaleva sequence.

Many characters of the Jormua ophiolite some 250 km to the north of the Outokumpu strongly support the concept of a 1.95 Ga break-up of the Karelian Craton and subsequent "Ligurian-type" amagmatic ocean opening (Kontinen, 1987; Peltonen et al., 1996; Peltonen et al., 1998). The close association of both the Jormua ophiolite and the Outokumpu ophiolite fragments with the upper Kaleva indicates their origin in a common formative setting. Compared to Jormua the Outokumpu ophiolite fragments carry significantly weaker narrow ocean ophiolite signature, however, which may imply that the Outokumpu ophiolite fragments were formed in a more advanced stage of the post 1.95 Ga ocean opening. Furthermore, the relative scarcity of mafic components in the Outokumpu ophiolite fragments may not be just a consequence of their advanced dismembering, but an indication of dominantly ultramafic nature of the new oceanic lithosphere, so that it was composed mainly of mantle peridotites with just minor (<5-25 vol.%) mafic intrusions, and that had only a patchy thin crust of mafic extrusive rocks. The black schists in the assemblage appear to represent sediments that were deposited early on the peridotitic seafloor, immediately after its slow extensional exhumation from beneath the separated continents.

The relative abundance of the black schists in the early stages of the deposition of the Upper Kaleva reflect shallow basinal conditions and low sediment input for the early postrift stage of the Kaleva Ocean, probably because of the underlying still after the break-up relatively hot and buoyant mantle lithosphere. With further opening and cooling of the early-formed oceanic lithosphere the basin was rapidly subsiding and received more sandy turbidite material. Periods of elevated organic background sedimentation seem to have occurred also during the subsequent sand-dominated deposition, resulting in thin black schist interbeds, partly preserved partly recycled into black sandy interbeds.

As we pointed out earlier, one of the most problematic aspects related to the Outokumpu ophiolite fragments is that how did they got incorporated among the OBS before their obduction. We proposed that this took place by transform fault tectonics shortly preceding the obduction. We note here that Kontinen (2002) has speculated that the boundary zone between

the Karelian Craton and Svecofennian domain would incorporate a transcurrent fault along which the Svecofennia was perhaps so late as somewhere after 1.86 Ga transported in its present position with respect to the Karelian Craton – as an already tectonically amalgamated protocratonic unit. If so, it is possible that the Outokumpu Allochthon had been obducted on the craton margin already before the emplacement of the Svecofennian protocraton. In this case incorporation of the ophiolite fragments among the OBS was related with a tectonic situation that no more is readily apparent in the rock record of southeastern Finland, and which is thus only speculatively reconstructable.

# Exploration implications

An important observation is the fact that previous studies of the OBS, despite of their many claims of the syngenesis of the OBS and the Outokumpu-type ores, have all failed to demonstrate features in the geochemistry or lithofacies of the OBS that could have been developed to really useful, practical exploration tools. This is not surprising in the light of the evidence we provided above of that the metal enrichment in the OBS was ultimately a normal black shale sedimentation process, which was completely unrelated to the hydrothermal Outokumpu ore formation. Below we review the few proposals that have been presented about he applicability of the OBS in defining targets for exploration of the Outokumpu type ores.

A spatial tie between calcareous black schists (CaO >3.13 wt.%), especially such that comprise greenish-grey 3 mm tremolite-rich layers, and Outokumpu type ores has been proposed by Loukola-Ruskeeniemi (1991). Our observations suggest that the association of calcareous black schists with serpentinite bodies is a universal aspect of the Outokumpu assemblage without any clear correlation to ore proximity. It is clear, also, that the calcareous black schists in the Outokumpu area do not show any metal enrichments or metal enrichment trends that would significantly exceed or deviate from those shown by the low-Ca black schists. And what comes to the presence of greenish-grey tremolite-rich layers in the OBS, they are a ubiquitous metasomatic veining feature along serpentinite margins all over the North Karelia Schist Belt, and locally present also in serpentinite bordering mica schists.

Loukola-Ruskeeniemi (1999) has recently proposed that the "S-rich laminated black schist cut by quartz sulphide veins, such as characterizes the Outokumpu deposits, could be used as a pathfinder in regional exploration for Cu-Zn-Co ores." Problem with application of the wide areal distribution of the critical "S-rich, laminated black shales", and the fact they show no lithological or geochemical metal-enrichment or depletion trends that would help to locate the more ore-critical domains. And what comes to the quartz breccia veining of the sulphidic blacks schists, which indeed is a common feature for instance in Kylylahti - if this phenomena really would be syngenetic with the sulphide ores, it would mean the latter would be structurally very late developments, having been formed in the brittle regime of deformation (cf. Fig. 7). Furthermore, the quartz veins themselves are not associated with any base or precious metal enrichment; thus, abundant quartz veins in the OBS rather dilute than upgrade metal concentrations.

Nevertheless, systematic analysing of black schists for base metals has historically been a common practise in association with exploration for Outokumpu type ores. This practise probably reflects the common idea of black schists being an integral part of the stratigraphy of the Outokumpu assemblage and to have some genetical or at least spatial tie-up with the ore formation (e.g. Peltola, 1960; Koistinen, 1981, Park, 1988). Our analysis of the black schist geochemistry shows, however, that if the aim is to find Outokumpu-type sulphides, systematic analysing of the black schists can be regarded more or less a waste of money and time. There simply is no evidence of Outokumpu type economical base or precious metal materialisations in the black schists, or no trends in the metal concentrations that would guide to Outokumpu-type mineralizations. Content of Co+Cu+Zn in the OBS appears to terminate to about 0.8 wt.% in maximum, and there is a distinct decrease in Co/Ni and Cu/Zn ratios with increasing metal content, which means that no trend in base the metal compositions of the OBS towards the Oku type ore sulphides is present (Figs. 14 and 15).



Fig. 14. Co/Ni versus Co+Cu+Zn (wt %) diagram for the OBS and some Outokumpu area sulphide deposits. For comparison median compositions of "Ni-poor" and "Ni-rich" blacks schists from Talvivaara (Loukola-Ruskeeniemi and Heino, 1996), and average composition of Bazhenov black shales (Gavshin and Zakharov, 1996) are also shown. Note the decreasing Cu/Zn with increasing metal content in the Outokumpu black shales, and that the black schists display here a trend away, not towards the sulphide ore compositions.

Finally, although syngenetic origin of the Outokumpu-type ores with the associated black schists seems utterly unlikely, one could still speculate whether they were the source of the metals by some secondary, either mechanical or fluid-assisted metal extraction/remobilisation process. The very differing lead-isotopes in the ores and blacks schists make also this type of scenarios very unlikely, however (cf. section 9.3.2).



Fig. 15. Cu/Zn versus Co+Cu+Zn (wt%) diagram for Outokumpu blacks schists and some Outokumpu area sulphide deposits. For comparison median compositions of the "Ni poor" and "Ni rich" blacks schists from Talvivaara (Loukola-Ruskeeniemi and Heino, 1996), and average composition of Bazhenov black shale (Gavshin and Zakharov, 1996) are also shown. Note that also in this diagram, as in the diagram in Fig.14, the Outokumpu black shales show decreasing Co/Ni with increasing base metal content, and a trend away from the sulphide ore compositions.

## 6.3. Outokumpu assemblage

#### 6.3.1. Metaserpentinites and metaperidotites

The serpentinite bodies in the Outokumpu assemblage range from just a few metres thick and a few metres long small lenses to large, up to several kilometres long and several hundreds of metres thick tabular to intensively folded and imbricated bodies (Gaál et al., 1975; Koistinen, 1981). The bodies that everywhere show faulted contacts comprise, but serpentinite, usually also a <5-25 vol.% component of deformed and metamorphosed basic rocks mostly present as dykes and small stocks enclosed in the serpentinites. The serpentinite-hosted metabasites yield U-Pb zircon ages at 1972±18 Ma for a pegmatoid gabbro from Horsmanaho (Huhma, 1986) and 1959±3 Ma for a coarse gabbro from Huutokoski (Huhma, 2002, written comm.). Significantly, similar basites as in the serpentinite bodies have nowhere been observed to intrude the enclosing Upper Kaleva metagreywackes.

The available detrital zircon age (U-Pb) data suggests that the Upper Kaleva metaturbidites enclosing the serpentinite bodies deposited subsequent to ca 1.92 Ga (Claesson et al., 1993); i.e. ca. 40 Ma later to the crystallization of the serpentinite hosted gabbros. This relationship attests to the allochthonous and exotic nature of the serpentinite bodies and supports the proposals that they would constitute an (dismembered) ophiolite complex (cf. Koistinen, 1981; Vuollo and Piirainen, 1990).

Whether the "Outokumpu Ophiolite Complex" (Vuollo and Piirainen, 1990) would really comprise a sample of true oceanic crust, like the Jormua complex (Kontinen, 1987), is still a debatable issue, since alternatively it could represent slices of "orogenic peridotite" tectonically incorporated into the Upper Kaleva metasediments (cf. Peltonen and Kontinen, 1997).

### Petrography

Serpentinites in the eastern part of the present study area, as e.g. in Kylylahti and Sola, consist of antigorite, whereas in the western part of the study area, as e.g. in Outokumpu or the Juojärvi--Heinävesi area, the dominant serpentine phases are lizardite and chrysotile (Haapala, 1936; Väyrynen, 1939; Vuollo and Piirainen,1990; Säntti et al., in press). A long-time controversy exists about the origin of olivine and enstatite occurring locally in the serpentinites. Haapala (1936) proposed that the olivines and enstatites represented relicts of primary magmatic olivine and orthopyroxene, whereas Väyrynen (1939) considered them metamorphic minerals derived from serpentine precursors and then variably reserpentinitized. Many subsequent workers (e.g. Park, 1983; Vuollo and Piirainen, 1989) have been supporting the interpretation by Haapala (op cit.).

Säntti et al. (in press) have recently studied the petrography of the ultramafic rocks in the Outokumpu assemblage in great detail. They found in agreement with Väyrynen (1939) that the precursor peridotites of the serpentinites most likely were more or less thoroughly serpentinized before the onset of the regional metamorphism. As a consequence of the regional metamorphism the serpentinites became replaced in the east (in lower amphibolite facies) by antigorite metaserpentinites, and in the west (in middle-upper amphibolite facies) by metaperidotites composed of metamorphic, neoblastic olivine, enstatite, talc and anthophyllite. The metamorphic olivines, enstatites and amphiboles in the metaperidotites are now extensively hydrated to post-peak retrogressive lizardite and chrysotile.

The main constituent in the metaserpentinites is always non-pseudomorphic antigorite as a fine-grained mass of interpenetrating, randomly orientated to sub-parallel blades and flakes (Fig. 16). Typical additional constituents include carbonate (magnesite) and talc, which are more abundant at the margins of the bodies, to an extent that locally antigorite is completely replaced by talc and carbonate, and soapstones (talc-carbonate rocks) are produced. In the core parts of the massifs, with increase in metamorphic grade antigorite is gradually replaced by olivine and/or tremolite porphyroblasts (Fig. 17). Distinct bands and schlierens rich chromite plus its oxide alteration products occur locally in the antigorite serpentinites. Being crosscut by pretectonic metabasite dykes, it is clear these bandings must represent pretectonic foliations. They strikingly resemble chromite bands and schlierens typical of many mantle tectonites. Occasionally coarser chromite grains preserve amoeboid and or lobate textures, very similar to chromites typical of strongly depleted harzburgitic-dunitic mantle residual peridotites (Fig. 16).

The metaperidotites frequently show massive, porphyroblastic or granoblastic-polygonal sructures (Fig. 18) without any clear preferred orientation implying crystallization in a relatively late kinematically static stage of the regional deformation history. Peak mineral mineral assemblages in the metaperidotites, ranging from talc+olivine via anthophyllite-olivine to enstatite-olivine, record a regional east to west increase in metamorphic temperatures. As we mentioned above, Säntti et al. (in press) provide petrographic and mineral chemical evidence that the olivines and enstatites are invariably metamorphic, neoblastic minerals, and that no other primary mantle minerals than occasionally chromite preserve in the metaperidotites (or in the metaserpentinites either).

Olivine in the metaserpentinites and metaperidotites has a total variation in Fo content between  $Fo_{82}$  and  $Fo_{96}$ . Ni content of the olivines varies between <0.01 and 0.44 wt.% and correlates roughly negative with the Fo content, which is a typical feature of metamorphic, neoblastic olivine suites (e.g. Peltonen, 1990). The enstatite in the metaperidotites is



Fig. 16. Scanned images of two samples of carbonate porphyroblastic antigorite metaserpentinites from southern part of the Kylylahti massif (R393/515.15-515.45). Coarse-grained anhedral, lobate to amoebic chromite grains as in these two samples are typical of the Kylylahti massif and strongly depleted mantle residual peridotites. Similarly coarse grain size and occasionally preserved lobate to amoebic shapes characterize also well-preserved chromite of the other Outokumpu area metaperidotite massifs.



Fig. 17. Scanned image of a sample of olivine-carbonate prophyroblastic antigorite metaserpentinite from the lower levels of the Kylylahti massif (R397/1036.65). Black=olivine, grey=carbonate, green=antigorite.


Fig. 18. Photographs of common rock types in the serpentinitized metaperidotite massifs of the Outokumpu area. (A) Weathering surface of a massive anthophyllite-olivine metaperidotite, Louhivuoret, Kaavi. (B) Diamond-sawn surface of an anthophyllite-tremolite-enstatite-olivine metaperidotite showing roundish-embayed porphyroblasts of gray enstatite in serpentinized, black anthophyllite-olivine matrix, Ruukinkoski, Kaavi,. (C) Diamond-sawn surface of an anthophyllite-olivine metaperidotite showing iridizing, lustrous prisms of anthophyllite embedded in serpentinized, black olivine matrix, Kultavuori, Kaavi. (D) Diamond-sawn surface of an olivine-tremolite metaperidotite showing serpentinized, black prisms of olivine in a gray matrix of tremolite, Puiroonkangas, Kangaslampi. (E) Diamond-sawn surface of an olivine-talc metaperidotite showing serpentinized, black prisms of olivine in a matrix of bluish gray fine-grained carbonate-talc, Saramäki, Outokumpu. (F) Diamond-sawn surface of an olivine-talc metaperidotite showing serpentinized, black prisms of olivine in a gray matrix of talc, Losomäki, Juankoski. More photographs of Outokumpu metaperidotites in Fig. 46.

(average 0.06 wt.%) and in other minor components, as metamorphic, neoblastic enstatites tend to be (e.g. Mancini et. al., 1996; Smith and Riter, 1997; Trommsdorff et al., 1998).

The composition and texture the chromite varies with metamorphic grade. In the metaserpentinites zonal alteration to ferrian chromite and chromian magnetite is typical for large chromite grains; the alteration being complete for small grains (Fig. 19a). The large, zonally altered grains have moderately aluminous relict cores (Cr# 0.4-0.7) surrounded by an inner alteration zone of ferrichromite and an outer one of Cr-magnetite. Nearly throughout alteration to ferrian chromite-chromian magnetite, or recrystallization to Cr-rich, Al-poor (Cr# 0.7-1.0) chromite characterize the metaperidotites; only very rarely do large chromite grains (5-10 mm) occur that still preserve unrecrystallized core domains of similar moderately aluminous chromite (Cr# 0.43-0.65) than the large zoned chromites in the metaserpentinites(Figs. 19b-c). Pervasive alteration to zoned ferrian chromite – Cr-magnetite is typical in the metaperidotite body cores while recrystallization to high-Cr chromite characterizes the body margins (Figs. 19d-f). In the highest-grade metamorphic domains SW of Outokumpu, the high-Cr chromite shows partial replacement by aluminous spinel, in samples where it is associated with chlorite.

The moderately high Cr# (0.4-0.7) from the relict chromite cores in the metaserpentinites and metaperidotites are compatible with the whole rock chemical evidence of that the serpentinites in the Outokumpu assemblage represented strongly depleted, mainly harzburgitic to dunitic mantle peridotites. The Cr# are similar as usual in mantle peridotites after 15-20 % melting in spinel stability field (cf. Hellebrant et al., 2001). In contrary, Mg# even in the best-preserved chromite cores, whether in the metaserpentinites or metaperidotites, are strongly affected by metamorphic alteration rendering them useless as a petrogenetic indicator.

In the following chapters, for the sake of simplicity, we often use the general term "serpentinite" instead of the more proper terms metaserpentinite (antigorite serpentinites in the eastern part of the NKSB) or serpentinized metaperidotite (chrysotile-lizardite serpentinites +relict peak-metamorphic olivine, enstatite, anthophyllite etc. in the western part of the NKSB). However, in occasions where the primary rock type is rather referred to, we will often use the term "peridotite".

# <u>Geochemistry</u>

The GSF dataset for the Outokumpu-Jormua Belt serpentinites includes 152 samples representing most of the known ultramafic bodies within the NKSB and KSB. For some of the bodies there are a few tens of samples, for some other maybe just one sample. The sampling is, however, considered covering enough to reveal the entire variation within the compositional spectrum of the serpentinites in the Outokumpu assemblage. This comes evident by that the over 1000 serpentinite whole rock analyses (XRF) in the Outokumpu database (OKU dataset), for map sheets 4222, 4224 and 4213, does not result in compositional variation that would exceed or essentially deviate from that shown by the GSF dataset. The OKU dataset for serpentinites is somewhat problematic, however, as it is plagued by considerable secular variation in analytical calibration (especially for Mg and Al). Therefore the GSF dataset is mainly used in the below discussion, if the Oku XRF dataset is referred, it is particularized.

The Outokumpu serpentinites are below discussed together with the compositionally very similar serpentinites of the Jormua Ophiolite, though to allow comparisons are usually shown in the included diagrams with different symbols. In the end of this chapter, the Outokumpu peridotites are discussed separately and in a more detail in an ore geological point of view for their Co, Cu, Zn and Ni geochemistry, i.e. for those elements that are the main metals in the Outokumpu sulphide ores. Average analyses of the main lithological components in the Outokumpu assemblage, and some reference data for comparison, are listed in Tables 4a-4b.



Fig. 19. Reflected light photomicrographs of polished thin sections of the various chromite types characteristic of the Outokumpu area metaserpentinites and metaperidotites. (A) Relict Al-rich chromite with ferrian chromite alteration rim in an antigorite metaserpentinite, Kylylahti, Polvijärvi (lower amphibolite facies). (B) Relict Al-rich chromite with a recrystallized high-Cr chromite rim in an anthophyllite-olivine metaperidotite, Piilukoski, Kaavi (upper amphibolite facies). (C) Relict Al-rich chromite showing recrystallization to high-Cr chromite at margins, Outokumpu (middle amphibolite facies). (D) Chessboard-textured, pervasively recrystallized high-Cr chromite with chlorite inclusions and a chloritic mantle in an olivine-anthophyllite-tremolite metaperidotite, Niinivaara, Kaavi (upper amphibolite facies). (E) Small, neoblastic high-Cr chromites enclosed in olivine (OL) partially altered to lizardite (Lz) in an olivine-enstatite metaperidotite, Outokumpu (middle amphibolite facies). (F) Small, neoblastic high-Cr chromite totally altered to lizardite (Lz) in an olivine-texture enclosed in olivine totally altered to lizardite (Lz) in an olivine-texture enclosed in olivine totally altered to lizardite (Lz) in an olivine-texture.

#### Major elements

The Jormua-Outokumpu serpentinites are uniformly very magnesian, showing MgO contents on a volatile-free basis usually between 35 and 50 wt.% and on average ca. 42.4 wt.%.  $Al_2O_3$  content varies typically between 0.4 and 3 wt.%, showing an average of ca. 1.9 wt.%.  $TiO_2$  is typically between <0.01 and 0.25 wt.%, with an average of ca. 0.08 wt.%. CaO contents are typically very low in core parts of large massifs <0.5 wt.%, but are markedly higher at the body margins and in the smaller lenses, obviously due to postemplacement Ca metasomatism. The very low Ca contents in the core parts of the serpentinites indicate pervasive serpentinization and removal of Ca from pyroxene already before peak-metamorphism.

On a volatile free-basis, bulk of the Outokumpu and Jormua peridotites correspond to depleted lherzolites, harzburgites and even dunites. Despite of the profound and multistage alteration of the serpentinites, Harker diagrams still reveal major element and trace element trends that are broadly similar with those of many depleted mantle peridotite suites (Figs. 20-21). These trends include e.g. that the relatively immobile and moderately incompatible  $TiO_2$ and  $Al_2O_3$  show good positive correlation for bulk of the samples, with a variation in  $Al_2O_3$  from 3 to 0.3 wt.%, implying as such 5 to 25 % total depletion with respect to primitive mantle source. Considering the multistage alteration-recrystallization history of the analysed serpentinites, their Al<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub> contents show remarkably little variation out of the compositional space of mantle peridotites. The antigorite metaserpentinites yield a somewhat higher average  $Al_2O_3$  content of 2.36 wt.% compared to the 1.59 wt.% of the metaperidotites. What is somewhat surprising, some of the lowest overall  $Al_2O_3$  and  $TiO_2$  contents, and hence probably highest degree of depletion, are shown by the metaperidotites in Outokumpu and Vuonos (1.09 wt.% Al<sub>2</sub>O<sub>3</sub> on average, n=36) and Luikonlahti massifs, i.e. those serpentinite massifs that are associated with the largest amounts of ore-grade Cu-Co-Zn sulphides.

The somewhat lower average  $Al_2O_3$  of the metaperidotites compared with metaserpentinites could potentially reflect metamorphic loss of alumina with increase in metamorphic grade. However, more probably the lower  $Al_2O_3$  in the metaperidotites reflects dominance of depleted peridotites in SW part of the study area wherefrom most of the metaperidotite samples come from. This view finds support from the fact that e.g. in the Kaavi and Juankoski areas metaperidotites show a similar average  $Al_2O_3$  content (2.54 wt.%, n=49) than metaserpentinites at Jormua and Polvijärvi (2.26 wt.%, n=69). Furthermore, there exists actually considerable local overlap in the alumina contents so that domains with very low  $Al_2O_3$  occur within the mostly "high- $Al_2O_3$ " bodies, as e.g. in Jormua, and vice versa.

In terms of SiO<sub>2</sub>/MgO ratios, there is no significant difference between the antigorite metaserpentinites and metaperidotites but both show about similar average ratios of 1.09 and 1.07, respectively. These are values significantly below the SiO<sub>2</sub>/MgO of 1.19 inferred for primitive mantle (McDonough and Sun, 1995) but well within the range of 1.00-1.10 defined by averages of the various continental peridotite xenolith suites and abyssal residual peridotites. In the Mg/Al vs. Si/Al diagram (not shown) both the metaserpentinites and metaperidotites plot tightly in the field defined by xenolith and abyssal peridotite suites. Altogether this suggests that Jormua and Outokumpu peridotites would have preserved their SiO<sub>2</sub>/MgO relatively unchanged, in spite of their complex hydration-dehydration history.Mg / Fe ratios (4 to 7) of the Jormua and Outokumpu peridotites are per a given Mg/Al somewhat higher than the Mg/Fe of most recent abyssal peridotites (Mg/Fe =4 on average). Neither is this feature necessarily an alteration indication since some cratonic peridotite xenolith suites, especially those from below interiors of the Archaean shields, also tend to be similarly "depleted" in Fe.

	n	SiO <sub>2</sub>	TiO <sub>2</sub>	$AI_2O_3$	Fe <sub>2</sub> O <sub>3</sub> t	MnO	MgO	CaO	Na₂O	K₂O	P <sub>2</sub> O <sub>5</sub>	S	Ctot	CI	Ва	Ga	Sr
		wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	ppm	ppm	ppm	ppm
Metasomatic ultramafic rocks	, Out	okumpı	ı-Jormı	ia belt:													
Metaserpentinite	69	41,03	0,08	2,01	8,17	0,09	37,65	0,67	0,01	<0.01	<0.01	0,07	0,52	75	6	6,3	4
Metaperidotite	155	39,86	0,06	1,38	7,76	0,10	37,17	1,71	0,01	0,01	<0.01	0,53	0,49	1451	15	5,2	12
Oliv-carb-talc rock	18	41,21	0,02	0,84	7,47	0,09	35,75	2,17	0,01	<0.01	<0.01	0,20	1,51	681	15	3,8	16
Talc-carbonate rock	35	37,23	0,03	1,17	6,25	0,11	31,66	5,59	0,01	<0.01	<0.01	0,76	4,99	62	10	3,2	47
Tremolite skarn	30	46,24	0,03	1,20	6,04	0,10	18,97	15,96	0,05	0,02	0,03	1,21	2,45	86	10	4,4	37
Diopside skarn	31	48,46	0,03	1,30	5,95	0,12	16,25	20,25	0,11	0,06	0,03	1,56	0,84	51	14	5,2	38
Oliv-carbonate rock	17	20,12	0,03	1,03	6,24	0,11	22,90	21,76	0,02	0,05	0,02	1,08	6,16	404	17	3,7	107
Carbonate rock	46	14,65	0,02	0,75	5,04	0,11	20,12	25,23	0,01	0,01	0,02	0,65	9,34	129	11	2,2	74
Quartz rock	88	89,68	<0.01	0,45	2,10	0,02	2,09	2,47	0,02	0,04	<0.01	0,98	0,71	47	14	2,2	11
Metasomatic ultramafic rocks	, Out	okumpı	and V	uonos:													
Metaperidotite	36	37,33	0,01	0,94	8,37	0,10	37,50	2,49	0,01	<0.01	<0.01	0,83	1,00	1425	12	4,4	8
Carbonate rock	18	12,44	<0.01	0,54	6,00	0,12	19,28	26,47	0,01	<0.01	0,02	0,48	9,54	71	7	0,8	86
Quartz rock	35	92,93	<0.01	0,42	1,65	0,01	1,24	1,41	0,02	0,04	<0.01	0,98	0,55	36	17	1,8	9
Upper Kaleva metasediments:	<u>.</u>																
Black schist	8	47,75	0,60	11,25	15,25	0,05	4,34	3,66	1,13	2,74	0,12	8,25	8,54	52	330	18,9	92
Mica schist WK1 <sup>ª</sup>	47	69,85	0,68	13,11	5,50	0,07	2,26	2,22	2,98	2,37	0,16	0,07	0,22	79	489	na	247
Pel. mica schist WK2 <sup>ª</sup>	6	63,23	0,83	15,42	7,38	0,08	3,23	2,36	2,84	3,36	0,16	0,06	0,07	139	613	na	223
Reference data:																	
Primitive Mantle <sup>b</sup>		45.0	0.20	4.44	8.96	0.13	37.81	3.54	0.36	0.03	0.02	0.025	0.012	17	6.6	4.0	19.9
Average UCC <sup>c</sup>		66,0	0,5	15,2	5,0	0,08	2,2	4,2	3,9	3,4	0,15	0,095	0,324	640	550	17	350

Table 4a. Average analyses of major and some trace elements in main rock types of the Outokumpu Assemblage.

<sup>a</sup> Lahtinen (2000).

<sup>b</sup> McDonough and Sun (1995).

<sup>c</sup>Taylor and McLennan, 1985; P<sub>2</sub>O<sub>5</sub>, S and Ctot from Wedepohl (1995).

	n	Со	Cr	Ni	Sc	V	Nb	Y	Th	Zr	Ŭ	Ni/Co	U/Th
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm		
Metasomatic ultramafic rock	s, Outoku	impu-Jorm	ua belt:										
Metaserpentinite	69	91	3079	2151	8,8	49	0,81	3,3	0,21	5,1	0,3	23,6	1,7
Metaperidotite	155	99	2621	2090	7,0	36	0,82	1,9	0,28	4,1	0,2	21,0	0,84
Oliv-carb-talc rock	18	86	2278	2171	5,8	26	0,65	0,9	0,37	1,2	0,5	25,2	1,2
Talc-carbonate rock	35	80	2326	1753	5,7	29	1,12	1,1	0,17	2,1	0,9	21,9	5,0
Tremolite skarn	30	111	1881	1627	8,5	41	0,38	5,1	0,15	3,1	5,1	14,7	34,2
Diopside skarn	31	112	2873	1752	10,5	44	0,53	5,3	0,20	2,8	11,9	15,6	59,1
Oliv-carbonate rock	17	76	2415	1359	8,6	35	0,75	3,9	0,26	2,4	8,0	17,9	30,8
Carbonate rock	46	73	2269	1220	6,8	29	0,69	3,0	0,27	2,2	6,8	16,7	25,1
Quartz rock	88	108	1909	1667	5,0	36	0,34	2,0	0,08	1,9	6,4	15,4	82,4
Metasomatic ultramafic rock	s, Outoku	impu and V	/uonos:										
Metaperidotite	36	120	3644	2213	6,2	31	0,22	0,6	0,05	1,8	0,1	18,5	1,7
Carbonate rock	18	64	3127	1118	3,5	24	0,21	2,3	0,27	1,7	4,3	17,5	15,8
Quartz rock	35	100	2092	1582	5,6	44	0,18	1,6	0,05	2,0	8,5	15,8	179,7
Upper Kaleva metasediments	<u>s:</u>												
Black Schist	8	35	136	441	17,0	623	9,05	30,6	6,99	114,4	16,9	12,5	2,4
Mica Schist, WK1 <sup>ª</sup>	47	14	106	45	15,3	128	9,20	23,7	8,93	217,0	1,8	3,2	0,20
Pel. mica schist, WK2 <sup>ª</sup>	6	21,3	137	65,3	20,5	164	11,2	26,5	9,27	203	2,00	3,1	0,22
Reference data:													
Primitive Mantle <sup>b</sup>		105	2625	1960	16,2	82	0,658	4,3	0,0795	10,5	0,0203	18,7	0,26
Average UCC <sup>c</sup>		10	35	20	11,0	60	25	22	10,7	190	2,8	2,0	0,26

Table 4b. Average analyses of relatively immobile trace elements and U in main rock types of the Outokumpu Assemblage.

<sup>a</sup> Lahtinen (2000).

<sup>b</sup> McDonough and Sun (1995).

<sup>c</sup>Taylor and McLennan, 1985; P<sub>2</sub>O<sub>5</sub>, S and Ctot from Wedepohl (1995).

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	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	ΣREE
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Metasomatic ultramafic ro	ocks, Out	okumpu-	Jormua k	<u>elt:</u>											
Metaserpentinite	0,87	2,02	0,30	1,24	0,37	0,06	0,44	0,08	0,48	0,11	0,33	0,05	0,37	0,06	6,78
Metaperidotite	0,61	0,94	0,15	0,67	0,21	0,06	0,27	0,05	0,30	0,07	0,21	0,04	0,22	0,04	3,83
Oliv-carb-talc rock	1,04	0,41	0,04	0,32	0,16	0,11	0,18	0,02	0,21	0,03	0,19	0,02	0,18	0,02	2,94
Talc-carbonate rock	0,80	1,21	0,17	0,63	0,18	0,03	0,18	0,04	0,18	0,04	0,12	0,02	0,14	0,04	3,76
Tremolite skarn	1,22	1,90	0,33	1,45	0,40	0,10	0,60	0,10	0,72	0,16	0,47	0,07	0,48	0,07	8,06
Diopside skarn	3,49	5,32	0,73	2,97	0,66	0,14	0,77	0,11	0,71	0,16	0,49	0,07	0,50	0,08	16,20
Oliv-carbonate rock	1,46	1,23	0,29	1,12	0,25	0,37	0,41	0,08	0,51	0,14	0,39	0,07	0,39	0,07	6,77
Carbonate rock	0,79	0,82	0,16	0,67	0,14	0,07	0,23	0,04	0,26	0,07	0,20	0,03	0,18	0,04	3,72
Quartz rock	1,47	1,65	0,27	0,87	0,18	0,08	0,24	0,04	0,24	0,06	0,18	0,03	0,18	0,03	5,51
Metasomatic ultramafic ro	ocks, Out	okumpu a	and Vuor	<u>ios:</u>											
Metaperidotite	0,17	0,36	0,06	0,25	0,07	0,03	0,09	0,02	0,08	0,02	0,06	0,01	0,07	0,01	1,30
Carbonate rock	0,65	0,83	0,11	0,56	0,12	0,06	0,18	0,03	0,19	0,06	0,16	0,03	0,16	0,03	3,16
Quartz rock	0,75	0,69	0,17	0,48	0,10	0,08	0,16	0,03	0,16	0,04	0,16	0,02	0,11	0,02	2,96
Upper Kaleva metasedime	<u>ents:</u>														
Black Schist	21,81	38,78	5,45	21,04	4,51	1,02	4,94	0,75	4,53	0,94	2,79	0,42	2,92	0,46	110,34
Mica schist WK1 <sup>ª</sup>	31,60	62,90	7,43	27,30	5,13	1,06	4,63	0,68	3,68	0,73	2,12	0,31	2,16	0,32	150,05
Pel. mica schist WK2 <sup>ª</sup>	33,2	65,4	8,02	28,9	5,55	1,15	5,04	0,75	4,12	0,79	2,31	0,32	2,19	0,32	158,1
Reference data:															
Primitive Mantle <sup>b</sup>	0,648	1,675	0,254	1,250	0,406	0,154	0,544	0,099	0,674	0,149	0,438	0,068	0,440	0,068	6,867
Average UCC <sup>c</sup>	30	64	7,1	26	4,5	0,88	3,8	0,64	3,5	0,80	2,3	0,33	2,2	0,32	146

Table 4c. Average analyses of REE in main rock types of the Outokumpu Assemblage.

<sup>a</sup> Lahtinen (2000).

<sup>b</sup> McDonough and Sun (1995).

<sup>c</sup>Taylor and McLennan, 1985; P2O5, S and Ctot from Wedepohl (1995).

	n	Ag	As	Au	Bi	Cd	Со	Cu	Мо	Ni	Pb	Sb	Se	Sn	Zn
		ppm	ppm	ppb	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Metasomatic ultramafic	rocks, C	Outokump	u-Jormu	a belt:											
Metaserpentinite	69	<0.1	41,2	4,8	0,01	<0.1	91	16	5	2151	13	2,28	0,12	<1	62
Metaperidotite	155	0,6	12,7	8,8	0,16	0,1	99	28	4	2090	10	0,11	0,86	1	94
Oliv-carb-talc rock	18	<0.1	13,2	5,0	0,01	<0.1	86	10	5	2171	12	0,18	0,15	<1	65
Talc-carbonate rock	35	<0.1	144,4	15,0	0,09	0,1	80	29	4	1753	10	0,14	0,75	<1	85
Tremolite skarn	30	0,5	44,1	15,2	0,35	0,4	111	68	5	1627	9	0,25	1,29	<1	169
Diopside skarn	31	0,6	12,6	4,3	0,40	0,5	112	161	4	1752	9	0,06	1,38	2	401
Oliv-carbonate rock	17	0,6	6,7	5,0	0,12	0,2	76	170	8	1359	12	0,05	0,90	<1	151
Carbonate rock	46	0,5	15,1	6,2	0,04	0,1	73	37	4	1220	14	0,30	0,24	<1	141
Quartz rock	88	0,8	33,6	5,2	0,06	0,2	108	64	6	1667	5	0,37	0,46	1	108
Metasomatic ultramafic	rocks, C	Dutokump	u and Vu	ionos:											
Metaperidotite	36	0,9	26,3	12,0	0,12	0,1	120	65	3	2213	3	0,15	1,06	<1	175
Carbonate rock	18	0,9	18,6	7,3	0,05	0,1	64	13	2	1118	5	0,30	0,24	<1	111
Quartz rock	35	0,8	31,9	5,0	0,05	0,2	100	51	15	1582	5	0,44	0,62	1	80
Upper Kaleva metasedi	ments:														
Black schist	8	0,7	75,1	5,9	0,35	14,5	35	304	81	441	34	1,45	15,39	1	1757
Mica schist WK1 <sup>a</sup>	47	0,067	0,42	0,34	0,10	na	14,1	25,6	na	44,9	na	0,028	0,13	na	84
Pel. mica schist WK2 <sup>a</sup>	6	0,061	0,63	0,40	0,12	na	21,3	31,7	na	65,3	na	0,021	0,15	na	115
Reference data:															
Primitive Mantle <sup>▷</sup>		0,008	0,05	0,001	0,0025	0,04	105	30	0,05	1960	0,15	0,0055	0,075	0,13	55
Average UCC <sup>c</sup>		0,055	1,5	1,8	0,127	0,098	10	25	1,5	20	20	0,2	0,05	5,5	71

Table 4d. Average analyses of chalcophile metals in main rock types of the Outokumpu Assemblage.

<sup>a</sup> Lahtinen (2000). <sup>b</sup> McDonough and Sun (1995).

<sup>c</sup>Taylor and McLennan, 1985; P<sub>2</sub>O<sub>5</sub>, S and Ctot from Wedepohl (1995).



Fig. 20. MgO, FeOt, TiO<sub>2</sub> and Zr versus  $AI_2O_3$  diagrams for Outokumpu area and Jormua metaserpentinites and metaperidotites (recalculated anhydrous). Data for Siberian Udachnaya cratonic mantle peridotite xenoliths (representing Archaean SCLM; Boyd et al., 1997) and modelled MORB mantle melting trend (Pearce and Parkinson, 1993) are shown for comparison.



Fig. 21. Ni, Cr, V and Sc versus Al<sub>2</sub>O<sub>3</sub> diagrams for Outokumpu area and Jormua metaserpentinites and metaperidotites (recalculated anhydrous). Data for Siberian Udachnaya mantle peridotite xenoliths (representing Archaean SCLM; Boyd et al., 1997) and modeled MORB-mantle melting trend (Pearce and Parkinson, 1993) are shown for comparison.

## First series transition metals Co, Cr, Ni, V, Sc, Zn

The concentrations of first series transition elements in the Jormua-Outokumpu serpentinites are within the range typical of depleted mantle peridotites. For example, the Cr concentrations vary typically from 1500 to 3500 ppm with an average of ca. 2700 ppm, and the Ni concentrations from 1500 ppm to 2500 ppm with an average of ca. 2000 ppm. Accordingly, plotted on a Ni/Al vs. Cr/Al diagram (not shown) the serpentinites define an obvious melt extraction controlled trend typical of mantle peridotite suites. The relatively little variations in concentrations of the first series transitional metals outside their mantle ranges suggests magmatic (cumulus) peridotites in the Outokumpu peridotite suite would be rare. A small part of the samples show high Cr concentrations out of the purely melting controlled space but these are usually samples with schlierens and shear bands enriched in chromite. Such tectonic chromite/chrome enrichments are typical for mantle peridotites.

It has to be noted, however, that, although all the transition metals correlate with  $Al_2O_3$  and MgO broadly as expected for mantle peridotites, the correlations are far from perfect. Two possible reason for this can readily be named, either the scatter reflects distributions after low-T and/or metamorphic alteration, or alternatively the relatively poor correlations reflect effects of mantle-stage fluid or melt infiltration events. The very similarity of the Outokumpu and Jormua peridotites in terms of their transition metal to Al distributions with some cratonic peridotite xenolith suites suggests the latter processes were the principal factor.

Sc (<8ppm) and V (<35ppm) concentrations in the most depleted Outokumpu metaperidotites are compatible with their  $AI_2O_3$  (0.5-1.5 wt.%) concentrations indicative of high degree (10-20%) of total melting (=source depletion+degree of partial melting). However, the Ni and Cr concentrations as quoted above are on average somewhat lower than one would expect for such highly depleted peridotites. In this respect there is more resemblance to some cratonic xenolithic peridotite suites than present abyssal or ancient ophiolitic peridotites.

Vanadium abundances in residual peridotites depend, but on degree of depletion (in basaltic components), also palaeo-redox states during formation of mantle lithosphere (e.g. Pearce and Parkinson, 1993; Canil, 2002). The low mobility of V during alteration and metamorphism means that V abundances should enable evaluation of redox memories of also ancient, altered peridotites. This would be useful in determining the palaeotectonic setting of formation of residual peridotite since peridotites from many arc-related peridotites, orogenic massifs, likewise large proportion of cratonic peridotites show V and AI (and MgO) covariations that suggests their formation at significantly higher oxygen fugacity compared to abyssal peridotites. V-Al<sub>2</sub>O<sub>3</sub> covariations suggests that the bulk of the Jormua-Outokumpu peridotites formed by 15 to 25% near-fractional melting of spinel Iherzolite under QFM to QFM+1 oxygen fugacity conditions. Another scenario could be that these peridotites were produced (depleted for basaltic component) at a  $fO_2$  similar to that recorded by present abyssal peridotites but at much higher pressures (>7 Gpa). We note that in terms of the V-Al<sub>2</sub>O<sub>3</sub> distribution the Jormua-Outokumpu peridotites are very similar with the peridotite xenoliths from the Udachnaya kimberlite, which is sampling mantle from below the Precambrian basement of the central Siberian platform. The origin of the apparently high oxidation character of some of the cratonic peridotites is not well known. One of the proposed explanations is that the cratonic roots are accreted from peridotites that originated as residuals of hydrous melting of mantle wedges above ancient subduction zones.

Although the great majority of the Outokumpu and Jormua serpentinite samples show V and Sc concentrations in the field of depleted mantle peridotites, there are a number of samples included that show V and Sc concentrations significantly above the normal mantle range. The sympathetic behaviour of Sc and V with Ti and AI for these samples suggests most probably of this enrichment would be of basaltic nature. representing refertilization/impregnation of the depleted peridotites by basaltic melts. A very likely explanation when one observes that many of the Sc-V-rich samples come from outcrops where there are abundant basaltic-gabbroic dykes. Basalt infiltrated peridotites appear especially common in Jormua, and in the serpentinite massif of the Kaavi structure, but occur also in Kylylahti and Sola massifs, for example.

# PGE

A suite of representative samples for Jormua, Outokumpu and Vuonos serpentinites had been analysed for their platinum group elements (PGE) in GTK already before the GEOMEX project. This data showed that the PGE concentrations in the serpentinites corresespond to their Cr, Ni and Co concentrations being systematically within the <0.5-1.5 times mantle range. In absolute terms this means the measured Ir, Pt and Pd concentrations systematically remained below 10 ppb level. Consequently, on the Ni/Cu versus Pd/Ir diagram of Barnes et al. (1988) Outokumpu serpentinites expectedly plot mostly within the field of mantle peridotites (Fig. 22), with some scatter towards more Cu-rich compositions. We will below deduct that the indicated minor Cu enrichment is related to synmetamorphic sulphur addition in the serpentinites.



Fig. 22. Metal ratio plot Pd/Ir versus Ni/Cu for Outokumpu-Vuonos and Jormua serpentinites (SP) and Outokumpu-Vuonos carbonate-skarn-quartz rocks (CRBR-SKA-QTZR). Compositional fields of mantle, komatiites, ophiolites, layered intrusions, ocean floor, high-Mg and boninitic basalts, flood basalts and associated sulphide veins (Barnes et al., 1988) are shown for comparison. Note that Pd abundances in many of the plotted samples were below the detection limit (3ppb) of the used analytical method, and that thus the Pd/Ir values are partly maximum values.

Both of the Jormua and Outokumpu ophiolitic complexes seem to exhibit thorough low PGE abundances, this concerning also the mafic parts of at least the Jormua complex (Peltonen and Kontinen, unpublished data) and sulphide deposits in association of the Outokumpu complex (section 9.2.7.). This finding is in marked contrast to outcome of many recent PGE surveys of ophiolites, which have revealed anomalous PGE values in almost every ophiolite studied, for their chromitites, ultramafic cumulates, sulphide bearing gabbros and sheeted dyke complexes. The most PGE mineralized ophiolites are usually interpreted to have formed in fore-arc and back arc terranes. Thus, the PGE-poor nature of the Jormua and Outokumpu complexes could be taken as one argument against their supra-subduction origin.

These are all elements that (excluding Th) show relatively immobile behaviour in most aqueous alteration processes and are highly to moderately incompatible in mantle melting. Nb and Zr belong to the high field strength elements (HFSE) while Th is a large ion lithophile element (LILE). In the Jormua-Outokumpu serpentinites the concentrations of the HFSE and Th are usually very low, e.g. Zr, for which the analytical data is fairly precise, is present fairly systematically in concentrations below 10 ppm, as it would be expected for originally depleted mantle peridotites (primitive mantle has 10.5 ppm Zr, McDonough and Sun, 1995). Th concentrations are mostly below 0.1 ppm and hence below the detection limit of the ICP-MS procedure (308M) used here as the routine method of trace element analysing.

Also the concentration of YREE are systematically very low, and especially in most Outokumpu samples below the laboratory certified detection limit of the 308M procedure. In order to get more accurate idea of the REE distributions, REE from a few selected samples from Jormua and Outokumpu were first chromatographically preconcentrated and then measured by the ICP-MS. These data show that both the Jormua and Outokumpu peridotites have in most cases relatively flat mantle-normalised REE profiles at 0.5-4 times of mantlenormalized levels (Fig. 23). The flat profiles are very dissimilar to the usually strongly melting controlled mantle normalised patterns of modern ocean-spreading-ridge, oceanic transform or arc-related (fore-arc, back-arc) residual peridotites, which all usually show MREE-HREE with positive slopes, and LREE-MREE varying from the mostly steeply positive profiles to flat or even negative (resulting in V shaped overall pattern), depending on amount of trapped/reacted melt or fluid (e.g. Johnson et al., 1990; Niu and Hekinian, 1997; Parkinson and Pearce, 1998; Ohara et al., 2002).

Clearly, in the light of the flat REE profiles neither the Jormua nor Outokumpu peridotites can represent simple melting residuals. This is seen also in that Zr in both the Jormua and Outokumpu sample sets shows very poor to bivariate correlation with, AI, Sc and V, and that there is also only relatively poor correlation between Yb and Al. Though as a group flat, in a more detailed scrutiny only a few of the mantle-normalised REE profiles appear literally flat, but actually some exhibit overall negative, some positive, and some somewhat more complex profiles. Putting the individual samples in their field context reveals that the REE profiles seem to reflect the abundance and nature of mafic dykes in the sample outcrops and/or neighbouring outcrops. This situation is more obvious in Jormua where there is usually proportionally more dyking and variation in the dyke compositions (OIB, E-MORB, carbonatite). In the light of this observation, the nonresidual characters in the trace element composition of the Jormua and Outokumpu mantle peridotites seem to originate from their interaction with mostly mafic melts that have percolated/channellized through them during their mantle evolution. Part of the chemical variation may be due to metasomatism by some more cryptic alkaline and/or carbonatitic melts/fluids, and undoubtedly also related to the post-mantle stage alterations. Unfortunately in case of peridotites with such complex alteration-metamorphic histories as the Jormua-Outokumpu peridotites, more exact clarifying of the underlying events/processes would be very difficult and out of scope of this work. It should be noted, however, that in terms of their incompatible trace element geochemistry the Jormua and Outokumpu peridotites clearly resemble more peridotites with long histories as part of subcontinental mantle lithosphere than peridotites of oceanic or supra-subduction lithospheres.



Fig. 23. Pyrolite-normalized (primitive mantle) REE profiles of metaserpentinites in Jormua and serpentinized metaperidotes in Outokumpu and Vuonos. Note the flat patterns that are strange for most abyssal or most ophiolite mantle peridotites, but more similar with patterns of some cratonic mantle peridotite suites.

# S, Ni, Co, Cu, Zn

These elements, plus iron and silica, are the main constituents in the Outokumpu type sulphide ores. As the serpentinites in the Outokumpu assemblage theoretically may have been the source of the sulphur and base metals in the associated sulphide accumulations, a more detailed scrutiny of S and base metal contents in the serpentinites is at place, and is given below. In this chapter we will use but the GTK and OKUXRF datasets, also the "OKUBS-dataset" as collected by M. Huhma in association with black schist oriented geochemical study carried out in Outokumpu during 1970s. The OKUBS dataset comprises 529 serpentinite analyses from the entire NKSB, all these samples are analysed for Cu, Ni, Co, Zn, Hg and S by AAS.

Sulphur content of the primitive mantle is 0,025 wt% (McDonough and Sun, 1995), and is likely to decrease with increase in degree of partial melting and melt extraction, though local enrichments may result in by separation of dense, immiscible sulphide droplets. Thus, the expected sulphur level in the Outokumpu metaperidotites, which most represent strongly depleted mantle, would be in the order of 0.025 wt.%, or rather less. Average sulphur content in the antigorite metaserpentinites of the map sheet 4224 is 0.27 wt.% based on the XRF analyses in the Outokumpu dataset, or 0,25 wt.% based on the XRF analyses in the GSF dataset. Notably, antigorite serpentinites of the Jormua Complex in KSB have much lower average sulphur content of just 0.033 wt.%. Compared with the antigorite metaserpentinites, the serpentinized metaperidotites from map sheet 4222 show significantly higher average sulphur content of 0.99 wt.%, based on the Outokumpu XRF dataset (n=976). The GSF dataset yields average sulphur content of 0.48 wt.% for the metaperidotites (n=152) the whole NKSB considered. It is to be noted that averages based on AAS or LECO determinations would not differ significantly. For example, the AAS data for 556 serpentinite samples in the OKUBS dataset, mostly from the area of map sheet 4222, yield an average S content of 1.11wt. %, which is notably similar with the 0,99 wt.% obtained by XRF for 976 samples from the same area.

The S concentrations measured for the Outokumpu area serpentinites exceed the expected mantle-like concentration level 10 to 100 times and locally more. The lowest sulphur contents are usually met in the interior parts of the bodies and the highest contents along the body margins, often in places where the serpentinites are in contact with sulphide-rich black schists. Origin of the sulphur from the Kaleva metasediments is supported by the lead isotope data from sulphur enriched metaperidotites samples from Outokumpu (cf. section 9.3.2.). Also the low Se/S ratios of the serpentinites, similar with those of the surrounding mica schists, indicate local metasedimentary source for the sulphur. Regionally the S content of the serpentinites is seen to increase with increasing metamorphic grade. These evidences leave little doubt about that most of the sulphur in the metaperidotites was added from the surrounding metasediments during the regional metamorphism.

**Nickel** concentration of primitive mantle has been estimated to 1960 ppm (McDonough and Sun, 1995). Ni is a strongly compatible element in mantle melting and fractionation of basalts, therefore its concentration should increase with increasing degree of melt extraction. Based on the OKUXRF data set, the antigorite serpentinites of map sheet 4224 and metaperidotites of the map sheet 4222 contain 2214 ppm and 2082 ppm of Ni, respectively. The entire GEOMEX area considered, the GTKXRF data set yields very similar averages of 2182 ppm of Ni for the antigorite metaserpentinites (n=20), and 2009 ppm of Ni for the serpentinized metaperidotites (n=152). For comparison, the antigorite serpentinites of the Jormua complex contain 2162 ppm Ni on average (n=49). These values mean that the OJOB metaserpentinites and metaperidotites are only slightly enriched in Ni with respect to the primitive mantle (1960 ppm Ni). The relatively high sulphur contents of the serpentinites consequences that most of the Ni resides in sulphide minerals, mostly in pentlandite. This is confirmed by the near total recovery of Ni from the serpentinites in solution by the agua regia or sulphide specific leaches. However, in some antigorite serpentinites and in the core parts of some larger metaperidotite bodies where S contents may locally be extremely low, significant part of the Ni resides in chrome magnetite rimming altered chromite grains. Also talc, variably

abundant in talc-olivine metaperidotites and especially in talc-carbonate rocks, may contain significant nickel.

There is a clear increase in Ni content in the metaperidotites with increase in sulphur content so that the more S rich samples (S>1 wt%) in the GTKXRF dataset contain 2556 ppm Ni on average. These metaperidotites also show a clearly lower average Ni/Co ratio of 15.8 compared with the average metaperidotite value of 21.1, indicating that the synmetamorphic sulphidation of the metaperidotites was associated with some enrichment in Ni, and also Co.

**Cobalt** content in primitive mantle has been estimated to 105 ppm (McDonough and Sun, 1995). Cobalt in mantle peridotites is only little affected by melt extraction. Cobalt is also a relatively immobile element in low temperature alteration processes. These facts are reflected in the very uniformly mantle-like Co contents of the Jormua-Outokumpu serpentinites, to a large degree regardless of their metamorphic grade. Accordingly, the average cobalt content for the antigorite metaserpentinites in the GTK data set (308M+511P) is 91 ppm (n=69), and for the metaperidotites 99 ppm (n=155), respectively. For comparison, the 559 serpentinite samples in the OKUBS dataset, most from the area of map sheet 4222 only, yield a very similar average Co content of 98 ppm. However, based on the GTK sample set, the extreme S richest portion (S>1 wt.%) of the metaperidotites is clearly elevated in Co with an average content of 162 ppm (n=24). As we pointed above, the relatively low mean Ni/Co (15.8) of these samples suggests that some cobalt was added in association with the synmetamorphic sulphidation of the metaperidotites.

*Zinc* content in primitive mantle is 55 ppm (McDonough and Sun, 1995). Zinc is a mildly incompatible element in MORB melting, and thus an element that should become slightly depleted in the residual mantle along with melt extraction. Based on the OKUXRF data set, antigorite metaserpentinites of map sheet 4224 contain 51 ppm of Zn and the serpentinized metaperidotites of map sheet 4222 100 ppm of Zn on average. Very similar values are indicated by the GTK data set that yields an average Zn content of 62 ppm for the antigorite metaserpentinites, and 94 ppm (median 62 ppm) for the serpentinized metaperidotites, now the whole Jormua-Outokumpu belt considered. Again, based on the GTK dataset, the S-richest portion of the metaperidotites (S>1 wt%) shows enrichment with an average Zn content of 257 ppm and Zn/Ni ratio of 0.045. For, comparison, the whole metaperidotite dataset yields an average Zn/Ni of 0,022, while this ratio in primitive mantle is 0.028.

**Copper** content in the primary mantle is usually assumed to be about 30 ppm, although there is a range in the published estimates between 18 and 30 ppm (e.g. McDonough and Sun, 1995; O'Neill and Palme, 1998). The fact that Cu/Zn ratios in MORB and bulk continental crust are significantly higher than Cu/Zn in primitive mantle imply that mantle melting should lead to depletion of the residues in Cu. This is confirmed by the low Cu contents (< 20 ppm) of the more depleted mantle peridotite suites (e.g. Boyd, et al., 1997). However, due to the strongly chalcophile nature of Cu, mantle domains enriched in Cu could theoretically result in by sulphide melt immiscibility and retention. The GTK dataset (308M+511P) indicates an average Cu content of <10 ppm for the metaserpentinites and 28 ppm for the serpentinized metaperidotites the whole NKSB considered. The OKU XRF dataset yields an average Cu content of 17 ppm for the metaserpentinites of the map sheet 4224, and 32 ppm for the metaperidotites of the map sheet 4222. The AAS based OKUBS dataset (n=556) yields an average Cu content of 31 ppm, again for a sample set representing mostly metaperidotites from the area of map sheet 4222. It should be noted that the measured Cu concentrations were often close to or below the effective detection limits of the applied analytical methods, and that it is therefore questionable how representative of the true concentrations these average values are. Probably the quoted averages are rather a bit too high than too low.

From a practical point of view, it is an important fact that there simply are no evidence in the extensive Ni and Co data by Outokumpu and GTK that any of the sampled Outokumpu – Jormua serpentinites would contain any type of economically significant nickel or cobalt enrichments. Like Ni and Co, also Zn and Cu contents of these serpentinites are more ore less systematically close to their expected mantle values. Nevertheless, the obvious synmetamorphic flushing of especially the metaperidotites by S-bearing fluids has the implication that probably only the very core parts of the largest serpentinite masses may be

truly pristine for their sulphur and base metal contents. In fact, due to the effects of the synmetamorphic sulphidation, which usually seem to have involved a slight metal addition, we cannot directly measure what exactly were the primary contents of e.g. Cu and Zn in the protolith peridotites. An approximation of the protholitic Cu and Zn contents is get, however, based on the usually high degree of depletion of the peridotites, which for e.g. for Cu would imply very low primary values, most probably significantly below 10 ppm (cf. e.g. Hattori, 2002).

# 6.3.2. Mafic and associated felsic rocks

## Framework of occurrence

Serpentinite bodies in the Outokumpu assemblage have for long been known to be associated with 5-25 vol.% mafic rocks, which have been described from Horsmanaho, Losomäki and Miihkali, for example (Koistinen, 1981; Park, 1983; Rehtijärvi and Saastamoinen, 1985). Besides being metamorphosed in amphibolite facies, these metabasites are frequently also highly strained (cf. Fig. 24a). Thus their exact nature remains often unresolved. Nevertheless, the available field and drill core evidence suggests major part of them would represent metabasaltic to gabbroic dykes and small stocks (usually less than 100m<sup>2</sup> by area) intrusive in the host serpentinites (mantle peridotites). Only a very small proportion of the serpentinite-associated metabasites, restricted almost to one occurrence in Losomäki, comprise features that more or less unambiguously suggest extrusive origin (Park 1983; Fig. 24d). In addition to the Losomäki metabasites, serpentinite-associated metabasites of possible extrusive origin are present only in Vehkalahti NE of Juankoski, where narrow stripes of highly strained and variably calc-silicate altered amphibolites accompanied by small serpentinite lenses occur intercalated in local mica schists.

Mafic rocks are most common in association with the Kaavi and Miihkali serpentinite massifs where the relative volume of metabasites may locally exceed that of the host serpentinite. The possible metalavas at Losomäki excluded (Fig. 24d), most of the metabasite occurrences in the Kaavi area, and also in the Miihkali massif, comprise medium to coarsegrained metagabbro to amphibolite usually in small bodies that are wholly enclosed in, or flank, often with irregular intrusive contacts, the host serpentinite bodies. Many of these occurrences are thus clear dykes or small pods/stocks, locally preserving apophyses in and chill margins against the enclosing serpentinite (Fig. 24c). Dike-in-dike intrusion features (Fig. 24b) are present in several metagabbro occurrences, which suggests emplacement of the protolith gabbro intrusions in an extensional tectonic environment. In addition to the obvious gabbro or metabasalt dykes and stocks, a smaller volume of metabasite is usually present in narrow pervasively chloritized lenses and layers in serpentinite. These highly altered, little studied rocks may comprise many mafic-ultramafic rocks types.

Importantly, several of the metagabbro bodies in Kaavi area comprise metarodingitic portions with diopside plus hastingsitic amphibole and plagioclase extensively replaced by grossular garnet (primarily hydrogrossular) and epidote-zoisite. Rodingitization is a process related to low-T serpentinization, hence the presence of metarodingites in the Kaavi metaperidotite massifs suggest that the metaperidotites had been serpentinitized already before start of the progressive metamorphism, probably before or during the obduction of the massifs. If the early serpentinization was of pre-obduction origin, then, the Kaavi massifs might represent relatively shallow, relatively pervasively serpentinized, and the Miihkali massifs with less rodingitized gabbros, deeper, less profoundly serpentinized sections of oceanic lithosphere.

Small intrusions of coarse-grained metagabbro are fairly common, although volumetrically not so abundant than in Kaavi and Miihkali, also in most of the serpentinite bodies of the Polvijärvi area, at Horsmanaho, Huutokoski, Kylylahti and Sola, for example. At the western margin of the Kylylahti complex there is a poorly known strongly tectonized zone where schistose and pervasively recrystallized metagabbros are closely associated with probably cogenetic felsic rocks of the oceanic plagiogranite or sodic rhyolite affinity. In addition to the thicker dykes and plugs of more ore less clearly metagabbroic amphibolites, the Polvijärvi serpentinites locally contain also narrow (mostly 5cm to 2 m) metabasite dykes, usually pervasively altered to chlorite schist, but occasionally with metagabbroic or amphibolitic core parts. Those dykes seem to be fairly abundant in parts of the in the Kylylahti and Sola massifs, especially.

As said above, metabasites in the Outokumpu assemblage are frequently severely tectonized, strongly schistose and folded (Fig. 24a), which attests for their pretectonic origin and emplacement among the enclosing ultramafic rocks. Even those metagabbros that in hand samples preserve clear pseudomorphic gabbroic textures, appear under the polarizing microscope severely recrystallized. Main mineral constituents in the metagabbroic dykes are typically hornblende, plagioclase (labradorite-bytownite) and epidote/clinozoisite. Uralite pseudomorphs after pyroxene are infrequently preserved in the coarsest metagabbro samples, and plagioclase, although frequently recrystallized to granoblastic mass, may still occasionally preserve outlines of the original coarse-grained magmatic grains. Minor to trace ilmenite and sulphide are usually present. Garnet is common in the metarodingites but rare in the ordinary metagabbros, except in some more iron-rich differentiates in Miihkali, Horsmanaho and Huutokoski, for example.

The chlorite-rich metabasite dykes in the lowest grade environments, as e.g. in Kylylahti and Sola, exhibit usually pervasive schistosity defined by the chlorite flakes, overgrown by criss-crossing slender prisms of peak-metamorphic amphibole. Thus the chloritization clearly is of pre-peakmetamorphic origin – but was it premetamorphic or perhaps an early greenschist facies metamorphic process remains obscure. With increase in grade from low amphibolite to middle and high amphibolite facies, the chlorite-altered metabasites progressively react to produce various garnet, cordierite, anthophyllite and green spinel bearing mineral assemblages depending of the nature of previous alteration, and synmetamorphic chemical exchange with the host rocks and local fluids.

As we described earlier in section 6.1.2., metabasites are present also in the parts of the epicontinental facies tectonostratigraphically immediately below the Outokumpu nappe complex. We distinguished two metabasite units in the epicontinental or Lower Kaleva tectofacies. The apparently lower/earlier of these groups, LKB1, comprises amphibolite sills and/or lavas associated with thin guartzite-carbonate-skarn-black schist horizons representing either tectonic slices of uppermost Jatuli, Lower Kaleva, or perhaps a previously unrecognised (deep self?) facies of the Upper Kaleva. Examples of this association include metabasites of Ranta-Kosula (Heinävesi), Retunen-Tahasniemi and Riihijärvi (Kaavi), for example. The LKB2 comprises amphibolite sills and/or lavas intruded/intercalated in mica schist and black schists obviously in the upper part of the Lower Kaleva tectofacies. As we will show below, intriguingly, the LKB2 metabasites, as e.g. those at Viitaniemi, Riihilahti and Heinävesi, have identical geochemistry with the serpentinite-associated, and hence possibly ophiolitic metabasites at Losomäki. This similarity raises a question of whether the Losomäki pillow lavas would really integrate to the adjacent serpentinites – or do they rather represent parautochthonous Lower Kaleva tectonically juxtaposed to the Losomäki serpentinites? Or had the Lower Kaleva and Outokumpu assemblage formed concurrently in a pericontinental environment where (thinned) continental and oceanic type basements existed side by side, and where basalts of similar chemical character had erupted on both types of basements?



Fig. 24. Photographs of metabasites typical in association with the serpentinite massifs in the Outokumpu area and in Jormua. (A) Strongly deformed, folded metagabbro, north of Teerijärvi, Outokumpu. (B) Dyke-in-Dyke gabbros, Losomäki, Juankoski. (C) Narrow, pervasively chloritized metabasite dyke in metaperidotite, Miihkali, Outokumpu. (D) Probable metabasaltic pillow lava, Käärmekalliot (Losomäki), Juankoski. (E) Sheeted metabasalt dykes, Sammakkomäki, Jormua. (F) Metabasaltic pillow lava, Kylmä, Jormua.

Outokumpu assemblage and their stratigraphic relationship with the underlying "epicontinental facies" would clearly provide crucial constraints for understanding the formative tectonic setting of the ultramafic-mafic complexes, and the associated massive sulphide ores as well. In the past the Outokumpu metabasites have been subjected to only limited geochemical-petrological study. Rehtijärvi and Saastamoinen published (1985) a brief study of the geochemistry of the Miihkali amphibolites and Park (1983) of the Losomäki amphibolites. We have undertaken a reconnaissance geochemical study including representative metabasite samples from most of the metabasite occurrences known in the Outokumpu and Lower Kaleva assemblages. The Lower Kaleva metabasites were dealt in chapter 6.1.2, a brief review of the results of our study for the serpentinite-associated, or "ophiolitic", metabasites is given below. Tables 5 and 6 summarize average chemical data for representative samples of possible extrusive (plus finegrained dyke) and metabasites from several of the here studied metabasite occurrences.

# Type occurrences, field and geochemistry aspects

# Losomäki metalavas

A part of the metabasites in the Losomäki area has been observed to show outcrop features supporting their origin as metabasaltic pillow lavas and pyroclastic rocks (Virkkunen, 1982; Park and Bowes, 1981; Park, 1984). The number of such outcrops in Losomäki is low, however, and as most of these few outcrops are now, after several previous stripping operations, in very poor observation condition, validity of the prior interpretations is difficult to evaluate. Nevertheless, based on the published descriptions, origin of these rocks as some sort of autoclastic metalavas/tuffs seems most likely. Virkkunen (1982) and Park (1984) interpreted the Losomäki amphibolites, largely based on their low Ti, Zr and Y (HFSE) contents, as low-K island arc tholeiite basalts.

Considering the huge variation in the major elements in the chemical data previously published form the Losomäki metabasalts by Park (1984), it is clear that he must have been sampling mainly highly altered materials less suitable for petrogenetic examination. We made in this work every effort to guarantee that the samples collected would represent the most pristine and mineralogically "orthodox" amphibolite available. The chemical composition of the collected samples being remarkably coherent and basalt-like (Table 5), it seems that this sampling goal was reached.

The Losomäki metabasalts with autoclastic features are systematically high in MgO (5.78-11.40 wt%, average of 13 samples MgO = 9.41 wt.%), have mostly normal basaltic SiO<sub>2</sub> (45-53 wt.%, average of 13 samples=50.1 wt.%), are high in Cr (428-1029 ppm) and Ni (97-292 ppm) and distinctly low in TiO<sub>2</sub> (0.36-0.46 wt.%), Zr (12-29 ppm) and Y (13-19 ppm). The high Mg numbers (0.71 on average) and high Cr and Ni together denote that the Losomäki metabasalts represent relatively little fractioned basaltic mantle melts. Compared to the E-MORB metabasalts of the Jormua Ophiolite (Fig. 24e, 23f), the Losomäki metabasalts have significantly lower REE abundances, 2.2-3.3 times mantle vs. 6.4-11.3 times mantle (Fig. 25). Also values of La<sub>N</sub>/Yb<sub>N</sub>, Gd<sub>N</sub>/Yb<sub>N</sub> and Nb<sub>N</sub>/Yb<sub>N</sub> ratios of the Losomäki metalavas are lower than those of the Jormua metabasalts, 0.37-0.78 vs. 0.40-2.20, 0.74-1.03 vs. 1.04-1.35 and 0.45-0.84 vs. 1.20-3.59, respectively. Significantly, however, both the Jormua and Losomäki metabasalts have Nb<sub>N</sub>/La<sub>N</sub> >1 and also Nb<sub>N</sub>/Th<sub>N</sub> >1. Though certain scatter by secondary Th and La mobility is clearly present, in final analysis the high Nb/La and Nb/Th appear primary features, however. In addition, minor negative Zr and Ti anomalies in mantle-normalised spidergrams characterize both the Jormua and Losomäki metabasalts, whereas the Jormua metabasalts appear slightly

Location	Losomäki	Miihkali	Luikonlahti	Vehkalahti	Vehkalahti	Kvlvlahti	Viurusuo	Viitaniemi	Riihilahti	Heinävesi	Jormua
	amphibolite	amphibolite	amphibolite	amphibolite	scarnoid a.	amphibolite	amphibolite	amphibolite	amphibolite	amphibolite	pillow lava
Ν	13	12	9	8	8	2	3	4	3	4	19
SiO2 wt.%	50,14	49,34	40,51	49,45	49,90	49,17	45,25	48,35	47,88	48,00	49,28
TiO2	0,41	0,40	0,93	0,32	0,29	0,57	0,91	0,36	0,41	0,33	1,11
AI2O3	15,55	15,64	15,08	16,73	12,70	15,24	14,61	15,78	14,44	15,34	16,69
Fe2O3	7,27	7,54	16,85	6,15	4,16	9,02	9,02	8,21	8,75	9,36	7,49
MnO	0,14	0,13	0,11	0,12	0,12	0,15	0,08	0,15	0,15	0,16	0,12
MgO	9,41	8,96	10,55	9,21	11,52	9,18	10,07	8,69	9,46	10,00	6,87
CaO	12,35	11,70	7,74	13,24	18,05	10,68	11,73	12,85	13,00	10,73	12,72
Na2O	1,97	2,40	1,21	1,85	1,13	2,36	2,22	1,96	1,64	1,71	2,62
K2O	0,25	0,18	0,78	0,46	0,25	0,30	0,71	0,56	0,31	0,26	0,11
P2O5	0,03	0,03	0,22	0,04	0,10	0,02	0,20	0,03	0,03	0,03	0,09
S	0,08	0,08	2,97	0,34	0,51	0,16	1,71	0,79	0,33	0,08	0,06
Cr ppm	765	232	526	855	798	695	538	481	742	396	526
Ni	226	116	457	245	348	75	289	162	226	137	184
V	198	194	210	198	174	264	307	198	189	190	254
Sc	44	49	36	48	35	58	49	49	43	48	45
Co	45	42	239	42	35	45	59	41	48	49	45
Cu	50	68	1362	41	46	102	144	99	59	73	57
Zn	77	56	1002	144	246	56	148	115	95	90	80
Y	14	15	25	13	12	17	24	17	16	14	22
Zr	23	21	57	17	19	22	55	18	24	18	73
Nb	1,5	2,3	5,0	1,1	1,7	0,6	3,5	1,7	1,6	1,0	8,0
Th	0,08	0,14	0,29	0,10	0,06	0,02	0,35	0,14	0,25	0,06	0,63
La ppm	1,23	1,40	11,38	1,40	1,54	0,90	4,45	1,15	2,60	1,08	4,64
Ce	3,47	3,97	18,95	3,44	3,52	4,14	9,33	2,94	4,72	2,29	11,59
Pr	0,60	0,62	2,53	0,58	0,57	0,92	1,35	0,46	0,74	0,38	1,91
Nd	3,39	3,15	11,88	2,99	2,76	5,22	6,31	2,31	3,63	1,97	9,52
Sm	1,08	1,01	3,47	0,89	0,82	1,58	1,96	0,79	1,06	0,64	3,23
Eu	0,41	0,46	1,05	0,41	0,37	0,72	0,70	0,29	0,41	0,30	1,24
Gd	1,69	1,64	4,30	1,26	1,26	2,30	2,95	1,39	1,53	1,11	4,29
Tb	0,30	0,30	0,69	0,24	0,23	0,39	0,53	0,25	0,31	0,24	0,77
Dy	2,14	2,19	4,18	1,73	1,60	2,54	3,66	1,99	2,15	1,86	4,98
Но	0,49	0,51	0,85	0,39	0,37	0,57	0,82	0,50	0,52	0,46	0,99
Er	1,54	1,57	2,38	1,23	1,17	1,62	2,50	1,75	1,70	1,54	2,91
Tm	0,24	0,25	0,34	0,19	0,17	0,24	0,36	0,27	0,25	0,25	0,49
Yb	1,60	1,63	2,26	1,31	1,26	1,61	2,54	1,95	1,72	1,74	2,86
Lu	0,24	0,26	0,32	0,20	0,19	0,25	0,39	0,29	0,27	0,28	0,44

Table 5. Average compositions of fine-grained, possibly extrusive/extrusive amphibolites from the Outokumpu area and Jormua ophiolite.

	Losomäki	Miihkali	Kylylahti	Kylylahti	Kylylahti	Kylylahti	Sola	Sola	Sola	Huutokoski	Jormua	Jormua	Jormua
	mgb	mgb	mgb	afb/low-Ti	dy/high-Ti	dy/alk?	mgb	dy/low-Ti	dy/high-Ti	femgb	mgb	femgb	dy/alk(oib)
n	20	18	4	2	7	1	1	4	3	1	17	11	8
SiO2 wt.%	46,84	48,44	50,02	49,17	26,76	21,36	50,41	34,51	28,00	51,80	51,12	43,25	38,59
TiO2	0,36	0,49	0,23	0,57	4,11	1,88	0,12	0,68	4,67	3,15	0,64	5,20	3,84
AI2O3	16,21	16,12	16,96	15,24	14,64	15,67	15,81	13,34	15,21	9,62	15,85	12,53	8,98
Fe2O3	6,91	7,03	6,74	9,02	14,40	26,93	6,88	20,19	23,49	20,70	7,97	20,20	10,21
MnO	0,14	0,13	0,11	0,15	0,06	0,07	0,10	0,07	0,11	0,22	0,15	0,32	0,16
MgO	11,08	9,86	9,18	9,18	26,29	22,94	10,34	19,27	23,28	4,27	9,22	5,29	20,51
CaO	12,89	12,24	11,93	10,68	2,85	0,97	9,81	2,75	0,36	7,75	11,56	8,74	10,92
Na2O	1,86	1,94	1,91	2,36	0,02	0,01	3,29	0,09	0,01	1,14	2,82	2,82	0,29
K2O	0,26	0,24	0,27	0,30	0,12	0,00	0,13	0,02	0,01	0,32	0,11	0,22	0,05
P2O5	0,02	0,03	0,02	0,02	0,29	0,80	0,00	0,02	0,07	0,06	0,03	0,43	0,39
S	0,03	0,10	0,01	0,16	0,95	7,37	0,01	0,18	0,68	0,07	0,01	0,33	0,05
Cr ppm	652	436	78	695	121	323	60	464	39	24	189	16	411
Ni	180	195	106	75	546	810	149	286	394	45	114	46	630
V	196	208	182	264	650	513	169	311	551	768	231	739	404
Sc	46	47	46	58	80	43	42	63	87	74	46	56	27
Co	35	43	na	45	130	82	41	146	164	52	41	65	82
Cu	36	54	69	102	117	340	44	147	371	97	51	146	89
Zn	50	57	43	56	128	364	41	91	135	134	49	168	54
Y	14	14	10	17	43	77	4	18	24	27	13	53	25
Zr	19	18	14	22	58	470	16	21	28	31	30	100	439
Nb	3,8	2,6	1,5	0,6	8,4	26	0,1	0,9	4,0	2,5	3,9	41	91
Th	0,09	0,13	<0.5	0,02	0,05	23,4	0,01	0,04	0,07	0,01	0,45	0,39	5,0
La ppm	1,27	1,55	0,49	0,90	4,24	79,60	0,29	6,82	6,50	0,71	2,19	9,53	108,50
Ce	3,36	3,77	1,73	4,14	10,87	159,00	0,48	14,83	21,45	2,86	5,00	26,60	187,13
Pr	0,56	0,58	0,33	0,92	1,95	19,50	0,11	2,39	3,87	0,59	0,93	5,25	19,96
Nd	2,95	2,96	1,95	5,22	11,01	74,60	0,53	12,15	19,14	3,82	4,31	21,13	69,41
Sm	0,97	0,90	0,67	1,58	3,46	14,20	0,27	3,30	5,07	1,80	1,59	6,53	11,03
Eu	0,44	0,41	0,38	0,72	0,15	2,09	0,28	0,24	0,66	0,83	0,73	2,30	4,35
Gd	1,49	1,40	0,97	2,30	5,52	15,90	0,38	3,27	4,59	2,82	2,13	10,05	9,84
Tb	0,28	0,26	0,17	0,39	0,95	2,39	0,08	0,48	0,74	0,55	0,38	1,26	1,29
Dy	1,98	1,90	1,19	2,54	6,60	12,60	0,65	2,95	4,11	3,89	2,50	10,30	5,69
Ho	0,46	0,44	0,27	0,57	1,44	2,57	0,13	0,61	0,87	0,90	0,53	1,90	0,94
Er	1,41	1,36	0,76	1,62	4,35	7,71	0,48	1,78	2,56	3,05	1,43	5,30	2,28
Tm	0,21	0,21	0,12	0,24	0,63	1,01	0,07	0,25	0,37	0,45	0,28	0,60	0,25
Yb	1,43	1,47	0,84	1,61	3,97	6,64	0,44	1,78	2,45	3,01	1,44	3,87	1,68
Lu	0,21	0,22	0,11	0,25	0,60	1,00	0,08	0,27	0,37	0,47	0,25	0,50	0,20

Table 6. Average chemical analyses for gabbroic and metabasaltic dykes enclosed in serpentinites in the Outokumpu area and Jormua ophiolite.



Fig. 25. Mantle-normalized extended REE diagram for Losomäki and Jormua metabasalts. For comparison also data for Jormua OIB, average N-type MORB (black line with light green dots) and E-MORB (black line with lavender dots) are shown. Note that compared to Jormua basalts the Losomäki basalts show significantly lower average REE level, but basically similar normalized profiles, suggesting a much higher degree of total melting in the Losomäki case, but a similar mantle source than that of the Jormua basalts.

depleted also in Y. The Ti/V ratios of Losomäki metabasalts between 5 and 16 are low compared to Jormua metalavas, which have Ti/V between 24 and 31. The low HFSE levels and Ti/V ratios of the Losomäki metabasalts are indeed compatible with their origin as arc-related melts, but on the other hand, these rocks systematically lack the more diagnostic features of island arc basaltic magmas, as for instance negative Nb anomalies in their mantle-normalized patterns. Furthermore, in terms of their Ti/Zr ratios the Losomäki metabasalts (Ti/Zr 92-118) are "normal tholeiites" similar to Jormua metabasalts (Ti/Zr 82-105) and N-MORB (Ti/Zr=102).

In close spatial association with the supposed autoclastic metalavas, there are also massive, fine-grained to medium-grained amphibolites at Losomäki, named to Rantala amphibolites by Park, 1984. The Rantala type amphibolites show sharp contacts against serpentinite in the outcrops, and the drilling by Malmikaivos demonstrate that they represent many small metabasite bodies enclosed in serpentinite. Therefore, these amphibolites appear to represent irregular shallow-level (fine-grain size) intrusions in the peridotite protoliths of the host serpentinites. The massive amphibolites are lower in Cr, higher in TiO<sub>2</sub> and REE relative to the amphibolites with autoclastic features, but otherwise these rocks show very similar chemical characters, as e.g. similar shapes for their mantle-normalised REE patterns.

### Losomäki metagabbros

In addition to the above described fine-grained and partly possibly extrusive amphibolites, there are also many small irregular stocks and dykes of medium to coarse-grained gabbroic metabasites in the Losomäki area serpentinites (serpentinized metaperidotites after mantle peridotites). These bodies sometimes show sharp, obvious intrusive contacts against the host ultramafic rocks. More often the contacts are, however, overprinted by metasomatic-metamorphic reaction bands composed of tremolite±anthophyllite. The gabbroic metabasites are usually strongly strained and often exhibit pervasive mylonitic fabrics. In central parts of bigger bodies original textural features of coarse-grained gabbro have been variably preserved, however.

We classified during the fieldwork the gabbro occurrences to gabbros (small stocks inside or directly fringing serpentinites) and gabbro dykes (usually 1-10 m wide dykes in serpentinite). There is probably no other difference between these types but the size and form of the intrusions, so in the following they are dealt with as a single population. The gabbroic metabasites share the similar, systematically high-MgO (8.42-15.40 wt.%, average of 20 samples=11.08 wt%), low-TiO<sub>2</sub> (0.14-0.68 wt.%) and low-Zr (3-41 ppm Zr) character with the Losomäki metabasalts. Geochemical consanguinity with the Losomäki lavas is indicated also by the mutual similarity of the metagabbroic and metabasaltic rocks in mantle-normalised REE distributions (cf. Figs. 25-26). However, the metagabbros show considerably larger variation in their REE abundances (0.6-6.5 times mantle), in TiO<sub>2</sub> (0.12-0.68%) and Cr (76-1892 ppm), for example. This indicates that though some of the gabbro dykes/stocks may represent just little unmodified melts similar to the Losomäki metabasalts, most of them probably represent considerable degrees of crystal cumulation in melt channels and small magma pockets.

## Vehkalahti and Suovaara amphibolites and skarnoid amphibolites

Thin layers (<200 m) of amphibolitic metabasites, locally with minor serpentinite, occur in mica schists in the Vehkalahti area E of Juankoski (cf. Äikäs, 2000). Minor mica schist enclosed intercalations/slivers of amphibolite are known also from Suovaara ca. 12 km NE of Vehkalahti. These amphibolites are systematically highly strained, medium to coarse-grained rocks observed with no preserved primary textures or structures. In many outcrops the amphibolites grade into carbonate altered, now calc-silicate-rich layers or domains that traditionally have been mapped



Fig. 26. Mantle-normalized extended REE profiles of gabbroic and metabasaltic stocks and dyke rocks enclosed in serpentinite massifs in the Outokumpu area and in Jormua. Plots are for the average data in Table 6. Note the striking similarity of the Outokumpu and Jormua gabbroic rocks in this diagram. Gb=gabbro dykes and stocks, fegb=ferrogabbro dykes and stocks, afb=amphibolitic dykes and amphibolites, low-Ti and high-Ti=low-Ti and high-Ti chloritized ferrogabboic/basaltic dykes, alk=chloritized alkaline dykes in Kylylahti, alk(oib)=chloritized alkaline dykes in Jormua.

as tremolite-diopside skarns (e.g. Huhma, 1971; Äikäs, 2000). The skarnoid components at Vehkalahti locally comprise layers and patches of sometimes distinctly bright green, coarsegrained chromian diopside and/or tremolite. Therefore the skarnoid metabasites at Vehkalahti sometimes have been erroneously mapped as Outokumpu type chromian skarns. In many outcrops it is seen that the chrome diopside-tremolite patches, often comprising very coarse-grained diopside, post-date the prominent schistosity in the host amphibolites.

The occurrence, though scattered, of small ultramafic bodies (mantle) along with the Vehkalahti amphibolites points to a similar, but a more dismembered rock association than at Losomäki. Therefore it is not surprising to see that also chemically the least carbonate-altered metabasites of Vehkalahti and Suovaara are very similar to the Losomäki metabasites, being similarly high in MgO (6.32-12.20 wt.%), Cr (255-1242 ppm), Ni (100-361 ppm) and low in TiO<sub>2</sub> (0.11-0.43 %) and Zr (7-25 ppm) (Table 5). Also in terms of mantle-normalised REE pattern shapes the similarity of Vehkalahti-Suovaara amphibolites with Losomäki metabasaltic amphibolites is very clear (Fig. 27).

The skarnoid Vehkalahti metabasites show mantle-normalised REE patterns that are systematically a bit flatter than those of the least calc-silicate altered amphibolitic metabasites. Intriguingly this holds, not only for  $La_N/Sm_N$  but also  $Nb_N/Sm_N$ . Maybe this indicates small difference in the magma characters and thus eruption styles? Maybe the magmas that are now skarnoid rocks were originally associated with more gases and hence more syngenetic fragmentation-porosity and hence show more posterruption carbonate-alteration?

## Viurusuo

In the Viurusuo area, ca. 10 km to the south of Outokumpu, a diamond drill hole by GEOMEX intersected about 30 m of variably altered, skarnoid to chloritic-amphibolitic metabasite, folded in a position between black and mica schists and Outokumpu type skarnquartz rocks flanking a size-able serpentinite body. Due to the only two drill holes in the environment, the exact stratigraphical relationships are not known, but there are again the two alternatives that the basite layer represents either an interbed in the local metasedimentary assemblage, or an "ophiolitic" metabasite obducted with the juxtaposed serpentinite body. We are inclined to support the latter alternative.

Three metabasite samples analysed from the Viurusuo basite show somewhat higher  $TiO_2$  (0.64-1.17 wt.%) and Zr (36-72 ppm) and REE abundances (Sm 3.8-6.2 times mantle) than the Losomäki and e.g. Riihilahti low-Ti metabasites. The most REE-rich sample (17-EPI-00) from Viurusuo actually has a mantle-normalised REE level and pattern approaching that typical of Jormua metalavas. Notably, also in terms of their  $TiO_2$  and Zr abundances the Viurusuo basites come quite close to the Jormua E-MORB (Table 5). In this respect and overall the Viurusuo metabasites closely resemble metabasites of the Luikonlahti complex.

### Luikonlahti

The southern margin of the Luikonlahti serpentinite complex hosts relatively abundant coarse-grained, diopside-amphibole-plagioclase±carbonate or locally anthophyllite+hornblende ±cordierite rocks that by their chemical composition are clearly basaltic or gabbroic in origin. Unfortunately, because the past Myllykoski Company often left in their maps and core reports a clear distinction between the Outokumpu type skarns and often skarnoid metabasites undone, the spatial distribution of the latter in Luikonlahti complex is only tentatively known.

The skarnoid metabasites in Luikonlahti contain but tremolite and diopside (often "chromegreen") also variably abundant plagioclase, hornblende, sphene, rutile and zircon, which distinguish them from the ultramafite-derived Outokumpu type skarns. Nevertheless, the



Fig. 27. Mantle-normalized extended REE profiles of the possibly extrusive and/or shallow level dyke rocks in association with the serpentinite massifs in the Outokumpu area and/or hosted in the immediately underlying Lower Kaleva type strata. Plots are for the average data from Table xxx. Note the very similarity of the Losomäki "ophiolitic" and Riihilahti "epicontinental" basalts, and more enriched, nearly Jormua E-MORB-like composition of the Viurusuo and Luikonlahti metabasites.

chromian nature of the diopside and tremolite and common presence of uvarovite in the skarnoid metabasites have led to their common but erroneous correlation with the Outokumpu type skarns. The skarnoid metabasites probably are derived form heavily carbonate-altered mafic protholiths, while the anthophyllite+hornblende±cordierite rocks obviously represent metamorphism of chlorite-altered versions of the same mafic protoliths. Due to the frequently more or less pervasive carbonate alteration and subsequent strong strain and metamorphic overprint, it is impossible to know to what extend the Luikonlahti basites were intrusive or extrusive.

The Luikonlahti basites show quite variable chemical compositions. The variations are large especially for the major elements like MgO, CaO and SiO<sub>2</sub>, probably reflecting mainly the often pervasive premetamoprphic and synmetamorphic alteration effects. Yet there is considerably less variation in terms of the more immobile components. The apparently least altered variants with close to basaltic CaO and MgO display TiO2, and Zr concentrations and shapes of REE patterns that are quite close to those typical of the Jormua E-MORB (Table 5). The concentrations of TiO<sub>2</sub> between 0.42 and 1.01 wt.%, Zr between 30 and 59 ppm and REE level of 0.5 to 1.5 times mantle, in the apparently better preserved samples, are only somewhat lower than in the Jormua E-MORB metabasalts (Fig. 27). These values and the systematically relatively high Cr (310-607 ppm) and Ni (235-672 ppm) in the Luikonlahti metabasites suggest they would represent somewhat less fractioned melts from a similar source than the Jormua E-MORB. The Luikonlahti metabasites resemble Jormua E-MORB also in that the least altered basites show relatively high Ti/V ratios between 24 and 34, similar to the Jormua values between 22 and 35.

No samples of the Luikonlahti cordierite-anthophyllite rocks, volumetrically subordinate to the skarnoid metabasites, were analysed during this study. Data provided by Takala (2001) shows that, in terms of more immobile elements, the chemistry of the cordierite-anthophyllite rocks is quite similar to that of the adjacent skarnoid amphibolites. For example, TiO2 in the cordierite-anthophyllite rocks ranges between 0.64 and 1.37 wt.% and Zr between 40 and 86 ppm. The concentrations of Cr (206-432 ppm) and Ni (86-205 ppm) appear somewhat lower in the cordierite-anthophyllite than in the calc-silicate altered metabasites, however. The relatively low SiO<sub>2</sub> (33.9-47.3 wt.%) and high MgO (10.2-18.6 wt.%) and total Fe (Fe<sub>2</sub>O<sub>3</sub>T=5.8-22.1 wt.%) of the cordierite-anthophyllite rocks is typical of low-temperature chlorite-altered metabasites. It appears clear that the skarnoid and cordierite-anthophyllite metabasites represent distinct alteration of the same basite protolith, the former carbonate alteration (CO<sub>2</sub> dominated fluid) and the latter chloritic alteration (H<sub>2</sub>O dominated fluid).

In association with the skarnoid and cordierite+anthophyllite metabasites, a minor but intriguing occurrence of hornblende+chlorite±olivine±garnet±spinel rocks occurs at Luikonlahti, restricted mainly in outcrops and subsurface immediately to the SW of the Pajamalmi open pit. Mineralogically these rocks resemble the garnet-spinel-bearing olivine-diopside-hornblendecummingtonite-chlorite rocks or "metaperidotites-hornblendites" of the Riihilahti prospect. Like their equivalents in Riihilahti, also the Luikonlahti "black skarns", as the Luikonlahti mine geologists called them, have obvious gabbroic-basaltic protolith (e.g. relatively high Sc of 27-41 ppm), but are yet distinctly low in SiO<sub>2</sub> (29.3-41.2 wt.%) and high in total iron (Fe<sub>2</sub>O<sub>3</sub>T = 20.0 – 41.2 wt.%). In the light of these values the "black skarns" probably also do represent, like the Riihilahti "peridotites", high amphibolite facies equivalents of pervasively in greenschist facies or lower temperatures chloritized metabasalt/gabbro. In a distinction to the Riihilahti "peridotites", the Luikonlahti "black skarns" do not show any truly high TiO<sub>2</sub>, Zr, Nb and P enrichments, however, and seem to derive solely from the same E-MORB like basalt/gabbro precursor as the adjacent skarnoid and cordierite-anthophyllite metabasites. The mineralogical difference between the cordierite-anthophyllite and spinel bearing metachloritite variants seems thus reflect some variation in the chlorite alteration of subsequent metamorphism. Maybe the spinel bearing "black skarns" represent an ultimate chlorite alteration?

### Miihkali amphibolites and metagabbros

The large but poorly exposed Miihkali serpentinite massif ca. 25 km to the N of Outokumpu

is one of the more basite-rich serpentinite massifs in the NKSB. Based on a few outcrop observations and fairly abundant, locally well-covering drill core data, Miihkali massif appears to contain an enclosed metabasite component of about 20-30 vol.% on average. In past part of these metabasites have been interpreted to komatiitic basalts, now deformed and metamorphosed into albite-actinolite schists (Rehtijärvi and Saastamoinen, 1982). However, the bulk of the metabasites are distinctly coarse-grained, gabbro-resembling rocks with heavily recrystallized labradorite-bytownite plagioclase and hornblende (uralite) as the main mineral constituents. Furthermore, our outcrop and drill core reviews implicated that most of the Miihkali metabasites do in fact represent intrusive dykes/sills in peridotite (now mainly serpentinized metaperidotite) not extrusive metabasalts. It must be noted, however, that due to intense deformation and rarity of outcrops in the Miihkali area, we cannot completely exclude that part of the more finer-grained, thoroughly amphibolitic rocks especially at the complex margins would be extrusive. Nevertheless, also the amphibolites in the drill hole Jumi-4 studied by Rehtijärvi and Saastamoinen (1982) seem to represent dykes/sill in serpentinite of mantle peridotite origin. Furthermore, unlike Rehtijärvi and Saastamoinen (1982), we did not observe albite-actinolite schists in the Jumi-4. Instead we found that the Jumi-4 amphibolites frequently comprise calsic plagioclase, hornblende and chlorite as their main mineral components.

The Miihkali metabasites are relatively high in MgO (8.42-15.40 wt.%), low in TiO<sub>2</sub> (0.11-0.97 wt.%), Zr (6-39 ppm) and in Y (14-29 ppm), and thus share the distinct low-Ti tholeiite character of the Losomäki metabasalts. The average compositions of the coarse-grained, clearly gabbroic and usually more pervasively deformed, finer-grained varieties do not significantly differ (cf. Tables 5-6, Figs. 26-27). As a group they show, like the metagabbros in Losomäki, a wide range in their Mg# and Cr content, from 0.58 to 0.87 and from 13 ppm to 2061 ppm, respectively. In further similarity to Losomäki gabbros, the Miihkali metabasites show a relatively wide variation in their REE abundances (Sm = 0.4-4.3 times mantle), but with only little variation in the shapes of the relatively flat mantle-normalised REE-patterns. These chemical features indicate that Miihkali gabbros-amphibolites, like the Losomäki gabbros, would most represent dyke cumulates, probably related to a Losomäki low-Ti tholeiite type parent melt. The finer-grained versions, in narrower dykes may represent near melt compositions. The wide variation in Cr abundances, relatively neutral behaviour of Sc, and dominance of plagioclase-uralite in the modes of the coarser variants of the Miihkali metabasites indicate they most probably originated as principally pyroxene-plagioclase cumulates.

#### Kylylahti, Huutokoski and Sola, metagabbroic amphibolites

The presence of metagabbroic amphibolites in the Horsmanaho and Huutokoski serpentinites has been known for some time (Koistinen, 1981; H. Huhma, written comm., 1988). Diamond drill holes reveal several small gabbro plugs and dykes also from inside of the Kylylahti and Sola serpentinite-talc carbonate massifs. The Kylylahti, Huutokoski and Sola gabbros all consist of mostly coarse-grained, thoroughly recrystallized labradoritic to bytownitic plagioclase and Mg-hornblende. The Horsmanaho metagabbros are especially coarse-grained, partly pegmatoid, and besides hornblende and plagioclase contain also some garnet and ilmenite (Koistinen, 1981). Also the Huutokoski metagabbros contain locally minor ilmenite and garnet. For this study a few representative metagabbro samples from Kylylahti, Huutokoski and Sola were analysed.

Four samples from the core part of a small plug of coarse-grained uralite-plagioclase metagabbro, altered for its margins thickly to chlorite schist, were analysed from Kylylahti (drill hole Oku-857, Table 6). REE abundances in all of the four samples are relatively low (Sm= 0.7-2.4 times mantle) and mantle-normalized patterns show flat HREE-MREE and depleted LREE. The moderate MgO (8.98-9.71 wt.%) and  $Al_2O_3$  (16.13-17.87 wt.%), low Cr (50-100 ppm), Ni (85-120ppm), TiO<sub>2</sub> (0.11-0.30 wt.%) and Zr (5-20 ppm), and relatively high Sc (52-52ppm) concentrations indicate together with the low REE level an origin as an evolved plagioclase-clinopyroxene cumulate. The LREE depleted nature of these gabbros also indicates that abundant cumulate clinopyroxene was present in the protholith modes.

In southern part of the Kylylahti massif, in addition of many narrow pervasively chloritic intervals (probably after thin dykes), the hole OKU-820 dissects a thicker section of medium to relatively fine-grained amphibolite of gabbroic-basaltic chemical composition. Four samples from this amphibolite show higher TiO<sub>2</sub> (0.34-0.59 wt.%), Cr (363-796 ppm) and Ni (73-264 ppm) but equally low Zr (11-22 ppm) and Y (8-18 ppm) than the Oku-857 gabbros. The mantle normalized REE patterns for these metabasites resemble those of Oku-857 metagabbros being flat for HREE-MREE and depleted in LREE but the overall REE level is higher (2.3-3.9 vs. 0.7-2.4 times mantle for Sm). Negative Ti and Zr anomalies in the mantle-normalised trace element profiles conflict with the otherwise obvious Losomäki low-Ti tholeiite melt chemistry, and push the interpretation towards gabbroic dyke cumulate origin.

The few exploration holes drilled at the western margin of the Kylylahti complex reveal presence of several small gabbro bodies either enclosed in serpentinite/talc carbonate rock or occurring at the ultramafite – metasediment contacts. Some of these bodies show distinctly well-preserved gabbroic textures, and based on Outokumpu XRF data also gabbroic-basaltic chemical compositions. In addition, some of the gabbroic amphibolites are intimately associated with strongly strained, pervasively schistose intermediate to felsic components, showing chemical compositions strikingly similar with the ocean-ridge type plagiogranites (below).

In the Sola complex, in addition of many narrow chloritized, fine-grained metabasite dykes (below), at least one several tens of metres wide body of coarse-grained gabbro is present, dissected by hole Sola-28. One sample from this gabbro body analysed during this work shows overall chemical composition, including mantle-normalised REE pattern, that is nearly identical with that of the Kylylahti Oku-857 metagabbros (Table 6).

One sample of ilmenite±garnet bearing, coarse-grained metagabbro was analysed from Huutokoski, where at least one gabbro body occurs, by field evidence clearly as a small intrusion inside a small antigorite serpentinite lens. The analysed sample is rich in  $TiO_2$  (3.15 wt.%) and total Fe (Fe<sub>2</sub>O<sub>3</sub>T=20.7 wt.%), low in Cr (24 ppm) and Ni (45 ppm), but also in Zr (31 ppm). The chemistry of this sample is thus similar to ilmenite bearing Fe-gabbroic mantle-dyke cumulates at Jormua. High Sc (57 ppm), and positive Nb and Ti spikes in mantle-normalised trace element patterns are compatible with presence of cumulate clinopyroxene and ilmenite, respectively. Origin as an evolved clinopyroxene-plagioclase-ilmenite cumulate is thus obvious for this rock.

# Kylylahti, gabbro-associated felsic rocks at the western margin of the complex

In a late stage of the GEOMEX project, occurrence of a zone of metagabbros associated with highly schistose felsic rocks was recognized within the western margin of the Kylylahti complex. The first hint of the existence of these rocks was by previous XRF data by Outokumpu Company for two drill cores (Oku-764 and Oku-766), which comprised intervals of rocks reported as quartz rocks but with peculiarly high Na<sub>2</sub>O up to 5 wt.%. More of similar rocks were dissected by the last exploration diamond drill hole M52/4224/R398 finished by GEOMEX during the late spring 2003. Analysing of there representative samples from this hole for major and trace elements showed that the sodic schists have compositions akin to oceanic plagiogranites or e.g. the rhyolites of the Icelandic Askja volcano or the Archaean Kidd Creek complex, Canada (cf. Table 7).

The western margin of the Kylylahti complex is not exposed and only sparsely drilled, hence the volumes and lithological association of the felsics as in the holes Oku-764, Oku-766 and

	Kylylahti <sup>a</sup> felsic schist	Jormua <sup>b</sup> plagiogranite	Kidd Creek <sup>c</sup> rhyolite	Kylylahti <sup>d</sup> mica schist
SiO2 wt.%	74,80	64,21	80,60	67,22
TiO2	0,20	1,04	0,08	0,73
AI2O3	11,47	14,59	10,20	13,49
Fe2O3t	2,41	8,55	1,20	6,08
MnO	0,02	0,13	< 0.03	0,06
MgO	1,71	1,12	0,29	2,7
CaO	2,65	2,47	0,85	2,13
Na2O	5,00	7,04	3,27	3,02
K2O	0,55	0,19	1,98	2,38
P2O5	0,06	0,25	<0.01	0,11
S	0,58	0,3	<0.03	0,16
Cr ppm	8	20	15	99
Ni	17	11	3	91
V	4	55		114
Sc	4	13	1	16
Cu	14	92	6	35
Zn	41	91	40	91
Zr	298	594	204	171
Y	157	110	99	21
Nb	30	57	23	9
Sr	59	101	34	159
Rb	16	5	44	91
Th	7,3	4,9	6,8	8,0
U	3,1	1,0	1,7	2,4
La ppm	52,40	44,50	47,08	25,50
Ce	124,33	110,50	105,08	52,45
Pr	15,63	14,93	11,48	6,16
Nd	68,60	66,00	51,78	23,40
Sm	17,17	17,25	12,80	4,47
Eu	2,25	4,18	1,70	0,96
Ga	20,90	20,25	13,87	4,29
al	3,62	3,33	2,63	0,59
Dy	24,23	21,88	13,27	3,29
HO	5,36	4,23	3,50	0,68
Er Tur	16,43	12,28	7,95	1,94
i m	2,40	1,/5	1,53	0,27
ΥD	15,77	11,30	9,25	1,95
LU	2,31	1,58	1,53	0,29

Table 7. Average composition of Kylylahti quartz-plagioclase schist, Jormua plagiogranite, Kidd Creek FW rhyolite (Canada), and Kylylahti mica schist

<sup>a</sup>Average of 3 quartz-plagioclase schist samples from R398, Kylylahti.

<sup>b</sup>Average of 4 quartz diorite-leucotonalite samples, Jormua.

<sup>c</sup>Average of 6 FW rhyolite samples, Kidd Creek, Canada, from Prior et al. (1999).

<sup>d</sup>Average of 2 representative Upper Kaleva mica schists, Kylylahti.

M52/4224/R398 is only poorly known. The three drill holes indicate 20-30 m thick layers or lenses of the sodic felsics in a zone that is at least 500 m long. The zone probably has a surface exposure (moraine covered) somewhere at X=6973200 and Y=4466350 wherefrom it plunges in an angle of 40-50 degrees towards the SSW.

Because of an overall high strain, no primary textures are preserved in the felsic schists but they show thoroughly recrystallized, medium to fine-grained, granoblastic-schistose fabrics (Fig. 28). Main mineral constituents are quartz, sodic plagioclase (albite-oliogoclase) and biotite. Sphene, rutile and zircon are common accessory constituents. Secondary tremolite and carbonate in late dykes and patches are commonly present.



Fig. 28. Fine-grained, plagiogranite-derived quartz-plagioclase schist in drill hole R398 in the western margin of the Kylylahti serpentinite massif. Secondary, metasomatic tremolite "skarn" bands as seen in the photo are typical for most sections of this rock in the hole R398.

rhyolite or plagiogranite type chemical composition with high SiO<sub>2</sub>(72.7-76.5 wt.%), Na<sub>2</sub>O (4.66-5.33 wt.%), Zr (223-369 ppm) and Y (149-177 ppm), and very low Cr (6.6-11 ppm), Ni (15-22 ppm) and Sc (2.7-5.0 ppm). Mantle-normalised trace element profiles of the more immobile trace elements of the three samples are mutually very similar and strikingly similar with the profiles of e.g. the Kidd Creek (Abitibi Belt, Canada) mine area rhyolites (Prior et al., 1999) or Jormua plagiogranites (Kontinen, 1987; Kontinen and Peltonen, 1998), but very different from those of the adjacent mica schists (Fig. 29). The chemical composition of the quartzplagioclase schist is actually about intermediate between the Jormua and Kidd Creek type compositions (Table 7).

In the light of the geochemistry, there cannot be much doubt about a magmatic origin of the Kylylahti sodic felsic schists. Their close chemical similarity with the ocean ridge type plagiogranites or spreading-ridge/plume type rhyolites (Figs. 29-30) is a very important message of the formative tectonic setting of the Kylylahti complex in particular, and the "Outokumpu belt" mafic-ultramafic massifs in general. This is an evidence strongly supporting origin in extensional oceanic setting, either in mid-ocean ridge or leaky transform, and thereby that the mafic-ultramafic massifs of the Outokumpu Allochthon really would represent true ophiolite fragments (fragments of oceanic lithosphere).



Fig. 29. Mantle-normalized REE patterns for samples from the highly deformed plagiogranites in the western margin of the Kylylahti serpentinite massif. For comparison patterns for representative samples of Jormua plagiogranites (Kontinen, 1987; Peltonen et al., 1998; Peltonen and Kontinen, 2004), Archaean rhyolites in the Kidd Creek mine area in western Superior subprovince, Canada (Prior et al., 1999) and Kylylahti mica schists are plotted.



Fig. 30. Rb–(Y+Nb) discriminant plot (Pearce et al., 1984) for Kylylahti plagiogranites. Data for representative samples of Jormua plagiogranites and late Archaean rhyolites at Kidd Creek mine are shown for comparison. Jormua and Kylylahti samples plot within the ocean ridge granite field, while the Kidd Creek rhyolites show a within plate signature. Note that although Rb is a relatively mobile element, the immobile Y and Nb put the Kylylahti, Jormua and Kidd Creek felsic rocks firmly in the within plate/ocean ridge territory. This is very important signature considering the past interpretations of magmatic rocks in Outokumpu "ophiolites" as products of subduction related magmatism.

#### Kylylahti and Sola, amphibolitic and chloritized metabasite dykes

Relatively narrow, usually <0.2-2 m wide, sometimes in their core parts partly amphibolitic, but usually wholly chloritized metabasite dykes are numerous in serpentinites and talccarbonate rocks in large parts of the Kylylahti and Sola complexes. Bimodal distribution in low Ti and high-Ti dykes, respectively low and rich in modal and/or normative ilmenite is a characteristic feature of these fine-grained, and usually pervasively chloritized dyke facies both in Sola and Kylylahti.

The samples considered here come all from inside or vicinity of the sulphide mineralised skarn-quartz rock zones of the Kylylahti and Sola massifs. Therefore most of the dykes show variable late-tectonic veining/replacement of variably tremolite-carbonate-quartz-sphene-rutile-sulphide-bearing skarn materials, whereas comparable replacement phenomena are nearly absent in the dykes within the adjacent talc-carbonate and serpentine rocks.

As one could expect, chemical compositions of the mostly pervasively chloritized, and carbonate-calc-silicate veined dykes show considerable variation, even in terms of the most immobile elements. The major element contents basically reflect the pervasive chlorite alteration. Accordingly, MgO is high (18-32 wt.%) and SiO<sub>2</sub> (21-38 wt.%) and Na<sub>2</sub>O systematically very low (<0.01-0.5 wt%). Alumina varies between 13 and 19 wt.% and total iron as  $Fe_2O_3$  between 8 and 21 wt.%. Like Na<sub>2</sub>O also K<sub>2</sub>O is usually very low (mostly <0.01-0.2 wt%), though there occur locally somewhat higher values up to 1.6 wt.%, related to late phlogopitization. Transition metals show wild variations (Cr=<10-620 ppm, Ni=120-3000ppm) reflecting the fact that most of the samples come from inside an Outokumpu-altered and sulphide-mineralized environment with much evidence of premetamorphic and synmetamorphic mobility of these elements. There is some more primary systematic variation in the distributions of the more immobile trace elements, however. For example, although systematically with deep negative Eu anomalies, several of the skarn-free chloritized dykes both in Kylylahti and Sola show flat REE distributions at about 10 times mantle level and that are thus, forgetting the deep Eu minimas, superficially resembling those of the Jormua E-MORB pillow lavas. However, the mantle-normalised extended REE patterns show distinct negative to positive Nb, Zr and Ti anomalies, which are usually absent in the Jormua pillow lava and sheeted dyke patterns, and which indicate Fe oxides were among crystallizing phases. Except for the often high  $TiO_2 \pm Nb$ , the other chemical features, such as e.g. low Zr (3-66 ppm) and P<sub>2</sub>O<sub>5</sub> (mostly <0.01-0.2 wt.%) and systematically flat chondrite-normalised HREE-MREE and low Nb/Yb ratios do not support alkaline character. Instead these dykes seem to represent highly evolved, partly "ferrobasaltic" fractionates probably from a low-Ti, low-Zr tholeiitic parent magma similar to the Losomäki low-Ti tholeiite. Here is worth to note here that Ti-rich metarodingitic gabbros from Louhivuoret in the Kaavi district (unpublished data by GTK/A.Kontinen) have very similar mantle-normalised extended REE patterns than the high-Ti dykes at Kylylahti.

We noted above that within the here sampled stringer-type skarn-related Cu mineralizations of Kylylahti and Sola; the chloritized dykes are often overprinted by late tectonic carbonate-skarn breccia veining/replacement. Compared to relatively skarn-free dykes, most the skarn-bearing dykes are enriched in LREE and show much lower Nb/La. We attribute this difference to mobility and addition of REE (especially LREE) in association with the skarn-replacement event. Noting the very low primary REE abundances of the peridotite host, most of the added REE necessarily was derived from the dykes themselves (redistributed from one part to one other in the dyke system) or from a source(s) external to the mafic-ultramafic assemblage. The few Sm-Nd isotope data from the REE enrichments with  $\epsilon$ Nd (1950 Ma) of ca.  $\pm 0$  suggest the former alternative would be more probable. This is so as the surrounding Kalevian metasediments have an average  $\epsilon_{Nd}$  (1950 Ma) at about –2 while the  $\epsilon_{Nd}$  (1950 Ma) for the basites in the Outokumpu assemblage cluster at around  $\pm 0$ .

From an ore geological point of view it is an interesting finding that the metabasite dykes from close association of Cu-mineralizations both in Kylylahti and Sola frequently show strong enrichment in especially LREE and very deep negative Eu anomalies in their mantlenormalised patterns. In Kylylahti some of the strongest REE enrichments were observed for samples with distinctly heavy sulphide (including chalcopyrite and sphalerite) enrichment. Although none of the here analysed REE-enriched Sola dykes showed similar scale skarn replacement as the many of the Kylylahti samples, yet their systematically elevated Co contents (103-160 ppm) and erratically elevated Cu values (up to 349 ppm) suggest their REE-enrichment also may be related to the generation of the adjacent Cu-Co mineralization.

# Keretti Co-Ni zone, metabasites

The Keretti Co-Ni mineralization is associated with a thin (usually <20 m), narrow (<100m) but lengthwise persistent (several km) zone of patchy occurrences of metabasitic rocks confined within a fold enclosure of the carbonate-skarn-quartz rock envelope of the Outokumpu serpentinite massif. In some previous views the Co-Ni metabasites have been considered as pervasively leached ultramafic rocks in an environment that was originally a stringer-mineralized zone below the main ore sheet (e.g. Treloar et al., 1981; Koistinen, 1981; Treloar, 1987). In its present position the Co-Ni-zone and the included metabasites are found some tens to 100 m above the roof of the main ore, paralleling the main ore, possibly for all of its length (Parkkinen and Reino, 1985). A similar feature is present also in Vuonos but was not studied here since no drill core of the Vuonos "Co-Ni zone" zone was anymore available in the Outokumpu stores. The origin of the Keretti Co-Ni metabasites as basaltic dykes in originally peridotite host is supported by their high, basaltic-level AI, Mg, Sc and V contents (Fig. 31), and their occurrence as typically 5 to 200 cm sharply-bound "intercalations" in the carbonate-skarn-quartz rocks of the Outokumpu assemblage (i.e. in altered mantle peridotites).

The metabasites in the Co-Ni zone are famous of their "anthophyllite-cordierite" assemblage once thought to be diagnostic of magnesium-metasomatism (Eskola, 1914; Eskola, 1933). The compositions actually range from green-coloured amphibole+chlorite schists (at the margins and outside of Co-Cu mineralization proper) to variably anthophyllite-gedrite, cummingtonite, chlorite, cordierite, garnet, phlogopite, spinel and staurolite bearing, porfyroblastic, usually brownish coloured rocks (inside the Co-Cu mineralised zone), in which orthoamphibole and cordierite prophyroblasts overgrow green-coloured chlorite, being themselves extensively replaced by brownish chlorite+-biotite/phlogopite and pinite, respectively.

Considering the wide variation in their (metamorphic) petrography, the Keretti Co-Ni metabasites show surprisingly uniform chemical compositions. All the analysed samples have Sc, V, Nb, Ti, Zr and Th abundances similar as in the Losomäki metabasalts. Mantle-normalized REE patterns (Fig. 31) are similarly flat for HREE-MREE than those of the Losomäki basalts but with a variation to much lower concentrations. Most samples are distinctly enriched in LREE and show deep negative Eu anomalies. Interestingly, some sulphide bands in the associated mineralization show relatively strong overall REE enrichment with excactly the same distribution as the metabasites (cf. Fig. 31). This indicates that the REE in the sulphide bands would be redistributed, during the ore-formation, or maybe later synmetamorphically, from the (earlier at lower temperatures) chloritized metabasites. This speculation finds support from that the  $\epsilon_{\rm Nd}$  (1950 Ma) values of the most strongly REE enriched Co-Ni zone samples and the sulphide bands cluster close to +-0 as it is characteristic of metabasites in the Outokumpu assemblage (section 9.3.3.). The deep Eu minimas imply strongly reducing fluids (cf. Bau and Möller, 1992).

# 6.3.3. Carbonate, skarn and quartz rocks

Although carbonate-skarn-quartz rocks are frequent phenomena at the margins of the serpentinite bodies all over the Jormua-Outokumpu belt, really nicely developed examples of the assemblage are restricted to the margins of the Outokumpu and Vuonos serpentinite massifs.


Fig. 31. Mantle-normalized extended REE profiles of representative samples from amphibole-chlorite schists, and from one REE-enriched sulphide band in the Outokumpu Co-Ni mineralization. The pattern of average Losomäki low-Ti (LOTI) metabasalt is shown for comparison. Samples depict with green colour comprise mainly hornblende and chlorite, samples depict with brown colour comprise in addition variably abundant, altered orthoamphibole, cummingtonite, cordierite and garnet.

The detailed cross section maps provided by Koistinen (1981) from Outokumpu and Vuonos indicate that the carbonate-skarn-quartz rock units there are hardly never thicker than 45 m, and are tightly bound to and folded with the mother serpentinite margins. Where apparently thicker domains of carbonate-skarn-quartz rocks occur, they are frequently due to shorthening and thickening by folding (cf. Fig. 32). Mineral assemblages in the carbonate-skarn-quartz zones are controlled by the regional metamorphic grade zonation. The mineralogical changes in the Outokumpu assemblage with shift from lower amphibolite facies metamorphism, as e.g. in Kylylahti and Jormua, to middle amphibolite facies metamorphism, as e.g. in Outokumpu, illustrated are illustrated in Fig. 32. More detailed information on the metamorphism of the Outokumpu assemblage is provided by Säntti et al. (in press).

Everywhere over the Outokumpu-Jormua belt the carbonate-skarn-quartz rock zones are highly deformed, schistose, lineated and folded. This holds also for the best preserved examples at Outokumpu and Vuonos (Figs. 32-33).

### Petrography

### Carbonate rocks

The zones of carbonate rocks in the Outokumpu assemblage are usually relatively thin (< 5m) and laterally discontinuous with frequent pinching and swelling (cf. Fig. 32). In Outokumpu, where the zonation in the carbonate-skarn-quartz rock assemblage is perhaps best developed, at the margins of the mother ultramafic massifs, serpentinitized enstatite-olivine metaperidotites grade via olivine-carbonate-enstatite+-tremolite rocks to olivine carbonate rocks to rocks (sagvandites) and further to the more pure carbonate rocks. Metamorphic olivine in the middle amphibolite facies olivine+carbonate rocks and sagvandites is sometimes distinctly bladed in appearance (Fig. 34), such rocks often have been dubbed as ophidolomites (in case of olivine-carbonate rocks) or even considered mistakenly as altered spinifex textured komatiites (in case of jackstraw-textured sagvandites). The olivines in these carbonate rocks are of purely regional metamorphic origin, however, missing in the equivalent carbonate rocks in the low amphibolite facies environments, as e.g. in Kylylahti and Jormua. The sagvandites and ophidolomites probably were developed by decarbonation/dehydration of talc-carbonate rocks that in the lower amphibolite facies occur between antigorite serpentinites in the massif cores and the carbonate-skarn-guartz zones at their margins.

The purest Outokumpu type carbonate rocks are greyish, medium to coarse-grained rocks with massive to irregularly tremolite-banded structure. Main mineral constituents are dolomite+-calcite and tremolite. Chromite, often in coarse to very coarse, frequently broken, cataclastic grains (Fig. 35b), similar to the chromite in the adjacent serpentinites (Fig. 35a), is a ubiquitous minor phase. Due to its commonly relatively coarse grain size (<1-12 mm), and dark black to brown colour, chromite is a conspicuous component especially in the purest carbonate rocks. A weak dissemination of iron sulphides and pentlandite is another frequent minor constituent. The large chromite grains, especially in the more pure carbonate matrixes, are often zonal (Fig. 36a), with core parts of translucent, deep red chromite (Mg# between 0.05 and 0.2 and Cr# between 0.5 and 0.6), and opaque rims grading from ferrian chromite to Cr-magnetite towards the grain margins. In middle amphibolite facies and higher grade carbonate rocks the lerger chromite grains are often recrystallized to spongy or chessboard textured grains of high-Cr, low-Al composition and surrounded by chlorite (Fig. 36b). Small grains dispersed in the carbonate matrix comprise variably ferrian chromite, Cr-magnetite or high Cr chromite, depending on metamorphic grade and fluid conditions.



Fig. 32. (A) Cross-section profile of the Outokumpu rock assemblage and its folding at Vuonos ore (Koistinen, 1981, Fig. 11). (B) Cartoon illustrating the metamorphic control of zoning in mineral assemblages and rock types in the Outokumpu rock assemblage. A=zoning in lower amphibolite facies, as e.g. in Kylylahti, B=zoning in middle amphibolite facies, as e.g. in Outokumpu (modified from Fig. 18 in Säntti et al., in press).



Fig. 33. Photographs of skarn-quartz rocks typical of the Outokumpu rock assemblage. (A) Highly lineated-schistose skarn-quartz rocks at the Vuonos Ni-deposit (photo by Tapio Koistinen). (B) Strongly foliated-tectonically laminated quartz rock with diopside-tremolite skarn bands in Vuonos (photo by Peter Sorjonen-Ward). (C) Tectonically banded-laminated quartz rock from next to a contact of the Outokumpu (Keretti) ore (photo by Esko Peltola). (D) Scanned image of diamond-sawn surface of a tectonically banded-laminated quartz rock from Horsmanaho (dark black grains are caltaclastically broken chromite).



Fig. 34. Photograph of an olivine-carbonate rock from Luikonlahti, showing long, serpentinized olivine prisms (brown) in a calcite-dolomite matrix (grey). This rock occurs between serpentinized enstatite-antophyllite rock and tremolite-diopside skarn at the southern margin of the Asuntotalo open pit.



Fig. 35. Photomicrographs and a scanned image of rocks in the Outokumpu rock assemblage at Outokumpu. (A) Serpentinized (chrysotile-lizardite) talc-olivine metaperidotite, Mökkivaara. (B) Carbonate rock, Mökkivaara. Note the large, 1-4 mm chromite grains both in the serpentinized metaperidotite and carbonate rock. (C) Scanned image of a diopside-tremolite skarn from Keretti. The sample shows schistose–lineated tremolite skarn (dark green) replaced by static diopside (light green), as is common in the diopside-tremolite skarns in the Outokumpu rock assemblage. (C) Typical quartz rock of the Outokumpu massif, showing strongly schistose-lineated, shear-banded quartz mylonite with strong peakmetamorphic static-granoblastic recrystallization ("annealing"). Width of the views ca. 40 mm, except for C ca. 50 mm. Photomicrograps in cross-polarized light.



Fig. 36. Photomicrographs of chromites in carbonate-skarn-quartz rocks in the Outokumpu rock assemblage. (A) Large chromite grain zonally altered to ferrichromite-magnetite in tremolitecarbonate rock, Oku12A/33.50, Outokumpu. (B) Spongy, recrystallized chromite in carbonate rock, Oku95a/175.30, Outokumpu. (C) Chromite in quartz rock, 1A-KYL-93, Kylylahti. (D) Aluminous chromite grain (diameter ca. 0.5 mm) recrystallized at margins to high Cr-low Al chromite, Oku-28A/118.60, Outokumpu. (E) A large, broken and hydrothermally leached chromite grain (original diameter ca. 0.8 mm) in quartz rock, surrounded by chlorite hosting small hydrothermal-metamorphic chromite euhedra, Oku-872/230.40, Kylylahti. (F) Broken fragments of originally one large chromite grain in quartz rock, Oku-808/557.00, Kylylahti.

#### Skarn rocks

Skarn rocks in the Outokumpu assemblage are present in two distinct "end member" varieties: (1) tremolite+carbonate skarns and (2) diopside+tremolite±carbonate skarns. Regional metamorphic temperature progression and related dehydration/decarbonation reactions controlthe regional and occurrence scale distribution of the two skarn types, so that tremolite skarns occur thorough the Outokumpu area, while the diopside skarns are restricted in the middle amphibolite and higher grade domains. Also uvarovite, for which the Outokumpu assemblage is world famous, is very rare in the low amphibolite facies skarns.

Tremolite skarns are typically grey green to dark green, usually nematoblastic-schistose rocks with a variation to almost monomineralic tremolite rocks but usually variably comprising variable amounts of tremolite (>50 vol.%), carbonate and quartz. Their typical position in the Outokumpu assemblage is between carbonate and quartz rocks or as irregular, discontinuous bands or layers inside the quartz rock regime (Fig. 33b). Contacts with carbonate rocks are often fairly abrupt, whereas relationship with quartz rocks is more gradational. Main mineral constituents in the tremolite skarns are typically tremolite, dolomite+-calcite and quartz, and olivine in the upper amphibolite facies (migmatite) environments. Common minor minerals include chromite and disseminated iron sulphides+-pentlandite. Eskolaite is fairly common trace mineral in the tremolite skarns, in Outokumpu for example. Distinctly green Cr-tremolite, Cr-epidote (tawmawite) and Cr-tourmaline are present locally and seem to have some positive correlation with Ni-sulphide enrichment. Graphite is a common constituent in the tremolite skarns often staining them dark grey or even black.

Diopside skarns in their most characteristic form comprise coarse- to very coarse-grained pale grey green to distinctly green (variably chrome-bearing) diopside with interlocking tremolite and dolomite+-calcite. The diopside skarns are structurally a relatively late development, overprinting schistosity in the associated tremolite skarns and quartz rocks (Fig. 35c). Many diopside skarn occurrences consist of kind of networks of irregular 5-50 cm thick veins, typically concentrated in zones between carbonate and quartz rocks. Most of the diopside in these skarns is in undeformed coarse grains that in many occurrences range up to several decimetres in size. Gem-quality Cr-diopside crystals with well-developed crystal facettes are present in places, in Outokumpu especially, but also in Saramäki and Luikonlahti. Coarse pyrrhotite in speckles and veinlets is a an ever present, often relatively abundant additional constituent. Chromite is not so common than in the tremolite skarns, and where it is present, it shows features of intensive alteration and recrystallization to high-Cr chromite. Uvarovite garnet is fairly common especially in the mixed type diopside-tremolite skarns in middle amphibolite facies, but is usually not present in the lower grade occurences, as e.g. in Kylylahti. It is worth to note, also, that uvarovite in North Karelia is not restricted in Outokumpu type rocks but occurs sometimes also in the skarnoid metabasites in the Lower Kaleva sequences, given metamorphic grade was sufficiently high.

As pointed out first by A. Huhma (1970), the skarns in Outokumpu assemblage are characterized by scarcity, usually by total absence of plagioclase, sphene and zircon. Using this character, they can easily be differentiated from the Cr-rich metabasite-derived Cr-diopside±uvarovite bearing skarnoids common in association with the Lower Kaleva metabasites as met e.g. in Riihilahti, Luikonlahti, Juojärvi and Savonranta areas.

### Quartz rocks

Quartz rocks are the most voluminous component in the Outokumpu zones at their type locality in Outokumpu, but may be almost missing in some other occurences, es e.g. in Luikonlahti and Kokka. Even in Outokumpu and Vuonos where the quartz rock zones attain their observed maximum thicknesses, they nowhere show undeformed thicknesses more than ca. 40 m. As we pointed above anything more is consequence of thickening by shortening and folding, as is so well demonstrated by Koistinen (1981) in his numerous detailed cross-sections from Outokumpu and Vuonos.

The quartz rocks in the Outokumpu assemblage are generally fine-grained; strongly schistose quartz-tremolite (±diopside) banded rocks that are usually grey to pale grey (pure quartz rocks) or grey green to green (tremolite±fuchsite bearing quartz rocks), and occasionally brownish grey in colour (variants particularly rich in fine-grained chromite). Presence of 1-5 vol.% of usually fine-grained pyrrhotite±pyrite±pentlandite in dissemination, speckles and thin, discontinuous schistosity parallel stripes is a ubiquitous feature. Often conspicuously well-developed mineral layer banding (quartz-tremolite±iron sulphides) is typically present both in hand-sample and outcrop scale (Figs. 33c-d).

The quartz is always present in several generations; the earliest generations are usually the darkest in colour and finest in grain size. It is to be noted that even the most fine-grained quartzes in these amphibolite facies metabirbirites are much coarser than quartz in unmetamorphosed or lowly metamorphosed birbiritic quartz rocks elsewhere (Fig. 37). In less strained variants the late quartzes typically occur in complex, irregular, twisty vein-like replacements or injections that show with younging increasingly coarser grain size and lighter colour. The more strained quartz rocks typically show a strongly schistose-lineated blastomylonitic fabric (Figs. 33c-d, 35d). Close to black schist contacts the best-preserved, least-strained quartz rocks are often very dark-coloured, sometimes almost black because of relatively abundant fine-grained graphite pigment. The more reworked variants of these graphite-bearing quartz rocks often contain angular fragments of graphite-pigmented very fine guartz and stylolite bands with graphite. With increase in strain and metamorphic grade, the guartz rocks get coarser grained and are characterized by blastomylonitic, "granulitic" fabrics. Common minor minerals include tremolite, diopside, carbonate, uvarovite, chromite, and infrequently epidote (tawmawite, allanite), phlogopite and fucsite-sericite. As first emphasised by Huhma (1970) plagioclase, sphene and zircon are in typical Outokumpu quartz rocks notably rare, usually completely non-occurring constituents. Diopside and uvarovite are absent form quartz rocks in the low amphibolite environments, like in Kylylahti, Sola and Jormua, for example.



Fig. 37. Photomicrograps for (A) lower greenschist facies metabirbirite from Eastern Metals, Quebec, Canada and (B) lower amphibolite facies metabirbirite from Kylylahti (Oku-803/676.43). The Kylylahti sample represents the "best-preserved", most fine-grained variation of quartz rock as occurring in the Outokumpu area. The comparison shows, that even the best preserved Outokumpu metabirbirites show at least 10 times larger grain size than the low-grade birbirites at Eastern Metals. Both photomicrograps in cross-polarized light.

Chromite is a constituent that in various forms is present in every quartz rock in their every known occurrence within the NKSB and KSB. Chromite is so characteristic that it was observed even in every single polished thin section of Outokumpu type quartz rock examined in the course of this work, and which were many. Chromites in the quartz rocks constitute morphologically, compositionally and in their alteration/recrystallization history a very complex group; many of the textural and compositional characters being controlled by metamorphic

grade. In less strained quartz rocks from the low amphibolite environments, large, often cataclastic and/or variably hydrothermally leached chromite grains (Fig. 36c-f) are common. In the more strained variants the large grains are sheared into streaks of streaks of variably hydrothermally leached small cataclastic grains and obviously hydrothermally reprecipitated euhedras. The large, cataclastic chromite grains have Cr# between 0.55 and 0.84 and Mg# with a large variation between 0.08 and 0.61. Compared with them, the porous, leached grains and tiny euhedras in the more tectonized hosts tend to show significantly higher Cr# between 0.69 and 0.99 and low Mg# between 0.05 and 0.29. Alteration towards magnetite compositions is uncommon, and Fe<sub>2</sub>O<sub>3</sub> contents are systematically low (<5 %). In the middle and upper amphibolite environments, large chromite chromite grains are less common, but are occasionally present in less-strained hosts. These large grains have cores with Cr# between 0.62 and 0.82 and high Mg# between 0.63 and 0.91. At their margins the large grains frequently show recrystallization to spongy or chessboard textured chromite high in Cr and low in AI (Fig 36d). Most chromites in the quartz rocks in the higher metamorphic environments are of the porous, leached and/or tiny euhedral morphological types as recognized in the regional antigorite zone, and also have broadly similar chemical compositions.

The porous, leached and tiny euhedral chromites obviously have a common origin by pervasive hydrothermal alteration, reflecting leaching and reprecipitation of chromite by hydrothermal fluids. Because similar hydrothermal alteration of chromites lack in lowly metamorphosed birbirites (as e.g. in Eastern Metals lower greenschist facies birbirites), we conclude that the hydrothermal alteration of the chromites in the Outokumpu assemblage in NKSB and KSB was related to syntectonic, upper greenschist to lower amphibolite facies metamorphic-hydrothermal processes.

### Geochemistry of the carbonate-skarn-quartz rocks

The carbonate-quartz rocks in the Outokumpu assemblage have usually been interpreted to metasedimentary carbonate and cherty rocks (e.g. Huhma, 1970; 1976; Mäkelä, 1975; Koistinen, 1981; Treloar et al., 1981; Treloar, 1987; Park, 1988). However, the mineralogy and geochemistry of these rocks abound in aspects that are strongly against such interpretations, and instead support origin of them by silicification and carbonation from the adjacent ultramafic, primarily mantle peridotite rocks (Haapala, 1936; Auclair et al., 1993; Kontinen, 1998). We describe in the below sections the general geochemistry of the carbonate-skarn-quartz rocks rocks while a discussion about mass balance issues related to their metasomatic origin is undertaken in chapter 7.4.

### Major elements

For the quartz rocks there are 88 representative samples in the GTK dataset. These yield a high average SiO<sub>2</sub> content of 89.7 wt.% (Table 4a). Many of the cleanest guartz rocks contain over 97 wt.% SiO<sub>2</sub> and thus are remarkably pure quartz rocks indeed. Averages for MgO and CaO are 2.1 wt.% and 2.5 wt.%, respectively, while average Al<sub>2</sub>O<sub>3</sub> is very low 0.45 wt.%. Forty six representative samples of the carbonate rocks have an average  $SiO_2$  content of 14.65 wt.%, showing that most of the Outokumpu type carbonate rocks must be low in silicates indeed composed dominantly of carbonate. Averages for MgO and CaO are 20.1 wt.% and 25.2 wt.%, reflecting the fact that the dominant carbonate species is dolomite. Most of the minor MgO and CaO in the guartz rocks are in tremolite and/or diopside (+carbonate). In the carbonate rocks tremolite and diopside are the main carriers of the minor SiO<sub>2</sub>. Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and alkali elements occur both in the carbonate and quartz rocks only in low to very low concentrations, reflecting the scarcity of plagioclase, aluminous amphiboles and Ti-rich minerals (sphene, rutile) in their modes. The systematically very low Al<sub>2</sub>O<sub>3</sub> (<<2 wt.%), TiO<sub>2</sub> (<0.1 wt.%), Zr (<10 ppm) and alkali element concentrations (K<sub>2</sub>O and Na<sub>2</sub>O <0.1 wt%) denote that both the carbonate and quartz rocks are practically free of any mineral components that could be considered to be of epiclastic, heavy or clay mineral origin.

The skarn rocks are in terms of their SiO<sub>2</sub>, MgO and CaO contents broadly intermediate to the carbonate and quartz rocks, and similarly show systematically very low in  $AI_2O_3$ , TiO<sub>2</sub> and alkali element concentrations. On average, the diopside skarns are a bit richer in SiO<sub>2</sub> (48.6 wt.%) compared to the tremolite skarns (46.2 wt.%). A more prominent difference is seen in CaO/MgO ratios, which are on average significantly higher in the diopside (1.25) than tremolite skarns (0.84). In comparison, the carbonate and quartz rocks have an average CaO/MgO of 1.25 and 1.18, respectively.

Phosphor contents in the carbonate-skarn-quartz rocks are systematically very low ( $P_2O_5$ <0.01-0.03 wt%). Total Fe<sub>2</sub>O<sub>3</sub> content in both the carbonate and skarn rocks is ca. 6 wt.%, while the quartz rocks have an average a significantly lower Fe<sub>2</sub>O<sub>3</sub> of only 2.1 wt.%. Manganese concentrations are low in the carbonate and skarn rocks (MnO ca. 0.10 wt.% on average), but like Fe concentrations, especially low in the quartz rocks, which frequently contain less than 0.01 wt.% MnO. Such systematically very low Mn and Fe concentrations indicate total absence of iron-manganese enriched layers that would be excepted in these rocks would they represent hydrothermal, exhalative deposits at subseafloor hydrothermal vents, as has been previously proposed (e.g. Borchert, 1954; Mäkelä, 1975; Treloar, 1987; Park, 1987).

The observed field relationships, petrographical and major element chemical data consistently provide evidence of that the skarn rocks in Outokumpu assemblage represented metamorphosed carbonate–silica mixtures, intermediate to those represented by the carbonate and quartz rocks in the assemblage. With regional metamorphic temperatures progressing above temperatures of ca. 300 °C, the original carbonate–silica mixtures reacted to produce first tremolite, then diopside±calcite, plus CO<sub>2</sub>.

#### Trace elements

With striking consistency, the carbonate, skarn and quartz rocks in the Outokumpu assemblage all have high to moderate abundances of the highly to moderately compatible first series transition metals Co, Cr, Ni, V, Sc, and Zn (Table 4b,d), and very low concentrations of the moderately to highly incompatible lithophile elements like REE, Zr, Y and Th (Table 4c). Moreover, in terms of the mantle-normalised more immobile transition metal and HFSE contents and profiles, the carbonate, skarn and guartz rocks are all mutually similar and strikingly similar with the adjacent serpentinites and depleted mantle peridotites (Fig. 38). The systematically very high mantle-like Cr and Ni contents of the Outokumpu-type carbonateskarn-quartz rocks unambiguously differentiate them from chemical-exhalative cherts and carbonate rocks that are nowhere known to contain even nearly similarly high concentrations of these elements (Figs. 39-40). Furthermore, the very low Th (mostly <0.5 ppm) and Zr (mostly <5 ppm) concentrations in the carbonate, skarn and guartz rocks strongly militate against their origin as radiolarian cherts, which even in open sea environments gain Zr and Th, if not by any other means, at least in wind-borne dust from the continents. Origin as radiolarite cherts is of coarse an unrealistic proposal, simply because there were not yet radiolarites in the Palaeoproterozoic oceans.



Fig. 38. Mantle-normalized trace element profiles of average Outokumpu type metaserpentinites, metaperidotites, carbonate rocks, skarn rocks and quartz rocks. In the light of this plot, showing mostly relatively immobile elements, origin of the Outokumpu type carbonate-skarn-quartz rocks as alteration products of the adjacent mantle peridotite-derived metaserpentinites and metaperidotites is clear. Note the relatively huge enrichment of the carbonate-skarn-quartz rocks in U, suggesting at lest mildly oxidizing environment for the primary carbonate-silica alteration.



Fig. 39. Cr, Ni versus Zr and Co, Cr versus Ni diagrams for carbonate-skarn rocks and serpentinites in the Outokumpu assemblage. Data for average late Palaeoproterozoic (LPP) dolostones and limestones (Veizer et al., 1992), various cherts (radiolarian, hydrothermal etc.) and pyrolite (primitive mantle) shown for comparison. Note the striking mutual similarity of the Outokumpu type carbonate-skarn rocks to serpentinites and pyrolite on these diagrams, and their very different plotting compared to the LPP carbonate rock averages.



Fig. 40. Cr, Ni versus Zr and Co, Cr versus Ni diagrams for quartz rocks and serpentinites of the Outokumpu assemblage. Data for various cherts (radiolarian, hydrothermal etc.) and pyrolite (primitive mantle) shown for comparison. Note the striking mutual similarity of the quartz rocks to serpentinites and pyrolites on these diagrams, and their very different plotting from cherts of any type.

Concentrations of REE in the typical Outokumpu carbonate and quartz rocks are universally very low. Typically the  $\Sigma$ REE content in these rocks is in the range of 3-6 ppm, which is less (!) than the  $\Sigma$ REE concentration of 6.87 ppm in primitive mantle. The REE concentration level and mantle-normalized REE profiles of the average carbonate and quartz rock are mutually similar and similar to the average Jormua-Outokumpu serpentinites and depleted mantle peridotites. Compared to the carbonate and quartz rocks, the skarns are somewhat enriched in total REE, with average concentrations of 8.0 ppm and 16.2 ppm for the tremolite and diopside skarns, respectively. In mantle-normalized profiles, compared to the quartz rocks, the skarns show a bit more enrichment in LREE, too. Several of the samples in the GTK skarn sample set representing the neighbourhoods of the Outokumpu, Vuonos and Kylylylahti Cu deposits, there is the possibility that the slightly higher total REE and LREE in the skarn averages could be related to the late syntectonic mobility of REE observed for the stringer zones ("Co-Ni zones") of these deposits.

Strontium concentrations in the carbonate-skarn-quartz rocks do rarely exceed 150 ppm, the quartz rock showing the lowest abundances (<1-70 ppm) and the carbonate rocks the highest (40-150 ppm). Barium concentrations in the carbonate, skarn-quartz rocks are systematically low (<<50 ppm). The universally low Ba of the Outokumpu assemblage together with the systematically low Mn and total Fe militate against involvement of hydrothermal subseafloor exhalative processes in any stage of the evolution of the carbonate-skarn quartz rock assemblage. The very low Mn and total Fe characteristic of the Outokumpu assemblage is an especially important aspect since the metal flux in oceans from seafloor hydrothermal vents comprises for overwhelming part Mn and Fe (e.g. Scott, 1997).

As we pointed out earlier the carbonate-skarn-quartz rocks have very similar PGE content and distribution as the adjacent serpentinites. Consequently, e.g. on the Ni/Cu versus Pd/Ir diagram of Barnes et al. (1988) the carbonate-skarn-quartz rocks plot very similarly as the serpentinites within the mantle field but with a slight scatter towards more Cu-rich compositions (cf. Fig. 22). There are two reason for this scatter. First, some of the quartz rock samples are from the vicinity of the Outokumpu and Vuonos ores, and thus probably show some "ore influence". Second, like the serpentinites, as we clarified before, also the quartz rocks probably have been gaining some minor Cu during the metamorphism. Most importantly, the fact that the carbonate-skarn-quartz rocks in Outokumpu assemblage have similar mantle-lke PGE abundances and distributions than the serpentinites (Figs. 22) is one more strong evidence of that these rocks, like the serpentinites, have been derived from mantle peridotite precursors by metasomatic alteration. The high, mantle-lke and relatively immobile Ir especially denotes that the carbonate and quartz rocks cannot represent any sedimentary carbonates or cherts; such rocks would contain at least a magnitude or two less of Ir.

Considering the pervasive alteration of the protolith mantle peridotites first into serpentinites and then further to carbonate and silica-rich rock types, the apparent immobility of PGE is a quite surprising finding. Where do the PGE in the serpentinites and especially in the carbonate-skarn-quartz rocks now locate, is an interesting question. Chromite is in these rocks the only primary phase that has to a degree survived from the original mantle protolith. Because Os, Ir and Ru in magmatic and mantle rocks have high affinity to chromite, it is then possible that this mineral and its oxide alteration products (ferrian chromite, Cr-magnetite) still would be the main PGE host, at least for the Ir and perhaps also Pt. In which form these PGE now exactly occur in the Cr-Fe spinels, remains unclear, but possibilities include that they might occur in solid solution or as minute inclusions of PGE sulphides/alloys. However, for the Rh, Pt and Pd it is more likely that they occur, similarly like Ni, remobilised/relocalised in the metasomatic-metamorphic sulphide phase.

### Carbon (graphite)in the quartz rocks

Organic derived carbon (graphite) is fairly common minor component in the quartz rocks, especially in such domains, which flank thick layers of black schists. These graphite-bearing

quartz rocks, which may contain graphite-bound carbon up to 3 wt.%, have been considered in some earlier views as "black chert" layers syngenetic with the adjacent black schists (e.g. Peltola, 1978; Loukola-Ruskeeniemi, 1992). However, the graphite-rich quartz rocks do not differ in their modal or chemical composition in any significant way from the less graphitic quartz rocks, but similarly contain chromite, lack zircon, are high in Cr, Ni and Co, and very low in Zr, for example. We propose that organic carbon in these quartz rocks was introduced by migration of hydrocarbon bearing fluids during the low T (<250 °C) part of their metasomatic-metamorphic alteration history. In fact, presence of hydrocarbons (petroleum) in unmetamorphosed carbonate-silica altered peridotites is a long since noted feature (e.g. Peabody and Einaudi, 1992).

# 7. Origin of the Outokumpu assemblage

#### 7.1. Metaserpentinites and metaperidotites

It is clear from the above presented data and discussion that similar as the Jormua serpentinites (cf. Peltonen et al., 1996; 1998) also Outokumpu serpentinites have to represent nearly exclusively residual mantle peridotites. An important follow-up guestion, and that is not only of academic but also profound ore geological importance, rises: Which type of mantle we are then dealing with? Do the Outokumpu serpentinites represent MORB source mantle or perhaps ancient, Archaean SCLM as has been inferred for mantle section of the Jormua complex (cf. Tsuru et al., 2000)? A SCLM origin is supported by the fact that in many significant aspects of their geochemistry the Outokumpu serpentinites are fairly similar with the serpentinities of the Jormua Ophiolite Complex. The similarity comes out especially clear in the usually distinctly flat mantle-normalised REE patterns and ubiquitous Zr (+Nb-Y-Th-HREE?) enrichment of both the Jormua and Outokumpu peridotites. In a significant difference, the proportion of highly depleted peridotites in most of the Outokumpu massifs is clearly higher than in Jormua, but similarly highly depleted peridotites are anyway present also in the Jormua complex. And, the more fertile compositions of the Jormua peridotites are not so much telling of their SCCL origin but their refertillization in basaltic elements by emplacement of the abundant 1.96-1.65 Ga basalt dykes ubiquitous in the Jormua mantle units.

We distinguished above two overlapping trends in the Zr (+Nb-Y-Th-HREE?) reenrichment of both the Jormua and Outokumpu peridotites, one that shows poor or no correlation, and the other with positive correlation with the basaltic elements AI, Sc and V. We related the latter enrichment trend to the interaction of the peridotites with the tholeiitic mafic magmas intruded ca. 1.95 Ga ago in the peridotites. Evidence from Jormua suggests that the former and more cryptic Zr (+Nb-Y-Th-HREE?) enrichment may be related to the OIB type dyke emplacement that preceded the emplacement of the ca. 1.95 Ga E-MORB type main suite magmatism in the Jormua peridotites. However, observations of similar OIB type dike than in Jormua from Outokumpu peridotites are yet rare, including just two possible candidates, one form Kylylahti and the other from Piilukoski, Kaavi. However, considering the usually pervasive alteration, high metamorphic grade and usually high strain of the dyke materials in the serpentinite massifs of the Outokumpu area, the "absence" of the early OIB dykes from Outokumpu may reflect just the difficulty of recognizing such dykes in the field, which is difficult even from the least strained parts of the overall much better preserved Jormua complex.

In ophiolite complexes the mantle sequences and basaltic lids are usually, though not always, in a cogenetic relationship, in a way that the former represent the residual after the melt extraction that produced the latter. This is, however, obviously not the case in Jormua complex where there are considerable field, geochemical and isotopic evidence of that the mantle this complex was not the source of the 1.95 Ga mafic rocks in its mafic parts, and that it would in fact represent completely unrelated, much older subcontinental lithospheric mantle (Peltonen et al., 1998; Tsuru et al., 2000; Peltonen et al., 2002, 2003). Though it was once thought that part of the Jormua mantle would dominantly represent Proterozoic 1.95 Ga mantle diapir, there are increasingly more evidence of that possibly the entire mantle sequence in Jormua was of

subcontinental lithospheric origin. This evidence includes e.g. Re-Os isotope data that suggests the Jormua mantle had been melted pervasively already 3 Ga ago (Tsuru et al., 1999), and Archaean xenocrystic magmatic zircons in the 1.95 Ga dyke rocks cross-cutting the Jormua mantle sequence (Peltonen et al., 2002, 2003). Peltonen et al. (2003) proposed that the SCLM in the Jormua Complex was exhumed by extreme crustal thinning and detachment faulting in the final stages of 2.0-1.95 Ga break-up of the Karelian continent.

Data for Re-Os isotopes, that seem to provide an especially powerful tool of mantle interpretations, are not plentiful for the Outokumpu serpentinites. The currently available data is restricted to the few data in Walker et al. (1996) for the chromitites at Sarvikangas, Kylylahti. Based on the Kylylahti chromitite data Walker et al, (1996) inferred a 1.95 Ga origin for the residual mantle parts in the Outokumpu massifs. As there is similar Re-Os results also from two highly altered chromitite boulders from the Jormua complex (Tsuru et al., 2000), which nevertheless for its main mantle parts clearly represents much older SCLM, one may ask how well the chromitite data form Kylylahti would represent the whole peridotite volume in the Outokumpu assemblage? The situation in Kylylahti could in fact be the same as in Jormua, and the peridotites outside of the immediate chromitite environments actually represent >3.0 Ga SCLM (cf. Tsuru et al., 2000; Peltonen et al., 2003). A possible hint of ancient SCLM origin of the Kylylahti serpentinites is provided by the U-Pb isotope data for presence of >2200 Ma zircons in one metabasite dyke observed during this project in Kylylahti massif, which indicates that the host peridotites (talc-carbonate altered) may be even older, and perhaps indeed represent SCLM of Archaean age (cf. section 9.3.1.).

Summarizing from the above discussion and that in section 6.3.1., it seems most likely that the serpentinites in the Jormua and Outokumpu ultramafic-mafic massifs would in the both cases represent SCLM peridotites strongly depleted in the more incompatible elements already before 3.0 Ga. And further that, the peridotite massifs both cases would register much later interactions with magmas which refertilized them, ubiquitously in the more incompatible elements like Zr, but variably also in some of the more basaltic elements like Al, V and Sc. From Jormua there is evidence of the dominant refertilization features would be related to the 1.95 Ga break-up of the Karelian Craton.

### 7.2. Mafic rocks

Our observations suggest that Outokumpu serpentinite massifs are associated with at least types of mafic rocks: (1) possible autoclastic (partly pillow?) fine-grained metalavas and tuffs, (2) coarse-grained, gabbroic dykes and small plugs, and (3) fine-grained, usually heavily chloritized, narrow basaltic dykes. Of these, type 2 gabbroic plugs/dykes, and type 3 basaltic dykes seem to be relatively common, while type 1 possible extrusive metabasalts, appear very rare, being more voluminous only in association of the Losomäki and perhaps Vehkalahti serpentinites.

The presumably extrusive Losomäki amphibolites show very distinct chemical composition in many aspects similar to the rare Phanerozoic low-Ti depleted tholeiites (LOTI) or boninites (Fig. 41). Even closer they resemblance low-Ti depleted tholeiites (Fig. 42), alias basaltic



Fig. 41. Losomäki low-Ti and Jormua E-MORB metabasalts plotted in a Ti/V versus Ti/Sc diagram discriminating between boninites, komatiites and mid ocean ridge basalts (fields from Piercey et al., 2001). For comparison average compositions of primitive mantle (BSE), N-MORB and Ontong-Java plume basalts are also shown. afb=massive amphibolite, pl-lava=pillow lava, dsdy=mantle-hosted sheeted dykes, sdy=shallow-level sheeted dykes, epiloti=low-Ti metabasites in Lower Kaleva type host environments. Note that the low-Ti tholeiites plot in this diagram in the boninite field, a better discrimination between boninites and low-Ti tholeiites is provided e.g. by the La/Sm vs. TiO2 plot in Fig. 42.



Fig. 42. Losomäki low-Ti and Jormua E-MORB metabasalts plotted on a La/Sm versus TiO<sub>2</sub> diagram discriminating between boninites, Tasmanian type low-Ti tholeiites (TLOTI) and mid ocean ridge basalts (MORB). For comparison data for Onega 1.97 Ga flood basalts and average compositions of primitive mantle (BSE), E-MORB, OIB, Ontong-Java plume basalts, and late Archaean Munro komatiites are also shown. afb=massive amphibolite, pl-lava=pillow lava, dsdy=mantle-hosted sheeted dykes, sdy=shallow-level sheeted dykes, epiloti=low-Ti metabasites in Lower Kaleva type host environments. MORB, TLOTI and Boninites fields from Wyman (1999).

komatiites, of some Archaean greenstone associations, where those rocks usually occur interfingered with ultramafic komatiite flows (e.g. Kerrich et al., 1998; Wyman et al., 1999; Smithies et al., 2005). The gabbros and basaltic dykes in the serpentinites show as a whole a wider compositional variation than the Losomäki LOTI, but overall in such frames that they seem to represent variable low-P fractionates from a parental magma similar to that of the Losomäki LOTI. A minor part of the metabasites as e.g. in Luikonlahti and Viurusuo show compositional variation towards the E-MORB (or rather T-MORB) compositions as typical of the Jormua metabasites (gabbros, pillow lavas).

A comparison with available models of mantle melting (e.g. Pearce and Parkinson, 1993) suggest that while the Jormua E-MORB could be produced by <5-15% fractional melting of peridotite broadly similar to modern E-MORB source, derivation of the Losomäki type low-Ti tholeiites from a similar source would imply significantly more, 15 to 35% melting. As this is clearly unrealistic for one stage melting, the Outokumpu LOTI metabasites likely do represent melting of more depleted mantle than typical MORB sources. The relatively low  $Gd_N/Yb_N$  of the Losomäki LOTI suggest that they were derived from a source earlier depleted in garnet stability field (>20 kb, >70 km), and hence enriched in elements with high affinity to garnet (as e.g. HREE). The Jormua E-MORB, which have  $Gd_N/Yb_N$  ratios >1, could well represent, or at least be similar to, those melts that were extracted from the Jormua-Outokumpu mantle before the LOTI stage.

Previously the Losomäki metabasites have been interpreted as island arc type low-K tholeiites originated above a subducting oceanic plate, in a back arc basin (e.g. Park, 1984; 1988; Vuollo, 1994). These interpretations were based mainly on the low Ti-Y-Zr character of the Losomäki and Miihkali amphibolites, indicating origin by high degree melting from strongly depleted mantle sources, as it is typical of primitive island arc tholeiites (e.g. Woodhead et al., 1998, and references therein). It should be noted, however, that the Losomäki low-Ti tholeiites do not show any of the more diagnostic chemical characters of suprasubduction-related magmas, like e.g. negative Nb anomalies in their mantle or MORB normalized trace-element profiles. On magmatectonic discrimination diagrams the Losomäki basites plot, depending of the diagram, either in MORB or combined MORB/low-K island arc tholeiite basalt fields. To specify the magma character, it has been proposed that the Miihkali and Losomäki basites would represent boninites (Vuollo, 1994). Absence of diagnostic boninite features like high SiO<sub>2</sub>, clear U-shaped mantle-normalized REE patterns or Zr spikes in the mantle-normalised spidergrams are lacking, however. If not unambiguously similar with either modern arc tholeiites or boninites, the chemical resemblance of the Losomäki basites to the low Ti depleted tholeiites from several Precambrian associations, especially to those from the Archaean greenstone belts is striking. The Archaean low-Ti tholeiites are often equated petrogenetigally and tectonically with the Phanerozoic low Ti-tholeiites and boninites, but for the same reasons as for the Losomäki low-Ti tholeiites, such a correlation must be regarded debatable.

It is increasingly evident that, at least during Precambrian, boninite-like rocks were emplaced also in clear non-suprasubduction formative settings (e.g. Smithies, 2002). An alternative source for low-Ti type tholeiites and boninites, to a mantle wedge above subducting oceanic plate, could be provided, for instance, by a step-wise ascending mantle plume or diapir in a rift setting (cf. Crawford et al., 1989), especially during Precambrian when overall mantle temperatures and thus also plume initiation temperatures likely were higher than now. In this respect is important to note that when plotted in Nb/Y vs Zr/Y or Zr/Nb vs. La/Nb diagrams (Fig. 43), both the Jormua and Outokumpu metabasites plot in the field of Islandic plume basalts, outside of the field of the North Atlantic N-MORB (cf. Fitton et al., 1997; Breddam, K., 2002). The geochemical similarity of the Jormua basalts to the more primitive melts from the Iceland plume, as e.g. those at Kistufell (Breddam, 2002) is prominent. Within the Icelandic plume array, the Outokumpu and Jormua basites plot in separate clusters, however, the Jormua basites showing significantly lower Zr/Nb ratios. As Nb-Y-Zr systematics is relatively insensitive to low pressure crystal fractionation, this difference likely reflects differences between Jormua and Losomäki in



Fig. 43. Zr/Nb versus La/Nb plot of Losomäki and Jormua metabasalts showing the fields of Iceland plume related basalts and representative N-MORB. For comparison averages of the 2.1 Ga Koli T1 and 1.96 Ga T2 tholeiite dykes (Vuollo et al., 1992), 1.97 Ga OIB-type Onega plateau basalts (OIB=noncontaminated, OIBC contaminated) (Puchtel et al., 1998), N-MORB, E-MORB, OIB, primary mantle (BSE), and upper continental crust (UCC) are shown. Note that the Jormua and Losomäki metabasalts both plot in the field of the Islandic plume basalts, and that crustal contamination that is apparent for the Koli T1, T2 and Onega OIBC is not indicated for the Jormua and Losomäki basalts. N-MORB and Iceland basalt fields from Fram et al. (1998).

terms of degree and depth of partial melting and/or source depletion through previous melt extraction. The high Nb<sub>N</sub>/La<sub>N</sub> (often >1) of especially the Jormua E-MORB but also Outokumpu low-Ti tholeiites further support a possible plume origin, as high Nb<sub>N</sub>/La<sub>N</sub> ratios are often considered a unique feature of modern plume magmas, thought to reflect a component of recycled oceanic crust in their source (e.g. Hofmann and White, 1982; Weaver, 1991). Importantly, the low Zr/Nb and La/Nb exclude any significant crustal or lithospheric mantle contamination of either the Jormua or Losomäki magmas.

One important finding of this work was that also many metabasite occurrences in the parautochthonous/autochthonous Lower Kaleva units, apparently structurally immediately underlying the Outokumpu Allochthon, as e.g. those at Viitaniemi-Virvujärvi, Riihilahti and in Heinävesi show the clear LOTI character of the Losomäki amphibolites. This raises the serious option that the Losomäki metabasalts would after all be part of the parautochthon, rather than represent an extrusive unit of a dismembered ophiolite complex – in spite of how alluring the latter interpretation would in this case be. In order to get also isotopic constraints for evaluation of this issue, and the source of the involved magmas, we introduced together with H. Huhma from GTK a Sm-Nd isotope survey for representative samples of both the serpentinite and Lower Kaleva associated metabasites.

Three samples representing the Losomäki metabasalts yielded  $\epsilon_{Nd}(1950)$  values between +0.2 and +0.5. Very similar  $\epsilon_{Nd}(1950)$  values between -1.2 and + 0.9 were obtained for ten metagabbro samples from the Losomäki, Miihkali, Kylylahti and Huutokoski serpentinites massifs. One metagabbro sample from Losomäki and two from Horsmanaho yielded somewhat

higher  $\varepsilon_{Nd}$  (1950) values between +2.3 and +2.7. Six representative samples from the metabasites in the parautochthonous units at Viitaniemi-Virvujärvi, Riihilahti and Heinävesi also turned out to have  $\varepsilon_{Nd}$  (1950) clustering around +-0, within a narrow range between -1.5 and +0.4. In the light of this data the similarity between the metabasites of the serpentinite associations and those in the underlying Lower Kaleva seems very clear but chemically also isotopically.

The fact that the  $\epsilon_{Nd}$  (1950 Ma) of the mafic magmas in the Outokumpu assemblage and Lower Kaleva cluster around +-0 implies that their source cannot have been in the MORB source type long-term depleted upper mantle that at 1950Ma had  $\epsilon$ Nd of +4 to +6 (e.g. Hegner and Bavier, 1991; Stern et al., 1995). The  $\epsilon_{Nd}$  (1950Ma) of the Jormua E-MORB, averaging to about +2, have been interpreted in terms of 1950 Ma melting of MORB source type mantle diapir, and contamination by SCLM during ascend upon surface (cf. Peltonen et al., 1998). However, as we pointed out previously, the low La/Nb, Th/Nb and Zr/Nb of the Jormua E-MORB basalts and Outokumpu LOTI do not support major contamination by continental crust or subcontinental lithospheric mantle. The fact that these ratios, and the +0 to +3  $\epsilon_{Nd}$  (1950 Ma) values of Jormua – Outokumpu basites, are in the expected range of 2 Ga old plume magmas (cf. Puchtel et al., 1998) makes it temping to propose that Jormua and Outokumpu metabasites would represent rather plume than either MORB-type or arc-type magmas.

## 7.3. Nature and formative tectonic environment of the mafic-ultramafic massifs

During the past twenty five years two fundamentally differing interpretations of the Outokumpu serpentinite-metabasite massifs have been proposed. Koistinen (1981) and Vuollo and Piirainen (1989), for example, have supported an ophiolite interpretation of the massifs, i.e. that they would represent fragments of dismembered oceanic crust and mantle. The ophiolite interpretation has been questioned by Park (1984, 1988), who interpreted the serpentinites as saxonitic-dunitic sills of the komatiite lineage, intrusive in the Kalevian metasediments and Outokumpu assemblage.

It is most clear from the above-presented evidence that the Outokumpu serpentinite massifs do not represent magma intrusions but tectonically emplaced, fault-bound bodies of dominantly refractory mantle peridotites. Equally clear is that none of the massifs is having a rock constellation or internal structure even close to that of an ideal ophiolite. Any evidence for large, layered gabbro or sheeted dyke units typical of well-developed ophiolites, are absent, for example. Some pillow lavas have been identified at the serpentinites, but only in very small volumes and in field settings where their relationships with the serpentinites are open to debate. It is worth to remark, also, that the serpentinites show geochemical features more similar to SCLM than MORB source peridotites.

The crucial features of the Outokumpu massifs suggest they would represent either "orogenic peridotites" or ophiolitic fragments of largely ultramafic oceanic lithosphere. Unfortunately, the poorly exposed and highly deformed Outokumpu massifs provide relatively little evidence for resolving between these two alternatives. However, the many similarities between the Jormua and Outokumpu massifs, such as the similar ages of their gabbros (section 9.3.1.), obvious SCLM character of their mantle peridotites (section 6.3.1.), plume signature in their basite components (section 7.2.), make it probable that they would represent petrotectonically consanguineous units. Noting the ample evidence of an ophiolitic origin of the Jormua Complex, this would render to that also the Outokumpu massifs, despite their far poorly developed ophiolite features, would ultimately represent ophiolite type massifs. The relative rarity of mafic rocks in the Outokumpu massifs can be explained by dominantly ultramafic oceanic floor, and the absence of any truly pelagic type sediments from their association by assuming them a near-continent formative tectonic setting, in which newly generated oceanic crust could have been rapidly buried below continent-margin turbidite fans. Hence, all the presently available relevant evidence put in the basket, origin as nascent oceanic lithosphere in a slow, magma-poor continental break-up setting, as envisioned by Peltonen et al. (1996; 1998) for the Jormua Ophiolite, seems the most probable formative setting also for the Outokumpu "ophiolites".

Phanerozoic and recent analogues of the Kainuu-Outokumpu ophiolites, in terms of the inferred original formative tectonic setting, are provided e.g. by the Northern Apennines ophiolites (e.g. Rampone and Piccardo, 2000), peridotites-gabbros within the West Iberia (Spain) passive margin of the Atlantic ocean (e.g. Cornen et al., 1999) and the Red Sea. In a significant difference, there where mantle exposed in association with Proterozoic ocean openings is usually of Iherzolitic composition, it in the Outokumpu massifs was mainly strongly depleted harzburgite. However, there is ample evidence from mantle xenoliths that mantle below several Archaean shield regions would comprise large portions of comparatively highly depleted harzburgite. Thus SCLM exhumed by early Proterozoic continental break-ups may well have been dominantly harzburgite instead of Iherzolite as during Phanerozoic.

In the light of the above scenario, Outokumpu mafic-ultramafic massifs would represent mainly Archaean SCLM mantle with an abundant component of low-Ti tholeiite basaltic-gabbroic mantle dykes. Abundant mantle dykes, although of E-MORB-like composition, are a distinct feature also in Jormua. Presence of low-Ti basalt intercalations in the Lower Kaleva continent-margin sediments, and autoclastic (including pillow?) structures in mantle fragment associated low-Ti basites in Losomäki, provide some evidence of that there may have been at least limited extrusion of the low-Ti tholeiite magmas on to the surface, too. Therefore a patchy thin mafic crust, like in Jormua, may have been a character of also the Outokumpu oceanic lithosphere. However, there is yet the possibility that the "pillow lavas" as e.g. at Losomäki actually belong to the autochthon. Either way, there are absolutely no evidence of thick ophiolite type crust of gabbros, sheeted dykes and pillow basalts in the Outokumpu ophiolite fragments. The lack of sheeted dyke units from the Outokumpu assemblage is a particularly notable difference compared to Jormua where they constitute, after mantle peridotites, the second most voluminous unit of the ophiolite.

The fact that there are LOTI metabasites not only with the serpentinites but also in the Lower Kaleva type parautochthonous units such as those at Viitaniemi-Viurvujärvi, Riihilahti and Heinävesi, suggests the LOTI type magmatism in the ophiolite floored embryonic ocean basin was preceded or concurrent with similar magmatism within the continental margin. We recognise that tectonic environments that allow basically similar situation of closely juxtaposed ensimatic and ensialic environments include but continental break-up basins also ensialic back arc basins. Back arc basin origin has been repeatedly proposed for Outokumpu assemblage, but as we pointed above, the lack of the more diagnostic subduction signatures in the geochemistry of the metabasites, and, in fact, any other arc messages in the geology of the Kaleva, do not much favour back arc scenarios.

The obvious plume signature in the Jormua and Outokumpu basalts is an important aspect to consider in modelling of the 1.98-1.95 Ga evolution of Kainuu-Outokumpu zone, especially as there is additional evidence of plume-related mafic magmatism of this time range also other parts of Karelia as from the Onega (Puchtel et al., 1998) and Koli areas (Vuollo et al., 1992), for example. The Onega, Koli, Jormua and Outokumpu basites seem to record an in time and space integrated shift in  $\epsilon_{Nd}$  (1950Ma) for crustally uncontaminated basalts from +3 for Onega (Puchtel, 1998) via +2 for Koli and Jormua (Vuollo et al., 1992; Peltonen et al., 1996) to ca. +0 for Outokumpu (this study). This trend seems to have been accompanied with a shift from a highly incompatible element enriched source for the Onega, via moderately enriched source for the Koli and Jormua, to the highly depleted source of the Outokumpu magmas, and a corresponding change from deep garnet stability to shallow spinel-plagioclase stability melting. It is conceivable that all this evolution was tightly related to the evolution of the apparently very large mantle plume at 2.00-1.95 Ga below the entire Karelian craton, and which possibly triggered the mantle processes leading to its break-up west of the present Svecofennian-Archaean boundary line (cf. Puchtel, 1988).

If the sequence of events in the inferred plume-induced 2.00-1.95 Ga break-up of the Karelian craton was as envisioned above, then the Outokumpu magmatism should be dominantly at least a somewhat younger event than the Jormua magmatism. The presently available precise age data suggests there would be only minor if any difference (less than 10 Ma) in ages of the metagabbros in Jormua and Outokumpu, and that the latter would be rather slightly older rather than younger. However, there are yet relatively few data for both Jormua

and Outokumpu, so it is yet not possible to relevantly reconstruct the related magmatic evolution.

Why then mainly E-MORB with  $\varepsilon_{Nd}$  (1950 Ma) of +2 in Jormua and low-Ti basalts with  $\varepsilon_{Nd}$ (1950 Ma) of +0 in Outokumpu? In a plume scenario a possible explanation would be that this reflects variation in the degree of melting, and proportion of those source components that contributed to the melting, such as deep primitive mantle, entrained astenospheric mantle and old recycled oceanic crust. If the Jormua and Outokumpu basites indeed were related to one plume, some overlap in their geochemistries could be expected, however, and indeed, there are some variation in the Outokumpu main tholeiite suite magmas towards E-MORB chemical compositions and positive  $\varepsilon$ Nd up to +3 as in Jormua, but it is yet not known how real and positively correlated these trends would be. As we noted above, the positive Nb anomalies in Jormua and Outokumpu metabasalts indicate a component of recycled oceanic lithosphere in their mantle source (for related theories of earths mantle evolution see e.g. Davies, 1998; Condie, K. C., 2001). One possible scenario is that the deeper Jormua melting involved a bigger proportion of this long-term isotopically depleted component, with positive  $\varepsilon_{Nd}$  (1950 Ma), while with further ascent and melting of the plume, in the Outokumpu stage, less of this presumably relatively easily fusible component was anymore available, and there was an associated shift in the  $\epsilon_{Nd}$  values towards bulk silicate earth-like ±0. Note that it is here assumed that the main plume component had a chemical and isotopical composition akin to the bulk silicate earth (primitive mantle).

Important from an ore genetical standpoint is that generation of low-Ti tholeiite magmas requires high degrees of high-temperature, shallow plagioclase-spinel stability field melting of a refractory mantle source, thus if a plume was involved and was the main source of the Outokumpu mafic magmas, it must have risen hot and high in the lithosphere. In the light of the lead isotope evidence for ca. 1.95 Ga origin for the Outokumpu sulphides (section 9.3.2.), ascent of hot mantle plume and related hot 1.95 Ga magmas to shallow levels below the inferred narrow, largely peridotite-floored Kaleva break-up sea may have been the ultimate cause of the formation of the Outokumpu type Cu-Co sulphides. Extension of the crust related to the plume impingement likely resulted in lithosphere-penetrating faults that acted as conduits for the low-Ti tholeiite magmas and that focused upflow of seawater circulated in the ocean crust. The 2.00-1.95 Ga mantle plume may have had an important role also in the earlier stages of the evolution of the Kalevian break-up ocean, modifying the marine and climatic conditions favourable to the deposition of the highly Cu-Ni-Zn-V anomalous black schists of the Talvivaara type that are associated with the low-Ti tholeiites in Riihilahti and Viitaniemi in the Outokumpu area, and widely present in the "Lower Kaleva" of Kainuu.

In a plume scenario the obvious amagmatic nature of the Kalevian break-up is a somewhat problematic aspect as the plume models suggest rapid production of large volumes of magma when they intersect the lithosphere. On the other hand as this stage probably is represented by the 2.0-1.98 Ga flood basalts as in the Onega Plateau and elsewhere on the Karelian Craton, much of the "magma fertility" of the plume in the 50-20 Ma later break-up stage may already have been consumed, explaining the low magma production. As we noted above low-Ti tholeiites and boninites are usually interpreted in terms of plume – arc or spreading-ridge – arc interaction (e.g. Crawford et al., 1989; Pearce, 1992; Kerrich et al., 1998; Piercey et al., 2001; Wyman et al., 2002). But as we pointed before, in this case there is no evidence of the subduction involvement.

A worthwhile remark is that low-Ti tholeiites and boninite-like basalts, as in the Outokumpu massifs, actually seem a particularly indicative omen of massive sulphide potential; judging from that they are an important component also of many other massive sulphide mining districts as e.g. the late Archaean Kidd Creek in Canada (e.g. Wyman et al., 1999), Flin Flon belt in Canada (e.g. Stern et al., 1995), Palaeozoic Finlayson region inYukon-Tanana terrane in Canada (e.g. Piercey et al., 2001), Cambrian Dundas and Adamsfield Troughs in Tasmania, Australia (e.g. Brown and Jenner, 1989), Troodos Ophiolite, Cyprus (Cameron, 1985) etc. Though the lithoassociations of these classical camps are usually related to subrasubduction processes, the driving factor behind the ore formation was not so much the geodynamical setting as such, but rather the high heat flows and thus enhanced possibility of vigorous

hydrothermal circulation, which are very likely related to environments of the low-Ti tholeiite/boninite type magmas, in whatever setting they erupted.

Finally, it is worth to note that boninite and related low-Ti tholeiite magmas are usually enriched in PGE and Au, but depleted in Cu, S and Se compared to average MORB, and exhibit incompatible like behaviour for PGE and Au. And that fractionation of such PGE enriched but sulphur undersaturated magmas could concentrate chalcophile metals in the liquid residuals (Hamlyn, et al., 1985; Hamlyn, 1986). The apparent absence of significant PGE enrichments in the case of the Outokumpu low-Ti metabasites may be related to absence of large magma chambers that did not favour extensive magma differentiation and related PGE concentration.

In conclusion, the Outokumpu "serpentinites" most probably represent ophiolitic fragments of ultramafic oceanic lithosphere generated after the 1.95 Ga plume-triggered break-up of the Karelian Craton and subsequent magma poor opening of the apparently largely mantleperidotite floored Kalevian Sea. The low-Ti depleted tholeiite type magmatism associated with the Outokumpu stage of the ocean opening implied local high heat flows and thus likelihood of enhanced seawater circulation in the newly generated oceanic crust of the Kalevian break-up basin.

#### 7.4. Origin of the Outokumpu-type carbonate-skarn-quartz rocks

The ubiquitous occurrence of coarse-grained chromite, the total absence of detrital heavy minerals such as zircon, and lack of sedimentary interbeds in the Outokumpu carbonate and quartz rocks, and their mantle-like distributions of the more immobile elements (transition metals, HFSE, REE), are all evidence that leave little doubt about the origin of these rocks: they clearly represent metasomatic, carbonated and silicified mantle rocks. The serpentinite-carbonate-skarn-quartz rock sequence of the Outokumpu alteration, and the variation in the major element composition across the alteration sequence is similar with that of listwaenite-birbirite type low-T carbonate-silica alteration zones observed at the margins of many ultramafic bodies elsewhere (e.g. Leblanc and Billaud, 1982; Buisson and Leblanc, 1985, 1986; Stanger, 1985; Peabody and Einaudi, 1992; Auclair et al., 1993; Tüysüz and Erler, 1993; Zhou and Robinson, 1994; Sherlock and Logan, 1995; Uçurum and Larson, 1999; Uçurum, 2000).

It is often described that the rock succession in the Outokumpu assemblage is gradational from serpentinite to carbonate rock and then via skarn rocks to guartz rock (e.g. Gaal et al. 1975; Koistinen, 1981). This is basically true, but it is worth to note that the interfaces between the carbonate and quartz rock zones zones are usually relatively abrupt, and the zones rather monomineralic, especially if we discount the partly purely metamorphogenic skarn components. The distinctly zonal nature of the primary carbonate-silica alteration, especially apparent in Outokumpu, suggests it was related to diffusion across the ultramafic-metasediment boundaries, driven by the associated steep chemical potential gradient. As diffusion through solids is slow, an aqueous intragranular fluid must have assisted it. Presenting a physicochemical model for such a diffusive system is out of scope of this work. Numerical models of the carbonate silica alteration performed prior to the GEOMEX (e.g. Peabody and Einaudi, 1992), and by Peter Alt-Epping in CISRO for GEOMEX (Ord et al., 2003) suggest that the process probably occurred at subgreenschist facies temperatures and that the involved fluid was CO<sub>2</sub>-rich, H<sub>2</sub>O-CO<sub>2</sub>-H<sub>2</sub>S-CH<sub>4</sub> fluid of low-T metamorphic character. However, we shortly consider below the overall mass balance of the Outokumpu alteration, and the possibly involved metal losses-gains.

The most notable compositions features of the Outokumpu metasomatites are the over 90 vol.% silica content of many of the quartz rocks, and the 90 vol.% carbonate (dolomite) content of many of the carbonate rocks, which intuitively imply dramatic, and differing losses and gains in major elements was associated with the alteration, given that the protholith was depleted mantle peridotite. For example, to get at the high CaO and very low SiO<sub>2</sub> in the purest carbonate rocks, starting from peridotite, obviously requires addition of abundant Ca and removal of great amounts of Si. Similarly, to get at the very high SiO<sub>2</sub> of the quartz rocks, often

in the range of 90 to 98 wt.%, undeniably requires nearly total removal of the abundant Mg±Fe in the peridotite protolith.

Any accurate mass balance calculations of the alteration are difficult in this case, as we lack accurate knowledge of the starting as well as end member compositions, which both have been blurred by the metamorphic, and in the case of the serpentinites also by retrogressive alteration effects. Nevertheless we have performed some tentative calculations using the chemical compositions of average Outokumpu-Vuonos serpentinite (2600 kg/km3) as the representative of the starting material, and the average Outokumpu-Vuonos carbonate rock (2850 km/m3) and quartz rock (2680 kg/km3) and as the end products (the values in parentheses give the rock densities applied in the calculations, the compositions are from Table 4). We here assumed that a throughout low-T serpentinization of the protolith peridotite preceded the carbonate-silica alteration.

To provide a basis for mass balance considerations we first calculated the masses of elements in a unit volume (m3) of the assumed protolith and end products. In a purely constant volume case, silicification of peridotitic rocks have been observed to take place more or less isovolumetrically (e.g. Hanor and Duchac, 1990), the protholith-endproduct mass differences indicate that the alteration of serpentinite to guartz rock was associated with addition of 1502 kg (152 %) SiO2, and loss of 958 kg MgO (97 %) and 135 kg FeOt (78 %), per one  $m^3$  of rock. Considerable losses (35-80%) are apparent for Ti, AI, Mn, Ca and Ni, while V, Cu, Y, and REE were gained (35-270%). In a pure isovolumetric alteration, masses of any possible conservative elements per unit volume would not change. Elements that show relatively similar masses in the unit volume of serpentinite and quartz rock, with only 0-20% difference, include Cr, Co, Sc and Zr. Aluminium, which is often considered one of the most immobile elements, was here clearly mobile, as assuming a constant AI would imply unrealistically high volume increase for the alteration. Assuming constant Cr implies also volume increase, but only in the order of about 20%. It must be emphasized that constant Cr and 20% volume increase would not at all change the basic result of the isovolumetric calculation; the silicification process necessarily involved addition of large amounts of Si with concomitant loss of nearly all of the Mg and most Fe from the system. One interesting option would be constant Si, but this scenario seems unlikely in the light of the Cr concentrations in the guartz rocks, they should be significantly higher if both Si and Cr behaved conservatively, or alternatively, massive Cr loss had occurred, for which there is no evidence. We did not make any estimation of the oxygen balance; previously Sherlock and Logan (1995) have observed that carbonate-silica alteration is a dominantly cation exchange process with little net gain or loss in oxygen.

A comparable calculation for isovolumetric alteration of average Outokumpu carbonate rock from serpentinite indicates that the carbonation process was associated with addition of 691 kg (1094 %) CaO, and loss of 635 kg (64 %) SiO<sub>2</sub> and 443 kg (45 %) of MgO per one m<sup>3</sup> of rock. Considerable losses (25-50%) are apparent for Ti, Sc, Ni, Co and Cu, while Cr, Y, and REE were apparently gained (30-500%). Elements that show relatively little mass difference (<20%) between the endmember rocks include Zr, V, Fe and Al. Showing a possible constant element is difficult, so maybe there was none. Applying constant Cr would imply considerable volume decrease of ca. 25 %, while constant Al would imply ca. 20 % volume increase. Such volume changes would not much change the basic result from the isovolumetric calculation, but it is clear that the carbonate alteration was associated with relatively massive addition of Ca and loss of Si and somewhat surprisingly also significant loss of Mg.

Noting that the volume ratio of the carbonate and quartz rock in the Outokumpu assemblage is about 1:8, one can calculate that the development of the carbonate-silica alteration fringes involved a large net addition of Si and large net loss of Mg, and also that significant mass of Ca  $(+CO_2)$  was added. The sources and sinks of these elements are an important, but difficult question to be resolved. Auclair et al. (1993) have proposed, based on evidence from the Eastern Metals listwaenites-birbirites, in Quebec (Canada), that the silica needed for the birbirite alteration was released by concurrent conversion of the adjacent serpentinite to listwaenite and talc-carbonate rock. They explained the zonatinon by assuming alteration in a dynamic environment, where a vertically uplifting serpentinite body was along its faulted contacts first altered to talc-carbonate rock, then listwaenite and finally to birbirite.

However, this model is in conflict with the fact that the Eastern Metals birbirites frequently comprise pseudomorphic serpentinite textures, which they cannot have inherited from the completely nonpseudomorphic listwaenites and talc-carbonate schists. Hence, the birbirites must have been produced separately or before the carbonate-rich rocks.

In the case of Outokumpu, due to the regionally pervasive progressive metamorphic recrystallization and equilibration of the quartz rocks (section 9.3.6, chapter 10), the original processes and silica source are very difficult to constrain. Carbon and Sr isotope data for the carbonate rocks indicate that their C, Sr and Ca were ultimately of marine origin (sections 9.3.4., 9.3.7.). Possible models include addition of Ca+Sr+CO<sub>2</sub> from seawater circulated by subseafloor convection trough the alteration zones, or from trapped formation waters in the enclosing Kaleva metagreywackes, or perhaps by leaching of carbonates clasts from the Kaleva metasediments. One important question is also where did the relatively large masses of Mg that were lost from the system end up? One possibility is that the Mg sink was in the phlogopitized mica schists that are usual along the contacts with the quartz rocks.

Calculations of mass fluxes of the metals Cu, Zn, Co and Ni in the carbonation/silicification processes, so important as such data would be, are inherently difficult because of the postalteration synmetamorphic effects on the metal budgets. The evidently very low contents of Cu and Zn in the mantle peridotite protolith (section 6.3.1.) and the relatively minor total volume of the altered rocks imply, however, that e.g. the large mass of copper (>1Mt) in the Outokumpu and Vuonos ore bodies simply cannot be by the Outokumpu type carbonate-silica alteration. Nor is there any clear indication that the carbonate-silica alteration would have been associated with significant Cu addition. The average Cu content of the quartz rocks is a bit elevated (39 ppm) over that of the adjacent serpentinites (30 ppm) and primitive mantle (30 ppm), but the probable reason to this "enrichment" was most likely minor introduction of Cu associated with the overall synmetamorphic sulphidation of the Outokumpu assemblage, a phenomenon which was more pronounced at the ultramafic body margins than in their cores, and which seems to correlate positively with the metamorphic grade. The lower average Ni/Cr ratios of the quartz rocks (0.75) and carbonate rocks (0.36) compared to that of the serpentinites (0.94) suggests some minor loss of Ni especially from the carbonate rocks. However, the values of Ni/Cr ratios in the serpentinites and quartz rocks are still notably close to the Ni/Cr of primitive mantle (0.75). Further, Co/Cr ratios in the serpentinites (0.038) and guartz rocks (0.045) are mutually about similar, and close to the mantle value of Co/Cr (0.04), all this suggesting immobility for Co, whereas the relatively low Co/Cr of the carbonate rocks (0.02) may indicate some Co loss. The very similar Zn/Cr ratios in quartz (0.038) and carbonate rocks (0.036) and serpentinites (0.036) probably inherits from the fact that most Zn in all these rocks probably locates in relatively inert chromite. Based on the Zn/Cr ratios, all these rocks seem to be a bit enriched in Zn over mantle (Zn/Cr=0.021), again most probably reflecting the slight synmetamorphic sulphidation of especially the margins of the highest-grade metaperidotite massifs.

In a summary, there is little evidence in the whole rock compositions for that the Outokumpu type carbonate-silica alteration was associated with any major losses or gains of the ore-forming elements Cu and Zn. Those minor deviations from expected about mantle concentrations/element ratios that are apparent for Cu and Zn are most probably related to minor addition of these elements by the regional metamorphic sulphidation of the ultramafic body margins. Ni/Cr and Co/Cr ratios, and also mass balance calculations suggest that there was outflux of some Ni+Co associated with the alteration process. This Ni+Co obviously ended up to the local Ni+Co enriched Kokka type "Ni-mineralization" zones, which were not considered in the above mass balance calculations.

One important issue related to the Outokumpu assemblage as an ore-formation environment is the exact timing of the carbonate-silica alteration. The timing would be done most accurately by isotopic methods, but which are in this case difficult to apply, foremost because of the more or less complete destroyal/recrystallization of any primary alteration minerals. We will discuss the existing isotopic data with timing significance later on in section 9.3., but below very shortly on the possible geological timing constraints.

One important constraint is by the observation of Koistinen (1981) on that the carbonatequartz rock fringes around the Outokumpu and Vuonos serpentinite massif0s would register, D1 included, the complete Svecofennian sequence of deformations. Another important constraint provided by Koistinen (1981) is his deduction that the Outokumpu serpentinite massifs were tectonically detached (from oceanic lithosphere), dismembered and tectonically distributed among the metaturbidites of the Upper Kaleva already before the pre-D1 thrusting/obduction of the Outokumpu nappes. These constraints clearly time the carbonate alteration subsequent to the tectonic emplacement of the serpentinite bodies among the Kaleva turbidites but nevertheless to predate the earliest regional deformations. Very importantly, this means that the carbonate-silica alteration was not a seafloor process but must have occurred inside an already tectonically stacked turbidite pile, perhaps already in an early stage of the obduction of the Outokumpu Allochthon, but certainly before the regional D1. This inference is compatible with the observation that silicification of peridotites is not known from the present ocean floors. We will later in this report, in section 9.3.2., present Pb isotope data that supports the geological evidence of synobduction or immediately subsequent timing of the alteration.

# 8. Outokumpu-type sulphide deposits in North Karelia

# 8.1. Explanation of the terms "Outokumpu-type Cu-Zn-Co-N±Au deposit" and "Kokkatype Ni deposit"

Outokumpu type sulphide deposits are here defined based on their distinct metal portfolio and unique lithologic environment of occurrence. Accordingly, Outokumpu type deposits are Cu-Co-Zn-Ni±Au sulphide deposits in close association with thin carbonate-silica, or listwaenite-birbirite, alteration fringes of refractory ultramafic bodies. In medium and high-grade metamorphic environments the listwaenite-birbirite rocks occur converted into marble-like dolomite rocks, tremolite-diopside skarns and quartz rocks. The Outokumpu type deposits usually comprise thin, narrow and sharply bounded sheets, lenses or rods of massivesemimassive sulphide, typically closely spaced along the listwaenite-birbirite rock – black shale (schist) interfaces. Thin but longitudinally extensive zones of generally subeconomic, disseminated, stringer or vein type mineralizations relatively rich in Co+Ni±Au may parallel the main massive-semimassive sulphide sheets/lenses, being hosted in the listwaenite-birbirite or carbonate-skarn-quartz rocks.

In addition to the usual Cu-Co-Zn-Ni±Au, Outokumpu type deposits frequently contain also minor Sn, As and Se, while metals such as Bi, Sb and Pb are usually present only in very low quantities, even in the most metal-rich parts of the deposits. Ba and Mn are distinctly low elements both in the ores and in their host environments, which typically completely lack volcanic rocks or hydrothermal sediments.

In the Outokumpu area the listwaenite-birbirite derived skarn-quartz rocks host subeconomic Ni mineralizations, some of them next to massive-semimassive Cu-Co-Zn sulphide shoots, but many far from and apparently unrelated with any Cu-Co-Zn enrichments. These Ni mineralizations, known as Kokka-type Ni mineralizations (Huhma, 1975), are characterized by very low Cu and Co concentrations and mantle-like Co/Ni ratios. In association with the Cu-Co-Zn deposits, as e.g. in the Keretti and Vuonos Co-Ni deposits, the Ni mineralization seems relatively older and overprinted by the Cu-Co-Zn event (Parkkinen and Reino, 1985).

Fig. 44 lists and shows on a geologic map the Outokumpu-type Cu-Co-Zn deposits presently known in North Karelia, and also a couple of the more significant Kokka-type Ni mineralizations. Tonnages and grades for these deposits are given in Table 8. The below sections comprise brief descriptions of all these deposits.



Fig. 44. Map of the Outokumpu type sulphide deposits in North Karelia, showing also distribution of the serpentinite containing part of the Outokumpu Allochthon, assuming here that the various serpentinite containing areas (cf. Fig. 3) would all represent one contiguous thrust unit. Cu-Co-Zn-Ni±Au deposits (**O**): (1) Outokumpu, (2) Luikonlahti, (3) Vuonos, (4) Saramäki, (5) Kylylahti, (6) Perttilahti, (7) Riihilahti, (8) Hietajärvi, (9) Kettukumpu, (10) Hoikka, (11) Sola. Co-Ni and Ni deposits/prospects: (**D**)(12) Outokumpu, (13) Vuonos, (14) Kokka, (15) Poskijärvet, (16) Petäinen. UK=Upper Kaleva, LK=Lower Kaleva.

	Cu	Со	Zn	Ni	Au	Ag	Fe	S	Tonnes
	wt.%	wt.%	wt.%	wt.%	gr/ton	gr/ton	wt.%	wt.%	Mt
Cu-Co-Zn deposis	ts:								
Outokumpu	3,8	0,24	1,07	,12	0,8	8,9	28,11	25,3	28,5
Vuonos	2,45	0,15	1,6	,13	0,1	11,0	24,8	17,5	5,89
Perttilahti	2,15	0,16	1,89	,145	na	na	25,	18,9	1,32
Kylylahti	2,63	0,39	0,76	,13	0,9	na	na	20,6	1,95
Sola	2,	0,1	1,	,15	na	na	na	17,	0,1
Saramäki <sup>a</sup>	0,71	0,086	,63	,05	na	na	17,87	12,39	3,4
Luikonlahti	0,99	0,11	,5	,1	na	na	25,	16,5	7,5
Hoikka	0,5	0,04	<0.1	,15	na	na	20,	15,	0,2
Riihilahti	0,72	0,09	,09	,03	na	na	9,05	3,84	0,7
Hietajärvi	0,78	0,17	1,82	,2	na	na	34,	18,2	0,33
Kettukumpu	0,44	0,07	,1	,18	na	na	15,	13,5	0,4
Co-Ni & Ni deposit	ts:								
Keretti Co-Ni	0,35	0,16	,1	0,47	0,15	na	6,3	3,9	1,
Kylyl. skarn zone	0,61	0,18	,39	0,33	0,9	na	na	8,9	1,43
Vuonos Co-Ni <sup>b</sup>	0,07	0,05	,07	0,33	,04	0,3	6,3	4,	1,
Vuonos Ni <sup>c</sup>	0,04	0,03	,04	0,2	na	0,3	na	2,5	5,5
Kokka	na	na	na	0,31	na	na	na	na	1,9
Kokka-type Ni <sup>d</sup>	0,02	0,035	,03	0,79	<0.01	<1.3	8,5	7,9	na

Table 8. Grades and tonnes of Outokumpu-type Cu-Co-Zn, Co-Ni and Ni deposits in North Karelia.

Data from Parkkinen (1997), except for Kylylahti from Pekkarinen et al. (1998), for Vuonos Ni from Parkkinen and Reino (1985) and for Kokka-type Ni<sup>d</sup> mineralizations from this study.

<sup>a</sup> Parkkinen (1997) reports 0.5 wt.% Ni for Saramäki, based on a scrutiny of the primary assay data.

from Saramäki prospect, 0.05 wt.% is probably a more correct value.

<sup>b</sup> Estimate for the most metal-rich part of the Vuonos "Co-Ni-deposit".

<sup>c</sup> Average mill feed of Vuonos Ni mine in years 1972-1977, from Parkkinen and Reino (1985).

<sup>d</sup> Average of samples with >0.3 wt.% Ni (n=24) from Kokka-type Ni-mineralizations for this study.

### 8.2. Western limb of the Outokumpu structure and Riihilahti

The ca. 2 km wide and 50 km long horizon of serpentinites and black schists defining the western limb of the Outokumpu structure, and which is often called the Outokumpu belt, is the host of the two economically most important Outokumpu type Cu-deposits in North Karelia, the Outokumpu and Vuonos deposits (Figs. 44-45). In addition, the belt comprises, as an obvious continuation for the Outokumpu-Vuonos system, a minor, relatively deep locating Cu-mineralization at Perttilahti.

The Outokumpu and Vuonos deposits, their geology as well exploration and mining history has been described in many contributions (e.g. Saksela, 1948; Disler, 1953; Vähätalo, 1953; Mikkola and Väisänen, 1972; Gaál et al., 1975; Peltola, 1978; Koistinen, 1981; Treloar et al., 1981; Parkkinen and Reino, 1984; Stigzelius, 1987; Gaál and Parkkinen, 1993). We are not going to repeat this description here in any detail, but will give only brief summaries of the both deposits, with focus on those features that we find important for their genetical understanding.

The Riihilahti deposit, though economically just an obvious fly, is nevertheless an oregenetically interesting case as a rare example of an obvious Outokumpu type deposit (by metal content) without no serpentinites in its immediate host environment. It should be noted, for clarity, that the Riihilahti deposit does not actually locate within the Outokumpu structure, but in the SW corner of the apparently underlying, presently unnamed thrust unit.

# 8.2.1. Outokumpu

### Location, exploration history and resource character

An unfortunate, confusing element in the literature of the recent years has been the practice to call the original Outokumpu deposit as Keretti deposit, and the Keretti and Vuonos deposits together as Outokumpu deposit. This reflects the recent ideas for that these two deposits originally formed one single, more or less contiguous deposit (cf. e.g. Mäkelä, 1997) but as they are in the present erosional surface separated by ca. 5 km of unmineralized rock, and to avoid confusion, we will below call the Outokumpu as Outokumpu and Vuonos as Vuonos.

The Outokumpu deposit is located for its most part within (below) the present Outokumpu town about in the centre the GEOMEX study area. Outokumpu was probably the first ever discovered clear Outokumpu type deposit, and probably still the largest one in its class (at least in terms of metal content). The first indication of the deposit came by discovery in the year 1908 of a several cubic metres size ice-borne Cu-sulphide ore boulder, in association with dredging of the Kivisalmi channel at Rääkkylä, ca. 50 km to the SE of Outokumpu. Subsequent exploration by Geological Commission of Finland, lead by Otto Trüstedt, resulted in the discovery of the Outokumpu ore, in the year 1910, as a result of a process that involved geological deduction to determine the probable provenance area of the float (Outokumpu was pointed out as one possible source by W.W.Wilkman and Benjamin Frosterus), detailed boulder tracking in the presumed provenance area, and in the end shallow diamond drilling (for a description of the exploration history see e.g. Stigzelius, 1987).

The Outokumpu ore comprised ca. 28.5 Mt of mineable ore that contained in average 3.8 wt.% Cu, 0.24 wt.% Co, 0.12 wt.% Ni, 1.1 wt.% Zn, 8.9 gr/ton Ag, 0.8 gr/ton Au and 25.3 wt.% S (Parkkinen, 1997). Metals in minor to trace concentrations included 0.015 wt.% Sn, 0.015 wt.% V<sub>2</sub>O<sub>5</sub>, 0.036-0.064 wt.% Mn, 0.005 wt.% Pb, 25-50 ppm Se, 45-75 ppm Mo, and 5-10 ppm Hg (Mikkola and Väisänen, 1972; Peltola, 1978; Papunen, 1987). The total copper metal content of the ore was a hefty 1 Mt. The mining of the Outokumpu deposit started 1913 and was continuing until 1989.

## Geological setting

As mentioned above, the Outokumpu deposit locates within the NE trending ca. 2 km wide horizon of black schists and serpentinite bodies that is defining the western margin of the Outokumpu structure (Fig. 44-45), and which is commonly called the "Outokumpu belt" ("Outokumpu jakso" in Finnish). The deposit is found in association with a long (>10 km), tubular (<1,2X<1.5 km in cross-sections) body consisting of tightly folded serpentinite, located along its NW margin in a few metres to tens of metres layer of carbonate-skarn-quartz rocks that are enveloping and being folded with the serpentinite (Fig. 45). Unfolded the serpentinite tube is found to consist a ca. 150-200 m thick, possibly 5 km wide and >10 km long sheet, the thickness and width estimated for the thickest part of the tube (Koistinen, 1981). The carbonate-skarn-quartz enveloped, folded serpentinite tube is enclosed in the Upper Kaleva metagreywackes, with usually a few metres to a couple of tens of metres thick layer of black schist in between.

The Outokumpu serpentinite massif comprises very few other components but serpentinite. Pervasively chloritized and metamorphosed obvious mafic dykes occur locally, but they are nowhere abundant, comprising far less than 5 % of the total volume of the massif. The serpentinites are in fact retrogressively serpentinitized (lizardite-chrysotile) metaperidotites, usually talc-olivine rocks in the middle part, and anthophyllite-enstatite-olivine to sagvanditic olivine-enstatite-carbonate rocks (Fig. 46) at the margins of the massif (Säntti et al., in press). The mineral assemblages of the metaperidotites and olivine-spinel thermometry indicate peak metamorphism in temperatures above 630 °C (Säntti et al., in press). Thermobarometry for garnet-cordierite-orthoambhibole rocks has yielded similar peak temperatures at ca. 3-4 kb pressures (Treloar et al., 1981).

The NW edge of serpentinite tube shows several shallowly to SW plunging and 20-50° SE dipping isoclinal folds, which are designated as F1 by Gaál et al. (1975) and Koistinen (1981), and what structure is somewhat imbricated by a couple of F1 axial-plane subparallel faults. The Outokumpu ore plate (below) is enclosed apparently for its entire length inside one of the F1 folds. In vertical cross-sections about perpendicular to the F1 axis (Figs. 47-50), the ore plate is seen to broadly follow the upper limb of the host fold, defined by the contact between serpentinite and fringing carbonate-skarn-quartz rocks. In a detailed investigation of the cross-profiles it is seen that, in many of them, the ore sheet actually truncates the serpentinite carbonate-skarn-quartz sequence (cf. Figs. 48-50), implying that the final emplacement of the ore has to post-date the carbonate-silica alteration of the serpentinite body margins.

The Outokumpu and Vuonos ores are often said to be hosted by the quartz rocks or quartzites (e.g. Koistinen, 1981; Papunen, 1987) in the Outokumpu assemblage. In the light of the mine cross-sections as in Figs. 48-50 from Outokumpu and in Figs. 58-59 from Vuonos, this is, however, a quite generalized and partly miss-leading statement. First, though it is true that the footwall of the Outokumpu ore plate is generally against quartz rocks, at the hanging wall it is for its large parts in direct contact to serpentinite and skarn-carbonate rock. In addition, parts of the lower edge of the ore plate are frequently found partly or completely enclosed in serpentinite (Figs. 48-50) and a narrow strip of its NE upper edge locally in mica and black schists (cf. Fig. 35 in Gaál et al., 1975). Second, though it is often so postulated (e.g. Peltola, 1978), the ore is in fact nowhere interbedded with the wall rock "quartzite", as already Mäkinen (1921) pointed out. Instead the contacts of the ore with the quartz rocks, as well as the other wall-rocks, are frequently very sharp, intrusive-like (Fig. 52), including that the ore material often brecciates the strongly shear-banded wall-rock quartzites (Fig. 51c; 52a-b; see also Vähätalo, 1954; Disler, 1954). Locally <1 cm to several dm thick ore veins in the wall quartz rocks cause layering-like features that often have been confused to primary bedding.



Fig. 45. Geological map of the "Outokumpu belt" and related main massive-semimassive sulphide deposits. The main map shows the surface projections of the known ore bodies. The longitudinal projections of the ore bodies are given in the lowermost diagram. The two other diagrams provide cross-sections over the thickest parts of the Outokumpu and Vuonos serpentinites, cross-section profiles of the Perttilahti end of the belt are given in Figs. 62-66. Data sources: Disler (1953); Huhma (1971); Gaál et al. (1975); Kauppinen (1978); Koistinen (1981) and for the Perttilahti deposit unpublished drill-core reports of the Outokumpu Company.



Fig. 46. Photograph of the main types of serpentinitized metaperidotite in the Outokumpu peridotite massif. From left to right: Talc-olivine; antophyllite-talc-olivine; antophyllite-olivine; anthophyllite-enstatite-olivine and anthophyllite-tremolite-enstatite-olivine metaperidotites. Olivine is in all the samples serpentinized extensively to chrysotile-lizardite. The rock types on the left side of the photo characterize the core, and the rock types on the right side of the photo the marginal parts of the massif. The mineralogical zoning reflects core-margin gradient in  $XCO_2$  of the peakmetamorphic fluid phase, due to  $CO_2$  infiltration. The  $CO_2$  was produced by decarbonation reactions in the carbonate-silica fringes of the serpentinite bodies. Note that chrysotile-lizardite is green in the serpentinite body cores, but stained dark black by magnetite dust at the body margins.



Fig. 47. Surface projections of the Keretti and Vuonos ore bodies according to Figures 12 and 13 in Koistinen (1981), cf. for Figure 41. Location of the cross-section profiles of the Keretti and Vuonos deposits in Figs. 48-50, 56 and 58-59 are shown.



Fig. 48. Cross-section profile 53 of the Outokumpu main ore body. For location of the profile see Fig. 47. Note the location of the ore body nearly entirely inside of serpentinized peridotite and its carbonate-skarn-quartz rock derivatives. Importantly, no sediments (exhalative or no other) are present among the carbonate-skarn-quartz rocks but these rocks represent thorough carbonate-silica altered peridotite. The diagram is compiled on the basis of drill core review of the first author and Urpo Kuronen, and drill hole reports of the Outokumpu Company.


Fig. 49. Cross-section profiles 47+20, 65, 71, and 81 of the Outokumpu main ore body. Rock colours as in Fig. 48, for location of the profiles see Fig. 47. Note the location of the ore entirely within the nonsedimentary, mantle derived serpentinites or carbonate-skarn-quartz rocks, and that the ore sheet also cuts through the serpentinite-carbonate-skarn-quartz rock alteration zonation. After cross-section profiles of the Outokumpu Company.



Fig. 50. Cross-section profile 68+20 of the Outokumpu main ore body, showing the Poikanen ("baby ore") "satellite" ore body below the NW edge of the main ore. Rock colours as in Fig. 48, for Location of the profile see Fig. 47. Also in this section the ore locates 100% inside of the peridotite regime and quartz rocks, which both below and above the ore are practically clean of Cu, often already <1 metres out of the ore contacts. After a cross-section map of the Outokumpu Company.

#### The main massive-semimassive ore

The main Outokumpu ore consists of a ca. 4 km long, >50-350 m wide and in average ca. 10 m thick ruler-shape sheet of semimassive-massive sulphide (Figs. 45,47), divided in two about equal-size subplates, which according Vähätalo (1954) showed an "en echelon inclined position" to each other. The ore had two surface exposures for its NE end, two, because the NE tip of the ore was found down-faulted by ca. 100 m (Fig. 45). Vähätalo (1954) called the two main subplates of the Outokumpu ore as the Lietukka and Kumpu ore bodies, and the down faulted NE tip of the latter as the Kaasila ore body.

Various classifications for the main ore types in the Outokumpu massive-semimassive ore have been proposed (e.g. Vähätalo, 1953; Disler, 1953; Gaál et al., 1975; Koistinen, 1981). Gaál et al. (1975) distinguished three principal structural types: (1) layered ore; (2) massive ore and 3) brecciated ore. Koistinen (1981) divided the ore in pyritic (mostly layered), and pyrrhotitic (mostly massive) types, considering the former a more primary and the latter a more recrystallized and remobilized facies. From the main ore types, the layered facies (Fig. 51a-b), especially the layered pyritic ore (cf. Fig. 4 in Papunen, 1987), has generally been considered as the most primary ore type, and the millimetre to metre scale compositional layering in it to represent modified sedimentary bedding (e.g. Peltola, 1978; Koistinen, 1981; Papunen, 1987). The breccia ore comprised the layered ore and wall quartz rocks as angular fragments up to 1-3 metre size in a matrix of massive ore (cf. Fig. 51c, 52a-b).

The total sulphide content in the pyritic ore parts was mostly below 50 vol.%. Parts of the pyritic ore were composed of massive, relatively fine-grained pyrite, but usually it showed, reminiscent of the Kylylahti ore (below), a banded to blebby structure (Figs. 53-54). Pyrite in all these variants occurred as mostly idiomorphic grains from a few millimetres down to 0.01 mm in size. Pyrrhotite, chalcopyrite and sphalerite were found unevenly distributed as plentiful fine-grained inclusions, interstitial to, in fractures or domains replacing the pyrite. The pyrrhotitic ore parts locally showed distinct quartz to sulphide banding similar to that of layered pyritic ore but were generally of more massive character (Fig. 51d). Compared to the pyrite ore type, the pyrrhotitic ore was on average richer in total sulphides and contained often more than 50 vol.% sulphides, usually complexly intergrown with granoblastic-graphic gangue quartz (Fig. 55). In the most pyrrhotite-rich ore parts there often occurred large idiomorphic pyrite cubes, often distinctly rich and zoned for cobalt. Various sulphide remobilization features were common inside of both the pyrite and pyrrhotite ore facies, and locally the ore materials showed also some tendency to late mobilization into fractures and associated limited replacement of the wall rocks (see Mikkola and Väisänen. 1972; Fig. 19 in Koistinen, 1981).

The pyrite and pyrrhotite ore types comprised about the same assortment of main sulphide minerals but in different ratios of abundance. The main sulphides included pyrite, pyrrhotite, chalcopyrite (locally with cubanite lamellae) and sphalerite. Cobaltian pentlandite, stannite and mackinawite were commonly present in minor to trace quantities. Minor magnetite occurred locally, especially in the layered pyrrhotite ore parts. Chalcopyrite, sphalerite, galena were found together with pyrrhotite highly concentrated in the late remobilizates in ore fractures. Altogether more than 40 sulphide species have been identified from the Outokumpu ore, but most of them only in trace abundances.

The dominant gangue mineral in the Outokumpu ore is quartz, to an extent that none of the tens of Outokumpu ore samples collected and examined during this study were even near to be quartz-free. The Outokumpu ore (Keretti) had an average SiO<sub>2</sub> content of 45 wt.% with >90 vol.% of the silica contained in quartz (Peltola, 1978). These values mean that the Outokumpu ore contains in average a bit more quartz (volumetrically) than sulphides. Importantly, Cr content in the ore proper, the very margins excluded, was very low (usually <<50 ppm) and chromite±eskolaite, ubiquitous minerals in the wall-rock serpentinites and carbonate-skarn-quartz rocks, were found in significant amounts only at the margins of the ore, with a higher probability in those parts of the ore where carbonate-skarn-quartz occurred as wall rocks. The



Fig. 51. Examples of structures typical of the Outokumpu (Keretti) ore body. (A) Sulphide bands in quartz rock at the ore contact. (B) Dominantly pyrrhotitic banded ore; though widely interpreted as sedimentary, the ore banding more likely is of tectonic origin as the ubiquitous shear bending in the host quartz rocks (cf. Fig. 33), which as silicified peridotites cannot have sedimentary layering. (C) Angular fragment of schistose-banded quartz rock floting in massive chalcopyrite-rich ore. (D) Massive, dominantly pyrrhotite ore. Photos from collections of Outokumpu Company, taken probably by Esko Peltola.



Fig. 52. Photographs of Contacts typical of the Outokumpu (Keretti) ore body. (A) Massive pyrrhotitepyrite ore with foliated quartzite fragment showing knife-sharp contact against foliated/shear-banded quartz rock. (B) Pyrrhotite ore full with fragments of folded/foliated quartz rock and in a sharp contact against dark, graphitic, shear-banded quartz-rock, a decimeter thick layer of reaction skarn along the contact. (C) Knife-sharp contact of massive pyrrhotite ore and diopside-tremolite schist (skarn). (D) Knife-sharp contact between pyrrhotite ore and serpentinitized metaperidotite, brittle fractures in ore filled by retrograde serpentine. The photos are from collections of Outokumpu Company, taken probably by Esko Peltola.



Fig. 53. Scanned image of a sample of blebby-banded pyritic ore typical in the middle parts of the Outokumpu main ore, Mökkivaara, Outokumpu. Width of the slab is ca. 11 cm.



Fig. 54. Scanned images of blebby pyritic ore from Outokumpu (left, Mökkivaara) and Kylylahti (right, Oku-870B/262.60). Note the coarse grain size of the gangue quartz and replacement of the finegrained pyrite blebs in the both cases by pyrrhotite and chalcopyrite. Width of the samples: left 45 mm, right 30 mm. quartz in the Outokumpu ore is on average significantly coarser in its grain size (typically 0.1-0.5 mm and up to several mm) than quartz in the wall-quartz rocks (typically <0.01-0.1 mm).

In the chalcopyrite-pyrrhotite rich more massive ore parts, considered recrystallized / remobilized variant from the more primary pyritic ore type, the quartz typically occurs in granoblastic-graphic intergrowths with the sulphides (Fig. 55). In the most sulphide rich parts of the pyrrhotite ore facies, the gangue quartz is often segregated and redistributed in 1-10 mm size, internally granoblastic, roundish balls dispersed randomly in the massive sulphide. In places the pyritic ore has a tendency to contain quartz-rich blotches and irregular quartz-rich discontinuos bands/veins/lenses in which the quartz is typically milky and often distinctly coarse-grained with grain sizes exceeding 10 mm. In many parts the ore showed distinct, 0.5 to 5 m thick relatively sulphide-poor selvages comprising mainly coarse-grained quartz; these are in Outokumpu drill core logs and mine maps reported to "disseminated ore". Based on our drill core observations the quartz-rich selvages frequently show knife-sharp contacts against the wall rocks, independent of their type.



Fig. 55. Scanned image of a thin section showing granoblastic-graphic sulphide-quartz intergrowth texture typical of the pervasively metamorphically recrystallized parts in the Outokumpu ore, sample K947/88.08. The sulphides comprise mainly chalcopyrite (light dull green) plus little sphalerite (black) and pyrrhotite (dark dull green). Width of the view ca. 30 mm.

# The parallel Co-Ni zone

A parallel zone of scattered Cu-Co-Ni mineralizations is present above the main Outokumpu ore (Fig. 56), probably for most of its length, but which is in terms of metal tenors

best developed, and hence also best studied/known for its SW end. This zone is informally known as the "Co-Ni zone" or "Ni parallel". The lower edge of the Co-Ni zone mineralization is typically some 150 to 200 m above and a bit to the NW of the upper edge of the main Cu-ore, and appears to be nowhere in a direct connection to it. As said above, the Co-Ni zone is metal-richest and most coherently mineralized for the ca. 600 m in its SW end.

The Co-Ni zone has some aspects that are distinct to the main ore environment. One is the frequent occurrence variably cummingtonite, anthophyllite, cordierite (usually extensively pinitized), staurolite, garnet, phlogopite and spinel bearing chlorite-rich rocks/schists, hosted as thin layers (usually < 1m) or patches in skarn(diopside-tremolite)-quartz rocks forming the bulk of the Co-Ni zone (Treloar et al., 1981; Parkkinen and Reino, 1985). Another distinct feature is the abundance of often very coarse-grained, usually highly zincian chromite in almost all the rock types in the zone (Treloar, 1987). And a third one is the relative cobalt-nickel (Copentlandite) richness of the included sulphide mineralization.

Economically interesting sulphide concentrations are restricted in the SW end of the Co-Nizone wherefrom a tattered sulphide mass of ca. 1 Mt at 0.35 % Cu, 0.16 % Co, 0.47 % Ni, 0.15 % Au and 3.9 % S has been invented (Parkkinen, 1997). In cross-sections this mineralization is found to constrain a few metres up to 25 m thick horizon, analogous in its shape and dimensions to the main ore plate, and also for its location in the hinge area of a tight F1 fold filled by quartz rocks grading via skarn-dolomite rocks to serpentinite at limbs (Fig. 56). The original maximum width (height) of the mineralized zone is not known because its upper edge is generally cut by the present erosion surface. The downward extent of the Co-Ni horizon is typically about 100 m. Notably, the carbonate-skarn-quartz rocks away from the Co-Nimineralised zone are distinctly barren of Cu-Co mineralization, excluding thus a "strata-bound" nature of the mineralization.

The names "Co-Ni zone" or "nickel parallel" are a bit misleading since the metal portfolio, texture or mode of occurrence of the economically interesting sulphides in the Co-Ni zone actually does not markedly differ from that in the main ore. We see this in that the economically interesting amounts of sulphides are frequently related to thin <1-20cm iron sulphide-chalcopyrite-pentlandite-quartz veins (Fig. 57) that are texturally and mineralogically very similar to the leaner variants of pyrrhotitic ore in the main ore. Many of these veins are particularly rich in pentlandite, presumably cobalt pentlandite, but significantly, similarly cobalt-nickel enriched pyrrhotitic portions are present at the lower edge of the main ore sheet, too. Moreover, the high proportion of the Ni-bearing skarn-rock gangue in the Co-Ni "ore bodies" explains part of the high Ni. Further, the sulphide-quartz veins, exclusively holding the Cu in the Co-Ni zone mineralizations, cut very sharply bound through the quartz rocks, tremolite and diopside skarns and also the anthophyllite and/or chlorite rich schists characteristic of the Co-Ni zone (Fig. 57), attesting to their very late structurally controlled final emplacement (similar to the main ore). The tremolite and diopside skarns being peak-metamorphic rocks there is little doubt of the late emplacement of the sulphide-quartz veins.

#### Ore genetically noteworthy aspects

Highly conflicting interpretations concerning the contact relationships of the Outokumpu ore have been proposed since the discovery of the ore. The early workers, as e.g. Mäkinen (1921) and Vähätalo (1954) were confident of that the ore was epigenetic, i.e. had formed later than its wall rocks. Since the notes of Borchert from the year 1954, most researchers have regarded the ore synsedimentary with their host "quartzites or cherts", however.

Our review of tens of representative drill cores over the contacts of the Outokumpu ore,



Fig. 56. Cross-section profile 83 of the SW end of the Outokumpu deposit. For location of the profile see Fig. 47.The location of the low-grade "Co-Ni zone", which is thought in some views to represent a submarine hydrothermal upflow zone once below the massive-semimassive sulphide body, is shown by oblique hatching. Note that both the main massive-semimassive ore body and the "Co-Ni zone" are located inside of altered peridotites, and that no metasediments (exhalative or other) are present among the ore-hosting rocks. The diagram is based on cross-section maps and drill hole reports of the Outokumpu Company.



Fig. 57. Scanned images of samples of schistosity-parallel sulphide-quartz bands characteristic of the parallel "Co-Ni zone" of the Outokumpu deposit. (A) Sharply-bound, 12 mm thick chalcopyrite-pyrrhotite-quartz band (vein) in coarse-grained quartz rock, Oku-832/80.82. (B) Chalcopyrite-pyrrhotite-quartz bands in quartz rock, Oku-832/84.10. (C) Very sharp boundary of a chalcopyrite-rich sulphide-quartz band in strongly lineated-schistose quartz rock with cataclastic chromite in thin shear stripes (black), Oku-835/68.40. (D) Sharp boundary of a chalcopyrite-pyrrhotite-quartz band in cordierite-anthophyllite schist (note a seam of massive pentlandite-pyrrhotite between the sulphide-quartz band and the cordierite-anthophyllite schist), Oku-835/72.50. Widths of the half-split drill-core samples are for all ca. 30 mm.

over its entire length and width indicated that it mostly has very abrupt and sharp contacts, irrespective of the wall rock type. Importantly, the review revealed no contact features that would unquestionably suggest syngenetic, sedimentary relationship of the ore sulphides and any of the wall rocks. This should be no surprise noting the occurrence of the ore for its most part inside carbonated and silicified peridotites (Auclair, 1993; Kontinen, 1998; cf. cross-section profiles in section 8.2.1). The unrelated nature of the ore and the quartz rocks, the dominant wall rock, is emphazised by the fact that the latter are, the very contacts of the ore sheet excluded, all over the ore environment remarkably low in all the principal ore metals except in Ni. Even in the Co-Ni stringer zone Cu and Co sulphides are confined to discrete sulphide-quartz veins, while the intervening carbonate-skarn-quartz rock domains are usually nearly barren of the pay metals.

The quartz-sulphide and sulphide mineral ratio banding in the layered ore facies and the similar looking calc silicate to quartz banding in the wall quartz rocks have usually been interpreted as bedding features (e.g. Peltola, 1978; Koistinen, 1981; Treloar, 1987). However, considering the origin of the quartz rocks as silicified peridotites, it is clear that at least their banding must be of nonsedimentary and largely metamorphic segregation/tectonic flow origin. We believe this most probably would be the case also for the banding in the layered ore type. We recall here Gaál et al. (1975), who after proposing that the ore layering would represent stratification plus strong S1, however, recalled that the evidence is that indecisive that as well the ore layering could represent purely metamorphic segregation parallel to S1.

Koistinen (1981) has proposed D1 isoclinal folding of the ore as a synsedimentary

interlayer together with its host carbonate-skarn-quartz rocks. Strangely, however, isoclinal fold forms are not seen in the shape of the ore plate, despite that such folds are in metres to tens of metres scale very common in all of its host rocks including the carbonate-skarn-quartz rocks (cf. Figs. 48-50). In many profiles the ore plate actually seems to inject into and truncate the tight isoclinal F1 fold patterns revealed by the metasomatic alteration zoning in the host assemblage. As we pointed above, truncation of the metasomatic zoning is most clear at the hanging wall contact of the ore. Recognising that the ore is >90 % inside of the altered peridotite without any associated syngenetic sedimentary components, it is most clear that to *its present position* the Outokumpu ore is most clearly a truly epigenetic, vein-like formation. In this respect we fully agree with Mäkinen (1921>), who stated: *"Att malmen är epigenetisk, d. ä. en senare bilding än kvartsiten, kan intet tvivel råda"*.

The cornerstones of previous seafloor exhalative models for Outokumpu ore have been interpreting the quartz rocks as chemical-exhalative metasediments on the seafloor and the parallel Co-Ni zone as an underlying fluid up-flow channel. The amount of volcanic or intrusive rocks in the Outokumpu-Vuonos complex is negligible; therefore simple in situ volcanic associated models are more or less irrelevant. Park (1988; 1992), apparently recognizing this, proposed that the serpentinites in the Outokumpu assemblage represented komatiitic sill that provided the thermal energy to run a convective hydrothermal system within the sill itself and the overlying metasediments to produce the associated ores. It is highly questionable, however, that the very depleted harzburgitic-dunitic serpentinites would represent magma of any type; instead there is strong chemical and mineralogical evidence to support their origin as tectonitic mantle peridotites (section 7.1.). Furthermore, a 200m thick komatiite sill hardly provides heat energy and metals enough to generate a 1 Mt hydrothermal Cu deposit. The thin deposit parallel nature of the stringer zone is another puzzle for seafloor venting models; at least the Co-Ni zone is nothing comparable to the extensive, kilometres deep funnel-shape alteration zones occurring below the demonstrably seafloor hydrothermal Cyprus deposits, for example.

# 8.2.2. Vuonos

## Location, resource character and exploration history

The Vuonos deposit, which locates ca. 6 km to the NNE from Outokumpu (Fig. 44), was found in the year 1965 by following the Outokumpu type rock assemblage from Outokumpu to NE, and utilizing trends in its Co/Ni ratio for targeting the exploration drilling. The deposits was mined in the years 1972-1986. The massive-semimassive main ore has no surface exposure, and it is often claimed to be one of the very few "blind ores" that in Finland ever have been located. Whether the Vuonos ore represents a truly blind deposit, or not, is a somewhat debatable issue, however. Namely, the massive-semimassive ore has a low-grade disseminated extension (part of the "Co-Ni zone" of Vuonos) in the SW part of the deposit and that is known to crop out below the glacial drift (Kauppinen, 1978).

The total reserve of the Vuonos main ore was estimated to 5.89 Mt at 2.45 wt.% Cu, 1.6 wt.% Zn, 0.15 wt.% Co, 0.13 wt.% Ni, 11 ppm Ag, 0.1 ppm Au, 17.5 wt.% S and 24.8 wt.% Fe (Parkkinen, 1997). The realized mil feed in the period 1972-1986 was 5.5 Mt of ore containing on average 2.13 wt.% Cu, 1.32 wt.% Zn, 0.14 wt.% Co, 0.12 wt.% Ni, 14.76 wt.% S, 10 ppm Ag and 12 ppm Se (Jouni Reino, pers. comm., 2005). In addition, in the years 1972-1977, 5.5 million ton of low-grade Ni-Cu-Co-bearing rock was mined, largely from an open pit (5 Mt ton) above the southwest central part of the main massive-semimassive ore. Mill feed of the Nibearing rock contained on average 0.04 wt.% Cu, 0.04 wt.% Zn, 0.03 wt.% Co, 0.2 wt.% Ni, 2.5 wt.% S, 0.3 ppm Ag and 3 ppm Se (Parkkinen and Reino, 1985). The mined Ni deposit contained a ca. 1 Mt portion of slightly more metal-rich rock at 0.07 wt.% Cu, 0.07 wt.% Zn, 0.05 wt.% Co, 0.33 wt.% Ni, 0.3 ppm Ag, 0.04 ppm Au, 4 wt.% S and 6.3 wt.% Fe (Parkkinen and Reino, 1985; Parkkinen, 1997).

Only a few drill cores from the Vuonos deposit were reviewed during this study, thus the following description of it is based mainly on descriptions what are available in published papers (Kauppinen, 1978; Koistinen, 1981; Parkkinen and Reino, 1985). Unfortunately no study

devoted to document the Vuonos deposit in detail was realized when the mine still was open and active. Now any comprehensive study would be difficult since the mine is water-filled, and because very scantily the drill core left from some critical parts of the deposit, as e.g. for the Co-Ni-parallel; those core have been completely utilized in past ore feasibility studies, or have been dumped.

#### Geological setting

The geological setting of the Vuonos ore is to a large degree identical with that of the above-described Outokumpu deposit (Fig. 45). The most significant difference is the somewhat lower degree of peak metamorphism, which is best seen in that anthophyllite and enstatitebearing metaperidotites, as in Outokumpu, lack in Vuonos where the serpentinites are derived dominantly from olivine+talc metaperidotites. Further, our observations suggest that there may be somewhat more mafic dykes within the Vuonos than in Outokumpu serpentinites, but probably no more than 5-10 % of the total volume. Also black schists, that are distinctly scanty in the immediate vicinity of the Outokumpu ore, are perhaps a bit more voluminously represented along the contacts of the Vuonos ore sheet. But even at Vuonos the ore-associated layers of black schists are thin and discontinuous compared to the thick layers outside of the immediate ore environment.

#### Main massive- semimassive ore

The Vuonos main ore has the same ruler-shaped general form as the Outokumpu main ore, though with considerably smaller dimensions. The ore body is >3800m long, 50-200 m wide and on average ca. 5 m thick (Figs. 45, 47). The lengthwise broadly taken nearly horizontal ore sheet located for its most part 130-150 m below the surface, with the exception of that the SW tip of the sheet was up-faulted ca. 50 m. In perpendicular cross-sections the ore plate had a dip of 5-20° to the SE, showing a straight plate-like (in SW part of ore) to slightly upwards-concave cross-section shapes (in NE part of ore).

The structural position of the Vuonos ore was very similar to that of the Keretti ore. Accordingly, the ore layer located in the core of one of the many 50-200 m scale tight to isoclinal, 50 degrees to SE (for axial plane) dipping folds along the NW margin of the Vuonos serpentinite massif. In a significant difference to Outokumpu, in some cross-sections of the ore a considerable part, 30-60 %, of its upper edge is found inside the Upper Kaleva mica schist - black schist environment, while the lower edge is similar to Outokumpu inside the serpentinite-fringing quartz rocks (Figs. 58-59). In the same way as in Outokumpu, the ore also in Vuonos had very sharp, intrusive-like contacts against its wall rocks, irrespective of the structural position, or whether the wall rocks were metasedimentary Kalevian mica or black schists or metasomatic carbonate-skarn-quartz rocks of the Outokumpu alteration assemblage.

Koistinen (1981) presented evidence of sedimentary interbedding and D1 isoclinal folding of the ore materials with the black schists and mica schists (metagreywackes) at the very upper/NW edge of the Vuonos ore sheet. However, our own observations to drill core from this environment brought out no evidence that would suggest the ore would really be *syngenetic and* 



Fig. 58. Cross-section profile 192.850 of the SW end of the Vuonos deposit. For location of the profile see Fig. 47. Note that the thicker lower edge of the ore is enclosed in the altered ultramafic rocks of the Outokumpu assemblage, whereas its thin upper egde is wedging inside Kalevian mica schists±black schists. The diagram is based an a cross-section drawing of the Outokumpu Company.



Fig. 59. Cross-section profile 194.150 of the Vuonos deposit. For location of the profile see Fig. 47. This is one of the Vuonos sections in which the upper edge of the ore is postulated to retain primary sedimentary bedding deformed into isoclinal F1 folds (Koistinen, 1981). Note, however, that Pb isotope data precludes syngenesis of the ore sulphides with the mica-black schists and that the carboanate-skarn-quartz rocks do not represent sediments (cherts or other) but carboanate.silica altered mantle peridotite. The profile is compiled based on cross-section drawings of Outokumpu Company, Fig. 14 in Koistinen (1981), and a review of some of the included drill holes by the present authors.

*interbedded* with the sedimentary wall rocks. Though apparently alternating layers of ore and metasediments are visible, the contacts the ore layers and black/mica schist layers appeared frequently "knife sharp", and based on thin section observations, even the thinnest ore "layers" wedging in the metasediments nearly free of micas, and based on chemical analyses also of the lithophile elements like zirconium, thorium, potassium, sodium etc., which in contrary are abundant in the enclosing black and mica schists. Therefore we are inclined to believe that the interfingering of the ore and metasediments even in the upper edge environment would be of purely nonsedimentary, injective or lode-fill nature.

Peltola (1980) distinguished two main structural types in the Vuonos deposit: layered and massive ore. The layered type was dominating in the upper edge and middle parts of the ore, while the lower edge comprised mainly the massive type, especially in those parts enclosed in serpentinite. In addition, as in Outokumpu, parts of the ore showed breccia fragments of the layered ore in matrix of massive ore. The lower edge of the Vuonos ore sheet had in several of the mid-ore cross-sections a pipe-bowl-like bulge of mainly relatively coarse-grained pyrrhotitic ore. According Koistinen (1981) the bulges at the lower edge of the ore were formed by a late-D1 mobilization process. The bulges were economically important as they contained, if not by their metal tenors, but from the point of view of mining and processing some of the best parts of the deposit.

The main ore minerals in Vuonos ore (in average) were 40 % pyrrhotite (mostly nonmagnetic hexagonal), 7 % chalcopyrite (+-cubanite), 2.75 % sphalerite and 0.3 % cobaltian pentlandite (Peltola, 1980; Parkkinen and Reino, 1985). In addition, minor pyrite, stannite, cobaltite and mackinawite were present. Most of the Vuonos ore was pyrrhotitic and pyrite was met in significant quantities only as scattered coarse porpyroblasts in pyrrhotitic ore, relatively more common in the thicker middle parts of the ore. The Cu-Zn richest parts of the ore were within its upper edge inside the country metasediments, while Co and Ni tenors were highest in the bulges at the lower/SE edge and in parts inside "quartzites" close to serpentinite. In a broad view, Cu showed increase towards the NE upper edge corner and cobalt towards the SE lower edge corner of the ore plate, and zinc some distinct enrichment for both the very upper and lower edges.

The massive and banded ore both contained on average of about 50 vol.% of quartz as the main gangue. In addition to quartz, the gangue typically comprised only some diopside+-tremolite. Other silicate minerals like e.g. micas occurred only in very low quantities. The gangue quartz was mostly relatively coarse-grained and showed both in massive and layered ore parts granoblastic aggregate or graphic intergrowth texture with the sulphides (Fig. 60). The banding in the Vuonos ore was defined by cm to dm thick layers of different quartz to sulphide and sulphide to sulphide ratios. Compared to the massive ore, the banded ore, especially inside sedimentary host environment, showed usually somewhat finer grain size, more quartz-sulphide and sulphide-sulphide intergrowth and more abundant and fine-grained sulphide inclusions in the gangue quartz.

# The parallel Co-Ni zone

In similarly to the Keretti deposit, there was a low-grade, disjointed Ni-Cu-Co-mineralized horizon above the Vuonos main ore sheet, traceable for ca. 2.5 km to the NE from the SW tip of the massive ore. The Ni-ore mining at Vuonos was targeted in the metal-richest SW part of this zone. The Ni-Cu-Co anomalous horizon extended as a steeply dipping, narrow (<10 m) layer from the surface down towards the upper edge of the semimassive ore and then subparallel with it to reach in places its lower edge (Fig. 61). The upper part of the horizon was characterized by patchy occurrences of cordierite, biotite-phlogopite, chlorite, muscovite, almandine, orthoamphibole, cummingtonite and plagioclase-bearing "mica-rocks" locally forming breccia-like networks in quartz and skarn rocks. In several locations a distinct "black wall" or metabasite



Fig. 60. Scanned image of a thin section showing granoblastic-graphic sulphide-quartz intergrowth texture typical for most of the Vuonos ore, K3278/79.63. The sulphides comprise mainly pyrrhotite (dark dull green), sphalerite (black-red) and chalcopyrite (light dull green). Width of the view 40 mm.

layer of chlorite-hornblende-biotite-phlogopite-carbonate schist occurred between the Ni±Cu±Co -mineralization at its hanging-wall serpentinite.

The Ni±Cu±Co mineralization comprised typically pyrrhotite+pentlandite+chalcopyrite+sphalerite. Where hosted in quartz rocks the sulphides occurred in fine-grained, irregularly distributed to banded disseminations, while in skarns, chlorite schists and mica rocks bulk of the sulphides were in relatively coarse grains in heterogeneous disseminations and blotchesveinlets. The Ni-richest parts of the mineralization were in the breccia-like portions of mica-rich rocks or in occasional small lenses of massive pyrrhotite in the skarn and mica rocks. The predominant Ni-mineral was pentlandite, occurring either in flame-like exolutions in pyrrhotite and/or as discrete coarser grains in pyrrhotite-pentlandite grain clusters. Ni content of the pentlandite varied from 30 to 36 wt.% (average 31.5 wt.%) and the cobalt content from 3 to 14 wt.% (average 3.8 wt.%). Pyrrhotite contained on average 0.35 wt.% Ni and 0.03 wt.% Co. Ni content in the total sulphide phase was about 3 %. For comparison, pentlandite in the semimassive ore contained on average 17 wt.% Ni and 33 wt.% Co, and pyrrhotite 0.18 wt.% and 0.10 wt.%, respectively.

## Ore genetically noteworthy aspects

There are little obvious differences in the host rock assemblages and ore-host rock relationships between the Outokumpu and Vuonos deposits. The most notable differences between the two deposits are that the Vuonos sulphide plate shows near complete metamorphic transformation to pyrrhotite ore, and also some more remobilization/wedging into the metasedimentary environment. The fact that about one third, locally more, of the Vuonos ore is found wedging inside the Kalevian metasediments has raised several proposals of the syngenesis of the ore and flanking sulphidic black schists (e.g. Peltola, 1978; Loukola-Ruskeeniemi, 1999). Little convincing hard evidence of such syngenetic relationship has been presented, however. Our review of a few drill cores dissecting ore-black schists contacts within the Vuonos upper edge environment resulted in observations of several knife-sharp intrusive-like



Ni ≥ 0.3 %



Cu ≥ 0.05 %



Co ≥ 0.03%



Zn ≥ 0.03 %



Fig. 61. Cross-section profile 193.750 of the Vuonos deposit, showing the relationship of the main massive-semimassive ore and the parallel "Co-Ni zone". Figure 21 from Parkkinen and Reino (1985).

contacts between the ore and the black schists, but none with sedimentary gradational relationship. Chemical analyses across the contact showed that black schist even at the very ore contacts frequently lack metal enrichment typical of the ore, being e.g. very low in cobalt and showing no enrichment in cobalt over nickel. Where significant Cu-sulphides occur in the ore contact black and mica schists, these sulphides are frequently found in veins and replacements reflecting secondary sulphide remobilization (cf. Huhma and Huhma, 1970).

Analogous to the Keretti Co-Ni zone, also the Vuonos Co-Ni mineralization has been interpreted as a remnant of a subseafloor channelway of hot, metal-bearing seafloor vent fluids, and that originally located below and fed the main ore body (Koistinen, 1981; Treloar et al., 1981). Certain skepticism on the validity of the vent models has been expressed, however. Parkkinen and Reino (1985) sate in their paper of the Vuonos Ni deposits: *"the special features of the formations [Co-Ni+-Cu occurrences] are due simply to the order of formation: first an extensive but thin and discontinuous Ni occurrence was formed, and this was followed immediately by the deposition or intrusion of the Cu ore. They added <i>"The source of the fluids and the location of the feeding channels will remain to be established"*. We had no opportunity to study the Vuonos Co-Ni environment, but we largely agree with Parkkinen and Reino (1985), as it is difficult to believe that the Cu mineralization in the Outokumpu and Vuonos Co-Ni zones would have preceded the pervasive carbonation-silicification that was generating their host skarn-quartz rocks.

# 8.2.3. Perttilahti

#### Location, resource character and exploration history

The Perttilahti prospect locates ca. 5 km to the NE of the Vuonos deposit (Fig. 44). Notably, the SW tip of the Perttilahti mineralization, as it is presently known, situates just ca. 1 km to the NE of the NE tip of the Vuonos deposit, falling somewhat to the NW of its down-plunge projection, however. The mineralization was discovered in 1982 by targeting drilling into the assumed down-plunge extension of the Vuonos deposit. Noting that the domain between the Vuonos NE and Perttilahti SW tips has never been drilled in detail, it is even possible that these two deposits were somehow connected and would in fact represent parts of a single deposit. Assuming that the Vuonos and Perttilahti deposits indeed formed a single continuous deposit, a >8 km long, 200-<50 m wide, 10-<1m thick straight-trending band of sulphide-quartz with dimensions gradually diminishing from Vuonos towards NE and Perttilahti is implied. The band would have had have an extraordinarily high average L/B ratio of ca. 80, and a L/T ratio of ca. 1600!

The Perttilahti ore body, as it is known from the present drilling, appears to form a <2-10 m thick, mostly less than 50 m wide, and at least 1.5 km, but probably 2.5 km long, ruler shaped sulphide-quartz shoot plunging in an average angle of about 5-6 degrees towards NE (cf. Fig. 45). The SW tip of the deposit is at depth of ca. 500 m, and the NE tip in depth of ca. 700 m. In the light of the present drilling data, there is a clear shrinking trend in the cross-dimensions and metal grades towards NE. An estimate based on the existing, very coarsely spaced exploration drilling suggests that the Perttilahti shoot would contain no more than 1.32 Mt at 2.15 wt.% Cu, 1.89 wt.% Zn, 0.16 wt.% Co, 0.145 wt.% Ni, and 18.9 wt.% S (Parkkinen, 1997). No formal estimate of Ag and Au tenors is available. A reanalysis by GEOMEX of 113 samples (old Outokumpu pulps) for Au from 13 drill core sections intersecting the Perttilahti mineralization suggest that Au concentrations in the massive-semimassive accumulations would be generally rather low; a maximum Au concentration encountered was 0.35 ppm. Gold contents observed in the immediate wall rocks remained systematically below 0.1 ppm.

# Geolgical setting

Not a single published geological description or even in-company (Outokumpu) report of

the geology of Perttilahti prospect seems to exist. The following description of the deposit is based on Outokumpu in-company drill core reports and geological cross-section maps compiled during this work. We also reviewed a few sections of drill-core dissecting the Perttilahti mineralization

Geological cross-section maps (Figs. 62-66) indicate that the sulphide concentration at Perttilahti occurs, like the Outokumpu and Vuonos ores, at margin of an intensely carbonatesilicified serpentinite body, enclosed in mica and black schists. The few drill core sections reviewed from Perttilahti in the course of this study featured lengthy sections of partly olivine porhyroblastic talc-carbonate rocks but unfortunately no serpentinite, which means that accurate estimation of peak-metamorphic temperatures is less straightforward. However, the ubiquitous presence of olivine porphyroblasts in the talc-carbonate rocks indicates peak hovering at about 550 °C or slightly above. Development of metasomatic, graphite-rich diopside+-tremolite skarns replacing presumably primarily carbonate-rich black schists (black marly shales) is a distinct characteristic of the Perttilahti black schist zones. Similar calc-silicate developments are a common feature also in black schists along the margins of e.g. Kylylahti Kalanen and Viurusuo serpentinites, for example.

# Deposit character

Black schists, though abundant elsewhere in the Perttilahti rock assemblage, are notably scarce in the exact ore environments. Hence, instead of black schists, the ore is more often seen in direct contact to mica schists, in several of the drill profiles so that significant parts of the ore sheet completely wedge inside the mica schists. For example, in the section 198.00 over two thirds, in section 198.50 about half, and in section 199.00 again over half of the ore sheet is inside of the country mica schists, the other wall rocks comprising Outokumpu-type skarns and quartz rocks. Contacts of the ore sheet against its wall mica schists and skarn-quartz rocks were in all those section we reviewed very abrupt, often "knife-sharp".

Based on core we reviewed for the massive-semimassive mineralization, it typically consists of pyrrhotite-chalcopyrite-sphalerite in a totally recrystallized and annealed granoblastic-graphic intergrowth with quartz+-diopside+-tremolite. In addition to the main sulphides, minor co-pentlandite and trace stannite are usually present. Most of the mineralization is apparently semimassive with dominantly quartz gangue, though also diopside+tremolite seem locally abundant; the ore sheet margins are particularly quartz-rich.

## Ore genetically noteworthy aspects

Perttilahti as a deposit appears to a large degree a repetition, perhaps even direct extension of the Vuonos deposit, with the flavor that compared to the latter, in Perttilahti even a relatively larger proportion of the deposit locates inside of the Kalevian mica schists. In a similarity with the Outokumpu and Vuonos ore environments, mafic rocks are scarce and chemical-exhalative sediments absent form the host rock assemblage also at Perttilahti. As the Perttilahti ore locates for its large parts, locally apparently nearly completely, and with very sharp contacts inside of the mica schist regime, the nature of the ore shoot as a sulphide-quartz lode is even clearer in Perttilahti than in Outokumpu or Vuonos. Whether this was a primary or remobilization feature is then the crux of the matter with these deposits.



Fig. 62. Cross-section profile 197.5 of the Perttilahti segment of the "Outokumpu belt". Rock colours as in Fig. 59. Compiled on the basis of drill core reports of the Outokumpu Company and drill hole plotting by Urpo Kuronen. For the location of the Perttilahti segment see Fig. 45.



Fig. 63. Cross-section profile 198 of the Perttilahti segment of the "Outokumpu belt". Rock colours as in Fig. 59. Compiled on the basis of drill core reports of the Outokumpu Company and drill hole plotting by Urpo Kuronen.



Fig. 64. Cross-section profile 198.5 of the Perttilahti segment of the "Outokumpu belt". Rock colours as in Fig. 59. Compiled on the basis of drill core reports of the Outokumpu Company and drill hole plotting by Urpo Kuronen.



Fig. 65. Cross-section profile 199 of the Perttilahti segment of the "Outokumpu belt". Rock colours as in Fig. 59. Compiled on the basis of drill core reports of the Outokumpu Company and drill hole plotting by Urpo Kuronen.



Fig. 66. Cross-section profile 200 of the Perttilahti segment of the "Outokumpu belt". This long profile is known also as the "Sukkulanjoki profile" (cf. Fig. 6 in Häkli, 1987). Rock colours as in Fig. 59. Compiled on the basis of drill core reports of the Outokumpu Company and drill hole plotting by Urpo Kuronen.

#### 8.2.4. Riihilahti

#### Location, resource character and exploration history

The Riihilahti prospect, ca. 15 km to the W of Outokumpu, encloses a small, low-grade Cusulphide mineralization entirely situated under the shallow (mostly 4-5 m) Riihilahti bay of Lake Juojärvi (Figs. 44, 67). First indications of the Cu mineralization were by floats of chalcopyritecontaining calc-silicate, tremolite-diopside "skarn" and garnet-cummingtonite rocks found by Outokumpu Company in the year 1956 from an area to the NE-E of the Riihilahti bay. Soon after the float finds, an outcrop of chalcopyrite mineralized garnet-cummingtonite rock was located in a small rocky island at the mouth of the Riihilahti bay. A small, tattered Cumineralization next to the discovery island was outlined by drilling in the year 1957 (Huhma, 1958). Outokumpu has performed additional drilling in several steps but without significant addition to the resource outlined by end of 1950s. There is a brief description of the Riihilahti deposit in Peltola (1978). Vesanto (1980) provides a detailed geological map (1:4000) of the Riihilahti area, and Merkle (1982) an extensive study of the geochemistry of the host rocks of the mineralization.

The prospect features a small, low-grade and disjointed Cu-sulphide mineralization estimated to contain ca. 0.7 Mt of rock at 0.72 wt.% Cu, 0.09 wt.% Zn, 0.09 wt.% Co, 0.03 wt.% Ni, 3.84 wt.% S and 9.05 wt.% Fe (Parkkinen, 1997). Occurrence of minor Au at Riihilahti has been known from since the finding of the first Cu-bearing ice-borne boulders from the deposit, some of which contained 0.1-0.5 gr/ton of Au (Huhma, 1958). A tentative Au survey by GEOMEX suggested that the Cu-Co mineralised rock body at Riihilahti might contain on average ca. 0.3 ppm Au and 6 ppm Ag.

## Geological setting

Different to any other of the here studied Outokumpu type deposits, the Riihilahti deposit is not associated with a serpentinite body enclosed in Upper Kaleva metaturbidites, but in a sequence of metasediments and amphibolites of clear Lower Kaleva affinity. The Lower Kaleva type host rocks define at Riihilahti bay a small, broadly E-W antiformal or domal looking structure (1x1.5 km) that is all around surrounded by Upper Kaleva type monotonitic metaturbidites (cf. Vesanto, 1980). An interpretation of the Riihilahti structure as a domal structure, instead of small klippe or intercalated sliver, is supported by the at least 600 m thickness of the Lower Kaleva type sequence indicated by holes drilled near vertically down in the Riihilahti structure in its E part of (VRL-97) and N and S of the Riihilahti mineralization (e.g. VRL-28, VRL-85 and VRL-89).

Stratigraphically the Lower Kaleva type sequence seems to comprise a several hundreds of metres thick lower unit of mainly metasedimentary wacke gneisses intercalated with a several tens of metres thick layers of graphite-sulphide-rich black schists in its top part, and an upper unit of 100-200 m of amphibolite with thin intercalations of arkosic wacke. Observations from the Varislahti area ca. 0.5 km to the NW of the Riihilahti mineralization suggest that this sequence would rest directly on an Archaean basement with only a thin layer of guartzites in between. Vesanto (1980) tentatively argued correlation of the Varislahti guartzites with Jatuli. However, an alternative interpretation could be that the guartzites in fact would correlate with Lower Kaleva "basal quartzites", such as the lowermost quartzites at Punamäki-Viitamäki area in Juankoski, or around the Juojärvi cupolas. It is worth to note here that like in Punamäki-Viitaniemi, also in Riihilahti part of the black schists in the Lower Kaleva sequence show Ni, Cu, Zn and V-rich concentrations approaching those typical in the Talvivaara metal-rich black schists in Sotkamo. The metavolcanic rocks at the top of the formation are dominantly high-Mg, low-Ti tholeiite basalts compositionally strikingly similar with the Lower Kaleva basites at Punamäki-Viitaniemi, Vehkalahti, Losomäki and Heinävesi, for example.  $\varepsilon_{Nd}$  (1950Ma) of -7 for one sample of the arkosic wackes intercalated with the amphibolites indicate derivation from purely Archaean sources, providing further evidence of the Lower Kaleva status of the Riihilahti host assemblage.



Fig. 67. Geological map of the Riihilahti formation. Location of the Riihilahti Cu-mineralization and the small Outokumpu-type serpentinite lenses N of it at Varislahti are indicated by arrows. Simplified from Vesanto (1980).

Mineral assemblages in chloritized/metamorphosed basic rocks (e.g. olivine-diopsidechlorite-green spinel, garnet-hornblende-cummingtonite) and presence of abundant granitic leucosome in the mica gneisses suggest at least middle amphibolite facies temperature conditions for the metamorphic peak at Riihilahti.

# The Riihilahti Cu-Co-Zn-Au mineralization

The prospect reports available from the archive of Outokumpu Mining describe that the Riihilahti mineralization would occur in close association with a small (<30 m x <50 m x 200m) "peridotite lens" in core of a small E-W trending synform of mainly metasedimentary rocks (Huhma, 1958). It should be mentioned here that the rock called "peridotites" in the Outokumpu reports should not be mixed with Outokumpu serpentinites, since instead of serpentine, these rocks consists variably of olivine, diopside, hornblende, cummingtonite, chlorite, garnet and green spinel. It is also important to note that, although Cu-Co mineralized, the "peridotite lens", is, however, not the sole or even main host of the economically interesting Cu-Co mineralization. Best parts of the Cu-Co mineralization in fact occur in the immediate surroundings of the "peridotite lens", mainly in tremolite-diopside "skarn" rocks, but to a degree also in garnet-cummingtonite and garnet-mica gneisses, and even in late granite dykes, (Fig. 67).

The rocks constituting the "peridotite lens" are mostly distinctly high in Fe, Ti, V and Zr, while relatively low in Cr and Ni. These as well as other geochemical features point to an origin of the "peridotites" from a highly fractionated, Fe-rich tholeiitic or mildly alkaline basaltic precursor rather than peridotite. This inference is supported by the fact that there are also garnet-cummingtonite and even amphibolitic rocks at the apparent lateral continuations of the peridotite lens sharing its critical immobile element characters. The XRF data of Merkle (1982) and Outokumpu Company support an interpretation of the peridotite lens as heavily hydrothermally altered, chloritized part of a 10-30 m thick layer of Ti-Fe-rich basalt overlain by a 5-10 m thick layer of mica gneiss and further the tremolite-diopside "skarns" that hosts the best parts of the Riihilahti Cu-Co mineralization. The mica schists immediately below and above the most heavily altered now "peridotite") part of the Ti-Fe-rich mafic layer are for 5 to 25 m thickness distinctly Fe-rich and rich in garnet (Fig. 68).

Calling the tremolite-diopside-rich rocks hosting the best parts of the Cu-mineralization as "skarns" or calc-silicate rocks appears a misnomer, too. Namely, the high MgO,  $Al_2O_3$ , V, Sc and Cr but relatively low TiO<sub>2</sub> and Zr of these "skarns" suggest that they also would derive from metabasalts, but in their case by carbonate alteration from low-Ti, high Mg basalt of the Losomäki type. The similarity with Losomäki, Vehkalahti and Viitaniemi skarnoid low-Ti amphibolites is clear. I should be noted, however, that also true metasedimentary skarns (calc-silicate rocks) do occur in Riihilahti, usually as 0.5-2 m intercalations in the thick black schist horizons in easern part of the Riihilahti dome.

Main part of the Cu mineralization at Riihilahti occurs in coarse-grained sulphide disseminations, blotches, veinlets and fracture fillings in the broad variety of host rocks listed above. The frequent occurrence of Cu-rich sulphides also in fractures of the late granitoid dykes/sheets that inject through the host rock assemblage indicates considerable late sulphide mobilization. Sulphide mineral constitution in the Riihilahti deposit is fairly simple, comprising pyrrhotite, chalcopyrite±cubanite exolutions, Co-pentlandite, and a little sphalerite and pyrite. Stannite and mackinawite occur infrequently in trace amounts. Notably, the sulphide phase of the mineralization has relatively rich average cobalt content of 0.83 wt.% and a relatively high Co/Ni ratio of 3.77. The Ni content of the sulphide phase is a high 0.22 wt.% typical for Outokumpu deposits, however. Most of the cobalt locates in fairly coarse-grained cobalt-pentlandite. Pyrrhotite and is low in cobalt and pentlandite exolutions, and hosts only ca. 0.1 wt.% of the cobalt in the mineralization (Hänninen, 1979).

The minor gold present in the mineralization seems to be concentrated, without any clear



Fig. 68. N-S trending cross-section profile 4 of the middle part of the Riihilahti deposit. The garnet-cummingtonite gneiss comprises mostly high-Ti metabasalt, wheras the metachloritite ("metaperidotite") represents its chloritized and high-grade metamorphosed variation. The skarnoid amphibolite is derived from Crrich, low-Ti metabasalt of the Losomäki LOTI type. With reinterpretations of the lithology, the profile is based on cross-section drawings of the Outokumpu Company and in Merkle (1978). Several of the included drill holes were reviewed during the GEOMEX. lithology control, in late shear zones where it occurs as native gold grains mainly enclosed in gangue silicates and at sulphide-silicate grain boundaries (Kontoniemi, 2001). Based on the obvious structural control of the gold, and its positive correlation with Bi and Sb, Kontoniemi (2001) suggested that the gold mineralization in Riihilahti would be related to a separate, late-orogenic "mesothermal" gold mineralization post-dating the main Cu mineralization. We note, however, that both the Bi and Sb contents at Riihilahti are rather low, even in the most Au-rich samples. Maximum observed Bi and Sb are no more than 1.7 ppm and 0.1 ppm, respectively. Given that similar and higher abundances of Au, Bi and Sb are common also in the Outokumpu ore, a separate gold mineralization event is hardly required to explain the presence of these elements also in the Riihilahti sulphides. More likely the gold initially deposited with the Cu sulphides, but was subsequently mobilized and concentrated with elements like Bi in late shear zones developed within the Cu-Co mineralization. Overall, there is very little evidence of late-orogenic, mesothermal, or any other type of gold mineralization in North Karelia Schist belt outside the Outokumpu type sulphide occurrences.

## Ore genetically noteworthy aspects

The here presented reinterpretation of the host rock assemblage of the Riihilahti deposit implies that the deposit is located in a pervasively altered domain of volcanic-sedimentary strata in the very uppermost part of the obviously Lower Kaleva type Riihilahti formation. Although the lithological environment of the Riihilahti deposit is thus drastically different from that characteristic of all the other Outokumpu deposits studied here, however, its metal fingerprint of Cu-Co-Zn-Ag-Au-Sn is highly Outokumpu-type. And, also the isolated mode of the pay-sulphides is a typical Outokumpu feature. In this case the sulphide mineralization is effectively restricted within a body less than 100m x 100m in its cross-section and 200 m in length. Outside of this small rock volume there is only little indication of any significant Cu-Co-Zn An mineralization or possible related hydrothermal alteration

One exception may be the occurrence of fuchsite and Cr enrichments in the metasediments below the W end of the mineralization, as seen e.g. in the hole VRL-85 (based on data in drill core reports of Outokumpu Mining), and which could be an indication of profound hydrothermal alteration and metal mobility, perhaps related to base metal leaching form the metasediments? Another interesting aspect is that the drill hole VRL-33 ca. 500 m to the NE of the known mineralization at Riihimäki hill dissects garnet-cummingtonite rocks similar to those at the known Cu-mineralization. Combined these observations raise the possibility that the Riihilahti deposit might be structurally controlled and primarily associated with a broadly SW-NE-trending fault/shear-zone across the Riihilahti bay. One possibly related aspect is the high, and apparently hydrothermally introduced P and REE content of many the high Cu samples from the Riihilahti mineralization, which raises the question whether the P, REE and perhaps also Cu-Co in the mineralization would be sourced from the local metal-enriched black schists, which also are partly distinctly enriched in P (0.5-1.5 wt%). Negative ɛNd(1950Ma) values obtained in this work from several ore-grade sulphide samples support interpretations that their REE enrichment, and thus perhaps also their ore metal enrichment, would be from the Lower Kaleva metasediments that yield  $\epsilon$ Nd(1950Ma) values ranging from -7 to -3.

What we find really peculiar is that although the Riihilahti mineralization is by its metal portfolio a most typical Outokumpu type deposit, it anyhow lacks the serpentinite body and carbonate-skarn-quartz rocks accompanying all the other clearly Outokumpu type deposits in North Karelia. This could be an indication of that the serpentinites were just a critical "ground-preparation" component for the ore formation process, providing a redox trap for syntectonic metal bearing fluids? And that, given right conditions, it could be possible also in other type environments than at carbonate-silica altered serpentinite lens margins. However, as there are small serpentinite lenses in mica schists at Varislahti only some 1.2 km to the N of the Riihilahti mineralization, we consider it is yet within the bounds of possibility that an intimate serpentinite context once existed also for the Riihilahti sulphides, but that this connection has been wrecked by subsequent tectonic displacement and/or erosion. Nevertheless, it is important to keep in mind that the Riihilahti sulphides at least now are nowhere in direct contact with or even close

to any Outokumpu-type ultramafic-derived rocks.

# 8.3. Eastern limb of the Outokumpu structure

# 8.3.1 Kylylahti

## Location, resource character and exploration history.

The Kylylahti prospect locates at the eastern margin of a volumetrically substantial but poorly exposed talc-carbonate – serpentinite massif ca. 1.5 km to the north of the Polvijärvi village, ca. 25 km to the NE of Outokumpu town (Fig. 44). First indications of Cu mineralization at Kylylahti were gained by reconnaissance exploration diamond drilling in year 1984. The discovery drilling was by the Oku-project (1979-1985), established in 1979 by Outokumpu Company to intensify exploration in the Outokumpu area before the then upcoming shut down of the Outokumpu (Keretti) and Vuonos mines (realized in 1989). The economically most interesting part of the deposit, the massive-semimassive "deep ore", was discovered in year 1985 by drilling at the assumed depth extension of the 1984 located shallower sulphide concentrations. By the end of a drilling campaign in the years 1983-1986, a massive-semimassive sulphide resource of 1.56 Mt 2.83 % Cu and 0.43 % Co was estimated to be present, for most in the deep SW part of the prospect, at a depth of 500-700 m (Hakanen et al., 1986). In addition to the massive-semimassive sulphides, 1.89 Mt of low-grade disseminations at 0.58 % Cu and 0.21 % Co was inferred to occur.

Subsequent exploration efforts by Outokumpu Company, in the years 1991- 1998, resulted in a better knowledge of the volumes and grades of especially the shallower parts of the deposit. However, largely because of technical problems and high cost of drilling to the required great depths (>700 m), the current main resource in the deep parts of the mineralized zone and its possible down-plunge extensions have remained only tentatively constrained and unexplored, respectively. Based on the most recent geological resource estimation (Pekkarinen et al., 1998), the Kylylahti mineralization should comprise at least 1.95 Mt of sulphides at 2.63 wt.% Cu, 0.39 wt.% Co, 0.13 wt.% Ni, 0.76 wt.% Zn, 0.9 gr/ton Au and 20.6 wt. % S in massive-semimassive lenses, most of this resource (70%) being located in the deep ore lens. In addition, 1.43 Mt of low-grade resource at 0.61 wt.% Cu, 0.18 wt.% Co, 0.33 wt.% Ni, 0.39 wt.% Zn, 0.9 gr/ton Au and 8.9 % wt.% S probably occurs in "disseminated" sulphide mineralizations paralleling the semimassive lenses.

Cu-Co sulphides are not the only economically interesting commodities at Kylylahti. In addition, there is considerable talc potential in soapstones, which have been briefly mined during the seventies. As a legacy of the past talc operations, the northernmost part of the Kylylahti massif is still under an active talc mining claim, hold currently by Mondo Minerals, which belongs to the Omya Group, a major worldwide "white mineral" miner and supplier.

# Geological setting

The Kylylahti massif locates at the nose of the in its surface pattern apparently synformal Outokumpu structure where the serpentinite-black schist- dominated "Outokumpu belt" running from Outokumpu through Vuonos and Horsmanaho to Kylylahti turns sharply to east to ramble southwards and towards the Sola serpentinite complex ca. 8 km to the S of Kylylahti (Figs. 2, 44). The Kylylahti massif consists of antigorite serpentinites, talc-carbonate rocks, carbonate-skarn-quartz rocks, and amphibolitic to chloritic metabasites, the latter comprising mainly altered and metamorphosed metabasalt and metagabbro dykes and small plugs enclosed in the metaultramafic rocks. The complex is imperfectly known to its surface map pattern, and poorly also for its overall internal structure. The structure of the massif is reasonably well known only for its eastern margin where most of the past exploration drilling has been done (but for Cu also talc). In its map pattern and in shallow cross-sections the complex appears to define an at 40-50 degrees SSW plunging tight synformal fold (Figs. 69-70). However, there is a serious

possibility that the surficial synform actually is a local synformal detail within hinge area of a much larger SSW plunging and somewhat transposed antiformal fold system (cf. Fig. 71). In any case it is clear that both the eastern and western contacts of the complex are very steep, near vertical to the depth of at least 600 meters. An overall impression rises that the complex would feature an N-S tight upright folded (to an antiform) and shear faulted, originally 100-200 m thick package of tectonically interdigitated metaserpentinites, metagreywackes and black schist, and which preceding the main phase of the upright folding/shearing and related shortening had a relatively flat-lying attitude.

Though metabasite dykes and stocks of gabbroic and metabasaltic origin are locally abundant in the serpentinites and talc-carbonate rocks, they nevertheless make no more than some 5-10 vol.% of the whole massif. A great deal the dykes are heavy in ilmenite and thus likely of ferrobasaltic nature. At the western margin of the complex there is a zone of extensively sheared metagabbros and associated Na-rich quartz-plagioclase rocks, the latter showing strong geochemical affinity to oceanic plagiogranites (section 6.3.2.). The narrow (<1m) mafic dykes are thoroughly altered to chlorite (+-amphibole), and are typically highly schistose, whereas the thicker ones may comprise amphibolitic, or sometimes clearly metagabbroic portions in their middle parts. The small plug-like gabbro bodies similarly show schistose, chloritic marginal parts and less strained, less altered amphibolitic to metagabbroic core parts. Based on information in drill core reports of Outokumpu Mining and that in Koistinen (1981), metabasite dykes and small metagabbro plugs do occur also in the serpentinite-talc carbonate massifs at Horsmanaho (ca. 6 km to the SW of Kylylahti), Sola and Huutokoski (ca. 7 km to the NNE of Kylylahti). It is worth to note that though the metabasite occurrences as described above are common inside the ultramafic massifs, none have been observed within the surrounding metagreywackes or black schists.

The prevailing serpentine species at Horsmanaho and Kylylahti is antigorite (Fig. 72). Interestingly, metamorphic olivine porphyroblasts, though they lack in the shallower parts of the Kylylahti massif, nevertheless appear, both in antigorite serpentinites (Fig. 17) and talccarbonate rocks, below the depth level of ca. 600 m. Stable coexistence of olivine with carbonate and antigorite in the deep serpentinites indicates that metamorphism at Kylylahti culminated at temperatures close to but probably slightly below ca. 520+-20 °C. The absence of olivine porphyroblasts in the surface parts of the Kylylahti but also Horsmanaho massif ca. 5 km SW of it, suggests metamorphic grade would increase in this area more rapidly towards the depth than laterally towards the SW.

## **Deposit description**

The Cu sulphide mineralizations known from Kylylahti locate all along the approximately S-N trending, nearly vertical eastern limb of the complex. In this environment a thick serpentinite cored body of ultramafic rock is found grading outwards (eastwards) to talc-carbonate rocks and further to several tens of metres thick zones of strongly schistose carbonate-skarn-quartz rocks typical of the Outokumpu alteration assemblage (Figs. 69, 73-74). The metasomatic carbonate-skarn-quartz rocks are all the way of the mineralized zone flanked by several metres to tens of metres thick layer of metagreywacke and metacarbonate intercalated, sulphide and graphite-rich, partly distinctly sulphide-laminar black schists, which eastwards abruptly grade into typical sand-dominated Upper Kaleva metagreywackes (mica schists). This basic lithoassemblage is deformed by apparently several episodes of folding and faulting (cf. Koistinen, 1981, 1993).



**Fig. 69.** Geological map of the Kylylahti massif, showing surface projection of the associated massive-semimassive sulphide mineralization and locations of the cross-section profiles presented in Figs. 70-71 and 73-74.



Fig. 70. Oblique cross-section profile Ob1 of the Kylylahti massif. For location of the profile see Fig. 69. The diagram is based on drill core reports of the Outokumpu Company and a review of the holes Oku-764 and Oku-765 by the first author. Drill hole plotting by Urpo Kuronen.

Two main types of Co-Cu-Zn sulphide accumulation are present in the Kylylahti mineralization: (1) semimassive-massive sulphide lenses between the zones of carbonate-skarn-quartz rocks and the black schists, and (2) a paralleling zone of skarn-hosted disseminations, veinlets, blotches and minor scattered semimassive sulphide lenses in carbonate-skarn-quartz rocks immediately flanking the semimassive lenses (Figs. 73-75).

# Semimassive lenses

The main sulphide concentration at Kylylahti occurs in a ca. 1.3 km long train of three main massive-semimassive guartz-sulphide lenses along the nearly vertically dipping eastern margin of the Kylylahti massif (Figs. 69, 73-75). The train of the near vertical sulphide lenses probably has a modest surface exposure at about section 73.700 in the NNE, wherefrom it plunges SSW towards the main "deep ore" body in section 72.650 at the depth of ca. 600 m. The north and middle lenses define a shallower plunge (10-20 degrees) than the deep ore lens (40-50 degrees). The north lenses are only 5 metres thick and 50 metres high at best, while the most voluminous "deep ore" lens has a thickness up to 30 metres and height up to 170 metres. All the ore lenses locate between or near the contacts of the ultramafic-derived skarn-guartz rocks and metasedimentary sulphide-graphite rich black schists. The contacts of the guartz-sulphide lenses are frequently very abrupt without any gradation either to the carbonated-silicified ultramafics or black schists. The deep ore lens occurs in synformal hinge of a sinistral, at 40-50 degrees to SSW plunging S-from shear fold (Fig. 74), an obvious parasite of the main Kylylahti fold. Several of the ore lenses show tendency to fold/protrude inside the black schist regime. Because of this, a large part of the "deep ore" lens, for example, is found inside of the black schist regime (Fig. 74). However, based on scrutiny of intersecting drill cores, contacts of the ore lenses and black schists are also in these cases very sharp and "intrusive-like", and definitely no features suggesting syngenetic-interbedded relationship of the ore materials and black schists



Fig. 71. Oblique cross-section profile Ob2 of the Kylylahti massif. The inferred, completely undrilled lower part of the serpentinite massif is in this strongly speculative diagram left undivided for lithology. The holes R397 and R398 were drilled by Geomex, the Oku-792 and Oku-793 are holes by the Outokumpu Company. Rock colours as in Fig. 70.



Fig. 72. Photomicrograph of typical antigorite serpentinite of the Kylylahti complex (Oku-857/83.90), showing carbonate (brown, granular) and talc (brown, flaky) replacing antigorite (grey, felty). The opaque (black) grain in the left-hand upper corner is chromite-ferrian chromite. Width of the view 46 mm, in transmitted, cross-polarized light.

are present. The abruptness of the ore-wall rock contacts is exemplified by the fact that the black schists even in the very contacts of the ore bodies lack any tendency towards cobaltenrichment typical of the Outokumpu sulphides. The contacts of the massive-semimassive lenses with the carbonate-skarn-quartz rocks are also sharp, and manifested by an abrupt jump in Cr content from negligible (<30 ppm) to very high (>1000 ppm) with changeover from the massive-semimassive sulphides into carbonate-skarn-quartz rocks.

Sulphide mineralization in the Kylylahti main sulphide lenses is for most part semimassive pyrite+pyrrhotite+chalcopyrite±spalerite with quartz as the main gangue mineral. In some sections the entire sulphide-quartz lens, and in many others significant parts of them are distinctly poor in total sulphides and constitute of just about medium to fine-grained quartz. Other gangue minerals than quartz include minor calcite, amphiboles, mainly tremolite, calcite and trace mica, rutile, sphene and "tucholite". In marked contrast to the quartz rocks of the Outokumpu assemblage, the ore lenses, even their quartz richest layers, do not contain chromite, and are poor also in Cr-rich silicates. Consequently, the Cr content of the semimassive sulphides is distinctly low (usually <30 ppm), and this indeed holds also for those ore lenses or parts of the ore lenses, which have high quartz contents. The in many drill section thoroughly low Cr content of the semimassive ore lenses implies they entirely lack intercalations of Outokumpu type ultramafite-derived quartz rocks. Systematically very low Al, Zr and K of the ore materials imply complete lack either of epiclastic (e.g. black shale) interbedding.

Four main textural-mineralogical ore types can be distinguished in the semimassive


**Fig. 73.** Cross-section profile 73.000 of the Kylylahti Co-Cu deposit, showing geological setting typical of its middle part (N ore body). The 1000 ppm Cu isopleth is for the Co-Cu sulphide dissemination flanking the massive-semimassive sulphides. Location of the profile is shown in Fig. 67.



Fig. 74. Cross-section profile 72.700 of the Kylylahti Co-Cu deposit, showing geological setting of the deep massive-semimassive sulphide lens in its SW part. The 1000 ppm Cu isopleth is for the Co-Cu sulphide dissemination flanking the massive-semimassive sulphides. Location of the profile is shown in Fig. 69.



Fig. 75. A perspective view of the Kylylahti Cu-Co-Zn deposit showing spatial distribution of the massive-semimassive lenses and the the paralleling disseminated, skarn-hosted mineralizations. Unpublished diagram of the Outokumpu Company.

lenses: (1) banded pyrite ore, (2) blebby pyrite ore (3) pyrrhotite ore, and (4) pyrrhotitemagnetite ore (Figs. 76-78). The banded and blebby pyrite ore types with variable component of pyrrhotite characterize most of the lenses, while the pyrrhotite-magnetite type is known about only from the inner parts of the deep ore lens.

From the main ore types, the banded pyrite type is characterized by relatively low tenors of the pay metals, also when comprising nearly massive sulphide. The banded-streaky appearance is due to alternation of pyrite or guartz-dominated, discontinuous, thin (mm-cm) stripes to more continuous, thicker (cm-dm) bands. Pyrite in this type is partly in very fine grains enclosed in the typically relatively fine-grained gangue quartz. Characteristic of the blebby pyrite ore type are large, up to several cm size pyrite blebs or blotches of mostly fine-grained pyrite+chalcopyrite±spalerite±pyrrhotite in a matrix of usually relatively coarse-grained granoblastic-granular quartz showing a tendency to coalesce into irregularly bounded veins or blotches (Fig. 77). The pyrite blebs contain sometimes core portions with reniform to even colloform-like growth features and frequently have coarse-grained, idioblastic and distinctly compositionally zoned (Co, As, Ni) pyrite at their margins. Coarse-grained pyrrhotite, chalcopyrite and sphalerite replacing pyrite are usual around the blebs and in irregular veinlets and bands (Figs. 54, 79), often associated with coarse-grained quartz or tremolite. The pyrrhotitic ore parts represent metamorphic recrystallization of the pyritic ore, showing similar massive, graphic pyrrhotite-chalcopyrite-sphalerite-quartz intergrowth textures (Fig. 78) as id typical of pyrrhotite dominated ores thorough the Outokumpu district. The pyrrhotite-magnetite ore type is restricted in a 5-10 m layer inside the deep ore lens, but which seems to persist across the whole deep ore lens. This ore type is characterized by presence of 2-20 cm thick layers rich in granular magnetite (up to 50 vol.%) in an otherwise mainly pyrrhotite-dominated ore (Fig. 78). Blue-green, iron-rich, alumina and Cr-poor amphibole, not yet more precisely identified (cummingtonite?), is an additional characteristic component of the pyrrhotitemagnetite ore type. It often occurs as abundant, hairy or "asbestiform" inclusions enclosed unoriented in the gangue guartz.

The lower edge of the deep lens in its SSW tip comprises a small volume of distinctly Asrich ore having a gangue dominantly of carbonate and with some tremolite, quartz, rutile, and pale-brown biotite. This As-rich ore is pyrrhotite-dominant with variable chalcopyrite, sphalerite, cobaltite and pyrite. Cobaltite is probably the main As carrier, but significant As in is found also in pyrite. Especially enriched in As in this ore type are large, apparently peak-metamorphic Copyrite cubes, which are zoned for and may contain up to 10 wt.% As.

## The Parallel zone of sulphide stringers and disseminations

Mineralization in the carbonate-skarn-quartz rock hosted "stringer zone" paralleling the semimassive lenses (Fig. 75) occurs mainly in coarse to fine-grained disseminations, blotches and veinlets, though locally tatters of semimassive sulphide with similar characters as the main semimassive lenses are included. Main sulphide mineral in the skarn-hosted mineralizations is frequently pyrrhotite that exists variably with pyrite, chalcopyrite, sphalerite, pentlandite and cobaltite. Minor to trace sulphide phases include e.g. mackinawite, and in several of the studied samples stannite. In addition, minor magnetite rich parts are occasionally present, especially in the deep ore environment where the parallel mineralization is most voluminous. Where the sulphidic skarn phase is replacing host-rocks of ultramafic derivation, as the case usually is, chromite in various forms, often also as inclusions in the sulphides (Figs. 82e-f), is frequently present.

The drill cores form the skarn-quartz zone mineralization provide plentiful evidence of the pay sulphides are dominantly in massive tremolite-carbonate skarn material secondary to and replacing/brecciating older schistose carbonate and quartz rocks (Figs. 80-81) . The mineralized skarn material typically consists of randomly radiating, coarse tremolite prisms with variable



Fig 76. Scanned images of Kylylahti banded byrite ore. The left image shows a fine-grained, more "primary" type with secondary pyrite blebs starting to develop by shearing and associated folding (Oku-902/365.00, hight of the slabs ca. 60 mm). The right image shows a more strongly tectonized, banded version probably from a protolith as in the left image (Oku-791B/653.00, width of the slab 30 mm).



Fig. 77. Scanned images of the Kylylahti blebby pyrite ore, showing blebs of fine-grained pyrite concentrated in bands of coarse-grained quartz and replacing fine-grained earlier pyrite. Note the clear syntectonic nature of the blebs. Samples: Oku-808/721.00 (left, width of the slab 30 mm); Oku-808/682.00 (right, width of the slab 30 mm).





Oku-808/698.00



Oku-808/729.00

# Oku-791B/648.00

Fig. 78. Scanned images of late metamorphic textures and structures of the Kylylahti massivesemimassive sulphides. (Oku-791B/648.00) Magnetite-pyrrhotite ore from the middle part of the deep ore lens. Note that magnetite and pyrrhotite in this sample enclose schistosity-defining trtemolite needles and mica flakes. (Oku-808/698.00) Large retrograde Pyrite IV idioblasts in pyrrhotite andchalcopyrite that are replacing fine-grained earlier pyrite. (Oku-808/729.00) Chalcopyritepyrrhotite ore showing granoblastic intergrowth texture of sulphides and quartz, as it is typical for thoroughly metamorphosed–Outokumpu ores. Width of the slabs 30 mm.



Fig. 79. Scanned images of shear banded blebby pyrite ore replaced by chalcopyrite and pyrrhotite (sample Oku-794/794.00). The right image provides 2 times enlargement of the upper part of the image in the left. In the enlarged image it is well seen that blebs/aggregates of syntectonic pyrite (Py) are "statically " replaced by coarse-grained pyrrhotite (Po) and chalchopyrite (Cp). In addition, an origin of the pyrite blebs/aggregates by syntectonic growth and replacement of earlier fine-grained pyrite is clearly evident. Note that part of the earliest pyrite is very fine-grained, and thus remains dark in the scanned images. Width of the slab 40 mm.



Fig. 80. Scanned images of a sample (Oku-788/305.47) showing structures and paragenetic relationships typical of the skarn hosted stringer mineralization parallelling the Kylylahti massive semimassive sulphide lenses. It is seen in the images that a schistose quartz rock (gray) is discordantly replaced by massive pyrrhotite and chalcopyrite rich in tremolite-carbonate skarn material. Similar structures as in this figure are ubiquitous in the Kylylahti stringer zone attesting to its late syntectonic origin. Note the sulphide poor nature of the quartz rock being replaced by the sulphidic skarn material. The left image shows the split surface, middle one the opposite curved surface, and right one the one the side of the half-split 40 mm drill core sample.



Fig. 81. More scanned images of mineralization features characteristic of the Kylylahti parallel skarnmineralization. (Oku-799/363.00) Coarse-grained tremolite-carbonate material replacing fine-grained quartz rock (grey). (Oku-800B/690.00) Sphalerite (ZnS), abundant rutile and phlogopitic mica replacing Outokumpu-type dolomite rock. Note that in the both samples sulphides (Cp=chalcopyrite, Po=pyrrhotite) are confined nearly 100% to the replacive skarn material, and that the nearly undeformed nature of the replacement textures strongly attest to structurally late timing of the skarnreplacement and related sulphide mineralization. Width of the both slabs ca. 30 mm. carbonate (dolomite+calcite) in the interstitial spaces. The massive texture of the mineralized, replacive skarn component is in marked contrast to the typically penetratively schistose-mylonitic texture of the host skarn-quartz rocks and their local amphibole-chlorite schist intercalations. Intriguingly, the mineralized carbonate-tremolite materials often seem to contain but tremolite and calcite, frequently also some sphene, rutile, zircon, plagioclase, biotite-phlogopite and apatite (Figs. 81; 82a-d), i.e. minerals that by definition lack in normal Outokumpu type carbonate-skarn-quartz rocks. The presence of these minerals is reflected in the somewhat elevated AI, Ti, Na, P, REE and zircon concentrations in the whole rock chemical compositions of samples from within the parallel mineralization (cf. Table 10a-b).

The plagioclase in the replacement skarns is often quite coarse-grained, and often remarkably fresh and free of any deformation features. Polysynthetic twinning is present in these plagioclases, which by optical estimation seem mostly very anorthitic (labradorite-bytownite) by their compositions. There is plenty of textural evidence under the microscope of that the plagioclase replaces carbonate and tremolite, and that sphene, rutile, apatite, phlogopite, and iron sulphide+pentlandite±chalcopyrite have been crystallizing concurrently. The sphene in the replacement skarns is often very coarse-grained and frequently with sulphide inclusions. The rutile is brown to honey yellow in colour and occurs typically in patches or vein-form aggregates of tiny needles or slender prisms, often enclosed in titanite.

A weak but genetically interesting sulphide mineralization occurs inside of the serpentinitetalc-carbonate environment some 100-200 m to the W of the main disseminated zone at the middle part of the Kylylahti mineralization. In section 73.700 this mineralization constitutes a pyrrhotite-enriched and weakly Cu (up to 0.4 wt.%), Co, Au anomalous "lens" with an upright cross-dimension of 5-25 x 200 m. The zone is characterized by veining and replacement of the host antigorite serpentinite by "skarn" material composed dominantly of mass of slender to asbestiform amphibole prisms, probably cummingtonite, magnetite and irregularly distributed veinlet and disseminated sulphides. Main sulphide minerals are pyrrhotite, pentlandite and chalcopyrite, in addition, e.g. trace stannite is present. Magnetite is present in blotches and vein networks, which in hand-size samples may amount up to 30 vol.%. Chromite inclusions in magnetite likewise sulphides are common attesting for the replacement of serpentinite. Cummingtonite occurs mostly in radiating prisms that show no preferred orientation. Overall impression is of late fracture-controlled, metasomatic replacement of the host antigorite serpentinite by cummingtonite, magnetite and concurrently deposited sulphides. XRF analyses in the Outokumpu XRF database indicate patchy presence of remarkably high zirconium contents ( $ZrO_2$  up to 400 ppm) in the lower part of this mineralized zone.

## Pyrite textures in Kylylahti sulphide mineralizations

As a part of our review of the Kylylahti deposit, we conducted a reconnaissance study of the ore pyrite. This was done since pyrite, being perhaps the most resistant of sulphide minerals to metamorphism, is in the amphibolite-grade Kylylahti deposit practically-speaking the only sulphide phase that could theoretically yield some information of the more primary ore formation events. Pyrite is also the most potential host for "invisible gold" in sulphide deposits (may contain Au in solid solution). Therefore understanding of the paragenesis and composition of pyrite would potentially clarify also the history of gold.

As described above, four main textural-mineralogical types were recognized in the massive-semimassive sulphides: (1) banded-striated pyrite, (2) blebby pyrite-pyrrhotite, (3) pyrrhotite, and (4) magnetite-pyrrhotite. Of these four types, only the banded and blebby pyrite ore facies comprise pyrite, or overall sulphides that could be of pre-peakmetamorphic origin. Fine-grained pyrite, **Pyrite I** (Fig. 83a), in narrow pyrite-quartz bands and enclosed in fine-grained quartz is typical for the banded ore type and is considered the most primary pyrite phase in Kylylahti. The blebby pyritic ore type seems to represent syntectonically reworked derivative of the banded



Fig. 82. Photomicrographs of some mineralogical-textural features characteristic of the Kylylahti skarn-hosted "parallel" mineralizations. (A) and (B) Tremolite, plagioclase, sphene and rutile as inclusions and intergrown with pyrrhotite (brown), chalcopyrite (yellow) and pentlandite (cream yellow). (C) and (D) Tremolite, sphene and carbonate as inclusions and intergrown with pyrrhotite, chalcopyrite and pentlandite. (E) Altered, recrystallized Zn-rich chromite (dark grey) enclosed in chalcopyrite (yellow) and sphalerite (pale grey). (F) Recrystallized Zn-rich chromite enclosed with chalcopyrite (yellow) in pyrite (cream white). A and C are taken in cross-polarized transmitted light, B and D-F in plane-polarized reflected light.



Fig. 83. For the figure caption see next page.

Fig. 83. Photomicrographs of some textures characteristic for the Kylylahti massive-semimassive sulphide lenses. (A) Banded-striated pyrite ore showing earliest fine-grained Pyrite I with some secondary coarsening (sample Oku-794/577.52). (B) A pyrite bleb replacing eary fine-grained Pyrite I, all sulphides

embedded in coarse quartz; (C) Detail of the internal texture of the pyrite bleb in A, showing that the bleb is sieved with tiny inclusions of chalcopyrite. (D) Pyrite II blebs in coarse-grained quartz (sample Oku-794/581.00). (E) Enlarged view of part of the Pyrite II bleb in D. Note the intimate intergrowth of Pyrite II and gangue quartz (black) in the middle part of the view. (F) Pseudocolloformal, concentric growth texture sometimes met in Pyrite II blebs. (G) Zoned Pyrite III typical of the margins of the Pyrite II blebs (sample Oku-794B/560.00). (H) Chalcopyrite-sphalerite -magnetite ore (spalerite=dark grey, magnetite=light grey) from the middle part of the Kylylahti deep lens (sample Oku-791B/644.00).

pyrite ore, in which the Pyrite I is reworked into the fine-grained pyrite, **Pyrite II** (83b-f), dominating in the blebs. Pyrite II sometimes exhibits growth-banded (with pyrrhotite, chalcopyrite and sphalerite) reniform, sometimes concentric colloform looking textures that distantly resemble growth-banded or colloform pyrite in seafloor hydrothermal sulphides (Fig. 83f). Such delicate textures as typical of Pyrite II in a weak quartz matrix would clearly have not survived the high strain typical of the Kylylahti ore environment and are thus indicative of relatively late, metamorphic (though not necessarily peak-stage) nature also the Pyrite II. Pyrite II blebs frequently enveloped by overgrowths of more euhedral, and often delicately zoned pyrite, **Pyrite III** (Fig. 83g), which is is free of fine-grained intergrowths with pyrrhotite and chalcopyrite, and which seems a clear metamorphic phase as it encloses monomineralic inclusions of metamorphic silicates. The growth banding of Pyrite II and growth zoning of Pyrite III imply considerable temporal fluctuations in the fluid chemistry during crystallization of these pyrite phases. Both Pyrite II and III are ubiquitously replaced by coarse-grained chalcopyrite and sphalerite (Figs. 54, 79, 83b-c). Resolving the important question about whether this replacement would represent remobilization of the Cu and Zn or their main emplacement in the massive-semimassive ore, would require considerable more petrographic and microanalytical mapping than we currently have. In addition to the above-distinguished pyrite generations, there commonly occur, especially in the pyrrhotite-dominated assemblages, also retrogressive pyrites, usually in the form of large cubes (**Pyrite IV**; Fig. 78), representing pyrite exolved from pyrrhotite along with the post-peak cooling.

Pyrite II and III are the most common pyrite generations in the Kylylahti massivesemimassive lenses, whereas Pyrite IV prevails in the pyrrhotite dominant skarn-hosted stringer-disseminated mineralizations. It is possible that solid solution of Au in pyrite II and III was the primary mode of occurrence of Au in Outokumpu-type deposits. The most gold in Kylylahti, and especially in the deposits of higher metamorphic grade as in Outokumpu, may then have exsolved from these more primary pyrites, forming native Au or electrum grains eventually ending in cracks of Pyrite III and IV where it now dominantly occurs.

## Au in Kylylahti mineralizations

As a part of review of the Kylylahti deposit, we undertook also a brief microprobe reconnaissance study of the mode of occurrence and chemical composition of gold in Kylylahti. The below sections paragraphs briefly summarize the results.

## Geochemistry of the gold

**Comparison of the Outokumpu and GTK Au assaying**. To get some idea of the comparability of the fire assay results by Outokumpu and the GFAAS data obtained during this study, a small number of primary Outokumpu sample powders of some of the most Au-rich samples (Au >1ppm by Oku fire assaying) were reanalysed by GFAAS at GTK. The correlation between the Outokumpu and GTK results turned out to be rather poor (Table 9). The GTK Au values were on average ca. 40 % lower than the fire assay results reported by Outokumpu Mining. One obvious reason of the differing results would be the supposedly poorer Au recovery of the aqua regia dissolution used for the GTK/GFAAS tests, especially in case if significant silicate enclosed gold was present. Nevertheless, two of the most gold-rich samples yielded results, which suggest that nugget effects may also be important. One of these samples, Oku-905/345.60-347.20, yielded only 1.47 ppm Au in the reanalysis by GTK versus

the 53 ppm Au reported by Outokumpu Mining. The other sample, Oku-801/151.90-154.10, yielded equal Au grades when the old pulp was reanalysed, but analysing the remaining half core yielded only 0.15 ppm and 0.01 ppm Au for two separate tests. Clearly there are heavy nugget effects involved, or, alternatively, some problems probably with the Outokumpu primary tests, perhaps in form of sample contamination.

Hole ID	From	То	OKME	GTK	S wt.%	Au ppm	Au ppm	Note
			Anal no	Anal no	OMKE	OKME	GTK	
					Fire ass.	Fire ass.	GFAAS	
OKU-905	345.60	347.20	9815330	L99007758	14.13	53.0	1.47	reanalysed OKME pulp
OKU-791	577.25	579.00	8524622	L99310768	1.65	13.7	9.75	reanalysed OKME pulp
OKU-791	581.15	583.70	8524624	L99310769	0.78	5.1	1.61	reanalysed OKME pulp
OKU-791	596.45	598.90	8524633	L99310770	7.29	4.3	3.73	reanalysed OKME pulp
OKU-795	640.70	642.50	8526335	L99310771	2.37	4.8	0.46	reanalysed OKME pulp
OKU-800B	596.50	599.15	8623007	L99310772	5.60	6.2	0.19	reanalysed OKME pulp
OKU-800B	691.40	692.65	8623043	L99310773	11.50	4.1	10.20	reanalysed OKME pulp
OKU-800B	692.65	694.15	8623044	L99310774	23.40	4.6	0.08	reanalysed OKME pulp
OKU-801	402.60	404.25	8623248	L99310776	4.41	3.9	2.03	reanalysed OKME pulp
OKU-803	740.20	743.15	8623677	L99310777	7.48	5.6	0.97	reanalysed OKME pulp
OKU-808	688.45	690.35	8624774	L99310778	26.80	6.8	0.68	reanalysed OKME pulp
OKU-810	690.45	692.35	8626000	L99310779	2.05	3.5	0.47	reanalysed OKME pulp
OKU-810	692.35	694.00	8626001	L99310780	0.74	6.3	0.49	reanalysed OKME pulp
OKU-810	694.00	696.50	8626002	L99310781	1.98	4.5	3.69	reanalysed OKME pulp
OKU-800B	618.20	620.35	8823588	L99310782	0.62	1.1	0.70	reanalysed OKME pulp
OKU-801	151.90	154.10	8623125	L99310775	1.13	55.6	69.60	reanalysed OKME pulp
OKU-801	151.90	154.10	-	L99319226	-	-	0.15	new sample, rem. half core
OKU-801	151.90	154.10	-	L00300963	-	-	0.01	new split of L99319226

Table 9. Kylyla	ahti: Comparison	of gold analyses	by Outokumpu	(OKME) and GTK.
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The average gold abundances in Kylylahti are rather low. The latest resource estimation by Pekkarinen et al. (1998) indicated an average Au content of ca. 0.9 g/t for the massive-semimassive lenses and carbonate-skarn-quartz rock hosted disseminations as well. The 15 massive-semimassive samples analyzed by us yielded an average of 0.26 g/t, while the 67 samples from the carbonate-skarn-quartz rock hosted mineralizations gave an average of 0.78 g/t. Recalling here the probably less than perfect Au recovery of the used assay method, these may be values a bit below the real concentrations. Carbonate-skarn-quartz rocks outside of the Cu-Co mineralized zones seem to be systematically low both in Au and Ag. Typical for talc-carbonate rocks, that usually is slightly enriched in As and Au, also the Kylylahti talc-carbonate rocks (soapstones) show unevenly distributed, typically up to tens of ppb level Au enrichments.

Location of Au and gold grain size. The research on Kylylahti gold included microprobe study of 24 polished sections from drill cores Oku-788, -791, -796, -801, -808, -810, -904, and -905. With the aid of optical and scanning electron microscopy possible gold grains were searched, measured for their size, and became chemically analysed and classified. The results indicate that most of the detectable gold occurs in <10 micron size grains with a gradual decrease in number of observed grains towards larger grain sizes (Fig. 84). In some cases several small gold grains were found coalescenced in clusters, which may potentially cause severe nugget effects in gold assaying. An example of such aggregate from sample Oku-808/730.00 is presented in Fig. 85, where two large 100  $\mu$ m -size gold grains occur associated with many thin gold veinlets and tiny surrounding grains.

Most of the Au (-Ag-Hg) grains occur within sulphides (57%), silicates host 33% of the grains, the rest are found within carbonates, phosphates (apatite) and silicates, or at sulphide-

silicate grain boundaries (Fig. 84). Pyrite and chalcopyrite are the most common sulphides that contain Au grains, while only minor amount of Au is enclosed in the other sulphide minerals(Fig. 84). Sphalerite, although a common mineral in some of the studied samples, was observed to be particularly scanty in gold grains. The chalcopyrite, in turn, was found to hosts more Au grains than its modal amount in the studied samples would suggest. Most of the Au grains in silicates were observed in quartz and only a few in diopside and amphibole (Fig. 84).

It is difficult to quantify whether the observed amounts of the metallic Au (-Ag-Hg) grains actually explain the Au assay results from Kylylahti. This is because some sulphides may contain substantial amounts of "invisible gold", especially in unmetamorphosed and lowly metamorphosed environments. Potential candidates in Kylylahti deposit include pyrite, especially the pyrite II and III, and perhaps cobaltite for which a literature review indicates substantial Au in solid solution. To check the Au content of pyrites characteristic of the massive-semimassive ores, two samples of blebby pyrite ore with mostly pyrite II and III were mapped for Au by normal electron microprobe (in GTK) equipped with the "TRACE"-program by CSIRO, Western Australia. The result was that pyrites in neither of the two studied samples did contain detectable amounts of gold. Minor signals were recorded, but none were significant enough to indicate concentrations above the detection limit that was approximately 20 ppm. This result does not necessarily mean that Kylylahti pyrites were entirely free of gold as substantial amounts of Au may yet be present diluted in the large volume of pyrite characterizing the two analyzed pyrite-rich samples. More likely, however, considering the relatively high amphibolite facies peak-metamorphism of the Kylylahti deposit, most of the Au, which originally may have been in the early pyrites I and II, has been separated to form metallic grains.

**Composition of gold grains.** Based on the GEOMEX survey, Au grains in the Kylylahti Cu-Co-Au deposit are rather heterogeneous for their chemical composition, containing generally considerable amounts of Ag in solid solution and native Hg possibly in mechanical solution. The following ranges apply for the Kylylahti gold: Au 13.51-97.81 wt.% (mean of 58.97 wt.%); Ag 0.46-64.24 wt.% (mean of 29.64 wt.%) and Hg 1.14-22.26 wt.% (mean of 10.55 wt.%). Thus, the gold is variably in the form of pure gold, electrum, Hg-bearing gold, Hg-bearing electrum, and Hg-bearing kustelite. Fig. 86 illustrates the chemical compositions of the "gold" grains in a 3D ternary plot.

There seems to be considerable variation in gold composition within the Kylylahti sulphide mineralizations, depending on the sample location. Relatively pure gold to electrum grains occurs in samples from core parts of the massive lenses and stringer zone, whereas grains in samples from ore parts closer to the black schist contacts comprise less pure, Hg-bearing gold. For example, in hole OKU-905, gold grains in a sample (Oku-905/346.45) from the hanging wall part of the stringer zone mineralization are of pure gold or electrum with negligible Hg-content, while in a sample (Oku-905/365.05) from a location close to the black schist layer at the footwall of the mineralization, the gold grains contain over 10 wt.% Hg. Particularly pure gold (>95 wt.% Au) was encountered in hole OKU-791 in a sample (Oku-791/578.70 m) well from inside the hanging-wall stringer zone, where the mineralization is in a fine-grained quartz rock. In contrast,



# Grain size distribution of Au (+Ag+Hg) grains

# Host minerals for native Au (+Ag+Hg) grains



Sulfides associated with native Au (+Ag+Hg) grains



Non-sulfides associated with native Au (+Ag+Hg) grains



Fig. 84. Diagrams illustrationg grain size, host minerals and associated sulphide and silicate minerals of gold in Kylylahti. Grain size in µm.



Fig. 85. SEM image of two relatively large, irregular-shaped gold grains (white) and many surrounding smaller grains in semimassive sulphide, sample 808/730.00. The gold grains are associated with spalerite-pyrite-chalcopyrite in a pyrrhotite dominated part of the Kylylahti deep lens.

distinctly Hg-rich gold was observed in a sample (Oku-808/688.80) just 35 cm away from a contact of a wedge of mica schists inside of the deep lens, and in an other sample (Oku-730.00) just 1 m away from a dark black schist related metacarbonate rock at the footwall of the deep lens. Particularly impure "gold" containing 50 wt.% Ag and 10 wt.% Hg was recognized at 684.35m in hole Oku-791 dissecting the Co-As -rich SW tip of the deep ore lens, there flanked by Cr-poor skarn and carbonate-bearing quartz rocks that show chemical affinity to carbonate interlayers in the adjacent black schists.

# Ore genetically noteworthy aspects

The Kylylahti deposit is the lowest metamorphosed and perhaps also least remobilised one of the Outokumpu type deposits in North Karelia, and therefore research-wise clearly the most interesting of them. The almost 150 °C lower peaktemperatures at Kylylahti compared to far best studied Outokumpu deposit makes a big difference in terms of sulphide mineral stabilities, although it is clear that even the "low", ca. 500 °C peaking at Kylylahti must have had a considerable modifying effect on the sulphide assemblages and chemical compositions of the ore sulphides. The location of the ore concentration in a prominent late fault/shear zone means that also pervasive syntectonic reworking of the ore materials, probably in several stages has certainly taken place. This practically means that if the deposit was premetamorphic, most of the textural and mineral chemical heritage of the primary sulphide formation inevitably has been destroyed.

The parallel skarn-hosted "Co-Ni type" mineralization is particularly well-developed feature



Fig. 86. Ternary plot of Ag-Au-Hg concentrations in Kylylahti gold grains.

in the Kylylahti system. From the structural evidence as briefed above, a late syntectonic origin of the skarn mineralization is very clear. This inevitably means that the parallel skarn-zone cannot represent a stringer zone below a seafloor exhalative sulphide accumulation. Many questions concerning issues like the nature and source of fluids that contributed in the sulphide deposition/redeposition? within the skarn zone, or the exact timing of the skarn mineralization, remain here open and should be addressed in future studies.

Though bodies of basic rocks are fairly common in parts of the Kylylahti complex, these mostly represent dykes or small intrusions, and no clear examples of extrusive components have been demonstrated so far. Furthermore, the volume of the basic rocks is far too small that they alone could represent the source of the metals or thermal energy that were required for the hydrothermal formation of the Kylylahti ores. Clearly, if the basic rocks and associated felsic rocks played a role, there must have been a stage in the evolution of the Kylylahti complex in which it was associated with a much bigger volumes of gabbroic-basaltic rocks than that it now incorporates.

The black schists flanking the in the Kylylahti ore bodies are distinctly metal and sulphiderich for metasediments, recalling a need of carefully examining their possible role in the ore forming process. The systematically abrupt, intrusive-like contacts of the massive-semimassive ore and the black schists and the different metal enrichments in the ore and the black schists likewise the drastically differing initial Pb isotope compositions do not favour sedimentary syngenesis. Some geochemical similarities, as e.g. the distinctly high As of both the ores and the adjacent black schists, and the high Hg of the gold in parts of the semimassive ore lenses, indicate that significant, probably syntectonic chemical interchange between the ore bodies and black schists may have been taken place. That such interaction has indeed taken place is supported by the variation of the Kylylahti ore sulphides in their Pb isotope composition from Outokumpu-type low <sup>207</sup>Pb/<sup>204</sup>Pb to black schist-like high <sup>207</sup>Pb/<sup>204</sup>Pb. Pb isotope data from the

interior parts of the relatively large deep ore lens suggests, however, that the primary metal

(Cu, Co) source cannot have been in the black schists (section 9.3.2.).

The present spatial organization of the Kylylahti mineralization is undoubtedly strongly affected, if not necessarily primarily controlled, by the late vertical fault(s) shaping the eastern margin of the host ultramafic massif. The control fault structure is clearly related to the several kilometres wide N-S "D2<sub>c"</sub> wrench (strike-slip) fault zone locating between Lake Viinijärvi and the Sotkuma "dome" (cf. Park and Doody, 1987). The entire kinematic history of the Kylylahti control fault is yet poorly understood, however, and difficult to study as currently observation only from drill cores (mostly unoriented) is possible. Therefore, it is impossible to say whether the D2c was the stage of the primary ore formation or just a stage of pervasive remobilization. That what is perfectly clear, however, is that the Kylylahti ore cannot represent an in situ sedimentary (exhalative or other type) sulphide accumulation; there are no syngenetic volcanic or sedimentary components in the host assemblage, and the structural evidence from the skarn-zone unambiguously demonstrates a syntectonic final-stage emplacement of the sulphides.

## 8.3.2. Sola

The Sola prospect locates ca. 7 km to the S of the above-described Kylylahti deposit, within the Sola serpentinite massiff at the eastern flank of the Outokumpu structure (Fig. 44). The geological environment at Sola is quite similar with that of Kylylahti, comprising a sizeable mass of antigorite serpentinite to talc-carbonate rocks, in two three lens like bodies fringed by thin zones of Outokumpu type carbonate-skarn-quartz rocks and enclosed in metaturbidite mica and black schists (Fig. 87). Drill profiles over the Sola complex indicate it would originate from a single sheet of serpentinite folded in relatively tight upright folds and then sheared to lenses along N-S trending nearly vertical fault planes, so that in its present surface pattern the complex now divides in three apparently separate lenses. A tiny semimassive sulphide concentration at ca. 0.1 Mt at 2 wt.% Cu, 1 wt.% Zn, 0.1 wt.% Co, 0.15 wt.% Ni and 17 wt.% S (Parkkinen, 1997) has been located within the relatively voluminous skarn-quartz rocks within the northern part of the westernmost of the main serpentinite lenses.

The three main lenses of the Sola complex all comprise antigorite±olivine±tremolite serpentinite and talc-carbonate rocks in their core parts and variably thick zones of Outokumpu-type carbonate-skarn-quartz rocks at their margins. The Outokumpu-type skarns are mainly carbonate-tremolite dominated, and only locally contain some diopside and/or uvarovite. Metabasite dykes, usually in a pervasively chloritized form, are fairy common in all the main lenses, especially in the westernmost lens, where the dykes locally account more than 20 % of the total rock volume. They are present in all the main lithologies of the Sola lenses, i.e. in the serpentinites, talc carbonate rocks as well as in their marginal zones of skarn-carbonate-quartz rocks. Twenty metres of medium to coarse-grained metagabbro enclosed in a skarn and talc-carbonate rocks are dissected by the hole Sola-28.

The westernmost of the Sola serpentinite-talc-carbonate lenses seems all over enveloped in a fairly continuous, a few metres to tens of metres thick shell of carbonate-skarn-guartz rocks. The tiny Cu sulphide showing discovered from Sola locates inside of a swelling of the carbonate- skarn-quartzite shell along the near vertical, about N-S trending eastern margin of the westernmost serpentinite lens (Figs. 87-88). Our review of drill core of this environment showed that the published resource estimate of the Sola "ore" (Parkkinen, 1997) has to be based on just one ca. 3 m long massive-semimassive sulphide intersection in the hole Sola-3/70.88-74.12, so it must be considered quite uncertain and optimistic. No description of the mineralization can be given as the relevant parts of the Sola-3 core have been completely utilized in previous studies. The tiny sulphide lens locates entirely inside carbonate-skarnquartz rocks, but noting that there are black schists just a few tens of metres above it, there is clearly the possibility that the sulphide lens represented materials displaced from an initial position between the rocks quartz

and black schists, i.e. as it seems typical of Outokumpu massive-semimassive sulphide lenses.



Fig. 87. A block diagram presenting surface geological map and hypothetical down plunge projection of the Sola massif, after Gaal et al (1975). The surface and hypothetical down-plunge projections of the Sola "Cu-ore" are shown by red dots, and the location of the cross-section profile 10.2 in Fig. 88 by a black line.

Weak, scattered copper mineralization appears to characterize the entire skarn-quartz rock shell around the W serpentinite body, but with the most notable pronouncements in the environment beneath the massive-semimassive lens at Sola-3.



Fig. 88. Cross-section profile 10.2 over the westernmost of the apparently three serpentinite lenses in the Sola massif, showing the location of the Sola massive-semimassive Cu-mineralization and other Cu-anomalous (typically 100-1000 ppm Cu) domains within the profile.

As noted above, there is no core left from the "Cu-Co ore" intersection in hole Sola-3. Corresponding Outokumpu drill core reports and assay data suggest it comprised of a vein or lens-like body of semimassive pyrrhotite with some chalcopyrite and little sphalerite in abundant quartz gangue. Further away from the supposed semimassive lens the Cu-Co-Zn mineralization occurs usually in form of weak sulphide (pyrrhotite+chalcopyrite+pentlandite±pyrite±sphalerite) disseminations and sulphide veinlets and shreds, usually in association with zones of increased quartz veining in the host skarn-quartz rocks. Local tattered Cu enrichments from 0.1-0.5 wt.% do occur almost all over the alteration shell of the westernmost serpentinite lens. As the intervening skarn-quartz rock domains are distinctly low in copper (<100ppm), its seems that the local copper sulphide enrichments would represent on overprinted feature, unrelated to the carbonate-silica alteration, or that there was effective mobilization of initially more evenly distributed syngenetic Cu sulphides in the now mineralised zones.

In addition to the Cu sulphide enrichments, the skarn-carbonate rock at the westernmost lens contains also scattered, thin (<15 cm) quartz-pyrrhotite veinlets that are low in Cu (<0.1 wt.%) and Zn (<0.01 wt.%) but distinctly enriched in Ni (0.5-1.0 wt.%). Compared to the chalcopyrite mineralizations, these Ni sulphide enriched veinlets are usually found in more inside positions of the alteration zone, and they are not associated with Co/Ni ratios significantly elevated above the background level. A third type of mineralization is found deep at the eastern margin of the lens, at the hole Sola-25, which dissects a Zn-dominated, partly semimassive sulphide concentration in a position between strongly sheared quartz rocks and blacks schists. In the best part of this mineralization, in ca. three metres of core (Sola-25/434.44-437.30), there is 1.73 wt.% Zn, 0.33 wt.% Cu, 0.24 wt.% Ni, 0.10 wt.% Co and 14.73 wt.% S.

Evidence for Cu-Co-Zn mineralization outside of the westernmost lens is scanty. Sola-27 dissects ca. 300 m below the central part of the complex a weak and scattered Cu mineralization in heterogeneous, partly vein-quartz-blotchy skarn-quartz rocks. In this showing within a 10m interval (Sola-27/ 482,65 - 492,40) there occur short parts (0.1-0.5m) at 0.1-0.5 wt.% Cu, but the average grades for the whole 10 m interval remain low (0.089 wt.% Cu, 0.064 wt.% Ni, 0.020 wt.% Co, 0.056 wt.% Zn, 2.02 wt.% S). In addition, the Sola-17 dissects at the western margin of the easternmost of the Sola main lenses, along a quartz rock–black schist interface, a semimassive Ni-Zn mineralization similar to the Ni-Zn mineralization at Sola-25. The best part of this mineralization (Sola-17/50.78-52.64) contains within ca. two metres 3.42 wt.% Zn, 0.33 wt.% Ni, 0.04 wt.% Cu, 0.004 wt.% Co and 20.17 wt.% S.

There was no data for gold available from Sola at the start of the GEOMEX project. As said above, any material from the massive-semimassive mineralization at Sola-3 was no more available for testing, but assaying for the low-grade Cu- and Zn disseminations in the Sola-3, and other above mentioned holes, suggests that there would be only little potential for Au. Namely, most of the analyzed samples contained less than 10 ppb Au. Maximum Au contents encountered by the GEOMEX exploration were from 29 to 259 ppb Au in hole R389 in the N-part of the complex, in a 5 m section of talc-carbonate rock with thin feather-joints filled by aphanitic antigorite and minor pyrrhotite+pentlandite+niccoline+safflorite (K. Västi, pers. comm., 2003). We note here that the talc-carbonate rocks in Kainuu-Outokumpu zone commonly show weak enrichment in Au and As, probably introduced in the synmetamorphic  $CO_2$  bearing fluids that were causing the talc-carbonate alteration.

# 8.3.3. Petäinen (Petäjäjärvi)

# Location and exploration history

The Petäinen (Petäjäjärvi) prospect is related to a small serpentinite lens ca. 10 km to the SW of the Liperi town. The serpentinite lens, about 0.5 x 2 km in its surface expression, is located for its most part below the small Lake Petäinen. Geologically the location is within the Kolehmala-Leppälahti-Petäinen serpentinite-black schist horizon (Figs. 44, 89), which defines the SE margin of the of the Outokumpu structure.

Outokumpu Company mapped the Kolehmala-Leppälahti-Petäinen zone in detail during 1950s. The mapping operation was conducted after outcrop and glacial-float observations for the zone indicated it was associated with Outokumpu type skarn-quartz rocks, and that these would comprise local Ni sulphide enrichments up to 0.5-1.0 wt.%. The Petäinen serpentinite in the SW end of the zone was observed a particularly promising target for Outokumpu type Cu and/or Ni. Between 1964 and 1978, in three main stages, 20 diamond drill holes totalling to 6416 m were drilled to test the prospect. Several of the holes intersected relatively thick Oku type carbonate-skarn-quartz rock zones within the folded and fault-imbricated serpentinite lens. Many of the holes intersected skarn-quartz rocks with scattered iron sulphide enrichments elevated in Ni, in many 5-10m intersections with up to 0.5 wt.% Ni, but without any significant Cu-Co enrichments.

It should be noted that during 1970s also the Malmikaivos Company intensively explored the Kolehmala-Leppälahti-Petäinen zone, mostly for the area between Leppälahti and Kolehmala. The company mapped this area in detail, made a number of exploration trenches at several targets, and drilled 10 diamond drill holes totalling to 1269 m. Like Outokumpu studies at Petäinen, also these studies failed to discover any Outokumpu type Cu-Co-Zn mineralizations. Only scattered, volumetrically insignificant Ni enrichments, similar to those observed by Outokumpu at Petäinen, were located within thin lenses of Outokumpu-type serpentinite-carbonate-skarn-quartz rocks both at Leppälahti and Kolehmala.



Fig. 89. Geological map showing the location and regional host environment of the Petäinen serpentinite body. The "sea" of metaturbiditic mica schists in which the small serpentineite bodies of the region are embedded, get migmatized SW of the line "MIGMATITES".

#### Geological environment

The Petäinen serpentinite lens is the south westernmost occurrence of Outokumpu assemblage in the "Sola-Kolehmala-Leppälahti-Petäinen zone" of serpentinite lenses and black schists at the SE margin of the Outokumpu structure (Fig. 89). The max. 500 m thick, 1.5 km long serpentinite lens dips at 60-70 degrees to the NW and seems to plunge at a shallow angle of10-15 degrees to the SSW. The rocks at the Petäinen area are near to upper amphibolite facies metamorphic grade; granitoid leucosome veining appears in the host metagreywacke gneisses some 5 km to the SW of Lake Petäinen.

In its general geology the Petäinen case is archetypical of Outokumpu-type prospects in North Karelia; an extensively carbonate-silica altered serpentinite lens enclosed in Upper Kaleva type metasediments (Figs. 89-90), in this case, however, in near migmatite grade mica and black gneisses. As most Outokumpu serpentinite massifs, also the Petäinen massif is a nearly pure mantle peridotite fragment. Besides serpentinite and its alteration products the lens irregular comprises minor only volume of pods and lenses of а anthophyllite±garnet±cordierite±corundum bearing amphibole-chlorite rocks, which probably are metamorphic products of chloritized basalt/gabbroic dykes. In the serpentinites, anthophyllite+enstatite+olivine is the typical peak-metamorphic mineral assemblage. All the peak phases show variably intensive retrogression to lizardite±chrysotile. Primary chromite is at Petäinen nearly totally recrystallized to secondary, spongy to chess-board-textured, high-Cr, low-Al chromite. Due to the relatively high-grade environment Outokumpu-type carbonate and skarn rocks comprise commonly olivine porphyroblasts and are recrystallized in coarse to very coarse grain sizes. The quartz rocks are also mostly distinctly coarse-grained and unusually whitish in colour.

# Metal content of the Petäinen serpentinites and Outokumpu-type metasomatic rocks

There does not exist much whole rock analytical data from the Petäinen ultramafic-derived rocks; those about dozen whole analyses made during this study indicate that the protolith peridotites were mostly very low in alumina ( $Al_2O_3 < 0.5 \text{ wt.}\%$ ) and thus of harzburgite-dunite origin. Based on the metal assay data by Outokumpu Company, Ni content in serpentinite samples is uniformly close to 2000 ppm, averaging to 2069 ppm with a standard deviation of 279 ppm (n=279). The average cobalt content being 87 ppm, this results a Co/Ni ratio of 0.042, which is slightly less than the 0.054 of primitive mantle. Abundances of Cu and Zn in the Petäinen serpentinite is 0.45 wt.% (n=146). The Co, Cu, Ni and Zn metal abundances are about what to expect for depleted mantle peridotite residua. However, the sulphur content is about 20 times higher than in mantle peridotites. As such high S in primarily very sulphur poor mantle peridotites must be of secondary, probably synmetamorphic origin, one could ask how much in the abundances of the chalcophile Cu and Zn were also by secondary addition. This is just to say that the very low abundances of Cu and Zn in the serpentinites may have been primarily even lower.

Compared to the serpentinites the Outokumpu type carbonate, diopside skarn, tremolite skarn and quartz rocks at Petäinen have somewhat lower average Ni abundances, 1623 ppm (n=44), 1623 ppm (n=64), 1224 (n=46) and 1876 ppm (n=299), respectively, and slightly higher Co/Ni ratios (0.046-0.056) but which are still close to the Co/Ni=0.054 of primitive mantle. However, the Oku-metasomatites are clearly enriched in both Cu and Zn compared to the serpentinites. The carbonate rocks and tremolite skarns show the highest average Cu and Zn abundances, with 123 ppm and 76 ppm of Cu, and 115 ppm and 129 ppm of Zn, respectively, while the average concentrations these metals in diopside and quartz rocks are clearly lower, 41 ppm and 56 ppm for Cu and 18 ppm and 25 ppm for Zn, respectively.



Fig. 90. Representative cross-section profile of the Petäinen prospect, schematically showing distribution of the tattered, low-grade (>0.3-1.0 wt.% Ni) Ni-enrichments observed in the profile. The profile modified after Huhma (1958), the inset map after Koistinen (1993).

# Outokumpu-type Co-Cu-Zn potential at Petäinen

The main reasons for the considerable exploration effort by Outokumpu company at Petäinen serpentinite obviously were: (1) the relative abundance of the Outokumpu-type carbonate-skarn-quartz rocks, (2) the local iron sulphide related Ni enrichments in the carbonate-skarn-quartz rocks, and (3) the local presence of chlorite+-anthophyllite rocks in association with the carbonate-skarn-quartz rocks, resembling those in the Keretti Co-Ni-zone.

The above-referred data show that on average basis the Petäinen carbonate-skarn-quartz rocks are not enriched in Co, Cu or Zn over the level typical of these rocks in the Outokumpu area, rather they are slightly depleted (cf. Table 4b). Moreover, in a Co/Ni diagram the Petäinen carbonate-skarn-quartz rocks are seen to plot more or less like the adjacent serpentinites (of mantle peridotite origin), showing no trend towards elevated Co/Ni typical of Outokumpu ore (Fig. 91). Actually none of the analysed 460 carbonate-skarn-quartz rock samples have a Co/Ni ratio elevated enough to indicate influences of Outokumpu type Co-Cu mineralization. Those few carbonate-skarn-quartz rock samples that show Co/Ni ratios over 0.1 are all samples abnormally low in Ni, but about "normal" in Co (compared to the main carbonate-skarn-quartz rock population). The samples in the Ni-richest (Ni>0.03 wt.%) quartz rock population have an average Ni content of 0.47 wt.% and an average Co content of 0.0171 wt.%, yielding a low average Co/Ni ratio of 0.037. These numbers bear a clear message of that the enrichment in Ni

in Petäinen quartz rocks is not associated with any relative enrichment in Co (same for Cu). Unfortunately there is only relatively little S data available from Petäinen rocks. The existing few data suggest that S and Ni contents would be strongly positively correlated, but with an associated negative trend in the sulphide phase Ni content. So, for example, the main population of the Petäinen quartz rocks (Ni 0.1-0.2 wt.%, av. sulphur content 0.79 wt.%) contains ca. 7 wt.% Ni in its sulphide phase, while in the Ni-richest (>0.3 wt.% Ni, average sulphur content 5.1 wt.%) quartz rock population has only ca. 3.5 wt.% Ni in its sulphide phase. In terms of Co, Cu and Zn the drop in the sulphide phase compositions with sulphur enrichment is even more pronounced.

Metal abundances in the locally occurring amphibole-chlorite schists are usually relatively low, too. Average metal concentrations based on the 44 samples analysed by Outokumpu Company are 47 ppm for Cu, 71 ppm for Co, 32 ppm for Zn, and 1094 ppm for Ni. Apart Ni, these are metal concentrations that one would expect for rocks of probable basaltic origin. The elevated Ni is most probably reflecting synmetamorphic diffusion from the enclosing serpentinites and skarn-quartz rocks. Six samples of particularly orthoamphibole-rich samples yield average metal tenors similar with the global averages of the chloritic metabasites: 78 ppm for Cu, 84 ppm for Co, 20 ppm for Zn, and 685 ppm for Ni. Average Co/Ni ratios for the dominantly chloritic and orthoamplibole-rich samples are 0.065 and 0.123, respectively. The low metal abundances and Co/Ni ratios (Fig. 91) clearly indicate that neither the chloritic nor orthoamphibole-rich rocks at Petäinen are associated with any copper-cobalt mineralization over the background.

The Outokumpu drilling at Petäinen prospect yielded seven 8 to 80 cm long intersections of semimassive pyrrhotite with minor pyrite and pentlandite, and which sections became classified by Outokumpu geologists to "pyrrhotite ore". Average Ni content for these seven samples is 0.69 wt.% and Co content 0.0298 wt.%, which yield on average Co/Ni ratio of 0.043 that is about exactly the Co/Ni ratio of 0.042 of the Petäinen serpentinites. One of these samples (Sr/Pe-4/232.32-232.50), is the only sample from Petäinen that has a Co content (766 ppm) and Co/Ni ratio (0.19) that deviate towards Outokumpu Co-Cu ore values, but even in this sample without any related elevation in Cu and Zn abundances or Cu/Ni and Zn/Ni ratios.

Overall, Petäinen is a good example of those many Outokumpu type prospects in the GEOMEX study area, which although comprising relatively abundant Outokumpu type carbonate-skarn-quartz rocks, nevertheless are barren of associated Outokumpu type Cu-Co-Zn mineralization. It cannot be overly emphasised that the Kokka-type Ni enrichments, frequent for these prospects, are not in Petäinen, nor elsewhere in the Outokumpu assemblage, associated with any metal trends towards Outokumpu type Co-Cu-Zn mineralization. The Kokka-type

Ni-enrichments rather seem to represent closed-system, probably syntectonic Ni and S redistribution within the carbonate-skarn-quartz rocks alteration shells, so that Ni+S enrichments in certain zones are balanced by depletions elsewhere. This phenomenon is well apparent in the Ni distribution of the large quartz rock data available from Petäinen (Fig. 92).



Petäinen, Co/Ni ratios

Fig. 91. Co versus Ni plot for the various rock types in the Petäinen massif. Note that there are no trend towards Outokumpu type Cu ore compositions in the Petäjäjärvi Co-Ni data despite of the plentitude of quartz rocks and occurrence of cordierite-anthophyllite rocks. This situation is annoyingly typical for many quartz rock rich but barren Outokumpu-type prospects, as e.g. in the Viurusuo-Juojärvi area SW of Outokumpu. Note that some of the amphibolite chlorite schists have Co-Ni contents similar of amphibolites and metagabbros as e.g. in the Miihkali massif.



Fig. 92. Histogram of Ni concentrations in quartz rock samples analysed from Petäinen. Based on AAS assay data of Outokumpu Company.

# 8.4. Miihkali structure

## 8.4.1. Saramäki

## Location, resource character and exploration history

The Saramäki prospect locates at the southern tip of the large Miihkali serpentine massif about 25 km to the NNE of Outokumpu (Figs. 44, 93). Though considerable in size, the Cu mineralization at Saramäki appears to be thoroughly of relatively low, by current measures uneconomic metal grade. Based on a tentative estimate by Saastamoinen (1972) referred by Parkkinen (1997), the economically most interesting part of the Saramäki deposit probably contains 3.4 Mt of mineralized rock with 0.71 wt.% Cu, 0.63 wt.% Zn, 0.05 wt.% Ni, 0.086 wt.% Co, 17.87 wt.% Fe, and 12.39 wt.% S. As a whole the mineralization, however, seems to contain at least 13.5 Mt tons of sulphide-mineralized rock with 0.36 wt.% Cu on average (Saastamoinen, 1972). The best individual sections include Jumi-27B/561.30-572.80 (11.50 m): 1.24 wt.% Cu, 1.31 wt.% Zn, 0.06 wt.% Ni, 0.32 wt.% Co and 24.6 wt.% Zn; and Jumi-60/743.95-752.68 (8.73 m): 1.13 wt.% Cu, 1.84 wt.% Zn, 0.07 wt.% Ni, 0.20 wt.% Co and 23.78 wt.% S. Though relatively low, these metal abundances, and the corresponding Co/Ni ratios clearly indicate that Saramäki deposit is an undoubted example of Outokumpu-type deposit (M. Huhma, 1969). The resource estimates of Outokumpu Mining do not include estimates for Ag and Au tenors, but a brief survey by GEOMEX suggests that the average Ag content of the massive-semimassive sulphides would be just 3-4 ppm, and that they would be relatively poor also in Au. The highest Au value of 20.5 ppb was observed for a particularly As-rich (864 ppm) semimassive ore sample.

The first indication of the deposit, which obviously has a surface outcrop in its SW tip, but which is covered by a relatively thick (>5 m) moraine blanket, was by a chalcopyrite bearing glacial float found in the late 1950s by a local resident. After several campaigns of boulder tracking, geological mapping, and geophysical survey in the years 1959-1967, the deposit was



Fig. 93. Geological map of the Miihkali massif showing the location of the Saramäki Cu deposit at its south tip. The Miihkali massif comprises mainly talc-olivine and olivine-carbonate-talc metaperidotites with some 5-30 vol.% component of metabasites, mostly as gabbroic dykes. There are antigorite metaserpentinites at the N end of the massif, and minor domains of carbonate-skarn-quartz rock alteration at Teerijärvi and Saramäki (Sara-aho) where the massif is more strongly tectonized and tectonically intercalated with black schists. Location of the cross-section profile 81.400 of the Saramäki Cu deposit in Fig. 86 is shown.

located by drilling in the year 1967. In the period 1967-1972 in total of ca. 15 km of diamond drill holes were drilled to outline the extent of the deposit. A few more holes were added during 1980s. As a result of this drilling the deposit can be said to be reasonably well outlined, and potential of yet undiscovered better ore in the prospected area must be considered low.

The past research of Saramäki deposit includes a study of its Ni-Co and Cu-Co distributions by M. Huhma (1969, 1972) and a master's thesis of its geology by Heinonen (1999). A brief general description of the deposit is included in Peltola (1978).

## Geological setting and deposit character

The Saramäki prospect is found at the very southernmost tip of the large, 15 km long and ca. 0.5 km thick, 40-50° E dipping sheet-like Miihkali serpentinite-mafite massif (Figs. 93-94). The Miihkali massif is exceptional among the Outokumpu massifs for its relatively high 5-50 vol.% mafic content, mostly as obvious gabbroic sills and dykes in the serpentinite and olivine blebby carbonate-talc rocks that are the main constituents of the complex. The deposit locates somewhat displaced of the S-end of the main Miihkali massive in a relatively thin (<50-100m), fault-controlled, 20-25 degrees SE dipping, and shallowly NE plunging horizon of highly tectonized black schists, tremolite-diopside-skarns and phlogopite-tremolite-carbonate rocks. In comparison of many other Outokumpu type prospects serpentinites are near absent at Saramäki; the mineralized zone contains only local thin slivers of mostly pervasively talctremolite altered ultramatic material. The sulphide mineralization shows the typical habitus of the Outokumpu type Cu-ores in North Karelia, being contained in an about 2 km long, 300 m wide and usually less than 20m thick sheet or ribbon of somewhat discontinuous, pinching and swelling sulphide concentrations (Figs. 93-94). The partly massive-semimassive, partly blotchydisseminated sulphide sheet has the same attitude than the controlling shear-fault zone, plunging at 25° to the NE and having a side inclination at 20-25° to the SE.

At the hanging wall of the sulphide sheet, there is a 20-80 m thick layer of highly tectonized, sheared black schists with abundant secondary tremolite-diopside±plagioclase, and carbonate-tremolite-phlogopite-chlorite "skarn" intercalations, which layer is in turn covered thickly by monotonous, pervasively schistose mica schists. At the footwall of the sulphide sheet, there is usually a thin (1-10 m) layer of black schist±tremolite±diopside skarn underlain thickly by monotonous mica schists. The country black schists, especially at the hanging wall of the sulphide horizon, are remarkably highly strained, pervasively schistose, and close to the sulphide horizon metasomatized to contain variably abundant microcline, tremolite and phlogopitic biotite. The most strongly sheared/altered black schists are often distinctly lightened in colour and show brownish to greenish hue depending on variation in abundance of secondary phlogopite and tremolite.

The massive-semimassive parts of the mineralization are mostly hosted in a 5-25 m thick layer of carbonate+tremolite±mica rock with portions of greyish, relatively coarse-grained, grain-size banded quartz+-diopside+-tremolite rock. The quartz-rich parts that contain some of the best Cu-enrichments in the deposit show features suggesting vein-type rhythmic deposition of quartz and sulphides. The "ore quartzite" frequently contains some graphite, in thin stylolite-like seams and roundish up to 1 mm size balls of probable silicified bitumen. Considerable part of the metal content of the Saramäki deposit is in sulphide veinlets, blotches and disseminations in the ore-zone carbonate-skarn rocks and to a lesser extent in black schists immediately flanking the semimassive lenses. The basic sulphide mineral assemblage in the Saramäki mineralizations is simple: pyrrhotite±chalcopyrite±sphalerite. There is relatively more chalcopyrite in the dominantly quartz-hosted ore parts while sphalerite is more typical of the sulphides with skarn-carbonate gangue. Accessory sulphides include arsenopyrite, cobaltite, Co-pentlandite and pyrite.

The Cu content of the sulphide phase in the Saramäki mineralization is ca. 2 wt.%, i.e. rather low compared to that of 8 wt.% in the prototype Outokumpu ore. The Co content in sulphide phase reaches ca. 0.4 % while that of Ni is on average ca. 0.2 %; these are both



Fig. 94. Cross-section profile 6981.400 of the Saramäki deposit. The deposit is located within a zone of tectonically intercalated thin sheets and lenses of extremely strained, partly mylonitic metabasite, black schist and some Outokumpu-type carbonate-skarn rocks. The mineralization is confined within a layer of dark to pale gray calcite-dolomite rock, locally replaced by quartz (probably originally veins) comprising some of the Cu-richest part of the deposit. Intriguingly, the Cu-deposit has exactly the same strike oriantation than the Outokumpu, Vuonos and Luikonlahti deposits suggesting a similar tectonic control of the final sulphide placing. The NE-looking profile is based on Outokumpu drill core reports, and a review of most of the included cores by the first author.

values rather typical of Outokumpu type sulphides (Huhma, 1969, 1972). Based on the GEOMEX data, Saramäki sulphides would contain about 50-60 ppm Mo, which is considerably more than the 19 ppm on average in the Outokumpu main ore. The Saramäki massive-semimassive sulphides show scattered enrichment also in As, in individual samples up to 500-1000 ppm, although usually As is present only in relatively low concentrations below 15 ppm. We attribute the uniformly relatively high Mo and sporadically high As in the Saramäki sulphides to syntectonic-metamorphic interaction with the adjacent black schists, usually enriched in these elements. Notable features of the Saramäki semimassive sulphides are their surprisingly low Cd, less than 10 ppm on average basis, and low, upper crust-like concentrations of Sb and Bi. The Pb concentration in Saramäki ore is very low, overall below 5 ppm; similar very low Pb seems a frequent feature of the higher metamorphosed Outokumpu sulphides.

The skarn layers in the black and mica schists above the Saramäki sulphide horizon are for most part, though not exclusively, plagioclase-bearing, and were considered by Huhma (1969) to represent metamorphosed calcareous facies of the country black schists. This is probably true for most of the graphitic or carbonate-rich and plagioclase-poor diopside+tremolite skarn variants. However, there are also abundant layers of plagioclase-rich variants that grade to amphibole-chlorite schists and that exhibit clear metabasaltic chemical compositions with high Al, Sc, V, and which thus more likely represent intercalations (tectonic?) of calc-silicate altered metabasite. The low Ti and Zr, and relatively high Cr of these metabasites indicate correlation with the low-Ti type basites within the serpentinites of the adjacent main Miihkali massif.

# Ore genetically noteworthy aspects

Outokumpu-type ultramafic or metasomatic ultramafic rocks are a distinctly rare component in the Saramäki assemblage. Closely associated with the ore horizon proper, there occur only thin (<10m), narrow lenses of tremolite+carbonate+talc schists, schistose tremolite skarns and phlogopite-carbonate rocks that are high in Cr and contain chromite, and which thus could represent altered, metasomatized peridotite. Though for most part low in Cr and thus probably black schist related, there are also high–Cr carbonate-skarn rock in the Saramäki assemblage, and that obviously represent Outokumpu type carbonate-skarn rocks. Importantly, however, any candidates for clear quartz-rocks of Outokumpu-type are absent. Banded quartzrich rocks hosting some of the best parts of the mineralization are in some of the old exploration reports considered Outokumpu type quartz rocks, but for such they are far too low in Cr (<<100 ppm). These "quartzites" are extremely low also in Ti, Al, Na, K, Mn, Rb, Zr and Y, which excludes their origin as epiclastic guartzites or cherts (cf. analysis data in Appendix 1 of Heinonen, 1999). Most probably these banded sulphidic "quartzites" represent rhytmically deposited guartz veins, or structurally controlled silica replacement. We note that also Huhma (1969) in his study of base metal ratios in Saramäki favoured an origin of the Saramäki "orequartzites" as quartz-vein materials rather than Outokumpu-type "chromian quartzites".

To summarize, the Saramäki deposit appears a quite distinctive case among the Outokumpu deposits. Connection to the Outokumpu assemblage is only weak, and the mineralization appears particularly clearly as a fault-controlled sulphide-quartz vein-type deposit. On the other hand, in its scarcity of ultramafic rocks the Saramäki appears a possible intermediate case between the Outokumpu (large volume of Outokumpu assemblage) and the Riihilahti (no Outokumpu assemblage at all) "end member" types of the Outokumpu mineralizations.

## 8.5. Kaavi structure

# 8.5.1. Luikonlahti

Location, exploration history and previous study

was largely drained in 1967 as part of the mine development.

Huopaniemi (1998) describes in detail the exploration history of the Luikonlahti mining camp and Tyni (1998) that of the Luikonlahti mine development. According to notes of Huopaniemi, first exploration efforts and official claims in the Luikonlahti area were done, by Hackaman & Co, already during the 1910s, after the find of Outokumpu ore. But it was just in the year 1929 when the first discovery of Outokumpu type Cu-Zn-Co sulphide mineralization of economic promise was made. Dr Heikki Väyrynen from the Geological Survey of Finland (Geologinen toimikunta) did this find, form a shallow exploration trench dug by spade men. The exploration work in the following two years outlined a small massive-semimassive Cu-ore body, later known as the Pajamalmi ore. The main Luikonlahti ore body, the Asuntotalo ore, was found 6.6.1944 by Erik Munsterhjelm who worked for Ruskealan Marmori in an exploration project lead by Dr Martti Saksela. He made the discovery find from an outcrop of massive sulphide that he had exposed near the S-shore of the Palolampi pond, from beneath a thin cover of rusty soil – using a spade. The distinctly rusty colour of the soil covering the outcrop had fixed attention of "Iso-Erik" (Big-Erik), who had previous exploration experience in Canada, wherefrom he had come to Finland, initially to do his military service as a Finnish citizen. By 1947 a resource of ca. 1.5 Mt ore had been outlined at the Asuntotalo showing, but which was considered uneconomic owing to the low Cu-grade and then poor accessibility of the occurrence. It was just ten years later, in the year 1958, when the whole depth extent of the Asuntotalo occurrence became apparent, as a result of a new drilling program by Malmikaivos Oy, in an operation managed by Erkki Heiskanen. A small satellite deposit at Kunttisuo had been located by drilling in the previous year 1957. The decision to open a mine and concentration plant at Luikonlahti was made in the year 1965. The first batch of copper concentrate was produced 1968. Mining at Luikonlahti came to an end in 1983 after utilization in total of ca. 6.85 Mt of ore (Tyni, 1997). The concentration plant is still in function producing talc concentrates.

During 1960s the geology and petrography of the Luikonlahti complex was described in several university thesis, as e.g. in those by Vorma (1956), Saikkonen (1962), Turkka (1962), Sarikkola (1963) and Björnberg (1965). Merkle (1978) provides a detailed study of the mineralogy and mineral chemistry of the Asuntotalo ore. Ruotoistenmäki (1978) has studied chemical aureoles around the sulphide bodies. Park (1988) has done a structural analysis of the Luikonlahti complex and its surroundings. Recently Takala (2002) has studied the petrography and geochemistry of the metabasic rocks in close proximity to the ore in the middle part of the Luikonlahti complex.

## Geological setting

The Luikonlahti deposit occurs within a serpentinite massif close to the contact between the SE margin of the Kaavi thrust structure and the NE margin of the Maarianvaara granite complex (Figs. 44, 95). The ca. 1.7 km long, 0.5 km wide, and at least 750 m deep, peanut shape serpentinite massif is enclosed in a horizon of carbonate rock-intercalated black schists in the Upper Kaleva-type gneissic monotonous greywackes of the Kaavi structure (Figs. 95-96). The host black schist horizon runs form Luikonlahti towards Petronlampi in the NNE but gets there rapidly thinner and free of serpentinite lenses. In the W-SW the black schist horizon seems to ramble towards the Hoikka mineralization (Fig. 95). Sheets and dykes of granite form the nearby



Fig. 95. Geological setting of the Luikonlahti, Hoikka and Kokka serpentinite bodies with Cu and/or Ni mineralizations. The rocks listed in the left column of the legend are of Upper Kaleva affinity, wheras the metasedimentary and metaigneous schists in the right column are probably of Lower Kaleva status. Abundant granite veining in the area W of the dashed red line. Location of the Hippos Cu-showing is shown by a star. The area covered by the map of the Kokka prospect area in Fig. 106 is indicated by a box. Modified after Huhma (1971).

1857±8 Ma (Huhma, 1986) Maarianvaara batholith criss-cross with sharply cutting contacts through the serpentinite massif, the ore and the surrounding mica and black gneisses (Figs 97-99). Many of the thicker granite sheets appear to be approximately subhorizontal. The known ore bodies and the mine development terminated to one such apparently subhorizontal major granite sheet below the 450 m depth level.

The main rock types in the interior parts of Luikonlahti serpentinite massif are tremoliteolivine and anthophyllite-enstatite-olivine metaperidotites showing extensive retrograde alteration to lizardite-chrysotile serpentinite. The peak-metamorphic assemblages of the ultramafic rocks and incipient melting in the enclosing metasediments indicate metamorphic peak temperatures at Luikonlahti exceeded 650 °C (Säntti, 1996). Evaluation of surface maps and cross-section diagrams of the massif and our own observations from drill cores show that it was wholly enveloped by a thin shell of Outokumpu type metasomatic carbonate and skarn rocks (Figs. 96). In most cases the original rock succession in the alteration sequence is disturbed by the deformation of the serpentinite massif about SW trending upright to slightly NW dipping tight folds, and the associated axial plane parallel imbrication and shearing; all this resulted in local infolding and wedging of the enclosing sedimentary rocks inside the serpentinite massif. Especially strong tectonic mixing is apparent for the S margin of the complex hosting the main Asuntotalo ore body. Park (1988) addresses most of the deformation of the Luikonlahti assemblage to regional "D2" thrusting and related local sheath fold propagation.

The Outokumpu type carbonate rocks at the margins of the Luikonlahti massif are typically olivine porphyroblastic, chromite-bearing and often show beautiful, decorative bladed to granoblastic intergrowths of olivine and carbonate (Figs. 34, 97). Complexly branching networks of typically 0.2-2 m thick veins and patches of bright green, coarse-grained diopside±tremolite±uvarovite "skarn" occur in the carbonate rocks and concentrated long the contacts between the carbonate rocks and serpentinites. Importantly, quartz rocks, similar to those ubiquitous e.g. in the Outokumpu and Vuonos massifs, are in the Luikonlahti massif relatively rare. This seems to be the situation in most of the serpentinite massifs in the Kaavi structure. In a review of some 20 holes from Luikonlahti for this study, many of the rock intervals named to quartz rocks in the Malmikaivos drill core reports turned out to be pale grey, phlogopitized and sulphidized arkosic and quartz wacke schists, or very coarse-grained vein quartz developments around the ore lenses or as to lateral extensions to them. Only in the Tirronen area, in the SW tip of the complex significant volumes of highly recrystallized, coarse-grained quartz rocks seem to be present.

The assemblage of the Luikonlahti massif is complicated by the occurrence of plagioclase bearing, diopside-tremolite rich skarnoid metabasites, most abundantly along the tectonically complex southern margin of the serpentinite massif. The most voluminous of the skarnoid units is the synformal "central-skarn" in the middle part of the complex (cf. Fig. 96). Whole rock chemical compositions of the skarnoid metabasites indicate their origin as metagabbroic and/or basaltic rocks of E-MORB tectonomagmatic character (cf. section 6.3.2.; Takala, 2002). The most diopside rich and plagioclase poor variants of the "sterile skarns", as the miners called the skarnoid metabasites, are sometimes difficult to distinguish from the "fertile" Outokumpu type skarns. This is because of their often relatively high Cr, causing bright green colours for the secondary diopside and tremolite, which is a typical feature of many Outokumpu type skarns. The maps and cross-section diagrams of the Luikonlahti massif produced by Malmikaivos Company reflect this difficulty, and often lump all the "skarns" in one single category, which considerably lessens the applicability of this material in detailed analysis of the internal structure of the Luikonlahti massif and exact lithologic association of the included ore bodies. An additional confusing element is that there occur, especially along the S-margin of the massif, also carbonate and calc-silicate rich units, which are not ultramafite-derived but are related to the black schists of the enclosing sedimentary assemblage. Metamorphosed in middle to high amphibolite facies conditions, also these carbonate rocks tend to show (serpentinized) olivine porphyroblasts, and may thus be confused with the (olivineporphyroblastic chromian) carbonate rocks of the Outokumpu type.


Fig. 96. Geological map of the Luikonlahti massif. Outlines of the Asuntotalo and Pajamalmi open pits (bold dashed line) and the surface projections of the Kunttisuo and Tirronen sulphide rods (white with black hatching) are shown. The map is drawn on the basis of unpublished maps and other data of the Malmikaivos Company.



Fig. 97. Scanned image of a sample of pyrhotite disseminated olivine-carbonate rock typical of the carbonate-skarn zones in the Luikonlahti massif. Dark green=serpentinized olivine, pale grey=carbonate, brown=pyrrhotite.

## The main ore bodies at Luikonlahti

There are three separate Co-Cu-Zn sulphide bodies in the Luikonlahti massif that have been mined in the past. All these bodies are closely associated with the narrow carbonate-skarn fringes that are folded/imbricated surrounding the serpentinite massif, usually in positions where the carbonate-skarn fringes are flanked by thick layers of distinctly graphite-sulphide rich black schist (Figs. 97-99). In total ca. 6.4 million tons of massive-semimassive sulphide was mined from the main Asuntotalo body at the SE margin of the complex. The ore contained in average 0.99 wt.% Cu, 0.11 wt.% Co, 0.1 wt.% Ni, 0.5 wt.% Zn and 16.5 wt.% S (Parkkinen, 1997). The other mined bodies, the Kunttisuo within the NW margin of the complex, and the Pajamalmi above the W part of the Asuntotalo ore, produced ca. 0.35 Mt and ca. 0.14 Mt of mainly massive-semimassive ore, respectively. The pay metal grades in these two lesser deposits were somewhat lower than in the Asuntotalo ore. In addition, a low-grade Cumineralization is known to occur within the carbonate-skarn-quartz rocks fringing the serpentinite complex at its SW tip in the Tirronen area, and minor showings also in the small carbonate-skarn-quartz rock occurrence at the NE corner of the Petkellahti bay (Fig. 96).

There are no published data for precious metal grades in the Luikonlahti ore bodies. Seventeen representative samples of massive-semimassive ore samples analysed during this study, most of them from the Asuntotalo ore, suggest that the average Ag content was ca. 5 g/t and that of Au negligible (systematically <10 ppb).

#### Asuntotalo ore

The overwhelmingly most important ore body at Luikonlahti was the Asuntotalo ore within the SE margin of the Luikonlahti massif (Figs. 96, 98-100). The NE-SW striking Asuntotalo body had a form of a near vertical standing, down-bowing boomerang with a total length of ca. 700 m. The both tips of the boomerang were exposed at the surface while the lower edge of the middle part reached a depth of ca. 480 m. In its middle part the ore sheet was ca. 200-300 m high and at best some 80 m thick. In many vertical cross sections the ore showed a tendency to two or more main vertical lenses one on top of each, separated by isthmus of barren or weakly mineralized (disseminated) "quartz-rock" in between (cf. Figs. 98, 100). Many veins and sheets of the Maarianvaara granite dissected the ore body with sharp contacts, locally engulfing bocks of it as xenoliths.

The lower edge of the middle part of the Asuntotalo ore occurred broadly taken between serpentinite and back schists in the NW, and between serpentinite and mica schists in the SE. There was usually a thin layer of schistose Outokumpu-type tremolite skarn in between the ore and the serpentinite, and a layer of diopside±tremolite skarn in between the ore and the country metasediments, though in many places the intervening skarn layers were missing and the ore was found in direct contact, in the NW against serpentinite, and in the SW against the country metasediments (usually against black schist but also mica schist/gneiss). In a notable difference to this basic setting, in the NE end of the ore sheet, its upper edge was for large part between the "sterile" skarnoid metabasites (diopside±tremolite±plagioclase) and Outokumpu-type diopside±tremolite±uvarovite skarns. The terrain immediately to the SE from the Asuntotalo ore zone is relatively scantily drilled and thus leess perfectly known. Based on maps of Malmikaivos Company, next SE of the ore zone there is a 50-100 m thick horizon of intercalated metasedimentary carbonate rocks, calc-silicate rocks and black schists, and then further in the SE dominantly mica gneisses.

Compared to the two other Outokumpu type Co-Cu-Zn deposits mined in North Karelia, i.e. Outokumpu and Vuonos, the environment of the Asuntotalo ore body is distinctly poor in Outokumpu-type (metabirbiritic) quartz rocks. Recalling that a considerable part of the skarns and carbonate rocks, especially along the SSE margin of the complex, actually are skarnoid metabasites and black schist related metasedimentary carbonates and calc silicates, even the volume of true ultramafic derived carbonate and skarn rocks seems relatively low for an Outokumpu-type environment.

The sedimentary origin of many of the relatively plentiful "ophicarbonates" at Luikonlahti is seen in their elevated Al<sub>2</sub>O<sub>3</sub> (3-7 wt.%), TiO<sub>2</sub> (0.2-0.6 wt.%) and Zr (10-40 ppm) contents attesting to presence of a significant epiclastic component. The moderately high chromium (<100-600 ppm) of these carbonate-skarn rocks more probably reflects synmetamorphic hydrothermal addition from the juxtaposed ultramafic rocks than a presence of "primary" chromite. A similar assemblage of both Outokumpu type ultramafite-derived carbonates and metasediment-related carbonates was in this study observed also in the environments of the Kylylahti, Saramäki and Hietajärvi deposits. It is also worth to note that the Luikonlahti "ophicarbonates" are often dominantly calcitic, as are e.g. the black schist-intrercalated metasedimentary carbonates at Kylylahti, not dolomitic as the Outokumpu type ultramafic rock derived carbonate rocks tend to be (irrespective of metamorphic grade).

Major part of the ore occurred in sharply bound semimassive-massive lenses sulphide and quartz, though there locally occurred also ore-grade disseminations, usually at the immediate contacts of the massive-semimassive lenses, typically in carbonate and calc-silicate rocks, but locally also in coarse-grained "quartz rocks". The main semimassive lenses showed frequently a Fig. 98.



Fig. 98. Cross-section profile 178 of the the Luikonlahti massif showing the Asuntotalo (on the right) and Kunttisuo ore bodies (on the left). For location of the NE-looking profile see Fig. 96. After unpublished data of Malmikaivos Company and drill core reviews of the present authors.



Fig. 99. Cross-section 194 of the the Luikonlahti massif showing the Asuntotalo (on the right) and Kunttisuo ore bodies (on the left). For location of the NElooking profile see Fig. 96. After unpublished data of Malmikaivos Company and drill core reviews of the present authors.



Fig. 100. Cross-section profile 210 of the the Luikonlahti massif showing the Asuntotalo (on the right) and Kunttisuo ore bodies (on the left). For location of the NE-looking profile see Fig. 96. After unpublished data of Malmikaivos Company and drill core reviews of the present authors.

few decimetres to a couple of metres thick quartz-rich selvages, in which the gangue quartz was usually coarse to extremely coarse and sulphide content often quite low, often just a few vol.%. It must be stressed that these quartz selvages were mostly low to very low in Cr and did not contain chromite, and that they thus unlikely represented metabirbiritic quartz rocks as in the Outokumpu assemblage. We recall that also in Outokumpu (Keretti) and Vuonos the ore lenses commonly had similar quartz-rich selvages, and which in many cases had similarly knife-sharp contacts against the wall rocks (metabirbiritic quartz rocks, black schists, mica schists etc.).

Asuntotalo ore was dominantly pyrrhotitic and with quartz as the main gangue mineral. Only a few, scattered patches of pyrite-rich ore were present (Matti Tyni pers. comm., 2000). About 40 vol.% of the ore contained, but quartz, also diopside and tremolite as abundant gangue. The diopside-tremolite rich ore was locally variably rich in coarse-grained magnetite. Reflecting regional peak-metamorphism at kinematically static conditions in temperatures exceeding 650 °C, the main pyrrhotitic ore type had a massive texture characterized by granular-graphic intergrowth of relatively coarse-grained (1-5 mm) guartz and sulphides (Fig. 101). The local pyrite-chalcopyrite patches contained coarse-grained Co-pyrite porphyroblasts in massive, coarse-grained chalcopyrite (Fig. 102). Merkle (1978) reported that he observed layering that possibly could be of sedimentary origin only in one of the 12 representative samples he had from the Asuntotalo ore. The contacts between the ore lenses and wall rocks were mostly very abrupt, often "knife-sharp". During this study such knife-sharp contacts of ore were observed against serpentinite, carbonate and calc-silicate rocks, black schists and mica schists. No evidence of sedimentary syngenesis, such as interbedding of the ore and sedimentary wall rocks, was observed in any of the drill core sections reviewed from Luikonlahti during this study.

Merkle (1978) provides a thorough ore-mineralogical study of the main semimassivemassive quartz+sulphide type ore in the Asuntotalo body. Based on ore optical and electron microprobe study of 39 polished sections on 12 ore samples he reports the following average composition: 47.3 vol.% gangue (mostly quartz), 42.9 vol.% pyrrhotite, 6.6 vol.% chalcopyrite, 1.4 vol.% sphalerite, 0.38 vol.% pentlandite and 1.5 vol.% minor ore constituents as e.g. pyrite, magnetite and graphite. Because the "besonderes erzeiche" nature and small number of samples included, this average cannot be considered as a representative average composition of the whole Asuntotalo ore, but rather a characterization of some best parts of the ore. Minor ore minerals observed by Merkle (1978) include (in alphabetical order): alabandite, cobaltite, chromite (zincian, chromite occurred in one sample only!), cubanite, gahnite, galena, hessite (Ag<sub>2</sub>Te), ilmenite, native lead, mackinawite, molybdenite, stannite, (Ag)pentlandite, (Co) violarite and uraninite. Most of these minerals occurred only in trace amounts, and many only sporadically. Interestingly, Merkle observed small balls (20-120 µm) of Si-C rich material, or "thucholite", enclosing small grains of uraninite and sulphides (chalcopyrite, pyrrhotite, mackinawite), fairly common as inclusions in the gangue diopside and seldom also in sulphides. Merkle (1978) argued the tucholite balls had an origin as microorganisms. Calcsilicate rich parts of the ore showed basically the same sulphide mineralogy as the common quartz+sulphide ore. These ore parts were, however, usually relatively richer in sphalerite, and especially magnetite, which locally was quite abundant (up to 10-40 vol.%). Locally the sulphide ore was flanked by near 100% Cu poor magnetite ore whose origin and relation with the sulphides is yet open.

The obvious discordant, dyke-like nature of the Asuntotalo ore sheet imply its origin either by (1) pervasive, perhaps repeated, mechanical or hydrothermal mobilisation and relocation of sulphides from some pre-existing proto-ore, or (2) by precipitation of quartz+sulphides directly into the vein-like ore bodies. Either way, the final emplacement of the ore materials must have been structurally a relatively late process. Unfortunately, the kinematically late, static hightemperature peaking of the regional metamorphism and related pervasive recrystallization of the Asuntotalo and other Luikonlahti ore bodies has completely destroyed the evidence that could help to make the selection which of the two hypothesis would the more probable one.



Fig. 101. Scanned image of typical Luikonlahti sphalerite-chalcopyrite-pyrrhotite ore. Note the relatively coarse-grained granoblastic-graphic intergrowth of the sulphides and quartz gangue. Width of the slab ca. 85 mm.



Fig. 102. Scanned image of chalcopyrite-pyrite ore from Luikonlahti, showing large metamorphic Co rich pyrite cubes in massive chalcopyrite. The dark patches interstitial of the sulphides comprise mainly graphite. Width of the slab ca. 12 cm.

## Kunttisuo ore

The Kunttisuo ore bodies are found partly inside, partly flanking the thin fringe (10-40m) of Outokumpu type carbonate and skarn rocks at the NNW margin of the Luikonlahti serpentinite massif (Figs. 96, 98-100). The mineralization is most substantial for its NE end, at Kunttisuo, where it forms an up to 30m high and 10 m thick steeply NW dipping lens between the serpentinite massif and a thick volume of black schists to the NW of it. To the SW of Kunttisuo the lens bifurcates into two rods, one plunging ca. 10 degrees and the other ca. 40 degrees to the SW, resulting in a two-forked structure reminiscent of pine-leaf. The two thin sulphide stripes or rods have down-plunge continuation for at least 500 m. The plane of the rods dips ca. 75 degrees to the NW subparalleling the contact of the serpentinite massif. Many dykes of the Maarianvaara granite intrude and crosscut the mineralization.

Interiors of the main Kunttisuo sulphide lens comprise semimassive to massive sulphide with relatively coarse-grained gangue of granoblastic quartz ±tremolite±diopside. The ore shoots frequently show decimetres to several metres thick quartz-rich and relatively sulphide-poor marginal selvages. The sulphide mineralogy of the Kunttisuo ore bodies is fairly simple as other species but pyrrhotite, chalcopyrite and minor sphalerite are very rare. Granoblastic-graphic intergrowth of 1-5 mm quartz and sulphide are characteristic of the ore textures.

Although the spatial arrangement of Kunttisuo ore bodies is clearly controlled by the carbonate-skarn rich alteration fringe of the serpentinite massif, they nevertheless do not show any clear evidence of syngenesis with any of the host rocks, but rather seem to represent kind of sulphide-quartz rich segregations or veins within the bounds of the alteration fringe. Evidence for an epigenetic, or at least pervasively remobilised nature of the Kunttisuo mineralization include e.g. that the ore stripes are found to project, apparently unfolded and with abrupt, sharp contacts through such a genetically, and in formation age highly varied rock collection as serpentinized metaperidotite, Outokumpu-type carbonate-skarn rocks, black and mica gneisses. In Outokumpu context another notable feature is that, as in the Asuntotalo ore environment, true Outokumpu-type (metabirbiritic) quartz rocks are surprisingly rare in the Kunttisuo host rock assemblage. Especially rare they are if the usually Cr-poor, quartz-rich selvages of the ore lenses, which unlikely represent silicified ultramafic rocks, are excluded.

The black gneisses/schists to the NW of the Kunttisuo ore are strongly deformed and recrystallized and have lost most of their primary sedimentary features. Sulphides extensively

remobilized in centimetre-scale irregular blotches and veinlets of coarse pyrrhotite±pyrite±sphalerite±chalcopyrite, and fine flaky graphite, are plentiful and attest to particularly sulphide and carbon-rich nature of the protolith black shales. In drill cores from the black schists intervals rich in quartz and plagioclase, or in coarse tremolite sheaves, are common, indicating presence of sandy and calcareous interbeds, respectively.

We observed a significant increase in the chalcopyrite content in the black gneisses at the immediate ore contacts, but yet no evidence of sedimentary or other type grading from the black gneisses into the ore. Instead in all those drill core sections where we observed the ore and black schists in direct contact, the contacts appeared all the way very sharp and suggestive of "intrusive-like" emplacement of the ore materials.

## Pajamalmi ore

The Pajamalmi ore refers to a small body of nearly vertical lenses of massive-semimassive sulphides ca. 50-70 m above of the SW part of the Asuntotalo ore (Figs. 96, 98). The original volume of the Pajamalmi bodies is not known as the mineralization is clipped by the present erosional surface. Geologic setting of the Pajamalmi ore lenses appears quite complex in fine detail as it seems that considerable part of the ore lenses located, instead of Outokumpu type "fertile" skarns", inside the basite-derived "sterile skarns" or plagioclase-hornblende-diopside rocks as locally common in the Luikonlahti massif. The main part of the Pajamalmi ore comprised massive-semimassive ore, largely similar to that in the above described Asuntotalo and Kunttisuo bodies. Cross-section maps and drill core reports of Malmikaivos indicate that there was, below the massive-semimassive lenses, a body of lowly copper mineralised, phlogopite-biotite-rich skarns grading in places to monomineralic mica rocks. These rocks appear genetically interesting, but since no relevant core could be located in the Luikonlahti depot, we could not study them.

### Tirronen mineralization

The environment of the Tirronen mineralization at the SW end of the Luikonlahti massif (Figs. 96, 103) is distinctive from that of the other sulphide occurrences at Luikonlahti as it comprises, in addition to the Outokumpu-type type carbonate and skarn rocks, also abundant Outokumpu-type quartz rocks (metabirbirites). The main sulphide body in the Tirronen mineralization consists of an at least 400 m long rod of small discontinuous, mainly semimassive sulphide concentrations and disseminations, mostly located within Outokumpu-type carbonate-skarn-quartz rocks between the serpentinite massif and flanking black schists. This sulphide rod or pipe has a moraine covered small surface exposure at the eastern slope of the Tirrosenmäki hill, wherefrom it plunges at an angle of about 45 degrees towards the NNE and apparently finally below the Petkellahti bay of Lake Retuisjärvi. The drilling data suggests the main sulphide pipe would continue to the NNE at least some 400m. Looking at the down plunge extensions, there is the possibility that Tirronen and Kunttisuo sulphide rods could actually join at the depth of ca. 500-600 m below the Petkellahti bay.

### Ore genetically noteworthy aspects

The Luikonlahti complex provides at first sight an excellent example of Outokumpu-type environment and associated sulphide ore formation. There is a sizeable serpentinized mantle peridotite body that shows thin metasomatic alteration fringe practically speaking all around its margins and several load-like Co-sulphide accumulations within this alteration fringe. However, much of this excellence is spoiled by the high metamorphic grade of the complex. The stable



Fig. 103. Cross-section profiles 420, 500 and 580 of the Tirronen mineralization at the SW corner of the Luikonlahti massif. For location of the profiles see Fig. 96.

occurrence of assemblage enstatite-anthophyllite-olivine in the metaperidotites indicates temperatures of at least 650 °C; spinel-olivine thermometry yields (post peak cooling)

temperatures between 650-680 °C. These are values consistent with the incipient partial melting and related throndhjemite leucosome veining of the metagreywackes surrounding the Luikonlahti complex.

Because of the high temperature peakmetamorphism, the textures of the Luikonlahti sulphides are thoroughly metamorphic and no prepeakmetamorphic features preserve. Merkle (1978) correctly points out the pervasive metamorphic status of the Asuntotalo ore, which he considered remobilized and recrystallized, possibly in several stages ("vermütlich mehrmals mobilisiert and rekristallisiert"). We fully agree with this statement; there is little question about the late, structurally controlled nature of the Luikonlahti quartz-sulphide shoots.

The Luikonlahti deposit is one of those Outokumpu deposits that irresistibly tempts one to think about the possibility of metal source in the serpentinite massif (or in the surrounding black schists) and diffusive, or perhaps some sort of electropotential early synmetamorphic concentration of the metals to form sulphide concentrations between the metasomatically altered serpentinite body margins and flanking sulphidic black schists, the latter providing the sulphur source. Subsequent syntectonic remobilization of the early sulphides could then have formed those distinctly epigenetic quartz-sulphide lodes and rods that these ore bodies now form. Unfortunately, study of this, or any ore genetical hypothesis for Luikonlahti, is seriously hampered by the apparently through late metamorphic remobilization, recrystallization and reequilibration of the sulphide bodies.

Origin of the Luikonlahti sulphide ores as volcanic-exhalative accumulations on the seafloor have been proposed, and the cordierite-anthophyllite and skarnoid mafic rocks of the complex considered volcanic rocks altered in related fluid upflow channels and the source wherefrom the ore metals were leached (e.g. Park, 1988; Takala, 2001). However, the total volume of mafic rocks in the Luikonlahti complex is far too small to represent a relevant source of all of the metals in the ore bodies. Moreover, anywhere in the Luikonlahti complex these rocks are rather strongly enriched than depleted in base metals. Consequently, if the ores really represented ultimately mafic volcanic associated sulphides, they now clearly are displaced far from the original sites of deposition and where the required volumes of the volcanic rocks (or mafic intrusive rocks) were present.

## 8.5.2. Hoikka

The Hoikka prospect encompasses a small Cu-showing ca. 3.5 km SW from the Luikonlahti Cu-Co-Zn mine (Fig. 95). The mineralization was discovered 1974 by Malmikaivos Company, which subsequently, in the years 1974-1975, drilled 17 short (50-180m) holes ashore and below the small Lake Hoikka, and in the isthmus between the Lake Hoikka and Kekäläislahti bay of Lake Retuisjärvi (Fig. 104). The total amount of the drilling was 1765 m. The Malmikaivos Company made no claim; therefore no report is available from the Ministry of Trade and Industry. It seems that neither any formal in company exploration report was ever prepared regarding the Hoikka prospect.

The main target of drilling at Hoikka was a narrow N-S trending, W dipping zone of Outokumpu-type rocks enclosed in local mica gneisses (Fig. 104). The thin zone of Outokumpu type rocks comprised serpentinites, talc-chlorite schists, carbonate rocks, diopside and tremolite skarns, black schists and minor quartz rocks. The drilling showed that this zone was associated with a tiny, low-grade, but in its metal portfolio clearly Outokumpu type sulphide mineralization of ca. 0.2 Mt at ca. 0.5 wt.% Cu, 0.04 wt.% Co, 0.015 wt.% Ni, <0.1 wt.% Zn and 15 wt.% S (Parkkinen, 1997). The actual sulphide mineralization comprises a thin sheet of semimassive to disseminated pyrrhotite-dominated sulphides, conformal with the narrow N-S striking and at ca. 55 degrees to the W dipping stripe of the Outokumpu-type rocks (Figs. 104-105). The northern tip of the mineralized sheet is exposed in a trench dug by Malmikaivos at 6980.44 (northing) and 4430.92 (easting). The mineralization, which has been traced downplunge to a depth of



Fig. 104. Geological map of the Hoikka-Tahasniemi-Melttusvirrat area showing the location and geological environment of the small Hoikka Cu-Co-Zn mineralization and Tahasniemi prospect. After unpublished maps of Malmikaivos Company and Huhma (1971).



Fig. 105. Cross-section profiles 22.800 and 23.000 of the Hoikka deposit. For location of the N-looking profiles, see Figure 104. After unpublished cross-section drawings of Malmikaivos Company and drill core reviews of the present authors.

ca. 100 m, is ca. 3 m thick at shallow levels (down to 50 m), but narrows rapidly below one metre in the depth. Near the surface the sulphide sheet is enclosed in impure quartz rocks, diopside skarns, talc chlorite schists and carbonate-rich metaperidotites. At deeper levels the metaultramafic rocks taper off, and the mineralization is enclosed in mica schists. Granite is abundant all over the prospect, cutting extensively also the mineralized horizon.

Although very small and low in metals, the mineralization at Hoikka is clearly of Outokumpu type, both in terms of its host rock assemblage and metal content. Looking at the available geological and geophysical maps suggest the mineralization would be located within the same horizon of black schists and serpentinite lenses as the Luikonlahti complex, being traceable from Hoikka via the Luikonlahti mine site until to Lake Suuri-Kyrpyli ca. 7 km to the NE of Luikonlahti. Excluding its interesting location, there is little in the existing data from the Hoikka area that would encourage further exploration, however.

It shoud be mentioned here that Malmikaivos has explored also the Tahasniemi area 0.5-1.0 km to the W-NW of the Hoikka prospect (Fig. 104). The exploration campaign during 1960s involved drilling of 14 shallow drill holes (ca. 1600 m) in a narrow N-S running horizon of quartzites, amphibolites, dolomites, calc-silicate rocks and black schists running N-S in the mica schists of the Tahasniemi spit in Lake Retunen. Despite the relatively abundant drilling, no indications of economical sulphides were located. The operation was probably based on a misscorrelation of the metasedimentary, either Jatulian or Kalevian quartzites, carbonate and calc-silicate rocks at Tahasniemi with the serpentinite derived carbonate-skarn-quartz rocks of the Luikonlahti complex.

## 8.5.3. Kokka

The ca. 9 km long, 1.5 km wide, curved Kokka serpentinite belt ca. 10 km to the NE of the Luikonlahti mine (Figs. 95, 106), was the target of several exploration campaigns between 1958 and 1985, first by Outokumpu Company, and then, after 1978 and passing of the mineral rights of the Kokka prospect from Outokumpu to Malmikaivos Company, by the latter. During the early vears of exploration for Kokka no claim reports were required by the Ministry of Trade and Industry. Therefore, and because also the in-company reports from Kokka are relatively few and thin, the exploration history of the Kokka serpentinite belt cannot be followed in detail. Anyway, over the years of the intense exploration, the two companies drilled altogether 97 holes totalling to 16147 m within the Kokka prospect and surrounding serpentinite belt. 8342 m of this drilling was by Outokumpu Company, and 7805 m by Luikonlahti Company. As a result of this drilling, two low-grade nickel mineralizations, Kokka "A" and "B" were outlined from within the SW margin of the sizeable serpentinite body to the SW of the Kokkalampi (Fig. 106). The volumetrically larger mineralization "A", originally discovered and outlined by Outokumpu Company, was estimated to contain ca. 1.9 million tons of rock at 0.35 wt.% of Ni, while the mineralization "B", located by Malmikaivos company some 600 m to the NW from the "A", was estimated to contain ca. 0.57 million tons of rock at 0.49 wt.% of Ni (unpublished documents of Malmikaivos Company).



Fig. 106. Geological map of the Kokka area showing the surface projections of the Kokka A and B Ni mineralizations. After unpublished maps of the Outokumpu and Malmikaivos Companies. Locations of the cross-section priofiles 10.250 and 9.650 in Fig. 107 are also shown.

The Ni-mineralizations at Kokka are hosted in 30-50 m thick units of medium-grained tremolite-carbonate and coarse-grained tremolite-diopside±uvarovite calc-silicate rocks along

the hanging wall contact of the gently SW dipping Kokkalampi serpentinite lens and structurally overlying black schists (Figs. 106-107). Locally the calc-silicate rock layer contains minor pods of quartz rock and quartz blebs, but, somewhat surprisingly, no thicker units of quartz rock are present. Both the A and B mineralizations have shapes of 5-10 m thick plates subparalelling the SW dipping hanging wall contact of the serpentinite. In case of the A body the SW dip is ca. 10-20 degrees, and for the B body ca. 40-50 degrees (Fig. 107). Drilling data indicate that the dip of the serpentinite-metasediment interface shallows near horizontal further SW of the mineralizations. The carbonate to calc-silicate rock layer at the footwall of the mineralizations grade downward through a heterogeneous tremolite+talc+dolomite -rich zone into serpentinized talc-olivine+-anthophyllite rocks. At the hanging wall the calc-silicate to carbonate rock layer has a sharp, sheared contact with the overlying black schist. Both the A and B mineralizations are located in continuation to a thin wedge of highly tectonized black schist being sheared and/or folded inside the layer of carbonate rock - calc silicate enclosing the Ni mineralizations (Fig. 107). Within the nose of the fold/shear wedge the black schists are locally distinctly fuchsite-rich and contain also Cr-tourmaline and apatite. The neighbouring diopside-tremolite skarns are locally very rich in uvarovite. The principal sulphide minerals both in the A and B Nimineralizations are pyrrhotite and Ni-pentlandite with infrequent minor gersdorfite. Chalcopyrite, and sphalerite occur only in trace amounts. The main Ni carrier, Ni-pentlandite, forms coarse, discrete grains in the dominantly carbonate and diopside-tremolite hosted parts of the mineralizations, while in black schist hosted ports it occurs mainly as narrow, irregular exolution flames in pyrrhotite.

The report by M. Huhma (1967) is one of the few documents existing about the exploration work done within the Kokka serpentinite belt. Information in this report shows that Outokumpu conducted among other investigations a study of the sulphide phase separated from the various rock types of the Kokka belt. This study showed that the sulphide phase of the carbonate and calc-silicate rocks hosting the Kokka A mineralization is relatively Ni-rich, sometimes comprising dominantly pentlandite, but that it is systematically very poor in Cu and Co. When the contact between calc-silicate rocks and black schists is approached from the side of serpentinite, the amount of sulphides tends to increase but with concomitant decrease in sulphide phase nickel concentration but slight increase in Cu and Zn, the latter metals, like the S, being obviously introduced from the black schists (Huhma, 1975). Importantly, the Ni/Co in the mineralized carbonate and calc-silicate rocks is more or less uniformly similar to that in the adjacent serpentinites, implying they would be devoid of Outokumpu-type Cu-Co -type mineralization. The complete lack of Cu-Co enrichment in the Kokka type Ni-mineralizations, in Kokka and elsewhere in NKSB, strongly indicates they were genetically entirely separate of the Outokumpu-type Cu-Co-Zn mineralizations.

The holes Kokka-28 and Kokka–29 drilled by Outokumpu Mining in years 1963-1964 intersected ca. 1 km south of the Kokka A prospect black schists tectonically interdigitated skarn (calc-silicate) rocks in a narrow zone between two size-able serpentinite bodies. This section comprises, with respect to Cu and Co, perhaps the most interesting drill profile within the Kokka prospect area (Huhma 1967). Although no clear Outokumpu-type Cu-Co-Zn mineralization is present, some of the black schist related calc-silicate rocks show some clearly elevated Co and Cu abundances of up to 300 ppm and 900 ppm, respectively. As elsewhere in the NKSB such Co-Cu enrichments in skarns had been found to indicate proximity of Cu-Co-mineralizations (Huhma 1967), the Kokka-28/-29 anomalies and the contacts of the nearby large serpentinite massifs became in years 1964-1968 examined by 12 more drill holes (ca. 3550 m). This drilling revealed short intersections of Cu-anomalous skarns (up to 0.27 wt.%/1.2 m) and Co-anomalous quartz rocks (best section up to 225 ppm/4.0 m) but nothing more significant.

In sum, although there are large serpentinite massifs in the Kokka belt and quite a lot of drilling has been done along their contacts, no clear indications of Outokumpu-type Cu-Co-Zn mineralizations have yet been encountered. Thus, some fundamental difference probably exists

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Fig. 107. Cross-section profiles 9.650 and 10.250 of the Kokka A and B Ni mineralizations, respectively. Based on unpublished cross-section drawings of Malmikaivos Company and review of some of the included drill holes by the present authors.

between the Kokka and Outokumpu type prospects with respect to their ore-potential. Some geological differences are clearly evident. One is the relative scarcity of metasomatic quartz rocks in the Kokka environment, compared to their abundance in the Outokumpu and Vuonos sulphide environments. On the other hand, guartz rocks are relatively rare in the Luikonlahti complex, too, and yet it hosts relatively large, although low-grade Cu-sulphide accumulation. It is noteworthy that the Cu and Co anomalies in Kokka-28/-29 are related nearly exclusively to black schist and associated, probably sedimentary skarn intervals, not in Outokumpu type ultramafic metasomatites (Huhma, 1967). Only in Kokka-28/119.9-120.5, there is a Cu-Co "anomaly" in carbonate-calc-silicate rock of possible ultramafic protolith; this interval contains 592 ppm Cu, 288 ppm Co, 1558 ppm Ni and 2750 ppm Zn, which are tenors on par with the maximum metal tenors observed in Kokka-28/-29. Although the Co/Ni ratio of 0,18 is clearly interesting, the relatively high Zn could be a sign of not-so-interesting syntectonic upgrading of black schist type sulphides also in this interval. Nevertheless, Huhma (1967) sees that the Kokka-28/-29 profile bears some resemblance to the Hietajärvi prospect, where scattered, weak Cu-Co anomalies occur in the metasedimentary wall rocks, also somewhat further away from the massive sulphide lenses. We note that in this respect the Saramäki prospect is similar.

The Poskijärvet Ni prospect (Losomäki, Ala-Poskinen) locates 2 km to the NNW of the Losomäki village, for its most intensively studied part below the Ala-Poskinen and Ylä-Poskinen lakes. Geologically the prospect is found within the northernmost tip of the large (7 km long and 1-0.5 km wide), ragged Losomäki ultramafic-mafic complex in the northern end of the Kaavi thrust structure (Figs. 44, 108).



Fig. 108. Geological map of the Losomäki area showing location of the cross-section profile Po-18/Po-1 of the Poskijärvet prospect in Fig. 109. Based on mapping of the first author and Virkkunen (1982).

The Losomäki complex consists ca. 70 % of serpentinized metaperidotites and ca. 30% of amphibolitic metabasites (Fig. 108), the latter representing partly intrusions in the serpentinite bodies and partly slivers of probable extrusive metabasalts tectonically interleaved with the serpentinite bodies (Park, 1983). The complex is intensely folded and fault-imbricated to be sandwiched with the local Kalevian metasediments that obviously include both Lower Kaleva and Upper Kaleva type units. The Lower Kaleva metasediments comprise metagreywackes, quartzose arkosic wackes and black schists with intercalations of mafic metavolcanic and sill rocks. The Upper Kaleva sediments that cover uniformly the area west of the Losomäki complex rests on an Archaean gneissic basement; separated from it by a ca. 60 m thick layer of black schists, carbonate rocks and mica schists (Fig. 109)

The serpentinites in the Losomäki complex are lizardite-chrysotile serpentinized talc-olivine and anthophyllite-olivine metaperidotites, for their peak assemblages corresponding to about 650±50 °C. Outokumpu-type metasomatites in the Losomäki area comprise chromite-bearing carbonate±olivine±tremolite rocks, diopside±tremolite skarns and quartz rocks, as it is typical of the Outokumpu alteration assemblage in middle amphibolite facies environments. As usual, the biggest concentrations of Outokumpu type metasomatites are present in locations where serpentinites are in direct contact with thicker layers of sulphide+graphite rich black schists. Because of the very intense late imbrication typical of the Kaavi structure, many serpentinite contacts at Losomäki are free of Outokumpu metasomatites, however. Exploration history of Poskijärvet prospect goes back to end of 1950s when boulder trackers of Outokumpu Company found from the Losomäki area several sulphidic (pyrrhotite-pyrite) skarn and quartz rock floats containing 0.25 to 1 wt.% Ni mainly in pentlandite. Scattered observations of similar rocks were made also in local outcrops. After geophysical, and moraine and stream sediment geochemical surveys in years 1963-1964, Outokumpu Company carried out in 1964 in the Losomäki area a drilling program of 12 holes, totalling to 2428 m. Two more holes were drilled in year 1970. These holes intersected Outokumpu-type formations with abundant serpentinites, but only minor skarn and quartz rocks. The located tattered skarn – quartz rock occurrences were observed to contain scattered portions little elevated in Ni (up to 0.3 wt.%) but with only background Cu and Co. Some black schists at the serpentinite contacts were observed to contain 0.1-0.3 wt.% Cu, up to 0.5 wt.% Zn and Ni up to 0.3 wt.%. The high Ni tenors of these black schists may indicate presence of Talvivaara-type Lower Kaleva black schist in the Losomäki area, or alternatively the high Ni reflects synmetamorphic diffusion from the adjacent ultramafic rocks.

Malmikaivos Company performed during 1970s and 1980s several boulder tracking and geological mapping operations and geophysical surveys in the Poskijärvet prospect area, and some more tentative operations also around the serpentinite bodies to the S of it. This work resulted in many new findings of Ni-sulphide bearing glacial floats, which in a few cases showed also slightly elevated Co and Cu, and some geophysical anomalies considered interesting exploration-wise. In the early 1980s Malmikaivos Oy performed within the Poskijärvet prospect, in two steps, in 1980 and 1981-1982, a drilling program of 18 holes totalling to 4108 m. This drilling was targeted mainly in the area of the southern corner of the Ala-Poskinen and within the isthmus between Ala-Poskinen and Ylä-Poskinen, where a bigger volume of intensely folded and faulted Outokumpu type carbonate-skarn-guartz rocks occur fringing a voluminous serpentinite body (Figs. 108-109). The metal tenors observed were usually very low, nothing more than normal for unmineralized Outokumpu type metasomatites. However, intersections of several metres of guartz rocks somewhat elevated in Ni were located by holes Po-1, Po-2, and Po-17. The best of these sections contained 0.43 wt.% Ni (9.7 m), 0.34 wt.% Ni (5.0 m) and 0.30 wt.% Ni (15.3 m), respectively. The best observed Cu-showing was for a 1.95 m long section of clear Outokumpu-type sulphide-dissemination in Po-15 at 230.45-232.40 m (Fig. 109), including a 0.5 m part with 0.58 wt.% Cu, 0.16 wt.% Co, 0.58 wt.% Ni, 0.40 wt.% Zn and 9.51 wt.% S. In another hole, Po-18, a thin quartz vein containing 0.38 wt.% Cu, 0.048 wt.% Co, 0.20 wt.% Ni, 0.12 wt.% Zn and 11.2 wt.% S was dissected. In years 1982-1983 Malmikaivos drilled further 11 holes (2056 m) at sites south of the Poskijärvet prospect but this drilling revealed no indications of either significant new Ni mineralizations or Outokumpu type Cu-Co mineralizations. In sum, the Poskijärvet prospect is in many ways similar to the Kokka prospect, also in that aspect that despite the rather extensive geological mapping, boulder tracking, geophysical and drilling programs (8592 m) performed within the prospect and in its surroundings, any truly promising metal showings have not been located. Nevertheless, some Outokumpu type altered carbonate-skarn-guartz rocks have been outlined in the northernmost part of the area, mostly below the Poskijärvet lakes, and which host weak, tattered Ni mineralizations, and a very minor, low-grade Outokumpu type Cu-Co-Zn showing. However, at current metal prices, the rambling low-grade Ni-mineralizations such as at Poskijärvet or even at Kokka are clearly without economical significance. The clear Cu-Co indication at Po-15/230.45-232.40m is intriguing, but the past drilling by Outokumpu and Malmikaivos seems sufficient to exclude the possibility that this mineralization would indicate Cu-Co potential of economic significance. The scarcity of Outokumpu-type carbonate-skarnguartz rocks outside of the immediate Poskijärvet prospect area is one more fact that does not encourage further Cu-Co exploration in the Losomäki area.



Fig. 109. Cross-section profile Po-18/Po-1 of the Losomäki prospect. The minor Outokumpu-type Cu mineralization dissected by the hole Po-15 is indicated by an arrow with "Cu". Constructed based on drill core reports of Malmikaivos Company and review of some of the included drill cores by the present authors. For location of the profile see Fig. 101.

Finally, it is probably so that the recognition of the probable pillow basalts at Losomäki in the beginning of 1980s (Park and Bowes, 1981; Virkkunen, 1982) was obviously one of the reasons why Malmikaivos Company at the same time intensified exploration of the area. Inspired by the pillow lava observations, the Losomäki Complex was probably considered to have potential of Cyprus type volcanic-associated massive Cu-sulphide deposits. However, there is no support in the Outokumpu and Malmikaivos assay data for anomalous Cu-Co tenors, or other clear evidence of Cu-sulphide mineralization, whatsoever, in any of the drilled and tested Losomäki metabasic rock units.

# 8.5.5. Hippos

Hippos refers to a minor Cu-showing 7 km to the east of Luikonlahti mine and 1.1 km to the north of Lake Sivakkajärvi (Fig. 95). The mineralization is exposed in a couple of shallow research trenches on a small hill approximately at 6986.72 (northing) and 4439.94 (easting), within the 1: 20 000 map sheet 4311 04 D.

The Hippos mineralization consists of a narrow (<2 m) sulphide bearing zone of quartz veins in mica gneisses, which according to the Sivakkavaara 1: 100 000 map sheet (Huhma, 1975) belong to the Archaean basement complex. The mineralized zone is conformal to a NNE-trending banding of the host mica gneisses. According Matti Tyni (pers. comm. 2000) Malmikaivos Company drilled one reconnaissance hole at the showing, but the core and related documents could not any more be located from the Malmikaivos stores. One representative sample analyzed during this work from a semimassive part of the narrow mineralization contained 0.84 wt.% Cu, 0.024 wt.% Zn, 0.011 wt.% Co, 0.033 wt.% Ni and 17.9 wt.% S. The contents of precious metals were low, 3.5 gr/ton for Ag and <15 ppb for Au. The Hippos sulphide mineralogy is dominated by pyrrhotite with minor chalcopyrite and pyrite. The gangue is over 90 % of quartz plus minor tremolite and plagioclase.

The location of the Hippos mineralization within the basement complex and its low Co content are features that seriously militate against interpretation of it as an Outokumpu-type mineralization. Intriguingly, however, the Hippos, Luikonlahti and Hoikka deposits all plot along a SW trending straight line that has exactly the same strike as what is get if a line is drawn through the Outokumpu, Vuonos and Perttilahti deposits. Whether this would be just a coincident, or have some genetical connotation, remains an issue to be clarified in possible future studies.

# 8.6. Savonranta structure

# 8.6.1. Hietajärvi

The Hietajärvi prospect locates on the side, partly below, the Savonranta-Heinävesi road ca. 15 km to the N from the Savonranta town (Figs. 44, 110). The included small Cu-Co-Zn mineralization was discovered in year 1955 during the construction of the Savonranta-Heinävesi road. Attracted by sizable magnetic-electromagnetic anomalies and scattered outcrop and float indications of Outokumpu type rocks, Outokumpu Company had been starting exploration (mapping, boulder tracking) in the surrounding Savonranta area already in the previous year 1954. Encouraged by the discovery of the Hietajärvi mineralization, Outokumpu carried out in 1955-1958 an extensive exploration program, including geological mapping, boulder tracking, geophysical surveys and drilling, over large areas in the Savonranta district. Since this program, the Hietajärvi prospect and the surrounding Savonranta area became geologically and geophysically surveyed and drilled by Outokumpu Company in several stages until the middle 1990s.



Fig. 110. Maps illustrating the geological setting of the Hietajärvi deposit. Dashed lines in the lower map show surface projections of the two main massive sulphide lenses in the deposit. Locations of the cross-section profiles in Fig. 111 are also shown in the lower map. After unpublished maps of Outokumpu Company.

Outokumpu exploration drilling in Hietajärvi consists of 23 drill holes in 1955-56, 6 drill holes in 1958, 5 drill holes in 1963 and 7 holes in 1983. In addition, 11 shallow shallow drill holes for a feasibility study were drilled in 1993. The more recent study effort includes a feasibility study in 1995, based on block samples from exposed parts of the mineralization. The feasibility study in 1993 was related to plans open-pit mining parts of the deposit to be processed at the then closing Enonkoski sulphide concentrating plant (30 km SW of Hietajärvi). The 1995 feasibility study was related to similar plans but with aim to process the ore at the Nivala plant of Outokumpu Company.

Over the past decades, related to the repeated drilling campaigns, several estimates of the ore reserves and mineral resources of the Hietajärvi deposit have been performed, but with only little differing results. The latest estimate of the proven and probable ore reserves is 241 000 tons of mostly massive-semimassive sulphide ore at 0.71 wt.% Cu, 1.21 wt.% Zn, 0.18 wt.% Ni, 0.15 wt.% Co, and 20.2 wt.% S (Isomäki, 1994).

The Hietajärvi mineralization is related to thin and conformable Outokumpu-type black schist-calc silicate rock-carbonate rock-serpentinite formation enclosed in mica schists. Mineralization occurs as two main, nearly E-W striking and 40-50 degrees to the S dipping lensoid bodies, one 200 m (E-lens) and other 100 m (W-lens) long (Figs. 110-111). Thickness of the mineralised unit varies between 3 and 20 m, being ca. 10 m by average. From hanging wall to footwall the rock succession for the lenses is usually: mica schist, thin layer of tremolite and sulphide-rich black schist, massive pyrrhotite ore with diopside+-tremolite gangue, and sulphide-disseminated (in places) diopside+-tremolite and serpentinite spotted carbonate rock. Several granite dykes crosscut the western lens. The hanging wall contact of the sulphide lenses is mostly very sharp while the footwall is gradational over a short distance. Majority of the ore consists of massive pyrrhotite with disseminated chalcopyrite and sphalerite as the main sulphide minerals, and diopside±tremolite±quartz, or seldom principally quartz, as the main gangue minerals. Nickel and cobalt pentlandite and linneite are present as minor sulphides.

The carbonate- skarn rocks at the Hietajärvi sulphide lenses are dominantly of clear Outokumpu type Cr-rich carbonate+-olivine (serpentinized)+-spinel rocks and diopside+-tremolite skarns, mineralogically and by texture, as one would expect for Outokumpu type carbonate-skarn rocks in upper amphibolite/migmatite metamorphic environment. So, although clear Outokumpu type carbonate and skarn rocks are present, the rest of the Outokumpu assemblage is absent. However, small bodies of serpentinized olivine-enstatite-talc-olivine rock (Fig. 110) are present at Paskosuo and litanniitty only some 1 km to the NNW and W of the Hietajärvi deposit, respectively. Thus, it seems quite possible that the Hietajärvi assemblage would represent a dismembered/fault-displaced slice of once more complete Outokumpu assemblage.

The nature of metal content, the ore sulphide and gangue mineralogy show that though small and of relatively low-grade nature, the Hietajärvi deposit is compositionally indisputably of Outokumpu type. The setting of the mineralization is also as usual for Outokumpu sulphides, that is, massive-semimassive lenses between a sulphide-graphite-rich black schist layer and Outokumpu metasomatites. In a difference, in this case there clearly was more remobilization of the sulphides as usually. However, little of the remobilization is recorded in the textures of the ore lenses, which reflecting the high-T peak of metamorphism now exhibit thorough the massive, coarse-grained granoblastic-graphic or "annealed" metamorphic texture (Fig. 112) typical of middle amphibolite facies or higher grade Outokumpu area pyrrhotite ores.



Fig. 111. Cross-section profiles of the southern and northern main sulphide lenses of the Hietajärvi deposit. After unpublished cross-section drawings of the Outokumpu Company and review of some of the included drill cores by the present authors.



Fig. 112. Scanned image of granoblastic-graphic sulphide-quartz intergrowth texture typical of the Hietajärvi massive ore. Width of the view ca. 70 mm.

## 8.6.2. Kettukumpu and Siiranlampi

Malmikaivos Oy discovered in 1975, in connection with field checking of a air-borne magnetic anomalies (GTK, high-altitude) in the Savonranta area, ca. ten kilometres S of the above described Hietajärvi deposit, a previously unknown, nearly unexposed, SE-NW trending thin band of Outokumpu-type serpentinite-skarn-quartz rocks and black schist. After routine magnetic and electromagnetic ground geophysical surveys, 23 diamond drill holes with a total length of 3183 m were drilled in years 1976-1977. The drilling resulted in localization of two small sulphide mineralizations hosted in carbonate and quartz-spotted diopside-rich calcsilicate rocks at the footwalls of the steeply SSW dipping small ultramafic lenses at Kettukumpu and Siiranlahti (Fig. 113). Diopside and tremolite skarns and carbonate rocks dominate in the heavily granite-intruded lenses, while serpentinite (serpentinized metaperidotite) and quartz rock occur only in minor volumes.

The largest volume of mineralized rock were localised from Kettukumpu where in a broadly E-W trending zone at the N-margin of the steeply to the SSW dipping ultramafic lens, one larger and three smaller separate lens-form bodies of Ni to Cu-Co-Ni sulphide mineralized rock occurs (Figs. 113-114). The largest of these lenses, 13 m by its maximum thickness, was encountered in four separate drilling profiles implying it had a total length of at least 250 metres. The nearly vertical to 45 degrees SSW dipping lens has a surface outcrop within the surface exposure of the host ultramafite lens wherefrom it plunges at ca. 30-40 degrees to the W. The ore mineralogy is dominated by pyrrhotite with subordinate amounts of chalcopyrite and cobalt pentlandite, and traces of sphalerite. Copper tenor in the mineralized rock volumes seldom exceeds 0.5 wt.%, while nickel is within 0.1 - 0.6 wt.% and cobalt ranges from 0.08 to 0.13 wt.%. The indicated size and metal tenors of the Siiranlampi target were even more modest. The largest of the Kettukumpu sulphide lenses are estimated to contain in total at least 0.3 Mt of



Fig. 113. Maps illustrating the geological setting of the Kettukumpu and Siiranlampi serpentiniteskarn lenses (lower map), and the sulphide mineralizations within the former (upper map). After unpublished maps of the Malmikaivos Company.



Fig. 114. Cross-section profile 59.300 of the Kettukumpu carbonate-skarn rock lens showing the related sulphide mineralizations. For location of the W-looking profile, and the holes R-6 and R-8, see Fig. 102. Based on unpublished cross-section maps of the Malmikaivos Company.

mineralized rock at 0.44 wt.% Cu, 0.18 wt.% Ni, 0.07 wt.% Co and 13.5 wt.% S (Huopaniemi, 1983). Considering the sparse drilling and considerable and irregularly distributed granite in the mineralized volume, this estimate must be considered rather optimistic.

The host assemblage and metal assortment of the Kettukumpu sulphides define it a clear example of low-grade, minor Outokumpu type mineralization showing considerable similarity with the Hoikka deposit E of Luikonlahti. Both these deposits are found in association of small, highly altered, mostly calc-silicate-bearing ultramafic lenses in high-grade (migmatite) metamorphic environments, and the mineralizations are small, of low-grade and heavily granite-intruded.

## 8.6.3. Suurlahti, Lapinsaari

Suurlahti is an Outokumpu type prospect ca. 6-7 km to the SE of the above-described Hietajärvi mineralization (Fig. 115). This prospect, which was studied by Malmikaivos Company in years 1979-1984, is included here as one of the most promising of the few yet underexplored Outokumpu type showings in the Savonranta area. One reason for the lacking interest of explorers to this occurrence has undoubtedly been that the critical rock horizon locates mainly below the Suurlahti bay of Lake Orivesi. The following description of the prospect is based on a brief internal report of Malmikaivos Company from the year 1984.

Malmikaivos got interested in the Suurlahti area in 1978, on the basis of chalcopyritebearing calc-silicate rock samples sent in the company by a local resident. In the follow-up in the field Outokumpu type skarn-quartz rocks with scattered indications of Ni and Cu sulphides were observed within the Suurlahti bay area, on the S shore of the Lapinsaari Isle and small rocky isles S of it (cf. Fig. 115).



Fig. 115. Part of the 1:100 000 geological map of Finland, sheet 4214, Rääkkylä (Lavikainen, 1985), showing location of the Suurlahti occurrence of Outokumpu assemblage with Cu indications, and also the find place of the Kivisalmi boulder. Blue=Mica schist and gneiss, Yellow=Quartz-feldspar gneisses (probably Archaean), Red symbols=Granite pegmatite dykes.

The subsequent geological mapping and geophysical surveys indicated potential of a

considerable size Outokumpu formation below the Suurlahti bay. Encouraged by this, in winter 1984 Malmikaivos drilled 3 holes totalling to 568 m to dissect a strong magneticelectromagnetic anomaly trending SE in the middle part of the bay. A ca. 100 m thick Outokumpu type serpentinite-skarn-quartz rock formation was dissected by the drilling but with no clear indications of significant Outokumpu type Cu mineralization in its association. The most interesting section comprised 3 m of skarn-quartz rock that contained 0,033 % Co and showed a Ni/Co ratio of 5, but only trace amounts of Cu.

Despite the less than promising results of the 1984 drilling by Malmikaivos, the Suurlahti prospect remains interesting, and one that is still clearly unexplored. After all, the geophysical and drilling data combined indicate it to comprise an at least 1200 m long and up to 130 m thick serpentinite-skarn-quartz rock formation of Outokumpu type. And, up to this, there are scattered indications of Ni up to 1.63 wt% and Cu up to 1.16 wt% in association of the iron sulphide concentrations in the skarn outcrops of this relatively sizeable body of Outokumpu type rocks. But of coarse, the underwater location in a lake environment of natural beauty are combined exploration-wise a big minus.

### 8.6.4. Kivisalmi boulder

The Kivisalmi boulder (Fig. 115), whose discovery in year 1908 sparked off the exploration process that in 1910 lead to the discovery of the Outokumpu deposit, is shortly discussed here. The boulder, although not an in situ ore showing, is included because the frequent dissident proposals of that its source was instead of Outokumpu in the Savonranta district. These proposals usually have been backed by evidence of W-E directed ice flow in the Savonranta-Kivisalmi area in the latest stage of the Pleistocene glaciations. It is worth to note here that, based on unpublished documents of e.g. Malmikaivos Company; during 1960s several more Outokumpu type sulphide boulders became found from the Kivisalmi area. It seems that these boulder finds further fuelled the ideas of that the Kivisalmi boulder would have had a closer source than Outokumpu.

However, the texture (Fig. 116), mineralogy and chemical comosition of the ore in Kivisalmi boulder strongly attest to Outokumpu ore as the source. This evidence includes e.g. the dominantly pyritic composition the discovery boulder, its high Co/Ni ratio, relatively low Ni and clearly elevated Sn content (Co/Ni=11.1, Ni 327 ppm and Sn 42 ppm, based on one sample analysed by us). Exposed ore with similar characters is currently known only from the Kumpu B and Kaasila outcrops of the Outokumpu ore.

In evaluation the Savonranta area as the source of the Kivisalmi boulder, its is important to notice that the Savonranta rocks have been peakmetamorphosed in middle to upper amphibolite facies in significantly higher temperatures than the Outokumpu rocks, having the consequence that any included Outokumpu type massive-semimassive sulphide deposits would now most likely be thoroughly pyrrhotitic as the Luikonlahti deposit in a comparable metamorphic environment. Needless to say that all the known small sulphide lenses from Savonranta area are indeed pervasively pyrrhotitic. It is possible yet that a very large deposit, something no less than the Outokumpu ore, could have been adequately buffered to escape pervasive pyrrhotization. It is, however, extremely unlikely that an exposed deposit of the Outokumpu size would remain unrecognised in the Savonranta area, which, after all, was intensively explored by Outokumpu and Myllykoski for more than thirty years between 1950 and 1990.

In summary, we conclude that it is more than probable that the Kivisalmi boulder derives from one of the outcrops of the Outokumpu (Keretti) deposit. The Kivisalmi boulder is clearly not a reason to explore Outokumpu type deposits within the Savonranta, or further NW in the Heinävesi and Tuusniemi areas.

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Fig. 116. Scanned image of a slab from the Kivisalmi boulder. Note the pyrite dominated sulphide assemblage and blebby structure as are typical for the ore in outcrops of the Outokumpu deposit.

## 9. Geochemistry of the Outokumpu-type ore deposits

The following chapter focuses on the geochemistry of the sulphide deposits in the Outokumpu assemblage. The discussion is divided in three sections. The first section defines the included sulphide mineralization types and elucidates variation in the average Cu, Co, Zn and Ni tenors of the presently known Outokumpu district deposits, largely based on published reserve/resource estimates (mainly Parkkinen, 1997). The second section examines and compares the metal enrichment patterns of the separate sulphide deposits and their host rocks, using mantle-normalized spider diagrams, based on new major and trace element data by GEOMEX/GTK. The third section provides an element-by-element examination of the geochemistry of the Outokumpu deposits, with a heavy bias on Outokumpu and Vuonos deposits, for which the available geochemical data is most abundant and widest by element selection. The applied deposit reserve/resource estimates are tabulated in Table 8, and the average compositions calculated from the GEOMEX/GTK data in Table 10. The chemical data produced for the modelling purposes during the GEOMEX project are all included in the GEOMEX assay database.

Comparisons with other massive sulphide types are done along with the treatment, much of this is with reference to the volcanic associated, first of all modern MOR (mid ocean ridge) ore ancient VMS (volcanic associated), Cyprus (ophiolite associated) and Besshi (sediment-volcanic associated) deposits, which are usually mentioned as possible analogues in discussions about the origin of these deposits.

	n	SiO2	TiO2	AI2O3	Fe2O3t	MnO	MgO	CaO	Na2O	K2O	P2O5	Ctot	Ва	Ga	Nb	Sr	Zr	Cr	v	Sc
		wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Co-Cu-Zn deposits:																				
Outokumpu	78	39,30	0,01	0,18	36,74	0,06	0,98	0,60	0,22	0,01	0,01	0,12	31	15,2	0,15	6	2,1	289	51	1,2
Outokumpu, CoNi-zone <sup>a</sup>	30	56,28	0,14	5,41	15,86	0,06	9,48	2,70	0,17	0,20	0,01	0,30	31	17,0	0,74	18	13,2	9968	141	28,5
Vuonos	17	45,30	0,02	0,36	37,91	0,09	0,35	0,45	0,08	0,06	0,01	0,20	32	18,9	0,26	14	4,0	31	49	1,8
Perttilahti	4	45,23	0,03	0,59	38,99	0,05	0,52	0,71	0,20	0,08	0,01	0,44	11	18,3	0,44	18	12,0	38	49	1,5
Kylylahti	13	40,32	0,02	0,25	33,88	0,09	1,69	1,86	0,11	0,04	0,01	0,42	48	14,9	0,53	6	6,3	124	54	1,0
Kylylahti, skarn zone <sup>a</sup>	67	49,76	0,52	3,53	15,84	0,05	9,79	8,90	0,35	0,25	0,09	1,77	114	15,6	2,32	32	37,1	1449	161	20,3
Sola Zn	4	34,66	0,02	0,41	27,75	0,12	6,10	9,09	0,21	0,01	0,08	1,85	25	25,6	0,13	41	10,1	234	40	2,6
Saramäki	7	51,71	0,04	0,77	25,56	0,05	3,21	5,73	0,15	0,13	0,10	1,72	26	4,0	0,45	38	9,3	23	42	1,2
Luikonlahti	6	42,21	0,04	1,66	37,49	0,46	4,03	2,89	0,45	0,35	0,01	0,13	6	10,1	0,33	11	22,1	126	22	2,0
Hoikka	2	31,54	0,08	4,62	29,44	0,15	11,20	10,53	0,42	0,42	0,02	0,14	60	15,5	0,69	53	17,1	198	101	15,0
Riihilahti <sup>a</sup>	48	36,65	0,60	12,73	23,95	0,10	7,66	6,08	0,67	1,05	0,23	0,48	210	26,1	4,65	70	67,9	539	224	26,6
Hietajärvi	1	36,08	0,01	0,54	19,56	0,12	11,65	16,03	0,01	0,01	0,38	0,23	6	3,6	0,18	27	20,8	11	34	1,1
Kettukumpu	1	16,79	0,03	0,99	38,28	0,05	7,33	13,37	0,04	0,04	0,05	1,30	14	7,1	0,28	73	11,2	40	36	2,3
Hippos	1	49,28	0,08	2,60	33,02	0,05	0,46	2,53	0,15	0,10	0,08	0,33	83	4,1	1,10	85	20,0	22	59	3,9
Ni-Mineralized rocks (Ni>3	3000 p	opm):																		
Outokumpu	7	60,70	0,09	2,89	11,60	0,05	9,94	7,40	0,11	0,35	0,01	0,30	22	9,0	0,71	21	8,8	7597	209	26,9
Vuonos	2	66,06	0,00	0,38	16,46	0,07	4,79	4,08	0,07	0,01	0,00	0,40	3	9,4	0,04	9	24,2	4870	41	7,2
Horsmanaho	1	25,20	0,07	6,40	31,20	0,30	3,42	13,80	0,01	0,01	0,03	0,48	32	11,0	0,79	128	4,5	17449	376	51,8
Kuikkavaara		na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
Kokka	9	33,52	0,11	6,38	9,65	0,07	12,41	17,64	0,38	2,13	0,15	3,34	147	13,2	0,83	69	11,2	4264	137	20,8
Poskijärvi	1	85,89	0,00	0,79	5,65	0,02	1,57	1,37	0,05	0,08	0,01	0,92	13	0,7	0,09	11	0,6	2013	52	5,4
Petäjäjärvi	3	46,28	0,03	0,84	13,62	0,06	8,00	12,48	0,03	0,05	0,15	3,25	18	1,0	0,14	112	3,8	1843	36	5,5
Average Ni-miner. rock	22	47,39	0,08	3,99	11,92	0,07	9,78	12,15	0,20	0,99	0,09	1,92	70	9,4	0,60	55	10,4	5491	144	20,2
Reference data:																				
Primitive Mantle <sup>D</sup>		45,0	0,20	4,44	8,96	0,13	37,8	3,54	0,36	0,03	0,02	0,012	6,6	4,0	0,66	19,9	10,5	2625	82	16,2
Average UCC <sup>c</sup>		66,0	0,5	15,2	5,0	0,08	2,2	4,2	3,9	3,4	0,15	0,32	550	17	25	350	190	35	60	11
MOR sulphides <sup>a</sup>		9,9			35,6			3,6					15500	47				25		
TAG sulphides <sup>a</sup>		19,2			43,8			2,8					95	8,0				23		

Table 10a. Average analyses of major and trace elements in Outokumpu-type Cu-Co-Zn and Kokka-type Ni mineralizations in North Karelia.

<sup>a</sup> Average for samples with Cu >0.1% and/or Co >500 ppm.

<sup>b</sup> McDonough and Sun (1995), <sup>c</sup>Taylor and McLennan (1985), P2O5 and Ctot from Wedepohl (1995), <sup>d</sup>Herzig et al. (1998).

U U		; 1 71					71											
	n	Th	U	Υ	La	Се	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Co-Cu-Zn deposits:																		
Outokumpu	70	0,10	5,8	1,4	2,92	3,32	0,31	0,88	0,17	0,09	0,23	0,04	0,22	0,05	0,12	0,02	0,12	0,02
Outokumpu, CoNi-zone <sup>a</sup>	27	0,08	7,0	17,2	46,34	55,36	5,23	16,12	3,02	0,13	3,27	0,54	3,01	0,66	1,71	0,24	1,33	0,19
Vuonos	17	0,22	7,1	1,5	0,92	1,49	0,22	0,85	0,18	0,16	0,23	0,04	0,19	0,04	0,12	0,02	0,11	0,02
Perttilahti	4	0,36	7,0	2,4	1,85	3,17	0,43	1,75	0,33	0,12	0,35	0,06	0,33	0,08	0,24	0,03	0,21	0,04
Kylylahti	11	0,11	4,2	6,2	5,31	7,16	0,71	2,52	0,60	0,12	0,81	0,15	1,08	0,24	0,68	0,10	0,60	0,08
Kylylahti, skarn zone <sup>a</sup>	31	0,42	12,1	32,5	38,43	57,20	7,09	25,20	5,49	0,37	6,37	1,12	6,08	1,38	3,57	0,55	3,14	0,49
Sola Zn	5	0,07	14,9	8,3	2,09	3,09	0,50	2,14	0,77	0,28	1,13	0,19	1,23	0,25	0,65	0,10	0,68	0,09
Saramäki	8	0,35	6,2	2,4	1,56	2,37	0,32	1,21	0,24	0,10	0,28	0,04	0,30	0,06	0,20	0,03	0,21	0,04
Luikonlahti	17	0,08	4,8	2,5	1,83	2,67	0,31	1,21	0,30	0,43	0,36	0,06	0,33	0,06	0,17	0,03	0,15	0,03
Hoikka	2	0,13	6,7	7,0	10,36	15,80	1,51	4,73	0,85	0,12	0,88	0,16	0,81	0,20	0,60	0,09	0,54	0,09
Riihilahti <sup>a</sup>	20	2,93	4,1	35,5	46,87	69,13	7,44	27,74	5,86	0,86	6,61	1,06	6,23	1,23	3,51	0,50	3,26	0,45
Hietajärvi	5	0,11	21,7	3,6	1,27	1,47	0,23	0,99	0,27	0,07	0,35	0,06	0,43	0,10	0,35	0,05	0,34	0,06
Kettukumpu	2	0,31	5,8	5,2	1,95	2,75	0,33	1,20	0,31	0,09	0,41	0,06	0,50	0,13	0,39	0,06	0,44	0,07
Hippos	1	0,96	9,3	7,1	5,02	9,33	1,35	5,57	1,19	0,28	1,31	0,16	1,00	0,20	0,59	0,07	0,43	0,07
Ni-Mineralised rocks (Ni	>3000	) ppm):																
Outokumpu	7	0,07	21,8	8,6	6,65	7,55	0,88	3,43	0,74	0,08	1,00	0,15	0,98	0,24	0,70	0,10	0,61	0,09
Vuonos	2	0,16	25,7	1,4	0,33	0,67	0,08	0,42	0,09	0,08	0,12	0,02	0,10	0,03	0,06	0,01	0,06	0,01
Horsmanaho	1	0,16	42,5	37,7	4,46	5,51	1,19	5,65	1,55	1,82	2,43	0,48	3,83	0,94	3,20	0,48	3,21	0,53
Kuikkavaara		na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
Kokka	9	0,46	19,3	7,1	2,64	3,46	0,66	2,80	0,62	0,23	0,84	0,13	0,85	0,19	0,58	0,08	0,55	0,08
Poskijärvi	1	0,01	2,4	2,2	0,82	0,70	0,15	0,59	0,15	0,04	0,26	0,03	0,30	0,07	0,20	0,03	0,13	0,02
Petäjäjärvi	3	0,04	13,1	4,3	1,15	1,04	0,25	1,16	0,27	0,08	0,40	0,07	0,52	0,11	0,30	0,04	0,26	0,04
Average Ni-miner. rock	23	0,23	20,1	7,8	3,46	4,12	0,62	2,60	0,59	0,21	0,81	0,13	0,89	0,21	0,63	0,09	0,58	0,09
Reference data:																		
Primitive Mantle <sup>D</sup>		0,080	0,020	4,300	0,648	1,675	0,254	1,250	0,406	0,154	0,544	0,099	0,674	0,149	0,438	0,068	0,440	0,068
Average UCC <sup>c</sup>		10,7	2,8	22	30	64	7,1	26	4,5	0,88	3,8	0,64	3,5	0,80	2,3	0,33	2,2	0,32
MOR sulphides <sup>a</sup>																		
TAG sulphides <sup>a</sup>																		

Table 10b. Average analyses of Th, U and YREE in Outokumpu-type Cu-Co-Zn deposits and Kokka-type Ni mineralizations in North Karelia.

 $^{\rm a}$  average for samples with Cu >0.1% and/or Co >500 ppm

<sup>b</sup> McDonough and Sun (1995); <sup>c</sup>Taylor and McLennan, 1985; P2O5, Ctot from Wedepohl (1995); <sup>d</sup>Herzig et al. (1998)

	n	Ni	Со	Bi	Se	Pb	Zn	Мо	Sb	Au	Cd	Sn	Ag	Cu	As	S	Se/Sx10 <sup>6</sup>
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb	ppm	ppm	ppm	ppm	ppm	wt.%	
Co-Cu-Zn deposits:																	
Outokumpu	78	1617	2564	0,72	24,2	48,7	18557	19	2,34	616	28,6	132,7	10,9	41570	81,6	24,8	97
Outokumpu, Co-Ni zone <sup>a</sup>	30	7410	2012	0,30	4,3	6,0	1877	48	0,21	383	1,4	6,5	2,6	11069	16,3	6,4	67
Vuonos	17	1560	1610	0,65	6,6	150,5	19948	17	1,84	92	33,5	134,6	12,1	27868	74,4	19,5	34
Perttilahti	4	1663	1710	0,40	3,2	8,5	18341	22	0,09	17	88,5	69,3	14,4	15953	13,4	21,9	15
Kylylahti	15	1674	4327	0,10	4,7	24,1	21171	29	3,76	258	30,9	18,9	9,2	30940	1202,8	24,6	19
Kylylahti, skarn zone <sup>a</sup>	67	2837	1262	0,06	2,8	11,5	3521	20	0,83	782	6,2	4,6	4,4	5659	256,6	8,7	32
Sola Zn	5	2929	411	0,01	17,2	10,3	34319	35	0,02	4	52,8	3,6	3,6	4508	28,7	18,2	94
Saramäki	8	532	614	0,06	2,0	3,9	4691	62	0,08	5	6,8	5,0	3,8	7159	84,6	14,8	14
Luikonlahti	17	1150	1124	0,30	1,1	2,7	11759	13	0,04	7	12,8	47,7	4,7	13825	15,5	25,6	4
Hoikka	2	1360	539	0,32	1,5	1,8	1338	18	0,03	8	8,0	1,3	4,1	6421	2,1	14,1	10
Riihilahti <sup>a</sup>	117	374	1052	0,16	6,6	20,1	1158	9	0,03	325	3,4	11,0	6,2	12359	7,6	5,4	122
Hietajärvi	5	2290	1896	0,44	1,2	5,4	11609	48	0,03	11	40,5	2,3	4,5	9674	2,3	28,4	4
Kettukumpu	2	2140	725	1,19	0,7	0,3	539	20	0,03	8	4,0	0,8	3,0	4231	1,9	24,5	3
Hippos	1	329	110	0,36	0,4	3,1	238	51	0,03	8	2,8	0,5	3,5	8353	0,3	17,9	2
Ni-mineralized rocks (Ni	>3000 p	<u>pm):</u>															
Outokumpu	7	4662	331	0,07	2,9	4,1	163	18	0,19	9	0,2	2,0	2,6	237	59,8	5,5	54
Vuonos	2	21698	1017	0,34	8,2	9,6	830	23	0,03	21	0,1	2,0	1,8	191	2,9	23,9	34
Horsmanaho	1	10442	504			45,0	264	6				5,0		415	8,0	10,9	
Kuikkavaara	1	18900	908	0,73	2,0	33,7	174	35	0,42	83	<1.0	na	<10	227	55,4	24,0	8
Kokka	9	5748	155	0,51	4,2	4,5	471	11	0,06	1	1,4	0,6	0,4	121	5,0	4,3	97
Poskijärvi	1	2987	131	0,06	0,2	0,3	56	3	0,12	8	0,1	0,5	0,2	93	35,3	3,0	7
Petäjäjärvi	3	8434	284	0,21	0,3	2,0	88	14	0,03	8	0,3	0,5	0,3	213	19,6	6,9	4
Average Ni-miner. rock	24	7725	339	0,31	3,4	6,1	323	15	0,11	10	1,0	1,1	1,23	188	26,1	7,7	44
Reference data:																	
Primitive Mantle <sup>b</sup>		1960	105	0,0025	0,075	0,15	55	0,05	0,0055	0,001	0,04	0,13	0,008	30	0,05	0,025	300
Average UCC <sup>c</sup>		20	10	0,127	0,05	20	71	1,5	0,2	1,8	0,098	5,5	0,055	25	1,5	0,095	52
Average MOR sulphide <sup>d</sup>		47	311	0,75	97	1200	104000	89	42	900	293	<1	111	40000	265	34	285
Average TAG sulphide <sup>d</sup>		10	234	na	14	59	4000	89	2	500	11	na	9	24000	43	42	33

Table 10c. Average analyses of chalcophile metals and S in Outokumpu-type Cu-Co-Zn deposits and Kokka-type Ni mineralizations in North Karelia.

<sup>a</sup> Average for samples with Cu >0.1% and/or Co >500 ppm.

<sup>b</sup> McDonough and Sun (1995);<sup>c</sup>Taylor and McLennan (1985), S and Ag from Wedepohl (1995),<sup>d</sup>Herzig et al. (1998), Bi and Sn from Goodfellow et al. (1999).

#### 9.1. General geochemistry

#### 9.1.1. Subdivision of the ore types, variation in Cu, Co, Zn and Ni

The sulphide accumulations in association with the Outokumpu assemblage can be divided into two distinct types: (1) those with Cu-rich sulphide phase, i.e. the Cu-Co-Zn massive-semimassive deposits of Outokumpu-type; and (2) those with Ni rich sulphide phase notably poor in copper, i.e. the semimassive-disseminated Ni mineralizations of Kokka-type. It has to be noted that the latter type, though an ubiquitous aspect of the Outokumpu assemblage, is of little economic significance; Ni tenors for economically interesting volumes are mostly low (0.5 wt.% Ni at best), and the accumulations are frequently of rambling nature. We have included here the Ni type, or Kokka-type, largely because the Ni disseminations in the carbonate-skarn-quartz rocks are a possible source of the high Ni characteristic of the Outokumpu Cu-Co-Zn sulphides, and because the Ni disseminations in the past have been interpreted as a synsedimentary facies of the massive-semimassive Cu mineralizations. A third mineralization type is represented by the Keretti Co-Ni zone, Vuonos Ni deposit and Kylylahti skarn-zone mineralizations, which should not be confused with Kokka type Ni mineralizations. Instead these Co-Ni stringer sulphide occurrences seem to represent a mixture of the Cu and Ni deposit types, where a Cu mineralization likely overprints a Ni mineralization (Parkkinen and Reino, 1985).

We first illustrate the distribution of the main ore forming elements with help of the **ternary** *diagrams Cu-Co-Ni, Cu-Zn-Ni and Cu-Zn-Co*.

On the ternary Cu-Co-Ni diagram (Fig. 117a) all of the larger Cu-Co-Zn-deposits plot close to the Cu apex, showing significantly higher Ni/Cu and Ni/Co than present day oceanridge sulphides, or most ancient hydrothermal massive-semimassive sulphide deposit types. In a high contrast, the Ni deposits plot in a tight cluster very close to the Ni apex, showing very similar Ni/Cu and Ni/Co ratios than their host mantle-derived Outokumpu-type metasomatites. Data points of some of the low-grade, smaller Cu-Co-Zn and the Co-Ni type deposits scatter intermediate between the larger Cu-Co-Zn deposits and Ni mineralizations. On the ternary Cu-**Zn-Ni diagram** (Fig. 117b) the larger Cu-Co-Zn deposits plot close along the Cu-Zn side, while the Ni-mineralizations plot also in this diagram very close to the Ni apex and mantle composition. Some of the lesser Cu-Co-Zn-deposits, and the Co-Ni stringer deposits all, plot also in this diagram scattered between the main group of the Cu-Co-Zn deposits and the Ni mineralizations. On the ternary Cu-Zn-Co diagram (Fig. 117c) all the Cu-Co-Zn deposits plot again close along the Cu-Zn join, while the Ni mineralizations together with their host rocks show a crude trend from mantle-like compositions towards black schist-like. Zn-dominated compositions. Again the Co-Ni mineralizations are found scattered between the main group of the Co-Co-Zn deposits and the mantle composition characterizing the Ni mineralizations and carbonate-skarn-quartz rocks.

The thre ternary diagrams all demonstrate a wide compositional cap between the Cu-Co-Zn and Ni deposits plus carbonate-skarn-quartz rocks, and lack of any trends in the metal contents to indicate their cogenesis.

A distinct, and obviously primarily genetically unlinked nature of the Cu and Ni sulphide mineratizations comes even more evident when the data are plotted on the *Ni-Co, Cu-Co and Zn-Co binary diagrams* (Fig. 118-119).

On the **Ni-Co diagram** the Cu-Co-Zn ores plot in a flat array with Ni/Co ranging from 0.33 to 7.1. In a high contrast, the Ni-mineralizations define an ascending linear array with the mantle Ni/Co ratio of 18.7. It is worth to note that also the carbonate-skarn-quartz rocks plot on this diagram remarkably identically with the mantle, and that the modern MOR, likewise ancient Cuprus and Besshi deposits show far lower Ni and Co abundances and, excluding the Cuprus deposits, also Ni/Co ratios (<0.3) than the Outokumpu sulphides. The mantle-like Ni/Co of the carbonate-skarn-quartz rocks and associated Ni mineralizations imply close system behaviour of Co and Ni inside the carbonate-silica alteration zones and that this alteration was not directly



Fig. 117, Part 2. (A) Cu-Co-Ni, (B) Cu-Zn-Ni and (C) Cu-Zn-Co ternary plots for average compositions of the Outokumpu-type Cu-Co-Zn deposits and Kokka-type Ni mineralizations in North Karelia. Primitive mantle composition after McDonough and Sun (1995) for comparison. HIE=Hietajärvi, HIP=Hippos, HOI=Hoikka, KET=Kettukumpu, KYL=Kylylahti, LUI=Luikonlahti, OKU=Outokumpu, RII=Riihihilahti, SAR=Saramäki, SOL=Sola, VUO=Vuonos, PER. Average data for the included deposits is from Table 9.

related with the formation of the Cu-Co-Zn ores. On this powerful diagram the Co-Ni formations do not significantly differ from the leanest massive-semimassive Cu-Co-Zn deposits. On the Cu-Co diagram the massive-semimassive Cu-Co-Zn and the Ni deposits define separate parallel ascending arrays with a high contrast in the associated Cu/Co ratios. Outokumpu alteration assemblage and Kokka type Ni mineralizations have Cu/Co ratio at about 0.7, which as being a bit higher value than the 0.29 of the mantle, implies slight contamination in Cu. Compared to the Ni mineralizations, the Cu-Co-Zn mineralizations have much higher Cu/Co ratios ranging between 4.5 and 20. These are, however, much lower values compared to the Cu/Co in the order of 100 typical of modern MOR or Cuprus and Besshi sulphides. On the Zn-Co diagram separation of the main mineralization types is less pronounced, because of the low Zn in some of the lesser Cu-Zn-Co deposits and the obvious slight Zn enrichment in the carbonate-skarn-quartz rocks and Kokka type Ni mineralizations. Being not associated with Co enrichment, the slight Cu-Zn enrichment in the carbonate-skarn-quartz rocks and Ni mineralizations is likely of a different origin than the Cu-Zn enrichment in the Cu-Co-Zn ores, probably by synmetamorphic addition. It is the obvious synmetamorphic immobility of Co that makes Co/Ni ratio superior over Cu/Ni and Zn/Ni ratios in tracing for signs of the Cu-Co-Zn mineralization processes.

There is a clear tendency among the massive-semimassive deposits towards higher Cu/Ni and Co/Ni with increase in deposit size. Riihilahti and Kylylahti are the most notable deviation from this trend showing the highest Co/Ni and second highest Cu/Ni after Outokumpu, in spite of their relatively small deposit sizes. The high Co/Ni at Riihilahti may reflect the unique absence of ultramafic rocks in its rock assemblage. This explanation does not work for the



Fig. 118. Ni, Cu and Zn versus Co plots for average compositions of Outokumpu-type MS-SMS deposits (bulk ore data from Table 10). For comparison, averages for mantle, MOR sulphides and Cyprus and Besshi massive sulphides are shown.
ultramafic-flanking Kylylahti deposit, however. The Sola Zn mineralization, sampled for this study in lack of core from its main Cu mineralization, exhibits also a deviating character, showing particularly low Co/Ni, Cu/Ni and high Zn/Co, which may reflect the particular intimacy of these sulphides with black schists.

It is important to note that the Co-Ni, or stringer type deposits from Keretti, Vuonos and Kylylahti all plot on the Co-Ni, Cu-Ni and Co-Cu diagrams intermediate to the massivesemimassive Cu- and Kokka Ni deposit types, consistent with proposals of their origin by overprinting of Ni-mineralized zones by Cu-Co-Zn mineralization (cf. Parkkinen and Reino, 1985). While the Cu-Co-Zn overprinting is clear for the best parts of the Co-Ni deposits, the low Cu/Ni and Co/Ni of the Vuonos "Ni-Ore" indicate mining for it involved chiefly digging for normal Outokumpu type carbonate-skarn-quartz rocks.

The very difference of the Outokumpu sulphides to modern MOR and Cyprus and Besshi deposits is very clear on the basis of the above presented diagrams. First of all, Outokumpu sulphides contain 1 to 2 orders of magnitude more Co and Ni. Some Besshi type sulphides have relatively high Co, as e.g. the giant Windy Graggy (1000±500 ppm ppm, e.g. Peter and Scott, 1999) and prototype Besshi (av. 558 ppm, Kase and Yamamoto, 1988) deposits, but the Ni contents even in these deposits are very low, typically <100 ppm on average basis (e.g. Slack, 1993).

The scatter in the binary diagrams is somewhat reduced, especially for the Kokka type Ni mineralizations, when the metal abundances are plotted as calculated into 100 % sulphides (Fig. 119). The distinct and obviously genetically unrelated nature of the Cu and Ni mineralizations is in these diagrams even more evident than in the bulk rock based diagrams, especially on the Ni-Co diagram. The Kokka type Ni deposits now plot in this diagram close to the average compositions of the carbonate-skarn-quartz rocks, and it can be seen that the Ni mineralization sulphides are actually poorer in Co, Ni, Cu (and Zn) than the serpentinite and carbonate-skarn-quartz rock sulphides. All the metaperidotite, metaserpentinite, carbonate-skarn-quartz rock and Ni mineralization sulphides have preserved their primary, protolith inherited mantle like Ni/Co ratios remarkably well. This means that there is absolutely no trend in the Ni mineralization sulphide compositions towards those typical of the Cu-mineralization sulphides. The relatively Co-Ni rich nature of the Keretti and Vuonos parallel mineralizations and Kylylahti stringers is more apparent in the light of the 100% sulphide compositions, justifying the referring of these mineralizations as "Co-Ni" mineralizations/zones.

## 9.1.2. Comparison of the sulphide phase compositions

In this section we examine and compare the metal enrichment patterns of the different Outokumpu district deposits and their usually relatively sulphide-rich wall rocks, using pie and spider diagrams (Figs. 120-125), the latter for sulphide phase metal concentrations from calculations assuming 100% distribution of total metals in a sulphide phase containing 37 wt.% sulphur (cf. Vähätalo, 1954). Though somewhat arbitrary, the sulphide phase normalized values make comparison between deposits/samples of different gangue amounts easier.

The average compositions of the studied Cu-ores and Ni-mineralizations used in the diagrams, are presented in Table 10. The averages are based solely on analytical data by GEOMEX/GTK. Because of the relatively small number of samples for most of the deposits, the average compositions in Table 10 should not be considered any sort of deposit grade estimates. The purpose of the GEOMEX geochemical study was rather to provide information about the general geochemical character and variation of the included deposits. For this purpose the sampling seems to have been overall adequately representative, and in case of some deposits (e.g. Outokumpu and Luikonlahti) even highly representative. Sample selection for the part of the semimassive-massive deposits was straightforward owing to the frequently very sharply bounded nature of the massive-semimassive bodies. For the less concentrated, "disseminated" or stringer-type deposits like the Riihilahti deposit, Outokumpu-Vuonos Co-Ni-parallels, and Kylylahti stringer (skarn) mineralization, samples with >1000 ppm Cu and/or >500 ppm Co were



Fig. 119. Ni, Cu and Zn versus Co plots for average sulphide phase compositions of the Outokumpu type deposits in the NKSB (calculated based on data in Table 10). For comparison averages for sulphide phases in mantle, modern MOR (TAG), Cyprus and Besshi deposits are shown. Note that the mantle point is calculated assuming bulk metal contents, 250 ppm sulphur and that all the metals were in sulphide phase, as it to a large degree is in the case of totally serpentinized peridotites.

accepted, as this procedure seemed to produce average composition reasonably close to the available reserve/resource estimations.

The pie diagrams in Figs. 120-121 show that Cu and Zn with subordinate Co and Ni are the dominant metals in all of the studied massive semimassive Cu-Co-Zn ores. Other metals rarely count together more than 0.8 wt. % of the sulphide phase. The trace metal budgets of the Cu-ores are dominated by As, Ag, Sn, Cd, Au, Sb, Mo, Pb, Se, and Bi listed in the order these metals are enriched in average Outokumpu ore over their primitive mantle abundances.



Fig. 120. Pie diagrams of relative metal abundances in average Outokumpu massive-semimassive ore, MOR (sediment-free) massive sulphides and Kokka Ni mineralization.



Fig. 121. Pie diagrams of relative metal abundances in the small and/or lean massive-semimassive Outokumpu type Cu deposits in North Karelia.

In a great contrast to the Cu mineralizations, the Ni-mineralizations are highly Ni dominant with only trace amounts of Co, Zn and Cu (Fig. 122). In the Ni-mineralizations absolute concentrations of the trace metals, except for As, Mo and Bi, are extremely low, mostly 5-10 times lower than in the Cu-ores (Table 10c). In this respect the Ni mineralizations are very close to "unmineralized" Outokumpu-type quartz rocks.

The Co-Ni stringer mineralizations are for their metal patterns at Outokumpu and Kylylahti intermediate to the Cu and Ni mineralizations, while in the Riihilahti deposit the metal distribution is quite like in the prototype Outokumpu deposit (Fig. 122).

The pie diagrams in Fig. 123 show that the metal distributions in the carbonate-skarnquartz rocks and the Kalevian black schists are very different, the former rocks being strongly Nickel dominated, while the latter are strongly Zn dominated. There is also relatively less Co in the black schists sulphides.

The metal distributions of the Cu-ores and Ni mineralizations are further illustrated and compared on the mantle-normalized spider diagrams in Figs. 124-125. The elements shown on the spider diagrams comprise all the major and trace metals considerd in the pie diagrams of Figs. 120-123. In the spider diagrams the elements are arranged from left to right in the order they are enriched in the average Outokumpu Cu-ore with respect to the primitive mantle, to provide a smooth reference pattern. Using bulk silicate earth (= pyrolite, primitive mantle) in the normalization was considered natural recalling the frequently intimate association of the Outokumpu deposits with metasomatically altered and metamorphosed mantle peridotites, and which thus may represent one of the more potential source of the ore metals. One advantage of using mantle-normalized spidergrams is that they directly show the factor by what a given metal in a given ore is enriched over its primitive mantle abundance.

The most enriched element in the sulphide phase of the average Outokumpu ore is As, which is enriched by a factor of about 2500 relative to the primitive mantle. In the prototype Outokumpu ore also Cu, Ag, Sn, Cd and Au show enrichment factors over or close to 1000, less enriched by 600 to 400 times are Sb, Mo, Zn, Pb and Se, whereas Co and Ni show much lower enrichment factors of 36 and 0.2, respectively. Comparison to other massive sulphide deposit types is difficult as massive sulphides are surprisingly poorly documented for their trace element geochemistry; our literature review yielded comprehensive trace element data only for present MOR surface sulphides (Herzig et al., 1998; Goodfellow et al., 1999). In terms of the Cu enrichment Outokumpu and MOR sulphide phases are about equal. Other metals that are about similarly enriched include As, Au and Bi. The surface MOR sulphides are significantly richer in Mo, Zn, and Se, and especially in Ag, Cd, Sb and Pb, but are much lower in Co, Ni and Sn. Due to post deposition zone refinement, interior/deeper parts of MOR sulphide mounds would show overall metal enrichment pattern more similar with that of the Outokumpu deposit, but the drastic difference in Co and Ni abundances would remain. The MOR interior sulphides in fact seem to contain less both Ni and Co than the MOR surface sulphides (cf. Herzig et al., 1998).

The mantle-normalized profiles of the sulphide phases in Fig. 124 reveal considerable metal spectral differences between the different Oku-type deposits. Most similar in their metal enrichment pattern with the prototype Outokumpu deposit are the other Outokumpu-zone massive-semimassive deposits, Vuonos and Perttilahti, though both these deposits are, compared to Outokumpu, significantly lower in Au and Se, and Perttilahti also in As, Cu, Sn, Sb and Pb. It seems that the drop in these elements In Vuonos and Perttilahti is correlated with drop in Cu content. In fact, Perttilahti could be included as the Cu-richest member in the lowgrade clan of Luikonlahti, Hietajärvi, Hoikka and Kettukumpu deposits, which all show strong relative depletion in As, Sn, Au, Sb, Zn, Pb, and Se compared to the Outokumpu ore. Kylylahti massive-semimassive sulphides exhibit rather similar metal enrichment pattern to that of the main Outokumpu ore, with the significant difference that they are relatively more enriched in As and depleted in Sn, Zn, Pb and Bi. The massive-semimassive sulphides of the Saramäki deposit exhibit rather similar metal enrichment pattern than the Kylylahti sulphides, although the overall metal enrichment level at Saramäki is lower and Au and Sb are relatively depleted. The Sola Zn mineralization is, compared to the Cu-dominated deposits, enriched in Cd, Mo, Zn and Se. It also shows a distinctly low Co/Ni ratio; in this respect the Zn-rich parts of the Kylylahti



Fig. 122. Pie diagrams of relative metal abundances in averages of Outokumpu Co-Ni zone, Kylylahti skarn-zone and Riihilahti striunger mineralizations. For comparison, similar diagram for Kokka-type Ni mineralisations is also shown.



Fig. 123. Pie diagrams of relative metal abundances in average Kokka-type Ni mineralization, Outokumpu type quarz rock and Upper Kaleva black schist.



Fig. 124. Mante-normalized metal profiles of sulphide phases of the Outokumpu type deposits in NKSB. The included elements ordered according to their relative enrichment in the Outokumpu ore, the enrichment factor increasing from left to right. Mantle values are from McDonough and Sun (1995). Profile of average MOR sulphides (in sediment-free ridges) is shown for comparison in the upper lefthand diagram (data sources Herzig et al., 1998; and Goodfellow, 1999).

deposit come close. The small Hippos showing, which possibly is not an Outokumpu type deposit at all; however, displays a general metal enrichment pattern that is not that dissimilar of the patterns of the low-grade Outokumpu type Cu mineralizations. Although there seems to be relatively slightly more Pb and less As, Ni and Co in the Hippos sulphides.

The Riihilahti deposit is related with special genetical interest because of its unique status as the only Outokumpu-type mineralization in North Karelia that lacks close association with peridotites (serpentinites) or their alteration products (metalistweanites and birbirites). In terms of metal enrichment Riihilahti is very Outokumpu-like, however. In fact more Outokumpu-like than e.g. the Luikonlahti deposit. It is also somewhat surprising that also the Outokumpu (Keretti) Co-Ni zone and the Kylylahti skarn-zone disseminated/stringer sulphides exhibit metal enrichment distributions quite similar to the Outokumpu distribution. There is, however, somewhat more enrichment in Mo, Au and Ni, and less Sn and Cd. The largest difference between Outokumpu Co-Ni zone sulphides and Kylylahti skarn-zone sulphides are the considerably higher Co and Ni and lower As and Sb abundances in the former. Average Cr contents of both of these mineralizations are high (Table 10a) and indicative of high proportion of peridotite derived gangue. Ni inherited in the abundant peridotite-derived gangue is the most likely explanation for the relatively high Ni of the Outokumpu and Kylylahti "Co-Ni" mineralizations.

The sulphide phases of the Kokka-type Ni mineralizations and the Outokumpu-type carbonate-skarn-quartz rocks show mutually very similar average metal enrichment patterns (Fig. 125). In both cases Ni and Co are quantitatively the most abundant metals (expect for Fe). However, the metals that show highest enrichment over their mantle abundances include As, Mo, Ag, Bi and Sb. Unfortunately, because of the usually very low absolute concentrations of these elements in both the Ni-mineralizations and carbonate-skarn-guartz rocks, often below the detection limits of the here applied analytical methods, their metal enrichment factors remain guite uncertain. Nevertheless, the metal profiles of the carbonate-skarn-guartz rocks and Ni-mineralizations, and certain degree also profiles of the Cu-poorest massivesemimassive Cu-ores, seem to be characterised by more or less significant positive As, Ag, Mo and Pb, Se and Bi spikes. It should be noted here that sulphidic black schists, which usually flank the carbonate-skarn-quartz rocks and contained Ni-mineralizations (and Cu-Co-Zn ores as well), are frequently strongly preferentially enriched in these same elements (cf. Fig. 125). But its should be reiterated that the absolute concentrations of Ag, Bi, Mo, Pb and Se are in the quartz rocks systematically very low. One notable feature is the Cu/As ratios that in the quartz rocks (av. Cu/As=ca. 2), black schists (av. Cu/As=ca. 4) and Ni mineralizations (av. Cu/As= ca. 7) are far lower than in any of the Cu sulphide deposits (Cu/As= >20 - >4000).

The high Cr in the Ni mineralizations (Table 10a) indicate, together with petrographic evidence of frequent presence of chromite, that the abundant gangue in these rambling mineralizations is systematically the ordinary carbonate-skarn-quartz rocks of the Outokumpu assemblage. And, as we stated above in the section about the Petäinen prospect, the Kokka type Ni mineralizations seem to represent closed system syntectonic redistribution of earlier formed Fe and Ni sulphides and silica inside of the Outokumpu alteration assemblage. In contrast, the low average Cr in the massive-semimassive Cu-Co-Zn ore bodies (Table 10a), despite their usual location partly inside, partly adjacent to the Cr-rich Outokumpu type carbonate-skarn-quartz rocks implies either extensive dilution of Cr abundances due to introduction of excess sulphur (sulphides) and perhaps also silica during the ore formation, or that large parts of the ores formed without any significant intercalations of their present wall-rocks.

## 9.2. Elemental geochemistry

The following discussion of the elemental geochemistry of Outokumpu sulphide deposits is mainly for the massive-semimassive Cu-Co-Zn-Ni+-Au deposits, with occasional comments on the associated Co-Ni (stringer) mineralizations and Kokka-type Ni mineralizations The following text is heavily biased to the large, well documented Outokumpu and Vuonos deposits for which we have most chemical data.



Fig. 125. Mantle-normalized metal profiles of sulphide phases in average Kokka-type Ni-mineralization, Outokumpu-type quartz rock and Outokumpu area black schist. The profile of average sulphide phase in Outokumpu main ore is shown for comparison. Note similarity of the Ni-mineralization and quartz rock profiles with the average black schist profile, suggesting metal contribution from the latter to the former. This may have taken place during the primary carbonate-silica alteration stage or later during progressive metamorphism.

## 9.2.1 Main suites of ore-forming elements

Applying statistical correlation analysis (aided with visual examination of element-element pair plots to overcome problems with "outlier samples" and multiple or nonlinear trends) on the Outokumpu and Vuonos ore system, from which a quite large number of samples (n=99) has been chemically analysed (all analytical work in GTK before the GEOMEX project), four distinct groups or suites of sympathetically behaving ore-forming elements can be delineated. These include the: (1) Co-S-suite: Co-S-Se-As; (2) Cu-suite: Cu-Sn-Ag-Sb-Au; (3) Zn-suite: Zn-Cd-Ga, and (4) Ni. We note that Sn, which is here included in the Cu suite, could as well be considered a Zn-suite element. It is also worth to note that the Co-S suite elements do not show positive correlation with any of the characteristic elements of the other suites. And, that Ni, though it is a fairly abundant element in Outokumpu sulphides, lacks correlation with about any of the here-considered metals. Also Pb and Bi seem to represent sort of background or overprinted elements.

In terms of these correlation patterns the Outokumpu sulphides are to a large extent similar with the other important types of hydrothermal massive sulphide deposits, especially the categories of VMS. The Cu-suite and S-Co-suites could combined be compared with the high-temperature suite Cu-Co-Bi-Se-In-Ni+-As+-Sn+-Ag+-Au, and the Zn-Suite with the low-temperature suite Zn-Cd-Ag-Pb-Sn-Sb-As-Hg+-TI+-W, these element suites being observed for many VMS. However, in marked difference to their behaviour in VMS, Co and As in Outokumpu sulphides do not show correlation either with Cu or Zn, and Ni behaves completely independent of other metals. Further, poor correlation of Pb with such metals as Zn and Ag seems a more or less unique feature of Outokumpu deposits, raising the question of to what extent Pb in this case was related to the principal ore-forming event.

It should be noted that the correlation coefficients mentioned below are all for bulk sample compositions; for the sake of simplicity, and to allow correlations with litophile elements. In

most cases applying of sulphide phase concentrations would not much change the reported correlations, which anayway should be taken with a grain of salt. Namely, in many cases the element distributions are far from being ideal for any correlation analysis.

## 9.2.2. Copper and Zinc

These are among the most abundant metals in most varieties of hydrothermal massive sulphides, and here Outokumpu makes no exception. The Zn and Cu in the amphibolite grade Outokumpu ores locate nearly quantitatively in coarse-grained metamorphically pervasively recrystallized and re-equilibrated sphalerite and chalcopyrite±cubanite.

Based on the published size and grade estimates, there is a very clear tendency of the Cu content in the Outokumpu deposits to increase with deposit size, both in terms of bulk ore and sulphide phase contents. So, the smaller deposits in the <1 Mt clan all contain on average less than 1 wt% Cu, while all the >1 Mt deposits, Saramäki excluded, contain more than 1 wt.% Cu. Excluding the small, poorly outlined Sola mineralizations, a tendency towards higher grade with increase in deposit size is obvious also for Zn, although the trend is much weaker than in the case of Cu. Within the bounds of individual deposits Zn and Cu show rather poor correlation; in the Outokumpu-Vuonos sample case there is only a weak positive trend (r=\*0.25).

In the Outokumpu ore the upper edge parts were its relatively Zn-richest domain, while its middle ore hanging wall and lower edge domains were relatively enriched in Cu and Co, respectively (cf. Fig. 1; Mäkelä, 1981). This situation has often been interpreted as an indication of that the Outokumpu ore originated with a Cu-Co rich "proximal" and Zn-rich "distal" facies and hence was a seafloor exhalative hydrothermal deposit akin to the Cyprus or Besshi deposits (e.g. Mäkelä, 1981). However, it remains problematic in frames of such models that Ni content is very high (for any type of seafloor massive sulphides) thorough the ore, also for its Zn richest parts. It is worth to note, also, that in its sister Vuonos ore the upper edge was but its Zn also Cu richest domain (Kauppinen, 1978). Therefore, and recalling the complex high amphibolite facies structural and metamorphic history of the Outokumpu deposits (cf. Koistinen, 1981; Treloare et al., 1981; Säntti et al., in press), there is the possibility that the metal zonations in the Outokumpu deposits, even in the well zoned Outokumpu main ore, were in fact due to pervasive differential mobilization of sulphides during their long-lasted and complex high temperature deformation and metamorphism. In the case of Outokumpu such processes have been documented (Väisänen and Mikkola, 1972; Koistinen, 1981), and they may have been far more extensive and important control of the ore metal distributions than have been considered likely.

Owing to their relatively high Cu/Zn ratios, as well as low Pb, in the past ore model speculations the Outokumpu deposits have usually been correlated either with Besshi or Cyprus type. With respect to the average Cu and Zn contents and ratios, there is indeed little that would be in opposition to such correlations, or correlation with several other massive sulphide types.

The Kokka-type Ni-mineralizations are systematically very low in Cu and Zn; the average level is about 200 ppm and 300 ppm, respectively. Concentrations of Cu and Zn in sulphide phases are significantly higher, 1100 ppm and 1400 ppm, respectively. Surprisingly, there is a clear tendency of the Ni mineralization sulphide phases to get leaner in Cu and Zn, as well as in most other metals, with increase in sulphur content.

# 9.2.3 Cobalt

Up to the systematically high Ni and very low Pb (below), high cobalt is one of the geochemically most distinct characters of the Outokumpu type Cu ores. Cobalt was an economically important by-product for all the past Cu mining in the Outokumpu ore field. In the pyritic ores/ore facies of the Outokumpu-type deposits cobalt locates dominantly in pyrite, whereas in pyrrhotitic ores the main host is Co-pentlandite. In addition, significant cobaltite may

occur in As rich ore parts, as e.g. in parts of the Kylylahti deposit. The variation in cobalt host mineralogy is clearly covered by regional metamorphic grade and related breakdown of the Co bearing pyrite to pyrrhotite and Co-pentlandite. So, in migmatite grade environments where all prepeak-metamorphic pyrite has been replaced totally by pyrrhotite, Co occurs almost exclusively in Co-pentlandite.

Like Cu grades, also Co grades in Outokumpu deposits increase with deposit size. So all the <1 Mt deposits except Hietajärvi (1700 ppm Co), contain on average 1000 ppm or less Co, whereas all the >1 Mt deposits, except Saramäki (860 ppm Co), contain more than 1000 ppm Co. In terms of sulphide phase compositions, there are deviations from this trend, the stringer type Riihilahti deposit shows up a particularly Co-rich deposit despite its small size, for example. The large Outokumpu main massive-semimassive ore contained 2400 ppm Co on average. From the other massive-semimassive deposits Kylylahti shows distinctly high average cobalt content of 3600 ppm.

The Co-Ni-parallels at Outokumpu and Vuonos, and as was mentioned above, the stringer type Riihilahti deposit have sulphide phases, which are relatively Co enriched, containing on average 15200 ppm, 4600, 7500 ppm of Co, respectively. These are clearly higher values than the 3100 ppm for Co in the sulphide phase of the massive-semimassive Outokumpu ore.

In the Outokumpu-Vuonos ore system Co shows significant positive correlation with Se (0.71\*\*\*) and S (0.61\*\*\*), and less significant affinity to As (0.23\*), while correlations with most other ore metals are mostly weakly to clearly negative. This implies with mineral chemical evidence from Outokumpu and Kylylahti that Co is one of the "primary pyrite-stage" elements. In Outokumpu and Kylylahti deposits, both the early, "primary" pyrites and late, clearly metamorphic pyrite idioblasts often show distinct zoning for cobalt (e.g. Väisänen, 1972; Hänninen, 1986). The presence of Co zoning even in the "primary" pyrites is a problematic feature, since theoretically the long-lasting amphibolite facies regional heating of these deposits should have homogenised any primary sulphides for their metal, including Co, distributions (Mizuta et al., 1998). Therefore it seems likely that Co zoning both in the "primary" and metamorphic pyrite swould record either synmetamorphic cobalt infiltration/cobalt pyrite generation or synmetamorphic pyrite dissolution and redeposition. More detailed study on the nature of the cobalt zoning should be performed before selection between these two alternatives can be attempted.

The Kokka-type Ni mineralizations show slightly elevated Co tenors of 150-300 ppm on average, with higher concentrations up to 500 ppm being usual for many individual samples. Cobalt abundances in the Ni mineralization sulphide phases are about the order of 1300-2200 ppm, but with a tendency of the Co tenors to decrease with increase in S. Average Co abundances for the Outokumpu type serpentinite and carbonate-skarn-quartz rocks range from 80 to 120 ppm depending on rock type. Due to the relatively low S of the Carbonate-skarn-quartz rocks, their sulphide phase is significantly higher in cobalt (2500- 5000 ppm) than that typical of the Kokka type mineralizations. However, both the Ni mineralizations (0.03-0.07) and carbonate-skarn-quartz rocks (0.06) show average Co/Ni ratios close to the primitive mantle Co/Ni value of 0.054 (McDonough and Sun, 1995). Thus a mantle origin of Co and Ni is indicated; there are no trends even in the Ni mineralizations.

From those massive sulphide deposit types that at least somehow show similarity to Outokumpu, only some Besshi, and to a lesser degree Cyprus type deposits show Co contents even approaching the high values of Outokumpu deposits. For comparison, the average cobalt content of the prototype Besshi deposits of the Sambagawa belt (Japan) is 558 ppm (Kase and Yamamoto, 1988) and that of the supergiant Besshi type Windy Graggy (>300 Mt of 1.38 % Cu) in British Columbia in Canada 1000+-500 ppm (Peter and Scott, 1999). Cobalt abundances in Cyprus-type, and modern ocean-ridge deposits are usually lower than in the Besshi deposits, typically in the order of a few tens of ppm up to a few hundreds of ppm (e.g. Herzig et al., 1998; Goodfellow et al, 1999; Petersen et al., 2000). Cobalt is a common associated metal also in the high sulphur end-member deposits of the iron oxide-Cu-Au clan, a typical example of these deposits is the Eloise Cu-Au deposit in Cloncurry District, Australia, which actually has quite Outokumpu-type metal pattern of Cu-Au-Co-Ni-Zn-As-Pb and Bi (cf. Baker, 1998).

Owing to the fact that the Outokumpu massive-semimassive sulphides frequently show much higher Co/Ni ratios (>1) compared to the mantle-like, or lower Co/Ni ratios (<0.1) in their usual host rocks, this ratio has been routinely used as an exploration tool helpful in locating of interesting targets within the alteration zones of serpentinite bodies. However, the fact that the "halos" of anomalous Co/Ni ratios around the deposits are usually very restricted, often nearly absent, greatly reduces the practical value of the Co/Ni ratios as ore indicator. Moreover, owing to the systematically very rare chalcopyrite and sphalerite in the unmineralized Outokumpu assemblage, looking after any visible chalcopyrite and/or sphalerite in the Outokumpu-type carbonate-skarn-quartz rocks provides certainly an nearly equally effective, but faster and cheaper method for discovering possible neighbourhood of an Outokumpu type mineralization.

## 9.2.4. Nickel

High nickel is a unique and perhaps most problematic geochemical aspect of Outokumputype massive sulphides. Namely, such high Ni contents that occur in the Outokumpu type deposits are not known to occur in any of the more common hydrothermal massive sulphide deposit types. Yet the Outokumpu deposits are frequently proposed to represent an example of either Besshi or Cyprus (Ophiolite) type massive deposits, even if with some flavours of their own (e.g. Treloar et al., 1981; Papunen, 1987; Gaál and Parkkinen, 1993).

There is considerable variation in the average Ni content of the studied Outokumpu-type deposits, ranging from 370 to 2900 ppm. With regard to sulphide phase compositions there is somewhat less variation; all the studied deposits contain in their average sulphide phase whopping amounts of Ni, from 1490 to 5940 ppm. There is a slight decrease with deposit size in the Ni tenors, more apparent in terms of the sulphide phases. Accordingly the <1 Mt deposits contain from 2890 up to 5940 ppm Ni in their sulphide phases, whereas the respective range for the >1 Mt deposits is from 2840 down to 1490 ppm Ni. The sulphide phase of the large Outokumpu deposit contains on average 1560 ppm Ni, the corresponding average bulk ore Ni concentration is 1200 ppm.

As we pointed above, Ni is an independently behaving element in Outokumpu-Vuonos ores, lacking a clear positive affinity to about any other element, except perhaps for Zn. The lack of significant correlation with Co (r=-0.02) is of particular importance. Namely, this is strong evidence of the Ni was not introduced concurrently, or from a common source with Co, and thereby a strong indication of that the metal enrichment in Outokumpu deposits would be of polygenetic origin. In contrast, most volcanogenic massive sulphides show strongly positively correlated distributions of Ni and Co, suggesting that the (highest temperature) ore-generating fluids were enriched in both these metals.

Especially high average Ni tenors (3300-3900 on average basis) are met in the Outokumpu and Vuonos Co-Ni zones and Kylylahti skarn zone, where the pay sulphides occur in bands and streaks (Keretti Co-Ni zone) or veins and blotches of semimassive Cu-ore and disseminations (Kylylahti) hosted in Outokumpu type carbonate-skarn-quartz rocks and confined narrow chlorite-rock layers (altered mafic dykes). Calculated for sulphide phases the Ni tenors in these mineralizations are pretty high, on average from 1.6 to 4.5 wt. %, the latter value referring to the Keretti Co-Ni zone sulphides.

Ni data for cross-sections over the Outokumpu ore show that dominantly pyritic ore parts would be Ni poorest facies of the ore, and that high Ni contents would characterise especially the pyrrhotitic margins of the ore sheets. This indicates the possibility of that at least a part of the ore Ni would be by synmetamorphic (?) interaction with the usually Ni-enriched wall rocks. The high Ni in the Co-Ni zone mineralizations, where preconditions for such interaction were particularly good, appears to support this type of scenario. Nevertheless, Ni concentrations are relatively high (for massive hydrothermal sulphides) also in the pyritic ore parts, usually between 500 and 1500 ppm, thus high Ni may not be solely a late, overprinted feature, but considerable Ni probably was added in the ore already during the "primary" pyrite deposition.

The Kokka-type Ni mineralizations contain 0.5-1.0 wt.% Ni for their best parts with peaks

up to 2 wt.% Ni. The corresponding sulphide-phase Ni tenors are usually between 3 and 5 wt.%. Average Ni concentrations in Outokumpu-type carbonate-skarn-quartz rocks are mantlelike between 1000 and 2000 ppm, depending on rock type. Because of the usually relatively low bulk S (ca. 1 wt.%), sulphide phases in the carbonate-skarn-quartz rocks are richer in average Ni than in the Kokka-type mineralizations, with a range from 4 to 9 wt.% Ni. Sulphide specific leaches and petrographic data indicate that Ni in the carbonate-skarn-quartz rocks would indeed reside more or less quantitatively in the sulphide phase (mostly in pentlandite).

Such high Ni contents as typical for Outokumpu sulphides would be considered extraordinary high in association about any of the more common types of hydrothermal Cu-Znmassive sulphides. Most volcanic associated massive sulphide deposits, for example, are practically free of Ni, with concentrations very consistently below 50 ppm. The average Ni content in the Japanese Besshi deposits is only 34 ppm (Kase and Yamamoto, 1988), in the Cyprus (ophiolite) type deposits the Ni range is 20-125 ppm (Hadjistavrinou and Constantinou, 1982), and in the present mid-ocean ridge sulphides <10-50 ppm depending on subtype (e.g. Foquet et al., 1996; Goodfellow and Zierenberg, 1999). Where Ni abundances above 100 ppm have been observed, they frequently have been interpreted as an indication of pronounced ultramafic component in the metal source (cf. e.g. Murphy and Meyer, 1998; Hannington et al., 1999). However, relatively low Ni concentrations, mostly between <20 and 250 ppm, seem to characterise also ultramafic-floored massive sulphides at modern mid-oceanic ridges (e.g. Murphy and Meyer, 1988; Bogdanov et al., 1997). This suggests that the well-established relative immobility of Ni in seafloor hydrothermal processes is that also in those environments where the metal source is dominantly ultramafic.

## 9.2.5. Gold

Some of the Outokumpu deposits contain recoverable amounts of gold. In fact the Outokumpu mine was for long the most important gold producer in Finland, with an annual yield of about 0.5-1 ton of Au. With respect to the massive-semimassive deposits, Gaál and Parkkinen (1993) and Parkkinen (1997) have reported that the Outokumpu ore contained 0.8 gr/ton, Vuonos 0.1 gr/ton and Kylylahti 0.64 gr/ton gold on average. The rest of the massivesemimassive occurrences appear very Au poor, however. The Co-Ni zone or stringer type occurrences seem all Au enriched. The Kylylahti stringer zone is reported with a mass of 1.43 Mt at 0.9 gr/t Au (Pekkarinen et al., 1998). According to Parkkinen and Reino (1985) the Keretti Co-Ni zone would include a mass of1 Mt at 0.15 gr/ton Au. A survey by GEOMEX showed that the Au enrichment in the Co-Ni zone is strictly restricted within the domains of visible chalcopyrite, outside of them the Au level drops immediately below 10 ppb. The Vuonos Nideposit was notably leaner in Au than the Keretti Co-Ni zone, and contained only 0.04 gr/ton Au for its Co-Cu-Ni richest part of 1 Mt (Parkkinen, 1997). Au content for the entire mass of 5.5 Mt "ore" mined from the Vuonos Ni deposit has not been published, but it must have been much below the 0.04 gr/ton reported for its Cu-Co-Ni-richest part. There are no formal estimate available of the Au content of the Riihilahti stringers, based on a reconnaissance study by GEOMEX the likely average Au tenor is somewhere around 0.3 gr/ton.

The mode of occurrence of gold in the Outokumpu deposits is imperfectly known. Vähätalo (1953) remarked in the Outokumpu ore at least part of the gold was in metallic grains; this was evident as native gold was recovered by gravity separation, as obvious mill-deformed, platy gold chips from 0.05 to 0.1 mm in diameter. Nevertheless, in his extensive petrographic work on the Outokumpu ore, comprising an optical study of more than 500 polished sections, Vähätalo (1953) observed native gold grains only in a few samples, most of them as tiny grains associated with sphalerite inclusions in chalcopyrite. A close association of Outokumpu gold with chalcopyrite appears from that in the concentration process Au followed chalcopyrite ending up into the anode mud of copper electrolysis. Based on our brief study of Au in the Kylylahti deposit (section 8.3.1.), and that of Hänninen (1982), Au in Kylylahti occurs mainly in native form, usually in tiny grains or their aggregates enclosed in sulphides (mainly in fractures of pyrite) and sometimes also in association of gangue silicates. Native gold has been observed also in Riihilahti stringers, there mostly in fractures of the gangue silicates

### (Kontoniemi, 2001).

Within the Outokumpu-Vuonos data set Au shows significant positive correlation only with Cu (r=0.31\*\*) and Ag (r=0.27\*\*). The poor correlation of Au with other ore metals is most probably a refection of its occurrence mostly in texturally very late, "remobilized" native gold grains as observed for the Outokumpu (Vähätalo, 1954) and Kylylahti ore (Hänninen, 1982; this study). It appears from the available data that only the large (>1 Mt) and/or Cu rich (>2 wt.%) Outokumpu deposits would contain significant Au, both in their massive-semimassive and associated stringer parts.

The Kokka type Ni-mineralizations, as well as the adjacent serpentinites and carbonateskarn-quartz rocks, all have systematically low Au abundances below the 10 ppb, which was the usual detection limit of Au analysis for this study. An exception is by the talc-carbonate rocks, as e.g. in Kylylahti, which show sporadic Au enrichments up to a few hundreds ppb. Vuollo et al. (1995b) have reported that also the Vasarakangas chromitites near the Kylylahti deposit would contain some Au, with concentrations up to 14 ppb, we assume this slight enrichment is most probably related to talc-carbonation of the host peridotite. Lahtinen has reported an average Au content of 0.34 ppb for the more sandy Upper Kaleva greywackes and 0.40 ppb for the more pelitic (micaceous) interlayers. Loukola-Ruskeeniemi (1999) reports a somewhat enriched median Au content of 3.8 ppb for the Upper Kaleva associated black schists.

#### 9.2.6. Silver

Silver is a ubiquitous trace metal in the Outokumpu Cu-ores, although the grades are systematically fairly low; none of the studied deposits contained more than ca. 10 ppm Ag on average basis. The maximum Ag concentration recognized during this study recognised was 33 ppm in a sample from Outokumpu. In the Outokumpu-Vuonos ore system Ag shows a very good positive correlation with Cu (r=0,78\*\*\*) and significant positive correlation also with Sn (0.48\*\*\*), Sb (0.39\*\*\*) and Au (0.27\*\*), i.e. with all the Cu suite metals of Outokumpu-Vuonos. Very good positive correlation of Ag with Cu is apparent in also for the other Cu deposits, independent of their subtype. In the Outokumpu-Vuonos sample set, Ag show some positive trend also with Zn, but the correlation (r=0.27\*\*) is clearly much looser than that with Cu. Surprising aspects in the geochemistry of the Outokumpu-Vuonos ores include that Ag shows absolutely no correlation with Pb, and also that samples with very high Zn (10-20 wt%) are often remarkably low in Ag (10-30ppm).

The very good correlation of Ag with Cu indicates Ag is for most part hosted in chalcopyrite that can accommodate several wt.% Ag (e.g. Hannington, 1999). Minor additional hosts include Ag-tellurides, native Au and argentian pentlandite, which have been observed in trace amounts in Kylylahti and Outokumpu deposists (this study; Vuorelainen et. al., 1972). In Kylylahti particularly abundant Ag-tellurides were found in a very Zn-rich sample (Oku-905/365.95) at the margin of a semimassive ore lens, this sample contained also kustelite (Hg-Ag-Au, >50% Ag) grains. In this case, much of the Hg and Te may be from the nearby black schists.

Ag-content in the serpentinites, talc-carbonate rocks and carbonate-skarn-quartz rocks in the Outokumpu assemblage, as also in the associated Kokka-type Ni-mineralizations, are negligible, mostly below the usual 1ppm detection limit of this study. This means that also the corresponding sulphide phases, especially of the Kokka-type Ni-mineralizations, would be relatively low in Ag.

Containing just 5 to 10 ppm Ag, the Outokumpu type sulphides are significantly lower in Ag than the average modern mid-ocean ridge sulphide deposits (110 ppm), ancient bimodal-mafic VMS (40 ppm), bimodal-felsic VMS (90 ppm) or SEDEX deposits (60 ppm) (Goodfellow and Lydon, 1993; Barrie and Hannington, 1999). However, similarly low average Ag than in Outokumpu are reported e.g. for Ophiolite-hosted (15 ppm) and Besshi-type massive sulphides (15 ppm) (Galley and Koski, 1999; Slack, 1993).

#### 9.2.7. Platinum group elements (PGE)

Platinum group elements (PGE) were not included among those elements that became routinely analysed for the GEOMEX studies. This was because a high accuracy PGE survey for tens of representative samples from the Outokumpu and Vuonos deposits, performed just before the GEOMEX project, had been shown, from an economical point of view, only very low PGE contents, both in the ores and their typical wall rocks. Some exploration quality Pt and Pd testing was carried out; the observed tenors were constantly insignificant, mostly below detection limits. The discussion below is based on the GTK high accuracy Outokumpu-Vuonos data, and is undertaken mainly for Ir, Pt and Pd for which the accuracy of the applied analytical method (714M) was best.

The PGE survey of the Outokumpu and Vuonos ores included 43 samples representing their various textural and mineralogical ore types and parts. The results of the survey indicate that concentrations of the relatively inert Ir in the Outokumpu-Vuonos ores may be remarkably high for massive sulphides, up to 4.50 ppb (Fig. 124). For comparison, Ir and Os concentrations of the modern ocean-ridge massive sulphides are in the order of a few to a few tens of ppt (parts per trillion) only (e.g. Bruggmann et al., 1998; Miller, 1998; Ravizza et al., 2001). Frequent presence of trace chromite±eskolaite in the Ir-rich samples, and a good correlation of Ir with Cr ( $r=0.87^{***}$ ), Sc ( $r=0.84^{***}$ ) and V ( $r=0.74^{***}$ ) suggest that the Ir would associate with chromite. The chromite/Cr-Ir rich samples came from the margins of carbonate-skarn-quartz rock or serpentinite enclosed ore segments, while chromium and Ir in samples from middle parts of the ore bodies and from ore segments inside metasediments were usually very low, below 50 ppm and 0.1 ppb, respectively.

The Pt concentrations in Outokumpu-Vuonos ore vary between <0.20 and 3.76 ppb averaging to <0.83 ppb. As there is a good positive correlation between Pt and Ir ( $r=0.52^{***}$ ), it seems that most of the Pt was also chromite associated and thus ultimately inherited from the wall rock peridotites. Pd contents range from <1 up to 11.70 ppb averaging to <3.3 ppb. In contrast to the partly extraordinary high Ir, these are now values that are fairly similar to those observed for the present ocean floor hydrothermal mound sulphides or hydrothermal massive sulphides in general (e.g. Miller, 1998). Pd/Pt ratios vary from <0.5 up to >40 with an average value at about 9, which is a much higher value than the Pd/Pt ratio of 0.55 in the primitive mantle (McDonough and Sun, 1995), or ca. 1.0 in the continental crust (Wedepohl, 1991), or 0.7 in the seawater (Li, 2001). Cu/Pd and Au/Pd ratios in the Outokumpu-Vuonos ore are very high,  $>1.75 \times 10^7$  and  $>2.09 \times 10^5$  on average, respectively. Though these values are high for any magmatic sulphides, they are nevertheless fairly similar to values obtained for modern ocean floor hydrothermal sulphides. The dominantly hydrothermal origin of Pd in Outokumpu-Vuonos ores is supported by the absence of any correlation of Pd with Ir and Pt (Fig. 124), and its significant correlation with Co (r=48\*\*\*) and Se (r=0.40\*\*\*). Significantly, however, Ni/Pd ratios in the Outokumpu-Vuonos ore, between 6.2x10<sup>4</sup> and 4.2x10<sup>6</sup>, are much higher than for any known VMS type ore. In the higher part of this range the Ni/Pd ratios overlap mantle values (cf. Barnes et al., 1988). Furthermore, Pd does not correlate either with Au or Cu.

The high pre-GEOMEX precision PGE survey did not include samples from the Co-Ni stringer or Kokka type Ni mineralizations, but a few exploration grade tests run during GEOMEX suggests Pt and Pd concentrations in these deposits would be similarly low as in their carbonate-skarn-quartz wall rocks (section 6.3.3.) or in the Outokumpu and Vuonos ores. That means that average tenors of both Pd and Pt in both the Co-Ni and Kokka type Ni mineralizations would be significantly below 5 ppb.

Finally, we note that Pan and Xie (2001) have reported two samples from Outokumpu with extremly high Pd concentrations of 954 ppb an 1042 ppb, and exreme fractionation for their Pd/Pt ratios, 235 and 166, respectively. Based on our results from Vuonos and Outokumpu, and the gangue mineral assemblage that Pan and Xie (2001) report for their samples:



Fig 126. Iridium versus Cr, Pd versus Pt, Pd versus Au and Pd versus Cu plots for 43 representative samples from Outokumpu and Vuonos ores. Note that Pd and Pt concentrations in part of the samples were below the detection limits; and that such data are in the diagrams plotted as half of the detection limits.

quartz-biotite-plagioclase-apatite±calcite; it may be that the two samples (from the University of Saskatchevawan economic geology collection) in fact were not from Outokumpu.

# 9.2.8. Tin

Tin is one of the more characteristic trace elements of the Outokumpu-type Cu-ores. However so that significant Sn enrichment is confined to the major deposits at the western limb of the Outokumpu structure, that is, in Outokumpu, Vuonos and Perttilahti deposits, whereas the remaining deposits show relatively minor to negligible enrichment. Individual samples of massive to semimassive ore in Outokumpu may contain up to 900 ppm Sn, although on average Outokumpu, Vuonos and Perttilahti contain far less, 133 ppm, 135 ppm, and 69 ppm Sn, respectively. From the other deposits Luikonlahti contains 48 ppm Sn on average, while the remaining small, low-grade deposits all less than 20 ppm. Positive correlation of Sn content with deposit grade and size has for long been known as a characteristic feature of hydrothermal massive sulphides (e.g. Hannington et al., 1999), and this seems to be the trend also for the Outokumpu deposits.

In the Outokumpu-Vuonos ores Sn is one of the "Cu-suite" elements, showing similar good correlation with Ag (r=48\*\*\*) and Sb (r=0.53\*\*\*) as Cu. However, having correlation with Zn (r=0.44\*\*\*) almost as good as with Cu (r=0.49\*\*\*), and good positive correlation with Ga (0.47\*\*\*) and Cd (0.42\*\*\*), Sn shows a considerable affinity to the Zn-suite elements, too. The Kokka-type Ni-mineralizations, likewise serpentinites, talc-carbonate and Carbonate-skarnquartz rocks in the Outokumpu assemblage are all nearly Sn free, with concentrations frequently below the 1 ppm detection limit in this study. Kalevian black schists contain 1.2 ppm Sn on average, and thus less than the average upper crust with 2.5 ppm Sn (Wedepohl, 1991). There is not many data available on Sn in the Upper Kaleva greywackes, but the few data that exist indicate <1 ppm concentrations.

According to Hannington et al. (1999), high Ag, Pb, and Sn in massive sulphides are usually related to relatively abundant felsic volcanic rocks in their metal source. Unfortunately, Sn is not systematically analysed for massive sulphide deposits. A comparison based on the available data suggests that Sn concentrations as in the Outokumpu and Vuonos deposits would be quite typical for massive sulphides especially of mafic dominated associations. Modern spreading ridge sulphides, for example, usually show similar tens to hundreds of ppm Sn concentrations, although with much variation showing some haphazard correlation with the environment of deposition. So, while sulphides from the sediment-covered Escabana Ridge, possibly representing modern analogue to the Besshi type deposits, contain 57-900 ppm Sn (Zierenberg et al., 1993), sulphides from Guaymas Basin in a broadly similar tectonic setting contain only 3 ppm Sn on average (Peter and Scott, 1988). Sulphides from sediment-starved ridges are generally relatively low in Sn; sulphides from Galapagos, Snake Pit (Fouquet et al., 1993a), TAG (Thompson et al., 1988), Southern Explorer, Axial seamount (Hannington et al. 1990) or East Pacific Rise (Fouquet et al., 1993b) all contain only 1-30 ppm Sn on average. Interestingly, high Sn abundances do not seem to require evolved crustal source, but relatively high Sn contents are recorded even for sulphides in deposits on a dominantly ultramafic substratum, as e.g. 55-1675 ppm Sn for sulphides at the Logatchev hydrothermal field (Murphy and Meyer 1998).

Kidd Creek (Abitibi, Canada) and Neves Corvo (Iberian Pyrite Belt) are examples of two large Zn-Cu-rich massive sulphide deposits in mafic-felsic volcanic and mafic volcanic-siliclastic associations that are for massive sulphides particularly rich in Sn, up to such levels that Sn concentrates from both of these deposits have been produced commercially (Bleeker and Hester, 1999; Hannington et al., 1999; Leistel, et al., 1998; Serranti et al., 2002). Most of the Sn in Kidd Creek is associated with the low-temperature polymetallic suite of Zn, Ag, Pb, Cd, Sn, Sb, As, Hg, ±In, ±W, an association typical for distal facies of also many other felsic-volcanic-hosted volcanogenic massive sulphide deposits. In Kidd Creek the Sn mineralogy is dependent on the ore type; it is cassiterite dominated in the sphalerite-rich upper parts of the ore lenses, whereas in the chalcopyrite-rich basal parts of the lenses most Sn locates in stannite and other Cu-Sn sulphides.

In the Outokumpu deposit Sn locates mainly in stannite (Cu<sub>2</sub>FeSnS<sub>4</sub>), According to Vähätalo (1953), the stannite occurs typically as small equidimensional grains in sphalerite, or less frequently in small grain aggregates or veinlets in chalcopyrite. We observed stannite mostly in chalcopyrite-sphalerite-rich ore parts, usually at contacts of chalcopyrite and sphalerite grains, as e.g. in Kylylahti, also as inclusions in late remobilized chalcopyrite replacing metamorphic pyrite. Thus, several generations of stannite is apparently present in Outokumpu deposits; early stannite associated with sphalerite-chalchopyrite and late stannite associated with remobilized chalcopyrite. Also rare cassiterite has been reported from the Outokumpu ore (Y. Vuorelainen, unpubl.) but no details are available. Cassiterite was not encountered in the course of this study.

# 9.2.9. Arsenic

Arsenic is along with Sn one of the more characteristic trace metals in the Outokumpu-type ores, although its concentrations, the relatively As rich Kylylahti excluded, only seldom exceed 200 ppm. In fact, there is considerable variation between the individual deposits, up to degree that some of them are nearly As free. From the massive-semimassive deposits, the relatively large and Cu rich Outokumpu, Vuonos and Kylylahti main ores show the highest concentrations, comprising respectively 82 ppm, 74 ppm and 1203 ppm As. In all the other deposits, massive-semimassive or stringer-disseminated, the average level is below 30 ppm. Similar to Sn, there seems to be a tendency for higher As in the larger deposits. The relatively small Kylylahti and Sola-Zn deviate from this trend, however, showing nearly one order of magnitude higher As level than the large Outokumpu deposit. It is worth to note that that these two deposits show a particularly close association with black schists.

A strong chalcophile nature of As in the Outokumpu deposits is apparent by its usual location in pyrite, in Kylylahti also in cobaltite, and the nearly complete absence of arsenides. Hence, it is not a surprise that arsenic in the Outokumpu-Vuonos dataset shows significant sympathetic covariation about only with S ( $r=0.43^{***}$ ). Some weak affinity to As is shown also by Bi ( $r=0.36^{***}$ ), Co (r=0.23) and Sb ( $0.22^{*}$ ). A negative correlation with Ni ( $r=-0.32^{**}$ ) suggests As would compete of vacancy in pyrite, in which these two elements indeed are mainly located, at least in the pyritic ore facies of Outokumpu and Kylylahti. The relatively weak correlation obviously reflects As mobility related to the metamorphic replacement of pyrite by pyrrhotite in large parts the Outokumpu, and overall in Vuonos ore body. The low As of the dominantly pyrrhotitic migmatite-terrane deposits may thus not be entirely due to the "small size-low grade effect", but rather be a consequence of synmetamorphic As loss.

Average As content in the Kokka type Ni mineralizations is 26 ppm. Quartz rocks in the Outokumpu assemblage contain an average 34 ppm As, tremolite skarns 44 ppm, diopside skarns 13 ppm, and carbonate rocks 15 ppm. These values indicate that, similar as the Cu-Co-Zn ores, also the Ni mineralizations and carbonate-skarn-quartz rocks are strongly enriched in As, compared to upper crust (2 ppm As) and primitive mantle (0.05 ppm As). Notably, also the Outokumpu-Jormua serpentinites are enriched in As, with average contents of 13 ppm and 41 ppm for the serpentinized metaperidotites and antigorite metaserpentinites, respectively. The soapstones (talc-carbonate rocks) are even more enriched in As, with sporadic contents often exceeding 100 ppm, indicating that a significant part of the As mobility in the Outokumpu system was related to relatively late CO<sub>2</sub>-rich synmetamorphic fluids. It is worth to note that calculated for average sulphide phase, the As content in the quartz rocks turn out to be pretty high 1269 ppm. This is a far higher value than the 122 and 126 ppm As in the average sulphide phase of the Outokumpu ore and Kokka type Ni mineralizations, respectively.

Although the absolute As concentrations in Outokumpu ores are not particularly high, it remains a fact that, on mantle-normalized basis, As is after Re the most enriched metal in the prototype Outokumpu deposit. The source of this As, and overall the ubiquitous As in the Outokumpu assemblage, posses an enigma. The source hardly was in the mantle represented by the serpentinites, nor in seawater, since both these are very low in As (cf. Taylor and McLennan, 1985; McDonough and Sun, 1995; Wedepohl, 1995). Looking at a possible As source, the black schists of the ore environments, being often fairly rich in As, come first in

mind; in terms of quantities they could easily have provided the As in the ores and the carbonate-skarn-quartz rocks. Support for such speculation comes from the fact that the most arsenous of the Outokumpu deposits, the Kylylahti deposit, is associated with some of the most As-rich black schists of the Outokumpu area.

If the As was added in the ores and their peridotite-derived host rocks from the adjacent black schists, when and how did this process occur? As arsenic is one of the characteristic elements of the listwaenite-birbirite type carbonate-silica alteration, this most probably occurred in association of the obduction stage/early burial metamorphic formation of the carbonate-silica fringes of the serpentinite bodies. This seems to require that either the Cu ores formed concurrently of the carbonate-silica alteration or then there was related addition of As in already existing sulphide proto-ores. The As enrichment in the talc-carbonate rocks suggests that more As in the Outokumpu system was added by metamorphic fluid infiltration with increase in the regional temperatures. The Co-As-Ni zoned pyrites in Kylylahti ore (Hänninen, 1986) provide clear evidence of at least significant As mobility, if not necessarily net As addition, also in the ore bodies also during the regional metamorphism.

# 9.2.10. Selenium

Selenium is a relatively low concentration trace element in about all of the here studied deposits. Only the large Outokumpu deposit contains some significant Se, 24.2 ppm on average; in all the other deposits there is less than 10 ppm Se on average. From the larger deposits Luikonlahti is particularly low in Se, with an average content of only 1.1 ppm. In terms of sulphide phases, the Se richest of the studied deposits is the Riihilahti mineralization, which has 45.3 ppm Se in its average sulphide phase. This is even a bit more than the 36.1 ppm of Se in the average sulphide phase of the Outokumpu ore.

In Outokumpu-Vuonos ore system Se correlates negatively with SiO2 (r=  $-0.41^{***}$ ), yet exhibiting only relatively weak positive correlation with S (r=  $+0.28^{**}$ ). Regarding the other elements in these ore bodies, Se shows good correlation only with Co (r=  $+0.71^{***}$ ). Based on its good positive correlation with Co, and weaker with S, Se could be considered a Co-S suite element. It is somewhat strange that Se shows absolutely no covariation with Cu (r= -0.03) and As (r= +0.00). Unfortunately, there are little published data about host minerals of the Se in the Outokumpu ore. Because selenides appear rare, it seems that the Se is distributed in the common ore sulphides, the good positive correlation with Co suggesting that a large part of it would be in pyrite.

Serpentinites, talc-carbonate rocks and carbonate-skarn-quartz rocks in the Outokumpu assemblage contain only little Se. Average Se contents in all these lithologies remain below 1.5 ppm. There is apparently little more Se in the Kokka-type Ni-mineralizations, the averages Se abundances of the here studied occurrences range between <1 ppm and 8 ppm. These numbers mean that the Ni-mineralization and carbonate-skarn-quartz sulphide phases would both contain ca. 10-30 ppm Se on average. Based on rather limited data, black schists in the "Outokumpu belt" would be relatively high in Se, containing 15.4 ppm Se on average. Elevated Se is a common feature of many black shale type sediments. In comparison, Se contents in the upper Kalevian mica schists are far lower, <0.2 ppm on average (Lahtinen, 2000).

The source of sulphur is obviously one of the more important issues in genetic models of sulphide deposits. Selenium is an element that has significant potential to tell of the sulphur sources. There are several reasons to that. First, Se as a highly chalcophile element follows sulphur in most magmatic and hydrothermal processes. Second, there are considerable variation in Se/S between the possible metal reservoirs of sulphur, for example: Primitive mantle has Se/S x10<sup>6</sup> ratio of about 300 (McDonough and Sun, 1995); mantle-derived magmatic rocks typically between 230 and 350; most magmatic sulphide ores between 50 and 930 (Hannington et al., 1999); while the average Se/S x10<sup>6</sup> in the upper continental crust is about 60 and in modern sea water only ca. 0.2 (Taylor and McLennan, 1985; Wedepohl, 1995). Third, metamorphism does not seem to affect Se/S ratios, although in granulite facies metamorphic conditions, there is already the possibility that oxidative and other desulfidisation

processes seriously increase Se/S ratios. Forth, there is usually only little fractionation in Se/S ratios during the fluid passage from the source regions to the sites of deposition. Significant fractionation, however, may take place at the site of deposition. So, that e.g. in case of volcanic associated MS sulphide deposits, the highest Se/S ratios occur generally in the lower parts of the massive accumulations and in the underlying stringer zones, reflecting the general trend of the Se/S ratios getting higher with temperatures of hydrothermal deposition (Rouxel et al., 2000)

The usefulness of Se/S ratios, especially in evaluating the source of S and Se of volcanicassociated massive sulphides lies in the fact that seawater has fairly constant and much lower Se/S ratio compared to Se/S typical in magmatic fluids, or in fluids that have leached magmatic sulphides. Se/S x10<sup>6</sup> ratios measured from native sulphur deposits at volcanic fumaroles range typically between 220 and 2100. Se/S x 10<sup>6</sup> ratios from sediment-free ocean ridge-related black smoker chimneys range between 450 and 2600. Seawater has a Se/S x10<sup>6</sup> ratio of about 0.2 (Hannington et al., 1999).

Se/S ratios in modern seafloor sulphide deposits show variation depending on the tectonic environment. In nascent back arc basins underlain by continental crust (e.g. Okinawa trough), Se contents and Se/S ratios in sulphide deposits are relatively low, whereas in the mature back arc basins (e.g. Northern Lau Basin) and in the ocean spreading ridge-related deposits Se contents and Se/S ratios are relatively high. These differences probably reflect the higher significance of magmatic fluid and/or leaching of basalt as source of S and Se for the midocean ridge deposits. Among ancient VMS sulphide deposits, Zn-rich deposits tend to have the lowest, and Cu-rich deposits the highest Se/S ratios. In Canadian Precambrian Cu-rich VMS deposits Se/S X10<sup>6</sup> ratios range typically between 500 and 1800 (Hannington et al., 1999). Besshi deposits in Japan have Se/S x10<sup>6</sup> ratios typically between 90 and 2200. The giant Neves Corvo deposit in the Iberian Pyrite Belt shows Se/S x10<sup>6</sup> ratios between 120 and 1600. The Se/S x10<sup>6</sup> ratios in some large VMS deposits like e.g. the Boliden and the giant Kidd Creek deposits are very high, ranging from 500 up to 15000 and 90000, respectively.

Among the Outokumpu-type deposits in North Karelia, the highest Se contents and Se/S x10<sup>6</sup> ratios are present in the Outokumpu (Keretti) deposit, averaging to 24.2 (16.5) ppm and 100 (57), respectively (medians in parentheses). Se contents and Se/S ratios in the other studied deposits, the Riihilahti deposit excluded, are even lower (cf. Table 10c). Compared with most VMS deposits, the Se contents and Se/S ratios in the Outokumpu-type deposits at the low to very low side (Table 10). Similarly low Se and Se/S ratios as in Outokumpu deposits are met about only in some sulphide deposits in modern nascent back arc basins. However, lithologic associations and general geochemistry of these deposits are significantly different from Outokumpu deposits. They are usually associated with arc-derived intermediate-felsic volcanic rocks, and compared to Outokumpu deposits, are much lower in Co and Ni and much richer in Zn, Pb and As. Among ancient VMS deposits only some Besshi-type or Cyprus-type (ophiolite-associated) deposits are similarly low in Se contents and Se/S ratios than the Oku-type deposits. But in a significant at difference, compared to Outokumpu deposits, both the Besshi and Cyprus deposits are systematically much lower in Ni.

The average Se/S X10<sup>6</sup> ratio of 100 in the large Outokumpu deposit is in fact close to the average Se/S x10<sup>6</sup> ratio of 52 in the upper continental crust or the average Se/S x10<sup>6</sup> ratio of 100 in the enclosing upper Kalevian metagreywackes (Se/S for the metagreywackes calculated based on data in the bedrock geochemistry database of GTK, accepting only data with S >0.1 wt.%). Thus, in the light of the Se/S ratios alone, sulphur in the Outokumpu deposit could well have been derived from the vast regional sulphur reservoir in the Upper Kaleva metagreywackes. Notably, Se/S ratios also of serpentinites, skarns, quartz rocks in the Outokumpu assemblage are fairly close with in the upper crust average. Kalevian sedimentary source of the S rocks in the carbonate-skarn-quartz rocks is supported not only by their low, crustal-like Se/S ratios but also their crustal-like Pb isotope compositions (cf. section 9.3.2).

In summary, the Se/S ratios in the Outokumpu-type sulphide deposits are similar or lower than typical of the upper continental crust or in the enclosing Upper Kaleva metagreywackes. These low Se contents and Se/S ratios suggest that Outokumpu-type sulphides would have only little magmatic sulphur in the sulphur budget. It is also clear that the Se contents and Se/S

ratios in the Outokumpu-type deposits are much lower than in most ancient or modern VMS deposits. There are some examples of modern back arc basin, ancient Besshi and ophiolite-associated massive sulphide deposits, which show similarly low Se/S ratios, but which all, however, are much lower in Co and Ni compared to the Outokumpu deposits.

# 9.2.11. Lead

Lead abundances in the studied Outokumpu-type ores are systematically very low. However, because of the usefulness of Pb isotopes in study of sulphide ore genesis, geochemistry and distribution of Pb even in these very low Pb deposits has some special interest.

None of the Outokumpu deposits contains more than 50 ppm Pb on average. Even the largest and Pb-richest Outokumpu deposit contains just 49 ppm Pb on average. Average Pb content calculated for the Vuonos deposit, based on the data collected during this study is 151 ppm, but because this value is biased by one especially Pb-rich (1370 ppm) sample, a median value of 46 ppm would obviously be a more representative average of this data. From the other studied deposits, Kylylahti and Riihilahti contain 20-30 ppm, and the rest less than 10 ppm of Pb on average. From the larger deposits, Luikonlahti is distinctly Pb-poor with only 3 ppm Pb on average.

The mineralogy and paragenesis of Pb in Outokumpu deposits would be of special interest in context of interpreting their Pb-isotope geochemistry. Unfortunately, both these subjects are currently only tentatively known/documented. It is well known, however, that Pb-sulphides such as galena are very rare in most of the studied ores. In most cases the little Pb present seems to locate in the main ore-forming sulphide minerals such as pyrite. Pb sulphides were very rare also in the relatively Pb-richest Outokumpu deposit. Trace galena occurred locally, mainly in sphalerite-rich ore, usually as tiny disseminated grains or crack-fillings. Vähätalo (1953) proposed a late paragenesis based on observations of galena-bearing "apophyses" shooting from sphalerite in chalcopyrite. In addition, megascopic to microscopic galena aggregates occurred infrequently in diopside skarns at ore contacts. During this study, galena was detected in Kylylahti ore as tiny (primary?) inclusions in pyrite, and as somewhat larger grains in association with sphalerite filling cracks in metamorphic pyrite and cobaltite cubes.

In the relatively Pb-rich Outokumpu-Vuonos deposits, Pb shows only weak or no correlation with S or the main ore-forming metals. There is a weak negative correlation with S and weak positive one with Zn, but no correlation with Cu and Co. From the trace metals in Outokumpu and Vuonos ores Pb has statistically significant correlation, positive, only with Bi (r=0.56 \*\*\*), Sc (r=0.40 \*\*\*) and V (r=0.39 \*\*\*). Similarly significant positive correlation Pb shows with lithophile elements like Th (r=0.48\*\*\*), Nb(r=0.48\*\*\*), Zr(r=0.44\*\*\*) and Hf (r=0.36\*\*\*), and somewhat weaker positive correlation with Sr (r=0.44\*\*\*), U (0.40\*\*\*), Rb (0.33\*\*), K2O (r=0.31) and SiO<sub>2</sub>(r=0.30). The Pb richest 10% percentile of Outokumpu-Vuonos samples is strongly enriched in all those lithophile elements that correlate positively with Pb. The affinity of Pb to the lithophile elements and to the margins of the ore bodies are problematic aspects with respect of Pb-isotopes studies. It could even be questioned how representative of the main ore metals Pb in these deposits actually is. Another weird feature of Outokumpu-Vuonos is very poor correlation of Pb with Zn (r=0.06) and Ag (r=-0.07). An explanation to this may be that during the tectonic deformation galena was remobilized and lost concurrently Ag by diffusion. Sevier remobilization may be the reason of poor correlation with the other ore metals, too,

Compared to the Cu deposits, the Kokka-type Ni mineralizations are even lower in Pb, with average concentrations in most cases between only 5 and 10 ppm. Moreover, a considerable part (25-95%) of this little Pb is of radiogenic origin, mostly uranogenic in situ Pb (section 9.3.2). Pb concentrations calculated for the Ni-mineralization sulphide phases hover around 20 ppm. The serpentinites, talc-carbonate and carbonate-quartz rocks in the Outokumpu assemblage are also systematically low Pb abundances mostly below 10 ppm. Because of the variable methods and relatively high detection limits applied during this study, the average

concentration levels for these rocks are not precisely known, however. According to a couple of precise measurements based on isotope dilution techniques, low-sulphur peridotites (now serpentinized talc-olivine rocks) in serpentinite body cores may contain as little as 0.05 ppm Pb, which is less than the 0.15 ppm Pb in primary mantle (McDonough and Sun, 1995). Significantly higher Pb concentrations up to 2 ppm were measured from sulphur-enriched serpentinites at the body margins. Isotope dilution data from carbonate-skarn-quartz rocks indicate Pb concentrations in these rocks would vary typically between 2 ppm and 15 ppm. Also in these rocks a variably large part of the Pb is of in-situ radiogenic origin (section 9.3.2).

Pb abundances in black schists in the Outokumpu area vary between 10 and 60 ppm; a large number of samples analysed in the Outokumpu AAS dataset yield a median Pb concentration of 34 ppm (Table 1). Pb abundances in the upper Kalevian metagreywackes are probably somewhat lower, a small set of samples analysed during this study indicate concentrations between 10 and 20 ppm.

It is clear that compared to most other massive sulphide ore types, the Outokumpu-type is distinctly low in Pb. Even the relatively Pb-poor Besshi- and Cyprus (ophiolite) type deposits contain significantly more Pb, typically from 100 to 2000 ppm (e.g. Kase and Yamamoto, 1988; Galley and Koski, 1999). Similarly low Pb as in Outokumpu deposits is typical of only such massive-semimassive sulphide deposits that are intimately associated with ultramafic rocks. These include magmatic Ni-Cu-(PGE) sulphides, Limassol Forest-type Cu-Ni-Co-As-Au ores (Panayiotou 1980, Foose et al. 1985, Economou and Naldrett 1984), and e.g. the North Zone mineralization of the Eastern Metals deposit in Quebec in Canada (Auclair et al., 1993) and the Durngoi Co-Cu-Zn-Au deposit in China (Yang, 1997). It is must be noted, however, that ultramafic-floored hydrothermal massive sulphides at modern spreading ridges do not seem distinctly Pb poor. In fact, data from the recently found ultramafic-floored Logatsew and Rainbow massive sulphides indicates Pb abundances in these deposits would be more or less similar with the "normal", basaltic-floored mid-ocean ridge massive sulphides, i.e. in the range of <100 ppm to several thousands of ppm (e.g. Bogdanov et al., 1997; Murphy and Meyer, 1998; Douville et al., 2002). Moreover, in comparison to typical Mid-Atlantic vent fluids, the Rainbow fluids are clearly enriched in Pb, and even more so in elements like Zn, Ag and Cd (Douville et al., 2002).

# 9.2.12. Molybdenum

Molybdenum is one of the on mantle-normalised basis moderately enriched metals in the Outokumpu Cu deposits. However, the actual bulk ore concentrations are rather low. The large Outokumpu deposit contains only 19 ppm on average, for example. Somewhat higher Mo is typical of the smaller Cu-mineralizations, especially for those that occur in intimate association with highly tectonized black schists/gneisses, like the Hietajärvi and Saramäki deposits, which contain 48 ppm and 62 ppm of Mo on average, respectively. Also the Co-Ni-zone at Keretti is somewhat enriched in Mo with an average concentration of 48 ppm and spikes up to 640 ppm. The relative Mo enrichment of the Keretti Co-Ni zone and the Saramäki deposit is better exemplified by the high Mo in the calculated sulphide phases, 271 ppm and 157 ppm, respectively. Also the sulphide phase in the Kylylahti stringer mineralization is somewhat enriched in Mo with an average content of 84 ppm. Mo in sulphide phase of the other Cudeposits range from 19 ppm to 63 ppm on average. Mo in the Outokumpu-Vuonos sample set shows good positive with Re (r=0.70\*\*\*), Y (r=0.52\*\*\*), Ce (r=0.68\*\*\*) and Yb (r=0.48\*\*\*), while there is only weak or insignificant correlation with any of the other analysed elements. Mo is positively correlated with As, Se and Sb in the Outokumpu black schists, but in Outokumpu-Vuonos ores Mo lacks significant correlation with these: Sb (r=0.19), As (r=0.14) and Se (r=-0.02).

The Kokka-type Ni mineralizations contain <10-25 ppm Mo on average, while the available analytical data indicates that Mo content in the carbonate-skarn-quartz rock of the Outokumpu type would be significantly lower, in most samples below 5 ppm, i.e. below the usual detection limit of the analytical methods used for Mo in this study. The average Mo concentrations of the Ni-mineralizations render to theoretical average sulphide phase concentrations in the range

from 20 to 120 ppm Mo. Because of the only imprecisely known Mo concentrations in the carbonate-skarn-quartz rocks, Mo content in their average sulphide phase cannot be reliably calculated, but may be somewhat higher than that in the Ni- mineralization sulphides. Mo concentration in upper Kalevian black schists is, as it is typical for black shale sediments, relatively high, 81 ppm on average. The few data of Mo in Kalevian metagreywackes all point to concentrations <5 ppm.

The Mo abundance level in the Outokumpu massive-semimassive Cu-deposits does not significantly differ from that typical for ancient VMS or modern ocean floor hydrothermal massive sulphides, which of the latter usually contain from 10 ppm up to 110 ppm of Mo on average (e.g. Goodfellow et al., 1999).

## 9.2.13. Antimony and Bismuth

Relatively low to very low Sb and especially Bi concentrations are a systematic feature of all the here studied Outokumpu type deposits. Average Sb concentration in the Outokumpu main massive-semimassive ore is 2.3 ppm, in Vuonos 1.8 ppm and in Kylylahti 3.8 ppm. The Outokumpu Co-Ni-zone contains 0.2 ppm, and the Kylylahti skarn-zone mineralization 0.8 ppm Sb on average. All the other here tackled deposits contain <0.1 ppm Sb on average basis. Average Bi concentration is very low <1 ppm in all the studied deposits, except for the volumetrically insignificant, very low-grade (Cu) Kettukumpu mineralization, which has an average Bi content of 1.2 ppm, based on two samples. Even the largest and highest grade (Cu) Outokumpu deposit is systematically very low in Bi, having an average Bi concentration of only 0.7 ppm.

In the Outokumpu-Vuonos sample set Bi shows significant correlation with Sb ( $r=+0.57^{***}$ ) Pb ( $r=+0.56^{***}$ ) and As ( $r=+0.36^{***}$ ) while none with other chalcophiles. As a curious aspect, Bi correlates positively with many lithophile elements, like Zr ( $r=+0.40^{***}$ ), Sc ( $r=+0.37^{***}$ ), Nb ( $r=0.37^{***}$ ), Hf (r=+0.34), Th (r=+0.34) and U (r=+0.27). In spite of its clear positive correlation with Bi, Sb shows far less lithophile behaviour, being in the Outokumpu-Vuonos system a clear Cu-suite element showing good positive correlations with Cu ( $r=+0.45^{***}$ ), Sn ( $r=+0.53^{***}$ ) and Ag ( $r=+0.39^{***}$ ).

Sb concentration in the Kokka-type Ni-mineralizations is on average basis <0.1 ppm and that of Bi <0.2 ppm. In comparison to the Ni-mineralizations, the ordinary skarn-carbonate rocks in Outokumpu assemblage seem to be a little higher in Sb, showing an average level of about 0.3-0.4 ppm, but yet similarly low in Bi with an average concentration level below<0.1 ppm. In the Kokka-type Ni-mineralization average sulphide phase concentrations remain below 2 ppm both for Sb and Bi. Concentrations in the carbonate-skarn-quartz rock sulphide phases probably are significantly higher, in the order of 5-10 ppm and 10-30 ppm, respectively.

Antimony concentrations in modern mid-ocean ridge-associated massive sulphides are usually on the order of 50-100 ppm for deposits at sediment-bare ridges, and somewhat higher, up to 600 ppm, for deposits at sediment covered ridges. Massive sulphides at intra-oceanic back-arc ridges show somewhat higher concentrations typically from 100 ppm (intra-oceanic) to 3000 ppm of Sb (intra-continental) (Herzig and Hannington, 1995; Goodfellow and Zierenberg, 1999). Bismuth values in massive sulphides at modern sediment-free ridges are quite low, only 0.75 ppm on average (Goodfellow and Zierenberg, 1999). Samples from sediment-covered ridges are usually more enriched, showing Bi abundances typically in the range between 30 and 100 ppm (Goodfellow and Zierenberg, 1999). Ancient sulphide deposits of the bimodal-volcanic-siliclastic type, like the Iberian Pyrite Belt deposits, or the Archaean Kidd Creek, are perhaps the most Sb and Bi enriched group of massive sulphides, with abundances of both of these elements characteristically ranging from several tens to thousands of ppm (e.g. Hannington et al., 1999; Marcoux et al., 1996).

As Selenium, also Bi and Sb are strongly magmatophile elements with a high tendency to concentrate in the volatile phase of volcanic eruptions. The systematically very low Bi and Sb in the here studied Outokumpu-type deposits could thus be taken as an evidence of unimportance of magmatic fluids or exhalations in their metal budget. In hydrothermal deposits Sb is usually

found enriched in their lower-T facies, whereas Bi is usually enriched in the higher-T facies. In Outokumpu-Vuonos deposit both Bi and Sb show more affinity to the "high-T" Cu-suite than the "low-T" Zn-suite. Distribution of Bi within the Outokumpu-Vuonos ores seems rather random, however, and in its lithophile aspects similar to that of Pb with which it shows significant correlation (r=0.56\*\*\*).

#### 9.2.14. Major elements and Zirconium

The Outokumpu type massive-semimassive Cu-Zn-Co deposits typically comprise 35-45 wt.% SiO<sub>2</sub>, whereas concentrations of all the other major elements are usually low (MgO=<1-4wt.%, CaO=<1-3 wt.%) or very low to negligible (TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MnO, alkali elements and P<sub>2</sub>O<sub>5</sub>) (cf. Table 10a). Noting in addition that sulphide-rich samples likely are over presented in our sampling, these values imply that gangue content of typical Outokumpu type ore is ca. 50 vol.%, and that the gangue comprises almost only quartz. The chemical results are supported by petrographic evidence of that the ore gangues frequently comprise only quartz±diopside±tremolite±carbonate with only occasional traces of allanite, chromite, chromian tourmaline, eskolaite, mica (phlogopite, fuchsite), plagioclase, chromian tourmaline, "tucholite" and uraninite. It must be noted that the chromian oxide and silicate gangue phases, although often considered a ubiquitous feature of Outokumpu ores, are in typical ore samples only a trace component or lack altogether.

Based on 78 samples analysed in this study from its various parts, the prototype Outokumpu deposit contains on average 39.3 wt.% SiO<sub>2</sub>, 0.98 wt.% MgO and 0.60 wt.% CaO. The very low average Al<sub>2</sub>O<sub>3</sub> (<0.18 wt%), TiO<sub>2</sub> (<0.01 wt%), Zr (2 ppm) and alkali element abundances (Na<sub>2</sub>O=0.22 wt.%, K<sub>2</sub>O <0.01 wt%) imply that only trace epiclastic sedimentary component, as e.g. in form of black schist intercalations, can be present, although this is sometimes proposed. A very similar result was obtained by 17 samples from the various parts of the sister Vuonos ore, while the other, grade-wise lesser deposits show a tendency to somewhat higher, but still distinctly low average Al<sub>2</sub>O<sub>2</sub> (<1 wt.%), TiO<sub>2</sub> (<0.08 wt.%) and Zr (<25 ppm).

MnO contents in most of the studied Outokumpu ores are distinctly low (<0.1 wt.%); in the large Outokumpu ore there is just 0.06% MnO on average (0.07% according to Peltola, 1978), for example. The Luikonlahti deposit is a notable exception with a relatively high average MnO content of 0.46 wt.%, the elevated MnO occurring in the diopside+tremolite+magnetite rich parts of the ore. Also in Kylylahti the tremolite+magnetite rich ore in the middle part of the deep lens is clearly enriched in MnO.

MnO is a low-abundance component also in the Kokka type sulphide mineralizations; they also rarely contain MnO in concentrations over 0.1 wt.%. Similarly low MnO is a systematic character also the carbonate-skarn-quartz rock zones in the Outokumpu assemblage. Average MnO is highest for the carbonate rocks (0.11 wt.%), while the quartz rocks are even lower in MnO, with an average concentration of just 0.02 wt.% for the 88 samples analysed during this study. The systematically low Mn and low total Fe contents across the Outokumpu association imply that Mn and/or Fe rich exhalites typical of distal facies of many modern and ancient seafloor hydrothermal ore environments are completely absent. Therefore, if the Outokumpu massive-semimassive sulphides overall would represent seafloor hydrothermal deposits, they most likely would represent "blind", "inhalative" deposits developed inside seafloor, not deposits at vents onto the seafloor. Further, the environment of the inhalations must have been largely ultramafic, based on the universal absence of volumetrically significant basic-felsic magmatic rocks in the ore assemblages.

#### 9.2.15. Chromium, Scandium and Vanadium

These are all elements with low solubility in most geological, including most ore-forming

fluids. Thus elevated concentrations of these metals in hydrothermal massive sulphide deposits are typically associated only with gangue inherited from volcanic or sedimentary host rocks.

Based on 78 samples in our database, the prototype Outokumpu deposit contains 289 ppm Cr on average. Average chromium concentrations in the other studied massivesemimassive Cu-Zn-Co deposits are mostly somewhat lower, in the range of 198 to 11 ppm. Though these values are fairly high for hydrothermal sulphide deposits, yet the many notations of high Cr as a special feature of Outokumpu sulphides (e.g. Treloar, 1987; Park, 1988) are somewhat misleading. Namely, there occur elevated Cr abundances usually only at the margins or edges of the ore bodies, whereas their interiors are frequently nearly devoid of Cr, showing concentrations typically below the 30 ppm detection limit of the Cr analysing for this study. In our data for Outokumpu a few high Cr samples from the edge parts and SW tail of the Outokumpu ore strongly contribute to the high average of 289 ppm. In comparison, a medium Cr content calculated for these same data would be only 56 ppm. The elevated Cr in samples form ore margins and edges reflects incorporation of the usually chromian wall rocks, which the ore in these environments brecciates, veins and replaces (cf. Vähätalo, 1954). It has been usual to correlate the guartz-rich layers/bands in Outokumpu ore, especially in their distinctly quartz-sulphide layered/banded parts, with the quartz rocks in the Outokumpu assemblage. This is, however, also an obvious miss concept, since even the most quartz-rich ore layers in the wall-rock free interior parts of ore sections usually contain only negligible amounts of Cr, usually less than 30 ppm. Significantly, also those ore margins that are against Kalevian metasediments usually show very low Cr concentrations. This is true even for the most quartzrich ore layers (>70% SiO<sub>2</sub>), in which one would expect to see high Cr contents about the order of 500-1000 ppm, given that the quartz layers would indeed represent true quartz rocks of the Outokumpu-type. It is important to note also that, based on our data for Outokumpu and Vuonos ores, there is no correlated behaviour between Cr and SiO<sub>2</sub>(r=+0.18), which one would expect if a variable interlayered quartz rock component was present in these ores.

As said above, our observations on the Outokumpu and Vuonos ores suggest that the type of wall rock controls the Cr content of the adjacent ore. We see this situation strong evidence of that the ore mass was emplaced in its present position as a fault-controlled quartz-sulphide vein. It seems that where the walls comprised chrome-rich rocks, there the vein scraped more chromium (mechanically and by chemical interaction), whereas in case of chrome-poor walls, there was significantly less such chrome intake. This is a promising study approach that should be further tested in future studies of the Outokumpu and particularly the Vuonos ore where the wall rock variation is greater.

The average V content of the prototype Outokumpu ore is 51 ppm and that of Sc 1.2 ppm. The average concentrations of these metals in the other studied massive-semimassive deposits are about similar or slightly lower. Both Sc and V appear to correlate positively with Cr and Ir, but unlike Cr also with SiO<sub>2</sub>, and also the trace lithophile components like K<sub>2</sub>O, Nb, Sr and Zr. This indicates that a part of the Sc and V probably locates in chromite in wall rock relicts, and a part possibly also in some, probably synmetamorphically introduced minor silicate component (in phlogopitic mica?).

Compared to the massive-semimassive ores, the Outokumpu Co-Ni and Kylylahti skarnzone sulphide samples are highly enriched particularly in Cr (thousands of ppm), but also in V (up hundreds of ppm) and Sc (up tens of ppm) (Table 10a). The elevated Cr is most probably related to the often-abundant chromite in the host carbonate-skarn-quartz rocks, while the Sc and V probably derive from the abundant chloritized basite dyke component typical of these environments. Also the Riihilahti samples show a strong host-rock/gangue effect; the low-Ti tholeiite origin of their skarnoid gangue shows up in their relatively high average Cr (539 ppm) as well as V (224 ppm) and Sc (26.6 ppm) abundances.

21 samples analysed here from the Kokka-type Ni mineralizations yield a high average Cr concentration of 5491 ppm, and indicate enrichment also in V (144 ppm) and Sc (20.2 ppm) over the average carbonate-skarn-quartz rock values (cf. Tables 4b and 10a). This could indicate that the Kokka type Ni-enrichments were generated by silica leaching and and related volume loss. We earlier observed that Ni enrichments in parts of the Outokumpu alteration zones are compensated by depletions in their other parts. In the light of the high Cr of the

Kokka mineralizations, this may be reflection of some serious redistribution of  $SiO_2$  rather than Ni.

#### 9.2.16. Rare Earth Elements (REE)

Due to the low solubility of Rare Earth Elements (REE) in most geological fluids, including most sulphide ore-forming fluids, their application as metal source tracers is usually limited. Potentially, however, REE may bear some information on the composition and physical-chemical nature, as oxidation state of the ore-forming fluids. And, if combined with Sm-Nd isotope data also of the source of the REE, an maybe also the pay metals. Thus, a complete suite of REE were analysed from all of the deposit modelling samples processed during the GEOMEX project. Representative samples from Outokumpu and Vuonos deposits had been analysed for REE in GTK already before the GEOMEX project.

The survey undertaken shows that REE concentrations in all of the studied Outokumputype massive-semimassive deposits are distinctly low, in large part of the studied samples below the primitive mantle level, and thus for many of the individual REE below the effective detection limits of the here applied analytical method (308M) (On the mantle-normalized diagrams in Figs. 127-135 data below detection limits is addressed by plotting them with half of the appropriate detection limit value). The average total REE concentration in most of the massive-semimassive ores is below 10 ppm; the value is 8.5 ppm for prototype Outokumpu deposit.

Most of the REE data (n=70) is for the prototype Outokumpu deposit. Based on mantlenormalised spidergrams of those samples for which more reliable data was obtained, three basic REE distribution types seem to characterize most part of the Outokumpu main ore. The three types are well covered by data from two drill core sections, K807 and K1024, from SW middle part of the ore sheet (Fig. 127). Of these two sections, the section K807 represents a relatively little "remobilized" part of the Outokumpu ore, while the K1024 has all the features that have been associated with pervasively remobilized and metamorphically recrystallized ore in previous studies of the deposit.

The K807 section is, as it is typical of the middle part of the Outokumpu ore, pyritedominated at footwall against quartz rocks, and somewhat more pyrrhotitic at the hanging wall against a thin layer of skarn-carbonate rocks grading into serpentinite. Samples from the pyritic footwall show Sm concentrations from 0.5 to 5 times mantle and mantle-normalized patterns with negative REE anomalies. In a sharp contrast, most samples from the hanging wall ore show significantly lower REE level (Sm <0.5 times mantle) and patterns with weak to steeply positive Eu anomalies. While the footwall pyritic and hanging wall more pyrrhotitic samples differ for their REE enrichment level and Eu anomalies, both seem to show about similar overall REE patterns with flat HREE-MREE and high La/Sm ratios.

The K1024 section comprises massive Cu-Zn rich pyrrhotite ore with abundant coarse cubes of metamorphic pyrite. The REE profiles of the K1024 samples are basically of similar shape with the K807 patterns but lack any distinct Eu anomalies. The concentration level is in the middle territory with respect to the range of K807.

The REE distributions in the more ore less pervasively pyrrhotitic Vuonos ore seem to depend on the host rock environment of the ore. A skarn-quartz rock enclosed ore segment intersected by hole Oku-223 shows for its most part mantle-normalized patterns with low REE level and distinct positive Eu anomalies (Fig. 128a), closely resembling the patterns of pyrrhotite ore in K807 in Outokumpu. However, a few samples from the hanging wall part of the section, closer to country mica schists, exhibit a higher REE level and less LREE anriched patterns with less distinct Eu maximas. Similar REE profiles as in the Oku-223 hanging wall samples seem to characterize the upper edge parts of the ore inside mica and black schists (Fig. 128b). The REE profiles of the Oku-223 hanging wall samples and samples from the upper edge ore in



Fig. 127. Mantle-normalized extended REE patterns for massive-semimassive sulphide samples from two representative drill hole sections, K807 and K1024, of Outokumpu (Keretti) massive-semimassive ore. (A) Section K807, footwall samples (dominantly pyritic) with negative Eu anomalies with orange symbols, hanging wall samples (pyrite+pyrrhotite) with positive Eu anomalies with red symbols. (B) Section K1024, all samples from massive coarse-grained, pyrite porphyroblastic pyrrhotite ore rich in chalcopyrite and sphalerite.



Fig. 128. Mantle-normalized extended REE patterns for massive-semimassive sulphide samples from the Vuonos deposit. (A) Plot for samples from drill hole Oku-223 intersecting an ore segment inside skarn-quartz rocks, for location of the hole OKU223, see Fig. 59. (B) Plot for samples from ore segments inside metasediments. Patterns for samples of the enclosing metasediments are shown for comparison.

sediments show notably similar shapes as the REE profiles of the enclosing mica and black schists, although in a distinction with a tendency to small positive Eu anomalies (Fig. 128b)

The Perttilahti deposits, which for large parts locates nearly completely inside the Kalevian metasediments, expectedly shows similar basically metasediment type patterns and REE concentration level as the metasediment enclosed parts of the Vuonos deposit (Fig. 129).



Fig. 129. Mantle-normalized extended REE patterns for massive-semimassive sulphide samples from the Perttilahti deposit. Pattern of average Upper Kaleva mica schist (WK1, Lahtinen, 2000) is shown for comparison.

Samples (n=15) from the nearly thoroughly pyrrhotitic Luikonlahti ore bodies are systematically very low in REE ( $Sm_N = 0,1$  up to 1), so that their REE pattern shapes remain here somewhat uncertain. Nevertheless, the samples seem to define similar bivariant distribution to patterns with either positive or negative Eu anomalies as the K807 section in Outokumpu (Fig. 130). The samples with positive Eu anomalies come mainly from magnetite and/or diopside-tremolite rich ore parts, whereas samples from the "normal" ore with dominantly quartz gangue typically exhibit pronounced negative Eu anomalies. The highest positive Eu anomalies were recorded for the most magnetite and/or tremolite-diopside rich samples.

Samples (n=11) analysed for REE from the Kylylahti semimassive-massive sulphides exhibit all but two negative Eu minimas (Fig. 131). Again, the REE abundance level is in most samples relatively low, in terms of Sm<sub>N</sub> from less than 0.1 to 1. The samples with Eu minimas are most from pyrite dominated ore. The two samples with Eu maximas come both from the magnetite-pyrrhotite rich sheet/wedge in the middle part of the deep ore lens. For their overall REE profiles the Eu negative Kylylahti samples resemble the foot wall samples in K807 section in Outokumpu.

Compared to Kylylahti, samples (N=7) from the semimassive parts of the Saramäki deposit show perhaps a bit less LREE enriched, and thus more the Kalevian metasediment like patterns, most with missing or minor positive Eu anomalies (Fig. 132). The REE abundence lewel is, however, mostly similarly low (Sm<sub>N</sub>=0.1-2). The small massive-semimassive deposits in Hietajärvi, Kettukumpu, Hoikka and Hippos exhibit all fairly similar REE geochemistry with the Saramäki deposit (cf. Figs. 132-133). With the difference, however, that there is a tendency to U-shaped normalized patterns, similar as are met also in the host tremolite-diopside skarns of these usually carbonate-skarn rock associated mineralizations.



Fig. 130. Mantle-normalized extended REE patterns for massive.semimassive sulphide samples from Asuntotalo and Kunttisuo ore bodies in Luikonlahti. (A) Samples with positive Eu anomaly. (B) Samples with negative Eu anomaly. Representative samples of Luikonlahti sulphidic black schists are plotted for comparison.



Fig. 131. Mantle-normalized REE patterns for samples of massive-semimassive sullphides from the Kylylahti depopsit. Representative samples of Kylylahti mica and black schists are ploted for comparison.



Fig. 132. Mantle-normalized extended REE patterns for massive-semimassive sulphide samples from the Saramäki deposit. Average Upper Kaleva mica schist (WK1, Lahtinen, 2000) and representative samples of Saramäki black schists are plotted for comparison.



Fig. 133. Mantle-normalized extended REE patterns for samples from minor Outokumpu type Cu sulphide deposits Hietajärvi, Kettukumpu, Hoikka and Hippos. Average Upper Kaleva mica schist (WK1, Lahtinen, 2000) and two representative Hietajärvi black schists are plotted for comparison.

Compared to the above tackled massive-semimassive deposits, most samples (N=10) from the Riihilahti deposit are slightly richer in REE. The higher REE abundance level (Sm<sub>N</sub>=1-15) in the Riihilahti samples could be realated to the relatively higher abundance of skarnoid silicate gangue in these "stringer-type" sulphides. It should be noted, however, that the REE pattern shapes of the Riihilahti samples are mutually quite similar and appear not to reflect the variation in the type/amount of associated gangue. The patterns are actually fairly similar than in the metasediment enclosed parts of the Vuonos deposit or in the smaller Outokumpu massive-semimassive deposits (cf. Figs. 133 and 134). Moreover, the patterns exhibit a clear enrichment in LREE over the amphibolitic low-Ti tholeiites in the Riihilahti sequence, and that as carbonate-altered (now skarnoid) seem to host a significant part of the Riihilahti mineralization.

Compared to samples from the adjacent massive-semimassive sulphide lenses, samples from the "stringer" zone Outokumpu Co-Ni and Kylylahti mineralizations are much higher in REE with average total REE concentrations of 156 and 181 ppm, respectively. Both these mineralizations are hosted in Outokumpu-type carbonate-skarn-quartz rocks, which outside the "stringer" zones contain less than 10 ppm total REE. This suggests that these "stringer" zones were enriched in hydrothermally added REE, which could be argued also for the above discussed Riihilahti stringer mineralization. Indeed, as the total REE content of ca. 20-50 ppm typical of the mainly low-Ti tholeiite dyke materials (now mostly chloritite) common in the stringer Co-Ni zones, in addition to the primarily very REE poor carbonate-skarn-quartz rocks, cannot explain the high REE, it is more or less clear that considerable net REE addition in the stringer zones must have occurred. Further support for REE mobility and enrichment is provided by sporadic extreme REE enrichments within both the Outokumpu and Kylylahti "stringers". Samples from such enrichments show total REE contents from 300 up to 3000 ppm and LREE enrichment up to 1200 times primitive mantle (Fig. 135). Notably, mantle-normalised REE patterns of these samples are quite similar with those of the most REE enriched samples of Outokumpu massive-semimassive sulphides, also showing high La/Sm ratios, steep Eu minimas and relatively flat HREE (Fig. 135). Interestingly, also many of the "peridotitic" and garnet-cummingtonite wall-rock samples from the Riihilahti mineralization show comparable REE enrichments and also guite similar mantle-normalised REE profiles (section 5.3.3.).



Fig. 134. Mantle-normalized extended REE profiles of chalcopyrite mineralized samples from the Riihilahti Cu deposit. Patterns of an associated low-Ti metatholeiitic amphibolite (8-EPI-00) and the average Upper Kaleva mica schist (WK1, lahtinen, 2000) are shown for comparison.



Fig. 135. Mantle-normalized extended REE patterns for some of the most REE enriched samples from Kylylahti (skarn-hosted parallel) and Outokumpu (Co-Ni) stringer zone mineralizations compared with patterns of some of the most REE enriched massive-semimassive sulphide samples from these deposits.

An important starting point for interpretation of the REE data is that the ore bodies conserving pyrite ore facies, pereserved only in Outokumpu and Kylylahti, probably represent the most primary cases we can have for the Outokumpu deposits. In the light of the Koistinen's

(1981) interpretation of that the Outokumpu ore originated with a lower, sedimentary pyrrhotitic layer, and upper, sedimentary pyrite layer would be true, it could then be an option that the layered distribution in REE patterns in the K807 was a very primary sedimentary feature.

There are several reasons to doubt a sedimentary origin of the K807 REE distribution, however. First, the ore segment intersected by the K807 is completely enclosed in the nonsedimentary ultramafic regime of carbonate-skarn-quartz rocks and serpentinites of the Outokumpu assemblage. Second, in the lesser metamorphosed Kylylahti deposit most of the dominantly pyritic ore seems to be characterized by negative Eu anomalies, while the positive Eu anomalies appear to be restricted on the undoubtedly pervasively metamorphosed (or syntectonic, metamorphogenic?) magnetite bearing parts of the ore. In addition, like in Kylylahti, also in Luikonti the REE patterns with the strongest Eu maximas are related to magnetite rich ore, which also in Luikonlahti seems an clearly synmetamorphic ore facies. Thus, some other than sedimentry control of the K807 type REE zonation must be sought for. Noting the fact that in Outokumpu ore, the ore facies in contact with carbonate-skarn rocks and serpentinite tend to be more pyrrhotitic with low REE and show Eu maximas, while ore parts in contact with guartz rocks tend to be more pyritic with relatively high REE and exhibit Eu minimas, it seems that redox character of the synmetamorphic dehydration/decarbonation fluids from the nearest wall rocks provided the principal control of the K807 type REE distributions. This does not say that the REE was neccesarily from the nearest wall rocks but that metamorphic dehydration/decarbonation fluids from wall rocks contributed to the REE deposition/zonation in the ore bodies.

The importance of the synmetamorphic influence of, and even REE contribution from the nearest wall rocks to the ore REE distributions is perhaps most clearly seen in the Vuonos ore, which has K807 type strongly LREE enriched REE patterns in the lower edge ore inside the ultramafic regime, while distinctly flatter, more metasediment like patterns in the upper edge ore in mica and black schists. In the case of the sediment enclosed ore, an contribution of REE from the sediments in the Vuonos upper edge ore is confirmed by Sm-Nd isotope data (section 9.3.3.). Remember, however, that we are here dealing with very low absolute quantities.

In addition, it must be recognized that, pervasive homogenisation of the ore materials for REE very probably occurred in those parts of the Outokumpu ore that became pervasively remobilized and metamorphically recrystallized. In our sampling for Outokumpu, samples from the hole K1024 represent such pervasively reworked ore. Effective homogenizing of the K807 type ore with distinct positive and negative Eu anomalies would obviously produce the K1024 type patterns without any pronounced REE patterns. Similar homogenization by durchbewegung and subsequent metamorphic recrystallization plus variable interaction with the wall rocks seems to explain the fairly homogenous REE distributions of the smaller massive-semimassive deposits.

That the REE patterns obviously vary depending and are controlled by metamorphic reactions in the immediate wall rocks suggests an origin of the Outokumpu and Vuonos ores as structurally (fault) controlled syntectonic-synmetamorphic lodes or fillings. But, although the wall rock influence for the REE distribution seems important, there is evidence of that significant part of the ore REE was added also in the ore forming fluids. One such indication is that at least the highest REE enrichments in Outokumpu main ore, as well as in the Outokumpu and Kylylahti stringer zones, clearly have more fractionated LREE than their usual serpentinite-carbonate-skarn-quartz wall rocks, or even the local mica-black schists. With more uncertainty, because the very low concentrations, this seems to hold also for the pyrrhotitic ore parts of the Vuonos and Outokumpu ore inside the low REE carbonate-skarn-quartz rocks and serpentinites. In every case, the average La/Sm ratio of 17 (n=70) of the Outokumpu massive-semimassive sulphides is significantly higher than the La/Sm of 6.2 of the Upper Kaleva metagreywackes (Lahtinen, 2000) and La/Sm of 6.6 of the upper crust (Taylor and McLennan, 1985). The nature and source of the REE in Outokumpu ore is further discussed with Nd-Sm isotope data in section 9.3.3.

Recent studies of sulphide deposits at modern seafloor hydrothermal vents have indicated very low REE abundances, and only little variation in the sulphide REE distributions with the nature of the basement underlying the vent sites (e.g. Murnae, 1994; German et al., 1999). This

is pretty much in accordance with the available data on the aqueous solubility of the REE, which suggest that modern vent fluids would have only very limited ability to mobilize REE (e.g. Wood and Williams-Jones, 1993). Against this background, it is surprising that many ancient supposedly sea-floor massive sulphides are relatively high in total REE. Examples of such deposits include e.g. the giant Neves Corvo of the Iberian Sulphide Belt and Archaean Kidd Creek deposits in Canada, which both are remarkably rich in REE; large parts of these deposits show total REE concentrations from 30 up to 300 ppm (e.g. Ruiz et al., 2002; Hannington et al., 1999b). However, more likely than an indication of hydrothermal REE mobility, the high REE as well as zircon in these deposits are a sign of their replacement origin and related REE-Zr inheritance from the replaced, usually acid, volcanic host-rocks.

In Outokumpu there is less evidence of wall rock replacement, and if it was for the carbonate-skarn-quartz rocks, their original REE content was very low and of flat mantle distribution, while e.g. the Outokumpu ore has an average REE pattern very strongly enriched in LREE with average La/Sm of 17. Which afterall, as pointed above, suggests an extraneous source of the ore REE. It is useful to reiterate here that the average La/Sm in the Kalevian metagraywackes is 6.2 (Lahtinen, 2000) and in upper continental crust 6.6 (Taylor and McLennan, 1985). Modern MOR black smoker fluids and sulphides have La/Sm ratios typically between 4 and 10.

About the only major class of sulphide deposits that unquestionably are associated with significant hydrothermal REE enrichment are the Olympic Dam type deposits of the iron oxide Cu+Au clan. In fact, the magnitude of REE enrichment and the mantle-normalised REE patterns of the most REE enriched samples from the Outokumpu deposits are surprisingly similar with those of the REE—rich heterolithic breccias at Olympic Dam (cf. Oreskes and Einaudi, 1990). This seems an intriguing similarity, although it has to be said that an average level the Olympic Dam ore is far more REE enriched than any of the Outokumpu ores, the stringer parallels and Riihilahti included. Nevertheless, the similarities in REE patterns between Outokumpu and Olympic Dam are clearly something worth to consider, an suggestion of that the principal ore forming fluids, or at least the REE mobilizing fluids, might have been fairly similar in the both cases.

In Olympic Dam the REE is located in bastnasite, florencite, monazite, xenotime and possibly britholite (Oreskes and Einaudi, 1990). We did not perform any detailed study of the mineralogical control of REE in the Outokumpu REE-enriched materials. Reconnaissance study of a few thin sections of the REE-rich rocks suggests presence of "allanite", sphene, rutile, zircon, apatite and several unidentified possible REE-host minerals. Based on chemical and mineralogical evidence, REE in the Olympic Dam deposit was introduced for most part probably as fluoride complexes (Oreskes and Einaudi, 1990), which is consistent with experimental and theoretical data that suggest REE in geological fluids would be transported most effectively as fluoride and carbonate complexes (Wood, 1990). Fluorine was not analysed during this study, but may be present in apatites abundant in some of the high-REE samples especially in Kylylahti and Riihilahti. On the other hand, the abundant late calcite in Kylylahti stringer zone points to an  $CO_2$  rich fluid.

Finally, our reconnaissance REE study suggests that, with further detailed REE study, especially for the here only briefly addressed Kylylahti deposit, considerably advances in deducting the genesis and of the Outokumpu deposit could perhaps be made. The dominantly pyritic nature of the Kylylahti massive lenses should help to figure out which patterns in the REE geochemistry are "primary" and which are purely metamorphic, or are the "primary" features also metamorphic and the deposit thus syntectonic-synmetamorphic.
In contrast to high enrichments of Ba and Sr in parts of many massive hydrothermal sulphide ores and in their immediate host environments, the Outokumpu deposits and their immediate wall rocks are distinctly devoid of any Ba and Sr enrichments. In this respect, among common massive sulphide deposits, only some Besshi and Cyprus (ophiolite) type deposits are comparable.

The larger of the Outokumpu area massive-semimassive deposits, Outokumpu, Vuonos and Luikonlahti all contain 35 ppm or less Ba on average. Compared to these, the smaller massive-semimassive deposits show somewhat more spread in their Ba concentrations, but yet within a very low abundance territory between 6 and 60 ppm. Low average Ba content of 31 ppm characterizes also the Outokumpu Co-Ni zone, whereas the average Ba contents of the Riihilahti and Kylylahti "stringer" mineralizations are significantly higher, 210 ppm and 114 ppm, respectively. The higher Ba in these stringer-sulphides reflects their exceptional, relatively metabasite-rich gangue assemblages.

In the Outokumpu-Vuonos ores Ba appears an erratically distributed element showing some tendency to positive correlation only with  $K_2O$  (r=0.27\*\*), CaO (r=0.25\*\*) and Sr (r=0.25\*). The sympathetic, although poor variation with potassium indicates that at least part of the Ba would locate in phlogopitic mica, which is met in trace abundances in marginal parts the ore sheets especially where in contact with mica-black schists.

Like Ba, also Sr is just a trace component in most of the studied Outokumpu deposits. The Outokumpu main deposit contains only 6 ppm of Sr on average, for example. The smaller deposits show somewhat higher average abundances between 6 and 72 ppm, the Sr content increasing with decreasing deposit size. The Riihilahti and Kylylahti stringer-mineralizations are in terms of the Sr content in the high-end, with averages of 32 and 70 ppm, respectively, obviously due to their exceptional, metabasite-rich gangues. In contrast to the erratically distributed Ba, Sr in the Outokumpu-Vuonos sample set shows clear positive correlation with gangue-related components, such as SiO<sub>2</sub>, MgO, CaO (r=0.54<sup>\*\*\*</sup>) and K<sub>2</sub>O (r=0.53<sup>\*\*\*</sup>), while correlation of Sr with lithophile trace elements such as Hf (r=0.80<sup>\*\*\*</sup>), Nb (r=0.91), Th (r=0.90<sup>\*\*\*</sup>), Zr (r=0.76) and Y (r=0.56<sup>\*\*\*</sup>) suggests that most of the Sr would be hosted in some Ca-Sr-HFSE-YREE rich trace mineral.

Notably, also the serpentinite and quartz rocks in the Outokumpu assemblage show very low average Ba and Sr values, below 20 ppm on average. The carbonate and skarn rocks are similarly low in Ba, but are compared to the serpentinites and quartz rocks clearly enriched in Sr with contents typically in the range of 30 to 100 ppm, and with peak abundances of up to 210 ppm in the carbonate rocks. The Sr enrichment of the carbonate rocks is explained by the geochemical affinity of Sr to Ca, which is strongly enriched in the dolomitic carbonate rocks.

Compared to the carbonate-skarn-quartz rocks in the Outokumpu alteration assemblage, the Kalevian black schists and mica schists show relatively high average Ba abundances, 330 ppm and 490 ppm respectively, i.e. abundances typical of siliclastic black shale and greywacke-derived metasediments. Also the Sr concentrations of the black schists and mica schists, on average 92 ppm and 250 ppm, respectively, are typical for siliclastic metasediments.

The overall low Ba and Sr, likewise Mn, in Outokumpu ore, and in the Outokumpu assemblage overall, indicates original absence, or alternatively total removal of any exhalative or inhalative Ba, Sr or Mn enriched hydrothermal accumultions in the Outokumpu ore environments. It is worth to note that Mn is in Outokumpu deposits an especially erratically distributed element lacking clear correlation even with Fe.

### 9.2.18. Uranium and Thorium

Uranium is one of the trace metals typical of the Outokumpu deposits, although the average deposit concentrations between 4.8 and 21.7 ppm are not particularly high for massive sulphide deposits in general. Despite of the bland concentrations, uranium is one of the more

4 to 10 ppm U range. In contrast to U, average Th concentrations in all of the studied deposits are extremely low; most of the deposits contain only from <0.1 to 0.4 ppm Th. The average Th content of the

most of the deposits contain only from <0.1 to 0.4 ppm Th. The average Th content of the prototype Outokumpu main deposit is less than 0.1 ppm, for example. The Riihilahti mineralization with an average Th content of 3.1 ppm is a minor exception to this rule, the higher than average Th obviously reflecting high abundance of relatively Th rich volcanic-sedimentary derived gangue in samples of this stringer or breccia type mineralization. Owing to the low Th, U/Th ratios in the Outokumpu deposits, the Riihilahti deposit excluded, are very high, ranging from 18 to 200. For Riihilahti the average U/Th ratio is a much lower 1.6, but which is a value still considerably higher than the U/Th =0.3 of average upper crust and primitive mantle.

In the Outokumpu-Vuonos dataset U shows good positive correlation with SiO<sub>2</sub> (r=0.58\*\*\*), MgO (r=37\*\*\*), CaO (r=0.54\*\*\*), Rb (r=0.50\*\*\*) and Sr (r=0.83\*\*\*), implying that it is associated mainly with the silicate gangue. Even better correlation U has with elements such as Nb (r=+0.83\*\*\*), Hf (r=+76\*\*\*) and Zr (r=+0.70\*\*\*). Correlation of U with Th is very good (r=+0.83\*\*\*) but somewhat less good with Pb (r=+0.40\*\*\*). U shows strong coenrichment also with Sc (r=0.61\*\*\*), V (r=0.61\*\*\*), Y (r=0.61\*\*\*) and HREE (U-Yb, r=+0.53\*\*\*), whereas correlations with S and the principal and trace ore metals vary from negative to insignificant. As said above, Th shows very good positive correlation with U (r=0.83) but even a better correlation with such lithophile elements as Nb (r=0.97\*\*\*), Hf (r=0.92\*\*\*) and Zr (r=0.86\*\*\*). The positive correlations of Th and U with Pb (Th-Pb, r=0.48\*\*\*; U-Pb, 0.40\*\*\*) reflect at least partly the radioactive decay of these elements to Pb.

As we already mentioned above, U (and Th) concentrations as in the Outokumpu ores, or higher, are common for massive sulphides, also for those occurring at present mid-oceanic ridges (e.g. Miller, 1998). In the present MOR sulphides U is mainly from seawater mixed in the ore-forming hydrothermal fluids before their venting and U added by postdeposition reactions of the mound sulphides with ambient seawater. So, potentially most of the U in Outokumpu ore bodies could be "initial" ore-formation stage U, but if the ore bodies have been subjected to the same metasomatic-metamorphic processes as their carbonate-skarn-quartz host rocks (below), also an abundant component of subsequently introduced metasomatic-metamorphic U would very probably be present. The strong association of U with lithophile elements supports importance of the latter process.

Metasomatic carbonate-skarn-quartz rocks shelling the Outokumpu serpentinite massifs contain typically from 4 to 10 ppm U, whereas there is usually far less, typically below 0.5 ppm U in their core parts. The Kokka type Ni-sulphides show the highest U enrichments for the carbonate-skarn-quartz rock environments, in the order of 10-40 ppm. It is important to note, that in spite of being enriched in U, the carbonate-skarn-quartz rocks, and the Ni mineralizations as well, are however similarly very low in Th (<0.5 ppm) than the adjacent serpentinites. The very low Th both in the serpentinites and carbonate-skarn-quartz rocks provides strong evidence of their metasomatic derivation of a common protolith, and also of the extreme purity of the carbonate-skarn-quartz rocks, usually between 15 and 150, and thus much higher than the U/Th ratio of ca. 0.3, imply, combined with the extremely low Th, purely hydrothermal origin of the U enrichment. We will later provide isotope evidence of an early tectonic timing of the U enrichment.

Petrographic and electron microscopical studies carried out during this work and before (Merkle, 1982) have indicated that the majority of the U, and that little Th, which are present in

Outokumpu ores and carbonate-skarn-quartz rocks, would locate dominantly in inclusions of trace uraninite in tiny nuggets of silicified bitumen, or "tucholite", which are rather common in these rocks. The carbon in the tucholite nuggets is associated with relatively low  $\delta^{13}$ C values, ranging between –5 and –15 (section 9.3.7), which suggests it was of organic origin, probably after petroleum, which is commonly present in unmetamorphosed carbonate-silica rocks as e.g. in California (e.g. Bailey and Everhart, 1964; Sherlock and Logan, 1995). Uranium, that is effectively soluble, as uranyl ion, only in oxidising fluids, was probably not introduced with the petroleum, but was rather reduced by it from earliest metamorphic fluids of oxidising character.

Upper Kaleva metagreywackes enclosing the Outokumpu serpentinite massiffs contain about 9 and 2 ppm Th and U, respectively, which are both values quite close to the average Th and U abundances in the present upper crust, 11.7 ppm and 2.8 ppm, respectively (Taylor and McLennan, 1985). As usual for black shale type sediments, the upper Kalevian black schists are enriched in U, containing 17 ppm of uranium on average. When the black schists have an average content of 7 ppm Th, they are found to have a low average Th/U ratio of 0.4, which is a clear indication of a dominantly authigenic origin of their U enrichment.

## 9.3. Geochronology and isotope geochemistry

#### 9.3.1. Uranium-Lead, zircon ages

## Previous study

Understanding ore formation in time and space in Precambrian environments requires high precision isotopic dating of the involved rock formations, in practise this means applying U-Pb zircon dating. Unfortunately, largely because of the usually very low zircon content in the serpentinites (mantle peridotites), serpentinite-derived metasomatic and also mafic rocks in the Outokumpu assemblage, high U-Pb zircon dates of Outokumpu rocks are rare. The only published zircon date is by Huhma (1986), who reports, based on four moderately discordant multigrain zircon fractions, an upper intercept age of 1972±18 Ma for a pegmatoid gabbro body intrusive in serpentinite at Horsmanaho. Recently H. Huhma (2003, written comm.) has obtained, based on five slightly to moderately discordant multigrain zircon fractions, a more precise upper intercept age of 1959±4 Ma for a coarse-grained, ilmenite-bearing gabbro intrusive in serpentinite at Huutokoski (cf. Fig. 137). Considering the involved errors, the Huutokoski date is very close to the 1950-1960 Ma ages obtained for the gabbros and plagiogranites of the Jormua Ophiolite Complex in Kainuu (cf. Kontinen, 1987; Peltonen et al., 1998). In the light of this new data the often-assumed somewhat older age of the magmatism in the "Outokumpu Ophiolite" than in Jormua Ophiolite is clearly a debatable concept.

Importantly, the 1960-1970 Ma ages obtained for the Huutokoski and Horsmanaho gabbros define the gabbro emplacement into Outokumpu serpentinites a significantly older event than the sedimentation of the enclosing upper Kaleva metawackes, that must have been taken place subsequent to 1920±20 Ma based on ages of their detrital zircons (Claesson et al., 1993; Lahtinen and Huhma, 2002, pers. comm.). This age relationship means that the gabbro-serpentinite bodies in the Outokumpu assemblage have to represent fault-bound, tectonically emplaced bodies. This conclusion is supported by the fact that though gabbro intrusions in the serpentinite bodies are common, they never are met in the surrounding metasediments. The relationship of the ophiolite bodies and Upper Kaleva is thus in Outokumpu basically the very same than in Kainuu (cf. Claesson et al., 1993; Peltonen et al., 1996; 1998).

#### Study during the GEOMEX project

During the GEOMEX project zircons for two rock types in the Kylylahti Complex have been dated. One of the samples, Oku-794B/490.00-492.70, is from zircon bearing plagioclase-carbonate-calc-silicate rocks locally occurring within the skarn-hosted stringer mineralization zone of the Kylylahti Cu-Co deposit. The other sample is from a zircon-bearing sphene-

ilmenite-apatite rich chloritized basic dyke located in talc-carbonate rocks in the southern part of the Kylylahti complex.

## Oku-794B/490.00-492.70

The Kylylahti skarnoid rocks represented by the sample Oku-794B/490.00-492.70 are characterized by variable, sometimes relatively high amounts of zircon, sphene, rutile, plagioclase and apatite, i.e. minerals that are very atypical for normal Outokumpu-type skarns (cf. Huhma, 1970). Based on drill core observations, these skarns developments sometimes clearly brecciate and replace ordinary Outokumpu carbonate-skarn-quartz rocks forming the bulk of the gangue in the disseminated zone of the Kylylahti mineralization.

In order to get age constraints for the replacement type skarns in the Kylylahti disseminated zone, a high density mineral fraction, thought to contain zircon, sphene and also monazite, from a particularly zirconium rich (470 ppm ZrO<sub>2</sub>) skarn sample, Oku-794B/490.00-492.70, were separated for dating. Zircon and sphene became recovered but no monazite. Presence of small amount of colourless, transparent scheelite in the heavy fraction suggests it possibly was misinterpreted monazite in optical inspection of thin sections. Another possibility is that the mineral grains suspected in microscopic examination to monazite, simply were larger, particularly clear, unzoned zircon grains. Nevertheless, moderate amount of clear, nonmetamict zircon distinctly free of any internal growth zoning was recovered and dated. Altogether six heavy fractions (+4.3) were variably abraded and analyzed. Five of the moderately discordant fractions plot along a line that yields an upper intercept age of 1926±11 Ma (Fig. 136). One fraction plots significantly aside of this line having a <sup>207</sup>Pb/<sup>206</sup>Pb age of 1982±6 Ma. We have no good explanation for the deviation of this particular fraction, which technically represents a similar abraded +4.3 density fraction than the other analysed fractions. All the analysed fractions are distinctly low in U (24-106 ppm), the deviating fraction showing the lowest U content at only 24 ppm. The problematic fraction has also a deviating <sup>208</sup>Pb/<sup>206</sup>Pb (Th/U ratio) ratio of 0.144, the other fractions having lower <sup>208</sup>Pb/<sup>206</sup>Pb between 0.041 and 0.109.

The titanite from the Oku-794B/490.00-492.70 turned out to have a very low U/Pb ratio and thus be unsuitable for dating. This was most unfortunate, since these titanites would most probably have dated the skarn-replacement event at Kylylahti. So because the titanites are clearly congruent with the replacement event, and since the peak temperatures at Kylylahti (500±20 °C) remained below the blocking temperatures (600-700 °C) of such relatively coarse-grained sphene as in the Oku-794B/490.00-492.70.

Because of the unclear origin of the host rock, the zircon age of 1926+-11Ma obtained for the Oku-794B/490.00-492.70 is difficult to interpret. It hardly dates the structurally late skarn-replacement event, and the location of the Oku-794B/490.00-492.70 inside of metasomatised mantle rocks excludes the possibility of detrital zircons. One possible scenario is that the Oku-794B/490.00-492.70 represents a pervasively skarn-replaced felsic dyke similar in origin to the felsic rocks at the western margin of the complex (cf. section 6.3.2.). The structureless, unzoned character of the analysed zircons suggests they rather had crystallized from basic magma, however. Maybe representing some variety of the mafic dykes common within the mineralized skarn zone. In any case, if the zircons really are of magmatic origin, the obtained age could mean that oceanic magmatism within the "Outokumpu Ophiolite complex" continued at least up to 1926±11Ma. Metamorphic resetting of the zircons in the max. 550 °C metamorphic temperatures at Kylylahti is considered unlikely.

In any case the 1926+-11Ma age for the zircons in Oku-794B/490.00-492.70 seems to set a clear upper age limit for the replacement skarn formation at Kylylahti. This is an important constraint noting the fact that the Co-Cu-Zn mineralization in the Kylylahti stringer zone is nearly



Fig. 136. Concordia plot of U-Pb data for zircons in sample OKU-794B/490.80-492.70 from a apatitetitanite-rutile-plagioclase bearing skarn domain within the Kylylahti skarn-zone mineralization.

exclusively confined to the replacement skarn component. Whether the skarn-related mineralization would represent remobilisation or more primary ore formation, is then another and far less clear issue.

## M52/4224-R393/422.40-427, chloritized alkaline(?) basic dyke at Kylylahti

Drill hole R393 in the S deep extension of the Kylylahti complex contains many narrow, pervasively chloritized basic dykes in serpentinites and talc-carbonate rocks. One of these dykes, enclosed in talc-carbonate rock at R393/422.40-427.00, was observed by core logging to be fairly rich in sphene and ilmenite, and by microscopic examination also in zircon. The dyke is pervasively chloritized, rich in secondary pyrrhotite and contains also some apatite, which is reflected in the relatively high  $P_2O_5$  content of 0.8 wt.% of the dyke. The relatively high Ti, P, LREE, Sc and Zr contents in the dyke point to an alkaline basaltic or perhaps lamprophyric origin. Recalling that chemically somewhat similar mantle dykes from the Jormua Complex have yielded Archaean zircons (Peltonen et al., 2003), zircons from the R393/422.40-427 dyke were separated and dated.

Separation resulted in relatively little zircon, compared to their apparent abundance in thin sections under the microscope, probably because of the mostly small size of the grains. The zircon population appears morphologically somewhat heterogeneous. Nevertheless, the majority of the grains are fine-grained, dull and short prisms. Uranium concentrations measured for the analyzed fractions were significantly higher than in zircons from Oku-794B/490.00-492.70, with a range from 474 to 1023 ppm. The relatively high U is reflected in strongly discordant and scattered data points (Fig. 137). Nevertheless, the <sup>207</sup>Pb/<sup>206</sup>Pb age of 2158 Ma for the most concordant fraction indicates that the zircons, or at least a considerable part of them, would be at least 2158 Ma old.

There are two alternative ways to interpret this data. The first would encompass that the dated dyke and zircons crystallized from magma about 2.16 Ga ago or earlier, and the second that the dyke is, let us say, 1.95 Ga old as the Horsmanaho and Huutokoski gabbros, but would



Fig. 137. Concordia plot of U-Pb data for zircons from sample R393/422.40-427.40 of a chloritized alkaline (?) mantle dyke enclosed in talc-carbonate rocks in southern part of the Kylylahti massif. Data for the skarn sample Oku-794B/490.80-492.70 and Huutokoski gabbro A1029 (Hannu Huhma, written comm., 2003) are shown for comparison.

contain but 1.95 Ga zircons also xenocrystic zircons that in this case had to be much older than 2.16 Ga. The latter case would be analogous with the alkaline mantle dykes in Jormua Complex, which solidified from magma at about 1.95 Ga ago but that contain xenocrystic zircons of 2.7-3.1 Ga in age (Peltonen et al., 2003).

In either case, the zircon data from the R393/422.40-427.00 dyke strongly suggest that, as in Jormua, the Kylylahti serpentinites might represent rather Archaean subcontinental than 1.95 Ga oceanic mantle (cf. Peltonen et al., 1998; Tsuru et al., 2000). Be this true, it would of coarse have serious influence on modelling of the "Outokumpu Ophiolite", which in recent years has been interpreted to obducted suprasubduction-type oceanic lithosphere (e.g., Vuollo, et al., 1993; Walker et al., 1996), and thus particularly ore potential.

## 9.3.2. Lead

The galenas form the Outokumpu ore are among the most "primitive", unradiogenic galenas analysed for Palaeoproterozoic (Svecokarelian-Svecofennian) hydrothermal sulphide ores in Finland. This has been frequently taken as an indication of mantle origin of the Pb and other metals in the Outokumpu ore (e.g. Vaasjoki, 1981; 1986), though also the possibility of lower crustal origin has been noted (e.g. Vaasjoki and Vivallo, 1990). Because it would be daring to rely upon that what are actually only very few data on trace galena form the very Pbpoor Outokumpu ore (50 ppm of Pb on average), during the past years Pb isotope analyses also for other materials from Outokumpu have been carried out. For example, Vaasjoki (1986) analysed pyrites from the Outokumpu ore and adjacent black schists. By this study he made the important observation that compared to the ore pyrites, which show relatively unradiogenic Pb isotope compositions broadly supporting the inference of a mantle origin of the ore Pb, pyrites in the black schists show much higher 207Pb/204Pb pointing to a long-lived crustal like source of their Pb. Since the work of Vaasjoki (1981, 1986) more samples from Outokumpu and also from Vuonos, Kylylahti and Riihilahti ores have been analysed in GTK, some of them during the GEOMEX project. Below we will give a short review and discussion of this unpublished data.

Before that, we want, however, remind of the uncertainties that necessarily are related to any Pb isotope work dealing with highly metamorphosed and Pb-poor deposits such as e.g. the Outokumpu deposits are. Most ore Pb isotope studies are done for obtaining data on initial Pb isotope composition of the ores, i.e. finding out the Pb isotope composition the ores had when they formed. This is, however, not always a straightforward task since the presently observed Pb isotope composition of a given ore sample is a complex function of its "initial" Pb isotope composition, in-situ decay of any contained or subsequently added U, possible concurrent and subsequent addition of Pb from sources unrelated to the ore-forming system, subsequent Pb loss etc. Obviously, the more closed a given sample has behaved since its formation, the better the chances to find out its "primary" Pb isotope composition. In practise this means that samples having as high Pb content and low <sup>207</sup>Pb/<sup>204</sup>Pb as possible are desirable. Because of this, many workers restrict their ore sulphide Pb isotope studies chiefly on galena and high Pb sulfosalts. The exceptionally Pb and galena deficient Outokumpu-type ores are a very challenging target for Pb isotope study.

Apart from the problems with the low Pb concentrations, there are certain uncertainties related with the analytics, too. Significant errors may arise e.g. if the run-time isotopic fractionation deviated significantly from the usual, which in this case was estimated to 0.12% a.m.u.It also has to be noted that most of the data applied below is based on single measurements, while routine galena analytics in GTK is normally reported as an average of four measurements (two separate dissolutions, two measurements from both). Hence there is somewhat more uncertainty with this than routine Pb isotope data by GTK.

### Results from Outokumpu-type ore bodies in North Karelia

Reflecting the very low Pb typical of Outokumpu ores (usually about 50 ppm or less in average) and their consequent extreme poverty in galena (or other Pb-rich ore minerals), all the new Pb isotope data used here are for bulk ore samples, and to a lesser extend bulk sulphides and pyrite separates. This is very unfortunate but unavoidable since no visible galena was observed in any of the numerous ore samples studied during this work. Even optical microscopic observations of galena were very rare, mostly for very small grains in distinctly secondary-looking positions, as in late cracks of metamorphic pyrites. From a genetical point of view, it is worth to note, however, that submicroscopic galena grains disseminated in pyrite were observed by scanning electron microscopy in some Kylylahti deep ore samples. Heavy sulphide separate from one such sample became analysed for Pb isotopes during this study.

Nevertheless, the new data from the ore bulk samples from Outokumpu and Vuonos ore bodies corroborate the idea that the Outokumpu ore galenas would register the Pb isotope composition these ore bodies had at the time of their formation. An indication of this is that the bulk ore samples plot in the uranogenic diagram roughly in an array that points to the composition of the two previously analysed ore galenas (G30 and G170, Fig. 138). Furthermore, some of the bulk ore samples show <sup>208</sup>Pb/<sup>204</sup>Pb ratios that are within error equal to the <sup>208</sup>Pb/<sup>204</sup>Pb of the ore galenas. Two galenas (G40, G489) analysed from skarn rocks next to Outokumpu ore show somewhat elevated <sup>207</sup>Pb/<sup>204</sup>Pb and <sup>208</sup>Pb/<sup>204</sup>Pb suggesting that these galenas register an input from the adjacent Kalevian metasediments, probably related to their 1.9 Ga formation and/or subsequent metamorphism (see below). Having only two galena determinations from the Outokumpu ore proper does not allow stringent evaluation of the initial Pb isotopic homogeneity/heterogeneity of the ore. The isotope ratios in the two analysed galenas are fairly similar, however. The calculated 74init15 values (values corresponding to <sup>207</sup>Pb/<sup>204</sup>Pb ratios at <sup>206</sup>Pb/<sup>204</sup>Pb=15) for both samples are 15.048, the measured <sup>207</sup>Pb/<sup>204</sup>Pb ratios being 14.716 and 14.731. The considerable scatter in 74init15 values calculated to the bulk ore samples, from 15.028 to 15.217, indicate variation towards more crustal-like Pb compositions but this may be, as discussed below, rather because of postdepositional than pre/syndepositional mixing.



Fig. 138. Uranogenic Pb isotope diagram for samples of bulk ore ore (error ellipses) and galena (error ellipses/PbS) from Outokumpu and Vuonos deposits. Two outlier samples rejected from the isochron age calculation giving the result in the inset box are shown by red squares. Stacey and Kramers (1975) average crustal growth curve is shown for reference.

If the altogether 16 sample bulk ore plus two ore galena samples analysed from Outokumpu and Vuonos main ore bodies are extended with two samples analysed for the parallel "Co-Ni zone" at Keretti, an attractive looking Pb-Pb isochron age of 1974±27 Ma is indicated (MSWD=35). However, the related "isochron" is strongly biased by the two "Co-Ni zone" samples, which both are rich in calc-silicate gangue and very Pb-poor (< 2.5 ppm Pb). Most of the little Pb in these samples is of in-situ radiogenic origin (below) and the rest probably from the nearby metasediments. The irrelevance of the two Co-Ni samples as ore samples, and the 1974±27 Ma "isochron" involving them, is apparent from the fact that a similar apparent Pb-Pb isochron age of 1981±28 Ma is obtained if the two Co-Ni-zone "ore" samples are replaced, for example, by the two completely Cu-unmineralized skarn-carbonate rock samples here analysed from Outokumpu and Vuonos. Omitting the Co-Ni zone samples, the remaining 14 bulk ore and 2 ore galena samples define an apparent Pb-Pb isochron with a slope indicating an age of 2059±99 Ma (MSDW=34). However, if two of the more radiogenic samples, which both show exceptionally high 74init15 values >15.17 and exceptionally high 208/204 >34.75 are rejected, the isochron age indication is considerably changed to 1943±85 Ma (MSWD=12, n=12). 74init15 values for this 12 bulk ore plus two galena sample set are all <15.12. Henceforth we will use the 1943 Ma line (Fig. 138) as a reference to the Pb isotope composition of the Outokumpu-Vuonos ores.

The 14 pyrites analysed from the Outokumpu ore, earlier by M. Vaasjoki and now during this study, define an apparent Pb-Pb isochron of 2008±170 Ma (MSDW=27), which is within errors quite similar with the ages form the bulk ore galena samples. However, the pyrite data is clearly too scattered to constrain a true isochron (Fig. 139). Splitting the pyrite samples in two groups, one with 74init15 <15.12 and the other with 74init15 >15.12 demonstrates the nature of the isotopic heterogeneity. Namely, the low-74init15 group (n=5) treated as an isochron indicates an age of 1838±190 Ma (MSWD=4.4), whereas the high-74init15 group (N=9) yields an age of 2050±110 Ma (MSDW=7.1). It appears that the pyrite separates would record more metamorphic modification than the bulk ore samples, and may constitute in this respect two separate groups. Furthermore, it should be noted that most of the pyrite samples from Outokumpu analysed by



Fig. 139. Uranogenic Pb isotope diagram for pyrites from Outokumpu ore (most of the data by Matti Vaasjoki, partly published in Vaasjoki, 1986). Stacey and Kramers (1975) average crustal growth curve is shown for comparison. The inset box gives the age correspondig to the slope of the line defined by the data points.

Vaasjoki in Denver show surprisingly high <sup>208</sup>Pb/<sup>204</sup>Pb ratios. Reanalyses of two of these pyrite separates during this study indicated significantly lower values, which suggests there probably was an analytical problem at least with the <sup>208</sup>Pb/<sup>204</sup>Pb determinations at Denver.

That a linear array on the Pb-Pb diagram would represent an isochron of age significance requires that the included samples (sulphides) all had the same age of formation, identical initial Pb isotopic ratios and remained closed since their formation. It is most apparent from the above sections that these prerequisites cannot be guaranteed in the Outokumpu-Vuonos case but instead there clearly is scatter in the data suggesting variation in the initial composition and/or by post-depositional open-system behaviour. One likely source of scatter in the data is the probable U±minor "crustal-type" Pb addition in the ores at about 1900 Ma ago when the usual immediate wall rocks, carbonate-skarn-quartz rocks, gained their U. Minor addition/loss of Pb was likely also during the long-lasted 1880-1800 Ma high-T metamorphism of the Outokumpu-system. Nevertheless, if some age figure for the Outokumpu ore formation has to be given, we consider the 1943±85 Ma by the Pb-Pb isochron based on the "screened" 12 sample Outokumpu-Vuonos sample set as the most appropriate, though yet only an approximate estimate.

Compared with the larger Outokumpu-Vuonos ores, the less thoroughly metamorphic but relatively small semimassive sulphide lenses at the *Kylylahti* deposit show significantly more heterogeneity in their Pb isotope composition (Fig. 140). For example, in the uranogenic Pb-isotope diagram all samples from the small middle ore lens plot well above the Outokumpu-Vuonos reference line, whereas samples from the much bigger deep ore scatter about along the reference line. The four bulk ore and four pyrite separates analysed from the small "middle ore" yield an apparent Pb-Pb "isochron" of 1839±160 Ma, whereas the four bulk ore and four bulk sulphide separates form the larger deep lens yield an apparent "isochron" of 1945±330 Ma. In comparison, eight bulk ore samples from the middle and deep lenses together indicate a Pb-Pb "isochron age" of 2117±570 Ma! Moreover, the four pyrite separates analysed from the middle lens plot along a line with a slope indicating an age of just 1755±270 Ma, whereas the four sulphide separates from the deep lens suggest a Pb-Pb "isochron" with an age indication of 2430±1600 Ma! Clearly, preconditions for obtaining any relevant Pb-Pb isochron age for the

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Fig. 140. Uranogenic Pb isotope diagram for bulk ore and sulphide concentrates from the Kylylahti deposit. Red square=deep ore, bulk ore sample; red diamond=deep ore, bulk sulphide concentrate; pink squares=middle ore, bulk ore sample; pink diamonds=middle ore, pyrite concentrate. The Outokumpu-Vuonos data (error ellipses) and related 1943 Ma isochron are shown for comparison, as well as the Stacey and Kramers (1975) average crustal growth curve.

formation of the Kylylahti deposit from the present Pb isotope data do not exist. Instead the various isochron fits discussed above serve well to demonstrate the heterogeneity of the Pb isotope composition of the deposit.

Importantly, however, the data from the Kylylahti deep ore strongly hint that the initial Pb composition nevertheless was similar with the initial Pb composition as inferred for the Outokumpu and Vuonos ores. First, as we mentioned above, on the uranogenic Pb diagram the deep ore samples roughly plot along the Outokumpu-Vuonos reference line. Second, the 74init15 values calculated for the deep lens bulk rock samples and sulphide separates (15.052-15.125) are fairly close to the 15.048 for the Outokumpu ore galenas. Third, <sup>208</sup>Pb/<sup>204</sup>Pb ratios measured for these samples range from 34.404 to 34.713 are also reasonably similar to the <sup>208</sup>Pb/<sup>204</sup>Pb ratios measured from the Outokumpu ore galenas (34.471-34.476).

We address the isotopic heterogeneity at Kylylahti largely to metasomatic-metamorphic mixing of the Outokumpu-Vuonos type ore Pb with Kaleva-type Pb. The bigger, significantly Pb-richer ore bodies like the Outokumpu and Vuonos bodies were obviously better buffered against secondary metasomatic-metamorphic effects. The significance of the Pb mass balance is underlined by the fact that, after all, quantitatively the Pb mobility associated with the metasomatism-metamorphism of the Outokumpu-system seems to have been quite limited.

During this study also five whole rock samples from the skarn-zone Cu-Co-Ni-Zn±Au mineralizations of the Kylylahti deposit were analysed for Pb isotopes, the samples representing heavily Cu mineralised to nearly unmineralized rock types. The gangue in all these five samples representing altered mantle peridotite, denotes they were initially very low in U, Pb and Th, and consequently very sensitive to secondary addition of these elements. All the five samples show relatively high U contents (7.9-24.4 ppm) and highly radiogenic Pb with the measured <sup>206</sup>Pb/<sup>204</sup>Pb ratios ranging from 49.02 to 264.34. In comparison to the high U, Th is very low (<0.01-0.11 ppm) in all of the five samples, confirming with the variably high Cr and Ni the supposed mantle peridotite origin of the gangue. Pb concentrations are rather low (5-12 ppm) but anyway much higher than in the protolith mantle peridotite (<0.15ppm), which means that practically speaking all Pb (as well as U) in these samples would be uranogenic in situ

decayed Pb or Pb from external sources. Calculations based on the determined U an Pb concentrations and U decay equations, and assuming closed system behaviour since 1900 Ma, suggest that 50 % to nearly 100 % of the present Pb would be in situ grown uranogenic Pb. The five skarn-zone samples plot in the uranogenic diagram loosely along the Kaleva Pb reference line and yield an isochron age indication of 1874±63 Ma. The <sup>208</sup>Pb/<sup>204</sup>Pb ratios measured from this sample set do not much differ from those typical for Outokumpu-type metasomatites (34.75-35.84). 74init15 values calculated for these highly radiogenic samples are too uncertain to be useful. First and foremost, this data demonstrates that practically speaking no Outokumpu-Vuonos type Pb is present in the skarn-zone Cu-Co mineralization.

To see how the exceptional environment of the small Outokumpu-type mineralization at *Riihilahti*, inside metasediments and metavolcanic rocks of the parautochthon, would be reflected in its Pb isotope compositions, a few Riihilahti "ore" and wall-rock samples were analysed during this study. Problematic for Pb isotope studies the Riihilahti deposit comprises practically speaking no massive sulphides (average S content of the mineralization regarded by Outokumpu as "ore" is just 3.8 %) but nearly all mineralization occurs in veinlets and disseminations in miscellaneous host rocks. Also, the average Pb content of the Riihilahti mineralizations is, typical of Outokumpu deposits, very low, <30 ppm, causing that no visible galena is present. Hence all the Pb data discussed below are from whole-rock samples containing various proportions of variable host rocks. Therefore it is somewhat surprising that the nine samples together define on the uranogenic diagram a relatively tight linear array (Fig. 141) with an age indication of 1839±20 Ma (MSWD 8.5). The isochron line based on the data point intercepts Stacey-Kramer (1975) global Pb growth curve at –94 Ma and 1885 Ma. In a worthy remark, sulphide and Cu rich samples and sulphide and Cu-poor samples treated separately yield both about the same isochron age indication.



Fig. 141. Uranogenic Pb isotope diagram for Cu mineralized samples from the Riihilahti deposit. Stacey and Kramers (1975) global growth curve is shown for comparison. The inset box gives the age correspondig to the slope of the line defined by the data points.

The <sup>208</sup>Pb/<sup>204</sup>Pb ratios of the Riihilahti samples are high and highly variable (35.17-43.31) reflecting the variable amounts of diverse silicate gangue (skarn, altered metavolcanic rock, mica gneiss) in these samples. The relatively sulphide and Cu-rich samples (>3% Cu) show significantly higher U/Th (=5.5 in average) than the sulphide and Cu-poor samples with (U/Th=0.7 in average). We conclude that the nine point 1839+-20 Ma Pb-Pb isochron from Riihilahti dates the S+Cu+Co+Ni+Au+U introduction in the Riihilahti mineralization. Considering

the ore petrography and field aspects of the deposits, this was likely a pervasive metamorphichydrothermal remobilization process that was associated with effective mixing of primary ore Pb with Kaleva-type Pb to yield the relatively high "initial" <sup>207</sup>Pb/<sup>204</sup>Pb indicated by the Riihilahti data. Noting the presence of small serpentinite lenses in the Varislahti area just about 1-2 km to the N of Riihilahti, we consider it was in bounds of possibility that the principal ore metals (Cu, Co, Zn, Ni) in Riihilahti deposit were remobilized from an pre-existing serpentinite-associated Outokumpu-type Cu-Co mineralization.

Pb isotope data from the other Outokumpu-type deposits in North Karelia are rare. One pyrite and chalcopyrite sample from a massive, very Cu-rich, coarse-grained pyrite-chalcopyrite ore sample from *Luikonlahti* were analysed during this study. The analysed pyrite and chalcopyrite both yield relatively unradiogenic, pyrite a bit more radiogenic compositions. On the uranogenic diagram both minerals plot slightly above the 1943 Ma Outokumpu-Vuonos reference line (Fig. 142). The measured <sup>208</sup>Pb/<sup>204</sup>Pb ratios of the pyrite and chalcopyrite are almost similar (34.56 and 34.55) and comparable to the <sup>208</sup>Pb/<sup>204</sup>Pb of about 34.55±0.06 in most of the Outokumpu-Vuonos bulk ore samples. Thus, in the light of this scanty data, there appears to be no significant difference in the Pb isotope composition in Luikonlahti ore compared to that of the Outokumpu and Vuonos ores.



Fig. 142. Uranogenic Pb isotope diagram for sulphide separates from Luikonlahti and Saramäki deposits. Red squares=Luikonlahti samples; red diamonds=Saramäki samples; tot.sul = bulk sulphide concentrate; cp=chalcopyrite; po=pyrrhotite; py=pyrite. The Saramäki data are unpublished analyses by Matti Vaasjoki. The Outkumpu-Vuonos ore data (blue error ellipses) and related isochron from Fig. 138 are shown for comparison.

Some older Pb-isotope data exists also for the **Saramäki** mineralization (anal. M. Vaasjoki). This data includes analyses for one bulk ore sample, two chalcopyrite and two pyrrhotite separates. All these samples show quite radiogenic Pb isotope compositions. On the uranogenic diagram the two chalcopyrites and one of the pyrrhotites plot close to the Outokumpu-Vuonos 1943 Ma reference line, whereas the bulk ore and the other pyrrhotite samples plot clearly above it (Fig. 142). The <sup>208</sup>Pb/<sup>204</sup>Pb values are high and highly variable (34.68-37.76) for Outokumpu-type sulphides, and show no clear systematics, hence an analytical problem similar that with the Outokumpu pyrites may be suspected here. Nevertheless, for the part of the uranogenic Pb the Saramäki deposit appears not to significantly differ from the Kylylahti middle ore or Riihilahti sulphides, which both show

significant mixing of Outokumpu-Vuonos Pb with Kaleva type (wacke sediment) Pb.

### Results from Kaleva metasediments and Outokumpu assemblage

To provide some reference framework for interpretation of the ore Pb isotope data, a number of samples from the ore-enclosing metasediments and carbonate-skarn-quartz rock metasomatites in the Outokumpu assemblage became also analysed for Pb isotopes. Results from this work are summarized below.

### Kaleva black schists

Pb isotope ratios for seven black schist (most highly sulphidic, one very high in C and P), one slightly graphitic metagreywacke (mica schist) and one black metacarbonate rock (carbonate-tremolite rock) samples from Kylylahti define a linear array (Fig. 143) with an age of 1914±21 Ma (MSWD=5.6) and pointing to an initial <sup>207</sup>Pb/<sup>204</sup>Pb well above the global average Pb evolution curve by Stacey and Kramers (1975). All the black schist samples show relatively high U and high to very high U/Th ratios, which is typical of black shale sediments reflecting their syndepositional to diagenitec enrichment in authigenic U. Thus the obtained isochron likely dates the syngenetic or diagenetic introduction of U in the black schists and thereby approximately their deposition. The Pb-Pb isochron indication of deposition of the Kylylahti black schists at 1914±21Ma is a very reasonable estimate considering that the youngest detrital zircons in the Upper Kaleva greywackes are about 1920 Ma in age (Claesson et al., 1993), and that the probable obduction age of the Outokumpu assemblage was about  $1900\pm10$ Ma. Compared to the whole rock samples, two pyrite separates from the Kylylahti black schists are much lower in radiogenic Pb, but yet plot about along the extension of the whole rock array. Combined the Kylylahti whole rock and pyrite data yields a line with an age indication of 1916±17 Ma (MSWD=5). We will below use this line as a reference of the variation of Pb isotope composition in the Kaleva metasediments.

In a considerable contrast to the Kylylahti case, five black schist samples analysed from Outokumpu, Vuonos and Sukkulansalo scatter on the uranogenic diagram along a line with an considerably younger age of 1868±120 Ma (MSDW=6.9). Added with three pyrite separates analysed from Outokumpu black schists the age indication remains similar at 1842±57 Ma (MSWD=5), which is almost exactly the same age as that resulting in from the Riihilahti "ore" samples. We address the observed difference in the Pb isotope compositions between the Outokumpu and Kylylahti black schists to metamorphic "updating" of the black schists at Outokumpu where regional metamorphism peaked in significantly higher temperatures (>630 °C) than in Kylylahti (<550 °C).

### Outokumpu alteration assemblage

Pb isotope data for one skarn, three carbonate rock and six quartz rock samples from the Outokumpu alteration assemblage were obtained during this study (samples represent several geographically widely spaced locations). These data plot in the uranogenic Pb isotope diagram, with some scatter, along a linear array with an age indication of 1908±27 Ma (Fig. 144). This



Fig. 143. Uranogenic Pb isotope diagram for whole rock samples from Kylylahti black and mica schists. Stacey and Kramers (1975) average crustal Pb curve is shown for comparison. The inset box gives the age correspondig to the slope of the line defined by the data points.



Fig. 144. Uranogenic Pb isotope diagram for skarn-carbonate-quartz rocks from the Geomex study area. Stacey and Karamers (1975) average crustal growth curve is shown for comparison. Note the extremely radiogenic composition of the Pb in the carbonate-skarn-quartz rocks. The inset box gives the age correspondig to the slope of the line defined by the data points.

the Oku-metasomatites, which as altered mantle peridotites initially contained only very little U (<0.02 ppm). The secondary nature of U enrichment in the carbonate-skarn-quartz rocks is confirmed by their very low Th concentrations (<0.01-0.2 ppm) and consequently very high, very mantle unlike U/Th ratios (30->2000). Notably, much of the U+Pb in the carbonate-skarnguartz rocks is incorporated in tiny uraninite+galena+sulphide aggregates in silicate enclosed tiny nuggets of silicified bitumen (="tucholite" by Peltola, 1978), which seem to have been very refractory to subsequent metamorphic resetting. U in the Oku-metasomatites being associated with bitumen suggests it was reduced by organic material; initially probably petroleum migrated in the quartz rocks from the adjacent black shales, most probably during the primary silicification process or soon after (cf. Peabody and Einaudi, 1992). The obvious petroleum migration in the guartz rocks suggests their formation during the early burial metamorphism when the black shales were still in the P-T conditions corresponding to the oil producing "window". This implies that the Oku-type carbonate-silica alteration must have taken place concurrent or very soon after the Upper Kaleva deposition. In the light of this and the post-1920 Ma deposition of the Upper Kaleva (cf. Claesson et al., 1993), the 1908±27 Ma Pb-Pb isochron age for the U addition in the Outokumpu metasomatites can be taken also a reasonably close estimate of their formation age.

The carbonate-skarn-quartz rocks seem to contain typically 2.5 to 13 ppm Pb, based on the available few high-precision isotope dilution data. High <sup>206</sup>Pb/<sup>204</sup>Pb ratios measured for these rocks (44.41-713.61) suggest that most of this little Pb would represent in situ grown uranogenic Pb. On the uranogenic diagram the data points plot along the Kaleva-Pb reference line, indicating that most of the minor "initial" Pb would be from the Kaleva (metasediment) type Pb reservoir, probably Pb introduced by the above inferred low-T petroleum migration. <sup>208</sup>Pb/<sup>204</sup>Pb ratios measured for the Oku-metasomatites are in most samples between 34.75 and 35.84, while a few samples show exceptionally high values between 36.60 and 38.84. These values mean that in terms of the <sup>208</sup>Pb/<sup>204</sup>Pb ratios the carbonate-skarn-quartz rocks are quite similar with the adjacent serpentinites (below).

In contrast to the fairly coherent Pb isotope data from the whole rocks, sulphide separates from four Outokumpu quartz rocks yield very scattered, highly radiogenic data (Fig. 145), indicating wild open system behaviour for the sulphide phase in these relatively sulphidic (usually 0.5-2 w% S) rocks. Best explanation to this is that the sulphide phase was very Pbpoor and hence very sensitive for about any post 1.9 Ga modifications. Importantly, however, all the analysed four sulphide fractions plot on the uranogenic diagram very differently of the Cu ore sulphides well above the Kaleva reference line. It seems that most of the U and Pb in the carbonate-skarn-quartz rocks would reside in the tiny inclusion nuggets of silicified bitumen they commonly contain, and which often enclose tiny aggregates of uraninite, galena and iron sulphides. Obviously the evidently early-formed bitumen nuggets have been very refractory to metamorphism.

### Outokumpu serpentinites

Six serpentinite samples, all from the Outokumpu massif, were analysed for Pb isotopes. These samples were selected to represent the sulphide poor serpentinites (serpentinized talcolivine rocks) typical for the core parts of the Outokumpu serpentinite body, and the sulphidic serpentinites (typically serpentinized anthophyllite-enstatite-olivine rocks) typical of its marginal parts.

The three body core samples all show very low Pb concentrations (0.05-0.11 ppm, highprecision isotope dilution data); well below the estimated primitive mantle average Pb content (0.15 ppm). Also S concentrations in these samples are very low (0.06-013wt.%) and below average primitive mantle level (0.025 wt.%). Compared to the body core samples, in the three body margin samples, the measures sulphur contents are much higher (1.15-9.59 wt.%), as are also Pb concentrations (0.39-1.9 ppm, isotope dilution data). These values show that while the Pb and S concentrations in the three body core samples are on a par with their inferred origin as depleted mantle peridotites, the margin-serpentinites clearly must be highly contaminated both in S and Pb.



Fig. 145. Uranogenic Pb isotope diagram for sulphide separates from Outokumpu quartz rocks (blue squares). Stacey and Kramers (1975) average crustal Pb growth curve and the 1916 Ma Kylylahti metasediment isochron from Fig, 144 are shown for comparison.

U and Th contents are very low both in the body core serpentinites and margin serpentinites, 0.02-0.16 ppm and 0.03-0.06 ppm, respectively (ICP-MS data). The low U in the margin-serpentinites is a bit surprising aspect, considering the usually quite high U in the adjacent carbonate-skarn-quartz rocks. This could reflect recent U loss from the serpentinites, which contain no reductant/refractory host for U similar to the silicified bitumen nuggets in the carbonate-skarn-quartz rocks. It is worth to note here that the measured U and Th concentrations do not much differ from the values estimated for the average primitive mantle (U = 0.023 ppm, Th = 0.0795 ppm).

All the six analysed serpentinite samples show highly radiogenic Pb isotope compositions with <sup>206</sup>Pb/<sup>204</sup>Pb ratios ranging from 16.70 to 47.03. The measured <sup>208</sup>Pb/<sup>204</sup>Pb ratios range between 35.09 and 35.65, except for one Pb-poor sample, which shows a value as high as 37.17, but with a high analytical uncertainty because of the very low Pb content. Basically the <sup>208</sup>Pb/<sup>204</sup>Pb ratios are quite similar to those measured from Outokumpu carbonate and quartz rocks. In the uranogenic diagram (Fig. 146) all the three body margin samples and the Pb-richest one of the core-samples plot along the Kaleva-Pb reference line, which suggests that they have gained most of their Pb from the surrounding Kaleva metasediments. The two very Pb-poor body core serpentinites plot below the Kaleva-Pb reference line and consequently show distinctly low 74init15. This could indicate mantle origin for the very little Pb in these samples, though due to the high analytical uncertainty related to these low Pb samples this conclusion must be taken with a grain of salt. Any meaningful isochron cannot be fitted to the serpentinite data.

Serpentinite margins getting regionally S richer with rise in the metamorphic grade suggests that most of the S was by synmetamorphic dehydration/desulfidation fluids. Whether the sulphidation of the serpentinite margins really was a purely synmetamorphic phenomena or perhaps a result of a more complex series of S adding processes, in either case, the very low Pb concentrations even in the most sulphide-rich serpentinite margins imply that the metamorphic fluids were very low by their Pb concentrations.

### Results from Eastern Metals deposit, Quebec Appalachians

The Eastern Metals deposit, visited by GEOMEX during the summer 1999, represents a





Fig. 146. Uranogenic Pb isotope diagram for serpentinitised metaperidotites from Outokumpu. Sulphidepoor serpentinites form core parts of the serpentinite massif are shown by brown squares, sulphide-rich serpentinites from the massif margins by brown diamonds. Stacey and Kramers (1975) average crustal growth curve and the Kylylahti 1916 Ma metasediment isochron are shown for comparison.

relatively young Outokumpu-type deposit (Ordovician). It is found in association with a small, serpentinized mantle harzburgite lens in the St Daniel Mélange within the Taconian Dunnage zone/terrane of the Quebec Appalachians. The Eastern Metals serpentinite probably correlates with the mantle section of the 480 Ma (crustal section) Thetford Mines ophiolite, which locates some 100 km to the SW of Eastern Metals. Metamorphism at Eastern Metals corresponds to the lower greenschist facies.

The Eastern Metals serpentinized harzburgite lens shows similar marginal silica-carbonate (birbirite-listwaenite) alteration than the Outokumpu serpentinites. There are also bodies of clear Outokumpu-type Cu-Co-Zn (S-zone) and Ni-Zn mineralization (N-zone) in association with the carbonate-silica rocks. Auclair et al (1993) consider Eastern Metals mineralizations epigenetic-hydrothermal and relate them to a Taconic (or even Acadian) fault and associated shearing along the serpentinite body margin, and place the metal sources in the adjacent metasediments (Cu-Zn) and serpentinites (Ni-Co-Au). The St Daniel Mélange, previously considered as an accretionary complex at a subduction zone (e.g. Cousineau, 1992), has recently been reinterpreted to a piggyback basin, which was unconformally developed on the obducting piece of oceanic crust now represented by the Thethford Mines Ophiolite (Schroetter, 2002). The St Daniel Mélange comprises ophiolite-derived mafic-ultramafic fragments and metamorphic rock fragments of continental origin as its main olistholitic sedimentary components. Locally there seems to be materials also from a Lower-Middle Ordovician island arc complex (Ascot-Weedon)(Cosieneau, 1992).

During summer 1999 GEOMEX excursion to Quebec, A. Kontinen collected several sulphide samples from the Eeastern Metals Cu and Ni mineralizations. Subsequently (2002) some of these samples became analysed for Pb isotopes in GTK. It was hoped that compared with the Outokumpu data this would shed some more light on the timing/metal source issues with the rare Outokumpu-type deposits. Below is a short report on the results.

The samples from Eastern Metals included one for pyrite-quartz veins in birbirite at Nzone, one for the massive pyrite+-polydymite+-minor sphalerite at N-zone, three samples for the Cu-Co-Zn mineralization at S-zone, and two samples from the flanking black shales. Though there is some variation in the uranogenic isotope ratios measured for the sulphides, there is no difference between the samples from the N-zone Ni-mineralization and S-zone Cu

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mineralization. Also the S-zone black shale sample has uranogenic ratios that do not much differ from those of the sulphide samples. The N-zone black shale sample shows a much more radiogenic Pb isotope composition, but also this sample may have had initial composition similar with the S-zone samples. Thorogenic ratios of the sulphide samples define a relatively narrow range between 37.558-37.701, with an average at 37.62. Compared to the ore sulphides the two black schist samples show clearly more radiogenic ratios of 38.273 and 38.522.

On the uranogenic diagram the Eastern Metals sulphides plot below the Stacey-Kramers (1975) global growth curve, and somewhat on the younger side of the related 500 Ma model isochron (cf. Fig. 147). Considering that the age of the Thethford Mine ophiolite is 480 Ma and that its obduction took place within 1-17 Ma of its formation (Withehead et al., 2000), the model age indication suggests origin of the Eastern Metals mineralization either in the pre-obduction oceanic setting or during the obduction. The average thorogenic ratio of the sulphides 37.62 is clearly too high that it would represent pure mantle value. On the thorogenic diagram the sulphide samples plot quite close along the Stacey-Kramers (1975) model curve with a geologically reasonable age indication of 500-550 Ma. The Eastern Metals Pb having <sup>207</sup>Pb/<sup>204</sup>Pb ratios significantly higher than Pb in the York Harbour deposit of the ca. 500 Ma old Bay of Island Ophiolite or in the present Mid-Atlantic (sediment-free) sulphides (cf. Fig. 147), a purely mantle origin for the Eastern Metals Pb and other metals seems unlikely. Also the average thorogenic ratio of the sulphides (37.62) is clearly too high that it time-integrated would represent pure mantle value.

Based on the lead isotope data, reported metal character and geological setting at Eastern Metals, we are inclined to think that both the birbirite-listwaenite alteration and Cumineralization were related to syntectonic/synsedimentary hydrothermalism in the St Daniel formation in its early piggy-bag basin stage. Olistholith mantle fragments that had been/were sliding in the tectonically active basin apparently became immediately silica-carbonate altered in relatively low temperatures. Somewhat later, fault-controlled higher-T fluids (250-350 °C) contributed to the Cu-mineralization (cf. Auclair et al., 1993). Metal sources seem to have been in the peridotitic ophiolite fragments (Ni-Co) and sediments (As-Sb-Pb-Hg) and volcanic rocks (Cu, Zn, Au) in the St Daniel Mélange and perhaps also in the (in the inferred piggy-bag stage) underlying ophiolitic/oceanic basement. Heat source to generate/run the hydrothermal flow in the piggy-bag basin may have been the still relatively hot (at the time of obduction) underlying oceanic lithosphere. It must be noted here that the obduction of Thetford Mines ophiolite occurred very short (1-17 Ma) after the magmatic formation of its magmatic part (oceanic crust). Also the presence of a high-T metamorphic sole below and obduction-related anatectic granites in the Thetford Mines Ophiolite support concept of relatively "hot obduction". Much of the ore petrographical and structural features of the Eeastern Metals deposit probably are related to the subsequent Taconian and perhaps even Acadian faulting/shearing that reactivated the synobduction faults and remobilized and structurally modified the sulphide deposit.

There are clearly many similarities in the Eastern Metals setting with the Outokumpu case. Isotope and structural evidence define the silica-carbonate alteration in both cases to a synobduction to early burial metamorphic process. In Eastern Metals the Cu mineralization event clearly post-dated the silica-carbonate alteration, thus this may have been the case also at Outokumpu. A synobduction/syntectonic origin would straightforward explain why both the Outokumpu and Eastern Metals, as well as the less well-known Deerni ore associations (cf. chapter 11) all lack rock the characteristic components of most massive sulphide environments, such as e.g. coeval volcanic rocks, barite zones, cherts, iron-manganese sediments etc.

#### Interpretation of the Pb-isotope data

### Origin of the Pb and other metals in the Outokumpu-type ores

The above scrutiny of the Pb data of the Outokumpu deposits was undergone for a large



Fig. 147. Uranogenic Pb isotope diagram for sulphide separates (red error ellipses) and samples of black schists (black error ellipses) from the Eastern Metals deposit, Quebec Appalacians. Stacey and Kramers (1975) average crust and Zartman and Doe (1981) mantle evolution curves are shown for comparison. Red square shows lead isotope composition of the York Harbour deposit at Bay of Island Ophiolite (Swinden and Thorpe, 1984) and the green square average composition of present seafloor sulphides from TAG hydrothermal site at Mid-Atlantic Ridge (26° 08'N) (Andrieu, et al., 1998). The inset box gives the age correspondig to the slope of the line defined by the Eastern Metals sulphide and black schist data points.

part with references to the possible Pb-Pb isochron age indications, first and foremost to demonstrate the involved isotopic heterogeneity. The best-case isochron for the Outokumpu and Vuonos deposits suggests that their deposition would have occurred 1943±85 Ma ago. However, it must be noted that even this 1943±85 Ga Outokumpu-Vuonos isochron is related with considerable uncertainty.

More useful than the isochrones, would in this case clearly be to look at the lowest Pb isotope ratios obtained for the sulphides, in hope to get some idea of the initial ratios and thereby of the possible source of the Pb and other ore metals. Unfortunately this approach is limited by the extremely low Pb typical of the Outokumpu deposits and scarcity of Pb isotope data for the principal components of the Karelian craton margin. On the other hand, considering the relatively large size of the Outokumpu-Vuonos deposits, one would expect that a large-size hydrothermal system was involved and that effectively homogenised the Pb flux in the deposits. Therefore it may well be that the Pb isotope data which we have for their bulk sulphides and rare ore galenas faithfully record the isotope composition of their initial Pb.

The plotting of the two ever-analysed Outokumpu ore galenas on the uranogenic diagram below growth curves for upper crust has frequently been used as an argument of mantle origin of their Pb and the ore Pb in general. However, independent reference for the Pb isotope composition of 1.95-2.1 Ga mantle being rare, it is difficult to evaluate how relevant such an interpretation would actually be. In fact, abundant data from data from the primitive 1.95-1.89 Ga Skellefte arc in Svecofennian of Sweden suggests that mantle values at 2.1-1.95 Ga may have been significantly lower than the values recorded by the Outokumpu galenas (cf. Vaasjoki and Vivallo, 1990). Thus it is quite possible that the Outokumpu galenas actually do register some mixing with crustal-like lead. Some, tough still vague support for this view comes from that thorogenic ratios in some of the Kylylahti bulk ore and bulk sulphide samples appear to marginally lower than in the Outokumpu ore galenas. It is worth to note also, that although most of the Outokumpu-Vuonos bulk sulphides and the two ore galenas plot along a line corresponding to an age of 1943±85 Ma, yet both Stacey-Kramers (1975) and Cummings and

Richards (1975) model ages for the two Outokumpu galenas are about 2100 Ma (Vaasjoki, 1981). Taken at its face value this age would mean that Outokumpu Pb was initially separated from its source already 150 Ma earlier than the 1943 Ma+-85 Ma indicated by the isochron of the Outokumpu-Vuonos ore samples.

As we mentioned in the beginning of the isotope part of this report, the Archaean lower crust below the Outokumpu district has been seen a possible alternative source of the Pb in the Outokumpu ore (e.g. Vaasjoki and Vivallo, 1990). Some relevance for the latter source alternative is actually provided by Pb isotope data on alkali feldspars from the about 1870 Ma Suvasvesi, Heinävesi, Onkivesi and Nilsiä granites (Halla, 20002; GTK, unpublished data), which indicate initial Pb isotope compositions in these granites were surprisingly close to those in the Outokumpu galenas (Fig. 148). These granitoids comprising considerable Archaean material based on Sm-Nd isotope evidence (Huhma, 1986), this data importantly demonstrates that theoretically was a suitable source of the "mantle-like" Pb of Outokumpu ore, but in mantle, also in the crust deep below the Outokumpu Allochthon. And that there was also a mechanism (granite intrusions and possibly related fluids) that at about 1870 Ma ago could have transported Pb from this source in the more upper parts of the crust.



Fig. 148. Uranogenic Pb isotope diagram for k-feldspars (red-filled error ellipses) from the 1870-1860 Ma granitoids at the western margin of the Karelian Craton. Data for k-feldspars from the 1.54 Ga Salmi Rapakivi batholith (Rämö, 1991) and galenas (PbS) from Outokumpu ore and associated skarns are shown for comparison. The age in the inset box refers to the isochron fit (black dashed line) shown for the 1870 Ma k-feldspars. The blue line is for Stacey and Kramers (1975) average crustal growth curve.

I must be noted, however, that there are some features in the Pb isotope ratios of the ore sulphides, such as the relatively low <sup>208</sup>Pb/<sup>204</sup>Pb ratios of the galenas and some of the least

radiogenic bulk sulphides, that actually militate against Archaean lower crust as the principal Pb source. Hence, and noting that the  $\epsilon_{Nd}$ (1870 Ma) values of the 1870 Ma granites between –2 and –4 (Huhma, 1986) do necessarily require extensive Archaean component, one might argue that the 1870 Ma granites indeed supplied the "mantle-like" Pb - but not necessarily from the Archaean crust below the NKSB – but more or less directly from mantle! An important aspect of the 1870 Ma granites should be taken in account here; they actually may be allochthonous as they are nowhere, absolutely nowhere, observed to intrude the Archaean basement. There is here a great contrast with the somewhat younger, 1.86 Ga Maarianvaara type granitoids which are in numerous locations showing intrusive contacts with the Archaean basement. There is a corresponding difference in the  $\epsilon_{Nd}$  values, too, as the Maarianvaara type granites have  $\epsilon_{Nd}$ (1870 Ma) values at –6, being in this respect similar to the ca. 1.80 Ga Kitee granite and 1.65 Ga Salmi rapakivi granite, that seem to comprise a large lower crustal component of Archaean age (Rämö, 1991).

We conclude that the Outokumpu galenas do not necessarily represent "pure" mantle Pb isotope compositions but most probably record at least some initial mixing with mantle-like Pb with more crustal-like Pb. Further, considering the 1.87 Ga granitoid Pb-isotope data, there seems to be alternatives to generate the isotope signature of the Outokumpu galenas. We mean alternatives to the present paradigm that involves hydrothermal leaching of Pb principally from mantle, and/or juveline mafic rocks in a seafloor. Clearly, the 1.87 Ga granite-forming processes in the western parts of Kaleva domain ended up with about the Outokumpu-type Pb composition in the k-feldspars. Whether the 1.87 Ga granites or related fluids really contributed to the Outokumpu mineralization is then on other question.

Importantly, however, what the Pb isotope data from Outokumpu, Vuonos and Kylylahti clearly constrain, is the large difference between the obvious initial lead compositions of the Upper Kalevian mica schists-black schists and the sulphide ores, which clearly precludes their syngenesis, and speaks also against any syntectonic scenarios positioning the metasediments as the principal metal source of the ores. One could of coarse prospect for scenarios with effective selective separation of Pb from Cu and Zn, in a way or other, but these seem difficult in the light of the high solubility of each of these metals in typical high-T hydrothermal fluids (e.g. Henley et al., 1984).

To a summary of the above discussion one can say that the presently available Pb isotope data on the Outokumpu deposits suggest they formed about 1943±85 Ma ago, that is, at some time between 1858 and 2028 Ma. And, that the principal source of the little Pb, and presumably also such more abundant base metals as Cu and Zn, in the deposits was either the mantle as represented by the host mantle fragments, or more hypothetically the mantle source component of the 1.87 Ma granitoids intrusive/obducted in the Outokumpu thrust belt in its western, more highly metamorphosed (migmatic) part. Model ages of the ore galenas may indicate separation of the ore Pb in sulphides already 150 Ma before the actual formation of the Outokumpu ore bodies; this could represent ca. 2.1 Ga sulphide protomineralization in the source mantle.

#### Timing of the Outokumpu-type silica-carbonate alteration

The reasonably tight nine point whole rock Pb-Pb isochron obtained for the Upper Kaleva black shales at Kylylahti suggests their deposition took place about 1914+-21 Ma ago. This indication is in perfect harmony with the constraints set by the about 1920 Ma age of the youngest detrital zircons in the Upper Kaleva greywackes (Claesson et al., 1993), and the about 1900+-10 Ma age inferred for their obduction onto the Karelian craton margin.

The ten point 1908+-27 Ma whole rock Pb-Pb isochron obtained for the Outokumpu type carbonate-skarn-quartz rocks indicates introduction of U in these originally very U-poor (mantle peridotitic) rocks concurrently with, or very soon after the Upper Kaleva deposition. The presence of obvious petroleum remains in these rocks supports alteration during the obduction or early burial metamorphism of the master serpentinite bodies, and when the Kalevian organic carbon-rich black schists (usual wall-rocks to the quartz-carbonate rocks) still were in the oil-producing P-T regime.

The above age constraints together with "stratigraphic" constraints from the typical Outokumpu occurrences require tectonic incorporation of the Outokumpu mantle fragments among the enclosing turbidite sediment perhaps already during their deposition but on no account no later than during the earliest stage of their obduction. Such a scenario is perfectly possible; for example, in a tectonic environment featuring subseafloor transform fault(s) in a metaturbidite covered ultramafic ocean floor, as we described earlier in section 6.2.2. Subsequent synobduction to burial metamorphic-metasomatic alteration of the peridotite fragments, under progressively increasing T and  $CO_2$ -richer fluid influence, was then responsible of the generation of the silica-carbonate rocks in the Outokumpu assemblage. With progression in the greenschist facies talc-carbonate rocks started to form.

If taken literally and ignoring the errors, the Pb-Pb isochron "age" of about 1943±85Ma obtained for the Outokumpu and Vuonos ores would constrain their formation a significantly older process than the <1.92 Ga Upper Kaleva deposition and the subsequent silica-carbonate alteration of the host peridotite fragments. One possibility to explain this relationship would be to assume, as we do in the GEOMEX ore model presented below, that the ore formation was related to (or started with) hydrothermal exhalative activity and associated sulphide deposition within the obviously sediment-starved, mantle-peridotite-floored oceanic basin, from which the host peridotite fragments derive, and which, based on evidence by the Jormua Ophiolite Complex, was opened W of the Karelian craton ca. 1950 Ma ago. Problematic for this basically attractive model is, however, as we pointed above, that there are no typical ocean floor exhalative sediments (carbonates, chert, anhydrite, barite, iron-manganese etc.) in association with the Outokumpu ores or in the Outokumpu Assemblage in general.

## 9.3.2. Rhenium-Osmium

Re-Os isotope works on the Outokumpu rocks are rare, including a study by Walker et al. (1996) on chromite and associated gersdorfite and laurite in chromitites from talc carbonatealtered mantle peridotites at Vasarakangas, Kylylahti. In addition, Tom McCandless has analyzed some samples from Outokumpu and Luikonlahti (at University of Arizona, samples provided by A. Kontinen). The results and interpretations by Walker et al. (1996) and MacCandless (written comm., 1999) are briefly discussed in the sections below.

### Vasarakangas chromitites

Walker et al. (1996) assumed that the Vasarakangas chromitites and their talc-carbonate host rocks would represent magmatic cumulates in an upper part unit of the mantle section in the "Outokumpu ophiolite complex". Their Re-Os data from Vasarakangas comprise  $\gamma_{Os}$  (1970) Ma) between -1.1 and +0.4 for eleven chromites, -1 and -1.2 for two gersdorfites, and -1.6 for one relatively large Os-rich laurite grain, all separated from chromitite blocks collected from a heap of waste rocks at the Vasarakangas talc guarry. Based on this data, and assuming that the chromitites would be ca. 1.97 Ga in age, Walker et al. (1996) proposed that the parent magma was derived from a mantle source having a broadly chondritic Os isotope composition (within  $\pm 2\%$  of the projected composition ). They further concluded that while the source of the chromitites was broadly chondritic, the variation in Os isotope ratios in the Vasarakangas samples required also another, more radiogenic Os reservoir. They attributed the relatively radiogenic Os in the gersdorfites and chromites to a variable synobduction contribution from seawater or continental crust. Walker et al. (1996) noted that the evidence from Vasarakangas of a nearly chondritic Os in 1.95 Ga upper mantle would support the theories about addition of significant Os and other highly siderophile elements in the Earth's upper mantle still after the Earth's core formation, probably by asteroidal and cometary bombardment.

Laurite with erchlimanite being the dominant primary PGM inclusions in many ophiolitic chromitites supports origin of the Vasarakangas laurite as a primary inclusion phase in chromite/olivine, and that its <sup>187</sup>Os/<sup>188</sup>Os ratio may thus indeed represent primary magmatic value. Whether the gersdorfite and chromite data would represent 1.97 Ga seafloor and/or

subsequent synobduction alteration, as Walker et al. (1996) suggest, is less clear, however. Talc-carbonate alteration being a typical regional metamorphic, greenschist to lower amphibolite facies process, associated with significant S and As in the carbonising metamorphic fluid, much of the radiogenic Os overprint could in fact be also synmetamorphic.

Walker et al (1996) considered a crude 1.97 Ga trend defined by chromite separates from one particular Vasarakangas chromitite sample (POL-10) to support the assumption of 1.97 Ga age of the chromitites, as well as the host mantle peridotites. However, two important comments should be made. First, the 1.97 Ga age POL-10C is highly depentend of one single data point, POL-10C, that has strongly deviating from rest of the chromitite-gersdorfite-laurite data, and which may record significant more recent Re addition. Second, instead of being dominantly of cumulate origin, as thought by Walker et al. (1996), the peridotites in the Kylylahti complex are in fact dominantly residual, as most peridotites in the "Outokumpu ophiolite" (section 7.1). Therefore, the 1.97 Ga age of the chromitites is fairly uncertain, and even if it would be correct, it does not mean that also the residual peridotites hosting the chromitite would necessarily be of the same age.

It is worth to recall here that the observation made during this work of >2150 Ma zircons in one mantle dyke in the Kylylahti talc-carbonate rocks (section 9.3.1.), suggesting that the mantle parts in the Outokumpu ophiolite would be much older than its 1.96 ga mafic components. Thus, the situation in Outokumpu could be much the same as in jormua where there is strong evidence of dominantly SCLM origin and >2.9 ga age of the mantle unit. This evidence include that Os isotope data from the best preserved accessory chromites in Jormua serpentinites have an average  $\gamma_{Os}$  as low as  $-5.1\pm0.8$  at 1.95 Ga, imlying the mantle section in the Jormua ophiolite must have been depleted for Re, and separated from convective mantle, already before ca. 2.9 Ga (Tsuru et al., 2000). Recent observation of Archaean zircons in mantle dykes in Jormua supports this view (cf. Peltonen et al., 2002, 2003).

There occur chromitites also in Jormua, identical for the chromite composition with he Vasarakangas chromitites, but like in Vasarakangas, unfortunately located in talc-carbonate rocks. Obviously related to the talc-carbonate alteration, also the Jormua chromitites exhibit distinct Re-Os isotopic heterogeneity with  $\gamma_{Os}$  (1950 Ma) ranging wild from –15 to +108. Though the mantle at Jormua seems at least 3 Ga old, the true age of the associated chromitites remains thus unknown. The chromitites in Jormua may either belong to the Archaean mantle suite or represent cumulates related to the 1.95 Ga E-MORB magmatism that formed the crustal part of the Jormua ophiolite. The latter scenario, i.e. broadly 1.95 Ga chromitites in Archaean SCLM could be the case also in Vasarakangas, but should be tested by analysing disseminated chromites from the host peridotites. Whether the chromitites would then be much younger, and related to the 1.97-1.95 Ga magmatic additions, remains, for both Jormua and Vasarakangas another yet unresolved question.

Vuollo et al. (1995) interpreted the presence of chromitites at Kylylahti as evidence of a suprasubduction origin of the "Outokumpu ophiolite complex". However, the relatively aluminous composition of the chromitites, and their extreme rarity in Kylylahti, as elsewhere in the "Outokumpu ophiolite complex", are rather opposing than supporting evidence of an suprasubduction origin. In fact the chemical composition of the Vasarakangas chromitites is almost identical with the chromitites in the Jormua Complex (Kontinen and Peltonen, 2002; Säntti et al., in press), which has clear nascent ocean type ophiolite characters (cf. Peltonen et al., 1996, 1998).

#### Re-Os data on the Outokumpu and Luikonlahti sulphides

As was mentioned in the beginning of this chapter, Tom McCandless has performed Re-Os isotope determinations on a few sulphide samples from Outokumpu and Luikonlahti. The following short summary of this work is based on his brief written communication from the year 1999.

According to McCandless, the studied Outokumpu sulphide samples comprise both Re and Os in relatively high and highly variable concentrations, rendering spiking for accurate analytics very difficult. There are also clear tendency towards open system behaviour in much the obtained data. After measuring a lot of samples from both Outokumpu and Luikonlahti, as an end result, isochrons were established, but with large errors. The best isochron was obtained for the Luikonlahti deposit, for which a five-point array indicates an apparent age of 1915±261 Ma, with an <sup>187</sup>Os/<sup>188</sup>Os initial ratio of 0.477. Based on this result, the following reasoning can be applied in interpretation of the source of the Os in Luikonlahti sulphides. As the mantle <sup>187</sup>Os/<sup>188</sup>Os ratio appears to have only slightly increased from the ca. 0.12 at the early Archaean, any significantly higher value, like the 0.477 for Luikonlahti, would indicate that radiogenic Os was involved. Then, noting the previous proposals of the 1.97 Ga ophiolite-hosted nature of the sulphides, and that the 1.95 Ga seawater already has a very radiogenic <sup>187</sup>Os/<sup>188</sup>Os ratio, over 1.0 in same parts of the Earth's ocean system, one could argue that the most likely source of the radiogenic Os was in the 1.97 Ga seawater. However, there is nothing in the data that would implicitly exclude a more direct continental crust-like source of the Os.

From a perspective of hydrothermal sulphides on seafloor, having seawater-like Os and more or less mantle-like Pb in Outokumpu type sulphides appears a somewhat conflicting situation, especially if we assume that the seafloor and metal source were comprising mainly mantle peridotite that tend to be relatively rich in Os. An explanation to this apparent discrepancy could be that Os in the mantle peridotites was, unlike Pb, inaccessible to the heated seawater. This could have been so as most Os in mantle peridotites is usually located in tiny grains of PGE minerals (laurite, erlechmanite, sperylite) enclosed in the relatively insoluble chromite. Actually most modern-day ocean floor hydrothermal deposits from sediment-free settings show similar behaviour, that is, the hydrothermal vent sulphides show mantle-like Pb, but yet seawater-like Os isotope ratios. In a summary, Osmium isotopic compositions of Luikonlahti sulphides are consistent with, although do not by no means prove, a seafloor hydrothermal setting of their deposition.

### 9.3.3. Samarium-Neodymium

In order to get more constraints for deducting the sources of the REE in the ore bodies, that of the sporadic high enrichments particularly, we performed some Sm-Nd isotope analyses on a set of ore samples from Outokumpu, Vuonos, Kylylahti and Riihilahti. The analytical work was done under the supervision of the third author of this report in GTK. Below is a short report summarising the main results.

Samples form the sporadic high REE enrichments in the massive-semimassive and stringer parts of the Outokumpu and Kylylahti deposits yielded  $\epsilon_{Nd}$  (1950 Ma) values between – 0.8 and +1.1 (all  $\epsilon_{Nd}$  values below are calculated at 1950 Ma referring to the apparent Pb isochron age of the Outokumpu-Vuonos deposits, cf. section 9.3.2). As most of these samples are relatively high in REE, but very low in lithophile elements like AI, K, Ti, Sc, Nb and Zr, the obtained  $\epsilon_{Nd}$  (1950 Ma) values from these samples most probably are for REE of more or less purely hydrothermal origin.

Two samples of massive ore with obvious metasediment affected mantle-normalised REE profiles from Vuonos (cf. section 9.2.16.) yielded both  $\epsilon_{Nd}$  (1950 Ma) values of –3.2, supporting the inference that the source of the REE in these samples was indeed in the adjacent Kaleva metasediments, which in Outokumpu and Kylylahti have  $\epsilon_{Nd}$  (1950 Ma) values typically between –3 and –1.5. This result probably can be generalized to concern ore with similar REE distribution also in any of the other here studied deposits, at least for those that are more intimately associated with metasediments, such as the Saramäki deposit, for example.

However, as the main parts of the ore bodies, the larger ones especially, tend to be very low in REE, the above data from more REE enriched samples may perhaps tell more of effects of secondary processes than actual ore formation related processes. The low REE ore parts are, however, analytically problematic as the Sm-Nd concentrations are too low to yield, by standard analytical means, well constrained Sm-Nd isotope data. We nevertheless tested for a few representative samples from the Outokumpu main ore. The test runs produced expectedly fairly imprecise results, but that nevertheless suggest  $\epsilon_{Nd}$  (1950 Ma) values around zero as in

the sporadic high REE samples from Outokumpu main ore and Co-Ni zone.

Thus, it seems that the bulk of the Outokumpu ore had  $\epsilon_{Nd}$  (1950 Ma) around zero. This could perhaps represent the Nd isotopic character of the primary ore forming fluid. The situation seems very similar at Kylylahti where high REE samples from the stringer zone also produce  $\epsilon_{Nd}$  (1950 Ma) close to zero. There are local, apparently wall rock controlled departures, as the evidence from the Vuonos ore clearly demonstrates, but these effects seem to be overprinted an a primary case of strongly LREE enriched REE patterns and  $\epsilon_{Nd}$  (1950 Ma) around zero. If the "primary "ore REE in Outokumpu and Kylylahti indeed had  $\epsilon_{Nd}$  (1950 Ma) of zero, this would imply that the surrounding Kalevian metasediments with significantly lower  $\epsilon_{Nd}$  (1950 Ma) values between -2 and -4 can not have been the source of this "primary" REE. This is telling analoguos with the Pb isotope data against syntectonic models with metal source in the Kalevian metasediments.

Unfortunately, because of the usually very low Sm-Nd concentrations, we do not have much comparative Sm-Nd isotope data from the serpentinites and carbonate-skarn-quartz rocks in the Outokumpu assemblage. But Nm-Nd data from Kylylahti, Horsmanaho, and Huutokoski and Miihkali mafic stocks and dykes indicate these rocks had  $\epsilon_{Nd}$  (1950 Ma) typically between –1.1 and +2.7. And, if Outokumpu area serpentinites were analogous with serpentinites in the Jormua complex,  $\epsilon_{Nd}$  (1950 Ma) values of about ±0 could be expected for them (cf. Peltonen et al., 1998). And, one sample of nonmineralized quartz rock analysed from Vuonos yielded  $\epsilon_{Nd}$  (1950 Ma) of –0.7. Hence, in the light of this scattered data, the "primary" REE in the Outokumpu and Kylylahti massive-semimassive and stringer sulphides may well be from the mafic and ultramafic rocks in the Outokumpu assemblage.

Like the Outokumpu Co-Ni and Kylylahti stringer zones, also the Riihilahti Cu mineralization and its host rocks are associated with sporadic high REE enrichments (cf. chapter 9.2.16). Two samples from strongly LREE enriched metachloritites ("metaperidotites") at the footwall of the mineralization yield  $\epsilon_{Nd}$  (1950 Ma) of –3.7 and –2.4. In comparison, two samples from adjacent garnet-amphibole rocks, that show less LREE enrichment, and apparently less alteration form a common high-Ti-Fe basalt protolith, show significantly higher  $\epsilon_{Nd}$  (1950 Ma) values of -0.2 and –0.4. In a high contrast, three samples of metasediment derived biotite-amphibole-garnet rocks, garnet-amphibole mica gneiss and cummingtonite-rich rocks also from the footwall of mineralization yield much lower  $\epsilon_{Nd}$  (1950 Ma) values between – 8.7 and –5.2. An arkosic metawacke (gneissic) from a location further from the mineralization yielded also an highly negative  $\epsilon_{Nd}$  (1950 Ma) value of –7.5.

Recalling the strong enrichment of REE over Nb, Ti, Sc and Zr in the metachloritites (cf. Fig. 4), it appears likely that their alteration involved addition of significant hydrothermal REE from some external source(s). In the light of the strongly negative  $\varepsilon_{Nd}$  (1950 Ma) values from the metachloritites contra near zero values in the obvious high-Ti-Fe basalt protholiths, there must have been an important component in this source with strongly negative  $\varepsilon_{Nd}$  (1950 Ma). Especially as there is indication by one amphibolite sample from a location outside of the mineralized area that the  $\varepsilon_{Nd}$  (1950 Ma) of the protolith may have been as high as +2.0.

Four samples selected to represent the most sulphide and Cu-rich parts of the Riihilahti "ore" yielded  $\epsilon_{Nd}$  (1950 Ma) values between -4.8 and -2.7, i.e. values that fall in the range of the metachloritite  $\epsilon_{Nd}$  (1950 Ma) values. Three of these samples, all with abundant skarnoid (diopside±amphibole) gangue of clear low-Ti tholeiite type metabasite origin, yield  $\epsilon_{Nd}$  (1950 Ma) values between -4.8 and -3.6. The fourth sample, from a sulphide-carbonate-quartz vein rich in chalcopyrite, yields  $\epsilon_{Nd}$  (1950 Ma) of -2.7. All the four ore samples have similar mantlenormalised REE profiles indicating significant enrichment in REE, especially in LREE, over the least altered Riihilahti low-Ti tholeiite amphibolites, representing the obvious gangue protolith (Fig. 134). Two samples from relatively non-altered low-Ti tholeiitic amphibolites of Riihilahti yield  $\epsilon_{Nd}$  (1950 Ma) values of -1.5 and -0.3. Thus, as in the case of the metachloritites, the Nd isotope ratios of the ore samples require that the added LREE had a strongly negative  $\epsilon_{Nd}$  at 1950 Ma. An isotopically suitable source for the indicated strongly radiogenic Nd was in the metasediments in the lower parts of the Riihilahti assemblage. In summary, there is geochemical and isotopic evidence from Outokumpu, Kylylahti and Riihilahti of that some REE was mobilized and carried in the primary ore forming fluids. The Sm-Nd data from Outokumpu and Kylylahti seem to exclude the Kalevian metasediments as an source of this "primary" REE, while they allow a local source in the adjacent serpentinites and associated mafic rocks. A more distant source seems unlikely since the Karelian granitoids nor Archaean basement that both posses both strongly negative  $\varepsilon_{Nd}$  (1950 Ma) are suitable sources of the significantly less radiogenic "primary" Nd in the Outokumpu and Kylylahti ores. Despite similarities in the REE patterns between Riihilahti and Outokumpu-Kylylahti ore samples; there is a drastic difference in their isotopic characters, the data from Riihilahti suggesting that the local (Lower Kaleva) metasediments were an important source of the apparently "primary" REE in the mineralizations. It is difficult to say, however, how primary the situation at Riihilahti really is. Noting the highly metamorphosed environment and tattered mode of occurrence of the Riihilahti mineralization, metamorphic overprinting and mixing may be there relatively more pervasive phenomena and overprint the real primary patterns.

The most pronounced REE enrichments in Outokumpu, Kylylahti and Riihilahti occur in hosts that comprise relatively abundant pervasively chlorite-altered metabasites (peakmetamorphically overprinted), which, like the associated, sporadic high REE enrichments, usually show enrichment in LREE and deep negative Eu anomalies in their mantle-normalised REE patterns Based on the deep negative Nb, Zr, and Ti minimas in the mantle-normalised profiles of the REE enrichments (cf. Figs. 4, 31 and 135), they really seem to record REE addition, not residual enrichment related to loss of e.g. alkali elements and/or calcium. This is somewhat surprising situation as chloritized basites are usually found depleted rather than enriched in total REE (e.g. Campbell et al., 1984; McLean and Hoy, 1991; Schandl et al., 1995; Roberts et al., 2003). The simplest explanation for the observed REE enrichment plus deep Eu minimas would be that it would represent hydrothermal remobilization and local enrichment of REE from already chloritized basites having experienced preferential Eu loss in reducing alteration fluids, perhaps from plagioclase completely exterminated in the chloritization process.

Two samples from relatively less-altered Outokumpu Co-Ni zone metabasites yielded  $\varepsilon_{Nd}$  (1950 Ma) values of –0.8 and –1.3, i.e. a bit lower values than  $\varepsilon_{Nd}$  (1950 Ma) values of +0.1 and + 0.6 obtained for two samples of the associated high REE-enrichments. In the light of these fairly similar values dominant part of the REE in the Co-Ni zone REE enrichment patches indeed seems to be leached and redistributed from the Co-Ni zone or equivalent basites. Unfortunately, the samples from the Co-Ni zone have too little spread in their Sm/Nd to yield an isochron of relevant age significance.

To summarize, the REE and Sm-Nd data from Outokumpu and Kylylahti suggest that the "primary" REE in these ores had  $\epsilon_{Nd}$  (1950 Ma) of ca. +0 or perhaps even slightly on the positive side, and that the source of the contained REE was in the serpentinite massifs and their mafic components. However, where in contact with Kalevian metasediments, the ore walls register lower, negative  $\epsilon_{Nd}$  (1950 Ma) indicating "diffusion" of REE from the metasediments. Much of this interaction probably took place during the late, high temperature stages of the regional deformation and metamorphism and unrelated to the ore genesis. The Riihilahti case with its very different Nd and Pb isotope composition and stratigraphical position but clear Outokumpu type metal content is very intriguing indeed and deserves more study in the future.

## 9.3.4. Rubidium-Strontium

#### Previous work

Published Rb-Sr isotope data of the Outokumpu rock assemblage are few. In a paper on the deep, saline ground waters in the Outokumpu area, Smalley et al. (1988) report a Rb-Sr

isochron based on whole rock serpentinite, feldspathic and mica-rich schist samples from the OKU-741 bore hole at Sukkulansalo. The isochron has a slope indicating an age of 1729+-40 Ma and initial <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.7094±0.0001(MSWD=5). Serpentinites in this plot had present day <sup>87</sup>Sr/<sup>86</sup>Sr ratios of about 0.71, feldspar-rich mica schists about 0.75, and mica-rich schists as high as 0.80. Smalley et al. (1988) addressed the young Rb-Sr whole rock isochron age indication obtained for this petrogenetigally diverse set of samples to a regional-scale pervasive thermal resetting of the Rb-Sr-isotopes in a late, postkinematic stage of the Svecokarelian regional tectonic-thermal evolution, assuming further that probably also minerals of the analysed samples would plot along the whole rock isochron. However, as no such late thermal event is known from eastern Finland, the youngest Svecokarelian granite intrusions being, for example, about 1800 Ma in age, we consider it more likely that the Rb-Sr isochron of Smalley et al. (1988) rather registers regional retrograde cooling below 350-300 °C, i.e. temperatures that seem to block the Rb-Sr isotope system in micaceous quartzo-feldspathic rocks.

### Rb-Sr isotope study during this work

During this study a small pilot set of samples form the Outokumpu assemblage, mainly from carbonate and skarn rocks from Outokumpu, Vuonos and Riihilahti, became analysed for Rb-Sr isotopes in GTK. The obtained few isotope data are relatively scattered, and, in lack of constraining data from several of the important components in the rock assemblage, difficult to interpret. It can be also questioned how much ability the Rb-Sr method overall has to deliver through the veil of element mobility and metamorphic resetting, which in the Outokumpu case have been fairly pervasive, as is demonstrated by the work by Smalley et al. (1988). Overall, Rb-Sr isotopes seem a less promising avenue to understanding of the Outokumpu system.

Data for two Rb-poor but relatively Sr-rich carbonate rock samples from the Outokumpu assemblage at Outokumpu and Vuonos are of potentially more straightforward significance, however. Namely, the very low <sup>87</sup>Rb/<sup>86</sup>Sr ratios in these samples allow reasonably reliable estimation of the initial <sup>87</sup>Sr/<sup>86</sup>Sr isotope values, and thus the possibility to evaluate the source of the abundant Ca in Outokumpu-type dolomite carbonate rocks. It is important to note here that the Outokumpu type carbonate rocks are strongly enriched in Ca (CaO up to 30 wt.%) and geochemically similar Sr (up to 210 ppm) relative to their strongly depleted mantle protolith peridotites that probably contained just a few ppm of Sr and less than 1-2 wt.% CaO. Although the protolith Outokumpu peridotites obviously were low in CaO, considering the relatively small volume/mass of the carbonate fringes, it is still possible that the Ca and Sr were sourced in them. Other source possibilities would include infiltration of seawater that is relatively high in Ca and Sr, or perhaps Kalevian formation waters that may have contained Ca and Sr in trapped seawater, or with burial and early metamorphism by infiltration of low-T diagenetic/metamorphic fluids that had leached Ca and Sr from carbonate clasts in the Kalevian wackes.

Of the two low-Rb/Sr carbonate rock samples, the Oku-24a/270.95-271.45 from Outokumpu has a particularly low <sup>87</sup>Rb/<sup>86</sup>Sr ratio of 0.0031 (0.12 ppm Rb, 110 ppm Sr). This sample yields an <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.70538 calculated at 1900 Ma. The other Sr-rich carbonate rock sample Oku-228/15.05-15.35, from Vuonos, has a bit higher <sup>87</sup>Rb/<sup>86</sup>Sr of 0.0356 (2.58 ppm Rb, 208.7 ppm Sr) and yields an <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.70485 at 1900Ma. These <sup>87</sup>Sr/<sup>86</sup>Sr values are significantly higher than the average <sup>87</sup>Sr/<sup>86</sup>Sr of ca. 0.7020 estimated for the 1900 Ma mantle, but well within the range of <sup>87</sup>Sr/<sup>86</sup>Sr values from 0.7047 to 0.7060 documented for the 1.91-1.85 Ga seawater (e.g. Mirota and Veizer, 1994; Whittaker et al., 1998). This suggest that instead of being migrated from the peridotites, the Sr and Ca in the Oku carbonate rocks more likely were introduced either in down circulated seawater, or infiltrated diagenetic-low-T metamorphic fluids that transported Ca and Sr from trapped formation waters or marine carbonate clasts in the enclosing Kaleva metasediments. This conclusion is supported by the C isotope data from the carbonate rocks, being also consistent with the inference of either sea water or dissoluted marine carbonate as to the main source of the metasomatising fluid (cf. Karhu, 1993, but see also the C-isotope section in this report).

#### 9.3.5. Sulphur

No new sulphur isotope study of the Outokumpu deposits was undertaken during this study. The following short summary and discussion of the Outokumpu sulphur isotope geochemistry is based on data and interpretations in Mäkelä (1974) and Luokola-Ruskeeniemi (1999).

The data by Mäkelä (1974) includes S isotope analysis for 258 sulphide separates (for pyrite, pyrrhotite, chalcopyrite and sphalerite) from the Outokumpu deposit, the samples representing the "primary" pyritic, remobilized pyrrhotitic massive and brecciated facies of the main ore, the small banded Poikanen satellite ore body, and a few nonmineralized quartz rocks from the footwall of the main ore. As a whole, the data in Mäkelä (1974) comprise a wide range of  $\delta^{34}$ S values, from -20 to +6 (Fig. 149). Within this broad overall range, the main Outokumpu ore body shows  $\delta^{34}$ S values between –10 and +6 ‰ with an average of –3.5 ‰, and a mode at ca. ±0. Compared to this, fine-grained pyrite from the quartz rocks at the footwall of the main ore show much lighter S isotope compositions between –20 and –14 ‰. The small Poikanen satellite ore body, dominantly of the banded ore type, has highly fluctuating sulphide  $\delta^{34}$ S values between -20 and ±0, most of the values falling in the range from –15 to –5, i.e. between the values typical for the main ore and quartz rocks.



Fig. 149. Histogram of  $\delta$ 4S values of Outokumpu sulphides (from Mäkelä, 1974). 1=sulphides from massive pyritic and pyrrhotitic ore from the main Outokumpu ore body; 2=remobilized sulphides in the main ore body, 3=sulphides from banded pyritic ore within the main ore body, 4=sulphides from banded pyritic ore in the "Poikanen" (Baby ore) satellite ore body and wall quartz rocks.

The  $\delta^{34}$ S values between -20 and -14 ‰ (n=8) for iron sulphides from the Outokumpu quartz rocks are considerably more negative than the  $\delta^{34}$ S values between -1 and -12 ‰ (n=11) reported by Loukola-Ruskeeniemi (1999) for iron sulphides from the black schists in Outokumpu and Kylylahti (Loukola-Ruskeeniemi 1999). While most of the latter data are for black schists from immediate contacts of the of Outokumpu and Kylylahti serpentinites and the Kylylahti deep ore, its is not clear how well this few data would represent the Outokumpu belt

black schists on a more general level. Two pyrite separates from the massive-semimassive deep ore lens at Kylylahti are reported by Loukola-Ruskeeniemi (1999) with  $\delta^{34}$ S values of –8.1 and –8.2, and two pyrites from the adjacent skarn-quartz rock-hosted stringer mineralization with  $\delta^{34}$ S values of –5.4 and –7.1. We note here that three of the samples, i.e. samples Oku-794B/562.25 and Oku-794B/567.30, 567.30, which are listed as Cu-Zn-Co ore samples in Table 7 in Loukola-Ruskeeniemi (1999), in fact all come from grey to black tremolite-carbonate rock ("skarn") intercalations in the black schists next to the western contact of the Kylylahti deep ore lens, not from within the ore proper (based on a drill core review of the first author). These samples have relatively low  $\delta^{34}$ S values between –6.4 and –16.00.

S isotopes for the relatively lowly metamorphosed Kylylahti would be of special interest, but the presently available data are yet few and scattered, and do not allow any far-reaching conclusions. The negative values of about –8, as reported by Loukola-Ruskeeniemi (1999) for the deep ore, could indicate that the Kylylahti mineralizations comprise some significant synmetamorphically added S from the adjacent sulphide-rich blacks schist. That would be consistent with the Pb-isotope evidence of synmetamorphic communication of the ore lenses and their wall-rock black schists (section 9.3.2.). There is yet evidently much more that detailed S isotope studies could tell about the mineralization processes of the paragenetically complex Kylylahti deposit, especially if modern high-precision in-situ analysis (as e.g. by ion microprobe) would be applied.

Mäkelä (1974) concluded on the basis of his abundant S isotope data for the Outokumpu ore that it was "deposited by volcanic exhalations discharged from a fissure type vent system on the seafloor". He based this interpretation mainly on the data from the sulphide ore – quartz rock – black schist – mica schist banded Poikanen satellite ore body, interpreting the fluctuating  $\delta^{34}$ S values (cf. Figs. 7 and 8 in Mäkelä, 1974) to reflect a pulsative variation in the relative proportion in which S was contributed in the ore layers and presumed interbedded sediments from the hydrothermal vent fluids (H<sub>2</sub>S,  $\delta^{34}$ S ±0?) and ambient seawater (SO<sub>4</sub>,  $\delta^{34}$ S +15?).

However, there are some obvious problems with the Mäkelä's (1974) interpretation of the Poikanen data. First, the quartzite layers in the Poikanen ore, which Mäkelä interpreted to sediment layers, clearly are layers of silicified mantle peridotite, as similar rocks elsewhere in Outokumpu assemblage. Second, our own observations form the Poikanen environment suggest that the sulphide to host rock banding in the Poikanen ore environment would represent, rather than sedimentary layering, merely syntectonic sulphide-quartz veining similar to the veining in the Keretti Co-Ni zone described above, in this case in tectonically interdigitated quartz rocks, black schists and mica schists in a tightly folded-sheared-fault displaced contact zone between the Outokumpu assemblage and Kaleva metasediments (cf. Fig. 12 in Koistinen, 1981). Thus, rather than by synsedimentary layering, the fluctuating  $\delta^{34}$ S values Mäkelä (1975) measured for the Poikanen ore, more probably do reflect sample scale variation in the ratio of ore veins to host rocks over the sampled intervals. The ore facies with  $\delta^{34}$ S values below ±0 in the Outokumpu main ore may represent similar "secondary" interlayering of the Cu-ore (veins) and host guartz rocks rocks.

Mäkelä (1974) studied also the effect of the ore remobilisation on the sulphur isotope compositions. He concluded that as a net effect, there was, on average, ca. 2.6‰ reduction in the  $\delta^{34}$ S values for sulphides in such ore parts that he considered remobilized. Mäkelä (1974) further concluded, based on partitioning of S isotopes between pyrite-pyrrhotite and pyrite-sphalerite pairs that the ore had isotopically equilibrated at about 350 °C, but left open if this would represent depositional or subsequent metamorphic equilibration. Considering the longevity and high peaking (>600 °C) of the metamorphic heating at Outokumpu, it appears most likely that the 350 °C obtained by Mäkelä (1974) represents blocking related to the postpeak retrogressive cooling of the Outokumpu system.

Compared to many Precambrian volcanic associated and modern mid-ocean ridge massive sulphide deposits, the Outokumpu deposit shows a wider variation in its  $\delta^{34}$ S values, with a range between -10% and +6%. Precambrian volcanic associated deposits usually show  $\delta^{34}$ S more or less systematically between -1.0% and +5% (Huston, 1999). Modern deposits at sediment-free mid-ocean ridges show sulphide  $\delta^{34}$  values usually in the same range as the

ancient volcanic associated deposits, mostly between +0‰ and +5‰, whereas deposits at sediment-covered ridges exhibit as a group a significantly wider spread between -4% and +13‰ (Goodfellow and Zierenberg, 1999). A part of the high variation in the Outokumpu values is probably because of the mechanical wall rock mixing plus subsequent diffusive equilibration. As both these processes were likely to cause shifts mainly towards lower  $\delta^{34}$ S values, the  $\delta^{34}$  values of the uncontaminated Cu-ore materials were obviously less varied and closer to the "magic" zero, or perhaps somewhat positive.

The around zero  $\delta^{34}$ S values in the Outokumpu sulphides have often been provided as an evidence of principally mantle origin of the involved sulphur and metals. It must be remembered, however, that S isotope studies for deposits of more complex origin than sedimentary derivation from marine sulphate, have often produced disappointingly ambiguous and difficult to interpret S isotope data (Faure, 1986). There are many reasons for this, starting from the fact that  $\delta^{34}$ S values of hydrothermal sulphide minerals do not depend solely on the isotopic composition of their S source but also on the environmental conditions at the source, during transport and at the site of deposition (e.g. Ohmoto, 1972). Furthermore, it is well known that sulphur isotopes in metamorphogenic ore deposits may have  $\delta^{34}$ S values close to zero, without any direct magmatic input into the mineralization process (e.g. Craw et al., 1995). In fact, since the Earth's crust on average and mantle (and directly mantle derived rocks) both have  $\delta^{34}$ S close to zero; both can obviously provide the ultimate source of sulphur with the about zero  $\delta^{34}$  signature. In a way, the zero  $\delta^{34}$ S is largely the zero hypotheses for hydrothermal sulphides.

In summary, discounting the secondary mixing and metamorphic effects along the ore body margins, the S isotope data from Outokumpu ore is certainly compatible with its origin as a exhalative sulphide accumulation on the seafloor – but so that also many other scenarios are possible. The perhaps most significant feature in the Outokumpu  $\delta^{34}$  data is the considerable number of positive  $\delta^{34}$  values for the main ore body that may point to role of seawater sulphate at some stage of the ore forming process.

Finally, it is clear that due to its high metamorphic environment the Outokumpu deposit is less than ideal subject of S isotope studies, especially if the deposit was indeed premetamorphic for its origin. In future studies the focus should be put on the Kylylahti deposits, which have seen some 150 °C less battering.

## 9.3.6. Oxygen

Published Oxygen isotope data from the Outokumpu assemblage and related sulphides ore bodies are rare, including only a few data for carbonates in Karhu (1993). In addition, a twelve sample pilot study for Outokumpu and Vuonos deposits was made in GTK just before the start of the GEOMEX project (by A. Kontinen and P. Peltonen). The pilot included 7 samples from representative quartz rocks from Outokumpu and Vuonos, and 5 samples from Outokumpu and Vuonos main ore bodies. The analytical results are given in Table 11. The following sections provide a summary and brief discussion of the results.

Five of the quartz rock samples was selected to represent the most "primary"-looking, greyish, fine-grained quartz rocks from the footwall sections of Outokumpu and Vuonos ores. Two of the quartz rocks samples were for their coarse-grained quartz-sulphide segregation veins typical of Outokumpu type quartz rocks. One sample was taken form a chalcopyrite-mineralized quartz rock at the contact of the Outokumpu ore. The remaining four samples are coarse-grained gangue quartz from the main ore bodies at Outokumpu and Vuonos. All the studied samples were already before separation very low in any other silicates but quartz and very low also in carbonates.

The measured  $\delta^{18}$ O values for the 5 quartz rock quartz separates show only limited variation from +15.2 ‰ to 16.3 ‰, with a part of this small variation possibly reflecting minor and variable presence of secondary vein quartz generations in the separates, despite of all the effort to sample the most "primary" fine-grained quartz rock component only. In searching for

Assuming that the fluid involved with the genesis of the quartz rocks was seawater with  $\delta^{18}$ O of 0 ‰ and a high water/rock ratio, one can calculate, using the quartz-water equilibrium fractionation equation (Matsushita et al., 1979), that the  $\delta^{18}$ O values from the Outokumpu quartz rocks would correspond to low temperatures of ca 140-150 °C. This scenario would be compatible with the other isotopic (Rb-Sr, C), petrographical (presence of petroleum/silicified bitumen) and structural evidence (alteration was pre D<sub>1</sub>), which consistently indicate that carbonate-silica alteration in Outokumpu-Vuonos was an early diagenetic-burial metamorphic process. Estimations of temperatures for silica-dolomite alteration of ultramafic rocks elsewhere range from 20 °C up to 200 °C (Weir and Kerrick, 1987).

However, in the Outokumpu case an alternative explanation for the ca. +16  $\delta^{18}$ O values in the quartz rocks would be that they actually record overprinted high-temperature regional metamorphic fluid -mineral equilibrium. Namely, it is well known that quartz veins in greenschist to amphibolite facies metagreywacke terrains worldwide typically have  $\delta^{18}$ O values between +14 ‰ and +18 ‰, reflecting equilibration with metamorphic fluids that usually have  $\delta^{18}$ O ranging from +8 ‰ to +14 ‰ (e.g. Gray et al, 1991; Jia et al., 2001). Although we do not have constraining data from the Kalevian metagreywackes, there is no reason to believe that the oxygen isotope compositions of the Svecokarelian metamorphic fluids somehow differed from the typical amphibolite facies fluid compositions. Therefore, the  $\delta^{18}$ O values between +16‰ in the quartz rocks could well represent values after thorough greenschist to amphibolite facies metamorphic.hydrothermal overprinting.

The  $\delta^{18}$ 0 values measured for the gangue quartz in the Outokumpu and Vuonos ore bodies show a variation from +13.6 ‰ to +18.4 ‰. Although the analysed four ore gangue quartzes probably do not constrain the whole range of  $\delta^{18}$ O variation in the Outokumpu-Vuonos ores, we believe more sampling would probably not much change the basic case. The observed  $\delta^{18}$ O values are considerably higher than what are usual for quartz gangue in most massive sulphide ores. The low  $\delta^{18}$ O values associated the massive sulphides, typically from +2 to +12 (Huston, 1999), reflect the high water/rock ratios typical of most sulphide systems, which forces the  $\delta^{18}$ O values of the alteration products towards the ±0  $\delta^{18}$ O value of seawater that is usually the dominant aqueous component in the ore-forming fluids (note that most massive sulphide deposits are submarine).

Also the two samples for the common quartz-sulphide veins in quartz rocks yield similar relatively high  $\delta^{18}$ O values than the quartzes in the sampled quartz rocks and ore bodies. The one sample representing the sulphide-poor, medium- to coarse-grained quartz veins, that are ubiquitous, in many generations, in the Outokumpu area quartz rocks, yields an  $\delta^{18}$ O value of +17.3 ‰. The other one, representing coarse-grained quartz-pyrite segregations/blotches typical in the more sulphidic quartz rocks in Outokumpu and Vuonos, yields a somewhat lower  $\delta^{18}$ O value of +15.9 ‰.

The result of our pilot O isotope study for the Vuonos-Outokumpu deposits was, a bit surprisingly, that the studied quartz generations, despite their different host rocks, origins and formation timings, all yielded  $\delta^{18}$ O values between +14 - +18. There are about no other alternative but to address the uniformity in the  $\delta^{18}$ O values to re-equilibration of the all components in the Outokumpu assemblage with respect to the regional metamorphic fluids. The thoroughly metamorphic-like and mutually similar fluid inclusion populations in quartzes through the whole Outokumpu system, in the ore bodies, wall quartz rocks and country mica schists support this conclusion (chapter 10).

In contrast to quartz in the quartz rocks and ore bodies, dolomite and calcite in the carbonate rocks of the Outokumpu alteration assemblage show a much higher range for their  $\delta^{18}$ 0 values, between +16.3 and +6.5, largely independent of variation in the usually low silicate

content or negligible graphite of the analysed samples. As calcite-dolomite pairs in carbonate rocks of eastern Finland commonly show pronounced disequilibria in terms of dolomite-calcite pairs, the variation in the carbonate  $\delta^{18}$ 0 values most probably stems from postmetamorphic interaction with various external fluids (Karhu, 1993).

### 9.3.7. Carbon

No new carbon isotope analysing was performed during the GEOMEX project, but the following review of C isotopes of the Outokumpu ore environments is based on some unpublished GTK data and those published by K. Loukola-Ruskeeniemi (1999). All this data is for carbonates and graphites in the Outokumpu type carbonate-skarn-quartz rocks and associated Kalevian black schists. The samples are mostly from drill cores for the Outokumpu, Kylylahti, Alanen and Jormua sites. The determinations of carbonate mineralogy (by XRD) and isotopic compositions of carbon and oxygen (by gas source mass spectrometry) have been performed mostly by J. Karhu at GTK, Espoo (for the analytical methods, see Karhu, 1993).

### **Carbonates**

Distinct assemblages of carbonate minerals characterize the different carbonate rich lithologies of the Outokumpu assemblage. Talc-carbonate rocks usually contain ferroan magnesite (breunnerite) as their dominant carbonate phase, but towards the body margins with increasingly more dolomite. Carbonate rocks in the zones of Outokumpu type carbonate-skarnquartz rocks typically contain dominantly dolomite with variable amounts of tremolite and calcite. In Kylylahti in the disseminated skarn-ore zone, abundant calcite is usually present along with dolomite.

The isotope ratios obtained for carbonates from the carbonate rich rocks of the Outokumpu assemblage show systematic variation depending on rock type (Fig. 150). Although probably partly due to metamorphic alteration and reactions, the large range of  $\delta^{13}$ C values cannot be ascribed solely to metamorphic overprinting. Instead, isotopically distinct source regions are clearly implied. The relatively low  $\delta^{13}$ C values of carbonates in talc-carbonate rocks, mostly between –5 and –15 ‰ suggest that a large share of the carbon in these rocks would be from from biogenic sources, most probably from the organic matter in the Kaleva metasediments. Carbonates from the dolomitic carbonate rocks in the Outokumpu alteration assemblage are distinctly enriched in <sup>13</sup>C relative to carbonates in the talc-carbonate rocks, most of the measured  $\delta^{13}$ C values being between +0 ‰ and –3 ‰. The highest  $\delta^{13}$ C values are close to 0 ‰, which could be an indication of marine inorganic carbon. Calcites from the Kylylahti stringer mineralization seem to have intermediate  $\delta^{13}$ C values, mostly between –4 ‰ and -7 ‰, falling between the extreme values of the two aforementioned groups. Looking just at the numbers, one possibility would be that the source of carbon in these calcites was magmatic. Proving this, however, would require other supporting evidence.

The observed isotopic differences should be considered with certain caution, as the sample material is areally quite biased. For example, a great majority of the Outokumpu assemblage carbonates analysed represent just the Outokumpu site. Nevertheless this data provides a clear evidence of that the carbon isotope composition in the alteration fluids was changing from seawater-like to biogenic-like with the regional temperature progression from subgreenschist



Fig. 150. C-isotope data for the main carbonate generations of the serpentinite-soapstone massifs in the Outokumpu-Jormua thrust belt. The available data define three apparent ly separate groups if some outlier samples are omitted, suggesting that carbon in carbonates in the Outokumpu-type carbonate rocks, soapstones and in Kylylahti skarn-hosted parallel mineralization were from isotopically different sources.

facies temperatures to greenschist facies and higher. It is useful to recall here that talccarbonate alteration is usually considered a greenschist facies to low amphibolite facies progressive metamorphic-hydrothermal alteration process. Obviously, with increase in temperature, proportionally more carbon in the alteration fluids was in CO<sub>2</sub> produced by oxidation of kerogen/graphite from the Kalevian black shales and graphite-bearing greywackes.

Karhu (1993) considered the seawater-like C isotope values in the Outokumpu-type carbonate rocks were an indication of their origin as marine carbonate sediments. However, as we have shown before, such origin for these systematically very Cr-Ni-Co-rich and chromitebearing carbonate rocks is not feasible, but instead they clearly represent metasomatic alteration of the adjacent serpentinites or their protolith peridotites. We still have the need to show a seawater-like carbon reservoir for the added carbon. Considering the early timing of the carbonate alteration, this source may have been in trapped seawater, or seawater-derived carbonate clasts in Kalevian sandy turbidites, or even in sea-water circulated down in the Kalevian sequence still during the early stages of the obduction of the Outokumpu nappe.

## **Graphite**

According to the data in Loukola-Ruskeeniemi (1999) black schist graphites from Outokumpu, Vuonos and Kylylahti have  $\delta^{13}$ C values between –24‰ and –30‰, while blacks schists samples from the W contact of the Kylylahti deep ore show somewhat lower values between –19‰ and 25‰. This data is compatible with the long since proven biogenic origin of most graphite also in Precambrian black shales and schists (Schidlowski, 2001). The somewhat lower  $\delta^{13}$ C from the black schists from ore body contacts at Kylylahti probably reflect presence of tremolite-carbonate intercalations and secondary skarn material in the sampled intervals (based on drill core observations by the first author).

Graphite is a fairly common mineral also in Outokumpu-type quartz rocks, especially at locations where they are in contact to black schists. Carbon isotope data for these graphites are rare, unfortunately. One sample analysed from Vuonos has yileded a  $\delta^{13}$ C of -24.4 (Loukola-Ruskeeniemi, 1999). In an unpublished report Kouvo (1962) provides C-isotope data

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for graphite from three quartz rock samples from Outokumpu; the <sup>13</sup>C values for these graphites are between –18.8‰ and –21.7‰. Interestingly, Kouvo (1962) had analysed carbon also for tucholite balls from two quartz rock samples with  $\delta^{13}$ C results of –23.4‰ and -25.4‰. This few data suggests that carbon in the Outokumpu quartz rocks would be of biogenic origin and most probably derived from the adjacent Kalevian black schists. As we infer elsewhere in this report, the graphite and silicified bitumen grains in the quartz rocks likely derive ultimately from petroleum introduced in the quartz rocks when the black shales passed through the "oil producing P-T window", most probably during the burial metamorphic stage of the Outokumpu nappe complex.

# 10. Fluid inclusions

Relatively few fluid inclusion data are available for the Outokumpu deposits, and that what exists is representing relatively old study, restricted mainly to the Outokumpu (Keretti) ore. The following review is based on the work by Kinnunen (1979, 1981, 1989), mainly on the qangue quartz of the Outokumpu ore. Kinnunen (op cit.) recognized three main types of quartz in the Outokumpu ore: 1) quartz in quartzitic (quartz rock) breccia fragments in the ore, 2) quartz in the banded and massive ore variants, and 3) quartz in late quartz veins in ore. According to Kinnunen (1979), inspire of clear differences in average grain size, extinction character and grain boundary characters between the main quartz types, their fluid inclusion populations are yet fairly similar. All the main quartz phases are devoid of primary inclusions, but usually rich in secondary inclusions, and also contain the main ore minerals and common calc-silicate gangue minerals as inclusions.

Kinnunen (1979, 1981, 1989) distinguished three main types for the secondary inclusions in the Outokumpu quartzes, here listed in the order of their magnitude of occurrence: (1) predominantly gaseous (>65 vol.% gas) inclusions, (2) "high-salinity" inclusions with water solution plus a solid crystal(s) and a gas bubble, and (3) aqueous low-temperature inclusions. All these three inclusion types Kinnunen (op cit.) considered to represent fluid trapped within healed microfractures, and be present not only in the more primary looking varieties of gangue quartz, but also in late quartz veins dissecting the ore. Consequently, Kinnunen (1979) considered all the inclusions secondary and unrelated to the ore formation proper.

Kinnunen (1979) describes that microfractures controlling type 1 gas-rich, and type 2 saltrich inclusions cross-cut the schistosity of the ore, usually at an angle of 50 to 70 degrees, and that the related inclusion trails often run subparallel through many adjacent quartz grains. Microractures controlling type 2 relatively liquid-rich inclusions cut quartz at variable angles and are usually restricted within single grains. These inclusions often define straight-trending inclusion-rich panels, which as fairly thick and irregular by their edges seem to be strongly recrystallized. Type 3 liquid-filled inclusions define wavy planes that appear only weakly recrystallised. Kinnunen (1979) considered that the trails of the type 1 gas and type 2 highsalinity liquid-salt inclusions would be about the same age, while the inclusion trails of type 3 liquid inclusions would appear somewhat younger.

The following brief descriptions of the main fluid inclusion types of the Outokumpu ore quartzes are based mainly on Kinnunen (1981):

Type 1 gas inclusions do represent 74-81 % of the total inclusions. These inclusions have an average diameter of 20  $\mu$ m, are typically elongated along quartz c-axis, and often show shapes of sharply edged negative crystals. Most of the inclusions are nearly gas-only although little liquid is sometimes seen in inclusion corners. Kinnunen (1981) observed that when heated type 1 inclusions homogenize to gas in temperatures between 310-350 °C, to crack with any further heating. Based on tentative measurements, liquid in the type 1 inclusions seem to freeze at about –90 °C and remelt at about –5 °C, which would indicate a salinity of about 7.5 %, in terms of NaCl equivalency. Observations on behaviour of inclusions when opened in glycerine and kerosene indicate that the gas in type 1 inclusions would be dominantly CO<sub>2</sub> and minor hydrocarbons. Kinnunen (1989) considered type 1 inclusions filled by intergranular metamorphogenic fluids.

Type 2 "high-salinity" inclusions comprise in room-temperature conditions usually aqueous liquid, a small gas bubble and a tiny anisotropic and/or isotropic daughter mineral. The average diameter of these inclusions is about 40 µm, and they usually show irregular shapes, though occasional negative crystal shapes may be present. Recrystallization related contraction necking of the inclusions was common, causing variation in phase content so that some inclusions are almost gas-only while some contain relatively large-size solid crystals. The inclusions nearly always have their longest dimension parallel with their host fracture. Refraction indices studies indicate that the isotropic solid in type 2 inclusions would in most cases be halite and the anisotropic one carbonate. By heating type 2 inclusions become completely filled to liquid at 230-300 °C, usually with partial dissolution of the anisotropic solid phase if present. Cracking of the inclusions takes place a bit above 400 °C with crystallisation of anisotropic crystals. According Kinnunen (1989) the group 2 type inclusions represent, like the group 1 inclusions, intergranular metamorphogenic fluids.

Type 3 liquid-filled inclusions comprise in room-temperature only water-rich liquid. These inclusions are usually flattened and irregular in shape. The average diameter is about 70 µm. Some of these inclusions may contain also a small gas bubble and/or small halite cube. The inclusions occur in well-defined, apparently unrecrystallized fracture planes. By heating the gas containing inclusions are filled to liquid at 190-240 °C temperatures. Referring to Arnold (1986), Kinnunen (1989) proposes that fluid inclusions as for type 3 very likely form under PT conditions close to room temperatures and most probably do represent trapped saline ground waters.

Chromian diopside and/or tremolite are locally abundant gangue in the Outokumpu ores, usually at margins of the ore bodies. In contrary to quartz, chrome-diopsides from Outokumpu, Luikonlahti and Hietajärvi ores were observed by Kinnunen (1981) to contain "excellent primary fluid inclusions". It should be noted here that Kinnunen (1981) defines primary inclusions to such inclusions that have originated concurrently with the primary crystallization of the host mineral. The description of the chrome diopside inclusions in Kinnunen (1981) is sparse, however. He only states that the fluid inclusions of the chrome diopsides were fairly similar in all the studied samples, containing usually aqueous liquid plus a gas bubble and one or more grains of an anisotropic solid mineral, and that the volume proportions of the included phases seem fairly constant for inclusions of one sample or between different samples. We have to add that because diopside in Outokumpu deposits is a definite metamorphic mineral, its fluid inclusions also must be of metamorphogenic origin.

Any interpretation of fluid inclusion data from Outokumpu must start from the fact that all the Outokumpu type deposits in North Karelia are multiply deformed and metamorphosed in the amphibolite facies. Marshall et al (2000) have recently reviewed the application of fluid inclusions in study of metamorphosed and metamorphogenic base metal deposits. They conclude that excluding the lowest metamorphic temperature regimes; metamorphism and deformation usually pervasively destroy and reset pretectonic fluid inclusion populations in sulphide ore deposits. Fluid inclusions in ore quartzes even in the prehnite-pumpeylite to lowest greenschist facies massive-semimassive sulphide deposits, as for instance those in the Iberian Pyrite Belt, are mostly secondary and filled by metamorphic fluids unrelated to the primary ore genesis (Cathelineau et al., 2001). Marshall et al (2000) end up in their review that for most metamorphosed deposits, at best, some information on their peak or near-peak metamorphic conditions may be attained, at worst, information only an retrograde re-equilibrate processes may be gained. Further, as both metamorphosed and metamorphogenic deposits usually contain (retrograde) metamorphic inclusions as their main populations, fluid inclusion data from metamorphic deposits alone can not discriminate between remobilisation of pretectonic or synmetamorphic emplacement of an ore (Marshall and Spry, 2000). Only in conjunction with other data, such as the geometry of the ore body and the relationship of the host minerals to the ore at large, a basis for genetic interpretation may exist.

The fluid inclusion study by Kinnunen (1979, 1981, 1989) demonstrates, as one would expect for these amphibolite facies deposits, that fluid inclusions in the quartzes of Outokumpu deposit would be entirely of secondary, metamorphic and post-metamorphic origin and

completely unrelated to the primary ore formation. The apparent lack of sulphide dither minerals in the Outokumpu fluid inclusions serves to underline their overprinted nature. The secondary fluid inclusions at Outokumpu are compatible either with premetamorphic-metamorphosed or synmetamorphic origin of the deposit, and other criteria are needed to make out the difference.

In summary, the data and interpretations of Kinnunen (1979, 1981, 1989) on Outokumpu fluid inclusions support the ugly preconception that Outokumpu deposits would unlikely preserve much fluid inclusion evidence of their prepeakmetamorphic histories. It must be recognized that even in the case that the Outokumpu deposits had a syntectonic-metamorpohogenic origin – because of the structurally late peaking and long lived nature of the regional metamorphic heating – there are only little chances that any fluid inclusions after the main ore formation stage would preserve. Yet fluid inclusion studies for the lowest metamorphic environments, as e.g. for Kylylahti, could possibly tell something about the nature of the fluids related to the latest major mobilisations of the ore materials.

## 11. Ancient and modern analogues

Any credible ancient or modern analogues for the Outokumpu-type deposits should share at least most of the following salient characteristics:

- Occurrence within a thrust terrain
- Intimate association of the sulphides with refractory mantle tectonites
- The polymetallic nature of the sulphides: Cu-Co-Zn-Ni-Cd-Sn-As-Ag-Au
- Extremely low Pb abundances of the sulphides
- Relatively high Ni content of the sulphides
- Presence of massive-semimassive and disseminated sulphides
- Derivation of sulphur and metals from both mantle- and crustal-like sources
- Syntectonic hydrothermal remobilisation and upgrading of the sulphides
- An obvious polygenetic origin

A profound literature survey indicated that reasonably close ancient analogues for the Outokumpu-type ore deposits are fairly difficult to find. However, at least three relatively welldescribed sulphide deposits share a decent number of the salient features of the Outokumpu deposits. These three deposits are: (1) the Deerni massive Cu-Co-Zn sulphide deposit of the A'nyemagen Ophiolite, Kunlun Mt., China (Haitian, 1992; Yang et al., 1997); (2) the *Eastern Metals* Ni-Cu-Zn deposit in the Dunnage zone of the Appalachian orogen, Quebec, Canada (Auclair et al. 1993); and (3) the Sykesville Fe-Cu-Co-Zn-Ni deposit in the Maryland Piedmont of Appalachian orogen, USA (Candela et al. 1989). In addition there are at least four other serpentinite-associated sulphide deposits showing interesting similarities with the Outokumputype deposits; these are: (1) the Ivanovka and Ishkinino Fe-Cu-Ni-Co sulphide deposits in South Urals (Nimis et al., 2003; Tesalina et al., 2003); (2) the Salamanca Co-Co-Zn-Au deposit in the Cordillera Frontal Range, Mendoza, Argentina (Bjerg et al., 1993); (3) the Limassol Forest Cu-Ni-Co-As-Au deposits in Cyprus (Panayiotou, 1980; Thalhammer et al., 1986); and (4) the Bou Azzer Co-As-Au deposits in Morocco (LeBlanc and Billau, 1982). A somewhat more far-fetched case is provided by the Cu-Ni-Co-U deposits of the **Singhbuhm** belt, Bihar, India (Sarkar and associates, 1986; Laznicka, 1993).

The Deerni (Derni, Dur`ngoi) Cu-Co-Zn deposit is found in association of a serpentinized
mantle peridotite fragment of the Anagyenen ophiolite within the South Ophiolite Zone of the east Kunlun orogeny (Haitian, 1992; Yang et al. 1997). The ophiolite zone comprises mainly allochthonous units of Permian-Triassic deep-sea metavolcanic and metasedimentary rocks intruded by Mesozoic granites. The Deerni deposit consists of several lensoid or sheet-from massive bodies hosted by pervasively carbonated-silicified parts of a ca. 0.5-1 km wide and 1.7 km long tectonic sliver of serpentinized mantle peridotites enclosed in a tectonic stack of graphitic slates, metasandstones and metavolcanic rocks (Fig. 151). The deposit has been reported with a mineable resource of 50 Mt of ore at 1.19 % of Cu and 0.5 gr/ton Au, including a reserve of 9.1 million tons at 1.53 % Cu, 1.00 % Zn, 0.07 % Co and 36.65 % S (http://www.thundrsword.com/derni.htm). No data for average Ni content is available, but the high Ni contents up to 0.74 % of ore pyrite (Yang et al., 1997) indicate bulk ore concentrations in the order of hundreds of ppm at least.

The Deerni ore bodies vary massive to banded in structure, with local disseminated facies. The main ore minerals are pyrite, pyrrhotite, chalcopyrite, sphalerite and magnetite. The usual gangue minerals include calcite, quartz, chlorite, mica, actinolite, ribeckite, talc and serpentine. The dominant ore texture is pyrite as fragmented, euhedral and anhedral grains up to 1 mm in diameter. The pyrite grains often contain chalcopyrite inclusions, show occasional growth bandings, and are variably replaced by chalcopyrite. Sphalerite and pyrrhotite occur interstitial to pyrite and chalcopyrite. Magnetite is largely restricted to the marginal parts of the ore bodies.

The ore bodies at Deerni are all sharply-bound lenses enclosed in the carbonatizedsilicified host peridotite, locally with thin overlying "hats", or even inclusions of sedimentary carbonate rock and slate. Though the host A nyemagen ophiolite is severely dismembered, Yang et al. (1997) still believe that the relationship of the peridotites, sulphide ores and their sedimentary "hats" would represent a primary sedimentary relationship, indicative of that at the time of the hydrothermal-exhalative ore deposition the basal mantle tectonites were exposed at the seafloor. To explain why large parts of the sulphide bodies yet are located enclosed inside the host serpentinite bodies, they infer that during the ophiolite obduction and subsequent orogenic movements, the ore bodies, together with some of their cover sediments, became tectonically enrolled inside of the peridotite massifs. Yang et al. (1997) consider that in a comparison with the common massive sulphide deposits types, the Deerni is closest to the Cyprus-type VMS deposits. With the notable difference, however, that the Deerni sulphides are significantly lower in Pb and higher in Ni. Yang et al. (1997) address this difference to the obvious ultramafic source of the metals in Deerni, compared to the obviously basaltic source of the Cyprus metals. However, also other opinions of origin of the Deerni deposit has been presented. Guolain (1991) has proposed that Deerni would be a magmatic-hydrothermal deposit related to the nearby Mesozoic biotite granites, and Wusheng and Jie (1996) that it should be considered a liquid-magmatic deposit formed deep in the mantle and brought in the shallow crust by subsequent tectonic processes.

The *Eastern Metals* Ni-Cu-Zn deposit in Canada represents another fairly clear Phanerozoic Outokumpu type deposit. The deposit is found at a carbonated-silicified margin of a peridotite lens (Auclair et al., 1993, Fig. 152) enclosed in the St Daniel mélange unconformally overlying the well-known Thetford Mines ophiolite (Schroetter et al., 2003). Similar to the Outokumpu deposits, the Eastern Metals deposit comprises of two distinct facies of mineralizations: disseminated to massive Ni-rich type (North zone) and semimassive to massive Cu-Ni-Zn-Co-Au type (South zone). Geologic reserves have been estimated to 0.35 Mt at 0.91 wt.% Ni for the N-zone and 0.87 Mt at 1.52 wt.% Cu and 0.15 wt.% Ni for the S-Zone. In addition both the N and S zone contain minor Zn and the S-zone also some significantly Au (up to 15 ppm in selected hand samples). Cobalt content in the N-zone sulphides is systematically relatively low (<350 ppm); while in the S-zone there is a considerable range in Co from 50 ppm up to 1600 ppm.

According to Auclair et al. (1993), deposition of the N-zone Ni-bearing pyrite±polydymite and associated sphalerite was related to the silicification of the serpentinite margins, quite as we have above proposed for the Outokumpu-type Ni-disseminations. The N-zone sulphides are very poor in Cu and Co and thus their formation probably was preceding or unrelated to



Fig. 151. Geological map of the Deerni deposit, modified from Fig. 13 in Haitian (1992). The graphitic sandstones-slates and associated metavolcanic rocks are Lower Permian, limestones Upper Carboniferous and granites Mesozoic and Cenozoic.



Fig. 152. Geology of the Eastern Metals (EM) deposit in Quebec, Canada. (Upper left corner) Geological map showing the geotectonic context of the EM deposit. (Upper rigth corner) Geological map of the EM deposit. (Lower right corner) Vertical cross-section A-B of the EM deposit. (Lower left corner) Photomicrograph of a sample from the South Zone Cu-Ni-Zn-Co-Au ore, showing chromite enclosed in pyrite extensively replaced by chalcopyrite. The maps and cross-section profile from Auclair et al. (1993).

generation of the Cu-dominated S-zone sulphides. Replacement of the Ni sulphides by a later Cu-Co-Au mineralization is thus believed to have occurred in the S-zone, controlled by a preexisting fault zone reactivated by a second event of deformation. While the apparent source of the Ni and Co in the Ni-mineralizations was in the carbonated-silicified serpentinites, the source of the Cu-Co-Zn-Au in the S-Zone is less obvious and was not discussed in detail by Auclair et al. (1993).

Although striking similarities exist between the Eastern Metals and Outokumpu, some clear differences are apparent, too. One is the considerably higher Pb content of the Cu-sulphides of the Eastern Metals sulphides, ca. 1100 ppm on average in the S-zone (Auclair et al. 1993), which is much compared to the very low <50 ppm of average Pb typical of Outokumpu deposits. The higher Pb at Eastern Metals points to that the metal source(s) was there in more evolved rocks than at Outokumpu. The Pb isotope data obtained from Eastern Metals sulphides support this conclusion (section 9.3.2).

The Fe-Cu-Co-Zn-Ni sulphide mineralization at **Sykesville** is hosted by banded magnetitesilica rich rocks between serpentinized ultramafic bodies and metasediments of the Morgan Run Melange, Maryland Piedmont. The Sykesville district produced in the period from 1750 to the beginning of the twentieth century ca. 7500 tons of metallic copper. The mineralizations consisted dominantly of magnetite, quartz, chalcopyrite, siegenite, sphalerite and pyrite, locally with some hematite and bornite. The ultramafic rocks in the Sykesville association are thought to have been exposed at the seafloor during the formation of the magnetite-quartz rocks and related sulphide mineralizations. Though interpreted as sedimentary BIF by Candela et al. (1989), the possibility remains that the magnetite-quartz rocks hosting the mineralizations in fact would represent silicified peridotite as the guartz rocks at Outokumpu. This seems conceivable as the magnetite-quartz rocks seem to be limited to contacts of ultramafic bodies and as they frequently contain chromite (detrital in opinion of Candela et al., 1989). Furthermore, the relatively magnetite rich nature of the Sykesville deposits may simply reflect somewhat higher oxygen fugacity during the Sykesville mineralization than at Outokumpu. We note here that abundant magnetite is known also in parts of several Outokumpu deposits, as e.g. in Luikonlahti and Kylylahti. As in Outokumpu, also in Sykesville the sulphide accumulations are notably poor in Pb. Candela et al. (1989) considered this an indication of origin of the sulphides far from any continental blocks, most probably from hydrothermal fluids upwelling either at an oceanic spreading ridge or a transform fault in an mafic-ultramafic oceanic crust. The sulphur was derived from the seawater and/or mafic volcanic rocks, and Cu and Zn from mafic volcanic rocks and Ni and Co from ultramafic rocks in the oceanic substrate.

In summary, the Sykesville bears many features in common with Outokumpu, such as e.g. the close association of Pb-poor and Ni-Co-rich Cu-Zn-sulphides with ultramafic rocks. The perfection of the analogy depends on the interpretation of the banded chromite-magnetitequartz rocks in the Sykesville association: i.e. do they indeed represent BIFs, or rather metasomatic quartz rocks derived from the adjacent peridotites, as the quartz rocks in Outokumpu.

The small, low-grade *Ivanovka and Ishkinino* Fe-Cu-Ni-Co deposits occur in the melanges of the Main Uralian Fault Zone (MUFZ), which in the south Urals separates an accretionary wedge in the west (Maksyutov Complex) from an fore-arc–island arc complex (Magintogorsk arc) in the east (Nimis et al., 2003; Tesalina et al., 2003). The Ivanovka deposit (ca. 180 km S of Magnitogorsk) at the western margin of the 2-25 km wide MUFZ comprises several closely spaced, 1-10 m thick, 100-200 m long lenses of massive, stockwork and disseminated sulphide in a talc-chlorite-carbonate-saponite-quartz altered mélange of serpentinized harzburgites-dunites, chlorite-altered gabbros, dolerites and basalts. The sulphides comprise pyrrhotite, pyrite, chalcopyrite and cubanite, with accessory cobaltite, sphalerite, Co-pyrite, Co-pentlandite, Ni-glaucotot and traces of native gold, bismuth and pilsenite. Ni is slightly enriched (0.2-0.4 wt.%) in ultramafic-hosted parts of the ore, whereas cobalt (0.04-0.1 wt.%) and copper (1.8 wt.%) are enriched in its mafic-hosted parts. The Ishkinino deposit (ca. 90 km SE of Ivanovka) at the eastern margin of the MUFZ comprises seven up to 15 m thick, and several tens of metres long sulphide-enriched lenses hosted in talc and talc-carbonate altered breccia of serpentinized harzburgites and dunites. The sulphides in

the ore lenses comprise massive to disseminated pyrrhotite and pyrite with chalcopyrite veins and nests of arsenopyrite pentlandite and violarite.

As a characteristic feature, the sulphide bodies both at the Ivanovka and Ishkinino contain a relatively large proportion of chromite (up to 3 vol.%). The high-Cr, low-Ti compositions of the chromites indicate a highly depleted nature of the protolith peridotites, and thus their probable origin in a fore-arc environment, which has been proposed as to the original formative environment also of the sulphides (Nimis et al., 2003; Tesalina et al., 2003). The ubiquitous chromite and fragments of altered ultramafic rocks in the Ivanovka and Ishkinino sulphide bodies suggests that if they indeed represent marine hydrothermal deposits, they were generated inside tectonized, broken ultramafic materials below the seafloor, not by deposition onto the seafloor.

The small, low-grade **Salamanca** Cu-Co-Ni sulphide deposit occurs in a fault zone in margin of a sheetform serpentinitized ultramafic body, which has been inferred to a tectonic sliver dislocated from basal part of a disrupted ophiolite complex (Berg et al., 1993). There is only little information on the geological environment of the Salamanca body, but the country rocks seem to comprise mainly greenschist facies metasediments. The sulphide mineralization (31500 tn of proven reserves) consists of discrete veins (up to 3 m), veinlets and disseminations comprising pyrrhotite, chalcopyrite±cubanite, sphalerite, Co-pentlandite and gold. Thin veinlets and disseminations of sulphides, including pyrrhotite, chalcopyrite and pentlandite, are a common feature in the adjacent serpentinites.

The subeconomic Cu-Ni-Co-As-Au deposits in the serpentinites of the *Limassol Forest* Plutonic Complex occur as lenticular or irregular bodies, veins and disseminations within a zone of highly sheared residual mantle peridotites immediately beneath the cumulates of the plutonic complex (Panayiotou 1980, Foose et al. 1985). The included main sulphides are pyrrhotite, chalcopyrite, pentlandite and arsenides. The origin of the Limassol Forest deposits is still highly controversial. First, Panayiotou (1980) considered them to magmatic sulphides that had been saturated from the magmas of the overlying plutonic complex and filtrated downwards into the underlying residual mantle peridotites. Later, however, Foose et al. (1985) and Economou and Naldrett (1984) have pointed out that the bulk sulphide compositions, particularly for the high Cu/(Cu+Ni) and low Pt/(Pt+Pd) values, are inconsistent with simple magmatic origin, but imply either pervasive modification and remobilisation of primary magmatic sulphides during serpentinization, or that the deposits are completely non-magmatic, i.e. hydrothermal, in origin. In the sulphides were hydrothermal, the metal source could have been in the silicates of the mantle tectonites. The bulk compositions of the Limassol Forest -type deposits bear some similarities with Outokumpu, but are characterised by significantly higher Sb and As, and are notably low in Zn.

The famous **Bou Azzer** serpentinite-associated Co-As-Au deposits (e.g. Leblanc and Billaud, 1982; Leblanc, 1986), that have so far produced >70 000 tons of cobalt, have been proposed as a close analogue for the Outokumpu type (e.g. Candela et al., 1989; Loukola-Ruskeeniemi 1999) or have been correlated with Limassol Forest type deposits (e.g. Cox and Singer, 1986). The similarity with Outokumpu comes closest for the sulphide host environment, since also the Bou Azzer deposits occur within quartz-carbonate altered (listwaenite-altered) margins of ophiolitic serpentinite massifs. However, in a significant difference to both Outokumpu and Limassol forest deposits, the Bou Azzer deposits are nearly free of copper and zinc.

The Bou Azzer comprises about thirty small deposits. The biggest of these, Ightem and Filon 7, contain resources of more than one million tonnes each. The deposits, which consist of lodes, veins, stockworks, complex shells and flat lenses of sulphides, all locate within quartz-carbonate altered margins of a 200m to 2000 m wide, 40 km long serpentinized harzburgite-dunite (mantle peridotite) massif. The bulk of mineralization is Co-Ni-Fe arsenides with accessory sulfoarsenides (skutterudite, gersdorfite, rammelsbergite, loellingite, nickelin, safflorite, glaucodot, arsenopyrite and maucherite etc.), copper sulphides, molybdenite and gold. It is believed that a Co-enriched "proto-sulphides" formed during the metasomatic alteration (post-obduction) of the serpentinized peridotites, and that later deformation, tectonic upgrading, remobilisation and recrystallization of these "proto-sulphides" resulted in the

structurally controlled mode of many of the present sulphide occurrences. The apparent source of the Co and Ni were in the peridotites whereas the As was probably derived from the overlying ignimbritic volcanics (Leblanc and Billaud, 1982; Leblanc, 1986).

The copper deposits of the **Singhbhum** belt miss one of the more important features of the Outokumpu type sulphides as they do not show any strong affinity to ultramafic rocks. What makes these deposits interesting, however, is their quite Outokumpu-type metal association of Cu-Co-Ni-Ag-Au-U-Se (Sarkar and associates, 1986; Laznicka, 1993). The Singhbum belt, or Sighbum thrust belt, refers to an arcuate, hundreds of metres to 15 kilometres wide, 30-50° dipping, >100 km long shear zone between a thick sequence of 2.4-2.3 Ga old Proterozoic metavolcanic-metasedimentary-metaplutonic rocks and the structurally underlying >3 Ga old Sighbhum Craton.

The Singbhum belt with its over 15 economically significant Cu deposits, is the historically most important Cu mining camp in India. The past cumulative production is over 3.5 Mt of copper metal, from deposits with a range of 0.7-2.5 % for average Cu content. In addition, the Singhbhum belt has produced >50.000 tons of U, >40.000 tons of Ni and minor Se, Ag, Te and Au. The Co content in Shinghbhum Cu-ores varies typically from 100 to several thousands of ppm, with Co/Ni ratios usually between 0.2 and 2 but locally much lower. All the Cu-deposits are hosted by ductile tectonites developed in the metaplutonics, metabasalts and metapelites of the Proterozoic sequence. The Cu usually occurs in cm to metres thick and hundreds of metres to 5 kilometres long "lodes", filled mainly by biotite-chlorite-quartz and locally muscovite-rich phyllonite. Some apatite and tourmaline are usually present. The dominant ore mineral in these lodes is chalcopyrite, often accompanied with lesser amounts of pyrrhotite, pyrite, violarite, valleriite, pentlandite, chalcocite and molybdenite. Minor magnetite, cubanite, bornite, tellurobismuth, millerite, heazlewoodite, sphalerite, ilmenite, uraninite, native copper etc. occur locally. The sulphides occur as disseminations, blebs and stringers, the latter usually aligned subparallel with shear-banding in the host tectonites. Interestingly, where ultramafic rocks in the country assemblage are dissected by the ore "lodes", there the Ni content of the "lodes" tends to increase up to a point that Ni sulphides become a feasible by-product of the Cu mining. This is a good example of environmental factor that may be behind also of the Ni enrichment of the Outokumpu deposits.

The models for Singhbhum Cu-deposits, which are highly deformed and pervasively metamorphosed in the amphibolite facies, have been many and controversial. The two main interpretations presently supported are: (1) the ore bodies represent highly deformed, remobilized and metamorphosed volcanic-hosted hydrothermal-exhalative deposits of the Cyprus type, or (2) the ore bodies represent syntectonic, metamorphic-hydrothermal and diffusive mobilization of metals from the wall rocks into the shear-zone controlled sulphide "lodes".

The closest *modern analogy* for the Outokumpu-type deposits is provided by the hydrothermal sulphide accumulations on serpentinized ultramafic rocks exposed at modern mid-ocean ridges. Recent exploration has demonstrated such deposits especially from within the slow-spreading ridges like the Mid-Atlantic Ridge, usually located off axis in places where the magmatic activity is minimal and where extensive listric faulting has exposed ultramafic rocks in dome-like structures. Where high-temperature, low pH fluid venting is associated, significant volumes of massive sulphides, either wholly or partially floored by the ultramafic (mantle peridotite) rocks do occur, examples of such environments include e.g. the Logatchev field at 14°45'N and the Rainbow field at 36°14'N (e.g. Bogdanov et al., 1997; Murphy and Meyer, 1998; Douville et al., 2002). Compared to sulphide deposits in dominantly basaltic seafloor environments, these deposits are significantly enriched in Cu, Zn, Co and Au, and to a degree also in Ni. The Ni contents of <20 to 450 ppm, based on data in Bogdanov et al. (1997) and Murphy and Meyer (1998) are significantly lower than in Outokumpu-type deposits, however. A surprising aspect is that the ultramafic-related seafloor deposits show similar enrichment in Sn (50-1700 ppm) as the Outokumpu deposit. However, despite of the many similarities in the host rock and metal association, using the modern ocean-ridge ultramaficassociated deposits as a model for the Outokumpu deposits is not completely straightforward. Firstly, the true importance of ultramafic rocks as metal source, is difficult to know since the

peridotite exposing modern vent environments frequently contain also significant basatic components (cf. e.g. Bogdanov et al., 1997, Fig. 1). Secondly, and related, it is quite likely that the ultramafic–floored high-T venting is anyway thermally driven by underlying hot mafic intrusions. The basalt-gabbro contribution to the metal budgets of the ultramafic-floored sulphides is evident in their relatively high Pb contents ranging from 55 to 3840 ppm (e.g. Bogdanov et al., 1997; Murphy and Meyer, 1998). Pb concentrations are relatively high also in the associated vent fluids (see e.g. Douville et al., 2002).

# 12. Foundations of genetic modelling of the Outokumpu-type deposits

### 12.1. Historical perspective – previous models

Genetical modelling of the Outokumpu-type ores has had a long history. Since the discovery of the Outokumpu ore in 1910 by O. Trüstedt, numerous ideas and models for the origin of these in many ways enigmatic deposits have been introduced. The sulphide type categories that have been associated with Outokumpu include (applying modern terminology) at least: (1) magmatic sulphides, (2) granite-related magmatic-hydrothermal sulphides, (3) sedimentary-exhalative (SEDEX) sulphides, 4) syntectonically remobilized syngenetic-diagenetic black shale sulphides, and (5) volcanic-associated massive sulphides (VMS). The single main reason to these highly varied and contradictory interpretations is certainly the pervasive amphibolite grade recrystallization and complex deformation of the Outokumpu deposits, rendering their interpretation to a real challenge.

The first documented proposal of the ore genesis is by *E. Mäkinen* (1921); in notes on the talk "Över geologin inom Outokumpu området" that he gave in a 1919 meeting of the Geological Society of Finland. According to the notes, the talk of Mäkinen was followed by a lively discussion, participated not only by the founder of the Outokumpu ore, O. Trüstedt, but also e.g. Norwegian professor J.H.L. Vogt and J.J. Sederholm. In his talk Mäkinen (1921) proposed that the Outokumpu formation comprised a large syntectonic intrusion of [serpentinized] olivine rocks largely inside and conformable with a layer of carbonate rocks, skarns and guartzites. Although he considered the carbonates and guartzites mostly interbedded sedimentogenic strata, for the part of the skarns he made a reservation that some of them could represent "metamorfa produkter av olivine- och serpentinsten". Mäkinen (1921) further considered that the Outokumpu ore represented a sulphide-impregnated breccia-zone within and broadly conformable to the carbonate-skarn-guartzite horizon. He found a scarcity of obvious host-rock intercalations in the ore and its very sharp contacts both clear indications of its epigenetic nature. Mäkinen was very confident about the epigenetic nature of the ore, stating: "Att malmen är epigenetisk, d. ä. en senare bilding än kvartsiten, kan intet tvivel råda". Furthermore, he argued that the pegmatite granite dykes at Outokumpu entirely post-dated the ore formation, representing injections into an already "färdigbildad" ore. To address the ultimate origin of the sulphides in the ore zone, Mäkinen (1921) proposed (obviously deeply touched by the recent studies of professor Vogt on Norwegian magmatic sulphide deposits) that the sulphides would represent a differentiate of the same magma as the nearby serpentinites. To explain the lack of Cu-Zn sulphides in the serpentinites, he proposed that "...sulfidmagman, redan förrän själva serpentinstenen började utkristallisera, hade utdifferentierats såsom en självständig magma och som sådan blivit injicerad i en breccierad zon i den liggande kvartsiten". In other words, Mäkinen suggested that the Outokumpu ore would represent an offset dyke-style magmatic sulphide ore body.

**O. Trüstedt** expressed in the discussion following the talk of Mäkinen (1921) a different view of the time succession of the pegmatite dykes and the ores, insisting that because the pegmatites were locally brecciated by Cu-Zn-sulphides, they could not be younger than the ore: "[O. Trüstedt]...förevisade prov på sådan pegmatiti från gruvan, där bärgarten blivit breccierad och brottstyckena ihopcementerade av de typiska malmmineralen." E. Mäkinen countered with pointing out that the breccia and sulphides in the pegmatites could have been caused by the action of late deformation. About the ore genesis he had the opinion that the sulphides in the

Outokumpu ore were ultimately derived from the nearby large, post-Kalevian (e.g. Maarianvaara) granite batholiths. Having had today's terms available, Trüstedt perhaps might have proposed that the Outokumpu ore would represent a granite-related magmatic-hydrothermal deposit. According to the notes from the meeting, *J.J. Sederholm* agreed with O.Trüstedt: *"Hr Sederholm var beträffande malmens uppkomst av samma mening som Trüstedt"*.

The study of **Eskola** (1933) had focus on the mineralogy of the chromian silicates and oxides at Outokumpu, but it also included some comments on the sulphide ore. He was probably the first worker who recognized the problematic status of the Outokumpu "dolomites" as sedimentary rocks, by stating that: "the occurrence of chromite in dolomite is strange indeed". Although failing to do a clear conclusion, he obviously was inclined to believe that the dolomites were formed by CO<sub>2</sub>-metasomatism from the nearby ultramafic rocks, pointing out that: "then we would easily understand the chromite crystals as relics from the primary phenocrysts once settled together with olivine". He also observed schistosity cross-cutting uvarovite+pyrrhotite veins in Outokumpu guartz rocks, which he saw a indisputable evidence of high hydrothermal mobility of chromium "the chromite, as well as all the other chromiumbearing minerals of this locality [Outokumpu], is in all probability of a hydrothermal origin". The local presence of chrome minerals (uvarovite, tawmawite, chromite) also in the Outokumpu ore made Eskola (1933) to believe that the sulphide ore formation was associated with introduction of chrome: "migration of the chromium and the replacement reactions had taken place contemporaneously with the forming of the ore, or a little earlier, but by no means later". Based on this assumption, Eskola (1933) further stated that the ore could "by no means have formed at the same time [or prior] as the mise-en-place of the serpentine rock occurred" but must represent, a perhaps considerably later development. Like Mäkinen (1921), also Eskola (1933) believed that the ore sulphides were derived from some kind of magma, but which unlikely was represented by the sulphide poor post-Kalevian granites or serpentinites in the Outokumpu assemblage. He settled to say: "although the Outokumpu ore, in all probability, has been derived from some magma, it is by no means necessary that the magma should exist at present as a rock and be exposed anywhere".

Väyrynen (1935, 1939) shared the then prevalent view of the Outokumpu assemblage as horizon of metasedimentary quartz sands and carbonate rocks and sheetform intrusions of serpentinized ultramafic rocks. He actually correlated the Outokumpu dolomites and guartz rocks with the Jatulian dolomites and quartzites in the Pisa area. The skarns in the Outokumpu assemblage Väyrynen (1935) however interpreted as "reactions skarns" that had gained their chromium in aqueous solutions released from the adjacent serpentinites by metamorphic dehydration reactions. At the time of Väyrynen's 1935, 1939 contributions the overthrust character of large parts of the Kalevian strata in the Outokumpu district had already been recognized (e.g. Wegmann, 1929; 1929; Väyrynen, 1937). Recognizing the distribution of the serpentinite bodies along the inferred thrust-faults, Väyrynen (1939) interpreted the bodies to olivine-rich crystal accumulations from syntectonic, thrust plane-controlled intrusions of "much more acid magmas". To explain the absence of mafic to felsic differentiates in association of the serpentinites, he proposed such components had become "squeezed further" along the thrust-faults, and ultimately extruded onto the earth's surface. Väyrynen (1939) was very confident about this interpretation and stated: "there is no other possibility than that the serpentinites must have originated from moving magma under a flat-lying cover".

Väyrynen (1939) saw that the Outokumpu ore had a very uniform mineral composition, was thoroughly massive, and had a very regular shape whose *"ramifications and bends"* had formed in connection with the emplacement of the ore. These features, and the frequently very abrupt, sharp contacts of the ore body, made Väyrynen (1939) believe that it represented a true magmatic intrusion. Having previously worked in Petchenga, and being thus familiar with peridotite-related magmatic sulphide deposits, he applied the magmatic model also to the Outokumpu ore: *"From these intrusions the pyrite ore magmas and other solutions containing sulphides, from which the Outokumpu ore and other copper and iron pyrite deposits, generally situated close to the serpentinites, originated, were separated...as in Petsamo."* Although he did not make it clear, it seems that Väyrynen (1939) thought that the ore magma was separated from those "much more acidic magmas" to which he related the serpentinites as

(contemporaneous?) olivine-rich cumulates.

Also Vähätalo (1953) and Disler (1953) considered the carbonate and quartz rocks in the Outokumpu assemblage to a sedimentary dolomite-guartizte horizon. Both they saw that the dolomite-quartzite horizon was at Outokumpu associated with a special structural "crushing zone", forming a perfect environment for injection of high-temperature hydrothermal solutions and related ore formation. Vähätalo (1953) distinguished three distinct structural varieties in the Outokumpu ore: 1) disseminated, 2) normal and 3) brecciated ore. The structural subtypes recognized by Disler (1953) were: 1) layered, 2) massive and 3) quartzite-fragment-containing ore. On the basis of the usually very sharp contacts of the normal and breccia ores with their host rocks, Vähätalo (1953) argued that these ore parts "must be epigenetic in their origin with regard to their wall-rocks" and that "...the crushing zone in the quartzite near the contact of serpentine has been a necessary tectonic condition for the [intrusive] development of the ore". The volumetrically minor, disseminated ore parts he addressed to hydrothermal replacement that in parts preceded, and in parts succeeded the emplacement of the normal and brecciated ore. From the nature and origin of the ore solutions Vähätalo (1953) had about the same opinion than Eskola (1944), i.e. that they were dense, highly viscose, high temperature (400-500 °C), "pneumotectic" (we could say "supercritical") solutions separated from some magma immediately after its crystallization. Based on the low Ni/Co ratios of the Outokumpu ore between 2:1 and 1:3, more akin to Ni/Co ratios in intermediate-felsic than ultramafic magmatic rocks, Vähätalo (1953) inferred that the parent magma of the ore solutions was probably granodioritic in composition. However, because plutonic rocks suitable to parental rocks are not exposed anywhere near the ore, he ended up to conclude: "the only possibility is to assume that the intrusive which the ore solutions derive from is situated somewhere below the schist formation".

Saksela (1957) was on guite different lines compared to the previous Finnish workers, as he saw that any relevant evidence of genetic link between any magmatism and the ore formation was largely missing, and overall considered such deposit models unlikely that require derivation/introduction of fluids and metals from beneath and through the Kalevian supracrustal package. He also saw that due to its dominantly massive nature the Outokumpu ore could not be of metasomatic origin, either. Saksela (1957) agreed with Borchert (1954) in that the ore materials were primarily synsedimentary in origin, but because of the lack of volcanic rocks in the Outokumpu assemblage, rejected the role of hot springs pushed forward by Borchert. Instead, Saksela (1957) proposed that low-grade synsedimentary-diagenetic sulphides, which are observed plentifull in the local sulphide-rich black schists, had been selectively remobilized by synorogenic, mesozonal tectonic-metamorphic processes to form the massive-semimassive Outokumpu ore. He must have assumed a structurally controlled final emplacement of the ore materials as he saw the massive ore filling "Klüfte und andere geeignete Holräume in den sedimentogenen Gesteinen". Saksela (1957) encapsulated his view of Outokumpu in the sentence: "Die Kupherlagerstätte von Outokumpu ist meiner Meinung nach ein schönes Beispiel der metamorpehen Abfolge".

Exhalative deposit models have been in favor since the aforementioned 1954 contribution by **Borchert**. In the opinion of Saksela (1957), Borchert's (1954) paper was of groundbreaking importance: "Neulich hat Borchert (1954) der Diskussion über die Entstehung der Outokumpu-Erze neuen Bahnen gewiesen". In this paper, which was a comment on the newly published papers of Vähätalo (1953) and Disler (1953), Borchert had been proposing that the Outokumpu ore represented, analogous with the Ergani-Meggen-Rammelsberg-type deposits in central Europe, a synsedimentary deposit at hot springs venting on the sea floor. This means that Borchert was the first who with clear terms was suggesting that Outokumpu ore would represent a metamorphosed SEDEX type deposit, as the Ergani-Meggen-Rammelsberg deposits are currently understood.

*Huhma and Huhma* (1970) and *Gaál et al.* (1975) argued that the origin of the carbonate and quartz rocks in the Outokumpu assemblage were genetically linked with the serpentinization of the Outokumpu peridotites. Huhma and Huhma (1970) saw that the quartz rocks represent chemical, colloidal silica precipitates, which formed through the *"action of the ultramafic magma, serpentinization and carbonization and were later metamorphosed into*  rocks resembling the quartzites". Gaál et al. (1975) refined this idea further, proposing that "serpentinization took place on the bottom of the geosynclinal sea" so that "during serpentinization first SiO<sub>2</sub> then MgO were freed in fluids that precipitated around the margins of the ultramafic masses". Huhma and Huhma (1970) and Gaál et al. (1975) did not make any specific comments on the ore genesis, while Huhma (1976) stated that "the ore invaded as a gel into the unconsolidated quartz rocks" [during the early flysch stage of the Kalevian geosyncline], and that "hence the Outokumpu ore is to be considered as a product of submarine processes".

*M. Mäkelä* (1974), based on interpretation of the results of his extensive investigation of the sulphur isotope variation in the Outokumpu ore, agreed with Borchert (1954) of a marine environment and hydrothermal-sedimentogenous origin of the Outokumpu ore, interpreting it as "a stratiform pyritic copper ore deposited by volcanic exhalations discharged from a fissure-type vent system on the [sediment covered] sea floor". Also *Peltola* (1978) thought that the Outokumpu and Vuonos deposits would be "*massive sulphide deposits of sedimentary-exhalative origin*" of "marine-volcanic association"". He insisted that the Outokumpu and Vuonos ores showed many sedimentary features to support this interpretation, such as graded bedding, preconsolidation folding and slump breccias, and that the ores had a clear stratigraphic affiliation with the enclosing sedimentary rocks, being controlled by a definite siliceous horizon with carbonaceous intercalations in the lower portion of the Outokumpu formation. The quartz rocks in the Outokumpu formation Peltola (1978) believed, referring to Huhma and Huhma (1970), to represent chemical sediments "formed by the serpentinization of intruding ultramafic magma".

*K. Mäkelä* (1980; 1981) suggested that Outokumpu along with some other Finnish sulphide deposits (Haveri, Pahtavuoma and Riikonkoski) would represent examples of Cyprus type strata-bound, volcanogenic massive sulphide deposits. He interpreted the Outokumpu serpentinites in terms of submarine ultrabasic lava flows, and their close association with metal-rich black schists as an evidence of syn-eruptive hydrothermal ore formation. He saw that metal distributions in Outokumpu and Vuonos ores were a clear indication of their origin at submarine hydrothermal vents. Further, Mäkelä (1981) was probably the first to propose that the Talvivaara Cu-Ni-Zn enriched black schists ca. 150 km to the N of Outokumpu in Kainuu would *"represent the distal facies of the Outokumpu-type ore forming processes"*, an idea that subsequently was supported by Loukola-Ruskeeniemi (below).

**Koistinen** (1981) interpreted the Outokumpu and Vuonos ores as multiply deformed and metamorphosed strata-bound, marine exhalative deposits associated with an ophiolite suite of mantle peridotites, gabbros, basalts, black shales, carbonate sediments and cherts. Based on a detailed analysis of the structural development and stratigraphy of the Outokumpu and Vuonos deposits, Koistinen (1981) inferred they had been deposited in two separate fault-controlled, oval shaped seafloor depressions, ca. 8 km apart, and both ca. 4 km in diameter. He addressed the deposition to sulphide precipitation from brine-pools collected in the two subbasins by hydrothermal fluids expelled along the basin controlling faults. This resulted in sulphide layers respectively 6-10 m and 3-5 m thick in the Outokumpu and Vuonos brine pools, comprising in both cases of a pyrrhotitic sublayer below a pyritic sublayer. Isoclinal folding in an early stage (D1) of the regional tectonism inverted the ore bodies, and deformed them into those linear, ruler-shaped plates as they now are. Subsequent episodes of regional deformation and metamorphism resulted in local fold thickenings-thinnings and fault displacements to the ore plate, and caused limited remobilisation and variable recrystallization of sulphides, but had otherwise only minor effect.

**Rehtijärvi** (1984) observed high concentrations of Br and CI and high Br/CI in many Outokumpu serpentinites. Some of the highest concentrations were observed in the serpentinites at the footwall of the Outokumpu main ore. Rehtijärvi (1984) assumed this was an indication of a halogen-rich composition of the primary ore-forming fluids, and thus evidence supporting marine exhalative origin of the Outokumpu Cu-sulphides.

Vähätalo (1953) was probably the first worker who noted that the patchy zone of sulphidic cordierite-amphibole-chlorite rocks occurring at the hanging wall of the Outokumpu ore might have some important telling of the genesis of the ore. Subsequently several authors, as e.g.

Koistinen (1981), Treloar, et al. (1981) and Park (1988, 1992), have interpreted this "Co-Ni" zone to comprise a deformed fluid upflow channel that originally located below the main ore. **Parkkinen and Reino** (1985), however, remained of that some of the features of the Co-Ni zones, as e.g. cordierite-amphibole-chlorite rocks and Ni enrichment, are in fact a relatively universal feature of contact zones between the serpentinites and mica schists/gneisses, occurring also in environments free of significant Cu-sulphides. They saw this to imply that *"the special features of the formations [Co-N+-Cu occurrences] are due simply to the order of formation: first an extensive but thin and discontinuous Ni occurrence was formed, and this was followed immediately by the deposition or intrusion of the Cu ore. They added "The source of the fluids and the location of the feeding channels will remain to be established".* 

**Papunen** recognized in his 1987 review of Outokumpu deposits that although they in many respects bear similarity to the Cyprus-type ophiolite-associated and Besshi-type mafic volcanic -clastic sedimentary associated deposits, they also have some unique features, like e.g. the high proportion of ultramafic rocks and lack of demonstrably extrusive volcanic rocks in their typical host associations. Papunen (1987) arrived at the conclusion that even if the Outokumpu deposits cannot be considered an independent type of massive sulphides, they nevertheless have so many special features that they probably should be classified as a new "subtype of sulphide ores associated with seafloor mafic and ultramafic volcanism". **Candela et al.** (1989) went further and suggested that the Outokumpu, Sykesville and Bou Azzer deposits represented an independent clan of [Outokumpu-type] sulphide deposits. According Candela et al. (1989) the basic features of the Outokumpu-type deposits would be: (1) Co-Ni-Fe-Cu-Zn mineralization, (2) a general sequence of ultramafic – mineralized zone (host rocks) – country rock, (3) subaqueous-subareal genesis of the host rock, and (4) ubiquitous chromite, possibly Zn-rich.

Like Koistinen (1981), also **Vuollo and Piirainen** (1989) interpreted the Outokumpu complex as a dismembered ophiolite complex, though in a subclass comprising mainly serpentinized peridotite fragments. The peridotite fragments they considered dominantly residual mantle dunites, harzburgites and lherzolites in the western, and mainly magmatic cumulates (dunites and wherlites) in the eastern part of the Outokumpu area. On the basis of the usually high-Cr, low-Al chromite in the residual peridotites, and the high MgO, Cr and Ni and low TiO<sub>2</sub> and Zr contents in the mafic metadykes/metavolcanic rocks in their association, Vuollo (1994) proposed that the Outokumpu ophiolite complex was formed in a suprasubduction environment, and it therefore, as considered typical of SSZ ophiolites, contained significant amounts of Cu-Zn-Co sulphide ore.

Unlike Koistinen (1981) and Vuollo and Piirainen (1989), *Park* (1988, 1992) regarded the ophiolite model of the Outokumpu assemblage as unfounded, and saw in it more evidence of ultramafic (95 % dunitic, saxonitic) sills intruded into a shallow marine, island-arc related sequence of metavolcanics (low-K tholeiites and shoshonites-shonkinites), pelagic shales, carbonates and chemogenic sediments [carbonate and quartz rocks in the Outokumpu assemblage], the latter including metalliferous exhalites. Park (1988, 1992) believed that the main phase of Outokumpu mineralization occurred concurrent with an early [sea-floor] serpentinization of the ultramafic sills, probably immediately following their intrusion and during their cooling. Hydrothermal circulation through the hot ultramafic sills [providing the driving energy of the fluid circulation] and enclosing metasediments *"debouched silica gel and brines rich in Mg, Cr, Ni, Co, Cu and Zn onto the contemporaneous ocean floor, and generated local chert-hosted Cu-Co-Zn and Ni-Co sulphide ores" (Park, 1988).* An areally extensive horizon of black shales enriched in Cr, Ni, Co, Cu and Zn and containing fuchsite and talc lamellae was deposited distal to the main sulphide deposits (Park, 1988, Fig. 5).

Also **Laznica** (1993, P. 249-253) doubted the ophiolite model of the Outokumpu assemblage, arguing, as Park (1988, 1992), that there are "too many departures from the ophiolite model", and that this assemblage would thus rather "be part of a diverse supracrustal assemblage established on mature quartz arenite and arkose, rich in carbonate", and which "grades upward into pelites augmented by ultramafics and mafics, topped by monotonous meta-turbidites". Laznica (1993) correlated the formative tectonic setting of the Outokumpu assemblage with his "pre-greenstone" association of greenstone belts, or the "rift-association",

seeing similarity in the rock assemblage also with that of the lower Proterotozoic Oswagan Group in the Thompson Nickel Belt of Manitoba. Laznicka (1993) doubted also the usual interpretation of the skarns, dolomites and quartzites in the Outokumpu assemblage as originally sediments, and suspected that they would more likely represent carbonised and silicified ultramafics. Subsequently Auclair et al. (1993) and Kontinen (1998) have expressed a similar view of their origin.

Gaál and Parkkinen (1993) presented a model in which they integrated formation of the Outokumpu ores with a break-up of the Karelian craton ca. 2.0 Ga ago, proposing that the carbonate and guartz rocks and sulphide deposits in the Outokumpu assemblage were related to submarine hydrothermal convection, leaching and deposition above the magmatically active spreading centre of the opening new oceanic basin. As to an explanation for the rarity of volcanic rocks in the Outokumpu assemblage, they proposed that the embryonic ocean basin was for large parts floored by serpentinized mantle peridotites, exposed either by "serpentinite protrusion", "block movements" or by "unusually fast spreading rate of oceanic crust". Gaál and Parkkinen (1993) further inferred that after the cessation of the hydrothermal activity, carbonand metal-rich muds (black schists) were first deposited under euxinic conditions to be then buried by a thick layer of greywackes. During the collision [of the Svecofennia to the Karelian Craton] the Outokumpu association was sheared off at its base, became co-folded with the greywackes, and obducted onto the continental crust to the east. Gaál and Parkkinen (1993) remarked that assuming an ultramafic floor of the ore deposition would greatly help to explain some of the more unique features of the Outokumpu deposits. They, however, pointed out that the strong initial dismembering and subsequent deformation of the Outokumpu assemblage makes any reconstructions of its primary environments necessarily highly hypothetical.

**Loukola-Ruskeeniemi** and her co-workers published during 1990s several papers on the geochemistry of the blacks schists in the Kainuu-Outokumpu area (e.g. Loukola-Ruskeeniemi, 1991; Loukola-Ruskeeniemi and Heino, 1996). In these works the relatively high metal enrichments characterizing the sulphidic black schists attached with the Outokumpu deposits were interpreted syngenetic with the ore formation. A point made public earlier by Mäkelä (1981), as we mentioned above. Loukola-Ruskeeniemi (1999) proposed that the metal rich black muds-shales in Outokumpu deposited in basins where the bottom waters were enriched in Co-Cu-Ni-Zn and S by hydrothermal fluids, and that the Co-Cu-Zn deposits precipitated from the same fluids beneath the black mud-shale horizons as they had developed thick enough to act as an effective cap. Subsequently, tectonic peridotites intruded in the assemblage of metal rich black muds and underlying sulphide layers. Alteration of the peridotites released Ca- and Si-rich material that precipitated between the black muds-shales and the ultramafic bodies. Tectonic and metamorphic upgrading resulted in massive ore bodies. According to Loukola-Ruskeeniemi (1999) *"this genetic model explains why the Outokumpu-type deposits are rare: the association of the Cu-Co-Zn ores with the serpentinites is coincidental"*.

Taking a retrospective look at the genetical modelling of the Outokumpu ores, the contribution of Borchert (1954) is indeed found to have had such turning point impact, as Saksela (1957) long-sightedly predicted. Before 1954 most researchers of the Outokumpu ores considered them "magmatic", either injections/intrusions of dense, relatively "dry" pneumotectic solutions (Eskola, 1933, 1944; Vähätalo, 1953) or true sulphide magma differentiated either from ultramafic or intermediate-acid parental magma (Mäkinen, 1921; Väyrynen, 1935, 1939). In great contrast, after 1954, nearly all researchers (e.g. Mäkelä, 1974; Peltola, 1978; Koistinen, 1981; Papunen, 1987; Park, 1988, 1992; Gaál, 1993; Loukola-Ruskeeniemi, 1999) have ended up support the submarine exhalative model first proposed by Borchert (1954). The canonized interpretation, since early 1960s, of the quartz rocks in the Outokumpu assemblage to chemical cherts has probably been the most important single "constraint" limiting the imagination of the post-1954 interpreters of the Outokumpu ores.

# 12.2. Constraints for deposit modelling – a discussion

# 12.2.1. Nature of the serpentinite bodies in the Outokumpu assemblage

Excluding one, all those ten (or so) Outokumpu-type sulphide deposits that are known from the NKSB occur at margins of serpentinite bodies. Only the small Riihilahti deposit in altered metavolcanic and metasedimentary rocks lacks serpentinites in its host rock assemblage. The Riihilahti mineralization is exceptional also in respect of that it seems to locate in the parautochthous Lower Kaleva instead of the allochthonous Upper Kaleva hosting the other deposits. But even at Riihilahti it is within bounds of possibility that the sulphides had a prehistory at an allochthonous serpentinite body immediately above the deposit and present erosion level, although this may have required some more sulphide remobilization as is usual for the Outokumpu deposits. Altogether, it appears a very reasonable starting point to assume that a close genetic link, in a way or other, would exist between the Outokumpu sulphides and ultramafic massifs. And that, hence, a good understanding the primary formative setting and subsequent alteration history of the ultramafic massifs would be one of the more important preconditions for understanding of the origin of the Outokumpu deposits.

The early workers usually considered the serpentinites ultramafic magmatic intrusions. The Outokumpu serpentinites were first called ophiolites by Wegmann (1928; 1929), with a reference to Steinman's (1905) concept of ophiolites as serpentinite and "diabase" intrusions in deep-sea chert horizons. Koistinen (1981) was probably the first to propose that the Outokumpu serpentinite bodies and associated mafic rocks would represent ophiolites in the modern sense of the term, i.e. be fragments of oceanic crust-mantle. The subsequent recognition of the Jormua mafic-ultramafic complex in the northern part of the Outokumpu-Kainuu thrust belt as a near complete Penrose type ophiolite (cf. Kontinen, 1987; Anonymous, 1982) was considered supporting an ophiolite interpretation of also the ultramafic-mafic bodies of the Outokumpu area (e.g. Gaál and Parkkinen, 1993). However, because the more diagnostic ophiolite units, such as sheeted dyke complexes and pillow lavas, that are present in Jormua, are lacking or very poorly developed in the mostly highly serpentinite dominated Outokumpu ultramafic-mafic massifs, one could, with good reason, to question their ophiolite status (cf. Park, 1988; Laznica, 1993).

There are many aspects that are common to the Jormua and Outokumpu mafic-ultramafic complexes, however, such as the ca. 1.97-1.95 Ga age of their gabbroic components, plume fingerprint of their mafic magmas, presence of sodic plagiogranites in both, and their common hosting in the <1.92 Ga upper Kaleva metaturbidites. These parallelisms could be considered evidence of their origin in a shared geotectonic setting. There are plenty of evidence from the Jormua complex supporting the hypothesis of the ca. 1.97-1.95 Ga magma-poor break-up of the Karelian craton and associated exposure of old lithospheric mantle on the seafloor, and with further divergence, opening of a narrow ocean basin floored by thin mafic crust. When evaluating the nature of the Outokumpu massifs, we ended up to support the concept that they would connect to the 1.97-1.95 Ga break-up basin, basically in similar way as the Jormua complex (cf. Kontinen, 1987; Peltonen et al., 1996, 1998; Peltonen and Kontinen, 2004), but representing ophiolite fragments detached from a slightly different, obviously dominantly mantle-floored segment of the newly opened ocean.

Modern passive margins (e.g. West Iberia, Cornen et al., 1999), likewise ancient passive margin ophiolite associations (e.g. Jurassic Ligurian, Rampone and Piccardo, 2000) provide evidence of that slow, amagmatic type ocean opening may indeed unroof wide segments of lithospheric to astenospheric mantle to flank continents. Mantle peridotites are exposed on the sea floor also in the slow-spreading mid-oceanic ridges, like in the Mid-Atlantic Ridge or the Gakkel Ridge (e.g. Bonatti et al., 1990; Brun and Beslier, 1996; Cannat, 1993; Cannat and Casey, 1995; Nicholls et al., 1981; Pickup et al. 1996) and also in oceanic transform zones. Though probably energetically not the most favourable environments, also the slow spreading ridges with mantle exposures are known to be associated with hydrothermal venting and related deposition of Cu-Zn rich sulphides, in places directly onto the ultramafic substructure (Bogdanov et al., 1997; Murphy and Mayer 1998). There, thus, should not be any obstacles either for hydrothermal sulphide accumulation in passive, magma-poor break-up settings, provided there were occasional shallow magma intrusions to provide enough thermal energy and/or metal source for local circulation and venting of hot metal-rich fluids. It is to be noted; also, that serpentinization of refractory peridotites is an exogenic process that alone may drive, albeit relatively low-T, hydrothermal circulation of seawater. Hence, a hydrothermal ore

formation at or below seafoor seems a perfectly feasible scenario for the Outokumpu deposits; despite that the seafloor probably was dominantly ultramafic. It should be noted, however, that if such a Cu poor reservoir as mantle peridotites was the principal Cu source, very large rock volumes must have been leached to provide all the Cu the Outokumpu ores contain.

Some aspects in the interpretation of the Outokumpu mafic-ultramafic bodies as incipientocean ophiolite fragments remain debatable, however. These include e.g. the highly depleted nature of the peridotites and the LOTI tholeiite nature of the associated gabbroic and basaltic rocks, and which previously have been interpreted as evidence of a suprasubduction origin the Outokumpu assemblage or ophiolite (Park, 1988; Vuollo and Piirainen, 1991), and thus of its separate origin from the rather MOR type Jormua complex. However, in terms of the peridotite compositions, there is considerable overlap between Outokumpu and Jormua; for example, REE profiles of both peridotite suites are mostly flat, and similarly highly depleted, harzburgitic peridotites as in Outokumpu are present also in Jormua. There is compelling evidence of that the peridotites at Jormua would represent Archaean, >3 Ga subcontinental lithospheric mantle (SCLM) exhumed in early stages of the 1.97-1.96 Ga break-up of the Karelian Craton (Tsuru et al., 2000; Peltonen et al., 2003). Therefore, and as Archaean SCLM is biased to depleted harzburgites, a serious alternative could be that also the Outokumpu harzburgites would represent dominantly SCLM. Our observation of >2160 Ma zircons in a metabasite dyke in the Kylylahti massif is a possible supporting evidence. However, more isotope study of both the Outokumpu peridotites and associated dyke rocks is required to test the SCLM hypothesis. We settle here to state that in the narrow ocean model, the Outokumpu peridotites could alternatively represent depleted astenospheric mantle, exhumed to the seafloor after a complete break-up of the continental mantle lithosphere.

The LOTI tholeiites in Outokumpu massifs exhibit a mixed tectonomagmatic signal; for example, they yield depleted tholeiite compositions as typical for suprasubduction magmas, but yet miss the more diagnostic signatures of subrasubduction origin, as e.g. negative Nb anomalies. Instead they exhibit a similar, though weaker, trace element signals of plume involvement as what are evident in the compositions of the Jormua basalts. Noting the shield wide evidence for 2.0-1.96 Ga plume and related mafic magmatism, we ended to propose the1.97-1.96 Ga break up of the Karelian Craton was actually plume triggered, and that the Jormua and Outokumpu 1.97-1.95 Ga magmas represented successive generations of melts from the plume. In any case, the LOTI tholeiites in the Outokumpu area are an important feature, which it shares with many classical massive sulphide districts. The connection of the LOTI tholeiites and sulphides probably is by the high temperature, relatively shallow mantle melting required for their genesis, and hence likelihood of steep shallow crustal thermal gradients at sites of the LOTI magmatism.

### 12.2.2. Nature of the carbonate-skarn-quartz rocks in the Outokumpu assemblage

Before the middle 1950s, it was popularly believed that these rocks represent sedimentary carbonate rocks and epiclastic quartzites. A dissident idea of a metasomatic origin of the carbonate rocks was proposed by Haapala (1936) but became vigorously opposed by Vähätalo (1953) and Disler (1953). Since the Borcherts (1954) contribution, an interpretation of the Outokumpu carbonates and quartz rocks as chemical carbonates and cherts was quickly adopted as an "official truth". During the 1990s occasional doubts about the sedimentary origin of the assemblage were presented, e.g. by Auclair et al. (1993), Laznicka (1993), and Kontinen (1998); all these authors proposing that an origin by silica-carbonate alteration from adjacent serpentinites was a more likely scenario. We found in this report that the chemical and mineralogical evidence of the nature of the Outokumpu carbonate and guartz rocks as alteration products of the adjacent serpentinites is insurmountably clear. Such uniformly Cr, Co, Ni and chromite rich while Zr, REE and zircon poor rocks as the Outokumpu carbonate-skarnquartz rocks simply cannot represent any sort of epiclastic or chemical sediments. The best analogy is by the listwaenite-birbirite type carbonate-silica alteration zones developed at margins of mantle peridotite bodies of many more intensely tectonized/disrupted ophiolite complexes.

Field relationships and isotopic evidence constrain, as we discuss elsewhere in this report, the carbonate-silica alteration in the Outokumpu assemblage a synobduction or immediately succeeding process. The presence of relicts of migrated hydrocarbons, probably petroleum, in the skarn-quartz rocks indicates the alteration took place at temperatures of ca. 100-250 °C as is typical of listwaenite-birbirite type alteration. We have no well-constrained explanation for the serpentinite-carbonate-silica zoning characteristic of the Outokumpu assemblage, but consider this an indication of that diffusion across the serpentinite-metasediment contacts was an essential component of the primary alteration process.

While there is no question about the dominantly nonsedimentary origin of the carbonateskarn-quartz rocks in the Outokumpu assemblage, one could still argue that some parts in it might yet represent hydrothermal sediments as cherts. That could be a likely situation if the silica-carbonate alteration of the peridotites occurred at seafloor seawater interface and was associated/driven by circulation of seawater in and out of the peridotites. Despite of our hard tries to locate such sediments during of the GEOMEX and previous/subsequent study in GTK, we have so far failed to show one. Furthermore, the numerical modeling of the silica-carbonate alteration of peridotite-serpentinite by Peter Alt-Epping during the GEOMEX, and before by Peabody and Einaudi (1992), consistently indicate that it involved rather a low temperature carbonic metamorphic than sulphatic seawater type alteration fluid. It is also most clear form the field evidence alone that the serpentinite fragments were tectonically detached form their source, and distributed among the host turbidites already before they were subjected to the silica-carbonate alteration.

### 12.2.3. Ore – host rock relationships

Our review of the past ore models indicated that since middle 1950s the Outokumpu ores have usually been interpreted in terms of strata-bound layers of exhalative sulphides on the seafloor (e.g. Borchert, 1954; Koistinen, 1981; Park, 1988; Gaál and Parkkinen, 1993). The views of Outokumpu sulphides as strata-bound or stratiform deposits owe much to the assumption that the Outokumpu-type carbonate-skarn-guartz rocks represented chemicalexhalative sediments, syngenetic or at least closely coeval with the sulphide deposits. However, the fact that these rocks in reality represent carbonate-silica altered metaperidotites (Haapala, 1936; Auclair et al., 1993; Kontinen, 1998; this study) greatly reduces the credibility of the concept of these ores as strata-bound/stratiform deposits. Another important factum is that all the known Outokumpu ores occur in environments that completely lack any types of syngenetic volcanic rocks or ocean floor hydrothermal sediments such as any types of cherts, silica or carbonate chimneys, Fe-Mn-rich metalliferous muds (umbers, ochres) etc. Furthermore, although syngenesis of the ores with the sulphidic black metamuds, that are common in the ore environments, has been proposed (e.g. Loukola-Ruskeeniemi, 1996; 1999), this is not likely in the light of the highly differing metal enrichment patterns and Pb isotope compositions, and the systematically sharp, nongradative contacts of the ore bodies and the black schists.

The cross-section maps of the prototype Outokumpu ore show that >90% of it locates inside serpentinite and the derivative carbonate-skarn-quartz rocks; therefore, the ore could actually be regarded as sort of ultramafic hosted deposit. The contacts of the Outokumpu ore have frequently been reported mostly very sharp, intrusive like; that was that what we also observed in our drill core studies. Furthermore, the wall rocks are mostly remarkably free of any ore-forming sulphides, at least anything further (>1 m) away from the actual contacts. And, most of the little sulphides that are present, appear diffunded or mechanically mobilized from the ore sheet (cf. Vähätalo, 1953; Huhma and Huhma, 1970). Only for its very uppermost edge the Outokumpu ore sticks out of its ultramafic envelope, wedging there locally in the black and mica schists of the Kaleva assemblage. Based on our observations on representative drill core from such locations, the ore has abrupt, sharp contacts also against the mica and black schists, which show no evidence of syngenetic enrichment in Cu and Co over the usual black schists background levels.

Then, if we look carefully at the cross-section maps over the Outokumpu main ore, for

which such data is extensively available, we note that the ore actually has a conformable relationship to none of the rock units in its host assemblage, but it in fact truncates with sharp contacts the entire rock sequence typical of the Outokumpu assemblage. This is especially clear situation for the upper contact of the ore sheet, which in numerous cross-sections is seen in contact against serpentinite for its lower edge, carbonate-skarn rocks for its middle part and quartz rock for its upper edge which locally wedges inside the mica and black schists of the Kaleva assemblage. Although the footwall contact is for most part against quartz rocks, even there one can see that the ore sheet truncates, not only the alteration zonation of the host assemblage, but also the F1 fold patterns contained in it (cf. Figs. 48-50). Overall, there can be little doubt about the relatively late syntectonic final emplacement of the ore. We are not at all wondering the early interpretations of the Outokumpu ore as a vein like intrusion of "ore magma".

Judging from the existing cross-section maps, published geological descriptions, and by our own scrutiny of representative core, the Vuonos ore is a very similar case with the prototype Outokumpu ore, with the exception that a larger part of the upper edge of the ore plate locates inside the Kalevian metasedimentary regime. Several workers (e.g. Peltola, 1978; Koistinen, 1981) have seen a clear stratigraphic affiliation of the Vuonos deposit with the black schists in its upper edge environment. However, our relogging and petrographical-geochemical studies on drill core from the upper edge ore sections revealed absolutely no evidence of sedimentary gradation between the ore and the black schists, but the ore to black schist contacts were invariably found, both lithologically and geochemically, "knife-sharp" and indicative of an epigenetic, load-like emplacement of the ore sheet.

The low-grade "Co-Ni zone" parallels of the Outokumpu and Vuonos main ore sheets have been interpreted as hydrothermal upflow zones originally below deposits that represent seafloor volcanic-exhalative sulphides (e.g. Koistinen, 1981; Treloar et al., 1981); although this concept has also been suspected (Parkkinen and Reino, 1985). The thin (mostly << 20 m), narrow (mostly <<100m) and long (at least >1 km) skarn-quartz rock hosted Co-Ni zones comprise volumetrically relatively minor layers lenses of chloritic schists, metamorphosed to chloriteorthoamphibole-cummingtonite±cordierite±garnet±spinel assemblages; these units have been interpreted as recording "calc-silicate units" (Koistinen, 1981) or more vaguely "rock units" (Treloar et al., 1981) affected by pre-metamorphic fluid movement and leaching. We found the chlorite layers as pervasively chloritized mafic dykes that are in variable extent ubiquitous in the Outokumpu massifs and their alteration zones as well. Our scrutiny of representative drill core from the Outokumpu (Keretti) Co-Ni zone suggests that much of the associated Cu-Co mineralization is in thin (1cm-50 cm) sharply bound quartz-sulphide veins very similar in mineralogy and texture with the main ore sheets; while the elevated Ni is reflects the relative abundance of the natively Ni-rich ultramafic derived gangue. Most of the Cu-Co bearing sulphide-guartz veins appear subparallel with the layering in their host rocks, but which clearly postdate the carbonate-silica and chlorite alterations. Furthermore, the systematically massive granoblastic textures of the ore veins suggest their emplacement post-dated also most of the penetrative deformation of the host chloritic and quartz rocks. Due to likelihood of pervasive recrystallization of the ore veins during the static metamorphic peak, this conclusion is somewhat uncertain, however. In any case, a syntectonic emplacement of the sulphide-quartz veins is clear judging from that a strong schistosity in the host chloritic dykes is sometimes sharply cut by the veins. Thus,

The Kylylahti deposit locates in a lithologically somewhat more varied, less deformed and significantly less metamorphosed environment (>100 °C lower peak) than the Outokumpu and Vuonos deposits, and therefore should keep the original ore versus rock features, as well as ore textures, better preserved than the Outokumpu or Vuonos deposits. The dominantly pyritic character of the massive-semimassive ore lenses, and many delicate ore textures, especially in the relatively large deep ore lens support this presumption. Study of the Kylylahti deposit is, however, hindered by its poor exposure and that presently only drill core observation and sampling of the ore zone is possible. Nevertheless, from the available plan and cross-section maps, and drill core observations, one gets a strong impression that the massive-semimassive sulphide lensoids would have formed exactly at the quartz rock to black schist interfaces at the margins of the host serpentinite bodies, and record just some relatively minor remodification by

later folding and remobilization, in places, however, to such extend that the ore lenses for their large parts wedge inside the immediately flanking black schists. Actually this seems, with some variation in the late deformation/remobilization, pretty much the situation of about the entire here studied Outokumpu deposits. In the other Outokumpu area deposits, the ore bodies record somewhat more remobilization than at Kylylahti, but in none of the cases, excluding perhaps the Riihilahti sulphides, even to that extend that there had occurred complete separation of the ore bodies from the quartz rock to black schist interfaces.

The skarn-hosted disseminated-stringer mineralization paralleling the Kylylahti massivesemimassive lenses provides some of the most pertinent information of the timing of the ore emplacement in the Outokumpu context. Namely, thorough the parallel mineralization, the pay sulphides are confined in a specific component of carbonate-tremolite "skarn" that is brecciating, veining and replacing the normal Outokumpu-type ultramafite-derived carbonate, skarn and quartz rocks and the contained basitic layers (dykes). Importantly, the mineralised skarn component veins and brecciates also a strong subvertical mylonitic schistosity ubiquitous in the host quartz rocks of the Kylylahti ore zone. This relation together with the systematically static textures and peak-metamorphic mineralogy of the replacement skarn materials dates the parallel mineralization syntectonic and synmetamorphic, possibly only slightly older than the actual metamorphic peaking.

The timing significance of the structural relationships in the Kylylahti parallel zone is not plain clear since one could the brecciating skarn related mineralization to late-tectonic reworking of an existing mineralization, assuming that the source of the remobilized ore materials were in the skarn zone itself or in the adjacent massive-semimassive bodies. Neither of these scenarios seems likely, however, since there are no evidence of pervasive internal reorganization of the sulphides in the parallel zone, and as the parallel mineralization seems a far too extensive and mineralogically-structurally complex feature to represent just sulphide remobilization from the semimassive-massive lenses. Furthermore, there are minor patches/lenses of massive-semimassive sulphides inside the parallel mineralization, showing close similarity in their textures, mineral compositions and in Cu-Co tenors to the main semimassive-massive sulphide-quartz lenses. Altogether, the parallel mineralization seems to have formed concurrently with the massive-semimassive lenses, and, hence, based on the structural evidence from the former, the whole deposit looks like a syntectonic formation.

One striking feature of the Cu mineralization at Kylylahti is that it is strictly confined along the near vertical N-S fault/shear zone defining the eastern contact of the Kylylahti ultramafic complex. As the sulphide lenses and paralleling disseminations about exactly obey the faulted contact zone, one cannot avoid rising the hypothesis that the boundary  $D_{2c}$  (?) faults and related folding controlled, not only the obvious limited remobilization of the ore materials, but perhaps also their initial deposition. Such scenario would be in perfect harmony with the skarn zone evidence of the structurally late emplacement of the ore sulphides. And, as we showed above, also in the case of Outokumpu and Vuonos deposits, we have evidence of late structural emplacement of the ore bodies. We are fully aware of the conflict we have here with the interpretation of Koistinen (1981), who proposed that the Vuonos and Outokumpu ores would record D<sub>1</sub> isoclinal folding of sedimentary layering. The idea of isoclinal D<sub>1</sub> folding of the ore is debatable, however. Namely, if indeed  $D_1$  folded, why would the ore sheets themselves, up to 400 m wide and 4000 m long, never outline outcrop and map-scale isoclinal or other tight fold forms, in spite of that they are ubiquitous in the surrounding Outokumpu assemblage. Quite the contrary, in numerous cross-section maps the ore bodies are seen to intersect the tight to isoclinal D<sub>1</sub> fold structures recorded by the host assemblage. Hence, we are inclined to suspect that the tight interlamination of the ore and its wall rocks at the upper edges of the Vuonos and Outokumpu ores, would in fact represent veining of the ore into previously tightly D1 folded host rocks, rather than isoclinal folding. Without access to the critical mine areas anymore, this is something that is difficult to prove, however. Fortunately, the problem of the emplacement timing can be resolved at Kylylahti in the very day when there will be sufficiently underground access to its more informative deeper ore parts.

The other Outokumpu type deposits, as e.g. the Luikonlahti, Hietajärvi, Saramäki, Riihilahti etc., occur basically in a very similar way than the above-described Outokumpu, Vuonos and

Kylylahti deposits. Because of their relatively small sizes and locations in middle to upper amphibolite environments, these deposits are, however, like the Vuonos deposit, all pervasively peakmetamorphosed to pyrrhotitic assemblages. It seems that the metamorphism was associated with an increase in the ability of the ores to flow plastically under stress, reflecting the lower shear strength of pyrrhotite compared to that of pyrite, and that of quartz rapidly decreasing with temperature increase. This may be one factor behind the distinct quartz sulphide banding in parts of Outokumpu and Vuonos deposits. In the lesser and higher-grade deposits much of the possible syntectonic plastic flow textures became recrystallized and annealed during the late, apparently long-lasted static regional metamorphic peaking and subsequent cooling.

### 12.2.4. Sulphide assemblages, microstructures and compositions

Detailed ore petrographic studies were a low priority in the GEOMEX modelling subproject. The main reason for this was the previous studies that claimed a premetamorphic, sedimentary origin of the Outokumpu deposits (e.g. Koistinen, 1981), and their subsequent amphibolite facies metamorphism. Namely, in this case, a more or less complete wipe out of the ores for their primary textures and structures could be expected; on the basis of what is known on sulphide mineral stabilities and mechanical properties, and recognizing the high temperature (520-770 °C) peaking of the regional metamorphism, apparent longevity (several tens of millions of years) of the metamorphic heating, and multiply deformed and highly strained nature of the Outokumpu ore environments. It is instructive to remember here that, for several of the deposits, the temperatures at their metamorphic peaking exceeded thermal stabilities of several of the in Outokumpu ores important sulphides, as e.g. chalcopyrite and pentlandite, which both have maximum thermal stabilities significantly below 600 °C for the relevant bulk ore compositions (cf. Vaughan and Graig, 1997). It is useful to recognize, also, that in a distinction to silicates, chemical equilibration of most ore sulphides takes place at geologically considered extremely fast rates, within tens of thousands of years to less than minutes, at any temperatures elevated above 300 °C (e.g. Barton and Skinner, 1979; Vaughan and Graig, 1997). Moreover, it must be noted that the common sulphides of copper, lead, zinc and Ni are all relatively soft and ductile at metamorphic temperatures, and that they show a high tendency to anneal even at submetamorphic temperature conditions (e.g. Stanton, 1972; Clark and Kelly, 1973; Cox et al., 1981; Marshall and Gilligan, 1987).

This all means that, although the relatively simple chemical compositions of the Outokumpu ores prevented any major modifications in the primary cross-sulphide mineralogies; the present ore textures, structures and mineral equilibriums, however, simply must be thoroughly metamorphic. Furthermore, because of the easy equilibration of most sulphide ores, they usually do not preserve, unlike many silicate rocks, the mineral assemblages and compositions that they attainted at the peak metamorphism. Therefore, that what we are observing in high metamorphic sulphide ores, such as in the Outokumpu ores, is (probably more often than what we would like it to be) about only retrograde textures, assemblages and equilibrium. In the Outokumpu ores only pyrite, which has a maximum low-pressure stability of 742+-1 °C, rising ca. 14 °C per kbar of confining pressure, could, in pyrite rich assemblages, represent a primary phase preserving its premetamorphic textures and compositions.

Nevertheless, to get some general idea of the deposit petrography, we studied microscopically several representative samples per each of the deposits sampled for this work. Much of the results of these studies were documented in association of the deposit descriptions, only a brief summary of the central findings is given below.

The Kylylahti deposit, having peaked in lower amphibolite facies at ca. 500 °C, is clearly the lowest metamorphosed one of the Outokumpu deposits; all the other deposits have been subjected to temperatures of at least 600 °C. Therefore Kylylahti should provide the best preservation of ore textures and mineral assemblages useful in determining the primary origin of the Outokumpu ores. In our reconnaissance petrographic study of the massive-semimassive lenses at Kylylahti, we recognized four distinct mineralogical-structural ore types: (1) banded-striated pyrite ore; (2) blebby pyrite ore; (3) pyrrhotite ore and (4) pyrrhotite-magnetite. Of these

ore types, a metamorphic origin of the pyrrhotitic types, by peak stage replacement and recrystallization of the pyrite ore facies, is most clear. The pyrite ore types occur in an interbanded way so that the blebby ore is found in clear tectonically reworked bands or lenses within the banded-striated pyrite ore. An ultimately sedimentary origin of the pyritic ore facies, as e.g. in a sulphidic cherty unit of the adjacent sulphidic black metamuds could be speculated, but the overall extreme poverty of the pyritic ore in any lithophile elements such as AI, K, Na and Zr militates against such an hypothesis. Importantly, the thoroughly low Cr content of the massive-semimassive lenses excludes their cogenesis also with the metasomatic quartz rocks of the Outokumpu assemblage. One possibility remaining is that the pyritic ore facies would represent syntectonic vein-fill type rhythmic deposition of silica and pyrite, modified by accompanying or later shearing. But as well the banding in the pyritic ore may be of a purely metamorphic-tectonic origin as the ubiquitous bandings in the adjacent, ultimately peridotite-derived skarn-quartz rocks must be.

Although the banded-striated pyritic facies seems the earliest component in the Kylylahti ore lenses, there are clearly more chalcopyrite and sphalerite in the paragenetically-structurally younger blebby and pyrrhotitic ores. A part of the chalcopyrite and sphalerite in the blebby ore bands locates in fine grains in the blebs; a part is in coarser grains replacing pyrite at the bleb margins. The finer-grained parts of the blebs often show poorly developed concentric and radial growth banding of pyrite, pyrrhotite, sphalerite and chalcopyrite. Although a pretectonic colloformal origin of these growth patterns could be argued, a syntectonic origin concurrent with the bleb formation seems more likely. Comparable pyrite textures have been described e.g. from the Rosebery massive sulphides, Tasmania, and have been there ascribed to syntectonic dissolution-reprecipitation (Aerden, 1994). A syntectonic origin of the Kylylahti pyrite blebs is supported by the fact that pyrites especially at the bleb margins frequently show oscillatory growth zoning (for Co, As, Ni etc.) as is typical of the peak-metamorphic to retrograde pyrite cubes in the pyrrhotitic ore parts. The preservation of the delicate growth patterns and the pyrite pervasivelv oscillatory zoning in blebs, in such complexly and deformed/metamorphosed environment as at Kylylahti, suggest they must have formed relatively late, probably near metamorphic peak. Further study is necessary to clarify if the chalcopyrite, Co-pyrite and sphalerite were deposited already along with the earliest pyrite components to be dissoluted-reprecipitated in the blebby ore bands, or was the Cu-Co-Zn mineralization perhaps an entirely syntectonic process with an extraneous source of the metals.

The pyritic ore facies in the Outokumpu deposit seems petrographically similar with the Kylylahti pyritic ore, although the peak-metamorphic static overprint in Outokumpu is clearly more severe. As in Kylylahti, also in Outokumpu and Vuonos parts of the massive-semimassive lenses show distinct compositional banding, which usually has been regarded sedimentary in its origin (Peltola, 1978; Koistinen, 1981; Papunen, 1987). In absence of other evidence but the mineralogical quartz-sulphide layering to support the hypothesis of sedimentary origin, we are inclined to associate the Outokumpu-Vuonos or banding with the very similar looking metamorphic-tectonic segregation-flow banding in their peridotite-derived quartzose wall rocks.

The deposits locating in middle-upper amphibolite facies terrains, like Luikonlahti, Vuonos Hietajärvi etc., have all been transformed pervasively pyrrhotitic, at the latest with the peakmetamorphism of the deposits. Of these deposits only the large Outokumpu deposit has escaped of pervasive pyrrhotitization. It seems that the Outokumpu ore already at the peak located in its present position for most part inside of the carbonate-skarn-quartz rocks of the Outokumpu assemblage, and that it thus was relatively protected for influx of reductive fluids required for decomposition of pyrite to pyrrhotite (cf. Ohmoto and Goldhaber, 1997). The preferred distribution of pyrrhotitic ore along the serpentinite contacts or inside serpentinite indicates that a supply of hydrogen in dehydration fluids from the serpentinites probably controlled the pyrrhotitization. In case of the other deposits like Vuonos, Luikonlahti, Perttilahti, Saramäki and Hietajärvi, which have a more intimate association of with the usually graphite bearing wall-rock metasediments, obviously were reduced by fluids generated by water-graphite reactions in the organic rich sedimentary wall rocks (cf. Ohmoto and Goldhaber, 1977). Although an isochemical metamorphism of massive sulphide bodies is usually taken as granted, there are certain trends in the trace metal compositions of the Outokumpu deposits that suggest this may not entirely apply here. Foremost, concentrations of As, Au, Pb, Sb and Se seem to be distinctly lower in the higher grade deposits, as at Luikonlahti. This, and myrmekitic intergrowth of sulphides and quartz in the pyrrhotitic ores hint of their limited partial melting. As such melt fractions likely were enriched in the aforementioned low melting point chalcophile elements elements (e.g Bailie and Reid, 2005), their escape from the ore bodies could explain the bias to low concentrations in the highest metamorphic deposits. In future studies this issue should be checked further.

It is clear that all the Outokumpu area deposits have seen the regional peakmetamorphism, and even that they are all thoroughly peak or near peakmetamorphic for their textures, structures, mineral assemblages and equilibriums. This does not tell, however, if the deposits were premetamorphic or synmetamorphic, but only says that resolving of that question will be very difficult.

### 12.2.5. Geochemical composition of the ores

The high Cu/Zn and Cu/Pb characterizing the Outokumpu Cu-Co-Zn deposits point to an origin from a ultramafic-mafic rather than acid-intermediate source association. On the other hand, the high Co/Ni >1 typical of the Outokumpu deposits has been considered an indication of granitic source. It is more probable, however, that the high Co/Ni is rather a reflection of the better solubility of Co over Ni in most ore forming fluids than a source signature. High Ni, low Se/S and Se/As likewise the low Ag, Bi, Sb and Pb are among such geochemical features of the Outokumpu deposits that warrant a more detailed discussion. In the following we will assume that these features would all be preserved unmodified from their "original" values. This is, however, a bit uncertain premise, as there is, as we briefed above, some evidence of that the effects of metamorphism to the concentrations of especially the more "volatile" ore elements may have been significant and differential.

# <u>High Ni</u>

The Outokumpu ores are, compared to most other Cu-Zn dominant hydrothermal massive sulphide types, peculiarly high in Ni, in some cases so Ni rich (up to >0.5 wt% Ni) that their origin even as magmatic sulphides could be argued. Importantly, also those hydrothermal massive sulphide ore types that show the most similarity with the Outokumpu type are systematically low in Ni. This concerns, for example, the modern ocean ridge and also ancient Besshi and Cyprus type sulphides, which hardly ever contain >100 ppm Ni, even in individual samples. Data from present mid-ocean ridge deposits suggest that low Ni contents would characterize even the ultramafic-floored hydrothermal vent fluids and sulphides (e.g. Bogdanov et al., 1997; Murphy and Meyer, 1998). Also massive sulphide deposits from ancient bimodal felsic-mafic associations are systematically very low in Ni, also for such deposits that have considerable volumes of ultramafic and/or mafic rocks at their footwalls, as e.g. the giant late Archaean Kidd Creek (Hannington et al., 1999) and some of the large deposits of the Iberian Pyrite Belt (e.g. Almódovar et al., 1995; Marcoux et al., 1996). Altogether, it seems that Ni was a highly immobile element in seafloor alteration processes, throughout the geological time, and independent of the lithological assemblage in the basement substratum. In terms of the overall metal pattern, from the common sulphide types, perhaps closest to the Outokumpu type come some deposits of the sulphur-rich end-member of the iron-oxide-Cu-Au clan, which may show a Cu-Co-Ni-As-Ag-Au dominated metal pattern very similar with Outokumpu type (e.g. Baker, 1998; Wang and Williams, 2001); although the average Ni tenors (<100-1000 ppm) also in most of these deposits remain significantly below the 1000-2000 ppm level typical of the Outokumpu deposits.

Another genetically important aspect of the Ni geochemistry in Outokumpu ores is that, at least in the Outokumpu-Vuonos system, Ni does not show clear correlation with any of the

other ore metals. This is a somewhat surprising feature noting that at least in the Ni-richest iron oxide-Cu-Au and volcanic associated deposits Ni tends to show positive correlation at least with Co (e.g. Barker, 1998; Hannington et al., 1999). One explanation could be that Ni in Outokumpu deposits was not among the "primary" ore metals, but was an irregularly overprinted or inherited element, signalling of a polygenetic origin of the metal enrichment.

The weak Ni-sulphide dissemination in the Outokumpu assemblage is usually genetically connected to the formation of the Cu-Co-Zn ores (e.g. Papunen, 1987). However, the weak Ni dissemination, and also the tattered Kokka type Ni mineralizations, are such a ubiquitous feature in the carbonate-skarn-quartz alteration zones, all over the Outokumpu area, that they very unlikely represent a syngenetic facies of the Cu-Co-Zn ores, especially as they normally do not show any tendency to Cu enrichment or elevated Co/Ni. Further, as we noted above, the Kokka type Ni mineralizations should not be mixed with the "Co-Ni mineralizations" as paralleling the Outokumpu, Vuonos and Kylylahti ores, and which seem to record overprinting of Cu-Co-Zn mineralization onto the universal Ni sulphide mineralization in the carbonate-skarn-quartz zones (cf. Parkkinen and Reino, 1985).

It should be remarked, too, that although there was the so-called Ni mine at Vuonos, all the economic deposits mined in the past were of the Cu-Co-Zn type. The Vuonos Ni mine utilized a tectonically thickened part of the carbonate-skarn-quartz rock shell of the Vuonos serpentinite, but which contained also tattered, weak enrichments in Cu-Co-Zn, apparently representing overprinting on the background Ni mineralization in the host carbonate-skarn-quartz rocks.

# Low Se/S ratios

The  $\delta^{34}$ S values in the main Outokumpu ore mostly between –2 and +2‰ have been interpreted as an indication of a dominantly mantle source of the ore sulphur (Mäkelä, 1975). The spatially closest possible source of isotopically mantle-like sulphur would be the mantle represented by the host serpentinites. However, in the light of the low 10<sup>6</sup> x Se/S values from <10 to 100 of the Outokumpu ores, mantle at least as a prime source of the sulphur seems an unlikely option. First, Se/S ratio estimated for primary mantle is about 300 (McDonough and Sun; Hattori 2002) and thus significantly higher than the <100 typical of Outokumpu ores. Second, the available data on sulphides in mantle xenoliths suggest Se is preferring the solid residue in mantle melting (e.g. Hattori, 2002), and that thus the primary  $10^6$  x Se/S values for such highly depleted peridotites as the Outokumpu peridotites probably were rather above than below the 300 of the primitive mantle. The high average Se/S x10<sup>6</sup> value of 2157 for ultramafichosted hydrothermal sulphides from the Mid-Atlantic Logatscev field suggests that mantle hosted seafloor copper sulphides indeed would have higher Se/S x 10<sup>6</sup> values than either primitive mantle (300) or basalt-floored ocean-ridge sulphides (120-300). Therefore, on the basis of the Se/S ratios, it seems unlikely that the highly depleted Outokumpu peridotites, or the highly depleted residual mantle they represent, were the sole, or perhaps even the dominant S-Se source for the Outokumpu ores. If taken at their face values, the low Se/S ratios of the Outokumpu deposits strongly indicate that the principal S source was either in the average upper crust or seawater, which presently have average Se/S x  $10^6$  of 53 and 0.14, respectively.

### High Se/As ratios

Se and As, which both are among the quantitatively more abundant trace metals in the Outokumpu deposits, form an pair of highly chalcophile elements that fractionates considerably in Earths magmatic differentiation processes. Thus, and as both these elements in the Outokumpu ore show clear affinity to the "primary" pyrite generations, Se/As ratios should provide, besides Se/S, another feasible means to evaluate the source of the sulphur and chalcophile trace metals in these deposits. Due to the relatively low Se but moderate As concentrations (for massive sulphides), Se/As ratios in Outokumpu massive-semimassive deposits are distinctly low, ranging from 0.3 in Outokumpu down to 0.004 in Kylylahti. These values are significantly lower compared to the average Se/As of 1.5 and 3.6 in primitive mantle

and theoretical primitive mantle sulphides, respectively (McDonough and Sun, 1995; Hattori, 2002), or as compared to the average Se/As of 4.0 in the mantle-floored Logatchew field sulphides (Murphy and Mayer, 1998). In comparison, average upper crust and seawater have Se/As of 0.04 and 0.13, respectively (Wedepohl, 1995; Nozaki, earth.agu.org/eos\_ elec/97025e.html). Thus, as the low Se/S, also the low Se/As ratios in Outokumpu sulphides militate against mantle as a dominant sulphur/metal source, while promote an important role of evolved crust or seawater - at least for the S, Se and As budget in the Outokumpu-type ores.

# Low Ag, Bi, Pb, and Sb

The low Ag as well low Pb and Sb in the Outokumpu ore sulphides speak against epithermal origin, or more generally, importance of low temperature aqueous sulphur complexes as metal carriers. The systematically low Bi and constant absence of highsulphidation minerals (bornite-enargite-tennantite) in Outokumpu deposits indicate that magmatic volatiles probably did not contribute to their genesis.

The low Pb in the Outokumpu deposits could be taken as a sign of very low, mantle-like Pb in their metal source. It must be noted, however, that there are clearly also other possible pathways, than an ultramafic-mafic source, to low lead in hydrothermal sulphides. For example, many Cu+Au±Co±Ni deposits of the Cu-Au(Fe-oxide) style are also extremely low in Pb despite of their assumed metal sources in relatively Pb-rich crustal rocks and hypersaline nature of the ore-forming fluids (e.g. Baker, 1998; Wang and Williams, 2001). The shear-zone related Shinghbum Cu-deposits are another example of very low Pb in spite of an apparent metal source of these deposits in dominantly mafic to intermediate-felsic crustal rocks (e.g. Ghosh, 1972). But then again, not are ultramafic-mafic sourced deposits always distinctly low in Pb but e.g. the mantle-floored massive sulphides at Logatchev field comprise actually not-so-low Pb in the range of 50-4000 ppm (e.g. Bogdanov et al., 1997; Murphy, 1998). These examples and theoretical considerations indicate, that the Pb content of hydrothermal sulphides is at least as much dependent on the physical-chemical parameters related to the transporting fluid(s) and deposition than the composition of the metal source. One clear trend is that high temperature syntectonic sulphide deposits are predominantly Pb poor, probably because in these systems the relatively good high temperature solubility of Pb in typical ore forming fluids allows more possibilities for separation of the Pb from the metals of somewhat lesser such solubility, as from Cu, and Zn, for example.

# 12.2.6. Isotopic constraints

# Pb isotope evidence of the metal source of the Cu-Co-Zn ores

Pb isotope ratios provide a powerful, but rarely unambiguous tool for constraining metal sources of sulphide ore deposits (Tosdal et al., 1999). To supplement the existing few Pb isotope data on the Outokumpu deposits, we determined Pb isotope ratios for a number of bulk ore samples from the in the Outokumpu context relatively Pb-rich Outokumpu and Vuonos deposits, and for comparison, also for a few samples from the other deposits. The Outokumpu and Vuonos bulk ore data we found plot on the uranogenic <sup>207</sup>Pb/<sup>204</sup>Pb vs. <sup>206</sup>Pb/<sup>204</sup>Pb diagram within a relatively tight array pointing to similar <sup>207</sup>Pb/<sup>204</sup>Pb ratios as what had been previously measured for a few galenas of the Outokumpu ore. The <sup>207</sup>Pb/<sup>204</sup>Pb ratios of the Outokumpu galenas plotting well below the average crustal Pb growth curves, as those by Stacey Kramers (1975) and Cumming and Richards (1975), have been interpreted as an indication of mantlelike source of the primary ore Pb (Vaasjoki, 1981). The new results for the Outokumpu and Vuonos bulk sulphides support this interpretation, and, noting the comparable geochemical behaviour of Pb, Cu and Zn in typical hydrothermal fluids (Henley et al., 1985), the concept that thus perhaps also the main metals Cu, Zn and Co in these two large sulphide bodies were derived from a mantle-like source. It could be added to this that the very low Pb content of the Outokumpu and Vuonos ores is consistent with, but as we noted above, does not necessarily require, a mantle peridotite, or directly mantle-derived mafic-ultramafic magmatic, and thus

### extremely Pb poor metal source.

The bulk sulphide Pb isotope determinations on the other, smaller Outokumpu area deposits showed, however, that in them a significant part of the ore Pb is likely from the local Kaleva sedimentary sources. This is particularly obvious for the intimately metavolcanite-metasediment associated stringer sulphides of Riihilahti, but also the smaller semimassive lenses of the Kylylahti deposit, which both yield Pb isotope values between the values of the nearby black schists and Outokumpu and Vuonos ores. However, samples from the relatively large Kylylahti "deep ore" lens, which is more separated from the local metasediments, yielded Pb isotope ratios similar to those measured for the Outokumpu and Vuonos bulk sulphide samples. This all suggests that, at least in Kylylahti, the primary Pb signature was the same as at Outokumpu and Vuonos, and that the tendency to Kaleva like isotope ratios would likely represent a later, probably synmetamorphic "contamination".

Although the available Pb isotope data thus provide a strong evidence of a mantle like source of the ore Pb, considerable uncertainty yet remains about where this mantle like source actually was. The most obvious source was the mantle represented by the host serpentinites, but the surprisingly Outokumpu-like feldspar Pb compositions of some the 1870 Ma granites in the western part of the NKSB suggest that, at least Pb isotopically, also an orogenic magmatic source could have been possible.

#### Pb isotope evidence of timing of the ore formation

Perhaps most importantly, the bulk sulphide and galena samples analysed from Outokumpu and Vuonos ores define on the uranogenic Pb isotope diagram, screened for a couple of obvious outlier samples, an apparent isochron of 1943±85 Ma (MSWD=12, n=12), which seems to date the time of the formation of the Outokumpu deposits. Although the uncertainty with the indicated age is large, it may not be only a fortuitous coincidence that comparable U-Pb zircon ages between 1972±18 Ma and 1952+-2 Ma are obtained for metagabbros and plagiogranites from both in the Outokumpu and Jormua ultramafic-mafic bodies (Huhma, 1985; Kontinen 1987, Peltonen et al. 1998, this report). Rather the Outokumpu-Vuonos Pb-Pb isochron could be seen as a strong evidence of that the Outokumpu sulphides were somehow related to the 1.95 Ga magmatism indicated by the gabbros-plagiogranites.

We ended above to an interpretation that the Outokumpu serpentinite bodies would represent, as the more northerly Jormua mafic-ultramafic complex, ophiolitic fragments from a Red-Sea type embryonic ocean developed subsequent to the 2.0-1.97 Ga break-up of the Karelian Craton (cf. Kontinen, 1987; Peltonen et al., 1996, 1998; Peltonen and Kontinen, 2004). On this account a straightforward interpretation of the apparently 1943±85 Ma Outokumpu sulphides would be that they would represent seafloor hydrothermal accumulations formed along with the 1.97-1.95 magmatism in the ophiolites, so that the magmatism (gabbro intrusions) provided the heat energy for driving the ore-forming hydrothermal activity.

We determined Pb isotope ratios also for a number of carbonate-skarn-quartz rocks from the Outokumpu assemblage. These whole rock data plot in the uranogenic Pb isotope diagram along a line with an age of 1908+-27 Ma (MSDW=669, n=10). The large MSDW implies considerable open system behaviour and thus the absolute age significance of the data is somewhat uncertain. Nevertheless, what this isochron seems to date is an early introduction of relatively significant amounts of extraneous uranium in the carbonate-skarn-quartz rocks, which, as mantle-peridotite derived rocks, initially had very low U (as well as Th and Pb) concentrations and U/Th and U/Pb ratios. As there is petrographic evidence of that significant uranium was added in association with the initial low-T, pre D1 carbonation-silicification process, it seems that the Pb-Pb isochron of the carbonate-skarn-quartz rocks approximately dates the time of the primary silica-carbonate alteration. The nearest and most likely source of the uranium was in the adjacent, relatively U-rich black schists, which based on data from the relatively lowly metamorphosed Kylylahti samples, yield an isochron age of 1914+-21 Ma (MSWD=5.6, n=9), which obviously dates the synsedimentary-diagenetic enrichment of the protholith black shales in authigenic uranium, and thereby yields the approximate age of the protolith black shale deposition.

The 1908+-27 Ma Pb-isochron age obtained for the carbonate-silica alteration agrees well with the structural and other field-evidence that constrain it an early pre-D1 process, but one which nevertheless must have post-dated the probably early syn-obduction stage tectonic fragmentation and incorporation of the protolith mantle bodies into the Upper Kaleva metasediments. Importantly, if the 1908+-27 Ma and 1943±85 Ma Pb-isochron ages of the carbonate-silica alteration and Cu-Co-Zn ore bodies, respectively, are taken at their face values, this would imply that of the carbonate-skarn-quartz rocks formed perhaps by as much as 40-50 Ma later than the Cu-Zn-Co ores.

The Pb isotope compositions of carbonate-skarn-quartz rock plot in the uranogenic Pbisotope diagram along the line definend by the samples from the Kalevian black and mica schists. This suggests that, but U, also some relatively significant metasediment-derived Pb was introduced with the primary carbonate-silica alteration, or during subsequent metamorphism. As the Pb contents of the carbonate-skarn-quartz averages to ca. 5 ppm, in absolute terms the Pb addition was very minor, however. The universally very low Pb in the carbonate-skarn quartz provides strong evidence of a remarkable regional Pb immobility throughout the post-obduction deformation-metamorphism of the Outokumpu Allochthon. This could well be an implication of those suitable preconditions for syntectonic base metal mineralization never existed within the allochton. The complete absence of signs of either base or precious metal mineralization, even in form of erratic sulphide veins, in the turbidite bulk of the allochton, is another strong indication that this indeed may have been the case.

#### Other isotopes

The five point Re-Os isochron obtained for the Luikonlahti deposit by Tom McCandless (written comm., 1999) produces an age of 1915+-261Ma, which is within the related large uncertainties similar with the Pb-Pb isochron age of 1943±85 Ma obtained here for the Vuonos and Outokumpu deposits. The Luikonlahti Re-Os isochron thus provides some further support for interpretations of the Outokumpu deposits as pretectonic for their ultimate origin. In addition, the Re-Os isochron points to a high initial <sup>187</sup>Os/<sup>188</sup>Os value of 0.477 for the Luikonlahti sulphides. As this value is well above the <sup>187</sup>Os/<sup>188</sup>Os value of 0.12 of the present, and likely also Proterozoic mantle, a source of radiogenic Os must have existed. This could have been, but upper crust, also seawater, which both already during Precambrian were strongly radiogenic for Os.

We observed in this work that  $\epsilon_{Nd(1950Ma)}$  values for samples from the Outokumpu, Vuonos and Kylylahti massive-semimassive ores vary so that samples from ore parts enclosed in metasediments tend to show wacke-type REE patterns, and yield negative  $\epsilon_{Nd(1950Ma)}$  from -5 to -3, while ore enclosed in serpentinite-carbonate-skarn-guartz rock environments tend to have more variable REE patterns, and  $\epsilon_{Nd(1950Ma)}$  values clustering around ±0. We addressed this situation to an indication of an introduction most of the ore REE concurrent with the final ore emplacement and/or during metamorphism from the local wall rocks. Though the REE of Outokumpu ores is usually very low, sporadic high concentrations do occur, especially in the stringer parts of Outokumpu, Kylylahti and Riihilahti deposits. Samples from these enrichments yield cNd(1950Ma) values around ±0 for Outokumpu and Kylylahti but significantly lower values from –3 to –5 for Riihilahti. It is not yet entirely clear whether these REE enrichments would be related to the primary ore formation stage or subsequent mobilisation of REE. Nevertheless, it is worth to note, that the  $\epsilon_{Nd(1950Ma)}$  data also form the high REE enrichments support importance of local sources in the ore REE budgets. Accordingly, REE in Outokumpu and Kylylahti stringers seems to derive mainly from the included metabasite component (dykes), which in the Outokumpu assemblage mostly have  $\varepsilon_{Nd(1950Ma)}$  also close to  $\pm 0$ , while in Riihilahti the ore REE seems to represent a mixture from the local Lower Kaleva metasediments and metabasites, which have very negative ca. -8 and close to zero  $\epsilon_{Nd(1950Ma)}$  values, respectively.

Previous studies and our own small reconnaissance study of Rb-Sr isotopes of the

Outokumpu ores and its host rocks attest to profound and complex metamorphic resetting of this isotope system in most of the included rock types. Probable closed system behaviour (during metamorphism and later) was observed only for some of the cleanest and Rb-poorest of the peridotite-derived carbonate rocks in the Outokumpu assemblage. Two samples from such carbonate rocks yielded <sup>87</sup>Sr/<sup>86</sup>Sr(1900 Ma) values that are significantly higher, 0.7049 and 0.7054, than the estimated <sup>87</sup>Sr/<sup>86</sup>Sr of ca. 0.7024 of the 1900 Ma mantle, but fall well within the range of <sup>87</sup>Sr/<sup>86</sup>Sr values from 0.7047 to 0.7060 documented for the 1.91-1.85 Ga seawater (e.g. Mirota and Veizer, 1994; Whittaker et al., 1998). This suggests seawater origin of the Sr and geochemically similar Ca in the carbonate rocks. But as we pointed earlier, a pretectonic origin of the carbonate-silica alteration at seafloor seems, however, an unlikely scenario, basically because the tectonic emplacement of the peridotite bodies among the Upper Kaleva turbidites preceded the carbonate-silica alteration, and as the alteration fluid was rather a aqueous-carbonic metamorphic type fluid than unmodified seawater. The source of Sr+Ca thus must have been in trapped seawater, or in carbonate rock fragments in the enclosing Kalevian metaturbidites, mixed/soluted in the early metamorphic fluid that contributed to the carbonate alteration.

More systematic sulphur isotope data exists only for the Outokumpu ore. The  $\delta^{34}$ S values for sulphides in the Outokumpu main massive-semimassive ore cluster around ±0 ‰ with a total range from -8 % to +6 %, while ore and guartz rock bands in a small satellite ore body, and at margins of the main ore sheet, show a much wider range between -20 ‰ and +1 ‰, with an emphasis on the more negative values (Mäkelä, 1975). Mäkelä (1975) addressed the wide variation in  $\delta^{34}$ S values in the banded satellite ore to "a submarine volcanic exhalative mechanism" involving fluctuations in the mixing ratio of sulphur from the vent fluid and ambient seawater. We considered above that quartz rocks with  $\delta^{34}$ S of -20 ‰ to -14 ‰ injected with ore veins with  $\delta^{34}$ S of +0±2 ‰ and subsequent variable peak-metamorphic equilibration is a more likely explanation of the  $\delta^{34}$ S pattern in the satellite ore. An urgent reason for this reinterpretation is that the quartz rock intercalations in the satellite ore do not actually represent sedimentary materials, as Mäkelä (1974) believed, but are normal chrome/chromite rich Outokumpu type quartz rocks of silicified peridotite origin. Interpreting the  $\delta^{34}$ S values of the main Outokumpu ore is difficult. One often proposed model is that the  $\delta^{34}$ S values mostly around ±0 indicate a dominantly mantle-like (mantle, mantle-derived igneous) source of the sulphur. It must be said, however, that  $\delta^{34}$ S values of ±0 ‰ are, by no means an unambiguous proof of mantle or magmatic origin but instead there are several possible routes to the zero value (see e.g. Ohmoto and Goldhaber, 1997). One such pathway would be by a very largescale syntectonic, say fault-controlled, hydrothermal system tapping S from large domains of the continental crust, which on average has to have a mantle-like  $\delta^{34}$ S value of ca. ±0‰. One fundamental difficulty in interpretation of the sulphur isotope data for Outokumpu is that we do not accurately know the 1.95 Ga seawater sulphate concentration and its sulphur isotopic composition.

The few available  $\delta^{18}$ O data for gangue quartz in Outokumpu ore define a range from +13.6 ‰ to +18.4 ‰. Similar values from +15.2 ‰ to 16.3 ‰ seem to characterize also the most "primary" looking quartz rocks in the Outokumpu assemblage. These values are significantly higher than the  $\delta^{18}$ O values from +2 to +12‰ that are usual for gangue quartzes with volcanic hosted seafloor hydrothermal massive sulphides (Huston, 1999). There are some examples of seafloor massive sulphides with gangue quartz of similarly high in  $\delta^{18}$ O as the Outokumpu quartzes, as e.g. from some deposits of Iberian Pyrite Belt, but in these cases the high  $\delta^{18}$ O have been found secondary, and to origin from re-equilibration with low-temperature metamorphic fluids (e.g. Cathelineau et al., 2001). Equilibration with regional metamorphic fluids seems the most plausible explanation of the high  $\delta^{18}$ O also in the Outokumpu case, in some yet unspecified stage of the obviously multistage, prolonged syntectonic remobilization of the ore materials.

# 12.2.7. Physico-chemical conditions of the Cu-Co-Zn mineralization

As we pointed above the high 500-700 °C peaking, and in its entirety obviously tens of millions of years of high metamorphic heating of the Outokumpu deposits consequences that their sulphide (or gangue) mineral assemblages, mineral compositions, fluid inclusions etc. will provide only very little, if any, information about pre-peak processes that may have contributed to the formation of these ores. It is most likely, also, that the present stable isotope compositions such as those for oxygen and sulphur in quartz and sulphides, respectively, are in these ores to a large degree reset, and primary ore-formation related fluid inclusions erased by peakmetamorphic equilibration processes. Therefore at best only highly speculative deductions of the primary ore formation conditions can be introduced.

Nonetheless, in the past some mineralogical characteristics of the Outokumpu ore, like e.g. the common presence of cubanite lamellae in chalcopyrite (cf. Vähätalo, 1953), have been used in attempts to set temperature limits for the primary mineralization. However, with present better understanding of the thermal stabilities of sulphide minerals, and the metamorphic history of the Outokumpu area, most of these features can be addressed to retrograde metamorphic cooling and blocking. As we stressed earlier only the "primary" pyritic parts of the Outokumpu and Kylylahti ore bodies have even some theoretical chances to preserve some information of the pre-peak ore formation conditions. Our observations from Kylylahti suggest that, although some of the pyrite ore sulphide microstructures and assemblages may indeed be prepeakmetamorphic, it is nevertheless by no means granted that even these features would record anything more "primary" than effects of some late reworking- remobilisation processes.

The high Cu-Co-Ni and relatively low Zn-Pb nature of the Outokumpu ores could be taken as indications of relatively high temperatures of the initial sulphide formation. However, many features suggest that these ores were polygenetic and have a more complex than one-stage metal addition history, and thus simple conclusions based on the present metal ratios or distributions may provide be a misleading basis for any conclusions of the physical-chemical conditions of the original ore formational process(es). Evidence of a polygenetic origin include, for example, that Co in the Outokumpu ore has statistically significant positive correlation with S, As and Se but not with Cu or Ni, and that the constantly relatively abundant Ni does not correlate with any other ore metal. Furthermore, textural evidence form the more primary Outokumpu and Kylylahti pyritic ore parts indicate late replacement origin of at least part of the chalcopyrite-sphalerite, which thus seem at least partly introduced by later Cu-Zn-rich introducing or redistributing fluid(s). Timing of the introduction of the enigmatically high Ni is difficult. The available microanalytical data and whole rock chemical data from Kylylahti and Outokumpu suggests that part of the Ni would be in the earliest fine-grained pyrites but that the pyrrhotite ore parts, especially those next to serpentinites, nevertheless would be the Ni-richest ore type. The latter feature suggests that considerable amounts of Ni may have been introduced still during the peak-metamorphic stage, by diffusion from the adjacent serpentintes and carbonate-quartz rocks.

It is interesting to note that the main Outokumpu ore body has a relatively high average Sn content of 133 ppm. Sn is of particular interest in massive sulphide context, as it seems to have a positive correlation with deposit grade and tonnage, at least in regard to volcanogenic massive sulphide deposits (Hannington et al, 1999). In most of the Sn-rich massive sulphide deposits, Sn was primarily deposited mainly as cassiterite at relatively low temperatures (Hannington et al., 1999; Serranti et al., 2002). In Outokumpu cassiterite is extremely rare, however, but most of the Sn locates in stannite, which by textural criteria seems to have exsolved from chalcopyrite and/or sphalerite. Noting that Sn in Outokumpu ore shows a statistically significant positive correlation with Cu, it is possible that it was originally introduced with Cu and deposited in chalcopyrite. If so, this would be indicative of relatively high original deposition temperatures exceeding possibly 400 °C (cf. Yajima and Ohta, 1979). This could represent a minimum temperature limit for the primary ore formation, or some more pervasive remobilization event.

The predominance of pyrite in the most primary looking ore facies in Kylylahti and Outokumpu indicates that  $fO_2$  during the "primary" sulphide deposition was above the pyrite-pyrrhotite equilibrium. Further speculation could be that the presence of minor magnetite in banded pyritic ore in Outokumpu, and rarity of acid replacement features in the ore

environments, may imply relatively neutral to only slightly acidic fluid during the "primary" pyritic stage. Furthermore, we note that that the rarity of Mn and Fe carbonates or their metamorphic derivatives in Outokumpu ores and their surroundings could imply that the ore-forming fluids were relatively low in  $CO_2$ . The rarity of Fe-carbonates but absence of high-sulphidation phases, such as bornite, even in the most copper rich ore facies, could be taken as an indication of moderately S-rich fluid.

The abundant magnetite in some recrystallized, pyrrhotitic parts of the Luikonlahti and Kylylahti could be an ultimately primary feature, but more probably it reflects locally elevated in the peak-metamorphic fluid. The magnetite-rich ore parts being mostly relatively rich in calc-silicate gangue suggest that the variation in local fO<sub>2</sub> conditions/magnetite content was controlled by decarbonation reactions, and hence basically abundance of carbonate gangue in the ore.

### 12.2.8. Serpentinites as metal source – mass balance constraints

Showing a source for the ore metals is one of the more pertinent, but unfortunately also one the most difficult tasks in modelling of sulphide ore deposits. Particularly difficult task it is in case such old, pervasively deformed and high temperature metamorphosed sulphide ores as the Outokumpu deposits. We attempted to determine the metal source(s) based on: (1) bulk metal contents and interelement ratios of the sulphides; (2) isotopic evidence; and (3) massbalance constraints. The first two of these approaches were discussed above. A simple massbalance analysis for one particular model scenario assuming the host serpentinite bodies as the prime source of the ore metals is introduced below.

Whatever we think about the genesis of the Outokumpu deposits, it remains a fact that in their present positions all the studied Outokumpu ore bodies appear very "epigenetic", pretty much as being structurally late, vein-like formations. Tactically assuming that the deposits indeed were primarily epigenetic and syntectonic; there are in the Outokumpu framework three main metal source alternatives: (1) the surrounding Kalevian metasediments, especially the black schists that are strongly enriched in all the main ore metals; (2) the mafic-ultramafic rocks in the Outokumpu assemblage; or (3) some more distant source as e.g. the granites intruding the Outokumpu Allochthon or perhaps the Archaean basement underneath the allochthon.

The relevance of the first and third source alternatives is best addressed by isotopic assessment, done elsewhere in this discussion. What regards the second alternative, there are two possible sub scenarios; either the ore metals derive from (1) unmineralized peridotites of the host ultramafic-mafic ophiolite fragments, or from (2) some contained Cu-rich protomineralizations that existed in the host mafic-ultramafic bodies already before their detachment/obduction. In the first alternative the metal availability was ultimately limited by both the total volumes and primary average metal concentrations of the host bodies, whereas in the second alternative, in the proto-ore stage, "immense" volumes of the source rocks, and perhaps in much different ultramafic to mafic ratio as in the preserved "ophiolite" fragments, could have been available to supply the metals into the assumed protomineralizations.

It can be calculated, based on the published reserve estimates for the Outokumpu and Vuonos Cu deposits, that they combined contained at least 1.22 Mt of Cu. Then, it can be estimated from the cross-section maps constructed by Koistinen (1981) that the total volume of ultramafic material in the Outokumpu-Vuonos serpentinite bodies was ca. 4 km<sup>3</sup>, this volume including also the parts of them that presumably have been removed by erosion. Then, it is known by the extensive drilling and whole rock analysing by Outokumpu Company that >90% of this 4 km<sup>3</sup> would consist of metamorphosed, serpentinized harzburgitic-dunitic mantle peridotite (or alteration products). Assuming now that the peridotites initially contained max. 30 ppm Cu on average (=the estimated Cu content of primitive, undepleted mantle), it can be calculated that the 4 km<sup>3</sup> of peridotite in the Outokumpu-Vuonos system contained in max. ca. 0.4 Mt of Cu, which is only about one third of the Cu in the present ore bodies. In other words, assuming 100% Cu extraction efficiency, no less than 13.5 km3 volume of peridotite was enough to supply the Cu in the Outokumpu-Vuonos ores. However, if the calculation is based

on a more realistic extraction efficiency of <20%, and <10 ppm Cu for such highly depleted peridotites as those at Outokumpu and Vuonos, one finds that just a source volume of about 300-400 km<sup>3</sup> of peridotite starts to be a realistic scenario. It is most clear that such volumes of peridotite were not present in the Outokumpu-Vuonos system, perhaps not even in the whole Outokumpu belt. The outcome is that if the ultimate source of the metals was in the ultramafic-mafic bodies, they must have contained protomineralizations developed already before the obduction of the bodies, in their oceanic formative setting, or then the Outokumpu mantle peridotites were hugely enriched in Cu for mantle peridotites for which there is absolutely no evidence, however.

#### 12.2.9. Implications of the deposit comparisons

Our literature search for possible Outokumpu analogous deposits showed that such are remarkably rare. Only a few deposits in association with ultramafic rocks of the ophiolite clan showed up enough common features to make them reasonably similar with the Outokumpu deposits, while peridotite-floored massive sulphides from mid-ocean ridge environments provide a possible modern analogue. The similarity of the ophiolite related and modern ridge deposits with the Outokumpu deposits is far from perfect, however, as deposits in neither of these associations posses, for example, the very high Ni typical of the Outokumpu sulphides. For the few clearly Outokumpu like deposits elsewhere, such as the Eastern Metals and Deerni, foremost the seafloor hydrothermal, but also many other and highly deviating genetic models have been proposed. The conflicting interpretations seem to reflect the difficulties rising from the characteristic occurrence of the Outokumpu type deposits in pervasively deformed and metamorphosed thrust belts, which allows that, although the deposits at first sight look pretty much syntectonic, structurally controlled accumulations, they nevertheless may represent extensive remobilization and sulphide migration from no more well reconstructable precursor deposits, which may have had long and complex syntectonic and earlier prehistories.

### 13. New model for the Outokumpu-type deposits

Based on the above-presented discussion on the known key characteristics of the Outokumpu deposits, we propose a new model of their origin. The model incorporates components that have been introduced for the Outokumpu type deposits already previously; here should particularly the papers of Gaál and Parkkinen (1993) and Auclair et al. (1993) to be mentioned. As a new element our model will introduce a concept of syntectonic mixing of Ni into the Outokumpu ores, from the ubiquitous low-grade Ni-sulphide dissemination in the Outokumpu assemblage, as to an explanation of their enigmatically high Ni. Therefore we will first discuss the origin of the Ni-sulphides in the carbonate-skarn-quartz rocks in the Outokumpu assemblage.

### 13.1. Origin of the Ni-sulphides in the Outokumpu assemblage

The ubiquitously high, 1500-3000 ppm Ni content of the Outokumpu carbonate-skarnquartz rocks, that would be a very strange property of any type of sedimentary carbonates and cherts, becomes readily understandable if these rocks are realized as carbonate-silica altered mantle peridotites. Noting that mantle peridotites comprise typically some 1800-2200 ppm Ni (and 90-110 ppm Co), it is only required that some S was introduced concurrent by the primary alteration, to ensure that the Ni (and Co) atoms liberated from the dissolving silicates and oxides (from magnetite by serpentinization) became simultaneously repositioned and fixed in nickeliferous sulphides. The observations from the lower greenschist facies Eastern Metals Cu-Zn-Ni deposit from Quebec Appalachians suggests that the carbonate-silica alteration was preceded by serpentinization of the protolith peridotite, and that most of the silicate Ni was relocated in fine-grained pyrite replacing magnetite after serpentinization of the protolithic olivines (Auclair et al., 1993). In the amphibolite facies Outokumpu rocks the primary nickeliferous pyrites have been metamorphosed to mainly Ni-poor pyrrhotite plus minor pentlandite. Sulphur- and Pb-isotope data combined with trace element data from Outokumpu and Eastern Metals suggest that the sulphur, and along with it, minor amounts of metals like U, Pb, As, and perhaps also some Mo and Sb, were introduced in the carbonate-silica rocks from the adjacent black schists. However, apart from As and U, the possible metal additions associated with the primary carbonate-silica alteration were quantitatively very minor, so that the present concentrations of Pb, Mo and Sb in the carbonate-skarn-quartz rocks usually are close to the detection limits of the here applied analytical methods.

Provided there was no volume change and no Ni gain/loss, silicification/sulphidation of typical mantle peridotite will produce a sulphide disseminated quartz rock that would contain ca. 2500 ppm Ni. Thus, the considerably lower average Ni abundance of about 1700 ppm in the Outokumpu-type quartz rocks suggests that the silicification process probably involved either significant addition of volume and silica, or alternatively significant Ni loss. The Kokka-type Ni enrichments within the skarn-quartz rocks are located in more or less clear shear zones within the metasomatically altered ultramafic body margins, and are associated, but with relative enrichment in Ni and iron sulphides, also local enrichments in Cr (largely in chromite), which could imply their origin involved leaching of silica, volume loss and passive enrichment of conservatively behaving Ni, Co and Zn. An analysis of the extensive Ni-Co-Zn data from the Petäinen prospect demonstrates further that, if larger volumes of the carbonate-skarn-quartz rock alteration fringes are considered, zones of low Ni compensate zones of high Ni. Drawing together, it seems that the Kokka-type mineralizations were related to close-system silica mobilization (leaching/redeposition) within the alteration fringes.

Of special significance to the genetical modelling of the Cu-Co-Zn ores is that the Ni sulphide disseminations in the carbonate-skarn-quartz rocks and Kokka type mineralizations do not show any tendency to elevated Co/Ni or Cu/Ni ratios, and, as we discussed above, by isotopic criteria seem 30-50 Ma younger by their formation time than the Cu-Co-Zn ores. It should also be emphasized that the present microstructures and silicate as well as sulphide mineral assemblages in the carbonate-skarn-quartz rocks are systematically pervasively metamorphic, recording complex modification by processes related to the regional metamorphic temperature progression, peak-stage equilibration and subsequent retrogression etc. The obliteration of mineralogical-textural inheritance of the initial low temperature carbonate-silica alteration stage has been in this case literally pervasive.

### 13.2. Model for the Cu-Co-Zn deposits

Our literature survey revealed that the polymetallic Cu-Co-Zn-Ni±Au deposits of the Outokumpu type (known as Deerni type in China) represent an extremely uncommon massive-semimassive sulphide deposit type that in several respects differs from any of the more common categories of massive sulphide deposits, including Cyprus and Besshi deposits to which Outokumpu is often compared. The most distinctive features of the Outokumpu ores include: (1) nonexistent to rare volcanic or subvolcanic rocks and (2) lack of obvious hydrothermal-exhalative sedimentary rocks in the ore environments; (3) often long, thin, narrow massive-semimassive ore bodies with very sharp bounding surfaces; (4) close association of the sulphides with carbonate-silica altered depleted mantle peridotites; (5) high Ni and Co content for hydrothermal Cu-Zn sulphide ore; (6) low concentrations of such trace elements as Bi, Sb and Se; (7) very low to extremely low Pb; (8) mantle-like Pb isotope ratios of ore galena and (9) relatively high  $\delta^{18}$ O values from +13 ‰ to +16 ‰ of the dominantly quartz gangue in the ores.

The unconventional features of the Outokumpu type deposits have provoked proposals that these deposits should be considered an independent class of massive sulphide deposits (Candela et. al., 1989), or at least a distinct subtype of "sulphide ores associated with seafloor mafic and ultramafic volcanism" (Papunen, 1987). We do very much agree with these proposals, and try in the following sections to figure out what were the unique processes and conditions that caused the special characters of the Outokumpu type deposits.

Before middle 1950s the metals in Outokumpu deposits were usually thought to derive from buried granite intrusions, or magmatism represented by the host serpentinite bodies. Although the available Pb isotope data the Heinävesi-type 1.87 Ga "late-orogenic" granites constrain them to an isotopically so-so suitable metal source; however, it is difficult to imagine how metal-carrying fluids from the granites would have avoided contamination by crustal Pb during their required travel through the at least 1.5 to 2 km of Kaleva metasediments (with crustal-like Pb) between the Outokumpu-Vuonos deposits and any possible source granites. A tightly channelized, fault-controlled fluid flow would have needed, but there is no filed evidence of such channels, or of Cu-Co mineralizations in association of any type of the granites met in the Outokumpu well with the early interpretations of the Outokumpu are as an offset dyke of massive sulphides from the adjacent peridotites. However, noting the abundant quartz+-calc silicate gangue and Cu-Co-Zn dominated metal enrichment of the Outokumpu deposits, their origin as magmatic sulphides of ultramafic rocks is clearly not a feasible scenario. Moreover, the host serpentinites derive from residual, not magmatic, peridotites.

Since middle 1950s models assuming volcanic-sedimentary exhalative origin of the Outokumpu deposits have been in favour. It has been proposed that the ores deposited either with the black schists or quartz rocks in the host assemblage, and that the serpentinites would represent syngenetic volcanic or intrusive rocks. But as we have clarified in this report, observations on drill cores for the contact relationships, and the different metal enrichments in the black schists and ores do not support, and their very differing sulphide Pb isotope compositions precludes their syngenesis. Sedimentary exhalative syngenesis with the quartz rocks is an impossible idea as the latter do not actually represent sediments at all, but instead silica-carbonate altered peridotites. And, the serpentinites indeed are altered residual mantle peridotites, not volcanic rocks of any kind, not even komatiites.

Syntectonic hydrothermal scenarios have also been proposed, assuming the metal source in the adjacent sulphide rich black schists. In syntectonic models also the serpentinites at the ore bodies could be considered a possible source of the metals. In the light of the very differing Pb isotope compositions and metal enrichment profiles of the ores and the black schists, syntectonic sourcing of the ore metals from the black schists seems an impossible scenario, however. The serpentinite bodies, then, seem too Cu poor and small to represent a serious source of syntectonic Cu extraction. Mass balance calculations performed by us suggest that even if 100% metal extraction efficiency, and a high Cu concentration of 30 ppm of undepleted mantle are assumed, in a closed system scenario, there was far too little Cu in the associated volumes of the Outokumpu-Vuonos serpentinites to deliver the >1.2 Mt Cu present in the associated ores. Clearly, if the serpentinite massifs were the metal source, they must have contained some sort of serious Cu enrichment, but for which there is no evidence.

So, if none of the previously proposed models were good enough, what would be? We try to answer below.

The question is difficult, however. Due to the pervasively metamorphosed and structurally reshaped nature of the Outokumpu deposits renders trace elements and isotope geochemistry may be about the only means we could hope to get some information about their possible prepeakmetamorphic origins. From such data available at the moment, the Pb isotope data and the large Outokumpu-Vuonos ore system appear the most significant. As we above concluded the very low Pb content, relatively unradiogenic, "mantle-like" initial Pb isotope composition, and the 1943±85 Ma Pb isochron age of Outokumpu and Vuonos ores, all point to that these deposits had an prehistory with the ca. 1.97-1.96 Ga obviously ophiolitic ultramafic-mafic fragments in the Outokumpu Allochthon. And, that the sulphides and Outokumpu ophiolite fragments probably were generated in the "Kalevian ocean basin", that opened by the 2.0-1.95 Ga break up of the Karelian craton, and existed until the ca. 1.90 Ga obduction of the Outokumpu Allochthon. The relative scarcity of mafic, especially mafic extrusive rocks in the Outokumpu system, and the very low Pb abundances of the ores consistently indicate that the deposition of the Cu proto-ore occurred in a segment of the inferred oceanic basin where oceanic mantle tectonites were extensively exposed and formed the principal environment of the metal/sulphur leaching and deposition. Suitable environments include e.g. magma-poor embryonic basins, slow-opening oceanic spreading ridges and oceanic transform fault zones that tend to locally expose mantle, and which are also known to be environments of sufficiently elevated heat flows and related convective hydrothermal circulation of seawater that may generate sulphide ores. The low Ti depleted tholeiite nature typical of the mafic rocks in the serpentinite massifs is a strong indication of that the thermal conditions of vigorous hydrothermal convection of seawater were present in the inferred ocean basin.

Although an origin of the Outokumpu ores as ocean sulphide accumulations seems thus plausible, the total absence of hydrothermalites from the ore environments and the extremely elongated/flattened shape of the Outokumpu-Vuonos-Perttilahti ore band demands some further explanation. One possible explanation is that the sulphides would represent originally inhalative deposition in fissure zones within the peridotitic ocean floor, which would provide at least a partial explanation for both the elongated shapes and the lack of hydrothermalites from the ore associations. As we discussed above, leaching of hundreds of km<sup>3</sup> of the peridotite could have provided the Cu in the Outokumpu Vuonos ores, while the Se/S and Se/As ratios of the ore sulphides point to that the ore sulphur was dominantly sourced in the ocean water. Hints of marine sulphate involvement are seen also in the  $\delta^{34}$ S values extending up to +6 in the Outokumpu main ore. Absence of crustal signature in the ore Pb suggests that at the time of the ore formation the formative fissure zone was not yet extensively covered by any continental derived sediments, or alternatively the sulphides precipitated deep enough in the mantle substratum that they were buffered for any external Pb influx.

Some 30-50 Ma after their deposition, somewhere around 1.9 Ga, the Cu-Co-Zn sulphides became transported, confined in dominantly peridotitic ophiolite fragments from the formative seafloor onto the margin of the Karelian craton. The detachment and dispersal of the ophiolite fragments in the Outokumpu Allochthon had been occurred shortly before or during the initiation of the obduction. The obduction process was accompanied or immediately succeeded by a metasomatic alteration of the outer margins of the dominantly peridotitic ophiolite bodies to carbonate and quartz rocks (listwaenites-birbirites). The low-T (100-200 °C) carbonate-silica alteration process was associated with transformation of the peridotite silicate nickel into sulphides making them weakly disseminated in Ni-bearing sulphides.

There are some aspects in the Outokumpu deposits that remain enigmatic and unexplained by sole seafloor processes. These include e.g. their super high Ni for any type ocean floor sulphides, also for those in ultramafic-floored associations, and their load-like epigenetic mode of occurrence at the serpentinite body margins, typically between the silica carbonate alteration cells and enveloping black schists. To provide a combined explanation for the high Ni and epigenetic, load-like occurrence of the ore bodies; and yet preserving the isotopically sane, and often proposed idea of their ultimately ocean floor origin, we propose a model that assumes two end member sulphide "proto ores": (1) the ca. 1.95 Ga Cu-Co-Zn oceanic sulphides, and (2) ca. 1.90 Ga early-tectonic Ni-sulphides in the carbonate silica alterations shells of the serpentinite bodies, and that syntectonic-synmetamorphic, structurally controlled mixing of these sulphides produced the present Cu-Co-Zn ores.

We infer that the apparently long lasted and complex syntectonic mixing process involved three essential phases: (1) Fluid assisted remobilization of the inferred Cu-Co-Zn proto-ore materials from their original formative locations (at least tens to hundreds of metres), (2) Redeposition of the relocalized materials at the margins of the host serpentinite bodies, and (3) Further mobilization of the redeposited sulphides by fault-controlled liquid-solid state processes causing their lode-like present mode of occurrence. The mixing of the Cu and Ni end member sulphides occurred by leaching or diffusion from the Ni-mineralised wall rocks along with the relocation pathways. Restricted more reworking-remobilization and ultimately extensive static recrystallization annealing of the sulphide materials occurred during the regional peakmetamorphism. Though genetically unimportant, these late events significantly upgraded the economic feasibility of the ore bodies by coarsening of the grain-sizes, simplifying the sulphide intergrowth textures, and transforming Co-pyrite to Co-pentlandite and pyrrhotite.

Location of the Outokumpu deposits typically in positions in between particularly thick units of the serpentinite fringing carbonate-quartz rocks and black schists, or apparently only slightly displaced from such preceding locations, suggests that the carbonate-quartz rock black schist

combination somehow contributed to the mechanisms that caused the final sulphide deposition. Maybe the fluids involved in the inferred remobilization process were generated by decarbonation processes in the ultramafic bodies and thus were oxidised. Assuming then that dehydration fluids emanating concurrently from the black schists should have been relatively reducing, mixing of the two fluids at the quartz rock– black schist interfaces cold have been the process controlling the final sulphide deposition.

However, because of the high late metamorphic overprint of the Outokumpu deposits, the sources and physicochemical characters of the fluids that actually were involved with the inferred remobilization process are, and will be, a very difficult issue to study. Presently we only can say that the nature of fluid inclusions and high  $\delta^{18}$ O values of +13 ‰ to +16 ‰ in the gangue quartz in the Outokumpu and Vuonos ores point to a pervasive interaction with metamorphic type fluids. The  $\delta^{18}$ O values may associate with the inferred lengthy remobilization process, although more probably with the peakmetamorphism.

We have calculated that in the case of the Outokumpu deposit the proposed model would imply mixing of 1 part of the Ni-end member sulphide phase with approximately 16 parts of the inferred Cu-proto ore end-member sulphide phase. And further that this would require mobilization of an amount of Ni that would be present in a volume of dolomite-skarn-quartz rock about twice larger than the volume of the Outokumpu main ore. Based on these, although simplistic calculations, the proposed model appears guite feasible for its mass balance. The mixing model implies that the Pb and S isotopic compositions of the Cu ores should show variations between the mantle-like compositions of the Cu and black schist like compositions of the Ni end members. Based on the available Pb data, this seems indeed to be the case as the larger, Cu-rich deposits are inclined towards mantle like Pb isotope compositions and the smaller and less Cu-rich deposits have more black schist-like lead isotope compositions. It should be noted that peakmetamorphic Pb introduction from the surrounding metasediments might have played here a bigger role, however. For the part of S isotopes, the present data from the black schists and quartz rocks, and the smaller Cu-Co-Zn deposits are too few to allow any serious evaluation of the proposed model. The negatively skewed distribution in the Outokumpu  $\delta^{34}$ S values by Mäkelä (1974) is undoubtedly something mixing related, but may reflect more sampling related mixing (black schist-guartz rock-ore) than actual distributions precisely in the Cu ore.

The proposed model, summarized in the cartoon of Fig. 153, adequately explains many of the apparently conflicting characters of the Outokumpu deposits. The model is consistent with both the distinctly epigenetic mode of occurrence of the ore bodies, and the geochemical and isotopic evidence that nevertheless strongly suggest an unradiogenic, mantle-like source and a pretectonic, probably oceanic hydrothermal extraction of the ore metals from this source. Further, the model gives a reasonable explanation for the high Ni content typical of Outokumpu deposits, which would be something very difficult to explain in purely ocean-floor hydrothermal model scenarios. The model also accommodates to the metasomatic, nonsedimentary origin of the quartz rocks in the Outokumpu assemblage, and also explains why the ores and their wall rocks completely lack true exhalative hydrothermalite components.

Finally, we are well aware that the proposed model is conflict with the structural deductions in Gaál et al. (1975) and Koistinen (1981) of that the Outokumpu and Vuonos ores would represent sedimentary developments that were about in their present positions already before the development of the "D<sub>1</sub>" tight-isoclinal folds that govern the structural pattern of their host assemblages. But if the host Outokumpu assemblage is correctly understood for its lithogenesis and "stratigraphy", a sedimentary origin of the ore materials starts to look a well debatable issue. Furthermore, a scrutiny of the mine cross-section maps suggested to us that the Outokumpu ore plate actually represents a lode crosscutting the D<sub>1</sub> folds in the host assemblage. However, within the framework of the above presented model, this does not necessarily mean that the ore was ultimately a post D<sub>1</sub> development, but only that its very final place taking must postdate at least the D<sub>1</sub>. Further elucidation of the structural timing of the Outokumpu deposits remains to wait the next opportunity to mine scale observation, hopefully soon possible at Kylylahti.



Fig. 153. A cartoon of the "GEOMEX Outokumpu model", illustrating the three main stages inferred in the model for the evolution history of the Outokumpu types deposits.

#### 14. Exploration implications

For exploration of Outokumpu type deposits within the NKSB the implications of the GEOMEX ore model are clear. (1) Outokumpu type semimassive-massive Cu-Co-Zn-Ni±Au deposits and disseminated Ni mineralizations can only be found in close association with the serpentinized mantle fragments (serpentinites), and only in the allochthonous part of the Upper Kaleva assemblage. (2) The quartz rocks and associated Ni-mineralizations in the Outokumpu assemblage are genetically unrelated to the Cu-Co-Zn-Ni±Au mineralization, and thus do not provide unambiguous aid in selection of favourable exploration targets. (3) The late strictly structurally controlled final emplacement inferred for the Outokumpu type deposits implies that application of lithogeochemistry as an exploration tool is of relatively limited value as only small-scale secondary metal "halos" around the ore bodies are likely to occur.

If there are problems in locating of the ore bodies in the Outokumpu assemblage by lithogeochemical methods, so it is also by geophysical methods, as the host serpentinites are usually strongly magnetic, carbonate-skarn rocks partly dense and black schists electrically highly conductive. Thus the best procedure in exploring for Oku type deposits really seems to be the traditional way of first locating serpentinite masses, *preferably large ones*, and then drilling them, for their marginal parts, with a reasonably dense cover. Noting that most of the large serpentinite masses outcropping in the NKSB already have been adequately tested, at least with regard to deposits of the Outokumpu (Keretti) to Vuonos size and grade, that are nowadays required to guarantee economical success, any successful future exploration would imply locating geophysically and/or by structural deduction, large, so far unknown "blind" serpentinite masses. Unfortunately, the analysis of the airborne geophysical data carried out during this project (see the geophysics subbproject report of GEOMEX) implicate that not many of such would be present in the study area, at least within the shallowest first 500 metres of the crust.

### 15. Alternative model scenarios and suggestions for further study

The above-presented "GEOMEX Outokumpu model" should be taken as a highest probability scenario on the basis of the currently available documentation, which, despite of soon almost a century of research, is still in many important respects incomplete and partly outdated. We remind about the incomplete and/or technically outdated nature of e.g. the existing oxygen and sulphur isotope, and fluid inclusion research, and note also that the study of the least metamorphosed, and thus potentially most informative of the Outokumpu deposits, the Kylylahti deposit, is still only in its very beginning. Consequently, and with a remark on the many troubles related to genetical modelling of such pervasively metamorphosed sulphide deposits as the Outokumpu deposits (for a discussion of the subject see e.g. Marshal and Spry, 2000), we would not be much surprised if, with appearance of new evidence, even major refinements to the here proposed model would be needed.

One obvious soft spot in the proposed model is in the inferred Cu-proto ore that remains a rather obscure concept; mainly as we cannot point at any "primary location" where the Cu proto-ore materials would have formed/resided before their final relocation in the present ore shoots. This is difficult because the host serpentinite+-mafic bodies any further than some tens of metres away the ores are usually totally devoid of any form of Cu-Co-Zn enrichment over the background. Although one possibility of coarse is that the now parallel Co-Ni zones represented those pathways. We also did not present any serious modelling of the source and physicochemical character of the fluids involved in the postulated liquid state remobilisation of the inferred Cu-proto-ore, or about the controls of the sulphide reprecipitation.

When assessing different model approaches for the Outokumpu deposits, we evaluated, impressed by their many epigenetic features, especially long and hard various "purely" syntectonic-synmetamorphic models. Another reason for the particular interest we had in syntectonic models was the possibility of steep redox gradients that probably existed across the

altered serpentinite body margins during their metamorphism (dehydration/decarbonation). But eventually found serious problems with syntectonic model. For example, the two most likely metal source candidates in such scenarios, the host serpentinite massifs and enclosing Kalevian metasedimentary rocks were found, the former volumetrically insufficient, and the latter Pb isotopically unsuitable. Another hypothetical metal reservoir could have been the Archaean basement or/and the regional Svecofennian granitoids. But the low Pb content and unradiogenic Pb of the ores would be difficult to explain if the metal source was in acidintermadiate granite-gneiss rocks, and if the presumably relatively high T fluids had to travel through kilometres of the Kaleva sediments comprising highly radiogenic Pb, as it is required in the granitoid-basement model scenarios. Furthermore, there are currently no supporting field evidence from the enclosing Kaleva of regional-scale syntectonic, e.g. thrust or shear zonecontrolled channelization of metal-enriched fluids to the ores.

From the point of view of exploration, we suggest that further study of the Outokumpu deposits should be focused on the GEOMEX model inferred fluid-assisted final emplacement of the ore bodies, to better constrain the control structures and check if they contained any geochemical or other readily identifiable forerunners or tails that could help in recognizing of the more promising exploration targets, and within them, ore bodies. In the more purely academic arena, more work should be directed in clarifying further the mineral paragenesis, oxygen and sulphide isotope geology of the Outokumpu deposits. To provide reasonable scope for interpretation, such studies should in future be extended over the ore bodies and Outokumpu assemblage to include sampling also for the associated serpentinites and regionally enclosing metasediments. Considering the complex tectonic-metamorphic histories of the Outokumpu deposits, there where appropriate modern in situ analytical methods (ion mass spectrometry, laser ablation spectrometry) should be applied, to enable analysis on the level of the various mineral generations. Applying of ion microprobe would also enable acquiring more and paragenetically better-constrained Pb isotope data for the trace galena both in the ore bodies and their host rocks, which would greatly improve interpretation of the presently available Pb isotope data. A fluid inclusion study by modern equipment and methods dedicated to clear out the exact nature and derivation of the fluids trapped in the ore gangue minerals should be realized. Although this would probably tell only about the very latest metamorphic effects, even the verifying of this would be very useful.

As most of the study listed above would benefit of sample material with as little peakmetamorphic overprint as possible, it would be best realized as part of a compressive, multidisciplinary study of the least metamorphosed of the Outokumpu deposits, the Kylylahti deposit. Special attention at Kylylahti should be put in absolute and structural timing of the skarn zone stringer mineralization, and the various pyrite generations in the massivesemimassive lenses and stringer zone as well. Combined with a systematic petrographic microstructural and microprobe chemical mapping of the various pyrite generations, and contact features of the massive-semimassive lenses, much about the timing and evolution of the Kylylahti mineralization would undoubtedly be found out. A presentiment of the present authors is that the Kylylahti deposit will prove out to be a dominantly syntectonic development. That would not be in conflict with the GEOMEX model that assumes a syntectonic, fluidassisted remobilisation final emplacement of the ore materials, but yet something that might provoke more interest to purely syntectonic models. We end this report by commenting that some mineralogical and geochemical features (apatite, allanite, LREE enrichment, C isotopes of calcite) of the Kylylahti stringer zone seem to hint of involvement of a possibly magmatically derived fluid (from granite intrusions in the depth?) in the genesis or remobilization of the ore sulphides.

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