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Geochemistry and origin of Haveri and Kiipu, Proterozoic strata-bound volcanogenic goldcopper and zinc mineralizations from southwestern Finland

by Kaarlo Mäkelä

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## GEOCHEMISTRY AND ORIGIN OF HAVERI AND KIIPU, PROTEROZOIC STRATA-BOUND VOLCANOGENIC GOLD—COPPER AND ZINC MINERALIZATIONS FROM SOUTHWESTERN FINLAND

by

## KAARLO MÄKELÄ

with 34 figures and 11 tables in the text

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This study is based mainly on diamond drilling data from two petrologically different Proterozoic occurrences: the vicinity of the extinct Haveri Au-Cu mine, and the Kiipu Zn ore prospect. The data consist of 314 AAS and XRF analyses performed on a total of 1117 m of split core.

The pyrrhotite-dominated auriferous and cupriferous massive sulfide deposits in the vicinity of the Haveri mine occur in basaltic metavolcanic rocks. The underlying metalavas and parent metalava breccias contain 49 % SiO<sub>2</sub> and display a typical tholeiitic differentiation trend with Fe enrichment and Mg depletion. Sulfur isotopes indicate a sea-water origin for sulfur in the ore, the rather fluctuating  $\delta^{34}$ S composition of pyrrhotites in the metalava breccia zone averages +6.3 °/<sub>00</sub>. Post-ore regional metamorphism has taken place at c. 550 °C temperature and 2.5 kbar pressure. The Haveri occurrence is correlated with Cyprus-type deposits and was probably generated in an initial-stage island arc.

The Kiipu zinc ore prospect is located in a pyritized and gahnitized alteration zone with streaks of compact sphalerite. The parent pyroclastic rocks in the alteration zone have a dacitic to rhyolitic composition (SiO, in the order of 63-73 %), and unaltered andesitic metalavas (SiO<sub>2</sub> 54 %) overlie the alteration zone. The intense alteration is attributed to the leaching of a pyroclastic pile by hydrothermal fluids resulting in the depletion of the system in Ca, Na (destruction and disappearance of plagioclase) and Si, and in the introduction into the system of K, Mg, Fe, S, Zn, Pb, Cu and Ag. The  $\delta^{34}$ S composition of pyrite in meta-andesite averages +1.5  $^{0}/_{00}$  and appears to be of magmatic origin.  $\delta^{34}$ S averages +1.0  $^{0}/_{00}$  in pyroclastic and +0.30/00 in altered rocks. A sea-water origin, possibly with some magmatic sulfur contribution, is proposed for the sulfur in the altered rocks. Post-alteration and post-mineralization regional metamorphism has not essentially changed the bulk chemical and mineralogical compositions of the metalavas and pyroclastic rocks; it has, however, produced isochemical cordierite, biotite, muscovite, anthophyllite, garnet and gahnite-bearing parageneses in the alteration zone resulting in the destruction of primary volcanic textures. The regional metamorphic conditions are approximated at 600 °C temperature and 3.0 kbar pressure. The Kiipu occurrence is correlated with Kuroko-type deposits generated in a mature island-arc environment dominated by calcalkaline volcanism.

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#### INTRODUCTION

#### Purpose

The purpose of this study is to describe, classify and compare with each other, and with other known occurrences in the world, two different strata-bound volcanogenic mineralizations from SW Finland, namely Haveri (actually the vicinity of the Haveri mine) and Kiipu. The emphasis is on their lithology, lithogeochemistry and ore-forming processes in terms of geotectonic processes (plate tectonics) and related magmatic evolution. Post-ore metamorphism is also discussed.

Haveri, a former producer of gold and copper,

was closed down in 1960. Kiipu is a zinc-ore prospect that was found in 1964 during geological field mapping by Outokumpu Co. The locations of the two targets are given in Fig. 1.

The Exploration Department of Outokumpu Co. carried out exploration in the vicinity of the Haveri mine and on the Kiipu prospect, under the supervision of the present author, in 1976—1977. Most of the material for this study was obtained from diamond drilling at these two sites.

#### Terminologic comments

In this study the term »strata-bound» implies deposits that are concordant with certain strata and that, in general, have syngenetic relations with them even though local epigenetic, discordant features may occur. Correspondingly, »stratiform» deposits are strictly syngenetic (e.g. synsedimentary) and concordant with a certain stratum.

The term »massive sulfide deposit» is genetical rather than descriptive since »massive» sulfide deposits commonly contain variable amounts  $(50 \pm 30 \%)$  of sulfides, the rest being gangue.

#### Methodology

The methods and course of investigation are briefly as follows. First, geotectonic processes (plate tectonics), related magmatic evolution, ore-forming processes and strata-bound volcanogenic massive sulfide deposits are examined in the context of the pertinent literature. Stratabound volcanogenic massive sulfide deposits appear to fall into two main groups: those related with tholeiitic magma series and which are known as the Cyprus type, and those related with calc-alkaline magma series and which are known as the Kuroko type. Secondly, the Haveri and Kiipu occurrences are examined separately. Their general geology, macroscopic and microscopic petrography, and major and minor element geochemistry are described on the basis of sample data. The geochemical examinations are visualized by the petrological



Fig. 1. Geological map of Finland showing the locations of Haveri, Kiipu and other Finnish deposits mentioned in the text. The geology is after Simonen (1971).
1 = Presvecokarelidic schists and paragneisses; 2 = Presvecokarelidic granulite; 3 = Presvecokarelidic orthogneisses;
4 = Karelian zone of Svecokarelidic orogeny; 5 = Svecofennian zone of Svecokarelidic orogeny; 6 = Orogenic plutonic rocks; 7 = Rapakivi granites; 8 = Jotnian sedimentary rocks.

diagrams and factor analyses. On the basis of these results the Haveri and Kiipu occurrences are fitted into geotectonic frames. For both cases the post-ore regional metamorphic conditions are deduced mainly from silicate mineral parageneses.

A total of 28 sulfur isotope determinations was performed. The sulfur isotope composition of Svecokarelidic sea-water and the sulfur isotope data from Haveri and Kiipu are discussed.

Some volcanogenic sulfide deposits, both abroad and in Finland, are discussed.

Finally, conclusions are drawn on the subjects presented.

The following  $SiO_2$ -based classification of metavolcanic rocks after Spitz and Darling (1975) is used:

metabasalt	<53 %	$SiO_2$
meta-andesite	53—59 %	$SiO_2$
metadacite	59-65 %	$SiO_2$
metarhyodacite	65-70 %	$SiO_2$
metarhyolite	>70 %	SiO <sub>2</sub> .

As geochemistry is one of the main topics in this study, representative diamond drilling (d.d.) holes were selected to obtain reliable rock type and analysis populations. For the Haveri occurrence d.d. holes Hvr-5, -7, -8, -9 and -10 were accepted. These holes are 300 to 1 000 m south of the extinct Haveri mine and within 800 m of each other. Their locations are given in Fig. 2. The holes were drilled at Slingram electromagnetic, and magnetic anomalies. The total length of the holes is 813.05 m. Of the intersections analyzed, a few irrelevant rock types (e.g. quartz and pegmatite veins) were rejected, and the total of 203 analyses, representing 732.40 m of split d.d. core, was accepted for further examination.

D.d. holes Ki-5 and -6 were accepted for the Kiipu occurrence. These two holes, which lie 1 100 m apart on the strike of an alteration

zone (Fig. 19), were drilled at Induced Polarization anomalies. Both holes intersected similar sulfide mineralizations in the same kind of alteration pattern within mainly pyroclastic parent rocks. The total length of the two holes is 471.70 m. A small group of analyses was omitted on the same grounds as at Haveri; thus relevant total data of 111 analyses, representing 384.45 m of split d.d. core, were obtained for the Kiipu occurrence.

The technical data and analysis numbers for the d.d. holes are given in Table 1.

All the samples represent continuous d.d. core. Most of the core was split with a core splitter; some ore intersections were split with a diamond saw, and some long (5-10 m) intersections of homogeneous rock types were crushed into pieces, roughly 10 cm long, of which every second piece was taken to make up a sample.

Rock-type contacts were the primary criteria in determining the sample lengths, which varied from 0.1 to 10.3 m. If necessary, these intersections were subdivided according to mineralizations and petrological criteria. Thus some homogeneous rock types were analyzed with sample lengths of up to 5-10 m, whereas some mineralizations were analyzed only at 0.1-0.5 m. The average sample length was 3.55 m. Errors that would have been caused by uneven distribution of sample lengths were eliminated by weighting the analyses with lengths. In the geometric statistical examinations means. weighted with sample lengths, were used for each rock type. Geometric means were preferred to arithmetic ones because the latter tend to emphasize extreme values in certain cases.

The thin and polished sections, the electron microprobe analyses (with a Geoscan I unit), the chemical analyses, and the drafting were all done at the Olari offices of the Exploration Department of Outokumpu Co.

The chemical analyses were performed as part of routine sulfide-phase atomic absorption spectroscopy (AAS) and whole rock X-ray

Hole number	Map sheet	x	У	Bearing	Dip	Length (m)	Analysis numbers	Number of analyses
Haveri:								
$Hvr - 5 \dots$	2142 02	6843.97	460.40	35°		136.30	778127-778145	39
							778147—778155	
$Hvr - 7 \dots$	2142 02	6844.50	460.55	35°		171.80	778159—778171	40
							778305-778310	
							778328-778331	
Hvr—8	2142 02	6844.60	460.63	35°	45°	200.60	778173—778184	54
							778186-778194	
		· · ·			ca		778223-778226	
Hvr—9	2142 02	6844.71	460.12	$0^{\circ}$		150.00	778227-778267	41
$Hvr = 10 \dots$	2142 02	6844.66	460.12	$0^{\circ}$	_	154.35	778268—778303	36
						813.05		210
Kiipu:								
Ki—5	2113 01	6745.52	465.68	315°		180.30	7623574-7623620	47
Ki—6	2113 01	6746.46	466.32	315°		291.40	7623823—7623907	85
						471.70		132
					Total	1284.75		342

Table 1

Technical data on diamond drilling holes and the analysis numbers employed in the text.

fluorescence (XRF) analyses. The methods used were as follows: A sample is jaw crushed to -2 cm and further swing milled to -200mesh. Some of the -200 mesh material is dissolved in concentrated nitric acid, diluted to standard volume and assayed on a Perkin Elmer 403 unit. Sulfur is analyzed by burning a portion of the -200 mesh sample in a resistance furnace; the gases are oxidized into sulfuric acid and titrated with a basic solution. Some of the -200 mesh material is pressed into a briquette, which is run on a Philips PW 1320 X-ray spectrometer. All the analytical data are systematically checked against standards. Of the analyses used in this study the following chemical components and elements were done by XRF: SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO\*, MnO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, As, Cr, Zr, Rb, Ba and Sr, and the following elements by AAS: Cu, Zn, Pb, Co, Ni, Ag and Au (after special sample treatment). The relative error of the AAS and XRF methods is c. 1-5 %. The sulfur determination detection limit is 0.05 % and that of Au 0.2 ppm.

Because the d.d. holes employed in this study were drilled for exploration purposes the sulfur contents in the analytical data are relatively high. To avoid errors in petrological examinations the sulfur contents were recalculated into dominant iron sulfide species, and an equivalent amount of iron was subtracted from the total iron. Thus in the pyrrhotite-dominated Haveri occurrence S was expressed as FeS, and FeO<sup>\*</sup> = (total iron — pyrrhotite iron) oxide; in the pyrite-dominated Kiipu occurrence S was expressed as FeS<sub>2</sub>, and FeO<sup>\*</sup> = (total iron — pyrite iron) oxide.

The analytical data and factor analyses were processed at the Outokumpu Co. Computer Center, Olari.

The geological maps of Figs. 2 (p. 18) and 19 (p. 41) were simplified by the author from unpublished Outokumpu Co. maps prepared for exploration purposes.

The photographs were taken by the author. The scale division in the field photographs is in cm.

## GENERAL ASPECTS OF PLATE TECTONICS, RELATED MAGMATISM, ORE-FORMING PROCESSES AND STRATA-BOUND VOLCANOGENIC MASSIVE SULFIDE DEPOSITS

#### The concept of plate tectonics

To understand the genesis of strata-bound volcanogenic massive sulfide deposits one must be aware of the large-scale geotectonic processes that take place in the Earth's crust and control magmatic evolution and related ore-forming processes. "The new global tectonics" of Dewey and Bird (1970), or plate tectonics (e.g. Le Pichon *et al.* 1972), is generally accepted as the main geotectonic process presently operating in the Earth's crust.

The concept of plate tectonics is based on the recognition of sea-floor spreading, continental drift and subduction. Plate-tectonic processes have been traced as far back as 1 000-1 300 Ma ago (e.g. Irving et al. 1974, Condie and Moore 1977). Conclusive proof of the existence of plate-tectonic processes older than that has not been found, although they have been suggested to have been active at least 2 500 Ma ago (e.g. Talbot 1973, Condie 1976, Mitchell and Garson 1976, Smith 1976). Despite certain secular compositional trends, mobile belts largely similar to present-day orogenic belts have existed since the Archean (e.g. Sutton 1967). Goodwin (1974) gives evidence of diagnostic features (e.g. island arcs) that can be traced throughout the evolution of the Archean crust of Canada and which refer to the plate motions observed in present-day plate-tectonic processes. In his model of the evolution of the Earth's crust, Tarling (1978) stresses the importance of the Archean-Proterozoic boundary (2 700 Ma ago),

since it was about that time that a major continental lithosphere was formed and the oceanic lithosphere was drastically thinned. In association with the thickening of the oceanic lithosphere it became possible for island-arc differentiates to be added to the continental margins even during Proterozoic times.

Models have been presented for the geotectonic evolution of the Archean(--Proterozoic) crust that require no, or only limited amounts of, crustal plate movements. These include Glickson's (1971) model, in which the evolution of Archean volcanic-sedimentary troughs was controlled by early nuclei of sodic granites and granodiorites emplaced in the primordial, oceanic crust, and the model of Baragar and McGlynn (1976), in which volcanic loading of a thin sialic Archean crust leads to downwarping, melting, plutonism and deformation.

Not enough is known of Finland's Proterozoic bedrock to tell for sure whether its geotectonic development can be explained on plate-tectonic principles. Nevertheless, because the concept of plate tectonics, together with the increase in data, is gaining in popularity as an explanation of Proterozoic (and even some Archean) structures, and because it serves as a good basis for comparisons, genetic classifications and correlations of ore deposits, plate tectonics, with the reservation given above, is applied in this study.

#### The structure of the Earth

The Earth is built up of three coinciding regions: the crust, the mantle and the core. The crust and the mantle are separated by the seismic discontinuity known as the Mohorovičic discontinuity, or Moho. The Moho is located 10—20 km beneath the oceans and usually 30-50 km beneath the continents. The following summarizes the crust and the mantle after Le Pichon *et al.* (1972) and Condie (1976).

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#### The crust

The crust is the region of the Earth that is above Moho. There are three major crustal divisions: oceanic, transitional and continental. The oceanic crust is 5 to 15 km thick. Island arcs and continental margins are the main regions of transitional crust, that is from 15 to 30 km thick. The continental crust is from 30 to 50 km thick, with thicknesses of up to 80 km in some areas.

The oceanic crust typically consists of three layers. From the top downwards these are:

- Layer 1: Thin sequences of chert, argillite and pelagic limestone. The average thickness of layer 1 is 0.3 km.
- Layer 2: Extrusive tholeiitic basalts that commonly display pillow structures and conversion to spilite. The average thickness of layer 2 is 1.4 km.
- Layer 3: The basalts of layer 2 pass downwards into gabbro with subsidiary diorite and trondhjemite. In some places the lower part of layer 2 and the upper part of layer 3 are intruded by conspicuous sheeted complexes composed of swarms of dolerite dykes intruded in succeeding orders into the spreading center. Layer 3 has a uniform thickness of 4.7 km. Below the third layer, i.e. below the Moho, the mantle consists of peridotite.

The transitional crust typically occurs in areas of island-arc systems, that is, arcuate chains of islands such as the Japanese Islands. Continental analogues of island arcs occur where the subduction zone plunges beneath a continental borderland, e.g. the Andes in South America. The transitional crust areas are characterized by calc-alkaline volcanic and plutonic rocks and by intense seismic activity. A negative gravity anomaly occurring at the outer margin of an island arc marks the site of a trench that is a surface manifestation of the Benioff zone.

The continental crust comprises cratonized shield and platform areas with an overall composition of granodiorite or quartz diorite. Magmatic intrusives within the continental crust display an alkaline trend.

#### The mantle

The mantle is that region of the Earth beneath Moho that extends down to c. 2 900 km. The mantle is vertically zoned into the upper and lower mantle; only the former is discussed here. The upper mantle extends for about 400 km down from the Moho and includes the lowermost part of the lithosphere and the upper part of the asthenosphere. The lithosphere (50—150 km thick) is the strong outer layer of the Earth, including the crust and uppermost parts of the mantle, that reacts to stresses as a brittle solid. The asthenosphere, on the other hand, which extends for 700 km down from the base of the lithosphere, is a weak layer that readily deforms by creep.

The primary, undifferentiated and undepleted composition of the upper mantle is assumed to be roughly 1 part basalt to 3 parts peridotite (Ringwood 1966). This hypothetical composition, termed pyrolite (pyroxene-olivine rock), is given in Table 3, column 14 (p. 24).

#### Magmatic evolution

Three main magma series are recognized on the Earth: the tholeiitic, calc-alkaline and alkaline series (Jakeš and White 1972). The alkaline series is mainly associated with the continental crust and is discussed no further in this account.

The main rock types of the oceanic crust and immature island arcs are the basalts and basaltic andesites of the tholeiitic series, whereas those in mature island arcs are mainly andesites and dacites of the calc-alkaline series (Miyashiro 1974, Ringwood 1974, Condie 1976, Condie and Moore 1977). The rocks of the island-arc-bound calc-alkaline series (and some tholeiites) tend to become enriched in incompatible elements (including Ti, K, P, U, Th, Ba, Rb, Sr, Cs, Zr, Hf and REE). These are a group of elements that are unable to substitute in the major minerals of the upper mantle (olivine, aluminous pyroxenes) and, depending on the heigth of the volcano above the Benioff zone, become enhanced in the liquid phase. The chief environments of tholeiitic and calc-alkaline magma production are the plate margins, either mid-ocean ridges or subduction zones. The tholeiites produced beneath the mid-ocean ridges and extending into their axial zones are very low in alkali elements and are therefore referred to as low-K tholeiites. The volcanic rocks of the calc-alkaline series occur mainly in island arcs and along continental margins overlying subduction zones.

According to empirical studies by Green and Ringwood (1967), a parent magma of olivine tholeiitic composition may fractionate at different pressures to yield distinctive basaltic magma types. In the following the main courses of these temperature—pressure controlled fractional crystallizations are discussed. Note that at decreasing temperatures fractional crystallizations are recorded, and at increasing temperatures melting events produce very similar meltsolid partitions. Under crustal conditions (partial) melting is the major factor in magma production (Green 1971).

During the early stages of fractional crystallization at pressures representing shallow crustal depths (i.e. at pressures < 5 kbar, < 15 km depth) the tholeiitic series is characterized by iron enrichment and magnesium depletion caused by the separation of olivine with much lower Fe: Mg ratios than the equilibrium ratios. In addition to iron enrichment, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO are also enriched in the liquid phase. However, the appearance of a very calcic plagioclase as a second phase curtails the Al<sub>2</sub>O<sub>3</sub> and CaO enrichment, and hence the tholeiitic fractionation trend into iron-rich, Na- and K-enriched quartz tholeiites with 50 % or more SiO<sub>2</sub> and 12—14 % Al<sub>2</sub>O<sub>3</sub> is maintained.

Further, in the course of fractionation at an empirical pressure of 9 kbar (representing 15— 35 km crustal depths), olivine is joined to orthopyroxene as a second phase in the olivine tholeiitic parent composition. Plagioclase only appears very near to the solidus. Owing to crystallization of large amounts of olivine and pyroxene(s) before plagioclase,  $Al_2O_3$  is notably increased while SiO<sub>2</sub> remains relatively constant at 47—49 %. Instead of Fe enrichment at lower pressures, this load pressure interval will yield high-Al olivine tholeiites.

In fractionations at up to 27 kbar empirical pressures (at depths of 35 to 100 km), the crystallization of pyroxenes and garnet from the parent magma yield olivine-rich alkali basaltic magmas.

The following model for the production of calc-alkaline magmas is given by Ringwood (1974). High water pressure is maintained by the dehydration of serpentine and hydrated magnesium silicates as the oceanic crust is subducted to depths of 100 to 150 km. Pyroxenites are formed through reactions with the overlying mantle material. Diapirs of pyroxenite rise upwards from the Benioff zone and partially melt to form magmas which, by amphibolecontrolled fractionation, produce the calcalkaline magmas typical of mature island arcs.

#### Ore-forming processes and strata-bound volcanogenic massive sulfide deposits

From the point of view of plate tectonics strata-bound volcanogenic massive sulfide de-

posits are formed largely in two different environments: the oceanic crust spreading center environment, and the transitional crust islandarc environment (e.g. Sillitoe 1972, Sawkins 1972 and 1976, Hutchinson 1973, Mitchell and Bell 1973, Mitchell and Garson 1976). The oceanic crust environment is characterized by tholeiitic magmatism and an island-arc environment, generally, by tholeiitic magmatism in its initial stage and by calc-alkaline magmatism in its mature stage. This genetical classification based on plate tectonics is reflected in the geochemistry and composition of the volcanogenic massive sulfide deposits related to these two environments. As in many of the studies on well-known type occurrences, in this study the volcanogenic massive sulfide deposits associated with tholeiitic magmatism, and which usually occur in the oceanic crust environment, are called the Cyprus type, and those associated with calc-alkaline magmatism, and which usually occur in the mature islandarc environment, are called the Kuroko type. In the following the petrology, geochemistry, ore-forming processes and plate-tectonic setting of these two main types are reviewed briefly.

#### The Cyprus type

Ophiolites are complexes of volcanic and plutonic rocks mainly of basic and ultrabasic composition (Miyashiro 1975). Coleman (1977) considers ophiolites as parts of the oceanic lithosphere incorporated in orogenic belts by plate-tectonic processes. Certain cupriferous massive sulfide deposits associated with maficultramafic volcanic piles of ophiolitic affinity are generated in deep water in ocean basins at sites of sea-floor spreading, i.e. mid-ocean ridges (e.g. Sillitoe 1972, Hutchinson 1973). These massive sulfides are temporally and spatially related to tholeiitic basalts, which constitute layer 2 of the oceanic crust. This layer overlies coeval dolerite dyke swarms (feeders) and gabbro complexes (layer 3), which, in turn, overlie and are derived through

partial melting from the ultrabasic rocks of the upper mantle. As components of oceanic lithosphere these massive sulfide deposits of ophiolitic affiliation are transported away from the midocean ridges by means of sea-floor spreading. On reaching the margins of the ocean basins, the massive sulfide deposits are underthrust along subduction zones beneath continental margins and island arcs. During subduction, some of the deposits are incorporated mechanically (obducted) into the continental crust as parts of slices of oceanic lithosphere (Dewey and Bird 1971, Sillitoe 1972).

Massive cupriferous sulfides of this type can also be generated at the sites of basalt extrusion in spreading ocean basins behind island arcs, or marginal basins (Sillitoe 1972, Mitchell and Bell 1973, Dewey 1974, Condie 1976, Pearce and Gale 1977).

The Cyprus-type cupriferous massive sulfide deposits, genetically associated with tholeiitic rocks of basaltic composition, are found all over the world, mainly in the Phanerozoic (Hutchinson 1973). Well-known examples are the massive sulfide deposits of Cyprus (Constantinou and Govett 1973) and of Newfoundland (Bachinski 1977). The copper-iron sulfide mineralization found in the Mid-Atlantic-ridge metabasalts (Bonatti *et al.* 1976) and the recent discovery of massive sulfides on the East Pacific Rise (Francheteau *et al.* 1979) verify the theory of the association of Cyprus-type deposits in areas of spreading oceanic crust.

In Cyprus some 90 massive sulfide deposits and prospects are genetically related to the Troodos ophiolite complex (Moores and Vine 1971, Sillitoe 1972). This Plutonic Complex is composed of hartzburgite, dunite, pyroxenite, gabbro and trondhjemite, and it grades upwards into a Sheeted Complex composed almost entirely of dolerite dykes overlain by Lower and Upper Pillow Lavas, mainly of tholeiitic basalt composition. The basalts are overlain by ferruginous and manganiferous sediments, grits, shales and cherts passing upwards into marls and limestones. The hartzburgite and dunite are considered to represent the depleted mantle; the gabbro and the lower part of the Sheeted Complex represent layer 3; the upper part of the Sheeted Complex together with the Lower and Upper Pillow Lavas represent layer 2; and the overlying (mainly chemical) sediments represent layer 1 of the oceanic crust. This is a typical sequence-type ophiolite complex (Miyashiro 1973b).

The massive sulfide deposits in Cyprus occur as irregular, elongated, lenticular bodies and are most common at the level of the contact between the Lower and Upper Pillow Lavas. The hanging walls of the orebodies are characterized by »ocher» composed of pyrite, silica and hydrated iron oxides. These are underlain by massive pyritic orebodies with the tenor of 1-4 % Cu, locally high Au and Ag contents and erratic Zn concentrations of a few percents in the upper parts of orebodies. The Co content of the ores is usually high, and Co: Ni > 1. The massive parts of orebodies pass downwards into stockworks of sulfide veinlets accompanied by silicification and propylitic alteration (Hutchinson and Searle 1971, Clark 1971, Constantinou and Govett 1973, Sillitoe 1972).

Not all authors, however, would agree with this plate-tectonic setting for the origin of the Troodos ophiolite complex in Cyprus. The chemistry of the Cyprus basalts led Miyashiro (1973a) to propose an island-arc origin based on a calc-alkaline fractionation trend, the frequency distribution of SiO2 and the FeO: MgO ratio of the lavas. Pearce (1975) suggested that the Troodos Massif was formed at a spreading axis in a marginal basin directly above a subduction zone; thus it may be possible to produce lavas with both mid-ocean-ridge and island-arc characteristics. Miyashiro (1974) maintains that some of the ophiolite complexes are remnants of volcanic masses in the initial and immature stages of island-arc formation.

Several attempts have been made to classify and/or subdivide the cupreous massive sulfide

deposits associated with basic to ultrabasic, tholeiitic volcanic rocks (e.g. Sawkins 1972, Mitchell and Garson 1976). All these deposits, however, share certain features that connect them with the main Cyprus type. These are:

- 1. Lithological association with submarine, usually pillowed ultrabasic to basic flow rocks of the tholeiitic magma series. Spilitic varieties are also met with. Association with basic pyroclastic rocks is far less common.
- 2. Distribution of metallic elements indicating concentrations mainly of Cu, Co and Au with lesser amounts of Ag, Zn and Ni, and negligible Pb. In the ore deposits Co: Ni  $\geq$  1.
- 3. Connection with spreading centers in oceanic crust areas: mid-ocean ridges, marginal and interarc basins, and initial island arcs.
- 4. Derivation of the ultrabasic to basic rock material through (partial) melting from the upper mantle. These parent magmas are rather »primitive» with little chemical differentiation or crustal contamination. The tholeiitic fractionation implies concentrations of incompatible elements into the melt.

The Cyprus massive sulfide deposits are generally explained to have generated during the formation of the layer-2 pillowed basalts (and thus to be bound to those volcanic units). The sulfides deposited partly as vent-area replacements but mainly as massive precipitates on the ocean floor (Clark 1971, Sillitoe 1972). Experimental and analytical studies indicate that the metals in mineralizing solutions probably originate from basalts through rock-sea water interaction at elevated temperatures (e.g. Corlis 1971, Bischoff and Dickson 1975, Mottl *et al.* 1979).

According to Mitchell and Garson (1976), rocks of the ophiolite suite are widely interpreted as thrust wedges of oceanic crust, or marginal basin crust, and upper mantle tectonically emplaced during continental or island-arc collision. Sillitoe (1972) explains that the Troodos ophiolite complex was generated at a mid-ocean ridge and was subsequently emplaced by collision of the African plate to the south with a subduction zone dipping northward.

#### The Kuroko type

The Japanese Islands form an island-arc system c. 2 000 km long that, like several other circum-Pacific island-arc systems, is underlain by a subduction zone along which the oceanic crust being created at the Pacific spreading system is consumed (Uyeda and Miyashiro 1974).

According to Horikoshi (1969) and Sato (1974 and 1977), the Japan-Sea side of the Japanese Islands forms a specific geologic province characterized by thick volcanic and sedimentary piles resulted from subsidence and violent submarine volcanism in the Miocene (roughly 13 Ma ago). This region is marked by numerous strata-bound »Kuroko-type» volcanogenic ore deposits along certain zones.

The Benioff zone is at a depth of roughly 150 km below the Kuroko zones, which were areas of high heat flow during the Miocene. Typical Kuroko deposits are polymetallic sulfide-sulfate deposits in which economic grades of Cu, Zn and Pb sulfides with Ag and Au occur together with Ba and Ca sulfates. A typical deposit is a lenticular pyrite-Cu-Zn-Pb orebody concordant with the surrounding sediments and volcanics. This stratiform orebody is commonly underlain by a stockwork orebody characterized by disseminated or network mineralization of pyrite and chalcopyrite distributed in a funnel shape in felsic lavas and pyroclastics. The stratiform orebody is usually topped by a thin bed of ferruginous chert. Japanese terms often cited for these ores are »keiko», or the siliceous epigenetic ore zone with iron sufides and chalcopyrite, followed by syngenetic »oko», or the yellow ore zone consisting mainly of pyrite with varying amounts of chalcopyrite; and »kuroko», or the black ore zone, which is a polymetallic sulfide zone consisting mainly of pyrite, sphalerite, galena, chalcopyrite, fahlores and barite (Shimazaki 1974).

The metal contents of Kuroko deposits are held to derive from underlying volcanic rocks (mainly pyroclastics) and to have been transported by hot circulating waters that originated mainly from sea water but, possibly, also from magmatic sources (Lambert and Sato 1974, Urabe and Sato 1978). The circulation of these hydrothermal fluids is driven by volcanic heat sources. By leaching volcanic piles the fluids become loaded with metal ions, and when entering the sea floor precipitate their metal load mainly as a result of falling temperature to form the stratiform Kuroko ore deposits. The sulfur in the sulfides of Japanese Kuroko deposits is derived through chemical reduction from coeval sea-water sulfate (Sasaki and Kajiwara 1971). The following physicochemical conditions, detected partly from fluid inclusions and mineral parageneses, are estimated to have prevailed at sites of Kuroko ore deposition: temperature is in the 200° to 260°C range, pressure is in the order of 30-50 atm, and fo, approximates 10-35 atm. The ore-forming fluids are saline (5 % NaCl) and the pH is weakly acidic (Tokunaga and Honma 1974, Large 1977, Urabe and Sato 1978).

A distinct alteration pattern recognized around the Kuroko ore deposits is related to the leaching effect of hydrothermal fluids. The alteration zones underlying Kuroko deposits are typically depleted in Na and Ca, and enriched in Fe, Mg, Mn, K and Si. This is termed the »Kuroko alteration» (Iijima 1974).

The Kuroko deposits themselves display a distinct zonation from the underlying Cu-rich epigenetic stringer ore zone to the syngenetic stratiform orebody where the base metals are zoned from Cu ores in the bottom to Zn ores in the middle and upper parts; Pb is concentrated at the very top (Shimazaki 1974).

The corresponding Precambrian massive sulfide deposits in calc-alkaline, intermediate to felsic pyroclastic environments are sometimes distinguished as a group of their own (e.g. the »Superior type» of Lambert 1976 and the »Archean type» of Large 1977). Although these deposits cannot be considered as exact analogues of Japanese Kuroko deposits they exhibit marked similarities such as association with submarine calc-alkaline volcanism, sulfide mineral composition and zoning patterns, wallrock alterations, and a geological setting in terms of plate tectonics.

One of the few differences is the general lack of lead in Precambrian deposits. Sangster (1972) explains this as a function of long-term geochemical evolution: the crust would not have had time to generate and accumulate Pb produced by radioactive decay of U and Th. Another explanation given by Lambert and Sato (1974) is that the Precambrian deposits are generally associated with andesitic volcanics whose Pb content was originally low.

Another difference is the presence of carbonates as gangue minerals in the Precambrian massive sulfide deposits instead of sulfates in the younger deposits (Sangster 1972, Lambert and Sato 1974). This difference probably arises from the scarcity of oxygen in the Early and Middle Precambrian (up to c. 2000-2500 Ma ago). The low fo<sub>2</sub> favors the precipitation of Ca(-Mg)-carbonates and even carbon, instead of Ca and Ba sulfates in higher fo2 ore-forming environments (cf. Ohmoto 1972). The low fo2 in the Early Precambrian has been proved by studies on iron formations. These studies suggest that until about 2000 Ma ago the atmosphere and hydrosphere were practically devoid of free oxygen. Around that time primitive photosynthetic organisms advanced biological oxygen mediation; the oceans were depleted in their ferrous iron load by the precipitation of huge essentially ferric iron formations and became saturated with O2, which thereafter escaped to the atmosphere

(LaBerge 1973, Cloud 1973). Dimroth and Kimberley (1976), on the other hand have found no evidence that an oxygen-free atmosphere has ever existed during the span of geologic history. The low fo, would explain why reduced sulfur species (Sr, S=) dominate over oxidized sulfur species  $(S_0, SO_4^{=})$  in Early and Middle Precambrian (up to c. 2 000 Ma ago) seas by a factor of 10, as assumed by Large (1977), compared with  $S_r: S_o = 1:100$ in present-day seas. (In the absence of other relevant data the Sr: So ratio of 10, after Large (op. cit.) is applied to the Haveri and Kiipu ore-forming environments.) The low fo2 causes different physicochemical conditions in Early and Middle Precambrian vs. Late Precambrian and Phanerozoic, and results in a general lack of barite and anhydrite, the existence of carbonates and carbon, and the dominance of pyrrhotite over pyrite in ancient deposits.

The third commonly recorded difference is the replacement of chlorite alteration, usually underlying Precambrian volcanogenic massive sulfide deposits (Sangster 1972), by siliceous alteration in Japanese Kuroko deposits (Iijima 1974). Large (1977) explains this difference as a result of the chemistry of the underlying parent rocks: the Precambrian deposits tend to be associated with intermediate volcanic piles that produce SiO2-undersaturated oreforming fluids, whereas the Japanese Kuroko deposits are associated mainly with rhyolitic volcanics that yield SiO2- (and K-)enriched fluids resulting in siliceous alteration pipes. The same phenomenon has been recorded from some Archean deposits (e.g. Kidd Creek and Millenbach, Canada).

Kuroko deposits are found in island-arc settings that develop above subduction zones. At active continental margins the volcanism tends to be subaerial (as in the present-day Andes), and the metal-bearing fluids give rise to magmatic-hydrothermal deposits typified by porphyry copper deposits (Sillitoe 1972). The study of plate tectonics reveals the similarity between ore-forming processes throughout the ages; hence even Precambrian volcanogenic massive sulfide deposits of felsic, calc-alkaline affiliation in island-arc environments are included under the heading »Kuroko type».

The following is a summary of the discussion so far. Volcanogenic strata-bound massive sulfide deposits are of two main types, called here the Cyprus and Kuroko types. (Each has several subtypes, but these are not discussed here.) The Cyprus-type massive pyrite and/or pyrrhotite deposits are generated at spreading centers in oceanic crust areas. These deposits are commonly associated with tholeiitic, pillowed basalts derived from the upper mantle. The plate-tectonic settings involved are those of a mid-ocean ridge, marginal or interarc basins, or shallow subduction-level initial-stage islandarc development. All these settings are characterized by the spreading of lithosphere, which allows the access to the ocean floor of (partly) melted basic to ultrabasic upper-mantle material of the oceanic crust type, generally from a depth of less than 30 km. The Cyprus-type deposits are commonly characterized by high Cu, Co and Au contents, low Zn, Ag and Ni, and negligible Pb contents. The Co: Ni ratio in the ore is  $\geq$  1. The metals are exhaled, or leached out by hydrothermal activities from the effusives; the sulfur originates mainly from sea water. The sulfides are deposited on the sea-floor under hydrothermal conditions.

The Kuroko-type massive pyrite and/or pyrrhotite deposits are generated in island-arc settings above subduction zones. These deposits are associated with submarine, felsic pyroclasticdominated, volcanic centers characterized by calc-alkaline magmatism, whose material is derived from depths in the order of 150 km, near the Benioff zone, through the partial melting of depleted and hydrated subduced oceanic crust and mixed sedimentary materials. The ore deposits commonly display a distinct zoning from Cu-rich bottom through Zn ore to Pb-rich top. The metals originate, through leaching by hydrothermal fluids, from felsic pyroclastic volcanic piles. Certain alteration phenomena are connected with the leaching and commonly result in the removal of Ca and Na from, and in the introduction of Mg, Fe, K and  $\pm$  Si into the parent rocks in the foot wall of the deposits. The sulfide sulfur is derived mainly from sea-water. The sulfides are deposited on the sea-floor under hydrothermal conditions.

Table 2 summarizes characteristic features of strata-bound volcanogenic massive sulfide deposits of the Cyprus and Kuroko type.

Table 2

Summary	of	characteristic	features of	Estrata-bound	volcanogenic	massive sulfide	deposits of	Cuprus and	Kuroko type
Summary	OI	characteristic	icatures of	strata-bound	voicanogenie	massive sumue	deposits of	Cyprus and	Kuloko type.

	CYPRUS TYPE	KUROKO TYPE
Plate-tectonic setting	Oceanic crust areas: spreading cen- ters at mid-ocean ridges, interarc and marginal basins, initial island arcs.	Transitional crust areas: mature island arcs.
Magma association	Ultrabasic to mainly basic tholeiitic (including spilitic) lavas. Magma derived from shallow crustal levels (15—30 km or less).	Intermediate to mainly acidic calc- alkaline pyroclastics. Magma de- rived from deep crustal levels (150 km or more).
Metal paragenesis	Cu(-Co-Au), minor Zn, Ag and Ni, negligible Pb. Co $\geq$ Ni.	Zn-Cu(-Pb-Ag-Au)
Metal zoning	Commonly lateral: Au-Co-Cu-Ni-Zn	Commonly vertical: Cu-Zn-Pb-Ag
Foot-wall alteration	Relatively weak	Distinct: $-Ca$ , $-Na$ , $+Fe$ , $+Mg$ , $+K$ $+Si$

#### THE HAVERI OCCURRENCE

The extinct Haveri mine is located in the commune of Viljakkala, roughly 35 km northwest of Tampere (Fig. 1). The deposit has been known since 1737. In the 18th and 19th centuries it was mined on a small scale for its magnetite content. Reinvestigation in 1935 indicated that the deposit contained economic grades of Au and Cu, and in 1942 Vuoksenniska Oy started mining operations. Gold was produced by the cyanide process and copper concentrates by flotation. By 1960, when the mine was closed down as unprofitable, a total of 1.5 million tons of ore containing 2.8 g/ton Au and 0.37 % Cu had been mined from an open pit and underground (Lupander and Räisänen 1954, Isokangas 1978). For detailed history of the Haveri mine, see Kaskimies and Sinisalo (1973, in Finnish).

In 1976—77 the present author supervized exploration drillings for Outokumpu Co. in the environment of the Haveri mine. Most of the material on Haveri for the present study originates from that work.

#### General geology

Fig. 2 is a simplified geological map of the Haveri region. The map area is relatively well exposed except for some large water-covered areas where geologic contacts have to be inferred, partly with the aid of geophysics. The basic metavolcanic and associated rocks around the Haveri mine, hereafter called the Haveri formation, form a distinct lithological unit with an area of c. 10 km<sup>2</sup> of steeply folded rocks. Assuming a consistent downward continuation, and allowing 50 % for erosion, it can be estimated that the Haveri formation originally contained c. 100 km<sup>3</sup> of rock.

According to Simonen (1953 and 1971), these basic metavolcanic rocks are part of the Tampere schist belt in the Svecofennian zone of the Svecokarelidic orogeny, whose orogenic, mainly granitic, plutonism culminated 1 800— 1950 Ma ago. Simonen (1953) gives the stratigraphy of the Tampere schist belt from top to bottom as:

	th	ickness
Basic volcanics	>	1 000 m
Conglomerates and associated sediments	700-	— 800 m
Basic and intermediate volcanics	800-	—1 500 m
Quartz-feldspar rocks	1 500-	-2 200 m
Varved sediments (graywacke-slates)	>	3 000 m
Total thickness	>	8 km

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On the basis of top determinations in the graywacke-slates, Simonen (op. cit.) includes the basic volcanics (the Haveri formation) in the uppermost stratigraphic unit. To the present writer's knowledge, the contact between the Haveri formation and the graywackeslates is not exposed. At Osara, Viljakkala, however, these two formations are separated by a water-covered distance of c. 200 m across the inferred contact. An exposure (map sheet 2122 11, x = 6844.05, y = 458.10, Fig. 2) of graded graywacke-slate indicates that the top faces to the southwest, away from the Haveri formation (Fig. 3). This implies that the Haveri formation underlies the graywackeslates. Even though Simonen's stratigraphic concept appears to be generally correct, the Haveri formation does not necessarily lie at the top of the roughly 5-km-thick column of graywacke-slates; it more probably lies at their lateral extension, possibly with partly interfingering contact relations.

Stigzelius (1944) proposed a submarine depositional environment for the Haveri basic volcanic rocks on the basis of primary structural features such as fluidal, pillow and amygdaloidal structures. Analyses indicated basaltic composition, SiO<sub>2</sub> c. 50.5 %, for the basic metalavas. The limestones associated with the basic meta-

17



Fig. 2. Simplified geological map of the Haveri region. 1 = Tholeiitic basic metalava and metalava breccia, metatuff, metatuffite, limestone, chert and black schist (the Haveri formation); 2 = Graywacke-slate and mica schist; 3 = Calcalkaline intermediate to acidic metavolcanic rocks; 4 = Granite, quartz- and granodiorite; 5 =Diamond drilling hole.

lavas were explained as chemical sediments precipitated on the surfaces or in the fractures of the effusive rocks.

Stigzelius (1944) divided the Haveri ores into four categories: iron ore, sulfide ore, gold ore, and shear or fault zone ore (Schölerz). The distribution of iron ore and sulfide ore in the Haveri mine displayed a subparallel »side by side» zonal arrangement (cf. op. cit. Figs. 41 and 42). The iron ore occurs mainly as magnetite disseminations in basic metavolcanics. The maximum iron contents in the iron ore are 40— 50 % HCl-soluble iron; the sulfur content is generally > 1 %, and c. 0.05 % P, 0.5-0.8 %  $TiO_2$  and 0.02 % V are encountered. The sulfide ore consists mainly of pyrrhotite, with chalcopyrite, magnetite and variable minor amounts of fahlores, sphalerite, molybdenite and ilmenite. The sulfide ores occur as stockwork- or network-type breccias and fracture fillings that together display folded and streaky structures (schlieren) within the basic rocks.

Most of the copper and gold in the Haveri mine displayed overlapping distribution patterns although they also occurred separately in parallel zonal arrangements (op. cit., Figs. 43 and 44). In production figures copper and gold show a clear positive correlation; in individual samples,



Fig. 3. Graded graywacke-slate from Osara, Viljakkala, 1500 m west of the Haveri mine. Stratigraphic top is to the left (southwest), away from the Haveri formation. The inferred contact lies 200 m to the right (northeast).

however, gold and copper and gold and sulfur display poor and erratic correlations. The copper and silver contents correlate positively and well. The shear zone ore, which occurs as fracture and fault-zone fillings, is composed mainly of pyrite with some pyrrhotite, chalcopyrite, cobaltite, arsenopyrite, and some gold.

In the opinion of Stigzelius (1944) the Haveri oxide, sulfide and gold ores are epigenetic, the metals and sulfur originating from hydrothermal solutions derived through magmatic differentiation from oligoclase granite; however, later Stigzelius (1976) suggested a volcanic-exhalative origin for the Haveri deposit.

Paarma (1947), who studied the mineralogy of the Haveri ore, identified and described abundances, modes of occurrence and properties of the following ore-forming minerals. Pyrrhotite, followed by chalcopyrite, is by far the most common sulfide mineral at Haveri. Pyrite occurs in two generations and seldom in sufficient abundance to be included in the main minerals. The only oxide minerals encountered were magnetite and ilmenite. Cobaltite is the most important cobaltiferous mineral. Glaucodote and gersdorffite occur together with cobaltite. In addition, small amounts of arsenosphalerite, molybdenite, pyrite, scheelite. tellurobismutite and hessite were found. Cubanite and valleriite lamellae occur in chalcopyrite. Native gold was met with mainly along grain boundaries of Co and As minerals and as extremely fine-grained, nebulous disseminations in cobaltite.

Ollila (1977) studied the distribution, petrography and geochemistry of the rocks in the area surrounding the Haveri mine. These metavolcanic rocks are mainly subalkaline, medium-grade metamorphosed basalts cut by granodiorite (stocks), metadacite dykes and biotite-amphibolite dykes.

The Haveri region is covered by the following geological maps: 1: 400 000, Sederholm (1913); 1: 100 000, Huhma, Salli and Matisto (1952), and Simonen (1952).

#### Petrography

#### Macroscopic descriptions

In hand specimens the Haveri metalavas are grayish green in color and rather massive in structure. Flow structures are visible (Fig. 4) on some outcrops. In some d.d. cores epidoterich and/or skarned bands indicate pillow rims, and thin metatuffite, chert or skarn layers indicate contacts between succeeding flow units. The flow breccia rocks are easily distinguished in outcrops (Fig. 5) and in d.d. cores by their heterogeneous structure and coloring. Most of



Fig. 4. Pillowed metabasalt from Haveri, Peltosaari, 800 m east of the Haveri mine.



Fig. 5. Basaltic metalava breccia from Haveri, Ansomäki, 900 m south of the Haveri mine.

these structures are broken pillow breccias, although some friction breccias have also been identified.

The Haveri metatuffs are usually dark in color and, except for being banded, rather massive in structure. As the degree of sorting increases, the metatuffs grade into metatuffites and mica schists. Black schists (or sulfide schists) are associated with the mica schists and are easily distinguished by their black color and smearing graphite contents. Limestone occurs in layers roughly 30 cm thick and interstitially with pillows and pillow breccias. Some of the interstitial material is skarned. Bands of white, hard chert 20—40 cm thick are found in d.d. cores allied with flow rocks.

The ore proper occurs as submassive to massive intersections (c. 0.5-1.5 m long) containing 20-80 % sulfides (pyrrhotite with some chalcopyrite and minor pyrite), most often together with metalava breccia and

metatuffs. The ore usually displays flowribboned, streaky breccia-like structures that are conformable with flow breccia structures and the layering of tuff. The ore also occurs as disseminations and dissemination bands forming »mineralized rocks» in all the above-mentioned rock types except for some massive flows.

In the opinion of Stigzelius (1944), the impregnation and breccia structures indicate that the Haveri deposit has an epigenetic origin. Because the mine is now flooded, it is no longer possible to study these features. However, the sulfide breccia structures seen in drill cores and on some outcrops in the vicinity of the Haveri mine appear to be syngenetic flow-breccia structures whose origin is explained on p. 35. Most of the impregnation-like structures seen in the cores are syngenetic oxide and sulfide disseminations in flow breccias, metatuffs and chemical metasediments. The magnetite disseminations in the metabasalts appear to be primary magmatic segregations (resulting from the high concentration of Fe in these tholeiitic rocks), whereas those in the metasediments correspond to the oxide facies of chemical sedimentation. Some chloritized fault zones with slightly mobilized sulfide material were seen in the cores and may correspond to the »Schölerz» of Stigzelius.

#### Microscopic descriptions

The Haveri basaltic metalavas are rather massive, homogeneous, plain rocks with plagioclase, hornblende and often also biotite as constituent minerals. The texture is usually granoblastic with blastoporphyritic or blastofitic relict features. The grain size of the groundmass averages 0.1 mm, and that of the plagioclase phenocrysts 0.5—1 mm. The following is a description of a typical basaltic flow rock (specimen Hvr-8, 156.85 m, Fig. 6).



Fig. 6. Photomicrograph of a Haveri formation basaltic metalava. Specimen Hvr-8, 156.85 m, nic. +, magn. 100 x. Plagioclase phenocryst (right center) in an equigranular plagioclase-hornblende groundmass.

Plagioclase occurs as groundmass equigranular grains, c. 0.1 mm in diameter, with  $An_{8-10}$  (X  $\sim$  Canada balsam). The larger grains average 0.5 mm in diameter and appear to be zoned blastophenocrysts with edges at  $An_{10-15}$ and centers up to  $An_{45}$  (max. X' $\wedge$ 010 = 26°). Except for saussuritization (epidote and sericite) in some of the large grain centers, the plagioclase crystals are clear and granuled, indicating more or less complete metamorphic recrystallization. The rock is cut by plagioclase veins 0.1 mm wide (An<sub>10</sub>) that apparently filled contraction cracks in a cooling flow.

Hornblende (Z = bluish green, Y = brownish green, X = pale brownish green,  $Z \wedge c = 17^{\circ}$ ,  $2V_X \sim 70^{\circ}$ ) occurs as euhedral grains 0.2 mm in diameter.

Sphene abounds among the accessory minerals as small, pale brown leucoxene grains and aggregates disseminated throughout the rock. Except for tiny inclusions in some plagioclase grain centers, abundant epidote occurs mainly as individual grains with diameters of 0.05–0.1 mm. Some grains display subidiomorphic monoclinic crystal habits and cleavages. It is a pale yellowish green,  $n_Z$ - $n_X = 0.026$  (from interference color),  $Z \wedge c = 3^\circ$ . These properties fit pistacite, which contains roughly 15–20 mol-% ferric component (Winchell and Winchell 1951).

Other accessories include small opaque, carbonate and apatite grains.

The texture of the Haveri formation metatuffs is usually granoblastic and equigranular, the grain size varying from 0.05 to 0.1 mm. They are commonly homogeneous and unsorted, except for some fine-grained tuffite layers that feature blastoclastic, graywacke-like textures. The thickness of the bands ranges from a few mm to a few cm. The following microscopic description is of a typical metatuff specimen (Hvr-9, 27.00 m, Fig. 7).

Plagioclase (An<sub>45</sub>, X > Canada balsam, max.  $X' \land 010 = 28^{\circ}$ ) occurs as granulated grains.

Hornblende (Z = bluish green, Y = brownish green, X = pale brownish green,  $Z \wedge c = 20^{\circ}$ ) displays poorly developed crystal habits and occurs as grain clusters and grain aggregate bands.

Dark brown (Z) biotite occurs as small flakes, and a minor part of it is altered to pale-colored chlorite.

Accessory minerals include sulfides, sphene, apatite (tiny inclusions in plagioclase) and zircon (a few grains in biotite with pleochroic halos).



Fig. 7. Photomicrograph of a Haveri formation metatuff of basaltic andesite composition. Specimen Hvr-9, 27.00 m, nic. +, magn. 100 x. Granoblastic plagioclase-hornblende-biotite rock.

Tuff material that was probably hyaloclastite in origin is commonly intermixed with the basaltic material in the metalava breccias.

Chemical sediments typical of the Haveri formation are limestone and chert. Under the microscope the limestones (e.g. Hvr-5, 100.70 m) are granoblastic, the grain sizes in the different layers varying from c. 0.2 to 1 mm. The limestones typically contain c. 90 % carbonate, 10 % opaque, some muscovite and pale green (X') chlorite. In some ore-rich layers the proportion of opaque is as much as 50 % and includes mainly pyrrhotite but also chalcopyrite, sphalerite and magnetite (identified in polished section).

The cherts (e.g. Hvr-10, 98.80 m) are granoblastic and equigranular with grain diameter of c. 0.1 mm. They contain roughly 95 % quartz, the remainder being biotite, hornblende and chlorite as minute grains, and streaks with larger grain sizes (up to c. 0.5 mm). The accessory minerals include opaques (pyrrhotite, pyrite, sphalerite), carbonate and zircon, the latter together with biotite and hornblende accumulations. The cherts typically display sooty pigmented streaks roughly 0.05 mm thick that probably indicate primary depositional banding. The granoblastic recrystallization is not consistent with this texture. Detrital heavy minerals, as well as other signs of blastoclastic textures, are absent.

#### Geochemistry

In this chapter the Haveri deposit is viewed on the basis of 203 whole-rock XRF and sulfide phase AAS analyses representing a total of 732 m of split d.d. core. Emphasis is on the basaltic metalavas and metalava breccias, which are the most important rock types from the ore-petrological point of view.

Many of the d.d. intersections were sulfide-(mainly pyrrhotite) bearing. To obtain petrologically reliable results, the rock types were classified according to their FeS contents. Only rocks with less than 5 wt-% FeS were included in the petrological diagrams and discussions. (According to Spitz and Darling (1975), a sulfur content up to 2 wt-%, corresponding to c. 5 wt-% FeS and 4 wt-% FeS2, does not essentially affect petrological examinations.) Rocks containing 5-20 wt-% FeS were called mineralized, and those containing over 20 wt-% FeS were called ore. As the d.d. targets were selected mainly on the basis of electromagnetic anomalies the proportions of »mineralized rock» and »ore» are relatively high in the data.

#### Major-element geochemistry

Table 3 gives the chemical compositions in geometric means, weighted with intersection lengths, of the main rock types in the Haveri formation. For comparison, analyses of tholeiitic rocks from other parts of the world are included.

Fig. 8 shows the frequency distributions of the main chemical components of the Haveri metalavas and metalava breccias; Figs. 9—11 are the petrological diagrams most commonly used. From these data it appears that the metalavas and metalava breccias do not differ essentially and can be classified as subalkaline, tholeiitic basalts with the following characteristics (Green and Ringwood 1967, Condie 1976, Sun and Nesbitt 1978):

- 1. The SiO<sub>2</sub> contents of the basalts are rather high, in the 49—50 % range. These rocks are classified as quartz tholeiites.
- 2. The FeO\* contents display an enrichment at c. 13-15 %, and the MgO contents a

#### Table 3

			10		otar no	11 45 10	0.100	- 0 04	pressea	40 1 00	•			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
sio	10 11	10 37	50.70	59.18	49.35	56.36	52 65	49.24	45 57	51 3	51 57	50.59	50.83	45.16
TiO .	1 71	1.68	1 76	1.04	1 66	1.03	0.42	1 64	210	0.96	0.80	1.05	2.03	45.10
$110_2$ .	12.96	12.20	13.03	16.49	14 79	16.49	15 70	14 54	12 70	14.8	15.01	16.29	14.07	3.54
Fa O	12.70	12.20	15.05	10.47	17.12	10.47	13.70	17.57	5 17	14.0	274	3.66	2.88	0.46
FeO									6.51		7.04	5.08	9.05	8.04
FeO*	14 43	15.02	13 58	7 73	13 10	10.37	9.56	12 49	0.51	10.5	7.04	5.00	2.05	0.04
MnO	0.23	0.27	0.23	0.28	0.27	10.57	7.50	0.20	0.23	10.5	0.17	0.17	0.18	0.14
MaQ	4 01	4.45	4 75	3 74	6.04	7.07	813	7 13	7.08	67	6.73	8.96	6.34	37 47
CaO .	11 50	12.85	11.63	4 31	12 12	4.63	9.36	10.92	10.59	10.8	11 74	9.50	10.42	3.08
Na O	1 50	1 63	1.61	1.58	1 94	3.65	1.73	2 30	2.66	27	2 11.74	2.80	2 22	0.57
K O	0.54	0.56	0.60	2 15	0.70	0.30	2.45	0.20	0.60	0.18	0.44	1.07	0.82	0.13
R <sub>2</sub> O.	0.14	0.50	0.00	0.21	0.70	0.57	2.45	0.20	0.00	0.10	0.44	0.21	0.02	0.15
Г <sub>2</sub> О <sub>5</sub> .	0.40	0.50	0.40	0.21				0.20	5.61	1.2	0.11	0.21	0.25	0.00
S .					0.06				5.01	1.2	0.45	0.01	0.91	
FeS	0.80	0.69	0.77	2.44	0.00									
100	98.63	99.22	99.12	99.15	100.03	00 00	100.00	98.86	99.12	993	100 11	100.28	100.00	00 36
	1 20.05	1	77.12	1 1.15	100.05	1	100.00	1 20.00	1 11.12	1	100.11	100.20	100.00	17.50
-O=S					0.03			_			-			
Total	98.63	99.22	99.12	99.15	100.00	99.99	100.00	98.86	99.12	99.3	100.11	100.28	100.00	99.36
C	110	76	0.0	007	022			100		107				
Cu	110	24	90	221	233			100		107				
Zn	20	15	20	10	4/			55						
PD	15	15	15	55	22			06						00
CO	20	20	21	116	23			160		170	20	25		1 (00
INI	52	30	34	110	40			108		170	30	25		1 600
Ag	17	1.16	16	16	1									
AS	265	262	10	40		05	200	121	-	267	50	10		2 000
7.	65	66				55	20	121		61	50	40		2 900
Lf	05	2				00	20		1	01	/0	100		
RD	603	110				1	29			9	5	10		
Da	140	412				100	110			105	15	115		
Sr	148	101			1	1100	110			105	1200	330		

Analyses of Haveri formation rock types (columns 1-5) and basic rocks from other parts of the world. Major chemical components are in wt-%, minor elements in ppm. In columns 1-4 FeO\* = (Fetotal-FeFeS) O, in other columns  $FeO^* = total$  iron as FeO. FeS = S expressed as FeS

- 1. Haveri metalavas, SiO<sub>2</sub> < 53 %, FeS < 5 %, n = 36, total 197.15 m of split d.d. core. Geometric means, weighted with sample lengths. Cr, Zr, Rb, Ba and Sr are averages of 5 XRF analyses.
- 2. Haveri metalava breccias,  $SiO_2 < 53 \%$ , FeS < 5 %, n = 19, total 107.25 m. Geometric means, weighted with sample lengths. Cr, Zr, Rb, Ba and Sr are averages of 5 XRF analyses.
- 3. Haveri metalavas and metalava breccias, FeS < 5 %. Geometric means, weighted with sample lengths, of total data including 36 basaltic metalavas and 19 metalava breccias, 4 andesitic metalavas and 10 metalava breccias, and 2 dacitic metalava breccias. Total n = 71, 384.50 m.
- 4. Haveri metatuffs, FeS < 5 %. Geometric means, weighted with sample lengths, of total data including 3 basaltic, 9 andesitic, 9 dacitic and 3 rhyodacitic compositions. Total n = 24, 74.45 m.
- 5. Average of 88 Haveri metavolcanic rocks at SiO2 43-53 % from Ollila (1977). The samples were collected from outcrops of Haveri formation rocks from around the Haveri mine. Analyses by Outokumpu Co., Exploration, Olari laboratory.
- Court Pillow Lava (and dykes), Troodos ophiolite complex, Cyprus. Pearce (1975, Table 6).
   Upper Pillow Lava, Troodos ophiolite complex, Cyprus. Pearce (1975, Table 6).
   Average of 4 Icelandic tholeiites. Mäkipää (1978, Table 1, analyses TH-3, -4, -7 and -10).

- 9. Average of 3 basic schists (metavolcanic rocks) associated with »Besshi-type» deposits from central Shikoku, southwestern Japan. Kanehira and Tatsumi (1970, Table 1, columns 1-3).
- 10. Average of 337 Archean tholeiitic basalts from the Eastern Goldfields region, Western Australia. Hallberg and Williams (1972, Table 2, column 1).
- 11. Island arc tholeiitic basalt. Jakeš and White (1972, Tables 2A and 2B).
- 12. Island arc calc-alkaline high-Al basalt. Jakes and White (1972, Tables 2A and 2B),
- 13. Nockolds' (1954, Table 7, VII) normal tholeiitic basalt (and dolerite).
- 14. Pyrolite, model composition. Ringwood (1966).

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40 50 60 70 % SiO2

Fig. 9. The Haveri  $Na_2O + K_2O$  vs.  $SiO_2$  diagram. O = Metalavas,  $\bullet =$  Metalava breccias. The dividing line between the alkaline and subalkaline fields is from MacDonald and Katsura (1964), and the high-alumina field from Kuno (1966). The subalkaline, low-Al character of the Haveri formation metalavas and metalava breccias is evident.

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Fig. 10. The Haveri AFM diagram. The dividing line between tholeitic (upper) and calc-alkaline (lower) fields is from Irvine and Baragar (1971). The tholeitic, high-Fe and low-Mg trend of the Haveri formation metalavas and metalava breccias is clearly indicated.



Fig. 11. The Haveri  $Na_2O-K_2O-CaO$ diagram. The Haveri metalavas and metalava breccias are in the basalt and tholeiite fields of Le Maitre (1976).



Fig. 12. Variation of the main chemical components and ore-forming elements in Haveri formation rock types. Geometric means, weighted with sample lengths, for each rock type.



Fig. 12, continued.



Fig. 12, continued.

corresponding depletion at c. 5—6 %. This is typical of the tholeiitic series.

- 3. The Al<sub>2</sub>O<sub>3</sub> contents fall within the low-Al group at c. 13 %.
- 4. The K content (0.6 %) is higher than that of primitive mid-ocean-ridge tholeiites and resembles that of island-arc tholeiites.
- 5. The 1.8 % TiO<sub>2</sub> content brings these rocks into a high-TiO<sub>2</sub> class that, together with low CaO: TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>: TiO<sub>2</sub> ratios, resembles mid-ocean-ridge basalts (Fig. 13).

The Haveri formation metalavas and metalava breccies appear to bear more resemblance to mid-ocean-ridge tholeiites (Mäkipää 1978) than to island-arc tholeiites (Jakeš and White 1972) and Archean tholeiites (Glickson 1971, Hallberg and Williams 1972).

Sugimura (1968) introduced the use of different indices, calculated from the main chemical components, to estimate the position of a volcano in relation to the Benioff zone. Applied to the Haveri metabasalts (Table 3, column 3), the indices are as follows.

- 1.  $\sigma = \frac{(Na_2O + K_2O)^2}{SiO_2 43}$  (all wt-%) = 0.6. This refers to a »strongly Pasific» position, i.e. the magma was derived from a very shallow
- depth (vs. »Atlantic» values of  $\sigma = 7-10$ ). 2.  $\theta = \text{SiO}_2 - 47 (\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3 (\text{SiO}_2 \text{ wt-}\%)$ , others mol-%) = 39.0 referring to a position comparable to such places as Kurile and Kamchatka (mean  $\theta = 41.6$ ), West Japan (mean  $\theta = 38.5$ ) and Indonesia (mean  $\theta = 36.0$ ) and indicating a shallow depth of origin for the magma ( $\theta$  around 40 referring to shallow origin, and  $\theta$  around 30 to deep origin).
- S.W.S. (simplest weighted sum) = MgO + 1.8 Na<sub>2</sub>O + K<sub>2</sub>O (all wt-%) = 8.25, a value close to Japanese tholeiites (S.W.S. = 10.63), referring to a shallow depth of origin for the Haveri basalts (vs. S.W.S. = 13.09 for Japanese and Korean high-alumina basalts,



Fig. 13. A plot of  $\text{TiO}_2$  abundance against CaO:  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$ :  $\text{TiO}_2$ .  $\bigcirc$  = Haveri metalavas (n = 40),  $\bullet$  = metalava breccias (n = 31). Basic data after Sun and Nesbitt (1978):

P = Pyrolite, model composition.

- IA = Island-arc low-Ti, high-Mg andesites from Papua and Bonin Islands.
- SPTK = Archean spinifex-textured komatiites.
- Bar. = Archean komatiites from Barberton, South Africa.
- MORB = Mid-ocean-ridge basalts. Many inter-arc-basin (Mariana and Lau) basalts, island-arc basalts and ophiolitic high-Ti basalts, including Bay of Islands (Newfoundland, Canada) and Troodos Lower Pillow Lavas (Cyprus), also fall within, or close to this field.

OPHIO = Low-Ti, high-Mg ophiolites, including Betts Cove, Rambler and Ming's Bight (Newfoundland, Canada) and Troodos Upper Pillow Lavas (Cyprus).

and 18.44 for olivine nephelinites from New Zealand, both of which rocks are of deeper origin).

All of the foregoing geochemical data refer to a shallow depth of origin (< 15 km) for the Haveri formation tholeiites. These data are in line with the empirical studies by Green and Ringwood (1967) discussed on p. 11. It can therefore be concluded that the Haveri formation tholeiitic magma was produced through the partial melting of the upper mantle (pyrolite) that resulted in the trend typical of tholeiitic Fe-enrichment in the melt while the Mg is lodged (mainly) in refractory olivine.

It is also possible that the Haveri formation was generated in the plate-tectonic setting of initial-stage island-arc development, when the chemistry of an oceanic crust still dominated the rocks forming over a shallow-seated subduction zone. In this sense the pillowed basalts of the Haveri formation can be correlated with layer 2 of the oceanic crust, and the overlying chemical, euxinic and partly volcanoclastic sediments with layer 1. Some of the massive d.d. intersections of Haveri metabasalts may be feeder dykes, and as such represent a transition between layers 2 and 3.

After the deposition of the tholeiitic Haveri formation, volcanism was dominated by a calc-alkaline trend that is indicated by the close spatial association between the calc-alkaline volcanic rocks (Fig. 2). Simonen and Neuvonen (1947) have described tholeiitic and calc-alkaline volcanic rocks to the south of the Haveri formation, and Seitsaari (1951) and Pihlaja (1974) have described calc-alkaline, mainly fragmental volcanic rocks east of the Haveri formation.

A close association between arc-tholeiitic lavas and calc-alkaline (andesitic) lavas has been reported by Condie and Moore (1977) from the Proterozoic Grenville Province, Canada. There the tholeiites are associated with the very initial stage of island-arc formation, and the younger, overlying calc-alkaline volcanic rocks with the more mature stages. According to the above authors, the Grenville tholeiites were produced by the partial melting of a descending (subducted), partly hydrated lithospheric slab (oceanic crust) at shallow depth (< 15 km), and the andesites from the partial melting of a dehydrated, eclogitized slab at greater depths. An analogous model could well be applied to the generation of the Haveri formation and its surroundings.

#### Minor-element geochemistry

The distribution of minor elements in the Haveri formation rock types is illustrated by Figs. 12, 17 and 18, and Table 3. The distribution trends of the ore-forming elements are discussed in more detail in the following chapter, »Ore-forming processes».

The following comments refer to the metalavas and metalava breccias. Regardless of the variations in Cu contents, the Zn: Pb and Co: Ni ratios are more or less constant at 1.7 and 0.8, respectively (calculated from values in Table 3, column 3). This implies a homogeneous source material and an intense Cu enrichment trend into the melt (the tholeiitic-basaltic magma) at mean 98 ppm (with some Zn and Ni peaks, cf. Figs. 17a and 18a). The overall contents of the following elements in the melt fraction were rather low: Zn 26 ppm, Pb 15 ppm, Co 27 ppm, Ni 34 ppm and Cr 265 ppm; the contents of the following elements were relatively high: Zr c. 65 ppm, Rb 5 ppm, Ba 510 ppm and Sr 130 ppm (with TiO2 1.76 %, K2O 0.60 % and P2O5 0.46 %). It thus appears that the basaltic melt fraction was enriched mainly in Cu (and possibly Au) and in incompatible elements, while the refractory fraction retained Cr (in chromite?) and the majority of the metallic elements, Co and Ni (in olivine and pyroxene(s)?), and Zn and Pb. The high availability of

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incompatible elements refers to an undepleted source, probably the pyrolite mantle.

Ten of the Au-rich samples were analyzed for Pt and Pd, but the contents of neither element exceeded  $\leq 0.01$  ppm (detection limit).

#### Gold distribution

Fig. 14 is a frequency distribution diagram of the gold in samples from Haveri containing 0.2 ppm (detection limit) to 5.0 ppm Au. The lognormal distribution pattern of gold is obvious. A total of 110 samples was included: 57 core samples (average length 1.7 m) from 6 d.d. holes, and 53 samples (approximate length 0.4 m each) from percussion drilling holes from Peltosaari, 600 m east of the Haveri mine. The samples consist mainly of »mineralized rocks», »ore», metalava and metalava breccia



Fig. 14. Frequency distribution diagram of gold in 110 samples, containing 0.2—5.0 ppm Au, from the Haveri formation.

Table 4

Correlation and factor matrices of the analyses containing 0.2—5.0 ppm Au from the Haveri formation rock types. Included are the 110 samples mentioned in the text.

Correlation matrix

	log Au	log Ag	log Cu	log Zn	log Co	log S	log Ni
log Au	1.00	0.23	0.19	0.13	0.12	0.11	0.05
log Ag	0.23	1.00	0.70	0.24	0.42	0.49	0.17
log Cu	0.19	0.70	1.00	0.23	0.47	0.39	0.03
log Zn	0.13	0.24	0.23	1.00	-0.25	-0.27	0.02
log Co	0.12	0.42	0.47	-0.25	1.00	0.86	0.36
log S	0.11	0.49	0.39	0.27	0.86	1.00	0.56
log Ni	-0.05	0.17	0.33	0.02	0.36	0.56	1.00

Rotated factor matrix

Factor	1	2	3	4	Comm.
log Au	-0.04 -0.13	0.12	0.02 0.17	0.99	1.00
log Cu	-0.06 -0.92	0.92	0.02	0.06	0.86
log Co	0.54	0.57	-0.48	0.09	0.85
log Ni	-0.07	0.00	-0.97	-0.05	0.95
Eigenv. %	41.4	22.5	13.9	12.0	
Principal loading	Co, S, —Zn	Cu, Ag, Co, S	—Ni, —S, —Co	Au	

and a few skarns and black schists, in other words, typical Haveri formation rock types.

In the course of exploration drilling the erratic and unpredictable distribution of gold in the Haveri core samples became obvious, a fact that was corroborated by the poor correlation with electromagnetic anomalies caused mainly by massive sulfides.

The poor correlation of gold with the other ore-forming elements is clearly displayed in the factor analysis run on the above-mentioned 110 analyses (Table 4). In the correlation matrix gold is poorly correlated with the other elements, and an individual gold factor stands out from the factor matrix (factor 4). Table 4 shows that Cu, Ag, Co and S from a group of elements that correlate relatively well (factor 2), Ni displays a moderate correlation with S and Co (factor 3), and Zn does not correlate with any of the elements included in the data (a negative loading in factor 1).

The reasons for the non-correlative behavior of gold, as well as the distribution characteristics

of the other ore-forming elements, will be explained in the following chapter as resulting from the precipitation of the elements from ore-forming fluids in the order Au-Co-Cu-Ag-Ni-Zn, which leads to spatially zoned proximal-distal arrangements.

A microprobe determination on gold was performed on specimen Hvr-5, 67.15 m. In this specimen there is a sub-compact band, with a syngenetic attitude (the band occurs concordant to the flow textures), composed of magnetite and ilmenite as a fine-grained dissemination in a basaltic flow rock. In the flow rock itself there is a pyrrhotite dissemination with some chalcopyrite. Native gold occurs as small inclusions in hornblende close to the oxide mineral band. The gold contained

Au	83.86 %
Ag	16.84 %
Cu	0.00 %
Total	100.70 %.

#### Ore-forming processes

On the basis of the data given in the preceding chapters the geochemical behavior of the oreforming elements in the Haveri formation are summarized as follows:

Gold is concentrated mainly in the proximal rock types (in the sense of Large 1977): Metalavas, metalava breccias, and their »mineralized» counterparts (calculated FeS content 5-20 %). The Au distribution correlates poorly with the other ore-forming elements but parallels them in a zonal arrangement.

Copper is rather consistently concentrated in »ore» intersections (FeS > 20 %) that are composed of massive pyrrhotite with chalcopyrite and minor pyrite. The mean copper content in the ore is 2535 ppm.

Cobalt is another consistent constituent of the orebodies, the mean being 295 ppm Co in the ore intersections. The commercial value of cobalt is roughly equal to that of copper.

Nickel displays maximum concentrations in »ore in metatuff» and black schist, with means at 478 and 471 ppm Ni, respectively, as opposed to 128 ppm Ni in ore, 139 ppm Ni in skarn and 30 ppm Ni in chert. The relative affinity of cobalt for proximal and of nickel for distal mineralization and rock types is indicated by Co: Ni ratios with the following trend:

Co: Ni = 2.3 at one in metalava bieccia	Co:	Ni	_	2.3	at	ore	in	metalava	breccia
---	-----	----	---	-----	----	-----	----	----------	---------

- 1.1 chert
- 1.1 basaltic metatuff
- 0.6 limestone
- 0.5 dacitic metatuff
- 0.5 skarn
- 0.3 ore in metatuff
- 0.1 black schist.

A low but consistent silver content is typical of orebodies at mean 5 ppm Ag. Silver correlates well with Cu, S and Co.

Zinc, unlike Cu, Co and Ag, displays maximum concentrations in distal rock types: skarn, limestone, metatuff and black schist (mean 430 ppm Zn in skarn vs. 70 ppm Zn in ore). The individual character of zinc distribution within the Haveri formation is further indicated by the independent zinc factor (with opposite loadings of Co and S) in the factor analysis (Table 4, factor 1).

Large (1977) has examined the zoning and ore-forming processes of massive sulfide deposits in volcanic terrains. He concludes that the massive sulfide ores within ophiolitic environments (Large's Cyprus type) are rich in copper with minor zinc and negligible lead, and that they are poorly zoned. The massive and stringer sulfide deposits within felsic volcanic piles (Large's Archean and Kuroko types) are typically zoned from a copper-rich base to a zinc + lead-rich top. All three types are underlain by hydrothermal alteration pipes and are considered to have been deposited at or just below the sea-water/rock interface. They occur towards the center of the volcanic pile and are termed proximal ores. The well-banded sulfide ore lenses (commonly Zn-Pb rich) and metalliferous sediments, which are not underlain by intense foot-wall alteration, occur within mixed volcanic-sedimentary environments; they were deposited directly onto the sea-floor from metal-bearing brines that had moved some distance from their fumarolic outlets and are termed distal ores.

Large (1977) has summarized the physicochemical conditions under which strata-bound volcanogenic massive sulfides are deposited. Cu, Pb and Zn may be transported to form massive sulfides in two distinct environments: 1. Reduced, high-temperature (> 275 °C), acidic to neutral pH environment; and 2. Oxidized, any temperature, any pH environment. More precisely, these physicochemical environments, calculated from mineral-solution equilibria reactions in the Fe–S–O system and partly based on experimental and fluid inclusion data, are as follows.

The temperature in the ore-forming fluids reaches 250°-350 °C. The fluids consist mostly of sea-water that enters the volcanic pile from the sea above, and whose circulation is driven by a volcanic heat source. These fluids become laden with ore-forming metal ions that they leach out of the volcanic rocks. The fluids are also responsible for the alteration phenomena that take place in the silicates within the volcanic pile by leaching out Ca and Na, and by introducing into the system K, Fe and Mg. Further, as the fluids move towards the sea floor, their temperature drops to c. 250 °C, and the dissolved oreforming material begins to precipitate as a stringer ore (pyrrhotite, chalcopyrite). The fluids enter the sea floor at 250°-200 °C, precipitating massive pyrite-chalcopyrite ore followed, along with falling temperature, by pyrite-sphalerite-galena ore.

The pressure during this process is that of the water column above the volcanic center, generally in the order of 40—50 bar. This pressure prevents a 1 M NaCl solution at  $120^{\circ}$ —300 °C from boiling on the sea-floor.

The pH in the high-temperature fluids is low at c. 3; it rises to 5—6 during the main ore-forming process and finally reaches 8 (present-day sea-water) upon mixing with sea-water. The fo<sub>2</sub> (oxygen fugacity) is low at c.  $10^{-45}$  atmosphere in the high-temperature fluids. It rises considerably with falling temperatures to c.  $10^{-35}$  and falls to c.  $10^{-60}$  (present-day seas) upon mixing.

The NaCl concentration of the fluid is considerable at c. 1 M. The role of Cl anions in transporting zinc in ore-forming fluids has been emphasized by Piirainen (1975).

The total sulfur content,  $\Sigma$ S, of the solution, including oxidized sulfur species (S<sub>0</sub>, mainly SO<sub>4</sub><sup>=</sup>) and reduced sulfur species (S<sub>r</sub>, mainly H<sub>2</sub>S), is rather low and varies from 10<sup>-4</sup>—10<sup>-2</sup> M. If it were higher, the sulfide mineral-solution equilibria would cause pyrite or pyrrhotite, depending on the level of oxygen fugacity, to precipitate from the fluid.

The concentrations of Cu, Zn and Pb in the ore-forming fluids are each in the 1—6 ppm range (Large 1977); the concentration of Au is roughly 0.1 ppb (Large 1975).

The ionic potential is assumed constant at 1.

In accordance with the concept of Large (1977), the ore-forming processes at Haveri were as follows. The ore-forming elements, except for the bulk of sulfur, were originally contained in the basaltic effusive rocks. As will be shown later, the elements were transferred from these rocks by relatively shallow leaching into fluids that originated from heated coeval sea-water. In the course of extrusive activities, with falling temperature and rising pH and fo<sub>2</sub>, first gold precipitated within the flow and flow-breccia units, or in their immediate vicinities, under (initial-)proximal conditions. The next phase to precipitate was iron (sulfide species), copper, cobalt and silver, and some nickel. The sulfur required was provided by the contemporaneous sea-water (cf. chapter »Sulfur isotopes»). Sulfides were precipitated at or close to the magma/sea-water interface. Some of the precipitating sulfides were trapped into the still flowing magma producing breccialike flowage structures in the flow brecciabound ores. Some of the nickel and the bulk of the zinc (including the meager available amount of lead) did not precipitate in the massive sulfide but remained in solution; they precipitated only under distal conditions, i.e. mainly together with distal-type chemical and euxinic sediments.

Figs. 15 and 16 summarize the mixing paths of the Haveri ore-forming fluids. The basic data are adapted from Large (1975 and 1977) and Ohmoto (1972). It is evident that gold tended to precipitate under (initial-)proximal conditions, temporally a little ahead of and spatially apart from copper, cobalt and silver. These, and to a certain extent nickel, precipitated together with the proximal(-proper) massive iron sulfide(s). Zinc, and partly nickel, precipitated only under distal conditions. Not enough lead was available to produce notable concentrations in any of the Haveri formation rock types. Thus this metal zoning appears to occur in a lateral rather than a vertical direction, the latter usually occurring in Kuroko-type deposits.



Fig. 15. The hydrothermal solution mixing path (A—B) of the Haveri occurrence in a  $fo_2$ —pH space at 250 °C,  $\Sigma S = 10^{-3}$  M and 1 M NaCl solution. The stability fields of the Fe-S-O minerals, the  $S_0$ :  $S_r$  line, and the chalcopyrite and sphalerite deposition fields between 6 and 1 ppm soluble Cu and Zn are from Large (1977). The gold deposition field between 0.2 and 0.02 ppb soluble Au is after Large (1975). The two  $\delta^{34}S$  countours for pyrrhotite at  $\delta^{34}S_{\Sigma S} = +18$   $^{0}/_{00}$  are after Ohmoto (1972).


Fig. 16. The sea-water recycling and hydrothermal solution mixing path (A—G) of the Haveri occurrence in a fo<sub>2</sub>—T field. The Fe-S-O mineral stability fields, the S<sub>0</sub>: S<sub>r</sub> line, and the chalcopyrite and sphalerite deposition fields are from Large (1977). The gold deposition field is after Large (1975).  $\Sigma S = 10^{-3}$  mol/kg H<sub>2</sub>O, 1 M NaCl solution. The chalcopyrite and sphalerite deposition fields are between 1—6 ppm soluble Cu and Zn, and that of gold between 0.02—0.2 pp soluble Au.

- A-B: Sea-water enters the recycling process; the hydrothermal fluid forms at 300°-350 °C and pH 3-4, dissolving metals from flows and hyaloclastite.
- B—C: Temperature decreases, and fo<sub>2</sub> and pH increase as the fluid approaches the rock/sea-water interface. Barren pyrrhotite may precipitate if sulfur is available. (The destruction of primary titanomagnetite may be associated with this, or some previous stage: the fluid reacts with titanomagnetite and dissolves the Fe-component, leaving behind ilmenite laths. This would cause a steepening grade in fluid fo<sub>2</sub> because of dissolved magnetite buffer.)
   C—D: Gold precipitates in this stage with or without pyrrhotite, probably mainly below the magma/sea-water interface.
- Copper and zinc remain in solution.
- D-E: Fluid emerges to the sea-floor at about 250°-275 °C. Pyrrhotite precipitates because sulfur is available from sea-water.
- E—F: The fluid leaves the pyrrhotite field; magnetite and, later, pyrite become the dominant iron mineral species. Chalcopyrite precipitates together with pyrrhotite, magnetite and pyrite. Zinc remains in solution. This stage apparently passes rapidly because of the rapid cooling of the hydrothermal fluid upon mixing with sea-water. Some of the ore precipitates in interstitial spaces in the still (partly) flowing basalt, and some gets trapped in it. The result is breccia-like flowage structures in the modes of occurrence of ore-forming minerals.
- F—G: Fluid mixes with sea-water, and temperature and  $fo_2$  decrease. The mixing path advances along the  $S_0$ :  $S_r = 10^{-1}$  line, keeping the dissolved Zn and some Cu in solution. Only when the mixing path emerges below the  $S_0$ :  $S_r = 10^{-1}$  line at »G» do the Zn and remaining Cu precipitate in distal environments, as chemical and euxinic sediments.

The spatial distributions of the iron sulfide and oxide minerals generally differ within the Haveri formation. Further, in the Haveri mine iron and sulfide ores are distributed in separate areas although they display largely parallel zoning (Stigzelius 1944, Figs. 41—43). This is explained by the precipitation of iron sulfides and oxides in different physicochemical environments. Only when the oxygen fugacity has risen to a sufficient level, usually with falling

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temperature, do the iron-oxide species (magnetite, ilmenite) start to precipitate at the expense rathe

At Haveri the magnetite and ilmenite usually occur in separate grains: magnetite in octahedral crystals without ilmenite exsolution lamellae, and ilmenite most often as lath-shaped crystals. Electron microprobe determination showed that the magnetite in sample Hvr-5, 67.15 m contained 0.52 % V<sub>2</sub>O<sub>5</sub> but that the coexisting ilmenite contained 0.00 % V<sub>2</sub>O<sub>5</sub>.

of iron-sulfide species (mainly pyrrhotite).

Fig. 17 is the Cu–Zn–Pb diagram and Fig. 18 the Co–Cu–Ni diagram of the main rock types in the Haveri formation. The proximaldistal mineralization relations discussed above as well as the element ratios can be readily observed in these figures. The following comments are appropriate (please also refer to the explanatory texts in Figs. 17 and 18). The metalavas and metalava breccias have a rather constant Zn: Pb ratio at c. 2: 1 and a rather constant Co: Ni ratio at c. 1: 1.

The mineralized and ore-bearing metalavas and metalava breccias are concentrated in the Cu corner with Co: Ni ratios generally > 1. These appear to be characteristic of the proximal ore type.

The metatuffs, including the mineralized and ore-bearing metatuffs, plot partly in, or close to, the Cu corner with a »tail» curving towards the Zn and Ni corners. Co: Ni < 1. This apparently indicates a transition from proximal to distal ore-forming processes.

Like the metatuffs, the skarns and limestones display trends from Cu-dominated, proximal distributions towards Zn- and Ni-dominated, distal ones. Only the chert samples, like the metalavas (breccias), display distributions in the



Fig. 17. The Haveri Cu-Zn-Pb diagrams.

- a. The metalavas and metalava breccias (calculated FeS < 5 %) display rather constant Zn: Pb ratios and concentrate towards the Cu corner.
- b. The mineralized (FeS 5–20 %) and ore-bearing (FeS > 20 %) metalavas and metalava breccias clearly concentrate in the Cu corner.
- c. The metatuffs and the mineralized and ore-bearing metatuffs display both Cu- and Zn-dominated distributions. d. The skarns and limestones display distributions similar to those of metatuffs. The chert samples concentrate in
- the Cu corner. e. The black schists appear to plot rather close to the Cu corner, and the mica schists (or »metatuffites») display a
- e. The black schists appear to plot rather close to the Cu corner, and the mica schists (or »metatuffites») display a trend towards the Zn corner.

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Fig. 18. The Haveri Co-Cu-Ni diagrams.

- a. The metalavas and metalava breccias exhibit rather constant Co: Ni ratios and a trend towards the Cu corner.
- b. The mineralized and ore-bearing metalavas and metalava breccias are concentrated in the Cu corner with relatively high Co contents.
- c. The metatuffs and mineralized and ore-bearing metatuffs display trends towards the Cu and Ni corners.
- d. The skarns and limestones plot in the same manner as the metatuffs; the cherts in the same manner as the metalavas
- and metalava breccias. e. The black schists show distributions similar to some ores (in metalava breccias); the mica schists follow the trend
- of metatuffs towards the Zn corner.

Cu corner, which indicates the close relation of chert to the proximal exhalite facies.

All in all, the proximal rock types (and elements) appear to consist of metalava, metalava breccia, chert and ore in metalava breccia (Au, Cu, Co). The intervening proximal-distal types include metatuff and black schists (Ni, Zn), and the distal types include limestone, skarn and mica schist (Zn, Ni). Lead is only relatively depleted from the parent metalava (breccias) and appears to be scattered in distal rock types without obvious concentrations.

According to Dimroth *et. al.* (1978), pillow breccias in the basalts of Royun-Noranda area, Canada, formed at the waning stage of eruption when the supply of fresh lava was reduced. Within the Haveri formation waning stages are marked by metatuffite intercalations in flow (breccias), by intercalated chemical and euxinic sediments, and by both proximal massive sulfides and distal-type mineralizations. The association of both Cyprus- and Kuroko-type mineralizations with waning stages of volcanic activity is well documented, e.g. by Sangster (1972).

In contrast to some other Cyprus-type deposits (Constantinou and Govett 1973), no distinct alteration pipes have been recognized underneath the orebodies drilled in the vicinity of the Haveri mine. The only alteration phenomena noted were the skarning of some pillow rims and spaces between pillows and some flow breccias, and the chloritization of wall rock in some ore intersections. Thus, the leaching pheneomena were apparently relatively rapid, partly contemporaneous with the effusion phases (deduced from the flow-ribboned sulfide structures) and partly associated with the waning stage of each flow pulse (deduced from the mineralizations that occur on top of the flow breccia units and interstitially between succeeding flow units). The leaching phenomena thus affected only a few meters on top of each flow (breccia) unit. Such an introduction of metals through shallow leaching over relatively large areas could well be termed exhalation, whereas »leaching proper» takes place during the postextrusional stages when the leaching effect is felt deep (several hundreds of meters) in the volcanic strata. The shallow leaching at Haveri also indicates relatively rapid cooling in each flow unit. Furthermore, there were apparently no near-surface intrusions to keep the water in circulation for extended periods; rather each pulse of basaltic magma surfaced from a relatively great depth.

# Pressure during the Haveri ore-forming processes

The metalava and metalava breccia intersections in the Haveri d.d. cores were macroscopically inspected for amygdularity and amygdule size. The general absence of amygdules refers to a deep-water environment (2 000 m +, Jones 1969, Moore 1965). However, a few intersections 2 cm to 1.5 m long were noted to contain amygdules with 5 vol-% (range 0.5—15 vol-%) and with diameters averaging 1.5 mm (range 0.5—2 mm). According to Jones (1969) and Moore (1965) this indicates a water depth of roughly 400 m, a depth that corresponds to 40 bar pressure, which would be approximately the minimum pressure at the emplacement site of the extrusions, and thus approximately the minimum pressure during the ore-forming processes.

Under the microscope the amygdules appear to be round or ellipsoidal in shape and composed of coarse-grained quartz with some carbonate.

D.d. hole Hvr-13 (not included in the analytical data), 500 m west of the Haveri mine, contained intersections with amygdule diameters up to 4 mm. This indicates a shallow water depth (low depositional pressure), which is reflected in the ore composition: considerably more pyrite with less pyrrhotite, chalcopyrite and gold than in the other holes. The effect of water depth on the ore-forming processes has been well documented by Plimer and Finlow-Bates (1978). They suggest that pyrite is far more abundant than pyrrhotite in submarine exhalative massive sulfide deposits formed at shallow depth (< 500 m).

Still larger amygdules have been reported by Ollila (1977) from outcrops in the Haveri region. The diameters of these amygdules, up to 1 cm, refer to a very shallow water depth. The flows carry no mineralizations. There are no indications of subaerial volcanism in the Haveri formation.

#### Metamorphism

In addition to the widespread regional metamorphic mineral paragenesis plagioclase (albite-oligoclase up to andesine)-hornblendebiotite-epidote the following metamorphic index minerals and mineral parageneses have been detected in the Haveri formation rock types.

Quartz-biotite-plagioclase-cordierite and quartz-biotite-plagioclase-staurolite occur in »pelitic» metatuffite.

Carbonate, quartz and tremolite (all these, and talc still present) have produced diopside

in skarned chert-carbonate rock. According to Miyashiro (1973b), this reaction takes place at c. 550 °C wat the threshold to the amphibolite facies». Wollastonite (forming at c. 600 °C) is absent. Brownish grossularite is present.

These mineral parageneses, and the tendency to low-An plagioclase together with epidote, refer to the metamorphic grade of low-temperature amphibolite facies. According to the data from Miyashiro (op. cit.) and Mueller and Saxena (1977), the metamorphic temperature reached 550 °C. In this temperature range staurolite is stable at c. 2.5 kbar pressure (Mueller and Saxena op. cit.).

As there are no indications of higher degrees of metamorphism, these values, temperature

#### THE KIIPU OCCURRENCE

In connection with the geological mapping performed by the Exploration Department of Outokumpu Co. an outcrop was found at the bottom of a gravel pit in Kiipu, a village in the commune of Jokioinen, in 1964. The outcrop displayed streaks of compact sphalerite in sericitized rock. This outcrop, lying in the alteration zone discussed in the text, gave the incentive to start exploration at the site some 12 km west of Forssa (Fig. 1).

In 1976 the Exploration Department of

Outokumpu Co. carried out exploration drilling on the property, under the supervision of the present author. The samples studied in the present study originated mainly from these d.d. cores. Although the known mineralization at Kiipu is uneconomic and a »massive sulfide deposit» has not (yet) been found in the area, the type of host rocks, alteration phenomena and mineralization refer to the possible existence of such a deposit, and the exploration work is being continued.

#### General geology

The geology of the area around Kiipu has been described by Neuvonen (1956), Härme (1960) and Lindroos (1980). The general geology of the Kiipu region has been compiled on the basis of these papers and the writer's own observations.

The Kiipu prospect is part of a rather undefined portion of the metavolcanic rocks in the Svecofennian zone of the Svecokarelidic orogeny (Simonen 1953, 1971). This continuous zone runs from central Sweden in the west (Gavelin *et al.* 1976) through southwestern Finland to Soviet Karelia in the east, where it terminates in the Karelian zone of the same orogeny (Fig. 1). In terms of plate tectonics the Svecofennian zone has been interpreted as a Middle Precambrian island arc (Hietanen 1975, Latvalahti 1979).

The Kiipu region appears to form a volcanic center with many pyroclastic units including primarily lapilli metatuffs, metatuffites and coarse meta-agglomerates. Metalavas also occur in the area; most of them are higher in, and flanking, the pyroclastic strata and are in a subordinate position in the alteration zone. The geological map in Fig. 19 has been simplified by the present author from the geological data gathered for exploration purposes by the Exploration Department of Outokumpu Co. and compiled by Lindroos (1980).

The main drilling target, the alteration zone, is only exposed in a few scattered outcrops. Information from percussion and diamond drilling indicates that the zone is covered by till overburden roughly 4 m thick. Some outcrops occur within a few hundred meters of the zone. The field photographs (Figs. 20–22) and some macroscopic descriptions are based on observations from these off-thezone outcrops, but they appear to be valid also to the d.d. cores. As the diamond drilling targets were chosen mainly from Induced

550 °C and pressure 2.5 kbar, appear to be valid approximations for regional metamorphic conditions in the Haveri region and to correspond to low-temperature and low-pressure amphibolite facies (see Fig. 33, p. 65).



Fig. 19. Simplified geological map of the Kiipu region. 1 = Basaltic metalavas; 2 = Andesitic metalavas; 3 = Intermediate to acidic pyroclastic rocks; 4 = Altered rocks; 5 = Granite and granitized volcanic rocks; 6 = Diamond drilling hole.

Polarization survey anomalies, the only obvious difference is the concentration of sulfides in the core samples. The area around the alteration zone (northern, central and eastern parts in Fig. 19) is moderately well exposed, but outcrops are lacking in the Loimijoki valley (the southwestern part of Fig. 19).

#### Petrography

#### Macroscopic descriptions

Meta-andesite outcrops 200 m east of d.d. hole Ki-6. There the rock is pale greenish on the weathered surface and displays flow struc-

tures in certain portions (Fig. 20). Elsewhere, the rock is rather massive, as is seen also in the d.d. core, dark greenish in color and cut by narrow pale-colored veinlets that represent the latest magma crystallization into contraction

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Fig. 20. A Kiipu metalava: massive meta-andesite with weakly developed flow structures.



Fig. 21. A Kiipu pyroclastic rock: weakly altered lapilli metatuff.

cracks. The meager pyrite and chalcopyrite contents of the meta-andesite are mainly concentrated in these veinlets.

Scattered outcrops of pyroclastic rocks are found in the Kiipu region. They range in grain

size from fine-grained metatuffites to metaagglomerates with bomb diameters that can be measured in meters. Fig. 21 represents a common type of pyroclastic rocks in Kiipu, a medium- to coarse-grained lapilli metatuff with intermediate to acidic composition and streaky, banded structure. The top determination (Fig. 19) is from an interlayered graded metatuffite (Lindroos 1980).

Outcrops of altered rocks are found 400 to 500 m to the northwest (on the foot-wall side) of the drilled alteration zone. The pyroclastic rocks grade into cordierite- and locally andalusite-bearing mica gneisses. Except for their schistosity these gneisses appear rather massive since recrystallization has destroyed their original volcanic structures. The porphyroblasts usually stand out from the weathered surfaces, which gives the altered rocks a mottled appearance (Fig. 22).



Fig. 22. A Kiipu altered rock: cordierite-muscovite gneiss. Cordierite porphyroblasts stand out from the weathered surface.

#### Microscopic descriptions

#### Metalavas

Under the microscope the Kiipu meta-andesite is a plain rock and granoblastic by groundmass. The constituent minerals are hornblende, plagioclase, biotite and, occasionally, quartz. The average grain size is 0.2 mm. Primary igneous textures are displayed by plagioclase: the largest grains are blastophenocrysts, the remainder of the mineral being equigranular groundmass. Some of the hornblende-ilmenite aggregates appear to be pyroxene pseudomorphs. The following is a description of specimen Ki-6, 40.60 m (Fig. 23). Hornblende occurs as grain clusters or as weakly developed rosettes. Z = bluish green, Y = dull green, X = pale yellowish green,  $c \land Z = 19^\circ$ ,  $2V \backsim 75^\circ$ . The diameters of individual grains seldom exceed 1 mm. Lamellar 100 twinning occurs occasionally.

Roughly 50 % of the plagioclase crystals are almost idiomorphic phenocrysts with diameters from 0.2 mm up to 1 mm. The other half is fine-grained groundmass. The plagioclase is oligoclase at the grain boundaries (An<sub>20</sub>, X'  $\leq$ O of quartz, X  $\geq$  Canada balsam) and oligo-clase-andesine at the grain centers (An<sub>25-30</sub>, max X'  $\wedge$  010 = 15°). Some of the large plagioclase grains are intensely sericitized.

Biotite occurs as flake decks whose diameters approximate 0.1 mm. Z = dark brown, X = pale brown to almost colorless. Prehnite is a common alteration product.

Quartz is a common accessory mineral occurring mainly as coarse-grained aggregates in veinlets. Ilmenite



Fig. 23. Photomicrograph of Kiipu meta-andesite. Clear plagioclase, dark hornblende. Specimen Ki-6, 40.60 m, nic. +, magn. 35 x.

is practically the only opaque mineral (identified in polished section) and abounds as ragged grain clusters or laths mainly together with hornblende and biotite. Sphene is usually associated with the same minerals, and as leucoxene around ilmenite grains. In another variety sphene abounds in biotite with only minor ilmenite. Tourmaline occurs as scattered small grains throughout the rock. Apatite is found as evenly disseminated small needles. Zircon is met with as small inclusions in biotite and hornblende, causing pleochroic halos in both of them. A few small, ragged carbonate grains have been encountered.

#### Pyroclastic rocks

The constituent minerals of Kiipu pyroclastic rocks are quartz, plagioclase, biotite, muscovite and often also microcline. The grain size of Kiipu metatuffs varies from very fine in some quartz-feldspar rock specimens to 1—2 mm in some plagioclase lapilli; the average is roughly 0.05 mm. The metatuffs are streaky and layered, the thickness of the layers being a few mm. The texture is granoblastic with weakly preserved blastoclastic (graywacke-like) features. Typical of these pyroclastic rocks is the gradual alteration, and finally complete destruction, of plagioclase towards altered rocks. A series of photomicrographs, Figs. 24 a—h, illustrates this phenomenon. The following is a description of a typical metatuff specimen (Ki-6, 43.55 m, Fig. 24a) with practically unaltered plagioclase. The constituent minerals of this specimen are plagioclase, quartz, biotite and muscovite, the grain size varies from 0.01 mm to 1 mm (average 0.05 mm), and the texture is granoblastic with blastoclastic relict features.

The composition of plagioclase varies from  $An_{5-10}$ ( $Z \ge Canada$  balsam, Z < O of quartz) in the small grains to  $An_{15-20}$  ( $Z \sim O$  of quartz) in the larger grains. Most of the big plagioclase lapilli are practically unzoned. Except for incipient saussuritization the plagioclase grains are unaltered.

The amount of quartz equals that of plagioclase. The quartz grains are granular and vary in size from 0.01 mm to as much as 0.7 mm in some quartz-plagioclase grain clusters. Biotite is very dark brown or even opaque (Z, X = pale brown) and occurs as flakes c. 0.08 mm long, disseminated in streaks. The very dark brown to opaque color refers to a high iron content (Winchell and Winchell 1951).

Muscovite is pale greenish to pale brown-greenish (Z, X = colorless) and occurs as ragged flake decks c. 0.1 mm long disseminated throughout the rock. The greenish color refers to an appreciable iron content (op. cit.).

The accessory minerals include opaque (mainly pyrite) dissemination mainly in streaks, microcline, carbonate, apatite and zircon (minute inclusions in biotite with pleochroic halos).

#### Altered rocks

The altered Kiipu rocks were logged and classified as follows according to their main mineral composition, in the order of increasing degree of alteration: cordierite gneiss, cordierite– muscovite gneiss, cordierite–biotite gneiss, and cordierite–anthophyllite–biotite gneiss. The following is a description of two typical altered rock specimens.

The cordierite-quartz-biotite-muscovite gneiss (specimen Ki-6, 185.40 m, Fig. 24f) displays a gneissose, foliated texture and streaky compositional layering. No primary textures are preserved, the rock being completely recrystallized, poikiloblastic and porphyroblastic in texture. The grain size varies from 0.3 mm in quartz to 1 mm in micas and to up to centimetres in cordierite porphyroblasts.

Cordierite occurs as large, ragged porphyroblasts enclosing other silicates, quartz and opaque. It varies from pale brownish yellow (X) to colorless. Some of the cordierite is altered to brownish or yellowish pinite with varying interference colors. The brownish color and the high birefrigence (0.011, from interference color) refer to a component composition of 50: 50 Mg: Fe (Winchell and Winchell 1951).

Quartz occurs as rather equigranular grains and small inclusions in cordierite.

Biotite (Z = brown, X = pale brown) is met with as rather randomly oriented flake decks. Much of the biotite is altered into pale green (X') chlorite with low birefrigence. Muscovite (colorless) occurs as flakes that are preferentially oriented parallel to the foliation of the rock.

The accessory minerals include opaque (mainly pyrite as cubes and dissemination streaks), pale green to dark green gahnite as porphyroblasts 0.5 to 1 mm in diameter, abundant small zircon inclusions in biotite (with pleochroic halos) and cordierite, a few small grains of colorless garnet, and some apatite.

The cordierite-anthophyllite-biotite-quartz gneiss (specimen Ki-6, 238.60 m, Fig. 24h) displays coarse-grained, poikiloblastic, porphyroblastic textures. The grain size varies from 0.05 mm in quartz inclusions to 2 mm in biotite and to up to several centimetres in anthophyllite and, especially, in cordierite.

Cordierite is pale yellowish to colorless (X) and fresh; it is pinitized only along fractures. Birefrigence (0.008, from interference color) and refractive indices (Z~O of quartz) refer to a composition of roughly 30 mol-% ferrous component (Winchell and Winchell 1951).

Anthophyllite occurs as splinters and rosettes and is almost colorless, optically positive with  $2V \sim 85^{\circ}$ , birefrigence c. 0.022 (from interference color). These properties refer to an iron component content of c. 20 mol-% (Tröger 1971).

Biotite (Z = brown, X = pale brown) is altered in some minor parts into green chlorite.

Quartz occurs as fine-grained inlusions in silicates. The accessory minerals include opaque (sulfide grains and small ilmenite laths), small zircon grains as inclusions in biotite and cordierite with pleochroic halos in both of them (dark in biotite and yellow in cordierite), and minor apatite.

#### Gahnite

Gahnite occurs as a consistent dissemination with c. 3 vol-% in the pyritized part of the alteration zone. The color of gahnite in a hand specimen is a dull dark green that upon exposure to the air often turns brown within a few months. The grain size is roughly 0.5 to 1 mm. In thin section gahnite occurs as porphyroblasts that are often ragged at the edges and display octahedral crystal habits. The paragenetic garnet



a. Practically unaltered lapilli metatuff. Except for incipient saussuritization the plagioclase is unaltered and clear. Clear: mainly plagioclase; dark: mainly biotite. Specimen Ki-6, 43.55 m, nic. +, magn. 35 x.



- b. Quartz-plagioclase-biotite(-muscovite) schist. An acidic metatuff with incipiently altered, turbid, saussuritized plagioclase. White: quartz; turbid: plagioclase; flaky minerals: mainly biotite. Specimen Ki-6, 76.60 m, nic. +, magn. 35 x.
- Fig. 24. A series of photomicrographs of Kiipu pyroclastic and altered rocks illustrating the degrees of plagioclase alteration, destruction and final disappearance in the course of progressive alteration.



c. Sericite-quartz-plagioclase-biotite schist. An altered acidic tuff with turbid, completely saussuritized, partly destroyed plagioclase. Turbid grains: plagioclase; white: quartz; flaky minerals: muscovite and biotite. Specimen Ki-6, 97.60 m, nic. +, magn. 90 x.



d. Biotite-sericite-quartz-garnet schist, originally an acidic tuff. Plagioclase is almost completely destroyed and is replaced by fine-grained sericite masses, pseudomorphic after plagioclase grains. Gray areas of high relief are sericite; white areas are quartz. Specimen Ki-6, 143.40 m, nic. +, magn. 90 x.

Fig. 24, continued.



e. Cordierite-quartz-muscovite-biotite-garnet gneiss, apparently of acidic tuff origin. Plagioclase absent. Cordierite is sooty brownish, pinitized and poorly crystallized. Muscovite at pale grey lower left corner; garnet porphyroblasts; white quartz; grey: biotite and some cordierite. Specimen Ki-6, 150.60 m, nic. —, magn. 90 x.



f. Cordierite-quartz-biotite-muscovite gneiss. Plagioclase absent; no original textures remaining. Cordierite occurs as well crystallized, somewhat pinitized porphyroblasts (white) with quartz inclusions. Flaky minerals are biotite and muscovite. Specimen Ki-6, 185.40 m, nic. +, magn. 35 x.

Fig. 24, continued.



g. Cordierite-quartz-biotite-garnet-gahnite gneiss. Plagioclase and original textures absent. Cordierite fresh. The rock is completely recrystallized, porphyroblastic and poikiloblastic by texture. Garnet left, cordierite center, gahnite right. Specimen Ki-6, 230.45 m, nic. —, magn. 35 x.



h. Cordierite-anthophyllite-biotite-quartz gneiss. Plagioclase absent. Cordierite fresh. Coarse-grained, porphyroblastic texture. Anthop hyllite splinters at top, cordierite at bottom. Dark-gray: biotite; black laths: ilmenite. Specimen Ki-6, 238.60 m, nic. —, magn. 45 x.

Fig. 24, continued.

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#### Table 5

Analyses of Kiipu rock types (columns 1–4) and calc-alkaline rocks from other parts of the world. Major chemical components are in wt-%, minor elements in ppm. In columns 1–4  $\text{FeO}^* = (\text{Fe}_{total} - \text{FeF}_{cS_2})O$ .  $\text{FeS}_2 = S$  expressed as  $\text{FeS}_{2}$ .

				2					
	1	2	3	4	5	6	7	8	9
SiO	54.08	72.56	66.57	63.95	54 20	71.66	73 53	65.0	65.80
TiO	0.82	0.52	0.59	0.58	1.31	0.38	0.33	0.76	0.71
Al <sub>2</sub> O <sub>2</sub>	16.87	15.09	15.43	16.30	17.17	15.58	12.49	14.22	12.57
Fe <sub>2</sub> O <sub>3</sub>					3.48	0.61	0.91	1.84	1.78
FeO					5.49	0.32	0.93	4.50	5.97
FeO*	8.84	0.49	2.06	4.22					
MnO	0.12	0.11	0.15	0.21	0.15	0.01	0.06	0.1	0.06
MgO	4.33	1.56	2.75	3.51	4.36	0.34	1.62	2.35	4.06
CaO	7.80	2.63	2.12	0.42	7.92	0.92	0.84	3.61	0.86
Na <sub>2</sub> O	3.24	1.94	1.30	0.45	3.67	4.62	1.61	3.03	0.70
K <sub>2</sub> O	1.61	2.57	2.71	3.24	1.11	2.03	4.08	1.90	2.71
P <sub>2</sub> O <sub>5</sub>	0.27	0.15	0.15	0.10	0.28	0.07	0.03	0.36	0.14
$H_2O+$					0.86	2.31	2.82	0.75	2.25
5	0.16	2.00	1.01	1 55				0.19	3.43
FeS <sub>2</sub>	0.16	2.00	1.01	1.55					
	98.14	99.62	94.84	94.53	100.00	98.85	99.25	98.61	101.04
$-0 = S \dots$	-		—				_	0.08	1.51
Total	98.14	99.62	94.84	94.53	100.00	98.85	99.25	98.53	99.53
Ca	72	16	60	102				150	150
Zo	12	110	125	346				150	100
DL	40	24	23	83				30	30
Co	21	15	24	25				50	50
Ni	52	45	39	24					
As	13	21	20	41					

1. Kiipu meta-andesite. Mean of 5 analyses, 5 m each, total 25 m of split d.d. core.

2. Kiipu rhyolite-class pyroclastic rock. Geometric means, weighted with sample lengths, n = 12, 41.00 m.

3. Kiipu pyroclastic rocks. Geometric means, weighted with sample lengths, of total data including 3 andesitic, 9 dacitic, 17 rhyodacitic and 12 rhyolitic compositions. Total n = 41, 170.60 m.

Kiipu altered rocks. Geometric means, weighted with sample lengths, of total data including 2 cordierite, 42 cordierite-muscovite, 17 cordierite-biotite and 2 cordierite-anthophyllite-biotite gneisses. Total n = 63, 178.85 m.
 Average calc-alkaline andesite of Nockolds (1954, Table 6, II).

6. Average »Lava dome volcanic rock» from the Kosaka mining area, Japan. Tatsumi and Clark (1972).

7. Average of 4 rhyolites associated with »Kuroko» ore deposits in Matsumine Mine, northern Japan. Data from Ogura (1972, Table 1).

8. Quartz-feldspar schist from the Vihanti mine field. Rouhunkoski (1968, Table 2, column 4).

9. Cordierite gneiss from the Vihanti mine field. Rouhunkoski (1968, Table 2, column 2).

porphyroblasts are colorless; they are usually a little bigger and with more euhedral crystal habits.

In thin section the color of gahnite varies from pale green or almost colorless to dark green when in contact with, or close to, sphalerite. Gahnite appears to be produced by prograde regional metamorphism from sphalerite through reaction with aluminous silicate(s). The sulfur thereby released forms pyrite. A typical gahniteferous paragenesis is cordierite-quartz-biotitegarnet-gahnite-pyrite (Fig. 24g). The intensity of the green color in the gahnite appears to have a positive correlation with the Zn contents, and the Zn contents in turn probably depend on the availability of Zn during the crystallization of the gahnite porphyroblasts. This was proved by electron microprobe analyses on gahnites in specimen Ki-5, 123.70 m: Dark green gahnites coexisting with sphalerite and silicates averaged 35.00 % ZnO-component whereas the pale green gahnites occurring alone in silicates contained 30.78 % ZnO-component.

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#### Geochemistry

In the following the Kiipu occurrence is viewed on the basis of 111 whole rock XRF and sulfide phase AAS analyses representing a total of 384.45 m of split d.d. core. Of these, 7 analyses are from metalavas (totalling 35.00 m), 41 from pyroclastic rocks (170.60 m) and 63 from altered rocks (178.85 m). The rock types were classified on the basis of visual (core logging) and thin-section examinations, and whole rock XRF analyses (classifications according to SiO<sub>2</sub> contents).

#### Major-element geochemistry

Analyses of Kiipu rock types are given in Table 5, expressed as geometric means weighted with sample lengths. For comparison, some selected analyses are cited from the literature. The distributions of the main chemical components are visualized by frequency distribution and petrological diagrams, Figs. 25—29.

In this context the following comments on each of the three main rock types are appropriate.





Fig. 26. The Kiipu  $Na_2O+K_2O$  vs.  $SiO_2$  diagram. • = Metalavas,  $\triangle =$  pyroclastic rocks. The dividing line between the alkaline and subalkaline fields is from MacDonald and Katsura (1964), and the high-alumina field is from Kuno (1966). The Kiipu metavolcanic rocks appear to be subalkaline, and the andesitic metalavas to fall within the high-Al field.

#### Metalavas

The metalavas range in composition from basaltic and site to rhyodacite  $(SiO_2 \text{ from } 51.98 \%)$ to 65.65 %). The mean of the five meta-and sites (25 m of core) is given in Table 5, column 1. Note the striking similarity to Nockolds' (1954) average calc-alkaline and site (Table 5, column 5). The diagrams in Figs. 26 and 27 indicate that the Kiipu metalavas fall within the fields of subalkaline, high-alumina, calc-alkaline and esites.

#### Pyroclastic rocks

The SiO<sub>2</sub> contents of Kiipu pyroclastic rocks range from 54.72 % to 75.12 %. The weighted mean of the 41 analyses is 66.57 % SiO<sub>2</sub> referring to dacite. The subalkaline, calc-alkaline character of these rocks is indicated by Figs. 26 and 27. The gradual passage from pyroclastic to altered rocks is visualized by the overlapping distribution of symbols in Figs. 27–29.

#### Altered rocks

Figs. 27—29 are petrological diagrams of the Kiipu altered rocks; they appear to be strikingly different in composition from the metalavas and pyroclastic rocks. The reasons for the alteration phenomena, with reference to other type examples, are discussed in the following.

Alteration phenomena surrounding Kuroko deposits in Hokuroku District, Japan, are described by Iijima (1974). A distinct alteration pattern, termed the »Kuroko alteration», is recognized around these deposits. This alteration pattern is the outcome of both Miocene submarine hydrothermal activity related to Kuroko mineralization and of normal burial diagenesis. Iijima reports the following characteristic major element alteration phenomena related to certain alteration zones in the stratigraphic column. K metasomatism is prominent mainly in the sericite-chlorite alteration zones underlying the Kuroko deposits. Leaching of Ca and Na is evident in all zones underlying the ore deposits; Fe, Mn and Mg are added to these zones.



Fig. 27. The Kiipu AFM diagram. The dividing line between tholeiitic (upper) and calc-alkaline (lower) fields is from Irvine and Baragar (1971). The calc-alkaline character of the main rock types of Kiipu is well demonstrated.

Fig. 28. The Kiipu  $Na_2O-K_2O-CaO$ diagram. The Kiipu metalavas are clustered in the andesite-dacite fields of Le Maitre (1976) and the pyroclastic rocks mainly in the dacite-rhyolite fields. In the altered rocks the trend is towards  $Na_2O$  and CaO depletion and  $K_2O$  enrichment. The overlap in the distribution of pyroclastic and altered rocks is due to the difficulty of distinguishing between unaltered and in-

cipiently altered pyroclastic rocks.

Fig. 29. The Kiipu K<sub>2</sub>O—(CaO+Na<sub>2</sub>O)— (MgO+FeO\*) diagram, or »the alteration triangle diagram». The depletion of the pyroclastic rocks in CaO and Na<sub>2</sub>O (destruction and disappearance of plagioclase) and the enrichment in K<sub>2</sub>O (muscovite, biotite), MgO and FeO\* (cordierite, garnet, anthophyllite) in the course of alteration is well illustrated.



Fig. 30. Variation of the main chemical components and ore-forming elements in Kiipu rock types. Geometric means, weighted with sample lengths, for each rock type.

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Fig. 30, continued.

Nichol et al. (1977, Table 1) have summarized the alteration patterns recognized in volcanogenic massive sulfide deposits ranging in age from Archean to Cenozoic as follows. The alteration zones display minerals such as montmorillonite, sericite, chlorite, calcite, quartz and kaolinite in association with the lowmetamorphosed deposits, and quartz, cordierite, anthophyllite, garnet, andalusite, kyanite and biotite with deposits of higher metamorphic degrees. As to the major element dispersion the alteration phenomena display enrichment mainly in K, Fe, Mn and Mg, and depletion mainly in Ca and Na. Elements unchanged comprise Ti and Al. Si is either enriched or depleted, depending on the case.

In the following remarks on the Kiipu alteration pattern the altered rocks are compared with the parent pyroclastic rocks (ref. Tables 5 and 6, and Fig. 30). CaO and Na<sub>2</sub>O (plagioclase) are markedly depleted, with some SiO<sub>2</sub> and P2O5 (apatite) from the altered rocks with respect to the parent rocks. The quantities of FeO\*, MnO, MgO, and the bulk of K,O, are greatly increased, as to some extent is FeS2. As to the alkalis alone the Na2O-K2O-CaO diagram in Fig. 28 shows very clearly the plotting of altered rocks in the K corner resulting from the enrichment in K, and the simultaneous depletion in Na and Ca by the leaching out of plagioclase (and apatite) by heated waters from the parent pyroclastic rocks. No natural igneous rocks fall within this field (cf. Le Maitre 1976).

Iijima (1974) also demonstrates the character of the Kuroko alteration by calculating the degree of enrichment of the main chemical components in the alteration zones as compared with the parent rocks. On the basis of electron microprobe analyses on fresh and altered parts of a rhyolite obsidian, Iijima (op. cit., Table 7) first demonstrates by an isovoluminous method that the content of  $TiO_2$  in a unit volume of rock remains unchanged even though large amounts of alkalis and silica are leached out, and abundant Mg, Fe, Mn and H<sub>2</sub>O, with a small amount of Al, are added to the altered glass. Using the stability of  $TiO_2$  minerals (gross immobility of titania) in this type of alteration Iijima then calculates the degree of enrichment of each main chemical component from the equation

 $\frac{[{\rm RO}/{\rm TiO_2}] \text{ altered rock}}{[{\rm RO}/{\rm TiO_2}] \text{ parent rock}} - 1,$ 

where  $RO/TiO_2$  is the mole ratio of a given component to  $TiO_2$ . The character of the Kuroko alteration pattern is clearly demonstrated with this method (Table 6, columns 6 and 7).

This equation was applied to the Kiipu altered rocks vs. the parent pyroclastic rocks. The results are presented in Table 6. An alteration pattern analogous to the Kuroko alteration described by Iijima (op. cit.) is clearly shown.

#### Table 6

Alteration coefficients of Kiipu altered rocks calculated from the length-weighted mean of each group and from that of the parent pyroclastic rocks (Table 5, column 3), from the equation

		1		1			
	1	2	3	4	5	6	7
SiO <sub>2</sub>	0.09	0.15	-0.30	-0.37	-0.02	0.46	-0.59
TiO <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al <sub>2</sub> O <sub>3</sub>	0.11	0.23	-0.17	-0.30	0.07	0.13	-0.17
FeO*	0.71	0.87	1.58	2.17	1.08	0.35	9.8
MnO	0.20	0.39	0.74	1.15	0.45	4.95	0.00
MgO	0.03	0.17	0.56	1.35	0.30	3.85	1.86
CaO	-0.40	-0.80	0.81	0.86	0.80	0.79	-0.93
Na <sub>9</sub> O	0.98	-0.59	-0.75	-0.93	-0.65	-0.71	-0.95
K"Õ	-0.33	0.42	-0.05	0.39	0.23	1.89	1.89
P <sub>2</sub> O <sub>5</sub>	-0.27	-0.38	-0.26	-0.17	-0.31		
FeS <sub>2</sub>	1.02	1.16	-0.27	0.33	0.56		
Cu	0.61	0.61	0.73	0.17	0.55		
Zn	0.45	1.99	1.66	1.38	1.82		
РЬ	1.14	3.63	1.26	3.16	2.67		
Со	0.18	0.06	0.10	-0.22	0.06		
Ni	-0.33	-0.41	-0.34	-0.46	-0.37		
As	0.97	0.16	-0.07	0.54	1.09		

1 = Cordierite gneiss (n = 2, 5.45 m of d.d. core)

2 = Cordierite-muscovite gneiss (n = 42, 116.45 m)

3 = Cordierite-biotite gneiss (n = 17, 51.05 m)

4 = Cordierite-anthophyllite-biotite gneiss (n = 2, 5.90 m)

5 = Weighted mean of 1-4 (Table 5, column 4).

For comparison, alteration coefficients for two types of alteration, detected in hydrothermal alteration zones surrounding Kuroko deposits in the Hokuroku district, Japan, are given from Iijima (op. cit., Table 8, FeO\* = total Fe as FeO):

6 = Sericite-chlorite alteration zone

7 = Kaolinite alteration zone.

#### Minor-element geochemistry

Along with the Kuroko alteration the concentration of sulfur and ore-forming metallic elements such as Fe, Cu, Zn and Pb is acknowledged in Kuroko-type deposits, generally regardless of their age, all over the world (Sangster 1972, Lambert and Sato 1974, Large 1977).

The distributions of minor (ore-forming) elements in Kiipu rock types are presented in Table 5 and Figs. 30 and 31. With reference to these data the following comments are brought up.



#### Metalavas

The minor elements display rather uniform distributions at mean 81 ppm Cu, 50 ppm Zn and 10 ppm Pb.

#### Pyroclastic rocks

At mean 69 ppm, Cu is slightly lower in pyroclastic rocks than in metalavas; in contrast Zn, at mean 125 ppm, and Pb, at mean 23 ppm, are relatively enriched in the pyroclastic rocks. The enrichment of Zn in calc-alkaline pyroclastic rocks, compared with flow rocks of the same series, has been documented from Canadian Archean rocks by Franklin *et al.* (1975) and Wolfe (1975).

#### Altered rocks

The altered rocks are enriched principally in Zn, with some enrichment in Pb. The Cu–Zn-Pb diagram (Fig. 31) shows the dominance of Cu in metalavas, the increasing Zn contents in pyroclastic rocks, and the Zn(-Pb) enrichment trend in altered rocks.

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Fig. 31. The Kiipu Cu-Zn-Pb diagram. The metalavas appear to approach the Cu corner; the pyroclastic rocks contain more Zn and Pb than the metalavas; and the majority of the altered rocks are enriched in Zn and Pb, with only a few samples close to the Cu corner.

The variation of Ni, Co and As in Kiipu rock types is displayed in Fig. 30. Co is quite indifferent at a constant level of roughly 20— 25 ppm. Ni decreases from 55 ppm in metalavas, through 39 ppm in pyroclastic rocks, to 24 ppm in altered rocks. As (XRF analyses) increases from 16 ppm in metalavas, to 20 ppm in pyroclastic rocks and 41 ppm in altered rocks. Gold was analyzed from some pyritiferous pyroclastic and altered rock intersections but only a few samples reached the detection limit of 0.2 ppm Au.

The Ni: Co ratios in metalavas, pyroclastic and altered rocks are 2.8, 1.7 and 0.9, respectively, and those for Cu: Zn are 1.6, 0.6, and 0.3, respectively.

In short the Kiipu metalavas belong to the subalkaline, calc-alkaline high-Al andesite class with mean 54 % SiO<sub>2</sub>, and the pyroclastic rocks average rhyodacite at 67 % SiO<sub>2</sub>. The alteration of pyroclastic rocks yields altered rocks enriched mainly in MgO, FeO\*, MnO and K<sub>2</sub>O, and depleted mainly in CaO and Na<sub>2</sub>O. This alteration pattern equals the Kuroko alteration described by Iijima (1974). With regard to the minor elements, Cu is rather evenly distributed between metalavas and pyroclastic rocks, whereas Zn is enriched in the

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Correlation matrix												
	SiO <sub>2</sub>	TiO <sub>2</sub>	$Al_2O_3$	FeO*	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	$P_2O_5$		
SiO	1.00	-0.93	-0.93			0.96		0.79	0.68	-0.43		
TiO <sub>3</sub>	-0.93	1.00	0.78	0.98	0.94	0.95	0.82	0.64	0.56	0.32		
Al <sub>2</sub> Ó <sub>2</sub>	-0.93	0.78	1.00	0.85	0.85	0.85	0.97	0.78	-0.69	0.22		
FeO*	-0.95	0.98	0.85	1.00	0.98	0.99	0.90	0.77	0.71	0.28		
MnO	-0.95	0.94	0.85	0.98	1.00	0.99	0.93	0.83	-0.80	0.28		
MgO	0.96	0.95	0.85	0.99	0.99	1.00	0.92	0.84	0.77	0.37		
CaO	-0.94	0.82	0.97	0.90	0.93	0.92	1.00	0.85	0.81	0.23		
Na <sub>2</sub> O	-0.79	0.64	0.78	0.77	0.83	0.84	0.85	1.00	0.95	0.37		
K,0	0.68	-0.56	-0.69	0.71	0.80	-0.77	0.81	-0.95	1.00	-0.17		
P <sub>2</sub> O <sub>5</sub>	-0.43	0.32	0.22	0.28	0.28	0.37	0.23	0.37	0.17	1.00		
FeS <sub>2</sub>	0.24	-0.19	-0.36	-0.12	0.00	-0.03	0.18	0.24	0.40	0.03		
Cu	0.23	-0.02	-0.37	-0.18	-0.34	-0.25	-0.43	-0.60	0.73	0.15		
Zn	0.67	-0.55	-0.57	-0.62	-0.74	-0.70	-0.73	-0.71	0.78	-0.46		
Pb	0.12	-0.27	0.13	-0.16	-0.21	-0.15	0.05	0.10	-0.04	-0.18		
Со	0.62	-0.34	-0.81	-0.40	-0.43	0.40	-0.69	-0.43	0.34	-0.13		
Ni	0.89	-0.80	-0.87	-0.83	-0.88	-0.83	-0.89	-0.67	0.65	-0.19		
As	0.85		-0.84		-0.79	0.76	0.80	-0.68	0.60	-0.28		

 Table 7

 Kiipu metalavas: Correlation and factor matrices of 7 samples representing 35.00 m of split d.d. core.

pyroclastic rocks. Further, Zn, Pb, Cu, Ag and S are enriched in the altered rocks, Co stays at a constant level, and Ni decreases from metalavas through pyroclastic to altered rocks. were run on the analytical data of the three Kiipu main rock types (Tables 7-9) and on the corresponding pooled data (Table 10).

#### Factor analysis

Factor analysis creates a minimum number of new variables that are linear combinations of the original ones in such a way that the new variables contain the same amount of information (Jöreskog *et al.* 1976). Factor analyses

#### Metalavas (Table 7)

The correlation matrix indicates that  $SiO_2$ and  $K_2O$  possess a moderate positive correlation. Another group with good correlations is formed by  $TiO_2$ ,  $Al_2O_3$ , FeO\*, MnO and Na<sub>2</sub>O, which do not correlate with metallic elements. The metallic elements Ni, As, Co, Zn and Cu generally correlate positively with each other and

Table 7, continued

						Rotated	factor ma	itrix			
<b>P</b> 0		7	Pla	6	27			Factor		6	
FeS <sub>2</sub>	Cu	Zn	РЬ	Co	N1	As	1	2	3	Comm.	
$\begin{array}{c} 0.24\\ -0.19\\ -0.36\\ -0.12\\ 0.00\\ -0.03\\ -0.18\\ 0.24\\ -0.40\\ 0.03\\ 1.00\\ -0.51\\ -0.27\\ -0.35\\ 0.55\\ 0.14\\ \end{array}$	$\begin{array}{c} 0.23\\ -0.02\\ -0.37\\ -0.18\\ -0.25\\ -0.43\\ -0.60\\ 0.73\\ -0.51\\ 1.00\\ 0.50\\ 0.06\\ 0.39\\ 0.47\\ \end{array}$	$\begin{array}{c} 0.67\\ -0.55\\ -0.57\\ -0.62\\ -0.74\\ -0.70\\ -0.73\\ -0.71\\ 0.78\\ -0.46\\ -0.27\\ 0.50\\ 1.00\\ 0.24\\ 0.36\\ 0.69\\ \end{array}$	$\begin{array}{c} 0.12\\ -0.27\\ 0.13\\ -0.16\\ -0.21\\ -0.15\\ 0.05\\ 0.10\\ -0.04\\ -0.18\\ -0.35\\ 0.06\\ 0.24\\ 1.00\\ -0.22\\ 0.35\\ \end{array}$	$\begin{array}{c} 0.62\\ -0.34\\ -0.81\\ -0.40\\ -0.43\\ -0.40\\ -0.69\\ -0.43\\ 0.34\\ -0.13\\ 0.55\\ 0.39\\ 0.36\\ -0.22\\ 1.00\\ 0.69\\ \end{array}$	$\begin{array}{c} 0.89\\ -0.80\\ -0.87\\ -0.83\\ -0.83\\ -0.83\\ -0.89\\ -0.67\\ 0.65\\ -0.19\\ 0.14\\ 0.47\\ 0.69\\ 0.35\\ 0.69\\ 1.00\\ \end{array}$	$\begin{array}{c} 0.85\\ -0.72\\ -0.84\\ -0.75\\ -0.79\\ -0.76\\ -0.80\\ -0.80\\ -0.68\\ 0.60\\ -0.28\\ 0.10\\ 0.51\\ 0.55\\ 0.35\\ 0.71\\ 0.95\\ \end{array}$	$\begin{array}{c} 1.00\\ -0.93\\ -0.94\\ -0.95\\ -0.94\\ -0.94\\ -0.94\\ -0.94\\ -0.74\\ 0.64\\ -0.38\\ 0.30\\ 0.20\\ 0.65\\ 0.12\\ 0.64\\ 0.90\\ \end{array}$	$\begin{array}{c} -0.05 \\ -0.08 \\ 0.11 \\ 0.09 \\ 0.24 \\ 0.18 \\ 0.26 \\ 0.57 \\ -0.74 \\ -0.10 \\ 0.79 \\ -0.90 \\ -0.90 \\ -0.001 \\ -0.01 \\ -0.21 \end{array}$	$\begin{array}{c} 0.03\\ -0.26\\ 0.32\\ -0.15\\ -0.16\\ -0.18\\ 0.03\\ -0.01\\ -0.43\\ -0.52\\ -0.24\\ 0.23\\ 0.76\\ -0.63\\ -0.01\\ \end{array}$	$\begin{array}{c} 1.00\\ 0.94\\ 1.00\\ 0.93\\ 0.96\\ 0.95\\ 0.98\\ 0.87\\ 0.95\\ 0.34\\ 0.98\\ 0.91\\ 0.72\\ 0.59\\ 0.82\\ 0.86\end{array}$	$\begin{array}{c} \text{SiO}_2\\ \text{TiO}_2\\ \text{Al}_2\text{O}_3\\ \text{FeO}^*\\ \text{MnO}\\ \text{MgO}\\ \text{CaO}\\ \text{MgO}\\ \text{CaO}\\ \text{Na}_2\text{O}\\ \text{K}_2\text{O}\\ \text{FeS}_2\\ \text{Cu}\\ \text{Zn}\\ \text{Pb}\\ \text{Co}\\ \text{Ni} \end{array}$
0.10	0.51	0.55	0.35	0.71	0.95	1.00	0.85			0.77	As
					Eige	nv. %	62.3	13.4	10.1		
					Princ loadi	ipal ng	SiO <sub>2</sub> Ni As Zn Co K <sub>2</sub> O -FeO* -Al <sub>2</sub> O <sub>3</sub> -MnO -CaO -TiO <sub>2</sub> -Na <sub>2</sub> O	FeS <sub>2</sub> Na <sub>2</sub> O —Cu —K <sub>2</sub> O —Zn	$\begin{array}{c} Pb \\ -Co \\ -FeS_2 \\ -P_2O_5 \end{array}$		

with SiO and  $K_2O$ . This indicates their homogeneous distribution in metalavas and their enrichment in SiO<sub>2</sub>- $K_2O$ -rich (acidic) varieties.

Being the result of homogeneous data factor 1 alone explains 62 % of the variation in the variables. The forementioned correlation relations are reflected in factor 1 as positive loadings of SiO<sub>2</sub>, K<sub>2</sub>O and metallic elements, and as negative loadings of the remainder.

#### Pyroclastic rocks (Table 8)

 $SiO_2$  does not clearly correlate with any other variable and displays a moderate negative

correlation with MgO. Correlating components can be grouped as  $TiO_2$ ,  $Al_2O_3$ , MgO and MnO, and CaO and Na<sub>2</sub>O. K<sub>2</sub>O reveals the best correlation with Pb, Zn, Co and FeS<sub>2</sub> indicating the enrichment of these components in the relatively K-rich and Ca–Na-poor (intermediate) varieties of pyroclastic rocks.

The high number (7) of factors is caused, except for cumulative eigenvalues of over 85 %, by relatively weak correlations between variables. Factor 1, explaining 26 % of the data, includes MgO, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MnO, Co, Cu and SiO<sub>2</sub>. Factor 2 could be designated a »pyrite factor» with negative FeO\* loading. Factor 3 is the  $CaO-P_2O_5$  »apatite factor». Factors 4–7 are

Correlation matrix											
	SiO <sub>2</sub>	$TiO_2$	Al <sub>2</sub> O <sub>3</sub>	FeO*	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	$P_2O_5$	FeS2
SiO	1.00	0.39	-0.32	-0.28	-0.25	-0.67	0.05	0.05	0.25	-0.36	0.22
TiO	-0.39	1.00	0.53	-0.22	0.48	0.57	-0.23	-0.14	0.31	-0.12	0.05
Al <sub>2</sub> O <sub>2</sub>	-0.32	0.53	1.00	-0.40	0.37	0.52	-0.23	0.09	0.22	-0.01	0.48
FeO*	-0.28	-0.22	-0.40	1.00	0.03	0.12	0.12	0.20	0.30	-0.05	-0.73
MnO	-0.25	0.48	0.37	0.03	1.00	0.68	-0.12	-0.05	0.27	0.15	0.06
MgO	-0.67	0.57	0.52	0.12	0.68	1.00	-0.18	-0.24	0.13	0.21	-0.03
CaO	0.05	-0.23	-0.23	-0.12	0.12	-0.18	1.00	0.58	0.34	0.70	-0.04
Na <sub>9</sub> O	0.05	-0.14	0.09	-0.20	-0.05	-0.24	0.58	1.00	-0.21	0.30	0.04
K"Õ	-0.25	0.31	0.22	0.03	0.27	0.13	-0.34	-0.21	1.00	-0.28	0.49
P.O	-0.36	-0.12	-0.01	-0.05	0.15	0.21	0.70	0.30	0.28	1.00	0.07
FeS,	0.22	0.05	0.48	-0.73	0.06	-0.03	0.04	0.04	0.49	0.07	1.00
Cu	-0.46	0.27	0.38	0.42	0.36	0.51	-0.59	-0.32	-0.08	-0.18	-0.22
Zn	0.03	0.27	-0.06	-0.03	0.10	0.07	-0.36	-0.18	0.55	-0.44	0.11
РЬ	0.15	0.22	0.27	-0.49	0.29	0.05	0.09	0.00	0.59	-0.05	0.72
Со	-0.44	0.48	0.25	0.04	0.39	0.65	-0.41	-0.49	0.42	-0.16	0.02
Ni	0.12	0.00	0.17	-0.35	-0.25	-0.12	0.17	-0.01	-0.07	0.10	0.31
As	0.01	0.00	0.11	-0.27	0.10	-0.12	0.16	0.17	0.22	0.01	0.47

Table 8

Kiipu pyroclastic rocks: Correlation and factor matrices of 41 samples representing 170.60 m of split d.d. core.

 Table 9

 Kiipu altered rocks: Correlation and factor matrices of 63 samples representing 178.85 m of split d.d. core.

Correlation matri
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	SiO <sub>2</sub>	TiO <sub>2</sub>	$\mathrm{Al}_2\mathrm{O}_3$	FeO*	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	FeS <sub>2</sub>
SiO <sub>2</sub>	1.00	0.51	0.08	-0.13	0.35	0.64	-0.26	0.25	-0.35	0.40	-0.19
TiO <sub>2</sub>	-0.51	1.00	0.21	0.10	0.67	0.54	0.39	-0.27	0.07	0.78	0.31
$Al_2O_3$	-0.08	0.21	1.00	-0.38	-0.03	0.07	-0.05	-0.04	0.35	0.09	0.21
FeO*	-0.13	0.10	-0.38	1.00	0.51	0.37	0.05	-0.21	-0.20	0.18	-0.41
MnO	-0.35	0.67	-0.03	0.51	1.00	0.56	0.35	-0.37	-0.12	0.55	0.06
MgO	-0.64	0.54	0.07	0.37	0.56	1.00	0.26	-0.33	-0.35	0.54	-0.07
CaO	-0.26	0.39	0.05	0.05	0.35	0.26	1.00	0.40	-0.17	0.48	0.13
Na <sub>2</sub> O	0.25	-0.27	-0.04	-0.21	-0.37	-0.33	0.40	1.00	0.14	-0.23	-0.19
K <sub>2</sub> O	-0.35	0.07	0.35	-0.20	-0.12	-0.35	-0.17	0.14	1.00	-0.18	-0.24
$P_2O_5$	0.40	0.78	0.09	0.18	0.55	0.54	0.48	-0.23	-0.18	1.00	0.46
FeS <sub>2</sub>	-0.19	0.31	0.21	-0.41	0.06	-0.07	0.13	-0.19	-0.24	0.46	1.00
Cu	-0.18	0.34	0.17	0.16	0.50	0.19	-0.18	-0.46	-0.04	0.35	0.36
Zn	-0.35	0.27	0.03	0.02	0.24	0.05	0.01	-0.06	-0.06	0.17	0.41
РЬ	-0.14	0.42	0.10	0.01	0.44	-0.06	0.21	-0.17	-0.08	0.34	0.59
Со	-0.49	0.26	0.26	0.07	0.12	0.58	-0.12	-0.24	-0.10	0.26	0.07
Ni	-0.25	-0.12	0.01	0.18	-0.12	0.51	0.02	0.03	-0.28	0.03	-0.26
As	0.13	0.17	0.08	-0.40	-0.05	-0.38	0.15	0.11	0.10	0.07	0.56

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#### Table 8, continued

						Rotate	d factor	matrix						
6	7	DL	6	NU	A				Factor				Comm	
Cu	Zn	PD	Co	181	As	1	2	3	4	5	6	7	Comm.	
$\begin{array}{c} -0.46\\ 0.27\\ 0.38\\ 0.42\\ 0.36\\ 0.51\\ -0.59\\ -0.32\\ -0.08\\ -0.18\\ -0.22\\ 1.00\\ -0.01\\ -0.22\\ 0.53\\ -0.14\\ -0.25\\ \end{array}$		$\begin{array}{c} 0.15\\ 0.22\\ 0.27\\ -0.49\\ 0.09\\ 0.09\\ 0.09\\ 0.09\\ 0.05\\ 0.72\\ -0.22\\ -0.22\\ -0.22\\ 0.47\\ 1.00\\ 0.21\\ 0.01\\ 0.01\\ 0.01\\ \end{array}$	$\begin{array}{c} -0.44\\ 0.48\\ 0.25\\ 0.04\\ 0.39\\ 0.65\\ -0.41\\ -0.42\\ -0.16\\ 0.02\\ 0.53\\ 0.48\\ 0.21\\ 1.00\\ 0.00\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0.00\\ 0.10\\ 0.00\\ 0$	$\begin{array}{c} 0.12\\ 0.00\\ 0.01\\ 0.017\\ -0.35\\ 0.25\\ -0.12\\ 0.017\\ -0.01\\ -0.07\\ 0.10\\ 0.31\\ -0.14\\ -0.21\\ 0.01\\ 0.00\\ 1.000\\ 1.000\\ 0.05\\ \end{array}$	$\begin{array}{c} 0.01\\ 0.00\\ 0.00\\ 0.11\\ -0.27\\ 0.10\\ -0.12\\ 0.16\\ 0.17\\ 0.22\\ 0.01\\ 0.47\\ -0.35\\ 0.33\\ 0.48\\ -0.10\\ 0.05\\ 1.00\\ 0.05\\ 0$	$\begin{array}{c} -0.78\\ 0.74\\ 0.74\\ 0.03\\ 0.61\\ 0.89\\ -0.16\\ -0.01\\ 0.10\\ 0.18\\ -0.01\\ 0.61\\ 0.05\\ 0.04\\ 0.62\\ -0.02\\ $	$\begin{array}{c} 0.33\\ 0.15\\ 0.44\\ -0.78\\ 0.30\\ 0.02\\ -0.09\\ 0.02\\ 0.67\\ 0.01\\ 0.91\\ -0.26\\ 0.18\\ 0.82\\ 0.07\\ 0.18\\ 0.26\\ 0.7\\ 0.18\\ 0.26\\ 0.07\\ 0.18\\ 0.26\\ 0.07\\ 0.18\\ 0.07\\ 0.18\\ 0.07\\ 0.08\\ 0.07\\ 0.08\\ 0.07\\ 0.08\\ 0.07\\ 0.08\\ 0.07\\ 0.08\\ 0.08\\ 0.07\\ 0.08\\ 0.0$	$\begin{array}{c} -0.24 \\ -0.18 \\ -0.08 \\ -0.05 \\ 0.11 \\ 0.11 \\ 0.84 \\ 0.28 \\ -0.19 \\ 0.00 \\ -0.46 \\ -0.29 \\ 0.02 \\ -0.13 \\ 0.11 \\ 0.02 \end{array}$	$\begin{array}{c} 0.00\\ 0.12\\ 0.18\\ -0.39\\ -0.51\\ -0.16\\ 0.00\\ 0.19\\ -0.15\\ -0.21\\ -0.18\\ 0.03\\ 0.87\\ 0.91\\$	$\begin{array}{c} -0.10\\ -0.17\\ -0.28\\ 0.05\\ 0.22\\ -0.41\\ -0.84\\ 0.19\\ -0.04\\ 0.02\\ 0.31\\ 0.18\\ 0.07\\ 0.56\\ 0.08\\$	$\begin{array}{c} -0.28\\ -0.17\\ -0.06\\ 0.10\\ -0.31\\ -0.09\\ 0.06\\ 0.11\\ -0.04\\ 0.02\\ 0.25\\ -0.06\\ 0.32\\ 0.27\\ -0.02\\ -0.02\\ -0.03\\ 0.02\end{array}$	$\begin{array}{c} 0.02\\ 0.42\\ -0.28\\ -0.13\\ 0.03\\ 0.12\\ -0.01\\ -0.00\\ -0.31\\ -0.16\\ -0.32\\ 0.75\\ 0.24\\ 0.38\\ -0.12\\ 0.1$	$\begin{array}{c} 0.86\\ 0.84\\ 0.94\\ 0.87\\ 0.84\\ 0.89\\ 0.93\\ 0.82\\ 0.79\\ 0.91\\ 0.95\\ 0.88\\ 0.87\\ 0.84\\ 0.86\\ 0.83\\$	SiO <sub>2</sub> TiO <sub>2</sub> Al <sub>2</sub> O <sub>3</sub> FeO* MnO MgO CaO Na <sub>2</sub> O Na <sub>2</sub> O FeS <sub>2</sub> Cu Zn Pb Co Ni
0.35	0.33	0.48	-0.10	0.05	1.00	0.06	0.36	0.08	0.01	-0.16	0.82	0.17	0.87	As
				Eige	nv. %	25.8	21.2	14.9	8.8	6.1	5.4	4.8		
				Pr	incipal ading	$\begin{array}{c} MgO\\TiO_2\\Al_2O_3\\Co\\Cu\\MnO\\-SiO_2\end{array}$	$\begin{array}{c} \operatorname{FeS}_2 \\ \operatorname{Pb} \\ \operatorname{K}_2 O \\ \operatorname{Al}_2 O_3 \\ -\operatorname{FeO}^* \end{array}$	P <sub>2</sub> O <sub>5</sub> CaO —Cu	Ni –MnO	Co —Na <sub>2</sub> O —CaO	As	Zn K <sub>2</sub> O TiO <sub>2</sub>		

#### Table 9, continued

					Rotated	d factor	matrix							
C.v.	7.0	Dh	Ca	NI	A				Factor				6	
	211	FD	Co	181	AS	1	2	3	4	5	6	7	Comm.	
-0.18	-0.35	-0.14	-0.49	-0.25	0.13	-0.55	-0.38	0.04	0.17	-0.11	-0.54	-0.23	0.83	SiO.
0.34	0.27	0.42	0.26	-0.12	0.17	0.89	-0.07	-0.06	-0.10	-0.19	-0.18	-0.07	0.89	TiO,
0.17	0.03	-0.10	0.26	0.01	0.08	0.16	0.22	-0.52	-0.03	-0.61	-0.02	-0.19	0.76	Al.O.
0.16	0.02	0.01	0.07	0.18	0.40	0.21	0.10	0.84	-0.07	0.20	0.06	-0.16	0.83	FeO*
0.50	0.24	0.44	0.12	-0.12	-0.05	0.74	-0.13	0.43	-0.13	0.01	0.14	-0.31	0.88	MnO
0.19	0.05	-0.06	0.58	0.51	-0.38	0.67	0.56	0.19	-0.18	0.15	0.13	0.06	0.88	MgO
-0.18	0.01	0.21	-0.12	0.02	0.15	0.63	0.09	-0.02	0.66	0.17	-0.05	0.16	0.90	CaO
-0.46	-0.06	-0.17	-0.24	0.03	0.11	-0.25	-0.01	-0.04	0.91	-0.10	0.01	0.18	0.93	Na <sub>2</sub> O
-0.04	-0.06	-0.08	-0.10	-0.28	0.10	-0.10	0.19	0.20	0.03	-0.91	-0.04	0.05	0.87	K,Ō
0.35	0.17	0.34	0.26	0.03	0.07	0.85	0.03	-0.13	0.03	0.15	-0.01	-0.25	0.83	P <sub>2</sub> O <sub>5</sub>
0.36	0.41	0.59	0.07	0.26	0.56	0.26	-0.28	-0.71	-0.08	0.29	0.25	-0.33	0.92	FeS2
1.00	0.34	0.26	0.30	-0.08	-0.01	0.23	0.03	0.02	-0.29	-0.04	0.21	-0.84	0.90	Cu
0.34	1.00	0.53	0.17	-0.29	0.32	0.08	-0.19	-0.04	0.03	0.02	0.89	0.23	0.90	Zn
0.26	0.53	1.00	-0.20	-0.57	0.75	0.37	-0.70	-0.13	-0.09	0.18	0.43	-0.12	0.89	Pb
0.30	0.17	-0.20	1.00	0.58	-0.31	0.21	0.75	-0.14	-0.19	-0.06	0.35	-0.17	0.81	Co
-0.08	-0.29	-0.57	0.58	1.00	-0.56	0.01	0.88	0.04	0.08	0.21	-0.12	0.06	0.84	Ni
-0.01	0.32	0.75	-0.31	-0.56	1.00	0.07	-0.71	-0.49	0.08	0.03	0.25	0.04	0.82	As
				Eigenv	. %	26.9	20.4	11.2	10.2	8.2	5.5	4.0		
				Princip	bal	TiO <sub>2</sub>	Ni	FeO*	Na <sub>2</sub> O	$-K_{2}O$	Zn	-Cu		
				loading	3	$P_2O_5$	Co	MnO	CaO	$-Al_2O_3$	Pb			
						MnO	MgO	-FeS2			$-SiO_2$			
						MgO	-As	-Al2O3			-			
						CaO	-Pb	-As						
						$-SiO_2$								

correlation matrix												
	SiO <sub>2</sub>	TiO <sub>2</sub>	$Al_2O_3$	FeO*	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	$P_2O_5$	FeS2	Cu
SiO <sub>2</sub>	1.00	0.38	0.26	0.40	0.22	0.19	0.27	0.26	0.32	0.25	0.36	0.47
TiO <sub>2</sub>	0.38	1.00	0.69	0.32	-0.53	0.42	0.08	0.19	0.19	0.09	-0.59	-0.47
$Al_2O_3$	0.26	0.69	1.00	0.14	-0.60	0.62	-0.11	-0.03	0.13	-0.12	-0.50	-0.47
FeO*	0.40	0.32	0.14	1.00	0.12	0.13	0.08	-0.36	0.58	0.25	-0.35	-0.43
MnO	-0.22	-0.53	-0.60	0.12	1.00	-0.22	-0.13	-0.07	0.04	-0.03	0.52	0.38
MgO	0.19	0.42	0.62	0.13	-0.22	1.00	0.53	0.12	-0.04	0.27	-0.26	-0.27
CaO	0.27	0.08	-0.11	0.08	-0.13	-0.53	1.00	-0.30	0.28	-0.29	-0.11	-0.21
Na <sub>9</sub> O	-0.26	-0.19	-0.03	-0.36	-0.07	0.12	-0.30	1.00	-0.66	-0.24	-0.08	0.13
K.O	0.32	0.19	0.13	0.58	0.04	-0.04	0.28	-0.66	1.00	0.34	0.17	-0.36
P <sub>2</sub> O <sub>5</sub>	0.25	0.09	0.12	0.25	-0.03	0.27	-0.29	-0.24	0.34	1.00	-0.17	-0.07
FeS.,	-0.36	-0.59	-0.50	-0.35	0.52	-0.26	-0.11	-0.08	-0.17	-0.17	1.00	0.75
Cu	-0.47	-0.47	-0.47	-0.43	0.38	-0.27	-0.21	0.13	-0.36	-0.07	0.75	1.00
Zn	0.08	0.32	0.39	0.27	-0.37	0.24	-0.30	0.22	-0.05	0.26	-0.48	-0.29
РЬ	0.50	0.41	0.52	0.29	-0.35	0.17	0.26	-0.29	0.61	0.16	-0.27	-0.44
Со	0.32	0.18	0.25	0.27	-0.07	0.13	0.01	-0.50	0.52	0.32	0.13	-0.14
Ni	0.11	-0.24	-0.14	-0.03	0.29	0.08	0.03	-0.33	0.24	0.01	0.63	0.25
As	0.06	0.50	0.72	0.02	-0.47	0.54	-0.19	0.10	-0.12	0.11	-0.38	-0.24

Table 10

Kiipu pooled data correlation and factor matrices including the metalavas, pyroclastic and altered rocks. Total

individual metal factors (Ni, Co, As and Zn, respectively) and indicate heterogeneous distributions of metallic elements in pyroclastic rocks.

#### Altered rocks (Table 9)

SiO<sub>2</sub> displays negative weak correlations with most of the other variables. Of the main chemical components TiO<sub>2</sub>, MnO, MgO, FeO\* and  $P_2O_5$  (and CaO) form a correlating group. This refers to a grouping caused by alteration processes and is reflected in factor 1. Of the metallic elements Cu, Zn, Pb, Co (and FeS<sub>2</sub>), and Ni and Co, display weak to moderate correlations. This is apparent in the factor matrix, where factor 2 is a »Ni-Co factor», 3 is an »As factor», factor 6 is a »Zn-Pb factor» and factor 7 is a »Cu factor». Further, with reference to groupings originating from alteration processes, factor 4 is a »CaO-Na<sub>2</sub>O factor» and factor 5 is a »K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> factor».

#### Pooled data (Table 10)

 $SiO_2$  does not clearly correlate with any of the other variables. A positively correlating group is composed of  $TiO_2$ ,  $Al_2O_3$  and MgO, with negative MnO correlation.  $K_2O$  displays negative correlation with Na<sub>2</sub>O. The metallic

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					Rotated factor matrix									
7		C	NU	1.				Fa	ctor				Comm	
Zn	PD	Co	INI	118	1	2	3	4	5	6	7	8	comm.	
$\begin{array}{c} 0.08\\ 0.32\\ 0.39\\ 0.27\\ -0.37\\ 0.24\\ -0.30\\ 0.22\\ -0.05\\ 0.26\\ 0.26\\ -0.48\\ -0.29\\ 1.00\\ 0.17\\ 0.07\\ -0.36\\ 0.36\end{array}$		$\begin{array}{c} 0.32\\ 0.18\\ 0.25\\ 0.27\\ -0.07\\ 0.13\\ 0.01\\ -0.50\\ 0.52\\ 0.13\\ -0.14\\ 0.07\\ 0.56\\ 1.00\\ 0.57\\ 0.04 \end{array}$	$\begin{array}{c} 0.11\\ -0.24\\ -0.14\\ -0.03\\ 0.29\\ 0.08\\ 0.03\\ -0.33\\ 0.24\\ 0.01\\ 0.63\\ 0.25\\ -0.36\\ 0.18\\ 0.57\\ 1.00\\ -0.21\end{array}$	$\begin{array}{c} 0.06\\ 0.51\\ 0.72\\ 0.02\\ -0.47\\ 0.54\\ -0.19\\ 0.10\\ -0.12\\ 0.11\\ -0.36\\ 0.24\\ 0.36\\ 0.13\\ 0.04\\ -0.21\\ 1.00\\ \end{array}$	$\begin{array}{c} 0.57\\ 0.79\\ 0.80\\ 0.50\\ -0.60\\ 0.51\\ 0.06\\ -0.23\\ 0.44\\ 0.33\\ -0.74\\ 0.50\\ 0.66\\ 0.38\\ -0.20\\ 0.36\end{array}$	$\begin{array}{c} 0.34\\ -0.14\\ -0.25\\ 0.38\\ 0.35\\ -0.29\\ 0.40\\ -0.74\\ 0.74\\ 0.74\\ -0.01\\ -0.39\\ 0.43\\ 0.64\\ 0.65\\ -0.46\end{array}$	$\begin{array}{c} 0.14\\ 0.06\\ -0.23\\ 0.11\\ -0.14\\ -0.61\\ 0.74\\ 0.00\\ 0.08\\ -0.41\\ -0.41\\ -0.35\\ -0.11\\ 0.01\\ -0.42\\ -0.50\\ -0.50\\ -0.28\\ -0.50\\ -0.28\\ -0.50\\ -0$	$\begin{array}{c} 0.00\\ 0.17\\ -0.32\\ -0.54\\ -0.41\\ 0.01\\ 0.36\\ -0.01\\ -0.19\\ -0.52\\ 0.24\\ 0.09\\ -0.37\\ 0.26\\ 0.15\\ 0.34\\ 0.24\\ \end{array}$	$\begin{array}{c} -0.20\\ -0.13\\ -0.04\\ -0.27\\ -0.37\\ -0.42\\ 0.04\\ -0.02\\ 0.03\\ 0.22\\ 0.03\\ 0.22\\ 0.41\\ 0.19\\ 0.24\\ -0.13\\ -0.05\end{array}$	$\begin{array}{c}0.46\\ 0.23\\ 0.11\\ 0.09\\ 0.02\\0.07\\ 0.04\\0.49\\ 0.18\\ 0.01\\ 0.01\\ 0.16\\0.15\\0.25\\0.08\\0.18\\ 0.31\\ \end{array}$	$\begin{array}{c} 0.36\\ 0.03\\ -0.09\\ -0.28\\ 0.07\\ -0.15\\ 0.08\\ 0.07\\ -0.15\\ -0.10\\ 0.50\\ -0.08\\ -0.34\\ -0.17\\ -0.16\\ -0.09\\ 0.01\end{array}$	$\begin{array}{c} -0.31\\ -0.25\\ 0.09\\ -0.23\\ 0.01\\ 0.14\\ -0.10\\ 0.10\\ 0.14\\ -0.10\\ 0.28\\ 0.09\\ -0.12\\ -0.25\\ -0.26\\ 0.22\\ -0.09\\ -0.09\\ -0.09\\ -0.01\end{array}$	$\begin{array}{c} 0.95\\ 0.80\\ 0.91\\ 0.91\\ 0.84\\ 0.93\\ 0.86\\ 0.87\\ 0.92\\ 0.92\\ 0.92\\ 0.82\\ 0.93\\ 0.87\\ 0.85\\ 0.89\\ 0.78\end{array}$	$\begin{array}{c} \mathrm{SiO}_2 \\ \mathrm{TiO}_2 \\ \mathrm{Al}_2 \\ \mathrm{O}_3 \\ \mathrm{FeO}^3 \\ \mathrm{MnO} \\ \mathrm{MgO} \\ \mathrm{CaO} \\ \mathrm{MgO} \\ \mathrm{CaO} \\ \mathrm{Na}_2 \\ \mathrm{O} \\ \mathrm{CaO} \\ \mathrm{Na}_2 \\ \mathrm{CaO} \\ \mathrm{FeS}_2 \\ \mathrm{Cu} \\ \mathrm{Zn} \\ \mathrm{Pb} \\ \mathrm{Co} \\ \mathrm{Ni} \\ \mathrm{As} \end{array}$
0.30	( 0.13	0.04	Eige Pr loa	nv. %	30.1 Al <sub>2</sub> O <sub>3</sub> TiO <sub>2</sub> Pb SiO <sub>2</sub> Pb SiO <sub>2</sub> MgO FeO* Zn K <sub>2</sub> O -FeS <sub>2</sub> -Cu -MnO	—0.46 19.7 K <sub>2</sub> O Ni Co Pb CaO —Na <sub>2</sub> O —As	$\begin{array}{c} -0.29 \\ -0.29 \\ 11.8 \\ -MgO \\ -Ni \\ -Co \\ -P_2O_5 \\ -FeS_2 \\ \end{array}$	-FeO* -P <sub>2</sub> O <sub>5</sub> -MnO		-Na <sub>s</sub> O -SiO <sub>2</sub>	4.3 P <sub>2</sub> O <sub>5</sub>	3.3	0.78	Δ8

111 samples representing 384.45 m of split d.d. core.

elements behave more or less indifferently.

Factor 1 explains 30 % of the variation in the variables and contains most of the main chemical components. Factor 2 indicates the negative correlation between K<sub>2</sub>O and Na<sub>2</sub>O that results from alteration processes. Factor 3 is the corresponding factor for CaO and MgO. Factors 4—8 together only explain 27 % of the variables and their loadings appear indifferent.

#### Ore-forming processes

In previous chapters the alteration phenomena and related ore-forming element distributions in the Kiipu rock types were examined. The alteration pattern was found to be the same as the »Kuroko alteration» reported by Iijima (1974). The following model for ore-forming processes in Kiipu was obtained on the basis of these data and on the principles of Large (1977), given on p. 34.

Contemporaneous sea-water entered the submarine pile of dacitic to rhyolitic fragmental pyroclastic rocks. The percolation was possibly driven by heat from a subsurface stock on the foot wall (north). Although such stocks have



Fig. 32. The Kiipu occurrence mixing path (B—C) of the hydrothermal solution in a  $f_{02}$ —pH space at 250 °C,  $\Sigma S = 10^{-2}$  M and 1 M NaCl solution. The stability fields of the Fe-S-O minerals, the So: Sr line, and the chalcopyrite and sphalerite deposition fields between 6 and 1 ppm soluble Cu and Zn are from Large (1977). The two  $\delta^{34}S$  contours for pyrite at  $\delta^{34}S_{\Sigma}S = +18 \ ^{0}/_{00}$  are after Ohmoto (1972). The field indicated by path A—B—C, representing a fully zoned Kuroko-type proximal ore deposit, has not (yet) been found at Kiipu. Path B—C represents the known zinc mineralization described in this study.

not been identified in the region, they may be granitized beyond recognition (cf. Fig. 19) or are not exposed on the present erosion level. During circulation the water heated to about 250°-300 °C to form hydrothermal fluids. These fluids followed a certain path affecting an area of about 3 km<sup>2</sup> (deduced from Fig. 19) before they finally surfaced at the sea floor. Within the volcanic pile the fluids destroyed plagioclase by leaching out Ca and Na, and introduced to the system mainly Fe and Mg. Also the ore-forming metals, Cu, Zn and Pb, may have been leached from the pyroclastic rocks and entered solution. Upon reaching the sea floor the fluids mixed with sea-water. causing a drop in the temperature and element concentrations, and a rise in fo<sub>2</sub>, pH and  $\Sigma$ S. Under these changing physicochemical conditions the metal load of the fluids precipitated pyrite, chalcopyrite, sphalerite and galena. Most of the sulfur was probably provided by contemporaneous sea-water (cf. chapter »Sulfur isotopes»).

Dominated by Zn(-Pb), the known mineralization likely represents a somewhat distal phase of the ore-forming process, whereas the proximal Cu-Zn-zoned massive sulfide deposit still has to be found.

#### Metamorphism

Regional metamorphic conditions in Kiipu can be approximated on the basis of certain index minerals and mineral parageneses.

Plagioclase is commonly calcic (except in some rhyolitic rocks where it is originally albite-oligoclase) and occurs in typical amphibolite facies parageneses, e.g.

plagioclase-hornblende-biotite-quartz,

plagioclase-biotite-muscovite-quartz,

biotite-muscovite-garnet-quartz,

cordierite-biotite-muscovite-garnet-quartz, and cordierite-anthophyllite-biotite-quartz.

Andalusite is the only one of the  $Al_2SiO_5$ species to have been met with. The iron-rich biotite and cordierite encountered in the parageneses, together with the absence of staurolite, indicate relatively low-pressure conditions at roughly 3 kbar (Miyashiro 1973b, Mueller and Saxena 1977). The absence of chlorite (except retrograde after biotite) and epidote, the existence of biotite-, cordierite-, garnet- and andalusite-bearing parageneses, apparently at the expense of staurolite-bearing parageneses, refer to a relatively high metamorphic temperature at roughly 600 °C (Mueller and Saxena 1977).

Sulfur isotope partitioning in several sulfide mineral pairs has been empirically studied by Kajiwara and Krouse (1971). They have established that sulfur isotopic fractionation is dependent, according to certain equations, on the temperature to which the sulfide systems were subjected. This enables sulfur isotope distribution in coexisting mineral pairs to be used as a geothermometer. For the mineral pair pyrite-pyrrhotite the equation is:

$$\Delta(\delta^{34}S_{\text{pyrite}} - \delta^{34}S_{\text{pyrrhotite}}) = 3.0 \times 10^{5}/\text{T}(^{\circ}\text{K})^{2}.$$

Three sulfur isotope determinations were performed on coexisting pyrite and pyrrhotite from the Kiipu pyroclastic and altered rocks (see Fig. 34 and Table 11). For these three determinations the mean  $\Delta = 0.4$  %/00. Applied to the above equation a minimum metamorphic temperature of 590 °C is obtained for the Kiipu rocks, a value that agrees well with that obtained from the silicate mineral parageneses.

In brief, the regional metamorphic conditions in the Kiipu region are those of mediumtemperature, low-pressure amphibolite facies at roughly 600 °C and 3.0 kbar (see Fig. 33).



Fig. 33. P—T diagram showing the main types of progressive metamorphism after Miyashiro (1973b). The positions of Haveri and Kiipu are shown on the diagram.

follows. Unweathered, sulfide-rich pieces of d.d.

core from 2 holes, Hvr-9 and Ki-6, were crushed

in a mortar and screened; the sulfide grains were

hand picked under a binocular microscope. The

#### SULFUR ISOTOPES

Sulfur occurs as four stable isotopes in nature; two of these are the most abundant, namely <sup>32</sup>S (95.0 %) and <sup>34</sup>S (4.2 %). The physicochemical properties of these two isotopes differ, and so their behavior in ore-forming processes also differs, resulting in diverse abundances in the sulfide and sulfate minerals of ore deposits. Thus, by tracing back the final sulfur isotope compositions we can establish the physicochemical conditions, e.g. T, fo<sub>2</sub> and pH, at the site of ore deposition that contribute to the solving the problems of ore genesis.

A total of 28 sulfur isotope determinations were done for the present study. The samples were prepared in the laboratory of the Exploration Department of Outokumpu Co. by the present author (except 3 that were flotated by Mr. V. Hyttinen). The method used was as

ming descriptions of the specimens subjected to verse sulfur isotope determinations, and the results, are given in Table 11. final The sulfur isotope analyses were done in the Laboratory of Economic Geology at the Hel-,  $fo_2$  sinki University of Technology as described

sinki University of Technology as described by Mäkelä and Tammenmaa (1977a). The precision of this system is 0.1  $^{0}/_{00}$ . The sulfur isotopes are expressed as the permil difference from the Canyon Diablo meteorite troilite standard according to the following equation:

$$\delta^{34}\mathrm{S} = \left[rac{(^{34}\mathrm{S}/^{32}\mathrm{S}) \text{ sample}}{(^{34}\mathrm{S}/^{32}\mathrm{S}) \text{ standard}} - 1
ight] imes 10^3$$

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#### Table 11

Sulfur isotope data.

#### MARINE JATULIAN IRON FORMATION

Specimen 704-0237 from K. Mäkelä (1976, Fig. 18).  $\delta^{34}S = 16.5 \ ^{9}/_{00}$  in pyrrhotite from a sulfide band in an iron silicate-magnetite-pyrrhotite-chert-banded chemical sediment.

### THE HAVERI OCCURRENCE

D.d. hole Hvr-9, all pyrrhotite samples.

Depth m	δ <sup>34</sup> S <sup>0</sup> / <sub>00</sub>	Rock type	Description
13.95	3.4	massive sulfide in basaltic metalava breccia	80 cm wide compact pyrrhotite ore between metatuffite and basaltic metalava breccia. Specimen 15 cm down from metatuffite/ore contact.
14.50	6.2	»	Same ore as above, specimen 10 cm up from ore/basaltic metalava breccia contact.
20.90	5.2	»	80 % pyrrhotite in basaltic metalava breccia as bands concordant to flow structures.
25.35	7.2	>>	As above, 95 % pyrrhotite.
26.60	6.5	»	Compact pyrrhotite brecciating basaltic metalava.
27.50	4.4	>>	60 % pyrrhotite in basaltic metalava as bands concordant to flow structures.
29.00	8.7	»	As above, 95 % pyrrhotite.
31.10	8.4	>>	50 $\%$ pyrrhotite in basaltic metalava as bands concordant to flow structures and as compact portions.
64.60	4.4	ore in metatuff	90 % pyrrhotite and 5 % pyrite in a 0.5-cm-wide band in basic metatuff.
71.70	4.7	»	As above, 0.7 cm wide band.
85.00	4.5	»	90 $\%$ pyrrhotite with chert in a 0.7 cm wide band in metatuff.
96.30	3.4	»	80 % pyrrhotite in a 35 cm wide band in metatuff. Sample from center of band.
121.80	0.0	ore in metatuffite	95 % pyrrhotite in a 10 cm wide band in phyllitic metatuffite.
148.00	0.5	»	0.5 cm wide compact pyrrhotite band in metatuffite.

Sakai (1968) suggested that the isotope composition of sulfide minerals is influenced by the temperature and pH of hydrothermal fluids. Ohmoto (1972) extended Sakai's concept and evaluated quantitatively the effects of physicochemical states of ore-forming fluids (T, pH, fo<sub>2</sub>,  $\delta^{34}S_{\Sigma S}$ ) on the sulfur isotopic fractionation. Large (1977) emphasized the importance of the quantity of reduced sulfur species (S<sub>r</sub>) in ore-forming solutions. At a high temperature (>250 °C) and mildly acid pH, where S<sub>o</sub>: S<sub>r</sub> < 1, H<sub>2</sub>S is the dominant sulfur species. It has been estimated that in the Precambrian the atmosphere contained less oxygen than it does at present (cf. p. 15). In the following the value S<sub>o</sub>: S<sub>r</sub> = 10<sup>-1</sup>, based on Large (1977), is applied to the ore-forming processes at Haveri and Kiipu.

THE KIIPU OCCURRENCE	
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Depth m	δ <sup>34</sup> S º/00	Mineral	Rock type	Description
7.00	1.6	Pyrite	Meta-andesite	Very weak pyrite dissemination (flotated sample).
38.25	1.4	>>	»	As above (flotated sample).
67.05	1.6	»	Acidic pyroclastic rock	1 mm wide compact pyrite band.
99.90	1.0	>>	Acidic metatuff	1 to 3 mm wide pyrite dissemination bands.
108.75	0.1	))	Pyrite-pyrrhotite ore	Massive, coarse grained sulfides in 15 cm wide tourmaline bearing pyrite-pyrrhotite-quartz vein.
108.75	0.1	Pyrrhotite	»	Same vein as above, pyrrhotite coexisting with pyrite.
127.95	0.5	Pyrite	Acidic metatuff	Pyrite dissemination bands (flotated sample).
159.80	0.4	>>	Cordierite-muscovite gneiss	Gahnite-bearing gneiss with 1 to 2 mm wide pyrrhotite-pyrite dissemination bands.
159.80	0.4	Pyrrhotite	»	As above, same location, pyrrhotite coexisting with pyrite.
201.40	0.7	Pyrite	»	Pyrite dissemination bands with garnet-biotite- hornblende in cordierite-muscovite gneiss.
208.60	0.1	>>	Cordierite-musco- vite-biotite-horn- blende-gahnite gneiss	1 to 2 mm wide pyrite-pyrrhotite dissemination bands.
208.60	0.4	Pyrrhotite	»	As above, same location, pyrrhotite coexisting with pyrite.
224.50	0.1	Pyrite	Cordierite-musco- vite-biotite-gahnite gneiss	Pyrite dissemination bands.

## D.d. hole Ki-6.

It is now generally accepted that the most obvious two primary sources of sulfur in strata-bound volcanogenic massive sulfide deposits are (e.g. Rye and Ohmoto 1974):

- 1. Deep-seated sources (mantle or homogenized crust, »magmatic sources»), and
- 2. Sea-water (mainly chemical reduction of sea water sulfate).

#### Svecokarelidic sea-water

There are few estimates of the sulfur isotope compositions of Precambrian seas. Thode and

Monster (1967) conclude that the  $\delta^{34}$ S-content of the oceans has changed with time and that

the minimum  $\delta^{34}$ S composition of the Precambrian Grenville series (1000 Ma old) sea-water was + 14.5 °/00. According to Vinogradov (1972), Middle Precambrian (c. 2100 Ma old) sea-water had  $\delta^{34}$ S = + 20 °/00. M. Mäkelä and Tammenmaa (1977b) give an estimate of + 14.6 °/00 for marine sulfur  $\delta^{34}$ S coeval with roughly 2100 Ma old sulfide ore deposits in Finnish Lapland.

A sulfur isotope determination done on the pyrrhotite from specimen 704-0237 (K. Mäkelä 1976, Fig. 18) yielded  $\delta^{34}S = + 16.5 \ 0/_{00}$ . This specimen represents the sulfide facies of Tuomivaara iron formation, a 200-m-thick chemically sedimented occurrence dominated by silicate facies of the Superior type (Gross 1965). The apparently coeval Pääkkö iron formation was dated at 2080 Ma by Sakko and Laajoki (1975). Both of these iron formations belong to the Marine Jatulian sedimentary facies of the Karelian schist zone of the Svecokarelidic orogeny. As the Tuomivaara iron formation is not visibly connected with volcanic rocks, the sulfur in its sulfide facies must originate from Marine Jatulian sea-water. The studies by Goodwin et al. (1976) on sulfur and carbon isotopes in Canadian Archean (2750 Ma old) iron formations also support a sea-water source for the sulfur in the sulfide facies of iron formations. They report sulfur isotopic fractionations caused by bacterial reduction of sulfate under anaerobic conditions.

According to Sangster (1968), the mean  $\Delta$  ( $\delta^{34}$ S sea-water sulfate —  $\delta^{34}$ S sulfide ore) in »sedimentary type» strata-bound sulfide deposits is 11.7 % according to Sasaki and Kajiwara (1971), it is 17.9 % of for Japanese Kuroko-type deposits. The cause is sulfur isotopic fractionation during reduction from sea-water sulfate. Schwarcz and Burnie (1973) maintain that in a shallow marine environment strata-bound sulfide deposits associated with clastic, marine sedimentary rocks, but not with volcanic rocks, display a flat  $\delta^{34}$ S distribution ranging from  $\delta^{34}S$  of sea-water sulfate to values by about 25 % lower. The values from these three sources are roughly  $\Delta = 15 \ ^{\circ}/_{00}$ , this figure applying to the Phanerozoic. However, as discussed on p. 15, in the Early to Middle Precambrian the sulfur in sea-water was largely in a reduced state,  $S_r: S_o = 10$ . Thus the  $\delta^{34}\mathrm{S}=+$  16.5  $^{0}/_{00}$  detected for Tuomivaara pyrrhotite would indicate, allowing for some fractionation, that the Marine Jatulian seawater  $\delta^{34}S_{\Sigma S}$  was roughly + 18 % a value that probably applies to Svecofennian sea-water as well (providing the seas were connected and contemporaneous). To obtain statistically reliable results on the  $\delta^{34}S$  composition of Middle Precambrian seas more studies on sulfur isotopes are required. One of the more rewarding subjects would doubtless be Finnish Superior-type iron formations.

#### The Haveri occurrence

Fig. 34 displays the sulfur isotope data from d.d. hole Hvr-9 as a depth function. All of the samples are pyrrhotite. The following comments refer to each rock type  $\delta^{34}$ S population.

#### Metalava breccia

The samples from the metalava breccia ore zone exhibit a rather variable, yet consistent,  $\delta^{34}$ S population that averages + 6.3 °/<sub>00</sub>. At the site of basaltic magma extrusion the seawater sulfate is chemically reduced at high temperature to sulfide species, mainly H<sub>2</sub>S (Ohmoto 1972, Mottl *et al.* 1979). The H<sub>2</sub>S readily reacts at the magma/sea-water interface with the metal ions (mainly Fe, Cu and Co as at Haveri) exhaled from the magma; it then precipitates sulfide minerals. THE KIIPU OCCURRENCE, d.d. hole Ki-6



THE HAVERI OCCURRENCE, d.d. hole Hvr-9



With reference to Ohmoto (1972), Rye and Ohmoto (1974), Large (1977) and the chapter »Ore forming processes», p. 33, the following approximate physicochemical conditions are estimated to have prevailed at the Haveri oreforming sites:  $T = 250 \degree C$ ,  $fo_2 = 10^{-40}$  atm.,  $\Sigma S = 0.001$  moles/kg H<sub>2</sub>O, pH = 5 (also cf. Figs. 15 and 16). The relatively high average of + 6.3 % in the sulfides indicates sulfate sulfide fractionation and the derivation of sulfur mainly from sea-water. The dispersion of pyrrhotite  $\delta^{34}$ S values (range + 3.4 %) of  $\delta^{34}$ S values (range + 3.4 %) to 8.7 0/00) is understood if the pulsating nature of volcanism leading to sudden changes in physicochemical conditions is taken into consideration. In this temperature range the smallest of changes in fo2 and pH will cause marked changes in the  $\delta^{34}S$  composition of sulfides (Ohmoto 1972). This is illustrated in Fig. 15 by the closely spaced  $\delta^{34}$ S contours for pyrrhotite at  $\delta^{34}S_{\Sigma S} = 18$   $^{0}/_{00}$ . (Note that these two contours apply to relatively young sea-waters with high  $S_0$ :  $S_r$ ; the fractionations are likely to be flatter in sea-water older than c. 2000 Ma.) The  $\delta^{34}S = -1 \ 0/_{00}$  contour unites with the  $S_o: S_r = 10^{-1}$  line and indicates that  $\delta^{34}S$  values lower than—1  $^{0}/_{00}$  are not likely to exist in this temperature (250 °C) field.

#### Metatuff

The homogenized  $\delta^{34}$ S distribution pattern (average + 4.5 %/00, range + 3.4 %/00 to + 4.7 %/00) indicates more stable conditions during pyrrhotite deposition in tuff. T and fo<sub>2</sub> have probably dropped, but the proximity of a volcanic center still dominates the ore-forming processes.

#### Metatu ffite

The pyroclastic rocks of the metatuff unit are overlain by metatuffites of epiclastic character.

This change in the volcanic/sedimentary strata is further reflected in the change of  $\delta^{34}$ S values from positive to negative ( $\delta^{34}$ S in tuffite averages  $-0.3 \ ^{0}/_{00}$ ). It is obvious that, with respect to the underlying metalava breccia and metatuff, T has dropped to c.  $100^{\circ}$ — $150^{\circ}$ C, fo<sub>2</sub> to  $10^{-40}$ — $^{-45}$ atm., and pH has risen to roughly 5. The lightening trend in  $\delta^{34}$ S composition indicates more complete isotopic fractionation. A similar geochemical boundary in an original sedimentary column has been well documented by M. Mäkelä (1977) from the Pahtavuoma copper deposit in Finnish Lapland.

The role of biogenic sulfur reduction under high-temperature (200°—250 °C) conditions is considered negligible because of the rapidity of chemical sulfur reduction reaction kinetics in this temperature range (Kajiwara and Krouse 1971), and because it is doubtful whether any life forms would survive under these conditions. Instead, bacterial reduction may noticeably speed up sulfur reduction at temperatures under 100 °C, e.g. in black schists and sulfide facies iron formations (i.e. distal ore-forming enviroments).

In conclusion, the bulk of the sulfur in the massive sulfide bodies of the Haveri formation likely originated through (partial) fractionation from sea-water. The degree of fractionation increased from metalava breccia-bound massive sulfide through metatuff to metatuffite.

The  $\delta^{34}$ S of the massive sulfides in Cyprus is roughly + 7 °/00, and the sulfur is considered to originate from sea-water (Clark 1971). Johnson (1972) detected  $\delta^{34}$ S values approximating + 4 °/00 in Cyprus and proposed a predominantly magmatic origin for the sulfur. The  $\delta^{34}$ S composition in the Ordovician Cyprustype massive sulfides of northern Newfoundland, Canada, is roughly + 13 °/00, and a sea-water sulfur origin has been inferred (Bachinski 1977). Fig. 34 displays the sulfur isotope data as a function of depth in d.d. hole Ki-6. Three of the samples are pyrrhotite, the remainder being pyrite. Coexisting mineral pairs are indicated by tie lines. The following comments are presented.

#### Andesitic metalava

The average  $\delta^{34}S$  of the pyrites in metaand esite is +1.5  $^{0}/_{00}$  with negligible range. This rock type is homogeneous, rather massive and, except for being metamorphosed, practically unaltered. The pyrite dissemination is weak but consistent. The total FeS2 content of the meta-andesite is 0.16 wt-%. No signs of sulfide remobilization are seen. Hence, there seems to be no doubt that the value obtained, +1.5 %  $_{00}$ , is the primary sulfide isotopic composition of the andesite lava, and that it is probably also the  $\delta^{34}$ S composition of that part of the mantle from which the lava was derived. Similar figures are reported from Germany by Schneider (1970):  $\delta^{34}S + 1.3 \, {}^{0}/_{00}$  for an olivine basalt and +1.6  $^{0}/_{00}$  for an alkali-rich basalt with explosive eruption character and associated pyroclastics. The  $\delta^{34}S$  of basic igneous rocks is generally given at 0 % (e.g. Coleman 1977).

#### Pyroclastic rocks

The pyroclastic rocks display a lightening trend in  $\delta^{34}$ S composition from  $+ 1.6 \ ^0/_{00}$  in practically unaltered pyroclastic rocks to  $+ 0.5 \ ^0/_{00}$  in incipiently altered rocks, the average being  $+ 1.0 \ ^0/_{00}$ . This lightening trend most likely indicates sulfur isotopic fractionation and derivation of sulfur (partly) from sea-water.

The compact pyrite-pyrrhotite-tourmaline-

quartz vein in pyroclastic rocks (Fig. 34) gave  $\delta^{34}S = -0.1$  %/% for both pyrite and coexisting pyrrhotite. This vein, however, apparently originates from an anatectic melt and intruded into its host rock during the climax of regional metamorphism. Being zero, the ( $\delta^{34}S$  pyrite -  $\delta^{34}S$  pyrrhotite) refers to a very high equilibriation temperature (> 600 °C, cf. Kajiwara and Krouse 1971) within the range of anatexis (Winkler 1974).

#### Altered rocks

The pyrites of the altered rocks display further lightening from the pyroclastic rocks, the  $\delta^{34}$ S distribution varying from  $+ 0.6 \ ^{0}/_{00}$ to  $-0.1 \ ^{0}/_{00}$ , and averaging  $+ 0.3 \ ^{0}/_{00}$ . This may indicate a primary, stratigraphically lightening trend in sulfur isotopic fractionation towards, or on, the sea floor and would refer to a more total sea-water origin of sulfur.

Smitheringale and Jensen (1963) detected  $\delta^{34}$ S distributions around 0  $^{0}/_{00}$  for ore deposits with sulfur of magmatic origin. However, according to the studies of Ohmoto (1972), sulfides with  $\delta^{34}$ S in the 0  $^{0}/_{00}$  range could have been chemically reduced from sea-water sulfate whose  $\delta^{34}$ S composition is considerable higher (e.g. +18  $^{0}/_{00}$ ) This is indicated by the two  $\delta^{34}$ S contours in Fig. 32.

To conclude, the sulfur in Kiipu meta-andesite is of magmatic origin with  $\delta^{34}S = 1.5$   $^{0}/_{00}$ . Sulfur was added to the Kiipu altered rocks, and there is a lightening trend in the sulfur isotopic composition from the parent pyroclastic rocks towards the altered rocks. Thus it is considered likely that the sulfur in the mineralizations originated mainly from sea-water. Some magmatic sulfur may have been incorporated.

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## DISCUSSION

A few modest attempts have been made to explain Finnish (and corresponding Swedish) bedrock in terms of plate tectonics (Kahma 1973, Piirainen et al. 1974, Piirainen 1975, Rickard and Zweifel 1975, Hietanen 1975, Rickard 1978, Löfgren 1979). In the opinion of the present writer, enough basic data of Finland's Middle Precambrian bedrock exist to allow more sophisticated conclusions to be drawn; this dominantly lithological information should, however, be refined into formational basin analysis, time-space, tectonic and metamorphic compilations. On the basis of such work it should be possible to trace the main geotectonic events in the development of Finnish bedrock, which, in turn, would greatly benefit exploration of ore deposits.

The two main regimes in the Svecokarelidic orogeny are the Svecofennian and Karelian zones (Fig. 1). The Svecofennian zone is thought to represent transitional crust (probably an island-arc system), with its dominantly calcalkaline volcanism, and the Karelian zone continental and oceanic crust (possibly, at least in part, a marginal basin), with its tholeiitic (and spilitic) basic to ultrabasic volcanic and dyke rocks.

Proximal-distal relations in strata-bound volcanogenic ore deposits have recently been reviewed by Plimer (1978), who divides stratabound volcanogenic ore deposits into those associated with calc-alkaline and tholeiitic volcanism (termed Kuroko and Cyprus types, respectively, in this study). Plimer further differentiates between proximal and distal facies of ore deposition within the two main types; the distal facies is characterized by a decreasing degree of hydrothermal alteration and Fe, Cu and S contents and, with increasing distance from the volcanic center, by increasing Zn, Pb, Ag, Mn, Ba and F contents. Plimer's conclusions are consistent with those presented in this study.

There is a great number of cupriferous volcanogenic massive sulfide deposits in the world whose geological and geochemical characteristics, in general terms, fit those previously explained as typical of the Cyprus type. These include the Besshi Cu deposits in southwestern Japan (Kanehira and Tatsumi 1970, Michell and Bell 1973, Michell and Garson 1976, Sawkins 1976, also see Table 3, col. 9, p. 24), those associated with the northern Newfoundland ophiolite assemblages (Upadhyay and Strong 1973, Strong 1974, Norman and Strong 1975, Bachinski 1977, Tuach and Kennedy 1978), and the Turkish Cu(-Co-Au) deposits in Ergani Maden and Küre district (Sillitoe 1972). It has been suggested that the Outokumpu Cu-Co deposit (Huhma and Huhma 1970, Peltola 1978) is of the Cyprus type (Kouvo 1976). Also the Pahtavuoma (Latvalahti 1973) and Riikonkoski (Geological Survey of Finland, Annual Report of Activities 1972, Lång 1978) Cu deposits likely belong to this category, since they occur within the central Lapland greenstone area, which, with its basaltic-spilitic volcanic and related rocks predominating in an area of 2 500 km<sup>2</sup> of folded strata (cf. Mikkola 1941), is thought to represent originally oceanic crust.

The Kuroko-type volcanogenic massive sulfide deposits of the world contain variable amounts of Cu, Zn, Pb, Ag and Au, and range in age from Archean (e.g. the Canadian deposits in the Noranda district, Sangster 1972, Spence and de Rosen-Spence 1975) to almost recent (Vanua Levu, Fiji, about 6 Ma, Colley and Rice 1975). On the basis of general geological milieu, host rocks, alteration phenomena and metal contents, the following Finnish Zn-Cu-Pb deposits are included in the Kuroko type: Vihanti (Rouhunkoski 1968, Rauhamäki *et al.* 1978, also see Table 5, columns 8 and 9 on p. 50), Pyhäsalmi (Helovuori 1978) and the Aijala-Orijärvi area (Latvalahti 1979).

## CONCLUSIONS

This study is based mainly on 314 AAS and XRF analyses representing 1117 m of split d.d. core from the vicinity of the Haveri gold-copper ore deposit and from the Kiipu zinc ore prospect.

The Haveri formation is composed of tholeiitic metabasalts and metatuffs, and of chemical and euxinic, and relatively scarce epiclastic metasediments. These refer to a low-energy, restricted sedimentation environment. The metals in the massive sulfide deposits were exhaled from basaltic flows, and sulfur was provided by contemporaneous sea-water. Both proximal and distal facies of ore-forming processes are recognized. The Haveri formation tholeiitic magma was generated through the partial melting of an undepleted source, probably in an oceanic crust environment. The chemistry of the Haveri tholeiites resembles partly that of mid-ocean-ridge basalts, partly island-arc basalts. The close spatial association between the Haveni formation and the overlying highenergy, thick-layered turbidites (the graywackeslate flysch-like formation, indicating a nearby source area and rapid filling of the depositional basin) and calc-alkaline volcanics point to the relative proximity of an island arc. Therefore an initial-stage island-arc location is favored as the depositional environment of the Haveri formation.

The Haveri occurrence is correlated with Cyprus-type deposits, which is a collective denomination for a group of deposits that are closely associated with dominantly basic submarine eruptions, usually with tholeiitic characteristics (including normal basalts and spilities). These tholeiitic magmas are derived from the mantle from shallow depths (c. 30—15 km or less) in spreading oceanic crust areas. The metal parageneses in Cyprus-type deposits include Cu, Co and Au with minor Zn and Ag and negligible Pb.

The Kiipu prospect occurs in a submarine

volcanic environment that is characterized by calc-alkaline, acidic pyroclastic rocks and intermediate (andesitic) metalavas. An alteration zone occurs within the pyroclastic rocks that was caused by heated circulating waters. The alteration attacked plagioclase by leaching Ca, Na, and some Si out of the system. The plagioclase was thereby destroyed, and its alumina component, during progressive metamorphism, finally turned into cordierite and andalusite. Contemporaneously with the leaching, Mg, Fe, K and ore-forming metals were introduced into the system. The sulfur in the ore-forming solutions originated from sea-water, possibly with magmatic sulfur contribution.

The conditions of regional metamorphism in the Haveri and Kiipu regions were estimated mainly from metamorphic silicate mineral parageneses. The values obtained were roughly 550 °C temperature and 2.5 kbar pressure at Haveri, and 600 °C and 3.0 kbar at Kiipu.

The Kiipu occurrence is correlated with a group of massive sulfide deposits known as the Kuroko type. This main type has been subdivided by several authors, mainly on the basis of differences observed in deposits formed during different geological ages. Such obvious differences, like the predominance of sulfates over carbonates and of pyrite over pyrrhotite in younger deposits, are, however, mainly caused by increasing fo2 with time, which is a biological, not a geological consequence. Certain important characteristics are common to all Kuroko-type deposits, and no major geological differences exist. The deposits are associated with calc-alkaline, andesitic to mainly rhyolitic fragmental volcanics in submarine environments. The ore deposits contain, usually in a stratigraphically zoned order, Cu, Zn and Pb. Ag and some Au are commonly present. The zoning implies an epigenetic alteration pipe with Ca and Na depletion; Fe and Mg enrichment and a siliceous stringer-type Cu ore

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within the pyroclastics; and an overlying or laterally extending syngenetic Zn(-Pb-Ag) ore with associated chemical sediments. In Precambrian deposits siliceous stringer ore is commonly replaced by chlorite-enriched stringer ore that may be the consequence of different parent-rock chemistries. The Kuroko-type deposits occur in mature island-arc environments, where the calc-alkaline magmas originate from the vicinity of a subduction zone at great depth (150 km or more).

The division of strata-bound volcanogenic massive sulfide deposits into two main groups is sound from the point of plate tectonics as well. The Cyprus-type deposits with their mantle-derived material (from a depth of c. 15 km) can only be generated in those areas of the Earth where spreading oceanic crust prevails. Such main areas are the mid-ocean ridges, marginal and interarc basins and initial stage island arcs. The Kuroko-type deposits, on the other hand, are generated in transitional crust areas, where advanced subduction has introduced contaminated and depleted oceanic crust and mixed sedimentary materials at great depths (150 km or more) from where the calc-alkaline magmas are derived at mature island arcs and continental margins. Even though the ore-forming processes themselves, eventually leading to the submarine precipitation of sulfides under hydrothermal conditions, are basically similar in both types, the forementioned differences in geotectonic setting and consequent magmatic evolution and metal contents substantiate the gross division into two main types. Table 2 (p. 16) summarizes the characteristic features of the Cyprus- and Kuroko-type deposits.

In this account no attempts were made to subdivide Cyprus- and Kuroko-type deposits even though specific local, regional, temporal or other characteristics do occur within these two main groups. On the basis of the characteristic similarities the following Finnish deposits are suggested to belong to the Cyprus type: Haveri, Outokumpu, Pahtavuoma and Riikonkoski; and the following to the Kuroko type: The Kiipu prospect, Vihanti, Pyhäsalmi and Aijala-Orijärvi.

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