Front cover: The photomicrograph of a Finnish diamond crystal shows typical surface textures on its octahedral face. The crystal was found by Dr. Petri Peltonen. It was fastened on an eclogite xenolith unearthed from Lahtojoki kimberlite pipe in Kaavi area, Central Finland. The main surface textures are microlamellae and trigons. These textures formed when the kimberlite magma etched the diamond crystal during its uplift from the mantle to the upper parts of the crust. Only the crystal faces, which protruded from the xenolith surface were resorbed. The article interpreting the morphological aspects of the Kaavi diamonds is on the pages 41 - 46. This photomicrograph was taken in transmitted light using Rheinberg method of colour filtering. This microscope method gives to the naturally colourless crystal a blueish hue and enhances its three-dimensional microtopography. The height of the picture area represents 0.72 mm, and the dimensions of the complete diamond crystal are 2.8 x 2.3 x 1.9 mm, 50x L 80 sample.

Photo: Kari A. Kinnunen

Back cover: Colourless diamond octahedron found from an eclogite xenolith. Locality is Lahtojoki, Kaavi, as in the front cover photomicrograph. The dimensions of the crystal are 1.9 x 1.8 x 1.5 mm. The crystal was photographed with dark-field illumination. Only the back octahedron face with distinct trigonal markings is in focus.

Photo: Kari A. Kinnunen
Geological Survey of Finland
Current Research 1999-2000

edited by Sini Autio

Geological Survey of Finland
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The publication contains 13 articles outlining the current research at the Geological Survey of Finland (GTK). The articles are divided into four categories. At the end of the publication there is a list of publications by GTK staff in 1999 and 2000.

The publication starts with articles on regional geological and petrological investigations. The project "Shear zone research and rock engineering" in Pori region has the main purpose to form a complete comprehension of the structure and fracturing of the bedrock for various applications. The Svecofennian layered mafic-ultramafic intrusions are part of the Paleoproterozoic Hyvinkää–Mäntsälä Gabbroic Belt which has been subject to mapping, research and exploration by a co-operation project of the Department of Geology and Mineralogy of the University of Helsinki and the GTK. Different rock types and formation environments have different oxygen and carbon isotope signatures and, therefore, stable isotope studies can be used as a tool for constraining the source of the fluids in the bedrock. The results of a test set of analysed samples from the alteration zones of gold deposits in Central Finnish Lapland are represented.

GTK's discovery of domestic raw material for paper pigments in western and southwestern Finland is presented in an article. A detailed characterization of diamond crystals is presented, because morphological studies are expected to provide solutions for the detection of the diamond source to avoid jewels from conflict countries. A thorough history on the lake iron ores and iron industry in Finland during the period 1811–1916 with a map crossing the country border and information on claims is published.

The first report on the main results of the "one thousand wells" project delineates the present-day well water quality in sparsely-populated rural areas. The presented sample preparation method suites well for fractionating different sulphur species in soil samples, but because of the relative errors in some steps, the estimation of major fractions is accurate. The result of a study identifies, how the land-use potential of bedrock areas in the Hämeenlinna–Riihimäki region has been investigated by using Geographic Information Systems (GIS).

The question, if the associated hydrothermal alteration can be outlined by interpretation of airborne geophysical data, was focused on the Cu-Zn-Au deposit at Hammaslahti. Characteristics of Proterozoic late-/post-collisional intrusives in the very thick Archaean crust in Isalimi – Lapinlahti area, Central Finland are presented. Information on the magnetic anomaly maps of central Finland - Russian Karelia and North Finland - Kola in scale 1 : 1,000,000 is given. The last study shows, how the fire and rescue services can easily learn to use soil vapor extraction method to reduce the environmental impact of chemicals spilt into the soils.

Key words (GeoRef Thesaurus, AGI): Geological Survey of Finland, current research, programs, bibliography, Finland

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PREFACE

As predicted in the preface of the previous volume of Current Research, GTK has made further advances in the service of society in the past two years. The present volume gives a representative cross section of the activities in this period, including traditional geological research, economic geology, environmental applications and geophysics - the latter having especially original contributions. The selection of papers reflects co-operation within a widening network of clients and partners, ranging from universities to mining industry, and from local municipalities to the European Commission.

GTK’s recent activities are clearly showing a trend of increasing involvement in environmental research. Much of this research, concerning for example climate change through geological times, pollution of marine sediments, environmental impact of mining and other applications, is ongoing or at the final stage. Most of this activity has been financed by the European Commission and will be published in the future. I hope you will be able to learn about these results in the forthcoming volume of Current Research.

Raimo Matikainen
Director General
PRELIMINARY REPORT:
THE "SHEAR ZONE RESEARCH AND ROCK ENGINEERING" PROJECT,
PORI AREA, SOUTH-WESTERN FINLAND

by
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Introduction

The collision between the Archean craton (3.1-2.5 Ga) and the Paleoproterozoic Svecofennian domain (2.0-1.8 Ga) occurred at about 1.91-1.885 Ga ago (e.g. Korsman et al. 1999). The early structures indicate overthrusting towards northeast in eastern Finland (Koistinen 1981). The following succession of island arc collisions show complex deformational history and metamorphism under amphibolite to granulite facies conditions. Juvenile (Huhma 1986) and partly recycled crust from unexposed Proterozoic protholith (Lahtinen 1994) was formed. Post-collisional granitoids intruded at about 1.885 Ga ago in the northern part of the Svecofennian and at about 1.80-1.78 Ga ago in the southern province (e.g. Korsman et al. 1999). The emplacement of the Subjotnian rapakivi and diabase magmas at about 1.65-1.57 Ga ago (Rämö 1991 and Laitakari et al. 1996), the following Jotnian graben formation and Postjotnian 1.25 Ga old diabase magmatism (Aro & Laitakari 1987, Elo 1994), caused large-scale movements and modification of the Svecofennian formations (Korja 1995, Korsman et al. 1999). Several plate tectonic evolution models (e.g. Lahtinen 1994) dealing with the Svecofennian domain have been produced to explain the crustal structure since the early model of Hietanen (1975). Korsman et al. (1999) connected the tectonic-metamorphic and magmatic evolution of the bedrock in southern Finland to the processes in the deep crust using integrated geological and geophysical deep seismic data.

The wide-ranging studies during the last twenty years have introduced much new and detailed information on the Precambrian geotectonic evolution in the territory. Unfortunately, the results have been directed to the geological community rather than to technical field planning programs. The known geological evolution can directly be linked to certain mechanical characters of rocks and weakness zones, thus, to features that are important for several geotechnical applications. The particular interest should be put on the brittle stage of crustal evolution represented by fracture zones and joint sets. The discussions between research geologists, geophysicists and engineering geologists could be encouraged to tighten mutual contacts. The recognized need for the cooperation was the reason to conduct the "Shear zone research and rock engineering" project in the Geological Survey of Finland (GTK) in 1998.

Pori region was chosen to be the study area (Fig. 1), because of the intensive studies already done in different exploration, mapping (Pihlaja 1994, Pihlaja & Kujala 1994) and international and domestic scientific research projects (BABEL Working Group 1993, Koistinen et al. 1996, Korsman et al. 1999). The area is covered by systematic high-resolution airborne surveys by the GTK, including the simultaneously measured geophysical parameters of total magnetic...
Fig. 1. The study and reference areas on the geological map of southern Finland, modified after Korsman et al. (1997 and 1999). The boundary between the main geotectonic provinces is shown as a thick brown line.
field, electromagnetic field and the Earth's gamma radiation. Regional gravity data covers the whole study area with a 5 km and a denser grid of 250 m (by Geodetic Institute and by GTK). The main features of Svecofennian structural evolution are well known (Hopgood 1984, Koistinen et al. 1996, Kilpeläinen 1998, Korsman et al 1999). According to Pietikäinen (1994) the study area is characterised by a block structure with wide shear zones bordering the blocks. The Kynskangas shear zone is the most remarkable dividing structure in the middle of the area. The latest crustal movements causing brittle structures, however, have attained less attention in the earlier studies.  

The main purpose of the project is to form a complete comprehension of the structure and fracturing of the bedrock for various applications. In the study area the geotectonic evolution can be followed from the early Svecofennian collision to the latest Jotnian and Postjotnian events. Thus, it is possible to construct a model of crustal structures with varying characters, from ductile shearing to brittle faulting and jointing, and bind them to the observed crustal processes by using the many-sided integration of geological, geophysical and rock mechanical information. This is the way we will become able to predict the variation of mechanical properties in bedrock and to form a more reliable model on our complex bedrock for the needs of various stages of civil construction and planning. This overview represents the ideas and preliminary results of the local structure and the jointing behaviour that are necessary for further benefiting in various application models.

**Tectonic structures in the study area**

The main geotectonic units of southern Finland are represented in the study area, in the Central Finland continental arc (Fig. 1). This gives good opportunities to establish the relations of different structures to an overall crustal history. In the Pori area the crust stabilized at about 1.87 Ga ago. Predominantly amphibolite facies thermal peak of metamorphism was at about 1.88 Ma ago, which is about 60-70 Ma earlier than in the south, in the so-called Southern Finland sedimentary-volcanic complex (Korsman et al. 1984, Korsman et al. 1999). This has a crucial bearing on the development of tectonic structures and their mechanical characters in these regions. While high temperature ductile deformation was still acting in the southern province, the bedrock behaved already in a rigid and brittle way in the north. This difference in the structural histories showed that correlative studies, which begun 1999 in the southern province were necessary (Pajunen et al. 2000, Pajunen et al., in press).  

The complex structural succession of the area is studied using the field methods described by Hopgood (1999). Pajunen (1986) described successive deformation structures in a shear-fault zone near the Archean-Proterozoic boundary, where polyphase shearing and faulting produced microstructures from the early ductile mylonitegnesisses and mylonites to semi-brittle, less recrystallized mylonites and, finally, to brittle microbreccias. Correspondingly, the generalized structural evolution of Pori region can be divided into the ductile deformation events with ductile shearing that occurred during the Svecofennian orogeny. Later processes were semi-brittle to brittle in character and were clearly related to younger than Svecofennian crustal processes. Schematic presentation of tectonic structures in the study area is given in Figure 2.

**Ductile stages of deformation**

In the study area the earliest identified deformation phases, at least up to the fourth, were connected to the Svecofennian orogeny and, in general, were ductile in character. The imprint of D1 is visible only in supracrustal rocks and is expressed as nearly bedding-parallel S1 foliation. The D1 structures may be strongly modified or even destroyed by the later processes.

Progressive metamorphism and partial melting of rocks, concurrently with the strong deformation D2, modified the crust penetratively. F2 folds are isoclinal to tight with strong axial plane foliation S2. S2 is the earliest foliation identified in the tonalitic granitoids in the area. It is accompanied by shearing along the fold limbs as indicated by gneissic to mylonite gneissic microstructures. In the most intensive, even up to tens of meters wide zones of high-temperature shearing, breccia migmatises were formed (cf. Pietikäinen 1994). The fragments contain F2 folds indicating that the shearing process was most effective during the late progression of D2. D2 structures are dominating the internal structures of the rocks, except in the areas of penetrative D3 shearing like within sub-areas 1 and 5. D3 was an outstanding event during which the earlier structures were deformed under a compressional N-S stress field, but the resulting structures differ significantly between the sub-areas. In the subarea 2, F3 folds are generally open, with a weak upright S3 foliation. S3, together with the strong S2, have resulted in a dominant, almost horizontal intersection lineation L2/3 trending E-W. In the central part of the sub-area 2a, the southwards overturned and tightened F3 folds indicate overthrusting towards south.
Fig. 2. Schematic model of the main tectonic structures in the study area. Numbers in boxes show the setting of the sub-areas discussed.
along D3 shear zones. Instead, in the sub-area 1, the stress during the D3 deformation was released commonly along blastomylonitic shear zones. They are recrystallised and neomineralised zones and are characterised by granitization; biotitization of amphibole and local porphyroblastic growth of potassium feldspar (cf. Pajunen 1986). The blastomylonitic structures indicate locally SW-side-up movement, whereas less recrystallised shear zones in the sub-area 1 indicate locally N-side-up movement (see Fig. 2). In the sub-area 1, the F3 folding was usually tight. The stretching lineation L3 varies in direction; mostly it is steep, dipping to NNE-NNW in the northwest and to ENE in the east of the sub-area. The resulting nearly E-W trending sliced structure of the crust is seen also in regional scale geophysical data where it is indicated by linear alternating zones of magnetic and electromagnetic anomalies. Sub-area 5 is a corresponding zone characterised by linear magnetic structure and shearing. In the E-W trending northern part, it is characterised by dextral, N-side-up overthrusting structures, whereas in its eastern part, a more horizontal dextral shear component is dominant. Both foliation and lineation dip steeply northeastwards.

The sinistral, 1-2 km wide Kynsikangas shear zone, sub-area 7, crosscuts the crust sharply and has deformed the earlier D3 shear zones. The shear zone is marked by magnetic reduction and its great lateral length indicates also a great dimension in depth. This stage is named here as a deformation phase D3-late, because a continued compressional N-S stress field without any indicated significant younging can explain the resulting structures. The structure is characterised by amphibolite facies, mylonite series rocks with less prominent recrystallisation than during the earlier stage of the D3 shearing. Horizontal lineation is very strong indicating horizontal movement. Lens-shaped bodies carrying earlier structures surrounded by shear zones are typical. On the aeromagnetic data this strain partition is expressed as partial destruction of

![Fig. 3. Preliminary division of the study area into sub-areas showing a coherent internal tectonic structure on the magnetic 3D-analytic-signal image (calculated by the horizontal and vertical derivatives). Sub-areas display continuity either in geophysical signatures or their intensity level.](image-url)
ferromagnetic minerals causing sometimes banded or spotted anomaly patterns.

D4 deformation is only locally and zonally expressed as nearly N-S trending symmetrical and asymmetrical dextral folding and concomitant shearing in amphibolite facies rocks in the sub-area 1, where it sharply cuts the E-W trending magnetic anomalies. Open gentle N-S-axial folding deformed the early structures causing ovoid interference structures, named as Fx in the Figure 2.

The ductile deformations, principally D3 and D3-late shearing, divided the crust into sub-areas that show coherent internal tectonic structure (see Fig. 2). Also geophysical patterns that correlate with regional structural fabrics divide the study area into sub-areas that display continuity either in geophysical signatures or their intensity level. The magnetic 3D-analytic signal image (Fig. 3) shows regions of coherent magnetic anomaly pattern and is generally used to outline magnetic provinces with different internal structure. At this stage of the study we have divided the area preliminarily into 8 sub-areas based on their tectonic and aerogeophysical signature.

**Brittle structures**

Brittle structures interest civil construction processes because of their geomechanical weakness. Particularly, the loose products of brittle deformation along narrow zones may be problematic. Sometimes these are not directly observable, because they may coincide with soil-covered valleys, but indications of these structures are commonly found on outcrops near the valleys possibly indicating larger brittle shear zones nearby. By careful examining the microstructures of these structural signs we can get necessary information on the character of these faults.

To get information on the fracturing at the bedrock in covered areas, an integrated analysis of magnetic, electromagnetic and topographic data was done. Apart from the shear and fracture zones, which outline structurally coherent provinces as shown in Figure 3, fault and fracture zones are generally expressed in the aeromagnetic data as weakly magnetic lineaments.

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**Fig. 4.** Linear structures as interpreted from an integrated analysis of magnetic, electromagnetic and topographic data (cf. Airo 1999). These structures mainly post-date the formation of magnetic minerals formed dominantly during the D2 and D3. These fabrics also crosscut the sub-area boundaries (Fig. 3).
crosscutting geological units. Since brittle faulting post-dates the main formation stage of magnetic minerals (D2-D3), it results in linear, abrupt disruptions of magnetic data - however, the indications may sometimes be very subtle. By utilizing processed aeromagnetic data in the combination with digital elevation data, systematic delicate, detailed-scale features were verified. These structural fabrics are observed to crosscut the province boundaries and traverse through the entire study area, which means that they were formed at a late stage in the tectonic evolution of the area.

The main orientations of the interpreted systematic, weakly or non-magnetic linear structures (Fig. 4) are 10-20° (blue), 40-45° (orange), 50-60° (black), 120-130° (dark red), 140-150° (pale red) and c. 80° (green). At the moment some interesting observations on the mutual relationship of these structures can be noticed.

The ca. 80° trending linear structure (green) appears in the sub-area 2 and in the NW part of the sub-area 1. Local brittle, altered zones dipping steeply south are found in the middle of the sub-area 2 (Fig. 2). Furthermore, Subjotnian diabase dykes have intruded into fractures in this direction. This feature seems to be less prominent in the western part of the area, where NW-SE oriented structures are better developed. Thus, it is probable that the main phase of the formation of this EW-trending feature is related to a Subjotnian tectonic process.

In the NW-part of the study area the Subjotnian diabase dyke swarms are typically NNW-SSE trending, dipping steeply westwards. They are closely connected to the strong linear structures in the same direction, 140-150° (pale red). Although this linear structure is identified over the whole area, it is clearly concentrated in the zone of the D3-late Kynskigans structure.

A semi-brittle mylonitic zone in the direction of 125° cuts the Subjotnian diabase dykes in the direction of 140-150° (Fig. 2). It coincides with a linear structure (red) that transects the whole area and is focussed in about 25 km wide zone continuing outside the study area. In the north this feature becomes less prominent. The structure is expressed as abrupt changes in the magnetic anomaly intensity indicating vertical block movements. Some changes in the magnetic anomaly intensity level can be identified also in the Jotnian sandstone province; the present position of the Postjotnian diabase laccoliths intervening the sandstone seems to be partly controlled by these features.

Very weak 40-45° trending linear features (orange) in magnetic data are observed in the southeastern part of the area, and some of them also cut the Postjotnian diabase dyke anomalies. Some field observations of very late brittle prehnite-filled fault-fractures follow this direction.

The almost N-S trending repetitive magnetic features (blue) are narrow zones that cut earlier magnetic structures. They correspond to topographic depressions such as long valleys, streams and lakes. Several observations of semi-brittle to brittle faults are in that direction, for example, dextral c. 20° trending semi-brittle zone that cuts the magnetic anomalies in the sub-area 1.

The latest structures of the crustal evolution have been generated under other, different mechanical conditions than the ductile structures resulting also in different fault rocks. The semi-brittle to brittle structures observed in the study area are microscopically very weakly recrystallised mylonite-series rocks and cohesive breccias and microbreccias. Locally, near the Jotnian sandstone boundary, pseudotachylitic structures are found. Typically the movements occurred along the old zones of crustal weakness. This is well established by microstructures showing ductile structures, which are cut by microbreccias. Locally, even three different cataclastic deformation events can be identified in one zone. These features are frequently met with, for example, in the Kynskigans shear zone. When comparing to the paleomagnetic results given by Mertanen et al. (in prep.) - one outcrop showing both Svecofennian, Subjotnian and Postjotnian events in the Pörkkälä-Mäntsälä shear zone - it is evident that reactivation is typical to many shear and fault zones (cf. Pajunen 1986).

**Jointing of bedrock in the study area**

When trying to produce a model for regional-scale jointing characteristics, it is important to study the relationship between jointing, tectonic structures and lithology. Tectonic and lithological properties are easily determined in the field and a large number of data is already available on geological maps and databases in Finland. A useful base for further predictions of the fracturing of the bedrock would arise, if general rules for jointing characteristics could be created. In order to study these relationships, the Pori region was divided into sub-areas on the basis of geophysical interpretation and structural geological analysis (Fig. 3). Some preliminary results for three sub-areas, 2a, 5 and 7b are presented below.

The main joint sets within sub-areas 2a, 5 and 7b show a clear connection to tectonic structures (Fig. 5). They also have corresponding features both in aeromagnetic, electromagnetic and elevation data. Magnetically the sub-areas 2a, 5 and 7b differ distinctively from each other. The magnetically quite smooth
and coherent sub-area 2a contains magnetic mica gneiss remnants in the weakly magnetic tonalitic intrusive rock. In the sub-area 5 the repeated positive magnetic anomaly bands with NW-SE orientation are caused by mica gneiss horizons. The Kynsikangas shear zone (sub-area 7b) contains magnetic banded local anomalies in a weakly magnetic background. All these magnetic structures are cut by non-magnetic linear features in various orientations, which are similar to those, obtained by structural analysis.

Open F3 folds with gently dipping axis to the east and parallel to the strong intersection lineation L2/3 (Figs. 2 and 5) characterize the sub-area 2a. One of the main joint sets cuts tensionally these stretched rock bodies. Within areas where the foliation S2 is gentle, one of the jointing surfaces coincides with this orientation. Horizontal joint sets are difficult to observe on the glacier-polished outcrops and, thus, the horizontal jointing is generally under represented in the diagrams.

Sub-area 5 represents a shear zone bordering the sub-area 2 (Fig. 4) in the northeast. The strong S2 was reoriented to the direction of D3 flattening and shearing, which characterizes the sub-area. Foliation and lineation dip steeply to the northeast. Tectonic structures and jointing show very systematic patterns as seen on the stereographic diagram in Figure 5. The maximum amount of joint sets is in the sub-area perpendicular to the main foliation S2+3 and steeply in the direction of the lineation. Typical to many areas is that the joint set follows the direction of the main foliation.

Fig. 5. Stereographic plots of foliations (red squares), lineations (green stars) and jointing (blue equal areas, \( N_s \) is number of joint sets) on the lower hemisphere of Schmidt’s net. The results of the sub-areas bordered in Figure 3 as 2a, 5 and 7b are shown.
The sub-area 7b borders the sub-area 2 bending its structures into this sinistral D3-late shear zone (Figs. 2 and 4). This zone is heterogeneous and there are slices, which have old tectonic structures within strongly sheared zones. In the D3-late shear zone all the earlier structures are variably reoriented into the shear direction and very intense horizontal lineation in this direction (L-tectonite) is typical. In Figure 5 the heterogeneous character of the zone is obvious. Lineations turn from the ENE to the NWN. The most concentrated foliation follows the trend of the Kynsikangas shear zone representing the intensified characteristics of old structures. Jointing shows very diverse directions in the sub-area 7b because of its heterogeneous tectonic structures. More careful studies are needed to determine the relationship between these two elements. So far, the main jointing direction cuts perpendicular the orientation of the shear zone and another joint set follows the D3-late orientation.

**Summarizing comments**

At this early stage of the “Shear zone research and rock engineering” project, it has become evident that the different ductile shearing structures in the bedrock (Fig. 2) can be exactly connected to the deformation history by their characteristic structures both in the field and microscope. These ductile Svecofennian shear structures have divided the crust into tectonic sub-areas or blocks (Fig. 3) that are only weakly affected by later deformations. Consequently, the main features seen on the magnetic and geological maps result from the early Svecofennian history.

However, the most problematic structures in civil construction are those, which were formed in the brittle cooled crust. According to our preliminary results brittle structures, although seldom easy to study in the field, show certain characteristics that can be used as key features in fixing them to the identified geotectonic processes. For example, the linear structures in the 140-145° direction as interpreted from the geophysical data (Fig. 4), are closely related to the Subjotian event according to their relationship to diabase magmatism, whereas the 125° trending structure is evidently younger. Both directions are identified also as fault zones in the field. Some geophysical features cut also the Postjotian diabase dykes. In future, it is very important to put much weight on the careful examining the characters of these structures that commonly show only minute evidence on outcrops.

It is an important observation that many of the joint orientations are inherited from the old ductile tectonic structures (Fig. 5). Because the tectonic features are easily identified in the field and have been compiled into geological maps and databases, continuing this work will open us methods to predict the jointing characters in the areas where original field data of jointing is small.

When the main features of the described tectonic structures are combined to an overall crustal evolution model, the classification and parameterisation of structures for various application purposes has a sound base.

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THE SVECOFENNIAN LAYERED MAFIC-ULTRAMAFIC INTRUSIONS 
IN MÄNTSÄLÄ, SOUTHERN FINLAND

by

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Key words (GeoRef Thesaurus, AGI): gabbros, layered intrusions, magmatism, mixing, mineral exploration, gravity methods, 
Paleoproterozoic, Mäntsälä, Finland

Introduction

The Paleoproterozoic Hyvinkää-Mäntsälä Gabbroic Belt (HMGB) has been subject to mapping, research 
and exploration by the Hyvinkää-Mäntsälä Exploration Project (HMEP), a co-operation project of the 
Department of Geology and Mineralogy of the University of Helsinki and the Geological Survey of 
Finland (GTK) (Eerola 2000, Kärkkäinen et al. 2000, Raitala 2000, Valli 2000). The field work was carried 
out during 1997-2000, and was supported by the Ministry of Trade and Industry of Finland. This paper 
presents an overview of the studies in the Mäntsälä area.

Regional geology

The HMGB forms a 150 km long and 20 km wide E-W trending zone of several 1.88-1.87 Ga mafic-ultramafic intrusions, occurring from Somero to the Wiborg Rapakivi Granite Complex in southern Finland (Fig. 1) (Koistinen 1994, Eerola et al. 2000, Raitala et al. 2000). These bodies are probable magma chambers of the metavolcano-sedimentary island arc sequence of Häme Belt (1.9-1.88 Ga) (Härme 1978, Kähkönen et al. 1994, Tiainen & Viita 1994) and coeval with granitic magmas, forming an extensive zone of magma mingling and mixing in the Svecofennian area (Eerola et al. 2000). The mafic intrusions are 
easily distinguishable in the aeromagnetic maps as high magnetic anomalies. All the investigated mafic-ultramafic intrusions show dynamic and non-dynamic 
layering, strong crystal fractionation, and magmatic differentiation (Eerola 2000, Eerola et al. 2000, Lallukka, 
in prep., Raitala 2000, Raitala et al. 2000), comparable with the classic layered intrusions emplaced in cratonic 
setting (e.g. Skaergaard Intrusion, Wager & Brown 1967, Larsen & Brooks 1994, Boudreau & Mc Birney 
1997, Mc Birney & Nicolas 1997). The Vähävesi, Karkkila and Hyvinkää (1.88 Ga; Patchett & Kouvo 
1986) gabbros are the major intrusions and several minor mafic-ultramafic bodies occur in the Somero, 
Mäntsälä and Pukkila areas (Fig. 1). The mafic intrusions of HMGB have been studied due to their 

Earlier works

The Mäntsälä region has been a subject of exploration campaigns since the middle of the 1940's (e.g. 
Viita 1994). The region has revealed several Cu-Ni sulfide occurrences and Fe-Ti-P prospects mainly found by amateur prospectors, and included in the GTK’s public archive of mineral occurrences (Saltikoff & Tarvainen 1990). Outokumpu Oy explored the intrusion’s potential for Ni and Cu in the 1960’s (e.g. Häkli 1963), but although the Mäntsälä region showed positive score in the Ni-Co factor analysis (Häkli 1970), the results for Ni were not considered good enough for detailed exploration (Huhma 1978). One of the most interesting indication for a significant mineralisation related to mafic-ultramafic intrusions of the Mäntsälä area is a glacial boulder of nelsonitic Fe-Tiapatite ore, with 11.3% TiO₂ and 5.4% P₂O₅, found by M. Lehtinen in 1963 from the shore of Lake Onkimaanjärvi (Pääkkönen 1964). Interesting geochemical indication is a Pd-anomaly in till in the Mäntsälä area (Koljonen 1992).

**Mafic-ultramafic intrusions in Mäntsälä**

The Mäntsälä region, located 60 km NE from Helsinki (Fig. 1), includes ten layered mafic-ultramafic bodies intruded within a metavolcano-sedimentary sequence (Fig. 2) (Kaitaro 1956, Härme 1978). The regional metamorphic grade is amphibolite facies (Kähkönen et al. 1994). Mafic-ultramafic intrusions comprise layered hornblendite-gabbros, hornblendites and anorthosites, with minor pyroxenites and peridotites. The largest intrusions are the Hirvihaara and Pitkäjärvi gabbros and Soukkio Complex (1.87 Ga; Huhma, 1986) (Fig. 2). Other intrusions are the minor Sahajärvi and Korkeavuori gabbros, and the Jussinkorpi, Joutsjärvi and Hunttijärvi hornblendites and anorthosites of Isolamminsuonio, Viitasuo, and Kotkakorpi (Fig. 2).

**Interaction of coeval contrasting magmas**

The mafic magmatism was associated with coeval granitoids, which is evidenced by magma mixing and mingling textures and structures (Fig. 3) (Eerola 2000, Eerola & Haapala 2000, Eerola & Törnroos 2000, Eerola et al. 2000). Based on these features, the authors described the Soukkio Complex as representing an MASLI-type intrusion (Mafic-Silicic Layered Intrusion, Wiebe 1993).

The Jussinkorpi and Hunttijärvi are small layered sub-volcanic net-veined complexes intruded in gneisses and schists, which were partially melted by the ther-
Pre-Cambrian bedrock map of Mäntsälä
Hyvinkää - Mäntsälä Exploration Project

Fig. 2. Precambrian bedrock map of the Mäntsälä region (after Kaitaro 1956).
Fig. 3. Mafic magmatic enclaves in the form of pillows, surrounded by granitic veins. The pillows contain granitic double-enclaves. Soukkio Complex in Haanmäki area, Mäntsälä. Photo T. Eerola.

Fig. 4. Non-dynamic layering in the Viitasuo anorthosite, Mäntsälä. Photo T. Eerola
below (cf. Wager & Brown 1967). Late-magmatic gabbro pegmatoids, similar to those described in the Skaergaard Intrusion (Larsen & Brooks 1994), intruded through mafic cumulates in the eastern margin of the intrusion (Eerola et al. 1998).

According with the concept of Boudreau and McBirney (1997), the well developed layering in the northern part of the Hirvihaara gabbro was mainly formed by non-dynamic processes (Eerola et al. 1998, Lallukka in prep.). Mafic cumulate layers have suffered syn- to post-cumulus processes, such as magmatic shearing and boudinage (cf. Nicolas 1992), occurring sometimes as autoliths (Eerola et al. 1998). Only non-dynamic layering has developed in the Viitasuo anorthosite (Eerola 2000) (Fig. 4).

Exploration

The HMEP carried out prospecting, geophysical surveys and geochemical sampling of selected target areas for Ni, Cu, V, Pd-Pt and Ti during detailed mapping of the intrusions. The most promising results are from relogging of the core from deep drilling hole MHA-2 of the Hirvihaara gabbro, with total length of 921 m, made by the Neste Oy (Särkkä & Puhakka 1990). A Cu-Ni sulfide mineralization with 0.33% Cu, 0.39% Ni was identified at the depth of 914.4 m, and with 110 ppb of Pt at 917 m and 0.57% Cu at 920 m (Eerola 2000, Kärkkäinen et al. 2000). The sulfide mineralization is located in coarse-grained basal pyroxenitic cumulate layers at the depth of 914-921 m, and contains pyrrhotite, chalcopyrite and pentlandite (Eerola 1999), with an average of 0.11% Ni and 0.27% Cu. There are no aerogeophysical anomalies indicating the occurrence of sulfide-bearing schists around the Mäntsälä mafic-ultramafic intrusions. Thus, the contamination of magma with sulfide-bearing country rocks, an important factor for the formation of magmatic Ni-Cu sulfide deposits in evolved magmatic systems (e.g. Li et al. 2001), probably did not occur in the Mäntsälä intrusions.

The magma mingling and mixing could have favoured the formation of Fe-Ti-P deposits in mafic-ultramafic intrusions of the HMGB (Eerola et al. 2000). The TiO₂ content is anomalously high in some intrusions in the Mäntsälä area: the marginal zone of the Hirvihaara Gabbro contains up to 4.2% of TiO₂ and the sheared synplutonic ultramafic dykes intruding the Viitasuo Anorthosite have 4.98% TiO₂ and 0.12% V (Eerola 2000).

Geophysical surveys

The GTK carried out regional gravity survey of 160 km² area (with 6-7 points per km²) at Mäntsälä during 1998-1999. The Hirvihaara Gabbro and Soukkio complexes are clear gravity anomalies whereas other intrusions result in weak anomalies in the 2nd derivative maps (Fig. 5). Gravity anomalies caused by intrusions coincide with the aeromagnetic anomalies. An interesting gravity high is located in the central part of Lake Kilpijärvi in the Soukkio Complex, but magnetic measurements do not show any clear magnetic anomaly beneath the lake (Valli 2000). Profile measurements (magnetic, slingram) were also made in some localities at the Hirvihaara Gabbro and in the Viitasuo Anorthosite (Valli 2000). The variation in geophysical parameters were in accordance with modal layering.

Geographical Information Systems

All the collected data of Mäntsälä is stored and integrated in a GIS-based package in the GTK’s open file archives (Eerola & Ajlani 2001). The data includes geological and geophysical maps, location and descriptions of field observations, chemical analyses and list of thin sections.

Final considerations and recommendations for the future

Although the HMEP’s aim was economic, all collected and studied data also serve in characterizing the tectonomagmatic evolution of the region and its relationship with the Svecofennian orogeny. Scientific results of this project will be published, and M.Sc. and Ph.Lic. theses of two authors are in preparation.

As the HMGB has revealed to be a wide zone of mingling and mixing, it could be one of the key-areas for the study of crust-mantle interaction in the Svecofennian.

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Student J. Bergström assisted in the fieldwork in 1997 and M. Ajlani drafted the maps.

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OXYGEN AND CARBON ISOTOPE COMPOSITIONS OF CARBONATES IN THE ALTERATION ZONES OF OROGENIC GOLD DEPOSITS IN CENTRAL FINNISH LAPLAND

by

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Introduction

In Central Finnish Lapland there are ca. thirty known gold mineralisations in an area covering ca. 4000 km², some of those being economically viable. The deposits are mostly associated with late shear zones in a greenschist facies metamorphic environment. A Pb isotope study of some of these gold mineralizations and their country rocks has given ages, indicating syn to late-orogenic ore formation during the Svecofennian orogeny (Mänttäri 1995). Therefore the gold mineralisations in Central Lapland seem to represent the orogenic ore type following the classification by Groves et al. (1998). According to Groves et al. (1998), orogenic gold deposits are ores that were formed during compressional to transpressional deformation processes at convergent plate margins in accretionary and collisional orogens.

Most of the gold mineralisations in Central Lapland are hosted by mafic and ultramafic volcanic rocks, and they are surrounded by alteration zones characterised by K-metasomatism with abundant biotitization and sericitization. Albition and carbonation are also typical features of the alteration zones. There are several interpretations for the origin of the fluids causing such alteration, the main alternatives being premetamorphic sea-floor hydrothermal and synmetamorphic fluid system connected with shear zones, as proposed for Central Lapland by Korkiakoski (1992) and Eilu (1994). Different rock types and formation environments have different oxygen and carbon isotope signatures and so stable isotope studies can be used as a tool for constraining the origin of fluids causing the alteration. In the case of the gold deposits, large quantities of fluid is needed to infiltrate the rock to precipitate gold in economic abundance. The high fluid-rock ratio should be reflected in the stable isotope compositions of host rocks. In this work, a test set of samples was analysed from carbonated rocks in the alteration zones of gold deposits (and also similarly altered rocks without gold) in Central Lapland (Fig. 1). For comparison, carbonates were also analysed from unaltered rocks at the neighbourhood of the alteration zones.

Analytical method

Carbonate was sampled from the fresh surface of a sawed rock using a dentist drill. From unaltered tholeiitic volcanite specimens carbonate was sampled from carbonate-bearing vesicles or veinlets. Isotope analytical methods were chosen according to the carbonate species in question. An aliquot of the sample powder was used to determine the proportion of calcite, dolomite and magnesite in the total carbonates by a semi-quantitative X-ray diffraction method described by Karhu (1993). Carbon and oxygen isotope ratios in carbonates were measured using the
conventional phosphoric acid method at 50°C for calcite and 100°C for dolomite and magnesite. The analytical methods are described in detail by Karhu (1993).

**Results and discussion**

**Oxygen isotopes**

The isotope ratios of oxygen and carbon in carbonates are given in Table 1 and illustrated in Figure 2. The δ¹⁸O values in altered rocks fall in a narrow range from 11 to 13‰ (SMOW), with a few outliers at lower and higher values. The small variation in oxygen isotope composition contrasts with the pattern observed in Archean hydrothermal carbonates associated with gold mineralizations in eastern Finland. There the variation in δ¹⁸O values is considerably larger relative to the variation observed in δ¹³C (Karhu et al. 1993).

The variable δ¹⁸O values in Archean deposits have been interpreted to be related to Proterozoic metamorphic overprinting (Karhu et al. 1993).

Unaltered carbonate bearing volcanic rocks in greenschist facies areas do not show any marked deviations from the isotopic composition of carbonates in the alteration zone. These regions include Saatopora, Iso-Kuotko and Atri. However, regions with peak metamorphic conditions in amphibolite facies show a different pattern. The volcanic host rocks of the Pahtavaara deposit have been metamorphosed in lower amphibolite facies with hornblende-plagioclase assemblages, whereas the gold-related metasomatic alteration took place in upper greenschist facies conditions (Korkiakoski 1992). The carbonates in the gold-related alteration zone are tightly grouped with δ¹⁸O values between 11.2 and 12.8 ‰, but both altered and unaltered rocks outside the immediate vicinity of the gold ore have distinctively lower δ¹⁸O.
<table>
<thead>
<tr>
<th>Outcrop</th>
<th>Sample no.</th>
<th>Site</th>
<th>Analyzed mineral</th>
<th>δ¹⁸O SMOW</th>
<th>δ¹³C PDB</th>
<th>Rock type, a = altered, u = unaltered</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSH-98-102</td>
<td></td>
<td>Kainotuskanka</td>
<td>cal</td>
<td>11.50</td>
<td>-2.74</td>
<td>mafic volcanic rock, u</td>
</tr>
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<td>PSH-98-103</td>
<td></td>
<td>Levi</td>
<td>dol/ank</td>
<td>14.05</td>
<td>-1.80</td>
<td>schistose mafic volcanic rock brecciated by brown carbonate veins, u</td>
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<td>1</td>
<td>Kuuskerimaa</td>
<td>dol/ank</td>
<td>11.58</td>
<td>-5.15</td>
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<td>-5.17</td>
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<td>mgs</td>
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<td>-2.83</td>
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<td>-5.01</td>
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<td>10.26</td>
<td>-8.74</td>
<td>pillow lava, 1.83 km NE from the main ore, u</td>
</tr>
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<td>2</td>
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<td>cal</td>
<td>10.06</td>
<td>-4.78</td>
<td>pillow lava, 1.83 km NE from the main ore, u</td>
</tr>
<tr>
<td>PSH-98-64</td>
<td>4</td>
<td>Pahtavaara</td>
<td>dol/ank</td>
<td>10.44</td>
<td>-1.23</td>
<td>talc breccia, 200 m N from the main ore, a</td>
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<tr>
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<td>4</td>
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<td>-1.76</td>
<td>tremolite rock, 200 m N from the main ore, a</td>
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<td>mgs</td>
<td>11.78</td>
<td>-2.08</td>
<td>barite vein with grey Fe-carbonate, main ore, a</td>
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<td>-4.11</td>
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<td>-1.18</td>
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<td>11.24</td>
<td>-2.39</td>
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<td>PSH-98-65</td>
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<td>Pahtavaara, open pit of the main ore</td>
<td>dol/ank</td>
<td>12.84</td>
<td>-4.42</td>
<td>biotite-amphibole schist, 30 m N from the ore, a</td>
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<td>-1.97</td>
<td>komatite, 200 m N from the main ore, u</td>
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<td>Atri, open pit</td>
<td>dol/ank</td>
<td>12.50</td>
<td>-5.84</td>
<td>carbonate breccia, a</td>
</tr>
<tr>
<td>PSH-98-76</td>
<td>1 b</td>
<td>Atri, open pit</td>
<td>dol/ank</td>
<td>12.83</td>
<td>-5.97</td>
<td>carbonate breccia, a</td>
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<td>dol/ank</td>
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<td>-5.20</td>
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<td>dol/ank</td>
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<td>Iso-Kursko</td>
<td>dol/ank</td>
<td>19.79</td>
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<td>cal</td>
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<td>mafic volcanic rock with crb-filled vesicles, u</td>
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<td>mgs</td>
<td>11.90</td>
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<td>chromian marble, without Au, a</td>
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<td>dol/ank</td>
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<td>-5.85</td>
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<td>-7.22</td>
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<td>Saattopora, open pit</td>
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<td>12.36</td>
<td>-7.68</td>
<td>coarse grained Au-bearing Fe-carbonate veins in N-S direction, cutting 96.1, a</td>
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<td>Saattopora, open pit</td>
<td>dol/ank</td>
<td>12.19</td>
<td>-6.87</td>
<td>coarse grained Au-bearing Fe-carbonate veins in N-S direction, cutting 96.1, a</td>
</tr>
<tr>
<td>PSH-99-96</td>
<td>4</td>
<td>Saattopora, open pit</td>
<td>dol/ank</td>
<td>12.44</td>
<td>-7.37</td>
<td>coarse grained Au-bearing Fe-carbonate veins in N-S direction, cutting 96.1, a</td>
</tr>
</tbody>
</table>

Oxygen and isotope composition of carbonates in the alteration zones of orogenic gold deposits...
values, between 10.0 and 10.4 ‰. Similarly, the unaltered tholeiitic amphibolite facies rock from Lauttasselkä (PSH-99-109) has a slightly lower δ18O value compared to the altered samples (Table 1). Sample PSH-99-106.1 differs from all other carbonate samples having a high δ18O value of 19.8 ‰. Calcite in this sample may represent late fluid infiltration at lower temperatures, possibly during weak weathering.

Oxygen isotope ratios of carbonates depend on the temperature of formation and the isotopic composition of the fluid. The isotopic composition of the fluid is, in turn, related to the source of the fluid and to the water/rock (W/R) ratio during alteration. Relatively homogeneous δ18O in alteration-related carbonates suggest large crustal scale processes with high W/R ratios. More variable δ18O values outside the cores of the alteration zones may result from differences in any of these factors.

**Carbon isotopes**

Compared to oxygen, the carbon isotope composi-

tion of carbonates show more scatter, with δ13C values varying from -8.7 to -0.8‰ (PDB, Table 1). No clear differences in carbon isotope values can be observed between altered and unaltered volcanic rocks apart from Pahtavaara, where the altered rocks generally have higher δ13C values compared to unaltered rocks (Fig. 2). The large spread in δ13C may be related to the presence of black schists in the host rock association of most gold mineralizations. Sedimentary organic matter is characterized by carbon depleted in 13C, and progressive additions of organic carbon to the fluid system will tend to shift the δ13C values to more negative values. Black schists have not been observed to occur close to the Pahtavaara ore deposits, and accordingly the δ13C values of the hydrothermal carbonates there are relatively high compared to other mineralizations.

**Concluding remarks**

Carbonates in gold related alteration zones in Central Lapland are characterized by relatively small
variation in $\delta^{18}O$ values compared to more spread in $\delta^{13}C$. Because oxygen isotope values are affected by both the fluid composition and the ambient temperature, it is difficult to draw any definitive conclusions about the source of the fluid. Furthermore, carbon isotope ratios seem to be more affected by local host rock lithologies. Nevertheless, in some study sites, such as Pahtavaara, the mineralized zone seems to have distinctive stable isotope characteristics, and stable isotope ratios may therefore have potential as an exploration tool. Apparently, each local fluid system has its own characteristics and detailed studies are needed for each prospect.

Acknowledgements

The authors want to thank Arja Henttinen from the Geological Survey of Finland for assisting in the analytical work. Terra Mining Co., especially Markku Kilpelä and Kari Niiranen from the Pahtavaara Mine, are thanked for helping to sample the Pahtavaara rocks.

REFERENCES

INDUSTRIAL MINERALS EXPLORATION IN SOUTHWESTERN AND WESTERN FINLAND

by

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Key words (GeoRef Thesaurus, AGI): mineral exploration, industrial minerals, limestone deposits, anorthosite, titanium ores, ilmenite, resources, Proterozoic, Finland

Introduction

In Sauvo, Nummi-Pusula, Kisko and Pohja the Geological Survey of Finland (GTK) has discovered new resources of calcite marble which are potential for paper pigment. Ilmenite exploration of which aim has been to find out domestic raw material of TiO₂-pigment in the Kälviä-Halsua area has also been successful and a new promising deposit has been discovered at Kairineva. The Mäntymäki anorthosite occurrence at Pihtipudas, was the main target of the Suomenselkä industrial minerals project.

GTK has drilled over 18 km during industrial mineral targets in southwestern and western Finland in 1999-2000. The drilling was directed into pigment minerals because of their increasing demand, over 3.0 Mt in 1999. In early 1999, GTK reported two potential calcite-marble deposits to the Ministry of Trade and Industry (MTI); the Genböle deposit in Dragsjärd and the Norrlammala deposit in Västanfjärd (Sarapää et al. 1999). After a tender process organised by MTI the Norrlammala calcite deposit was acquired by Omya Oy, who has carried out industrial scale mining and beneficitation tests. At present a feasibility study of the deposit is under way and Omya Oy has applied a mining concession in Norrlammala.

In late 2000, GTK reported calcite deposits to MTI; Järvenkylä at Sauvo and Kalkkimäki at Nummi-Pusula. In addition to these, Iso-Sorro, Multsilta and Hyypäämäki marble deposits from Kisko and Kuovila from Pohja and Illo from Västanfjärd will be reported to MTI in the near future (Fig.1). Preliminary laboratory scale beneficitation tests from drill core samples of all these deposits indicate that the ISO-brightness of concentrates correspond to those of commercial ground calcium carbonate (GCC) products (Table 1).

Calcite deposits in southwestern Finland

The GTK has explored for calcite marbles since 1994 within the 1.9 Ga aged Kemiö - Mäntsälä Belt (KMB) of Svefennian Domain. The KMB is mainly composed of high-grade metamorphic felsic volcanoclastic rocks, mafic and intermediate volcanic rocks, mica gneisses and granites. The schist belt continues to the Bergslagen area in Sweden, where marbles and ore deposits are even more common. In the KMB, multiphase folding and metamorphism have thickened and purified the originally rather thin carbonate sediments of shallow marine environment into high-quality marble deposits (Reinikainen, in prep.).

Järvenkylä calcite deposit

The Järvenkylä deposit was studied by detailed geological mapping, magnetic ground measurements and by drilling of 17 holes, altogether 1776 m (Seppänen et al. 2000).

Järvenkylä calcite deposit, situated 35 km southeast from Turku, comprises of an E-W trending, 600 m long and 10-50 m wide, almost vertical calcite marble layer. The country rocks are granite, granite pegmatite and granodiorite, (Figs. 2 and 3). The calcite marble of Järvenkylä deposit is very coarse-grained (4-10 mm),
The indicated mineral resource estimate of the Järvenkylä deposit to the depth on 5 m is 1.9 Mt with decrease the average calcite content. Accessory generally white in colour and it contains over 90% CaCO₃. The resource estimate is 80.3% CaCO₃. The resources to the depth of 125 m by drilling of 29 holes, altogether 1636 m.

The carbonate deposit, bordered by granites, is composed of two separated lenses (northern and southern), which are 80-120 m wide and at least 400 m long (Figs. 4 and 5). Kalkkimäki deposit comprises alternating, 10-25 m wide layers of calcite and calcite-dolomite marble, which are separated by 5-10 m wide granodiorite sheets and quartz-plagioclase rock layers. Calcite marble is coarse-grained, light-gray or white and there are occasionally 1-2 mm flakes of graphite. Calcite content in the calcite rock ranges from 70 to 95%. There are also thin interbeds that are composed of quartz, feldspars, tremolite and phlogopite. Calcite-dolomite marble is a medium-grained, gray in color and composed of about equal amount of calcite, dolomite and calc-silicate minerals: diopside, tremolite, forsterite, phlogopite and chondrodite. Wollastonite-calcite rock, in the contact zone of the deposit, composed of alternating beds of calcite, quartz, wollastonite and diopside.

The indicated mineral resources of Kalkkimäki generally white in colour and it contains over 90% calcite. There are some granite intercalations, which decrease the average calcite content. Accessory minerals are diopside, quartz, tremolite and wollastonite. The indicated mineral resource estimate of the Järvenkylä deposit to the depth of 75 m is 1.9 Mt with 80.3% CaCO₃. The resources to the depth of 125 m is 3.2 Mt with 82.4% CaCO₃. The resource estimate is based on geological mapping and systematic sectional diamond drilling. On geological basis it can be estimated that to the depth of 300 m inferred resources will be 4.5 Mt, which together with indicated resources give a mineral resource of 7.7 Mt calcite rock.

**Kalkkimäki calcite-wollastonite deposit**

The Kalkkimäki deposit was studied by detailed geological mapping, magnetic ground measurements and by drilling of 29 holes, altogether 1636 m (Reinikainen et al. 2001).
The deposit estimated to the depth of 75 m in 800 m interval are 9.6 Mt marble (Table 1). The resources include 3.95 Mt calcite marble containing 81.6% calcite, 3.7 Mt calcite-dolomite marble with 70.1% carbonate and 1.95 Mt wollastonite-calcite marble, in which there is 57.5% calcite and 14.7% wollastonite. The beneficiation tests of the wollastonite-calcite marble were done by Partek Nordkalk Co. at Lappeenranta, and a concentrate contained about 84% wollastonite.

**Table 1. Indicated and inferred* mineral resources of some industrial mineral deposits based on systematic sectional diamond drilling.**

<table>
<thead>
<tr>
<th>Deposit</th>
<th>Resources/ depth</th>
<th>Ore content</th>
<th>ISO-Brightness &lt; 45 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Järvenkylä</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite marble</td>
<td>1.9 Mt/ 75 m</td>
<td>80.3% calcite</td>
<td>91.2-94.7 %</td>
</tr>
<tr>
<td></td>
<td>3.2 Mt/ 125 m</td>
<td>82.4% calcite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.7 Mt/ 300 m*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kalkkimäki</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite marble</td>
<td>1.95 Mt/ 75 m</td>
<td>81.6% calcite</td>
<td>91.1-92.9 %</td>
</tr>
<tr>
<td>Calcite-dolomite marble</td>
<td>3.7 Mt/ 75 m</td>
<td>70.1% carbonate</td>
<td>88.2-90.4 %</td>
</tr>
<tr>
<td>Wollastonite-calcite marble</td>
<td>1.95 Mt/ 75 m</td>
<td>14.7% wollastonite</td>
<td>57.5% calcite</td>
</tr>
<tr>
<td>Iso-Sorro</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite marble</td>
<td>1.8 Mt/ 75 m</td>
<td>72% calcite</td>
<td>91.1-92.1 %</td>
</tr>
<tr>
<td>Dolomite marble</td>
<td>6.0 Mt/ 100 m</td>
<td>55% dolomite</td>
<td>90.4-92.3 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30% calcite</td>
<td></td>
</tr>
<tr>
<td>Multsilta</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite marble</td>
<td>20 Mt/ 150 m*</td>
<td>67%</td>
<td>91.8-93.3 %</td>
</tr>
<tr>
<td>Hyypämäki</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite marble</td>
<td>17 Mt/ 100 m</td>
<td>80%</td>
<td>92-93.7 %</td>
</tr>
<tr>
<td>Kaovila</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite marble</td>
<td>10 Mt/ 100 m*</td>
<td>80%</td>
<td>91.1-92.1 %</td>
</tr>
<tr>
<td>Peräneva</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ilmenite deposit</td>
<td>4.5 Mt/ 70 m</td>
<td>16.1% ilmenite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14 Mt/ 200 m*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 2. The calcite marble deposit at Järvenkylä. Base map©National Land Survey of Finland, permit to publish 326/MYY/01.**
Carbonate deposits in the Kisko-Pohja area

Iso-Sorro calcite-dolomite deposit, Multsilta, Hyypiämmäki and Kuovila calcite deposits are located in Kisko-Pohja area, where metamorphic grade is lower than in other parts of the KMB. The country rocks are composed of felsic and mafic metavolcanic rocks, also iron formations and massive sulfides with associated cordierite-antophyllite-rocks.

Iso-Sorro calcite and dolomite deposits

The Iso-Sorro calcite deposit was studied by detailed geological mapping, magnetic ground measurements and by drilling of 56 holes, altogether 4596 m. The deposit comprises of an E-W trending, 1600 m long and 10-100 m wide, almost vertical carbonate formation surrounded by mafic metavolcanic rock. The western part is mostly composed of calcite marble, in the eastern part dolomite marble is more common than calcite marble. Calcite marble is 5-50 m wide and dolomite marble 20-100 m wide. The marbles are thickest in fold hinges. The calcite marble is medium-grained, grey and contains 50-90 % calcite, 4 % dolomite, amphibole, phlogopite and occasionally quartz. The dolomite marble is fine-grained and it contains 50-95 % dolomite, 5-40 % calcite, amphibole and phlogopite.

The indicated calcite marble resources based on geological mapping and systematic sectional diamond drilling of the Iso-Sorro deposit to the depth of 75 m is 1.8 Mt with 72 % calcite and 5 % dolomite and 1 Mt with 55 % calcite and 30 % dolomite. Indicated dolomite marble resources to the depth of 100 m are 6 Mt with 55 % dolomite and 30 % calcite. The dolomite marble is suitable for agricultural use and as dimension stone.

Multsilta calcite deposit

The Multsilta deposit, at Kisko is parallel to the Iso-Sorro deposit and locates 0.5 km north from it. The Multsilta calcite marble occurs as a 20-130 m thick layer between mafic and felsic metavolcanic rocks (Fig 6). The marble is medium-grained, grey and contains 50-82 % calcite, quartz, phlogopite and tremolite. The inferred calcite resources of the deposit to the depth of 150 m are 20 Mt with 67 % calcite. The estimate is based on geological mapping and drilling of 9 holes, altogether 1079 m.

Hyypiämmäki calcite deposit

The Hyypiämmäki deposit, at Kisko locates 1 km north from the Multsilta deposit. The calcite marble forms a vertical of 20-50 m thick and at least 1000 m
Fig. 4. The calcite-wollastonite deposit at Kalkkimäki. Base map © National Land Survey of Finland, permit to publish 326/MYY/01.

Fig. 5. A cross section of the Kalkkimäki calcite-wollastonite deposit.
long layer between felsic and mafic metavolcanic rocks and iron formation (Fig. 7). The marble is medium-grained, white or grey in colour and contains 75-95% calcite. The other minerals are quartz, tremolite and mica. The indicated calcite resources of the deposit to the depth of 100 m are 17 Mt with 80% calcite based on geological mapping, magnetic ground measurements and drilling of 40 holes, altogether 3750 m.

**Kuovila calcite-wollastonite deposit**

The Kuovila calcite marble at Pohja, in the central part of the Uusimaa Belt is currently being studied by GTK. The deposit is about 1500 m long and 30-120 m wide, and it is composed of alternating, 15-50 m wide of calcite and calcite-wollastonite marble layers (Fig. 8). The Kuovila deposit is surrounded by pyroclastic felsic metavolcanic rocks, mafic metavolcanic rocks, garnet skarns and granite. The inferred calcite resources of the deposit to the depth of 100 m are 10 Mt with 80% calcite based on geological mapping, magnetic ground measurements and drilling of 28 holes, altogether 3117 m.

In 2001, a drilling program will be targeted to the western, wollastonite-rich part of the deposit.

**Ilmenite deposits in the central western Finland**

In 1993, GTK started active ilmenite exploration in central west Finland and since then four economically interesting deposits have been discovered and studied. The deposits are Koivusaarenneva, Lylyneva, Peräneva and Kairineva (Fig. 9). The ilmenite deposits are hosted by small, layered mafic intrusions, which were emplaced at 1881 Ma into tonalitic bedrock (Kärkkäinen 1999a). The main rock type is metamorphosed gabbro or gabbro-norite, which contains several mineralised layers of massive and disseminated ilmenite, magnetite and ilmenomagnetite. The deposits can be classified as mafic intrusion hosted magmatic titanium ore. The concentration of ilmenite has been interpreted to be a result of stepwise magma flow within a chain of small mafic intrusions (Kärkkäinen 1999b). Ilmenite concentrates of commercial quality (44 - 45.6% TiO₂) have been processed from Koivusaarenneva and Peräneva ilmenite.
The Peräneva ilmenite deposit has been explored during 1997-2000 in Kälviä municipality. The ilmenite deposit is hosted by the Peräneva gabbro and is situated two kilometres to northwest of the previously (1993-1996) studied the Koivusaarenneva ilmenite deposit (Fig. 10). The deposit was discovered by drilling to geophysical anomalies which were interpreted to be ilmenite mineralisation in a mafic intrusion.

The Peräneva ilmenite deposit is almost vertical, broken sheet that is composed of three separate mineralized units within gabbro. The length of these units varies from 200 m to 400 m, and they include both disseminated and massive ilmenite in 10 to 60 m layers thick. Ilmenite and magnetite occur as individual grains, ilmenomagnetite grains are rare. The indicated resource is 4.5 million tons with the average grade of 16.1 wt % ilmenite based on 42 drill holes, altogether 4043 m. The middle unit includes 2.4 million tons of 18.7 wt % ilmenite. The estimate extends down to the depth of 70 metres from the bedrock surface. The soil cover is 10 m, and it includes 2 to 3 metres peat, and 7-8 m till. Based on the gravity studies the ilmenite rich units continue at least to the depth of 200 m, and accordingly the inferred resource is 14 million tons.

The Kairineva ilmenite deposit

The Kairineva ilmenite deposit was discovered at the end of 2000. It is situated in the Halsua municipality 3.5 kilometres to southwest from the Peräneva deposit. The ilmenite deposit forms an almost vertical 450 m long and 50 m wide sheet of massive ilmenite ore in a gabbro intrusion surrounded by tonalities. A ten meter thick overburden, 3 m peat and 7 m till covers the deposit. Nine drill holes intersected ilmenite-
Fig. 8. A cross section of the Kuovila calcite-wollastonite deposit.

Fig. 9. The geological map of the Kälviä-Halsua area.
rich mineralization. Within the 34 m intersection of the drillhole R503 the average composition of the ore is 32 % ilmenite, 14 % magnetite, and 0.18 % vanadium. Ilmenite and magnetite occur as individual grains so they can be separated. Electron microprobe-analyses show that ilmenite contains 49.5 % TiO₂, 0.18 % V and 0.01 % Cr.

Mäntymäki anorthosite deposit

The Mäntymäki anorthosite deposit in mid-Finland was studied by the Suomenselkä industrial minerals project in 1999-2000, and the deposit is now claimed by SP-Minerals Oy. Within seven hectare outcrop, the anorthosite is homogenous and it is composed of bytownite (An70-80 %) and minor hornblende (Ahtola & Sarapää 2000). It contains 27.7 % Al₂O₃; 1.7 % Na₂O, 13.1 % CaO and 4.6 % Fe₂O₃ tot and 0.3 % TiO₂ (average of 21 samples). At present the deposit is being studied as potential raw material to ceramic and rock wool industry. Previously the only suitable anorthosite for this purpose has been the Lapinlahti anorthosite in eastern Finland.

Summary

The Järvenkylä, Kalkkimäki, Iso-Sorro, Multsila, Hyypiämäki and Kuovila calcite deposits host economically interesting calcite resources in terms of quantity and quality. They all have good potential for paper quality GCC-production.

The Peräneva, Kairineva and Koivusaarenneva deposits represent the richest part of ilmenite concentration in the ilmenite province of mid-western Finland.

REFERENCES


PHOTOGRAPHIC INTERPRETATION OF MORPHOLOGY AND SURFACE TEXTURES OF DIAMOND CRYSTALS FROM KAAVI KIMBERLITE PROVINCE IN FINLAND

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Key words (GeoRef Thesaurus, AGI): diamond, crystals, kimberlite, xenoliths, morphology, surface textures, photography, Kaavi, Finland

Introduction

Characterization of morphology and surface textures is required for the exploration and marketing of diamond crystals. In Finland, the recently discovered kimberlites and their xenoliths in the Kaavi area have been described thoroughly in a number of studies (Griffin et al. 1995, Peltonen et al. 1999, Peltonen 2000, O’Brien & Tyni 1999), but description of the morphology of diamond crystals have received only a minor attention. Elsewhere the morphological characteristics of diamonds have been examined in detail and the earliest publications date to early 1900’s (e.g., Fersmann & Goldschmidt 1911, Tolansky 1960, Orlov 1973, Sunagawa 1995). The more recent studies conclude that the main primary morphologies of diamonds are octahedral, cuboid and fibrous. It is now generally agreed, that partial dissolution of crystals (resorption) explains the rounded rhombic dodecahedras (Mendelsohn & Milledge 1995), which earlier were interpreted as primary forms.

Detailed characterization of diamond crystals is needed, because the country of origin is an integral information of contemporary diamond trade. Clients want to know the source of their stones used in jewellery as some diamonds (so called blood stones) are exported from conflict countries: Angola, Sierra Leone and Democratic Republic of Congo among others. Morphological studies are expected to provide solutions for the detection of the diamond source.

Material and methods

For this study only five diamond crystals were examined under the microscope, because most of the crystals are under the control of mining companies. However, photographs scanned from Laapas (1994), Tyni (1998), Tyni and O’Brien (1997) and from other published sources were used as a supplementary research material. In total 46 individual diamond crystals of commercial size, which were all from the Kaavi area, were analyzed from this photographic material. The diameter of the diamond crystals in these published photographs ranged from 1 to 5 mm (mean 2.8 mm).

The five diamond crystals studied microscopically originated from xenoliths and were found during Geological Survey xenolith research conducted by Dr. Petri Peltonen (see Peltonen 2000). He generously gave some of his material to the author for the present study provided that nondestructive methods were used. It is noteworthy that in some of the eclogitic xenoliths studied the diamond contents were around 1 vol.% (Griffin et al. 1995). These five crystals originated from the Kaavi kimberlite province in Central Finland from its most diamond rich pipe (see Tyni & O’Brien 1997 for localities). The size of the crystals ranged from 0.2 to 5 mm consisting of microdiamonds as well as macrodiamonds of commercial size (diameter over 0.8 mm).

The morphology and surface textures of the diamond crystals were studied with optical microscopes and photographed using oblique illumination com-
combined with Rheinberg colour filter technique (see Kinnunen 1995). Secondly, the combination of transmitted crossed polarized light and oblique lightning in was adopted for some of the observations. With this technique inner stresses, dislocation structures and some other lattice imperfections could be depicted. It was possible to examine how these features are connected with the crystal morphology and surface textures. The interpretation continued from image analysis procedures to a literature review. The key references consulted in the identification of the specific characteristics were Tolansky (1960), Orlov (1973), Gurney (1986), and Mendelssohn and Milledge (1995).

**Results**

The diamond crystals manually detached from the eclogitic xenoliths (Fig. 1) were octahedra with smooth faces and polycentric development of faces. One crystal was distinctly pseudohemimorphic (see definition in Bulanova 1995). Its unresorbed part resided inside the xenolith while the resorbed part projected from it (Fig. 2). This crystal confirms that the resorption took place in the kimberlite magma. No diamonds were found in the peridotitic xenoliths.

Most of the diamond crystals separated from the kimberlite matrix were intensively resorbed. The proportion of resorbed to unresorbed crystals were about 9 to 1 (in total 46 crystals studied from the photographs). Primary morphologies representing octahedrons, twinned crystals and aggregates of coalesced single stones were rare among the crystals, because of the prevailing dissolution had lead to the resorbed forms. Therefore, the most common diamond forms were the resorbed ones: rounded dodecahedrons and transitional forms between octahedrons (Fig. 3) and dodecahedrons.

Well-defined dissolutorial surface features were observed on the resorbed crystals (Fig. 4). They were classified and identified following the terminology defined by Orlov (1973). Plane faces were characterized by trigons (pointed and flat-bottomed) and microlamination (Fig. 5). The arrangement of trigons was linear (Fig. 6) or connected with the boundaries of anomalous interference patterns (Fig. 7). This shows that the plastic deformation areas as well as particular dislocation areas localized the trigons. Rounded surfaces were distinguished by striations, hillocks (pyramidal and drop-shaped), etch pits and discoïd and imbricate sculptures. Highly resorbed crystals exhibited channels, chip defects and rarely corrosive frosting.

The crystals are most commonly yellowish brown,

![Fig. 1. Mantle xenolith (Ca-garnet clinopyroxene eclogite) and a partly exposed diamond octahedron on its surface. The protruding faces of the diamond crystal are resorbed whereas the other faces are intact. The sample was found by Dr. Petri Peltonen from the Kaavi kimberlite. The diameter of the diamond is 1.9 mm. Photo: Kari A. Kinnunen.](image-url)
rarely colorless and very rarely brownish with greenish tint. Because of the small number of crystals studied no relationship could be shown between the crystal morphology and color.

Fig. 2. The unfastened diamond octahedron shown in Figure 1. The crystal face, that was in contact with the xenolith, is unresorbed. The diameter of the diamond is 1.9 mm. Photo: Kari A. Kinnunen.

Fig. 3. Resorbed diamond octahedron derived from the Kaavi kimberlites. The diameter of the crystal is 0.48 mm. Colour filter and shadowing used in the photomicrography. Photo: Kari A. Kinnunen.
Fig. 4. Well-defined dissolitional features with pronounced trigon formation on the surface of a Kaavi diamond crystal. The width of the photomicrograph is 1.14 mm. Dark-field photomicrograph. Photo: Kari A. Kinnunen.

Fig. 5. Trigons and microlamination on the octahedral face of the Kaavi diamond. The width of the photomicrograph is 1.14 mm. Colour filter and shadowing used in the photomicrography. Photo: Kari A. Kinnunen.
Photographic interpretation of morphology and surface textures of diamond crystals...

Fig. 6. Trigons showing linear orientation on a Kaavi diamond crystal. The width of the photomicrograph is 1.14 mm. Colour filter and shadowing used in the photomicrography. Photo: Kari A. Kinnunen.

Fig. 7. Relationship between the surface textures and inner stresses in the Kaavi diamond crystal shown in Figure 6. The grouping of trigons is connected with the boundaries of anomalous interference patterns, which define domains of plastic deformation. The width of the photomicrograph is 1.0 mm. Combined crossed polarized light, lambda plate and oblique illumination used in the photomicrography. Photo: Kari A. Kinnunen.
Interpretation

The primary octahedral habit of the diamond crystals detached from the eclogite fragments is in agreement with the observations from other kimberlite fields (Bulanova 1995, Fig. 2 in Haggerty 1999). The morphology and surface textures of the Finnish diamond crystals in xenoliths compared to the ones found in kimberlite matrix show that the dodecahedroids evolved from the resorption in kimberlite magma. The pseudohemimorphic crystal found protruding from the xenolith surface is a conclusive evidence for this. The surface textures of the resorbed crystals indicate that the crystal growth mechanism had operated in solution by means of layer-by-layer expansion, 2DNG (two-dimensional nucleation growth) as interpreted by Sunagawa (1981,1995) for other diamond localities. The textures verifying this interpretation are particular trigon types outcropping on dislocation trains and the presence of widespread microlamination. Plastic deformation of the diamond lattice is illustrated in some crystals by the clustering of the trigons on specific bands and by the presence of channels.

Conclusions

The morphological types and their particular surface features as described here are typical to diamonds exposed from kimberlites in general. The observations indicate that the morphology cannot provide an equivocal evidence of the source area. Moreover, the studied Archangelska diamonds, as described by Garanin and Posukhova (1995), are very similar to the Finnish stones. The percentage of unresorbed to the resorbed crystals stays around 10% in the diamond crystals analyzed from the Finnish kimberlite pipes. This appears to suggest modest diamond grade for gem quality stones to be gained in large scale mining. However, as Pattison and Levinson (1995) pointed out in their study of diamond resorption: "each kimberlite pipe is typically formed by several intrusions and intrusion phases of varying character that contain their own grade and morphological, textural and color characteristics of diamonds."

In spite of these questions, the high diamond content (1 vol.%) observed in some of the eclogitic xenoliths implies, that small scale mining focussed largely on xenolith separations could prove profitable. Diamond crystals, rough and cut, could be marketed as genuine Finnish stones much in the same way as Canada has recently begun to sell its diamonds with the Ice Bear inscription authenticating their provenance. The prices of genuine Finnish diamonds may well rise above the common world-market level as has already happened with some Finnish gem materials and large gold nuggets. Characterization of the diamonds would be an integral part of the future venture.

REFERENCES

LAKE ORES AND IRON INDUSTRY IN FINLAND
DURING THE PERIOD 1811 – 1916

by
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Introduction

The practice of manufacturing iron for domestic use has been well known for time immemorial. Iron oxides were reduced to metal by heating ore with charcoal in various kinds of heaters. First, small pits filled with earth or sometimes hearths were used, fuelled by wood and blown with bellows (Furuhjelm 1877, Mustonen 1894, Nikander 1928, Tylecote 1976). Towards the end of the 19th century, a more sophisticated method, using bloomery furnaces with single-fill charging of ore were used. The soft iron thus produced was directly suitable for hammering. The so-called pig-iron, produced in the still more sophisticated continuously filled furnaces was suitable, however, for casting only, and the malleable rod iron had to be produced in a separate furnace.

In the 1850’s puddling became widely known. It was an epoch-making turn in manufacturing malleable iron and changed the use of lake and bog ores. Puddling involved smelting pig-iron with slag in an air furnace. When the melt was being stirred, air oxidated the carbon and, above all, the phosphorus, and by this way the harmful constituents could be removed.

The Nyby iron works built on the lands of the Suila estate in the 1530’s is considered the first industrial plant in Finland. It aimed at beneficiating the iron ore of the recently founded Ojamo mine in Lohja. The first actual blast furnace was built in 1616 at Mustio. Later, important blast furnaces were founded e.g. at Billnäs (1641) and Fiskars (1649) in Pohja, at Taalintehdas (1686) in Dragsfjärd, and at Teijo (1686) in Perniö, where today iron-based industrial activities are still continuing. In these iron works the primary raw materials were domestic and imported iron ore. The machinery operating tilt hammers and blowing were powered by flowing water. Consequently, the iron works were always built along rapids or rivers.

The increase in general industrial production and growing need of iron started as early as the end of the 18th century. After the annexation of Finland to Russia in 1809, the direct ties to Sweden were broken and importing iron ore from the Swedish mines grew more difficult. The authorities began to pay more attention to mining industries in Finland, the Office of Commissioners of Mines was founded, and the promotion of mining resulted as the issue of a declaration by the Czar on 3 October 1821. The Office of Commissioners of Mines was even changed into the Bureau of Mines in 1858. The objective was to develop the iron industry in order to produce a surplus for exported iron, particularly to the markets of St. Petersburg. Notable results were achieved by government’s enhanced mineral prospecting, practical guidance, own mining, and supporting domestic industry.

As agriculture and industrialization advanced, the need of pig-iron for casting increased in Finland as well. Since the import of iron ore and pig-iron from Sweden to Finland was restricted, the iron works had to utilize more and more domestic lake and bog ore (Laine 1955). When Sweden removed restrictions in
export of iron ore and pig-iron in the 1850’s, the utilization of mined iron ore was resumed in western and southern Finland. During the Crimean War (1853 - 1856) export to the western world was blocked. Consequently, Finnish iron was much sought after especially in St. Petersburg. The sudden post-war reduction in the year 1858 export towards Russia reflected the economical crisis of the previous year (Joustela 1963).

The close vicinity of the St. Petersburg smelting works and the Russian arms factories in Olonetz attached the interests of Russian businessmen to eastern Finland lake and bog ores (Holmberg 1857, Solitander 1882, Laine 1948, 1955, Saltikoff & Puustinen 2000). Consequently, the Raivola works (1800) at Kivennapa, and the Sumpula works (1827) at Rautu were founded by Russians in the Karelian Isthmus in the 19th century. The iron works of St. Anna, that exported large amounts of pig-iron across Lake Ladoga to St. Petersburg, was built at Suojärvi in 1809. It was founded by a court lady, the countess Anna Alexeyevna Orlov-Tchesmensky, who also owned the parishes of Salmi, Suojärvi, Korpiselkä, and Soanalhti. Similarly in central Finland, in the latter half of the 19th century, the iron works such as Haapakoski at Pieksamäki (1842), Huutokoski at Joroinen (1858), and Oravi at Rantasalmi (1868) were founded. Soon afterwards, the ownership of these plants was transferred to Nikolai Putilov from St. Petersburg. At the same time, Nils Ludvig Arppe constructed the greatest blast furnaces of Finland at Möhkö (1837) in Ilomantsi and Värtšilä (1851) in Tohmajärvi.

Prior to 1809, at least 32 iron works had been operated in Finland, and by the early 1900’s, a minimum of 115 iron works or bloomeries had been active (Bremer 1824, 1825, Hultin 1897, Laine 1907, 1948, 1950, 1952, 1955). These numbers include iron works located beyond the present Finnish border on the Ladogan Karelia and the Karelian Isthmus. An example from among the Finnish iron industry is provided by the history and restoration of the iron works of Leineperä at Kullaa, founded in 1771, which was still operational in 1987, although its activity was somewhat transformed (Härö 1994). On the other hand, the Värtšilä industries, that were created during the time of Nils Ludvig Arppe, provide an example of an iron works developing into a modern industrial plant (Kaukoranta 1935). However, the rise of the Finnish modern mining industry began only after the early 1900’s (Puustinen 1999).

### Raw materials for the iron works

During the first decades of the 19th century, the Finnish iron industry relied on mined iron ores located mainly in the southern parts of Finland (Bremer 1824, 1825, Holmberg 1858, Puustinen 1997). A statistical presentation of the importance of lake and bog ores as basic raw material for blast furnaces is set out, giving the average amounts of ore used during periods of several years (Table 1) and on an annual basis (Fig. 1). Over the period of 1811 - 1915, a total of 1.13 million tonnes of mined iron ore and 2.29 million tonnes of lake and bog ore were used in blast furnaces. The annual average consumption was 10 777 tonnes of mined iron ore (31.1 %), and 23 897 tonnes of lake and bog ore (68.9 %).

Comparing the consumption of lake and bog ore with that of mined ore, the peak period of the former was in 1861 - 1877 with 75.8 % of the total of iron ore consumed then. The year 1860 stands out as the relative peak year, when 37 883 tonnes of lake and bog ore were used, corresponding to 81.6 % of the total of iron ore used that year. Surprisingly enough, the peak year for the amount of lake ore utilization in blast furnaces in Finland was the year 1900 with 59 880 tonnes. The amounts of ore material raised from lakes and bogs (Furuholm 1881) can also be compared with

| Table 1. Average utilization of iron ore in blast furnaces by time periods during 1811 - 1915 in Finland (records from Furuholm 1881, Laine 1907, 1948, Mäkinen 1920), and number of lake and bog ore claims (according to the archive records in the National Archives). |
|-----------------|-----------------|-----------------|-----------------|
| Periods         | Iron ore tonnes | Lake and bog ore tonnes | Lake and bog ore claims |%
| 1811 - 1852     | 5 238           | 2 554           | 32.8             | 31 |
| 1853 - 1860     | 8 974           | 27 796          | 75.6             | 170|
| 1861 - 1877     | 12 902          | 40 390          | 75.8             | 241|
| 1878 - 1886     | 16 879          | 32 015          | 65.5             | 71 |
| 1887 - 1907     | 17 015          | 46 393          | 73.2             | 20 |
| 1908 - 1915     | 13 899          | 4 809           | 25.7             | 2  |
| Average for     | 10 777          | 23 897          | 68.9             | 76 |
the amount of ore used in blast furnaces. It is noted that the amount of lake ore raised is slightly larger than the amount used, which might be explained by losses due to refining or transport.

Bog ore accounted for 14.6% of the total lake and bog ore in 1851 - 1862 (Laine 1955). Following that period of time, the ratio of bog ore decreased gradually, due to new bog ore districts could not be claimed any longer after the year 1877. Apparently, the last blast furnace having beneficiated bog ore was Sumpula which ceased operations in 1882.

A periodicity in the utilization of lake and bog ore in blast furnaces can be observed. The period 1811 - 1852 belonged to the pre-industrial era with relatively small use of iron ores in general. In 1853 - 1860, utilization of lake and bog ores started a noticeable increase. This period includes the increased demand for iron reflecting the Crimean War (1853 - 1856), as well as the decline in the export to Russia in 1858 with no significant effects.

The period of 1861 - 1877 forms the first distinct peak involving steady growth of use. The French-German War (1870 - 1871) and the Russo-Turkish War (1877 - 1878) occurred during that period of time, and also the drop in 1878. During 1878 - 1886, between two peak periods, the lake and bog ore beneficiation was only 65.5%. The other peak period is in 1887 - 1907, which ended in a collapse. Blast furnaces using lake ore declined definitively during the period 1908 - 1915.

Distribution of lake and bog ore

According to Aarnio (1915), lake ore deposits occur mainly in the provinces of Kuopio and Mikkeli. The area can be approximately restricted in the south by a line drawn through the cities of Savonlinna and Mikkeli and through the northern ends of the lakes Päijänne and Näsijärvi, and on the other hand, in the west by a line drawn from the northern end of Lake Näsijärvi to Lake Oulujärvi. This is primarily due to the fact that lake ore occurs mainly on such lake bottoms where the soil type surrounding the lakes is sand or gravel, and the lakes are rich enough in humus to allow the retention of iron. An example of solitary, notable islets of lake ore deposits is the corner formed by Pusula, Lake Pyhäjärvi, Loppi, Tammela, and Somerniemi, where sand and gravel eskers with bogsm form a suitable ground for the deposition of lake ores. For several decades, most of the lake ore smelted in the Högfors blast furnace at Karkkila came from this area, specifically from the lakes Liesjärvi, Heinäjärvi, and Pyhäjärvi (Aarnio 1917).

Lake ore is found in shallow lake shores, at the depth of 1 - 3 m, it is yellow, brown or blackish, with porous or brittle texture (Aarnio 1915). It is shaped round and flat, or bean-shaped bits, or as wider plates, and accordingly, lake iron is called bean, coin, or cake ore respectively. The bean ore was considered the best, and the cake ore the worst, because the latter was difficult to raise, as well as generally poorer in quality. Bog iron occurs as lumps and cakes in bogs and narrow streams normally beneath a 15 - 60 cm thick layer of soil. The iron content of lake ore varies considerably reaching as much as 46% Fe at its best (Aarnio 1917). The mineralogical and chemical composition, structural types and their origins of ferromanganese lake ores in some Finnish lakes have recently been discussed by Halbach (1976) among others.
Regulations concerning claims

After Finland had been annexed to Russia, the Swedish Law from 1734 remained in force, and its principles are still in force today. The Swedish Mining Legislation contains laws and decrees at least from the years 1551, 1649, 1723 (on the prerogative rights of the Crown to ores), 1741 (on granting claim and mining licences), as well as 1757 (the prospecting rule). Despite the various social changes that have taken place in Finland, the Finnish Mining Acts have always displayed a uniform pattern and contents. The following sections from the Mining Legislation will clarify the temporal distribution of lake and bog ore claims.

In 1542, southern Finland's mighty Councellor of State, Erik Fleming, was granted privilege to undertake mining at Ojamo in Lohja (Hultin 1897, Neovius 1911). Already in 1538, Erik Fleming was given the Lohja parish as a fief, and now he made a plea to King Gustav Wasa of Sweden that he be granted rights to engage in mining activities, as he had recently discovered an iron or steel hill. As a result of this petition, on 9 September 1542, the King permitted that for the good of the country such gifts given by God could be utilized, and that Lord Erik was granted the right without hindrance to mine and smelt rocks and whatever the Lord Almighty would give him from this work, iron or steel, however on condition that the Crown should be donated every 12th kippunta (corresponding to 170 kg) of pure iron, were it soft iron, cast iron, or pig-iron. As to the pit and coal timber, that were necessary for the mining activity, Lord Erik would have to make arrangements with the owners of the forests, nevertheless being under obligation to inform the King on the development of this mining work. Finally, the King forbids his bailiffs and sheriffs to cause hindrance to the aforesaid mining activities. The licence granted by the King of Sweden is interesting in that it corresponds to modern mineral exploration and mining rights, and the government claim fee and the tax on profits.

The ordinance on legal prospecting of ores and substances of the mineral kingdom, as well as on the right to raise them and manufacture them into products from the year 1857 decreed that objects of legal prospecting were formed by all metals and ores, found in bedrock, soil layers, on the bottoms of lakes, bogs or swamps. Ordinary limestone and quartz may not be legally claimed but only for mixing material or lining material for use in smelting plants. In other words, it was possible to claim lake and bog ore, but the limestone and quartz required by industrial furnaces had to be claimed. The claim owner was to be a private person.

A regulation given by the Senate in 1877 stated that limestone and quartz, as well as bog ore, could be claimed only with a permission granted by the Senate. Claiming bog ore was prevented because the raising work often required extensive removal of loose earth which caused unnecessary harm to agriculture.

A prospecting and mining rule decreed in 1883 that minerals for prospecting are iron and its ores, with the exception of bog ore. Lake ore was allowed to be claimed only if it were utilized and further processed in an industrial plant that was already in operation or under construction. The claim owner was to be a private person. This law was devised to prevent superfluous claims of lake and bog ore. The iron works had rights to more lakes than they could utilize, which was a hindrance to free competition.

An ordinance from 1902, which alters the prospecting and mining regulation of 1883, ordered that in addition to the location of the lake ore, the area in squares be given, and an annual obligation to work the site is specified. Finally, it was ordered that prospecting rights of lake ore will be lost if the establishment for which the claim has been made, ceases to be the prospector's property, or in case the claim is made for an establishment under construction and the claim owner has failed to comply with the period of time allowed for its construction.

The Mining Act of the year 1932 decreed that a Finnish citizen and company, cooperative society, association or other group has the right to claim and beneficiate iron, with the exception of bog ore. The Act also stated that a lake ore deposit may not be claimed otherwise than with the view of utilizing it in an existing iron works or one to be established.

The Mining Act from 1943 stated that a Finnish citizen and company, association or other community has the right to prospect and claim iron with the exception of bog ore.

The Mining Act of 1965 decrees that Finnish citizen and company, cooperative society, association or other community or foundation has the right to prospect, claim and beneficiate iron only if it is located in the bedrock. Consequently, claiming lake or bog ore was no longer possible. It was only now that quartz and lime feldspar were added to mining minerals, although it is possible to claim and utilize quartz only when it occurs in the bedrock.

Temporal distribution of lake and bog ore claims

This work looks into the period between the year 1811 and 1916, which is soon after the Finnish War.
1808 - 1809, as well as the time when the so-called Old Finland was annexed into the Grand Duchy of Finland in 1811, i.e. 105 years prior to the last lake ore claim in 1916. The material concerning claims has been collected from original sources stored in the National Archives (Vuorihallitus 1811 - 1884, Teollisuushallitus 1885 - 1903, Kauppa- ja teollisuushallitus 1904 - 1918). Claims register records for the year 1875 (Furuhjelm 1877) are provided as an example of the printed claims register. The information that was gathered for the present work included claim register number, owner, parish (corresponding to the present-day municipality), name, starting year, and location if given. Geographical locations of claims were established separately later on the level of the present day topographic map sheets in scale 1:20 000.

During the period 1811 - 1959 a total of 7 320 lake ore claims and 450 bog ore claims were made, i.e. 7 770 claims in all (Fig. 2). The period to be investigated is the time immediately after the Finnish War 1808 - 1809. Apparently, because the society was in turmoil, the successor to the Swedish Mining Collegium certainly did not keep any records on lake and bog ore claims in 1811 - 1813. The latest lake ore claim was made by the company Oy Wärtsilä Ab when applying for the extension for lake Koitere in Ilomantsi in 1916. All bog ore claims date to 1817 - 1877. The cessation of bog ore prospecting in 1877 is due to the alteration of the prospecting rule.

As stated above, it can be seen that the annual amounts of lake and bog ore utilized in blast furnaces falls into several time periods (Table 1 and Fig. 1). Comparing these periods of time with the temporal distribution of the claims (Fig. 2), partly coinciding features can be detected.

Towards the end of the period of 1811 - 1852, the forthcoming increase in iron production was being prepared for, and, consequently, during the period of increase in 1853 - 1860, approximately 170 claims per year were made. During the peak period of 1861 - 1877 a total of 241 claims, and during the 1878 - 1886 interval, 71 claims were made. On the other hand, during the last production peak, only 20 annual claims were made, and at the end of the whole time span under investigation, only two were made.

A single peak year of claims is the year 1867, when alone 741 claims were recorded. Because the lonely peak of 1879 is produced by the 458 claims by Adolf Törngren, which in addition did not lead to establishing a plant, it can be stated that no more lake ore claims were made after the 1877 Mining Act amendment. The use of lake ore as an important raw material for iron works continued till 1906. This is explained by the fact that the iron works operated utilizing previously granted claims.

During the period 1941 - 1959, 21 lake ore claims were still made with the objective of investigating the manganese potential of the lakes south of Ilisalmi. In this respect, the company Oy Vuoksminka Ab hoisted a total of 8 860 tonnes of lake ore during 1944 - 1947 with the average content of 29.0 % Fe and 14.0 % Mn from the lakes Kirmajärvi, Nerkkoonjärvi, Onkivesi, and Porovesi.

In addition to ore and coal, various kinds of additives were needed in the iron works. As a result, during the years 1811 - 1877, claims were made for limestone in 137 cases and quartz in 43 cases.
Regional distribution of lake and bog ore claims

Locations of the lake and bog ore claim sites were established on the basis of the original archive material stored in the National Archives and on a topographic map sheet level. Therefore all claim sites appear in the middle of their pertinent map sheet which causes
certain angularity in the map (Fig. 3).

Claims dating to prior to 1811, i.e. to the time of the Swedish Rule, were not recorded in this work. It is self-evident that by then mined iron ore, as well as lake and bog ore was being hoisted for utilization in iron works. Between 1811 and around 1838, the main part of the claims were made in the provinces of Ladogan Karelia, North-Karelia, and North-Savo, and only thereafter to provinces such as North-Ostrobothnia, Kainuu and Central Finland.

Practically no claims took place on the coastal areas of Finland during the time period investigated (Fig. 3), where the number of lakes is relatively small as well. Excluding the few cases in Ylitornio and Rovaniemi, no claims were made in Lapland either. Outside the Central Finland lake district, individual islets are distinguished however, e.g., the lake districts of Loppi and Tammela, Ikaalinen and Parkano, Lappajärvi and Kortesjärvi, and the Ylitornio lake districts. Other claims on the coastal areas concerned mainly bog ore, out of which Koivisto in the Karelian Isthmus, and Mantsila in the Salmi parish in the Ladogan Karelia stand out.

An interesting observation is the absence of lake ores immediately south of the Salpausselkä, from Hanko to Imatra. The area constitutes a Quaternary geological unit of its own, where the soil rich in clays has not been favourable for the formation and deposition of lake ores.

The regional distribution of the claims by parishes in the Central Finland lake district will be dealt with separately in this work. The map (Fig. 3) also shows concentrations of claims near lisalmi in the provinces of North-Savo, around Nurmes and Valtimo in North-Karelia, and around Kuhmo, Sotkamo and the Lake Oulujärvi area in Kainuu. As a general observation, the regional distribution of lake ores described in this work follows well the lake ore distribution collected by Aarnio (1915).

Distribution of lake and bog ore claims by parishes

During the years 1811 - 1916, lake and bog ore claims totalled 8,797, covering the area of 218 parishes (Table 2). The most significant parishes as to the number of claims were Kuhmo 338 (3.8 %), Karttula 329 (3.7 %), Juva 302 (3.4 %), Suonenjoki 268 (3.0 %), Pieksämäki 250 (2.8 %), Ilomantsi 225 (2.6 %), Suistamo 223 (2.5 %), Impilahti 207 (2.4 %), Punkaharju 190 (2.2 %), and Mikkeli 187 (2.1 %).

On examination of the ratio of number of claims per parish-area, the most notable concentration is located upon a relatively narrow zone trending southwest-northeast from the central part of the province of South-Savo to the southwestern corner of North-Savo, i.e. from Sulkava to Tervo (Table 2). Another concentration lies between the eastern part of South-Savo and the northeastern tip of South-Karelia, i.e. from Savonranta to Uukuniemi. Practically only small areas exist outside the above mentioned areas, in North-Karelia from Kihetelysvaara and Pyhäselkä to Eno, and also in the Ladogan Karelia at Impilahti and Suistamo.

Lake and bog ore claim owners

The applicants for lake and bog ore claims were almost invariably owners of iron works. Through claims they aimed to secure the supply of raw-material for their industrial plants or they were planning to construct an iron works. Only 2 % of owners out of the total 7,770 claims, were private persons, merchants or farm-owners (Table 3). The largest groups were formed by small individual iron works companies (2,964 claims, 38.1 %) and specially

Table 2. Regional distribution of Finnish lake and bog ore claims from 1811 to 1916 by parishes (according to the archive records stored in the National Archives) and in relation to the land area of the parishes. The intensity factor is defined as number of claims per square kilometre and multiplied by 100.

<table>
<thead>
<tr>
<th>Parishes</th>
<th>Number of claims</th>
<th>Area km²</th>
<th>Intensity factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Karttula</td>
<td>329</td>
<td>468.2</td>
<td>70.3</td>
</tr>
<tr>
<td>Kesälahti</td>
<td>163</td>
<td>387.3</td>
<td>42.1</td>
</tr>
<tr>
<td>Virtasalmi</td>
<td>105</td>
<td>263.2</td>
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<tr>
<td>Punkaharju</td>
<td>190</td>
<td>498.4</td>
<td>38.1</td>
</tr>
<tr>
<td>Suonenjoki</td>
<td>268</td>
<td>719.6</td>
<td>37.2</td>
</tr>
<tr>
<td>Tervo</td>
<td>126</td>
<td>347.4</td>
<td>36.3</td>
</tr>
<tr>
<td>Sotkamo</td>
<td>183</td>
<td>588.7</td>
<td>31.1</td>
</tr>
<tr>
<td>Rautalampi</td>
<td>159</td>
<td>548.6</td>
<td>29.0</td>
</tr>
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<td>Pieksämäki</td>
<td>250</td>
<td>945.1</td>
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<td>Juva</td>
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<td>25.5</td>
</tr>
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<td>Mänttä</td>
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<td>81</td>
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<td>Rantasalmi</td>
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<td>Hankasalmi</td>
<td>86</td>
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<td>15.0</td>
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<td><strong>5,304</strong></td>
<td><strong>1,692.5</strong></td>
<td><strong>5.2</strong></td>
</tr>
</tbody>
</table>

Table 2. Regional distribution of Finnish lake and bog ore claims from 1811 to 1916 by parishes (according to the archive records stored in the National Archives) and in relation to the land area of the parishes. The intensity factor is defined as number of claims per square kilometre and multiplied by 100.
Nikolai Putilov (2,438 claims, 31.4%), a private person. Other owners of claims were Adolf Törngren (5.8%), Nils Ludvig Arppe (3.9%), and the work group formed by Miron Smirnoff and Alexander Gajewsky (3.0%), merchants from Joensuu.

Nikolai Putilov (1820-1880) was a Russian tycoon, Collegial Counsellor, and later an actual Counsellor of State. In 1868, he bought the Russian state-owned large steel and arms factories in St. Petersburg. In Finland, he acquired the Huutokoski works at Joorinen, and the Haapakoski works from Piekšämäki in 1857, and, in addition, founded the Oravi works at Rantasalmi in 1868. The claims of Nikolai Putilov from 1858 to 1876 were located mainly in the provinces of North-Savo, South-Savo, and South-Karelia, with the objective to assure a continuous flow of raw materials to his industrial plants. The great number of Putilov's claims is reflected in the fact that his claims were recorded as a separate memorandum at the Finnish Bureau of Mines (Vuorihallitus 1880).

Adolf Törngren (1824-1895) owned the linen factory and blast furnace of Tampere, the Hietalahti dockyard in Helsinki, and expanded the Nuu-tajärvi glass factory. A special feature is that all of his 453 claims date to the year 1879 in the provinces North-Savo and South-Savo. Soon afterwards the 1883 mining rule prevented speculation with these kind of claims.

Nils Ludvig Arppe (1803-1861) is considered the pioneer of Finnish industry. He owned among others timber businesses the Värtsilä sawmill and blast furnace, the Möhkö iron works at Ilomantsi, and the Läskelä sawmill at Harlu. Arppe's 306 claims during the years 1850-1898 were situated solely in the vicinity of the iron works district in the province of North-Karelia (including Korpiselkä), and of Ladogan Karelia in Suistamo.

The disappearance of blast furnaces using lake ore

In the 19th century, hoisting lake ore was more economical than mining iron ore. Although the iron content of the lake and bog ore hoisted almost equalled that of the mined ore, utilization of lake and bog ore encountered difficulties due to the large quantities of harmful constituents, especially phosphorus. On the other hand, the use of mined iron ore was also sometimes difficult due to sulphur and occasionally titanium.

The industrial revolution took place towards the end of the 19th century in Finland. Steam became the most important source of power, and mineral coal replaced charcoal. Simultaneously, import of cheap iron from Russia started and the old-fashioned iron industry of Finland suffered economically.

In 1859, the Senate declared limitless free export of pig-iron made from lake ore to Russia. This resulted in a marked increase in exports, and particularly for the iron works founded in the eastern Finland lake district which depended primarily on exports for their operation. Later export restrictions resulted in a significant decrease in the iron works' feasibility, and the exports to Russia declined almost totally after the year 1907 (Laine 1955).

The primary reason for the cessation of the iron export to Russia was that the Finnish iron industry was unable to compete with Russia's own iron production, also at the same time, large amounts of cheap rolled iron began flowing in from Russia (Laine 1955, Joustela 1963). All this resulted in the Finnish blast furnaces using lake ore to face a rapid closure and death. The Haapakoski at Piekšämäki and the Kuokkakoskensoski at Nurmes ceased operations in 1905, followed by the Högors at Karkkila in 1906, the Möhkö at Ilomantsi in 1907, and the Souru at Kattula and the Salamhi at Vieremä in 1908. After 1908, the lake ore smelting

<table>
<thead>
<tr>
<th>Claim owner</th>
<th>Period of time</th>
<th>Number</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small iron works companies</td>
<td>1811 - 1916</td>
<td>2,964</td>
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</tr>
<tr>
<td>Nikolai Putilov (iron and steel works company)</td>
<td>1858 - 1876</td>
<td>2,438</td>
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</tr>
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<td>Adolf Törngren (iron works company)</td>
<td>1879 - 1879</td>
<td>453</td>
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</tr>
<tr>
<td>Nils Ludvig Arppe (iron works company)</td>
<td>1850 - 1898</td>
<td>306</td>
<td>3.9</td>
</tr>
<tr>
<td>Miron Smirnoff and Alexander Gajewsky (merchants)</td>
<td>1867 - 1868</td>
<td>232</td>
<td>3.0</td>
</tr>
<tr>
<td>Johan Edvard Hällström (iron works company)</td>
<td>1822 - 1874</td>
<td>227</td>
<td>2.9</td>
</tr>
<tr>
<td>Alexander Grigorjeff, Sergei Soboleff and others (merchants)</td>
<td>1866 - 1874</td>
<td>182</td>
<td>2.3</td>
</tr>
<tr>
<td>Gustaf Herman Löfström (minister from Impilahti)</td>
<td>1844 - 1865</td>
<td>179</td>
<td>2.3</td>
</tr>
<tr>
<td>Antti Juhana Mustonen (iron works company)</td>
<td>1865 - 1882</td>
<td>173</td>
<td>2.2</td>
</tr>
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<td>Alexander Schleisner (iron works company)</td>
<td>1867 - 1872</td>
<td>160</td>
<td>2.1</td>
</tr>
<tr>
<td>Paul Wahl (iron works company and trading house)</td>
<td>1853 - 1901</td>
<td>154</td>
<td>2.0</td>
</tr>
<tr>
<td>Lupikon rauta- ja teräsyhtiö (mining company)</td>
<td>1870 - 1881</td>
<td>152</td>
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</tr>
<tr>
<td>Private persons or other small companies</td>
<td>1824 - 1905</td>
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</tr>
<tr>
<td><strong>Totalling</strong></td>
<td></td>
<td>7,770</td>
<td>100.0</td>
</tr>
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</table>

54
furnaces still left operating were the Juantehdas at Juankoski till the year 1911, the Jyrkkäkoski at Sonkajärvi till 1918, and the Värtsiä till 1920.

Following the history of granted lake and bog ore claims, one is also following a history of mineral exploration. The location of claims also reflect the geographical and geological areas where prospecting has been carried out, as well as where raw materials for blast furnaces and bloomery furnaces were obtained.

Acknowledgments

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REFERENCES


CHEMICAL COMPOSITION OF WELL WATER IN FINLAND – MAIN RESULTS OF THE “ONE THOUSAND WELLS” PROJECT

by
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Introduction

Geological Survey of Finland (GTK) has completed the existing national groundwater data file by collecting and analysing 1002 water samples from shallow dug wells and drilled bedrock wells. Also a few captured springs were included in the sampling grid. Samples were collected during the 1999 field season between May and September and analysed during the year 2000. The purpose of the survey was to delineate the present-day quality constraints of well water in sparsely-populated rural areas. This is the first report on the main results of the project and more detailed information will be published in near future.

The first nation-wide hydrogeochemical survey, carried out in 1978-1982 by the GTK, was reported in the first part of the Geochemical Atlas of Finland (Lahteron et al. 1990). Later the Ministry of Social Affairs and Health together with the Finnish Environment Institute (earlier National Board of Waters) published a second nation-wide well water survey which was carried out in 1990-1991 (Korkka-Niemi et al. 1993). The results from these surveys were quite similar. However, bacteriological and aluminium determinations, which were missing in the GTK’s survey, were included in the second survey. Since the last survey, the water analytic methods have been considerably developed, and new methods such as ICP-AES and ICP-MS, have been adopted. In the project of “the one thousand wells” commenced in 1999 two “new” elements (I, Sn) and many other dissolved components (e.g. Br, Ba, Sr, Li, Rb, V, As, Tl, Sb, Bi, Se, D/H, ¹⁶O/¹⁸O) are analysed. Comprehensive nation-wide and reliable groundwater chemical data on these elements are virtually lacking. The most interesting of such elements are Br, I, B, Tl, Se and Th. Furthermore, information on the regional distribution of Al, As and Rn in groundwater has so far been insufficient.

Materials and methods

Sampling and analytical procedures

Water samples were collected from springs (n=124) and dug wells (n=615) by filling plastic buckets with water. Drilled wells (n=263) were sampled by pouring enough water from taps to ensure a fresh uncontaminated water sample. In field, water temperature (°C), pH, electrical conductivity (mS/m, +25 °C), content of dissolved oxygen and carbon dioxide (mg/L) were determined. From each site one 500 ml bottle filled with unfiltered water and one 100 ml bottle with filtered (<0.45 μm) and acidified water were collected for major anion analysis and ICM-MS and ICP-AES analysis, respectively. From drilled bedrock wells one 100 ml bottle with unfiltered water for total-α determination, one 10 ml bottle for radon analysis and one
50 ml bottle water for isotope analysis were collected. In the GTK chemical laboratory pH, electrical conductivity, values of colour and KMnO₄-number were measured and concentrations of 43 elements and compounds were analysed. In the GTK stable isotope laboratory the isotopic composition of oxygen was analysed from 984 samples. The isotopic composition of hydrogen (D/H) will be analysed in the future from approximately 150 samples. Radon concentrations were measured from the major part (919) of the sample population by STUK Radiation and Nuclear Safety Authority.

Special field observation sheets were filled to collect information on the local topography, soil composition, land use in the vicinities and the condition of the well. Also the possible sources of contamination (fertilizers and wastes from animal husbandry, deicing salts, traffic exhausts, etc.) and access of contaminated surface runoff into the wells were evaluated as they are anticipated to have a strong impact on the water quality of shallow groundwater. The total depth of shallow wells and the groundwater level and sampling depth were measured, as well as the colour and turbidity were ocularly recorded.

The sample quality control is based on three methods: 1. Each sampling group collected a blank sample every week. The blank samples (distilled water) were prepared in the field similarly to the proper filtered and acidified samples; 2. Duplicate samples were collected in every 30th sampling sites. Both samples were analysed twice to provide data for balanced ANOVA (Agterberg 1974) and scatter diagrams (Fig. 1); and 3. The chemical laboratory used their standard protocols for the internal quality control.

Selection of sampling sites in the hydrogeological provinces

To facilitate a reasonable and representative sampling network over the whole country, Finland was divided into four hydrogeological provinces (Fig. 2, Tarvainen et al. 2000, cf. also Korkka-Niemi et al. 1993): 1. The southern Finland coastal belt stretches up to the Salpausselkä ice-marginal formations, included the South and Southwest Finland and Ahvenanmaa (Åland) archipelagos studded with big number of skerries and islands. The area is characterized by clay deposits in the low-lying areas and by bedrock outcrops in the higher regions. There are scattered glaciofluvial deposits (eskers) in the most parts of the area while the large Salpausselkä ice-marginal formations characterize the northern border area. Small littoral and till deposits occur frequently at the hill foots; 2. The western coastal belt reaches from the Pori area to the northern end of the Bothnian Bay. The western coastal belt stretches up to the water divide in East where terrain is higher and where the relative height differences are larger. The broad coastal plain, cut by numerous rivers, is dominated by clay and silt deposits and bounteous peat lands while till deposits are getting more common eastward; 3. The central Finland lake district encompasses the main part of the large lake basin. In the East the region is bordered by the lake Pielinen and Kainuu hill area. Numerous lakes, overburden of till and small peat lands, but lesser clay deposits are the characteristic features of the area; 4. Northeast Finland (Koillismaa) and Lapland are the most hilly and mountainous areas in this country. The till-covered hills, often peaked by broken bedrock and rock fields are separated from each others by large flat peat.

Fig. 1. a) Scatter diagram of Al concentrations in the normal and duplicate samples b) Scatter diagram of Al concentrations in the normal and replicate analysis.
Fig. 2. Map showing place names referred to in the text and the distribution of electrical conductivity values (mS/m, 25 °C) of the dug wells measured in field in the connection of water sampling in the summer 1999. The lines show the borders of the hydrogeological provinces (cf. text): 1. The southern Finland coastal belt; 2. The western coastal belt; 3. The central Finland lake district; 4. Northeast Finland (Koillismaa) and Lapland.
lands. Large rivers flow in broad and flat river valleys flanked frequently by extensive sand deposits.

The above division of Finland into the four hydrogeological (and sampling) provinces is based on the dominating topographical and Quaternary geological features and density of water courses. The areal distribution of clay and silt deposits, which are controlled by both topographical conditions and late- and postglacial development of the area, has a strong impact on the water quality whilst it is also the main basis of the hydrogeological division presented above. The bedrock of Finland is composed of Archaean and Proterozoic igneous and metamorphic rocks which are covered by thin layers of Quaternary deposits. Due to repeated glaciations during the last two to three million years the surficial deposits are composed only of glacial and late glacial deposits such as till, glaciofluvial sand and gravel, glacial and postglacial clay and silt deposits which are extensively covered by recent peat layers.

The density of sampling sites broadly reflects the extent of the groundwater utilization from private wells in the respective provinces. The largest number of samples were collected from the Central Finland lake district (3), where people frequently use drinking water from their own wells. Likewise the large population in the southern Finnish coastal belt (1) emphasizes the large number of water samples collected from there. In the western coastal belt (2) fewer private wells are used as domestic water sources and, consequently, a smaller number of wells were sampled. The number of the samples in Northeast Finland and Lapland is smaller compared to other parts of the country, due to the sparse population and the small number of wells.

In addition to the hydrogeological provinces described above, the sampling sites were categorized into four aquifer types. Because glacial till is the most common soil type it is obvious that the majority of wells are dug into till deposits. However, the most important economical groundwater reserves are in sand and gravel deposits in glaciofluvial formations such as eskers and ice-marginal formations (Salpausselkä), in spite of the fact that they represent only 3-4% of the area in Finland. Due to their importance, the sand and gravel aquifers are purposely over-represented in this well water survey. Another reason was to achieve a population large enough for a reliable statistical treatment. Only 7% of the water samples were taken from dug wells, which are placed in till or sand deposits covered by clay. About 25% of the water samples were collected from drilled bedrock wells which duly represents their frequency in this country.

Regional quality of well water

Main characteristics of water: Temperature, EC, pH, O₂, CO₂, total hardness (dH), alkalinity, colour and KMnO₄ number.

The median and mean temperatures of the dug well water samples, +6.8 °C and +7.2 °C respectively, measured in the connection with sampling, are higher than the real groundwater temperatures, which longitudinally decreases from the level of 5.0-7.0 °C in South Finland to 2.0-3.5 °C in North Finland (Kahri 1963). The warming of sampled water is still more clearly seen in the wells drilled into bedrock (+8.0 °C and +8.2 °C), which generally were sampled by pouring water from taps.

The springs and a few metres deep shallow dug wells represent shallow groundwater percolating near the ground surface. Hence, it is evident that the average values of electrical conductivity, which reflects the content of electrolytes dissolved in water, are smaller than in groundwater pumped from the appreciably deeper (in general 40-60 m) drilled wells (Tables 1 and 2). The highest values of electrical conductivity (15-45 mS/m) were measured in southern and southeastern Finland (province 1 in Fig. 2) and the lowest values (3-15 mS/m) in northeastern Finland and Lapland (province 4). Statistically the electrolyte content in well water is strongly affected by the areal distribution of clay deposits. In the coastal regions the occurrence of relict sea salts, trapped in the pore waters of fine-grained sediments and in fractures of the underlying bedrock, have an especially strong impact on the water quality. Also the anthropogenic contamination in the densely populated areas (urban sewages, fertilizers and animal dungs, deicing salts and traffic in general, industrial refuses, gravel excavation, etc.) is an important source of electrolytes in groundwater. Furthermore, the airborne fallout is higher in South Finland than elsewhere in the country although it has a meaningful effect in intact uncontaminated waters only. The groundwater from aquifers confined by overlying clay and silt deposits and water from drilled bedrock wells show appreciably elevated electrical conductivity values.

It is noteworthy that in this survey, which was carried out in 1999, the electrical conductivity values in groundwater are significantly lower than in the earlier survey dating back to the years 1978-1982 (cf. Lahermo et al. 1990). This finding may suggest that the general quality of shallow groundwater has not deteriorated during last twenty years. This reasoning does not, however, compile with the aquifers confined by the covering clay deposits, and groundwater in bedrock fractures, where water quality has not appre-
The central Finland where the bedrock is largely composed values of the bedrock groundwater are statistically changed. not any meaningful differences in the average pH level of water from the dug wells in this survey (1999) compared with the results from the earlier surveys in 1978-1982 (Lahermo et al. 1990) and in 1990-1991 (Korkka-Niemi et al. 1993). However, present pH values of the bedrock groundwater are statistically higher than those measured in the earlier survey in 1978-1982 (median pH 6.9) but slightly lower than in

### Table 1. Characteristics of the waters sampled from the well dug into the overburden.

<table>
<thead>
<tr>
<th>Element</th>
<th>Unit</th>
<th>N</th>
<th>2%</th>
<th>Median</th>
<th>Mean</th>
<th>S.D.</th>
<th>98%</th>
<th>Max</th>
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<tr>
<td>pH, field</td>
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<td>698</td>
<td>5.5</td>
<td>6.4</td>
<td>6.46</td>
<td>0.532</td>
<td>7.8</td>
<td>9</td>
</tr>
<tr>
<td>EC, field</td>
<td>mS/m, 25°C</td>
<td>709</td>
<td>2.72</td>
<td>12.5</td>
<td>16.4</td>
<td>13.5</td>
<td>56.3</td>
<td>106</td>
</tr>
<tr>
<td>t</td>
<td>°C</td>
<td>706</td>
<td>1.9</td>
<td>6.8</td>
<td>7.21</td>
<td>2.99</td>
<td>13.4</td>
<td>19</td>
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<td>CO₂</td>
<td>mg/l</td>
<td>699</td>
<td>3</td>
<td>3.4</td>
<td>38.8</td>
<td>26.3</td>
<td>110</td>
<td>200</td>
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<tr>
<td>O₂</td>
<td>%</td>
<td>693</td>
<td>6.82</td>
<td>60.9</td>
<td>57.9</td>
<td>25.4</td>
<td>98.3</td>
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<td>Colour</td>
<td>mgPt/l</td>
<td>737</td>
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<td>13.4</td>
<td>17.2</td>
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<tr>
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<td>Hardness</td>
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<td>2.84</td>
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<td>HCO₃⁻</td>
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<td>14.6</td>
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<tr>
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<td>I⁻</td>
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<td>700</td>
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<td>2.12</td>
<td>6.78</td>
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<td>739</td>
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<td></td>
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<tr>
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<td>&lt;0.1</td>
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<tr>
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Geological Survey of Finland, Special Paper 31
Chemical composition of well water in Finland - main results...
Table 2. Characteristics of waters sampled from the wells drilled into the bedrock.

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the 1990-1991 survey (median pH 7.2).

In addition to temperature, also the content of dissolved oxygen (O₂) measured in the ventilated wells does not represent the real conditions in intact groundwater. A distinctive feature is, however, that groundwater occurring in bedrock fractures, generally veneered by tight till and clay deposits, contains notably less dissolved oxygen (median/mean 40%/45 %) than more effectively aired shallow dug wells (median/mean 57%/60 %).

Ventilation has also affected the dissolved CO₂ contents. Part of CO₂ undoubtedly escapes when groundwater percolates into wells, in the course of bailing, pumping, storing and, finally, while sampling the water. In spite of these conditions, it is noteworthy that the CO₂ content is lower in the bedrock.
groundwater (median/mean 17/28 mg/L) than in the more diluted well waters (median/mean 34/39 mg/L). This is due to the fact that the dug well waters are more acid than the circum-neutral or slightly alkaline water pumped from the drilled bedrock wells. In analogy with this a relatively larger portion of inorganic carbon is in the form of bicarbonate in the water from the drilled wells than in the dug wells.

Total hardness is the function of abundance of dissolved alkaline earths (mainly Ca and Mg) in water. According to the international standards the hardness of Finnish shallow groundwater, expressed in German degrees (one German degree or °dH is equivalent to 10 mg/L CaO) is particularly low. Most of the samples fall into the categories of very soft (1-4 °dH) and soft water (4-8 °dH), which is a typical characteristic to groundwaters in the areas composed of geochemically inactive granitic basement rocks poor in carbonate minerals. Regionally, the hardest groundwater is met in the southern Finland coastal belt while the softest waters are encountered in Northeast Finland (Koillismaa and Lapland (Fig. 3)).

Bicarbonate or hydrocarbonate, determined as alkalinity (mmol/L), is the most abundant anion in Finnish groundwater both in waters from the dug wells (median 32.9 mg/L and mean 51.9 mg/L) and from the drilled bedrock wells (median 83 mg/L and mean 103 mg/L). It overwhelmingly constitutes the buffering capacity of natural water, which is conspicuously higher in the southern Finland coastal belt, and in the parts of western coast in the Oulu-Tornio-Tervola area, than elsewhere in the country (Fig. 4). The reasons for this condition is the abundance of clay and silt sediments commonly confining aquifers and the occurrence of carbonate rocks in these areas. The most weakly-buffered groundwater is encountered in East Finland and in parts of North Finland in areas where bedrock is mainly composed of Archaean (and

Fig. 3. The distribution of total hardness in German degrees (°dH) in waters from the dug wells (a) and drilled bedrock wells (b) sampled in the summer 1999.
Proterozoic) granitoids.

Colour and KMnO₄ consumption values are good indications of organic coloured material, generally various sorts of humus, dissolved in water. Particularly poorly protected shallow wells are susceptible for contamination caused by humus-rich runoff which is clearly seen also in the data presented in this study. The relatively largest number of elevated colour and KMnO₄ consumption values are encountered in the western coastal areas and central parts of the country characterized by slowly rising, low-lying land (crustal upheaval, maximum one metre per one hundred years, is caused by glacial isostasy) rich in clay and silt deposits and extensively paludificated wet lands.

**Anions:** HCO₃⁻, SO₄²⁻, Cl⁻, Br⁻, F⁻, I⁻, NO₃⁻, PO₄³⁻ and SiO₂⁻

The regional distribution of the most abundant anion, bicarbonate, is discussed above with alkalinity.

Sulphate is among the most abundant anions in groundwater. The median and mean SO₄²⁻ concentrations in the dug wells are 10.4/14.6 mg/L and in the bedrock wells 12.2/19.9 mg/L. The largest number of elevated SO₄²⁻ concentrations are encountered in the southern and western coastal belts (Fig. 5). The distribution pattern is at least partly explained by the occurrence of sulphur-rich clay and silt deposits (Palko 1994) and remobilizing of relict sea salts from the pore water in fine-grained sediments and fractured bedrock. The occurrence of primary sulphide minerals in the soils and bedrock in East Finland (e.g. Outokumpu area) is a supplementary source of sulphates in groundwater. The airborne SO₄²⁻ fallout is higher in South Finland than elsewhere in the country (Lahermo et al. 1994), but it has a meaningful effect as an additional sulphate source only in exceptionally weakly mineralized waters, such as soil water and very shallow swiftly circulating groundwater.

As far as their concentrations are concerned by far the most abundant halogenide (Cl⁻, F⁻, Br⁻, I⁻) is chloride. It is notable that in the bedrock wells there is a much larger number of high Cl⁻ concentrations (median and mean 8.7/52.7 mg/L) compared with the well waters from the overburden (median and mean 3.8/7.9 mg/L). Due to the marine effect most of the elevated concentrations in the drilled wells are located along or nearby the coast line. About 7% of the samples from the drilled bedrock wells exceeded the upper recommendable Cl⁻ concentrations (100 mg/L).
while in the dug wells only one case is found. Bromide behaves largely similarly to chloride while occurring in much lower concentrations (median and mean in dug wells 0.01/0.025 mg/L and drilled wells 0.02/0.20 mg/L, respectively). Also bromide is overwhelmingly of marine origin and, hence, the elevated concentrations are bound to the coastal areas rich in fine-grained bottom sediments. Although very low concentrations of iodine (median and mean in dug wells 2.1/6.8 μg/L and drilled wells 3.0/10.7 μg/L, respectively) has similar characteristic to the afore mentioned halogenides as far as its areal distribution is concerned. This survey confirms the earlier known observation that the in Finland natural iodine concentrations in groundwater are too low to fulfill the intake amounts required by metabolism and the balanced human nutrition.

In geochemical point of view fluoride differs from the other halogenides discussed above. Fluoride is strictly a geochemically-controlled element in the environment. Into natural water it is mainly derived from fluorite or fluorspar (CaF₂) and apatite minerals, as well as from micas and amphiboles, where OH-groups can be diadocically replaced by F⁻-ions, both of them representing roughly the same dimension of their ionic radii. Anorogenic rapakivi granites in southeastern (the Viborg rapakivi batholith) and southwestern Finland (the Laitila, Vehmaa and Ahvenanmaa rapakivi batholiths) contain by far the highest average fluorine contents compared to other rock types. Fluoride anomalies in groundwater in the rapakivi areas reflect the high bedrock fluoride content (Lahermo & Backman 2000). The median F⁻ concentration in the dug well waters is <0.1 mg/L. In the drilled bedrock wells median and mean F⁻ concentrations are 0.15 mg/L and 0.70 mg/L, respectively, while the concentrations in groundwater in the rapakivi granite areas are roughly one order of magnitude higher (mean 2.5 mg/L in drilled well waters in the rapakivi granite areas).

Nitrate is among the most deleterious dissolved components in water as its elevated amounts in groundwater are predominantly derived from the anthropogenic contamination often intertwined with bacteriological pollution. The current upper permissible NO₃⁻ concentration (25 mg/L) is exceeded in 8% of the samples collected from the dug wells and in 5% of samples from wells drilled into bedrock while the median and mean concentrations in the mentioned groups are 3.2/8.4 mg/L and 0.26/5.4 mg/L, respectively. The new national safe limit (Anon 2000) for the
public water utilities (more than 50 consumers) will be 50 mg/L which is in line with the EU directives. This limit is exceeded only in 2% of the samples. The passing of a prospective act for small water supply units, i.e. private one-household dug wells and wells drilled into bedrock, is underway.

It is noteworthy that, deemed on the basis of their NO$_3^-$ concentration, the shallow dug wells seem to be more contaminated than the wells drilled into the bedrock. The results of this survey are in a good agreement with the hydrogeochemical mapping performed earlier by the GTK (1990) and by the National Board of Waters and Environment and the Ministry of Social Affairs and Health (Korkka-Niemi et al. 1993). Background concentrations in the most pristine areas in the North Finland are <1 mg/L. Regional differences of nitrate are not conspicuous, instead elevated NO$_3^-$ concentrations caused by “point source” contamination are occasionally encountered all over the country.

Phosphate occurs in groundwater in very small concentrations only (median <0.02 mg/L). This is due to its affinity to form sparingly-soluble complex compounds, such as Fe- and Al-phosphates, and to get sorbed by the Fe-Mn-oxyhydroxides. The highest PO$_4^{3-}$ concentrations are found in the western and southern parts of the country or along the coastal areas where agricultural activities are most intense.

Silicic acid, determined as SiO$_2$, is among the most common dissolved (partly colloidal) component as far as its gravimetric concentration is concerned. The median and mean values do not differ much in the dug well waters (12.9/13.9 mg/L) and in waters from the drilled bedrock wells (13.8/14.6 mg/L). In the dug well waters SiO$_2$ correlates positively with EC. The highest SiO$_2$ concentrations are found in the coastal areas. In the drilled well waters SiO$_2$ correlates with the SO$_4^{2-}$, PO$_4^{3-}$, Fe, Mn, Li, Mg concentrations and alkalinity. Detailed information is missing, however, about the speciation of silica and its ability to form complexes with inorganic and organic ligands.

**Cations:** Ca, Mg, Sr, Ba, Be, Na, K, Li, Rb, Al, Fe, Mn, Zn, Cu, Ni, Co, Cr, V, Ti, Pb, Sn, Cd, Mo, B, As, Sb, Bi, Tl, Se, U and Th.

The most common alkali earths (Ca, Mg, Sr) behave similarly with each other while Ba and particularly Be have geochemically a divergent character. The most common alkali earths, calcium (median and mean in the dug wells 11.4/15.2 mg/L and drilled wells 16.0/28.1 mg/L) and magnesium (median and mean in the dug wells 2.4/3.8 mg/L and drilled wells 4.5/6.7 mg/L) are the main components in constituting of water hardness. Hence, the areal distribution patterns of Ca and Mg are virtually identical with that of total hardness (see Fig. 3). The same is true with strontium occurring in much smaller concentrations (median and mean in the dug wells 60/79 μg/L and drilled wells 81/190 μg/L) while the areal distribution of barium (median and mean in the dug wells 18/28 μg/L and drilled wells 14/26 μg/L) differs conspicuously. The highest Ba concentrations are encountered in the central part of Finland in the area partly coinciding along with the Ladoga-Bothnian Bay (Raahe) sulphide ore belt (Fig. 6). This regional feature is more clearly seen in the Ba contents of the dug well waters than in the drilled bedrock well waters. As barium occurs statistically in somewhat lower concentrations in South Finland, where total dissolved load and components derived from the contamination in groundwater are higher than elsewhere in country, barium seems to be mainly derived from the weathering of biotite, barite and potassium feldspar.

Beryllium, the lightest member in the group of alkali earths, occurs in groundwater in very small concentrations (median in dug and in drilled wells <0.1 μg/L). As far as its geochemical behaviour is concerned, beryllium has nothing common with the other alkali earths, however. The elevated Be concentrations are strictly bound to rapakivi granites or related coarse-grained K-rich granites in Southeast and Southwest Finland (Fig. 7). Hence, its distribution pattern is practically identical with that of fluoride. Vesely and others (2000) have reported Be concentrations up to 5 to 10 μg/L in Czech freshwaters with high F content in acid sensitive areas. In the less acid groundwaters of the Finnish rapakivi granite areas Be concentrations are typically 0.3 - 1.2 μg/L.

The most common alkali metals in groundwater are sodium (median and mean in the dug wells 4.2/7.0 mg/L and drilled wells 9.0/36.2 mg/L) and potassium (median and mean in the dug wells 2.8/5.0 mg/L and drilled wells 3.0/4.4 mg/L), while the lightest one, lithium (median and mean in the dug wells 0.8/2.8 μg/L and drilled wells 3.3/6.6 μg/L) and heavier one rubidium (mean and median in the dug wells 2.7/5.0 μg/L and drilled wells 1.8/3.2 μg/L) occur in much lower concentrations. It is noteworthy that, against the general tendency, statistically higher Rb concentrations are encountered in the waters from the dug wells than in water pumped from the drilled wells. Relatively the largest number of elevated Na concentrations are delineated along the coast line, particularly when the water pumped from the drilled bedrock wells is concerned (Fig. 8). Sporadic high Na concentrations elsewhere in the country were plausibly derived from the local sewage contamination or from de-icing salts.
Fig. 6. The distribution of Ba concentrations in the waters from the dug wells (a) and drilled bedrock wells (b) sampled in the summer 1999.

Fig. 7. The distribution of Be concentrations in the waters from the dug wells (a) and drilled bedrock wells (b) sampled in the summer 1999.
The regional distribution of potassium in the groundwater does not show any meaningful pattern. This suggest that the few elevated K concentrations originate from the local pollution, which is supported by the similarity of its distribution pattern with nitrate. Correlation coefficient between potassium and nitrate originate from the local pollution, which is supported by the similarity of its distribution pattern with nitrate. Correlation coefficient between potassium and nitrate is .486** in the dug well waters. Rb correlates even stronger with potassium (r = .656**). Nothing more can be concluded about rubidium either in this respect.

Aluminium concentrations vary within four orders of magnitude. Concentrations are notably higher in the dug well waters in the overburden (median and mean 18.5/101 μg/L) than in the waters pumped from drilled bedrock wells (2.5/30.0 μg/L). This is due to the lower pH level and abundance of humic material in the shallow groundwater. It is probable that Al has an affinity to form complex compounds with the organic ligands which is also supported by the finding that there are many elevated Al concentrations in the well waters in the rapakivi granite areas (Fig. 9). The plausible reason for this is the formation of soluble Al-fluoride complex compounds (see also Lahermo et al. 1996). In 11% of the dug wells the Al concentrations exceeded 200 μg/L, the upper permissible value for household water, whereas only 1% of the analysed waters from the drilled bedrock wells are over the above limit.

Similarly to aluminium, also iron and manganese concentrations vary more than four orders of magnitude. The median Fe concentration in the dug wells is <0.03 mg/L and in the drilled bedrock wells median and mean concentrations are 0.03/0.49 mg/L, respectively. The values for manganese are median and mean in the dug wells 0.004/0.06 mg/L and in the drilled wells 0.017/0.11 mg/L. Relatively largest number of elevated Fe concentrations are encountered in the western coastal belt which is, in places, characterized by humus-rich shallow groundwater. Although Fe and Mn are not harmful elements as far as health consequences are concerned, they cause aesthetic and technical problems. The recommended concentration limit set for iron (0.5 mg/L) in small water supply units was exceeded in 6% of the analysed dug wells and in 13% in the drilled bedrock wells while the corresponding figures for manganese (0.2 mg/L) were 7% and 14%, respectively. If compared to the Fe- and Mn-concentrations set for the public water utilities (0.2 and 0.05 mg/L, respectively) a much larger number of the sample population would exceed the limits. The highest Fe and Mn concentrations analysed in this survey are 27.6 mg/L and 5.33 mg/L in the dug wells and 39.9 mg/L and 4.14 mg/L in the drilled bedrock wells, respectively. The figures presented above demonstrate that Fe and Mn are among the most harmful ones causing technical-aesthetical problems in the practical water supply activities.

The other common heavy metals encountered in groundwater, although in smaller abundances, are zinc, copper, nickel, cobalt, chromium and vanadium. Median and mean Zn concentrations in the dug wells and drilled wells are 10.4/44.2 μg/L and 21.7/84.9 μg/L, while the corresponding values for Cu in the dug wells are 2.5/14.1 μg/L and in the drilled wells 9.1/32.3 μg/L. The related figures for the Ni concentrations are 0.8/3.3 μg/L and 0.6/1.8 μg/L, Co concentrations 0.09/0.77 μg/L and 0.04/0.42 μg/L. Median and mean Cr concentrations are 0.20/0.33 μg/L in the dug wells and the median in the drilled wells is <0.2 μg/L. In the dug wells median and mean V concentrations are 0.20/0.39 μg/L and in the drilled wells 0.16/0.49 μg/L, respectively. In this survey none of the sampled well waters exceed the upper allowable Zn, Cu and Cr concentrations (3.0 mg/L, 1.0 mg/L, and 0.05 mg/L). The irregular distribution pattern of the anomalous heavy metal concentrations in the well waters suggest that most of them originate from technical contamination in wells and in the water distribution and storage systems.

High concentrations of lead are considered harmful when dissolved in household water. Its concentrations in the analysed dug well waters (median and mean 0.04/0.25 μg/L) and in drilled well waters (0.15/0.42 μg/L) are, however, very low. The upper permissible limit for lead (10 μg/L) was exceeded only in one dug well. The quality of this well has been monitored since 1993, and lead concentrations exceeded the limit 10 μg/L only in 1999. In 2000, the concentration was again considerably lower (2.6 μg/L). The reason for the variation is not known. Tin concentrations are also very low (median <0.5 μg/L) and only in 10 water samples the Sn values were over the detection limit. Cadmium is among the most deleterious elements in the environment as far as its consequences on human health are concerned. Also Cd concentrations are very low both in the waters from the dug wells (median 0.02 μg/L and mean 0.04 μg/L) and drilled bedrock wells (median <0.02 μg/L). The upper safe limit for Cd (5 μg/L) was never exceeded in this survey (while maximum Cd concentration in a dug well was 1.3 μg/L).

Molybdenum is a geochemically interesting dissolved component which seems to be concentrated mainly in the southern part of the country, particularly in the rapakivi and other granite areas (Fig. 10). Its median and mean concentrations are appreciably
Fig. 8. The distribution of Na concentrations in the waters from the dug wells (a) and drilled bedrock wells (b) sampled in the summer 1999.

Fig. 9. The distribution of Al concentrations in the waters from the dug wells (a) and drilled bedrock wells (b) sampled in the summer 1999.
higher in the dug wells (0.13/0.30 μg/L) than in the drilled bedrock wells (0.50/2.31 μg/L), but none of the analysed samples exceed the upper recommended safety limit (70 μg/L). Boron is more bound to marine factors, i.e. proximity to the sea coast and occurrence of marine clay and silt deposits, than to the petrological composition of the bedrock and overburden. However, the effect of the bedrock and overburden composition cannot be ruled out in Central and North Finland (Fig. 11). Only 2.3% of the analysed waters from the drilled bedrock wells exceed the upper permissible B concentration (0.30 mg/L). 

Arsenic is among the most deleterious dissolved components in water when the concentrations exceed several tens of μg/L, which is common in wells drilled into certain geological environment: black schists, metavolcanic rocks, amphibolites and gabbros. The median and mean values in the dug wells are 0.14/0.35 μg/L and in the drilled bedrock wells 0.16/1.0 μg/L, respectively. The upper permissible safety concentration for arsenic (10 μg/L) is never exceeded in the dug well waters but in the drilled wells 3% of the sample population exceeded this limit. Even the highest analysed As concentration (23.6 μg/L) was much below the highest ones detected earlier in the parts of As-inflicted areas in Finland (Backman et al. 1996, Kurtto et al. 1998, Kurtto et al. 1999, Loukola-Ruskeniemi et al. 1999). It seems that the used sampling network does not delineate any notably As-anomalous provinces and even the known As-rich areas have not been detected by the sampling density used for this survey. However, the southern Finland coastal belt comes out as an province of higher As concentrations (Fig. 12). Antimony and bismuth occur at extremely low concentrations (median and mean in the dug wells 0.03/0.05 μg/L and in the drilled wells 0.02/0.04 μg/L for Sb and median for Bi <0.03 μg/L in all well types) and no connection with the geology can be found.

Thallium is an interesting element due to its highly toxic properties. It occurs, however, at very low concentrations (median <0.02 μg/L), hence it does not pose any environmental problem in Finland. A few elevated Tl values (0.05-0.19 μg/L) are in the rapakivi granite areas in southeastern and southwestern Finland, and in the western coastal belt (Fig. 13). Also silver occurs in extremely low concentrations (mostly <0.01 μg/L) and a few elevated concentrations are found in the same areas as those of thallium.

Selenium has been at the focus of general interest since 1980s due to its importance in the metabolism and in human and animal nutrition. Because the Finnish environment is exceptionally poor in selenium,
the nation-wide Se increment into fertilizers was commenced in 1985 (Wang et al. 1994). This activity resulted in a notable rise in Se concentrations both in the agricultural products and, consequently, in the Se intake of populace. The Se concentrations are equally low both in the dug wells and in the drilled wells (median <0.5 µg/L). None of the concentrations reach the upper permissible level (10 µg/L). The few elevated Se concentrations do not suggest any connections to the geological environment. Hence, they are presumed to originate from the fertilizations and, in a few cases only, from sulphide minerals in the bedrock or overburden.

From long-lived radioactive elements uranium is the most abundant element dissolved in the groundwater. A noticeable feature in the hydrogeochemistry of uranium is its skewed distribution and that the concentrations are much higher in the bedrock water from the drilled wells than in the water from the overburden. Median and mean concentrations are 0.09 µg/L and 0.85 µg/L in the dug wells and 0.64 µg/L and 13.7 µg/L in the drilled wells, respectively. These are lower than the population weighted average concentrations presented by STUK. In the drilled well waters uranium concentrations are usually more than ten times higher than those of other long-lived radionuclides. In the dug wells the disequilibria between uranium and other radionuclides is not so large. The larger abundances of uranium in the dug wells occur in the western part of Viborg rapakivi massif and in the neighbouring granite areas (Fig. 14). Markedly high U concentrations are found also in the southern and western parts of the country in granitic bedrock areas. As far as the drilled wells are concerned the U distribution pattern is more irregular. Concentrations are conspicuously higher in South Finland than elsewhere in the country while the rapakivi areas do not show up at all. Thorium occur in very low concentrations and, apart from uranium, Th concentrations do not differ much from each other in the dug wells and in the wells drilled into the bedrock (on the average <0.02 µg/L, maximums 1.5 µg/L and 1.41 µg/L, respectively). In groundwater thorium is much less soluble than uranium. This is due to that thorium is easily removed from water by precipitation or by adsorption onto the clay or rock minerals. The areal distribution patterns for thorium, although quite dispersed, resemble broadly those of uranium. Both the toxicity and radioactivity affect the restrictions set for uranium. Concentration limits of 20 – 100 mg/L for toxicity has been used in a number of countries. WHO has proposed a maximum permissible concentration of

Fig. 11. The distribution of B concentrations in the waters from the dug wells (a) and drilled bedrock wells (b) sampled in the summer 1999.

[Image of distribution maps]
Fig. 12. The distribution of As concentrations in the waters from the dug wells (a) and drilled bedrock wells (b) sampled in the summer 1999.

Fig. 13. The distribution of Tl concentrations in the waters from the dug wells (a) and drilled bedrock wells (b) sampled in the summer 1999.
2 mg/l. In Finland, the limit given for radioactivity in drinking water corresponds to a uranium concentration of 70 – 500 mg/l. Concerning the limit of 2 mg/l given by WHO, less than 8% of the dug wells but as much as 35% of the drilled bedrock wells would be in this respect unsatisfactory.

Radon

Radon ($^{222}$Rn) belongs to the radioactive decay series of uranium ($^{238}$U). Occurring as gas, its concentrations (median and mean 12.0/38 Bq/L in the dug wells and 140/310 Bq/L in the drilled wells) and hydrogeochemistry can not be compared straightforwardly with those elements occurring as dissolved solids. Radon is over 60 times more soluble than oxygen in water at 10°C temperature (Lowry & Brandow 1985). Due to its gaseous form, there is a great disequilibrium between radon and the other uranium series radionuclides. In the drilled well waters radon concentration can be more than thousands of times higher than those of other long lived radionuclides. There are, however, similarities in the distribution patterns of radon with those of uranium and thorium. The main part of South Finland forms by and large the most anomalous Rn area without any discernible smaller provinces (Fig. 15). Based on Radiation Act in 1992, STUK (1993) has issued Safety Guides to present the safety requirements for different practices. ST-Guide 12.3 of 1993 stated that the annual dose from drinking water supplied by waterworks, or water used in the production of food and beverages, should be less than 0.5 mSv. According to this safety guide the radon concentration in water must not exceed the value of 300 Bq/l. This was exceeded in less than 2% of the dug wells and in 27% of the drilled bedrock wells. The regulations for private wells are under preparation. STUK recommends an action level of 1000 Bq/l for private well users. Radon concentration over 1000 Bq/l was not exceeded in the dug wells but it was exceeded in 5% of the drilled bedrock wells. This is a lower figure than the estimate of the population weighted average presented by STUK.

Stable isotopes of oxygen and hydrogen

Studies of shallow groundwaters in temperate climates have shown that the isotope ratios of hydrogen and oxygen ($\delta$D and $\delta^{18}$O, given as a per mil differ-
ence vs. VSMOW standard) closely represent the local mean annual precipitation (Clark & Fritz 1997). The isotope values of precipitation, in turn, are linearly related to the annual mean temperature, especially in the middle and high latitudes (Dansgaard 1964). The results of a recent groundwater monitoring program suggested that such correlation is characteristic also to groundwaters in Finland (Backman et al. 1999), and the new data confirm the pattern. In shallow groundwaters the highest δ18O value, -11.1 ‰ is found in southern Finland, and the isotope ratios show a systematic decrease to values as low as -16.8 ‰ in Lapland (Fig. 16). No systematical differences can be observed between the shallow dug wells and the drilled bedrock wells. The isotope shift occurs mostly parallel with a change in the mean annual surface temperature from +5°C in southern Finland to -3°C in northern Finland. As no reports on the isotopic composition of precipitation in Finland have been published, these groundwater data give the first approximation of regional variations in the isotopic composition of precipitation.

Conclusions

The quality of Finnish dug well waters is affected by geological, marine, atmospheric and anthropogenic factors including the quality of the well, pump, pipes and related equipment. The As, F and Rn concentrations exceeding the upper permissible limit in groundwater are the most common health-related problems in well waters. Nitrate derived from the anthropogenic contamination has been reported to be one of the major problems in the dug well waters in the earlier studies. However, the new national safe limit of 50 mg/l was exceeded only in 2% of cases. Uranium concentrations in the drilled bedrock well waters are high compared to the proposed international limits, but there is no national safe limit for uranium. Acidity, the amount of dissolved organic compounds as well as high Al and Fe concentrations commonly cause technical-aesthetic problems.

In this survey which was carried out in 1999, the electrical conductivity values and nitrate concentrations in groundwater representing till as well as sand and gravel aquifers are statistically lower than in the earlier survey dating back to the years 1978-1982. Thus the general quality of shallow groundwater has not deteriorated during the last twenty years. This reasoning does not, however, compile with the aquifers confined by the covering clay deposits, and groundwater in the bedrock, where water quality has
Fig. 16. The distribution of the isotopic composition of oxygen in the waters from the dug wells and drilled bedrock wells sampled in the summer 1999. The data, composed of 980 analyses, have been smoothed by Alkemia Smooth interpolator using 100 km radius (Gustavsson et al. 1997).
not appreciably changed. The quality of bedrock well waters is closely related to the composition of the surrounding bedrock.

Two new elements were included in this survey: I and Sn. Although occurring in very low concentrations, iodine (median in dug wells 2.1 μg/L and drilled wells 3.0 μg/L, respectively) has a similar characteristic to the other halogenides (Cl, F, Br) as far as its areal distribution is concerned: the highest concentrations are located along or nearby the coastline. The iodide concentrations of groundwater in the basement rocks are too low to fulfill the intake amounts required by metabolism and the balanced human nutrition.

Tin concentrations are also very low (median <0.5 μg/L) and only in 10 water samples the Sn values were over the detection limit.

REFERENCES


A PROEDURE TO INVESTIGATE THE LAND USE POTENTIAL OF BEDROCK AREAS, AN EXAMPLE FROM THE HÄMEENLINNA-RIIHIMÄKI REGION

by

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Introduction

The new Finnish Land Use and Building Act, that was approved on January 19, 1999, gives local authorities more extensive powers to make independent decisions on the matters of land use planning. The common aim of the new Act is to improve both the good living environment and the ecologically, economically, socially and culturally sustainable development. These principles were already considered in the previous Act. The new Act has specified them. Among the aims of the land use planning are the maintaining of biodiversity, promotion of environmental conservation, prevention of environmental hazards and economic use of natural resources.

The new Act also includes the goals of national land use that have been approved by the Finnish Council of State. The main aims comprise of themes as: functional community structure, cultural and natural heritage, recreation, natural resources and special areas with natural and cultural values. Additionally the international agreements considering the biodiversity and climate changes are included in the goals.

This study on the land use potential of bedrock areas is a sub-project within PSSD-project. PSSD (Planning System for Sustainable Planning) is a transnational GIS development project, which is one realization of the European regional development fund, INTERREG II C. The project started in 1998 and it was completed in the beginning of 2001. The PSSD-project is administrated by the Regional Council of Päijät-Häme on behalf of the South Finland Regional Alliance. It has partners from Finland, Denmark and Germany. The main idea of PSSD was to develop a GIS-based planning method, application and decision support system for promotion of sustainable planning in the Baltic region. The results of the project have been published in the Methodical Report, the Technical Toolbox Report and the Administrative Final Report. However, the most comprehensive presentation of the results is offered by the Planner's TOOLBOX which can be found from web page at http://www.pssdtoolbox.net.

Geological Survey of Finland (GTK) and the Regional Council of Häme have carried out a co-operative study on the land-use potential of the bedrock areas in the Hämeenlinna-Riihimäki region. Eight municipalities are included in the research area. This study endeavours to develop a GIS-based procedure to investigate the potential land-use of the bedrock areas. The aim is to investigate the distribution of bedrock areas which need protection and bedrock areas for possible exploitation. This is done by considering the various limitations of the utilization of rock material and rock material suitability.

Aim and purpose of the study

The pressure to exploit bedrock material for construction purposes is growing in Finland. Simultaneously the need to protect bedrock areas for scientific,
scenic and other purposes has been identified. For the aims of sustainable land use planning a comprehensive geographical information processing method has been developed to identify the current state of the land use of bedrock areas.

The land-use potential of bedrock areas in the Hämeenlinna-Riihimäki region has been investigated by using GIS. The purpose of the study was to identify a suitable way to delineate the bedrock hill areas and to examine the distribution of the needs for protection and for the potential exploitation of the bedrock areas within the study area. The GIS has been used as a tool to manage and analyze various data in the study area.

In Finland, the comprehensive nationwide GIS databases are a significant asset for regional planning purposes. The Regional Council of Häme has developed GIS-oriented methods as an essential part of regional planning and has gathered extensive databases. Simultaneously there is a requirement to develop GIS-analysis methods for planning purposes and for environmental impact assessment. GIS methods are an efficient way to analyse vast amounts of spatial information for different land use planning purposes. The combination of vector and raster data techniques gives opportunities to classify and evaluate information.

Delineation of bedrock areas

The first objective of the study was to find out an appropriate way to delineate morphologically distinct hilly areas of bedrock i.e. areas where the overburden is on an average less than 2 to 4 metres thick. The topographic database of the National Land Survey of Finland has information on bedrock outcrops and cliffs (National Land Survey of Finland 1998a). This data has been completed with Quaternary geological mapping data of GTK (Geological Survey of Finland 2000a). This database has information of bedrock areas where the overburden is less than one metre and also of small outcrops and striae. These two databases need to be enhanced with the supplementary information gained from the analysis of the Digital Elevation Model (DEM) of the National Land Survey of Finland (National Land Survey of Finland 1998b). The final delineation combined with the hillshaded Quaternary geological map from a part of Loppi municipality is presented in Figure 1.

Classification of bedrock areas

There exists a requirement to obtain a rough estimation of the land use potential in bedrock areas by considering their protection needs and suitability for exploitation. For practical reasons the bedrock areas have been classified in the end result map into three classes: protection, inspection and exploitation. Protection class includes areas that have strong protection needs. The bedrock areas that do not have strong protection limitations compose the exploitation class. Areas that need more close inspection when considering their potential land use either for protection or exploitation are included in the inspection class. The processing of bedrock protection is done by using a 2-level approach. The limitations are divided into main and secondary levels. The suitability of bedrock material and utilization factors are managed as one level.

The calculation of scenic parameters (visibility, viewed etc. calculations) from the DEM material was studied briefly and found out to be too time-consuming to be feasible for the purposes of our study. Moreover the scenic values are considered to have been adequately taken into account in our GI-method. This has been achieved by the incorporation of the various valuable landscape areas and the buffer zones around the lakes and nature protection areas. Also the valuable bedrock areas study includes a scenic value evaluation.

Limitations for bedrock exploitation

The main limitations of bedrock exploitation are nature protection, valuable landscapes and protection zones of lakes and conservation areas. The secondary limitations of bedrock exploitation are level 2 valuable landscapes, densely populated areas and possible hazardous rocks. The table 1 illustrates these limitations of bedrock exploitation.

The level 1 nature protection areas comprise the areas of the Natura 2000-programme (Suomen ympäristökeskus 2000) which are based on nature and bird directive areas of the European Union. In these areas the exploitation of bedrock material is not allowed. They are the most valuable nature areas.

The level 2 nature protection areas consist of the areas that are included in the official and ratified Regional Plan (Hämeen liitto 1999, 2001). These areas are conservation areas (S), nature reserves (SL1 and SL), ancient historic sites (SM), protection areas of historic buildings and milieu (S2), landscape protection areas (S1), farming and forestry areas with valuable natural landscape (MY) and recreation areas (V). Additionally this level includes valuable bedrock areas of international, national and provincial level (1-4 grade) investigated by Finnish Environmental Institute (Suomen ympäristökeskus 1996). Geologically and geomorphologically valuable bedrock areas in-
Quaternary deposits

- Bedrock terrain, overburden less than 1 meter thick
- Till
- Gravel
- Sand
- Fine sand

Fig. 1. The figure illustrates the hillshaded Quaternary geological map which has been used to check the delineation of bedrock areas. Black line indicates the delineation of bedrock areas. Digital Elevation Model (DEM) © National Land Survey of Finland. Permission number 340/MYY/01.

vestigated by GTK belong to this group too (Kananoja 1999). These areas are presented as points with a 200 metre buffer zone. These areas are of international, national, provincial or local importance.

The level 1 valuable landscape areas comprise urban areas (A) and areas of agriculture (MT) of the Regional Plan (Hämeen liitto 1999, 2001). Valuable bedrock areas of local level (5-6 grade) investigated by Finnish Environmental Institute belong to this level (Suomen ympäristökeskus 1996). The 500 metre buffer zone around the lakes and nature reserves (Natura 2000, SL, SL1) is also included in this level. The information on the Building Register has been buffered with a 200 metre buffer zone (Population Register Centre 2000).

The level 2 valuable landscape areas are composed of a 500 to 1000 metre buffer zone around the larger lakes (area over 50 hectares), areas for farming and forestry, where attention is paid recreational and environmental matters (MU) and areas of cultural and natural landscape (ma) of the Regional Plan (Hämeen liitto 1999, 2001).

The settlement areas are presented as a 250x250 metre grid. The threshold of population density is over 20 citizens per square kilometre.

The possible hazardous rocks include black shales,
rocks with possible radiation risk and asbestos bearing rocks. In the area of the Regional Council of Häme no asbestos rocks have been observed. Information on the rocks with a possible radiation risk was collected from GTK’s reports (Seppänen 1983, 1985, 1987). The anomalies are digitized as points in the dataset. A buffer of 50 metres has been calculated for the points. Information on black shales is divided in two categories: 1) known black shale bearing formations, evident in either outcrops or drill cores and in the geophysical map composite, and 2) interpreted black shale bearing formations with no outcrop or drill core evidence but of which geophysical anomalies are similar to those of known formations. In the research area, there are only interpreted black shale rocks (Arkima 1999).

**Rock material suitability**

The information on the bedrock is composed of three different types of datasets. Hard rock aggregate data is verified in field and laboratory, bedrock mapping data is based on field observations but it has generalizations. Data on dimension stones is based on available geological, geophysical and other studies but also on a limited amount of field verifications. According to the quality and suitability of the rock material the bedrock areas have been divided into five different classes: verified hard rock aggregate deposits of good quality, estimated hard rock aggregate deposits of good quality, potential dimension stone deposits, verified bulk stone and other bulk stone deposits.

Verified hard rock aggregate deposits of good quality include bedrock areas that have been verified and evaluated into classes A, I, II or III. Verified bulk stone deposits consist of bedrock areas with class >III aggregate (Vuokko et al. 1999, 2000, Vuokko 2000). Bedrock mapping data (Geological Survey of Finland 2000b) have been reclassified according to the general suitability of the rock types for hard rock aggregate. Estimated hard rock aggregate of good quality compiles verified hard rock aggregate deposits of good quality but it has not as strong status as the areas with verified data. Other bulk stone deposits consist of bedrock areas that do not include any of the three categories mentioned above.

Potential dimension stone deposits have been delineated during the investigations. This data has only two values: potential dimension stone deposits and deposits non-potential for dimension stone (Härmä 1998).

**Evaluation**

All information on the limitations for bedrock exploitation and rock suitability has been converted to raster format. The grid cellsize is 25x25 metres. The evaluation of grids has been done within each level. The stronger the protection status is, the higher the positive numeric value of the grid cell. Bedrock areas have been evaluated with negative numeric values depending on the suitability of rock material. The bedrock
areas of good quality have the most negative numeric values.

Converting the data into raster format makes it easier to compare different datasets. In this study, the end result was obtained by summing up the grid-layers. In limitations for bedrock exploitation each subclass combines of an individual grid-layer. On the other hand, the suitability of rock material is one grid-layer. Therefore the protection values are cumulative in the calculations. The more there are protection factors for one area, the less suitable it is for exploitation.

**Main limitations for bedrock exploitation**

The main limitations of bedrock exploitation have been divided into three categories based on the strength of protection factors. The data has been valued according to the following system:

- **Value 8:** Nature protection, level 1
  - NATURA-areas

- **Value 5:** Nature protection, level 2
  - Protection areas from Regional Plan (codes S, SL, SL1, SM, S1, S2, MY, V)
  - Valuable bedrock areas of international, national and provincial level (classes 1-4)
  - Geologically and geomorphologically valuable bedrock areas (buffer 200 metres; international, national, provincial or local level)

- **Value 3:** Valuable landscape, level 1, protection zones
  - Valuable culture landscape areas and settlements from Regional Plan (codes MT, A)
  - Valuable bedrock areas of local level (classes 5-6)
  - Settlements, 200 metres protection zone for dwelling and free time buildings
  - 500 metres buffer zone for lakes
  - 500 metres buffer zone for nature protection areas (Natura 2000, SL1, SL).

**Secondary limitations for bedrock exploitation**

The secondary limitations combine the information on areas that have possible limitations for exploitation. The data have been evaluated according to the following system:

- **Value 2:** Valuable landscape, level 2
  - 500 - 1000 metres buffer zone for lakes (area over 50 ha)
  - Recreational forests from Regional Plan (code MU)
  - Cultural landscape from Regional Plan (code MA)

- **Value 2:** Settlements
  - Population density over 20 citizens/km²

- **Value 3:** Possible hazardous rocks
  - Lithological areas having possible natural radiation risk
  - Proposed black shale rocks.

**Rock material suitability**

This part classifies the delineated bedrock areas according to their suitability as rock material. The field-verified hard rock aggregate has the strongest status. At first stage, the bedrock areas have been evaluated according to their suitability for hard rock aggregate production. The reclassified bedrock mapping data has been joined to the bedrock areas after this stage. The information on dimension stone potentiality has been added at the last stage. Nevertheless it has a same status as the estimated hard rock aggregate deposits of good quality.

Finally the synthesis of bedrock areas have been evaluated according to the following system:

- **Value -5:** Probable (verified) hard rock aggregate deposit of good quality

- **Value -4:** Possible (estimated) hard rock aggregate deposit of good quality (interpretation from bedrock map)

- **Value -4:** Potential dimension stone deposit (partly verified, mostly interpretation)

- **Value -3:** Probable (verified) hard rock aggregate deposit for general use, i.e. bulk stone

- **Value -3:** Possible (estimated) hard rock aggregate deposit for general use (interpretation from bedrock map), i.e. bulk stone.

**End result**

The evaluated grids have been combined to produce one grid dataset and a corresponding map. An important issue in this combination is the size of the raster datasets. They have to be exactly of same size to get the correct result from the summation of the grids. The evaluated grids have been summed up and the resulting grid datasets have been divided into three classes. The distribution of the three classes is:

- <2: Exploitation class
- 2-2: Inspection class
- >2: Protection class

Figure 2 illustrates the end result map from a part of Loppi municipality.
Conclusions

The land use planning of the bedrock areas is a planning theme gaining more importance as the conflicting pressures of protection and exploitation increase. This is due to the growing need for hard rock aggregate exploitation simultaneously with a clear demand to protect the most valuable bedrock areas because of their nature (geological and biological) and scenic values.

The developed tool demonstrates the strengths of GIS-based analysing methods for the decision support compared with the traditional planning procedures. Almost 30 different numerical map and database materials were used as a base of information. A 3-category bedrock area classification was produced from these data by the application of vector and raster analyses. Substantial cost reductions can potentially be achieved by the utilization of the described work method.

Based on the end result map it is evident that both protection, inspection and exploitation classes are presented. The synthesis map illustrates that the chosen class limits will give results that contain relatively large areas in every part of the pilot area which are suitable for exploitation. The protection areas and zones locate in the appropriate places in relation to the aims of functional protection and development of settlement structure. The areal extent of the areas of inspection class is quite large. These areas divide the exploitation and protection areas under evaluation in such a way that will give flexibility for the planners and decision makers to deal with and accept plans and exploitation permits.

The developed bedrock classification method is considered to be appropriate and evidently sufficient for the general regional and communal land use planning. The method is a suitable tool when striving...
to achieve the objectives of the new Finnish Land Use and Building Act that include sustainable development, good living environment and sustainable use of the natural resources. The method has also potential for the various environmental impact assessments in the regional and general planning level.

REFERENCES


SULPHUR SPECIATION - METHOD VALIDATION AND TESTING

by
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Key words (GeoRef Thesaurus, AGI): chemical analysis, soils, pollution, sulfur, chemical fractionation, methods, testing, Monchegorsk, Russian Federation.

Introduction

Effects of acid rain on terrestrial ecosystems have been studied intensively for many years. The anionic components of acid rain, mostly sulphate and nitrate, often constitute even more significant additions to the ecosystems than $H^+$. Sulphate can leach cations from soils but on the other hand cation leaching can be reduced if the soils have the capacity to adsorb sulphate (Singh 1984b). Possible retention mechanisms include microbial sulphate immobilization, sulphate adsorption on hydroxides and clay minerals, and precipitation of aluminium hydroxy sulphate minerals (Mayer et al. 1995). In forest soils, a large part of sulphur is in the organic constituents ester sulphate and C-bonded sulphate (David & Mitchell 1987). This pool of organic sulphur obviously regulates sulphate flux in soils (Novák & Wieder 1992, Novák et al. 1996). Detailed information on sulphur speciation in soils is necessary in understanding sulphur cycling and the effects of pollution in soil geochemistry.

Inorganic sulphur forms include sulphates ($SO_4^{2-}$), elementary sulphur ($S$) and other metal sulphides (e.g. FeS). Sulphates can occur in soil solution or as adsorbed sulphate or as insoluble forms. Several other oxidised sulphur species can also exist or be formed e.g. bisulphide ($S_2^-)$, polysulphide ($S_{2n}^-$), thiosulphate ($S_2O_3^{2-}$) and dithionite ($S_2O_4^{2-}$) e.t.c. Organic sulphur forms are generally divided into ester sulphate group (organic sulphates containing C-O-S linkages, e.g. choline sulphate, phenolic sulphates, sulphated polysaccharides) and carbon-bonded sulphur in which sulphur is directly bonded to carbon (mainly sulphur bound in amino acids, proteins, vitamins, aliphatic sulphones, sulphonates and sulpholipides) (Tack et al. 1997). The objective of this study was to develop a quick and simplified analytical procedure to fractionate sulphur in soil samples into its inorganic and organic constituent compounds.

Materials and methods

Accurate determination of the reduced forms of inorganic sulphur is difficult because they can easily be oxidised on exposure to air. In this study, two different drying methods were used (freeze drying and oven drying at 70°C) to find out if the preparation method effects different sulphur species.

For the extraction of inorganic sulphates solutions containing different concentrations of phosphate, carbonate, chloride and water can be used. In this study, the mobile sulphate fraction of soil is extracted with water and the adsorbed sulphate is extracted with phosphate solution. Both extracts contain also a small portion of other sulphur forms in addition to sulphates. Because the extracts are measured with ICP-AES, the concentrations are total sulphur concentrations.

After these two extractions, the sample was treated with two reducing agents. Mono- and disulphides and elementary S were reduced to $H_2S$ using Cr(II). The evolved $H_2S$ was collected to aqua regia by oxidation to sulphate. Total sulphur concentrations of the solutions were analysed using ICP-AES.

Organic ester sulphates were separated from the residue after the above treatments using HI-reduction. The C-bonded sulphur was calculated by sub-
tracting the water soluble, phosphate soluble, Cr-reducible and HI-reducible sulphur from the total sulphur.

Using this fractionating procedure samples from three different test sites were analysed. Test sites were situated in Kola peninsula in the vicinity of Monchegorsk Ni-Cu-smelter and they were affected by varying airborne deposition of heavy metals and sulphur.

**Apparatus**

The freeze drier used was HETO FD 8.0 (Heto-Holten A/S, Allerod, Denmark).

The distillation apparatus is presented in Figure 1. An electric heating mantle was used in the distillations.

A Thermo Jarrell Ash 61E Polyscan set up to determine 32 elements simultaneously was used in this study. The emission line for sulphur was 182.040 nm.

Ion-chromatograph was Dionex 2000i equipped with a conductivity detector.

**Reagents**

* Sulphur standard solution *was prepared from a multielement stock solution provided by Inorganic Ventures Inc. containing 200 μg/ml S. Stock solution was diluted 1:10. Matrix matching to 20% aqua regia for each solution in ICP-AES measurements was used.

* Aqua regia*: hydrochloric acid (HCl) and nitric acid (HNO₃) were combined at a proportion of 3:1. The solution has to be prepared just before use.

\[ NaH₂PO₄ (0,032 M): 4.4157 \text{ g (M = 137.991 g/mol)} \]

is dissolved to 1000 ml distilled water.

\[ CrCl₃ \text{-solution (1 M): 133.22 g CrCl₃·6 H₂O (M = 266.45 g/mol)} \]

is dissolved to 500 ml 0.5 M HCl.

* Cr(II) solution*: Zinc pieces were washed with 1 M HCl. 1 M CrCl₃ solution was added to a vessel containing zinc pieces under a continuous flow of argon. The solution reacts with zinc reducing Cr³⁺ to Cr²⁺. The reaction takes about 10-30 minutes during which time the solution turns from dark green to dark blue. The solution was prepared daily.

* HI-solution*: Hypophosphorous acid (H₃PO₂, 30-32%), formic acid (HCOOH, 98-100%), hydriodic acid (HI, 57%) were combined at a proportion of 4:2:1. The solution was prepared just before use.

**Procedures**

**Sampling**

Profile samples from three test sites were collected in July 1999. Test sites were chosen at different distances from Monchegorsk Ni-Cu-smelter (Fig. 1). On test site 3, the visible effects of pollution from the smelter were severe. The erosion was clearly seen and the organic horizon and the leaching horizon were missing. On site 2, the effects of pollution were clear but they were not as distinct as on site 3. Distance to the smelter was greatest for test site 1 where the effects of the pollution were not visible.

The parent material was at the test sites 1 and 2 basalt till (stony sandy till) mixed with glaciolacustrine silt and at the eroded site 3 glaciofluvial silty sand (Räisänen, M-L. personal communication, 2001). The texture of the <2.0 mm fraction in horizons varied from sand (E, B) to loamy and clayey sand (BC, C) at the site 1, from fine sand (E, B) to sand (BC, C) at the site 2 and from sand (B1) to silty and clayey sand (B2, BC, C) at the eroded site 3.
Sample preparation

Samples were divided in the laboratory into two subsamples. One subsample was dried in 70 °C and the other was freeze dried. Dry samples were sieved with nylon sieves to less than 2 mm. Both subsamples were analyzed in a similar way.

Sulphur speciation procedure (Fig 2):

Total sulphur

1.0 g of sample was weighed in a borosilicate tube, 9.0 ml hydrochloric acid and 3.0 ml nitric acid was added. The sample was left standing overnight and after that it was digested in 90 °C for two hours. After digestion the volume was made up to 60 ml using distilled water. After centrifugation the supernatant was used for ICP-AES analysis.

H₂O soluble sulphur

3 g of the material to be analysed was weighed into a 50 ml polyethylene centrifugal tube. 30 ml of water was added and the tube was shaken horizontally for 30 minutes (215 rpm/min). The resulting suspension was centrifuged (10 min, 2900 rpm) and filtered through 0.45µm membran filter (Schleicher & Schuell) and sulphur content was analysed by ICP-AES. Matrix matching to 20 % aqua regia was used in ICP-AES measurements. Some of the test solutions during method development were analysed by ion chromatograph for SO₄²⁻.

NaH₂PO₄ soluble sulphur

After the H₂O-supernantant was poured off, 30 ml of 0.032 M NaH₂PO₄ was added and again the mixture was shaken for 30 minutes. After centrifugation and filtering the sulphur content of the supernatant was analysed. Matrix matching to 20 % aqua regia was used. Some of the test solutions during method development were analysed by ion chromatograph for SO₄²⁻.

Cr²⁺-reducible sulphur

The residual soil from the above steps was transferred into a round bottom flask to which a Dimroth condencer was attached (Fig. 3). After the system had been purged with argon for 10 minutes at a bubbling rate of 1-2 bubbles/s, 20 ml of Cr(II)-solution was introduced to the reaction vessel and the suspension was brought to boiling. The evolved hydrogen sulphide is carried by argon gas stream into a vial containing absorbing solution which was either 30 ml of 1:10, 30 min.

Fig. 2. Sulphur speciation.

Fig. 3. Distill a tion apparatus. 1. 250 ml flask, 2. Syringe with thin needle, 3. Silicon septum, 4. Reflux condencer, 5. Absorption vial (30 ml), 6. Electric heating mantle.
0.05 M NaOH or 12 ml freshly prepared aqua regia. After 1 hour 40 minutes the solution was removed. To NaOH solution 200 µl H₂O₂ was added to ensure oxidation of sulphide to sulphate (Shan et al. 1992). After matrix matching to 20 % aqua regia the sulphur concentration of the absorption solutions were analysed using ICP-AES.

**HI-reducible sulphur**

After a new absorption solution was installed, 42 ml of HI-solution was added slowly to the reaction vessel. The suspension was boiled for 1 hour and 10 minutes. The absorption solution (NaOH or aqua regia) was removed and the sulphur was analysed using ICP-AES after matrix matching to 20 % aqua regia.

**Carbon-bonded sulphur**

The C-bonded sulphur was calculated by subtracting the water soluble, phosphate soluble, Cr-reducible and HI-reducible sulphur from the total sulphur.

**Method development**

**Comparison of drying methods**

To find out the effect of sample preparation method to different sulphur fractions two different drying methods were compared. The effect of drying method was clearly seen only in the fraction of NaH₂PO₄-soluble sulphur (Fig. 4). In oven drying, the samples were exposed to air and the reduced forms of inorganic sulphur were oxidised to sulphates. Thus, in the samples that were dried in 70°C the sulphate concentrations were higher than in the freeze dried samples.

**Water soluble sulphur and NaH₂PO₄-soluble sulphur**

Water was used to extract mobile sulphur compounds from soil samples. When the sample was extracted with phosphate solution the adsorbed sulphate ions were replaced with phosphate ions and transferred into the solution.

Soil solution ratio 1:10 was used (Shan et al. 1992) in both extractions. Repeatability of the extractions was studied using four samples with different sulphur concentrations (Table 1). The effect of extraction time was also studied (Table 2). Using 30 minutes extraction time 90 % recoveries were achieved considering 960 min extraction time as total water soluble S-fraction. Also Singh’s (1984b) studies confirm that 30 min extraction time is adequate.

When testing the effects of extraction time some of the extracts were measured with ICP-AES and with ion chromatograph (Table 2). The sulphur concentrations from IC-measurements were smaller than the concentrations obtained using ICP-AES. The IC-measurements give the concentration of sulphate-sulphur whereas the ICP-AES measurement gives the total sulphur concentration in the solution. The results indicate that both water and phosphate extract

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**Figure 4** Phosphate soluble sulphur in freeze dried and oven dried samples.

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Table 1. Results of water-soluble and phosphate soluble sulphur, repeatability tests.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H₂O-extraction</th>
<th>NaH₂PO₄-extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>Sulphur concentration mean (mg/kg)</td>
</tr>
<tr>
<td>5.3</td>
<td>7</td>
<td>3120</td>
</tr>
<tr>
<td>7.3</td>
<td>5</td>
<td>11400</td>
</tr>
<tr>
<td>8.3</td>
<td>5</td>
<td>36</td>
</tr>
<tr>
<td>98.3</td>
<td>6</td>
<td>281</td>
</tr>
</tbody>
</table>

Table 2. Effect of extraction time on a) water soluble and b) phosphate soluble sulphur. Results are expressed as the average of n replicate determinations ± the standard deviation.

<table>
<thead>
<tr>
<th>a) Extraction time (min)</th>
<th>Sample 5.3 ICP-AES</th>
<th>IC</th>
<th>Sample 7.3 ICP</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>2</td>
<td>2960 ± 3</td>
<td>2710 ± 148</td>
</tr>
<tr>
<td>30</td>
<td>3</td>
<td>2970 ± 21</td>
<td>2630 ± 85</td>
</tr>
<tr>
<td>60</td>
<td>3</td>
<td>3000 ± 30</td>
<td>2670 ± 42</td>
</tr>
<tr>
<td>210</td>
<td>3</td>
<td>3050 ± 35</td>
<td>2700 ± 61</td>
</tr>
<tr>
<td>480</td>
<td>3</td>
<td>3080 ± 27</td>
<td>2770 ± 32</td>
</tr>
<tr>
<td>960</td>
<td>3</td>
<td>3180 ± 30</td>
<td>2860 ± 90</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>b) Extraction time (min)</th>
<th>Sample 5.3 ICP-AES</th>
<th>IC</th>
<th>Sample 7.3 ICP</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>3</td>
<td>262 ± 4</td>
<td>189 ± 2</td>
</tr>
<tr>
<td>40</td>
<td>3</td>
<td>264 ± 9</td>
<td>188 ± 5</td>
</tr>
<tr>
<td>60</td>
<td>2</td>
<td>294 ± 8</td>
<td>210 ± 16</td>
</tr>
<tr>
<td>230</td>
<td>2</td>
<td>299 ± 4</td>
<td>211 ± 9</td>
</tr>
<tr>
<td>435</td>
<td>2</td>
<td>297 ± 7</td>
<td>207 ± 13</td>
</tr>
<tr>
<td>960</td>
<td>3</td>
<td>299 ± 7</td>
<td>204 ± 6</td>
</tr>
</tbody>
</table>

also non-sulphate which may be lost if IC-analysis is used.

**Cr³⁺-reducible and HI -reducible sulphur**


Effect of the time and amount of added reagents to these reductions was studied. Sum of these fractions remained constant even when the reaction times were changed (Fig. 5). If the time used for Cr(II) reduction is not long enough, or if the amount of the reagent is not sufficient before HI-solution is added, the Cr-reducible sulphur compounds left in the mixture will be oxidised by HI-solution. Conditions for Cr-reduction must be chosen carefully so that the fractionation succeeds. Best recoveries and repeatabilities for Cr-distillation were achieved using 100 minutes distillation time and adding 20 ml Cr(II)solution. For HI-distillation optimum time and reagent amount were 70 minutes and 42 ml (Table 3).

At first 0.01 M NaOH solution was used in absorbing the H₂S formed in the reaction. In ICP measurements alkaline solutions can cause nebulization problems and high concentrations of Na lead to severe interferences. To avoid these problems, and also to avoid diluting that comes from matrix matching of the samples, the efficiency of aqua regia as collecting solution was tested. Freshly prepared aqua regia contains gaseous oxidizing compounds (e.g. chloride, nitrosylchloride and nitrogen oxides) which oxidize hydrogen sulphide to sulphate. The results show that freshly prepared aqua regia was as good as alkaline solution in absorbing H₂S (Table 4).
Results and discussion

The results of the samples collected from Kola peninsula are presented in Table 5. Proportional values of each fraction from total sulphur in the freeze dried samples were also calculated (Fig 6).

Freeze drying of the samples is a recommendable preparation method because it does not change the sulphur constituents in soil samples. This was proven also by David & Mitchell (1987) who also found out that oven drying at 65°C causes changes in concentrations of extractable sulphate. Canfield et al. (1986) determined total sulphur and chromium reducible sulphur from field moist samples, freeze-dried samples and from samples dried in room temperature. According to their results sample preparation has no clear effects to these sulphur fractions.

Table 3. Results from Cr(II)-reduction and HI-reduction distillations of sample 98.3 using different distillation times and reagent amounts.

<table>
<thead>
<tr>
<th>Cr(II)-distillation</th>
<th>HI-distillation</th>
</tr>
</thead>
<tbody>
<tr>
<td>t (min) reagent amount (ml)</td>
<td>mg/kg S</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
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<tr>
<td>80</td>
<td>20</td>
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<tr>
<td>100</td>
<td>20</td>
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<td>70</td>
<td>42</td>
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<tr>
<td>50</td>
<td>42</td>
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<tr>
<td>50</td>
<td>42</td>
</tr>
<tr>
<td>50</td>
<td>42</td>
</tr>
</tbody>
</table>

Table 4. Cr-reduction results of sample 98.3. Absorption solutions for \( H_2S \) NaOH or aqua regia.

<table>
<thead>
<tr>
<th>Absorption solution</th>
<th>Cr(II)-reduction S mg/kg</th>
<th>RSD %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 M NaOH n = 12</td>
<td>599</td>
<td>9.7</td>
</tr>
<tr>
<td>aqua regia n = 5</td>
<td>599</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Total sulphur

Highest concentrations of total sulphur were found in the organic horizon in the test sites 1 and 2.

In the most polluted site (site 3) the concentration was highest on the uppermost part of the B-horizon. E-horizon and C-horizons have low S-concentrations. In the C-horizon, the S-concentration correlates with the geology of the area and is at all sites below 50
### Table 5. Sulphur concentration of samples collected from the Kola peninsula. All fractions. Proportional value from total sulphur for each fraction is given as percentages.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Lowest depth (cm)</th>
<th>Water soluble S (mg/kg)</th>
<th>Phosphate soluble sulphur (mg/kg)</th>
<th>Cr-reducible sulphur (mg/kg)</th>
<th>HI-reducible sulphur (mg/kg)</th>
<th>C-bonded sulphur (mg/kg)</th>
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<tr>
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<td>0</td>
<td>1490</td>
<td>57.3</td>
<td>3.9</td>
<td>13.0</td>
<td>9.6</td>
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<tr>
<td>E</td>
<td>4</td>
<td>55</td>
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<tr>
<td>B1</td>
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<td>514</td>
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<td>44</td>
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<td>1.3</td>
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<td>6.3</td>
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</tbody>
</table>

Oven dried samples | | | | | | |
| O       | 0                 | 1340                    | 47.3                             | 3.5                        | 22.1                      | 1.6                       | 37.3                       | 2.8                        | 159 | 11.8 | 1075 | 80.3 |
| E       | 2                 | 54                      | 8.5                              | 0.2                        | 0.5                       | 6.1                       | 11.6                       | 10.2                       | 19.7| 31   | 59.8 | x    |
| B       | 14                | 657                     | 12.8                             | 3.4                        | 13.8                      | 21.0                      | 21.7                       | 1.3                        | 13  | 1.9  | 59   | 1.9  |
| BC1     | 26                | 303                     | 10.3                             | 3.4                        | 12.8                      | 21.7                      | 21.7                       | 1.9                        | 13  | 1.9  | 59   | 1.9  |
| BC2     | 45                | 89                      | 1.0                              | 0.7                        | 3.9                       | 1.3                       | 43.8                       | 7.8                        | 16  | 18.3 | 23   | 25.5 |
| C       | 65                | 31                      | 3.8                              | 1.2                        | 3.6                       | 6.3                       | 13.4                       | 5                          | 17.2| 10   | 31.8 | x    |

Freeze dried samples | | | | | | |
| O       | 0                 | 1490                    | 67.4                             | 4.5                        | 26.1                      | 1.7                       | 69.4                       | 4.6                        | 243 | 16.3 | 1086 | 72.9 |
| E       | 2                 | 54                      | 6.7                              | 0.2                        | 2.0                       | 11.2                      | 20.2                       | 11.2                       | 20  | 4.9  | 24   | 45.1 |
| B       | 14                | 659                     | 17.2                             | 2.6                        | 256                       | 38.9                      | 30.4                       | 4.6                        | 64  | 9.8  | 156  | 23.8 |
| BC1     | 26                | 327                     | 11.3                             | 3.3                        | 102                       | 31.0                      | 20.6                       | 4.3                        | 14  | 3.4  | 150  | 46.0 |
| BC2     | 45                | 89                      | 5.6                              | 0.8                        | 19.2                      | 21.8                      | 18.9                       | 1.9                        | 14  | 1.9  | 32   | 36.2 |
| C       | 65                | 29                      | 2.6                              | 1.3                        | 4.2                       | 13.6                      | 45.6                       | 5                          | 15.8| 5.8  | 18.5 | x    |

**Note:** If a result is missing, it is indicated by an asterisk (*) in the data column. The concentration of C-bonded sulphur was calculated by subtracting concentrations of water soluble, phosphate soluble, Cr-reducible and HI-reducible sulphur from the total sulphur concentration.

x = result missing, * = concentration of C-bonded sulphur was calculated subtracting concentrations of water soluble, phosphate soluble, Cr-reducible and HI-reducible sulphur from the total sulphur concentration.

mg/kg.

In the test sites of this study, the total sulphur concentrations of B-horizons are high compared to values Reimann et al. (1998) found in their studies from the same area. In their median concentration for B-horizons is 162 mg/kg and for C-horizons 30 mg/kg.

Novák et al. (1996) found a positive correlation between sulphur concentration in the A (0) horizon and atmospheric S loads. Kashulina and Reimann (2000) concluded that admixture of mineralogical material is the major factor influencing total S concentrations in the O- and E-horizons. In the B-horizon, S can derive from the soil material or it can be linked to organic material. The mobile fraction can also accumulate into B-horizon.

**Water soluble sulphur**

Because the sulphur concentration of water and phosphate extracts was measured using ICP-AES, the results contain also other sulphur compounds than sulphates.

The proportion of water soluble sulphate was small in all samples (1-10%). The highest proportions were found in the E-horizon of the sites 1 and 2. In the test site 3, where the O- and the E- horizon are missing, the highest proportion was in the C-horizon. In all sites the
Fig. 6.1  a) a view from the test site

b) proportional values of each fraction calculated from total sulphur

c) test pit

Fig. 6.2  a) a view from the test site

b) proportional values of each fraction calculated from total sulphur

c) test pit
absolute amounts of mobile sulphate are low. The highest concentrations are in the uppermost horizon.

Kashulina and Reiman (2000) studied the effects of sulphur pollution in the Kola district. According to their results pollution influences the availability of S in the B-horizon. The proportion of water extractable S was found to increase from 1-2% in the background catchments to almost 20% in the polluted areas. They also found a high proportion of water-extractable S in the C-horizons of podzols and concluded that it is due to effects of strong S-deposition.

**NaH₂PO₄-soluble sulphate**

Proportions of adsorbed sulphate were greatest in the B-horizons in all test sites (30 - 65%). The smallest proportions were in the organic horizons. The concentrations in the B-horizons are high at all sites, most of them even higher than the mean of the total sulphur concentrations Reimann et al. (1998) found in their studies. In the sites 1 and 2, the absolute and the proportional values are small in the O- and E-horizons and in all plots in the C-horizon.

Nömmik et al. (1988) studied sulphate stores and sulphate adsorption capacity of Swedish forest soils. Their results show that in typical Scandinavian forest soils the inorganic stores are higher in the B-horizon than in other horizons. He did not find a correlation between the atmospheric S deposition and sulphate adsorption. He found a positive correlation between the indigenous soil content of phosphate-extractable sulphate and the capacity of the soils for additional adsorption of added sulphate. Also Gobran et al. (1998) studied sulphate adsorption-desorption of Spodic soils. A sequential batch technique was used to leach mineral horizons with forest floor leachate containing different concentrations of sulphate. They found that the sulphate retention of all horizons increases linearly with the increasing SO₄²⁻ concentration in the solution. Results also show that the retention of SO₄ by the Bs horizons was distinctly higher than by the Ah horizons. They suggest that the most obvious mechanism in the sulphate retention is the specific adsorption of SO₄²⁻ on hydrous oxides and the precipitation mechanisms of basic sulphate minerals.

**Cr³⁺-reducible sulphur**

In all test sites, the highest proportions of Cr-reducible sulphur are in the C-horizon and the highest absolute amounts in the uppermost horizon in all sites. In the E- and C-horizon, the concentrations are lowest.

Reduced forms of sulphur have been studied in
detail in samples of anoxic environments like sediments and bogs (e.g. Nriagu & Soon 1985, Henneke et al. 1997). With the developed method useful information about the pool of reduced sulphur compounds and its participation to sulphate flux in soils can be obtained.

**HI-reducible sulphur and C-bonded sulphur (organic sulphur fractions)**

The proportion of HI-reducible sulphur varied from 10-20%. The C-bonded sulphur variation between different horizons was very large (24 - 80%) and the highest proportions were in the O- and E-horizons. David and Mitchell (1987) have studied sulphur flux in forest soils. In their studies, the C-bonded S was the dominant S constituent in all horizons and the next largest fraction was the ester sulphate. They conclude that sulphate shows rapid conversion to organic S components, especially to ester sulphates in the O horizons. In the mineral horizons, the sulphate is initially retained as adsorbed sulphate. Houle and Carignan (1992) reported high organic S proportions in coniferous boreal forest soils, carbon bonded S 51 - 68 % and ester sulphate 29 - 37 %. They argue that forest ecosystems in a steady state with respect to organic matter do not accumulate organic S in response to increased atmospheric S loading even though organic S is dominant in most soils.

**Conclusions**

The developed method suites well for fractionating different sulphur species in soil samples. It is a useful tool in research work where effects of heavy deposition of sulphur cycling are studied. Because the relative errors are rather large in some steps, the estimation of minor fractions is not very accurate.

The effect of drying methods is clearest in the amount of adsorbed sulphate. Oven drying gives higher results than freeze drying because reduced S compounds may oxidise during oven-drying. For this reason freeze drying is a recommendable preparation method.

Total sulphur in all the fractions is easily determined using ICP-AES. Freshly prepared aqua regia is a convenient collector for H,S when the solution is to be analysed with ICP-AES.

**Acknowledgements**

I would like to thank all the people working in the Barents Ecogeochemistry project, especially Galina Kashulina from Kola Science Centre (INEP) and Jouni Aarrevaara (GTK) for collecting these samples and arranging the transport of the samples to Finland. Also I would like to thank Marja-Leena Räisänen for helping me in the soil classification of the test sites.

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Sulfide deposits, black schists, hydrothermal alteration, Proterozoic, Hammaslahti, Finland

Key words (GeoRef Thesaurus, AGI): geophysical methods, airborne methods, magnetic methods, gamma-ray methods, massive sulphide deposits, black schists, hydrothermal alteration, Proterozoic, Hammaslahti, Finland

Introduction

The geophysical response for variation of magnetic mineralogy and radioelement relations characteristic of a sediment-hosted massive sulphide deposit were investigated in the Pyhäselkä region in eastern Finland. The specific question was if the associated hydrothermal alteration can be outlined by interpretation of airborne geophysical data. The study focused on the Cu-Zn-Au deposit at Hammaslahti, where the geological and geochemical factors have earlier been described in detail (Loukola-Ruskeeniemi et al. 1991).

Aerogeophysical surveys have traditionally been successful in exploration for base-metal bearing sulphide mineralisations. Since 1972 the Geological Survey of Finland (GTK) has carried out high-resolution low-altitude (c. 35 m) airborne surveys and has developed the so-called three-in-one system measuring simultaneously the magnetic and electromagnetic fields and the earth’s gamma-radiation. The electromagnetic dual-frequency system was particularly designed for exploration and mapping of base-metal bearing sulphide mineralisations. Most known sulphide deposits in Finland are spatially related to the early Proterozoic metamorphosed black shales (so-called black schists), which are geophysically easy to map. This is because of their typically good electrical conductivity and strong magnetic properties, particularly the high remanent magnetization owing to their monoclinic pyrrhotite content. Black schists are commonly also well expressed in the airborne gamma-radiation data. Since massive sulphide deposits are generally characterized by hydrothermal alteration of their host rocks, it is expected that changes in the relative concentrations of uranium, thorium and potassium would be detected in the regional radiometric data.

Close to the Hammaslahti deposit, about 10 km to the northwest, the so-called Mulo schists are geophysically distinctive, but so far they are not known for economical base metal deposits. In this paper, their geophysical similarities and differences are compared with the Hammaslahti region rocks.

Geological and geophysical setting

The sediment-hosted Hammaslahti massive sulphide Cu-Zn-Au deposit is situated at the Archean-Proterozoic boundary close to the eastern margin of the Early Proterozoic Svecofennian province. Decreased overall magnetization characterizes this boundary zone (Fig. 1) but it contains local N to NW trending narrow magnetic anomalies, which mainly are caused by pyrrhotite-bearing metamorphosed schists or ultramafic igneous rocks. Several base-metal bearing sulphide deposits are known along this metasedimentary belt, such as Hammaslahti, Kylylahti, Luikonlahti, Alalen and Talvivaara. The correlation based on the
geochemical and geophysical data for the black schists from this belt (Airo & Loukola-Ruskeeniemi 1991) contains classification of black schists from an ordinary graphite-bearing shale to the ore-prognostic type. Hammaslahti and Mulo schists belong to a NNW trending metasedimentary basin of age 2.0-1.9 Ga (Ward 1987). Tholeiitic metabasalts have erupted in the rifted basin, which is mainly composed of metaturbidites and characterised by intercalated highly magnetized and electrically conductive black schists and other graphite-bearing schists. The Archean granitoids and greenstone belts are seen as moderately magnetized regions in the East in Figure 1.

**Hammaslahti and Mulo schists**

Black schists are characterized by their commonly distinctive magnetic properties due to their monoclinic pyrrhotite content and by their high electrical conductivity, which is a result of their high graphite content.

**Hammaslahti Cu-Zn-Au deposit**
- massive sulphide deposit in Eastern Finland, about 20 km SSW of Joensuu
- situated close to the Archaean-Proterozoic boundary and the Outokumpu Cu-Zn-Co district
- Outokumpu OY mined 7 million tons of ore grading on average 1.16% Cu and minor amounts of Zn and Au
- mining active during 1973-1986
- mineralisation is hosted by hydrothermally altered Early Proterozoic metaturbidites
- the hanging-wall is characterised by a steeply W-dipping sheared black schist layer
- major sulphide minerals are pyrrhotite, chalcopyrite, pyrite and sphalerite
The high-amplitude N to NW trending magnetic anomaly bands seen in Figure 2 are mainly caused by the black schists. The same zones in Figure 3 are variably electrically conductive. The best conductors are graphite-bearing phyllites and mica schists, which are distinguished from black schists by their generally weak magnetization. The magnetization and electrical conductivity of the black schist horizons decrease south of Hammashlahti mine (Figs. 2 and 3).

The structural control of Hammashlahti sulphide deposit is apparent from the magnetic horizontal gradient image (Fig. 4). The curved structures (trend enhanced by blue) of the metasedimentary basin are disturbed by a series of NW-SE trending faults. These are thrust faults along which the Svecofennian rocks were placed onto the Archean basement complex from west to east (Ward 1987). The Mulo schists are located along the same thrust faults (also trend enhanced by blue). Evidently the strong magnetization of Mulo schists is caused by the increased amount of monoclinic pyrrhotite due to deformation along the thrust surface. Based on the magnetic gradient image the Hammashlahti sulphide mineralisation is located at the intersection of a thrust fault and an almost NS trending fracture zone (enhanced by red), which parallels the axial plane of the Hammashlahti synclinal structure. Some of the NW-SE trending faults are associated with weak positive magnetic anomalies indicating intrusion of mafic dyke rocks along these fracture zones. The same fault trend is characteristic of the Archean basement province east of Pyhäselkä area, but there the early Proterozoic mafic dyke swarms are much more numerous.

The airborne gamma-ray ternary image in Figure 5 maps broadly the main lithological variation of the area, although the radioelement content of the surficial cover complicates the interpretation. The tectonic diamond-pattern of the Pyhäselkä region is determined by the large-scale tectonic framework of the area. The shapes of lakes and mires follow this pattern. The western margin of late Archean granitoid and gneiss province is marked by dominant K + Th signatures. Westwards the dominance of Th grows due to the metaturbiditic material in the sedimentary basin of the Svecofennian province. The E-W trending esker in the centre of the image is high in all three elements, K + U + Th, and it divides the map area into two slightly different parts. The southern part is low in all three radioelements, although with dominant K, which largely reflects the K concentration in soils. The northern part is higher in all three elements, particularly the province which contains the Mulo schists. According to the different typical colours in Figure 5, the radioelement concentration within the bedrock unit, which contains the Hammashlahti deposit, differs from the neighbouring units. This unit is particularly low in K and Th, except the local K maximum precisely at the sulphide mineralisation. Potassium depletion due to hydrothermal alteration associated with Hammashlahti deposit is known from geochemical evidence (Loukola-Ruskeeniemi et al. 1991). The local increase of potassium is probably due to sericitisation, which is typical of the mineralised zones in Hammashlahti.

Data sets and methods

Field mapping. Block samples from 14 different places around the Hammashlahti deposit were collected to complement the existing data from the area and data from the GTK’s petrophysical database. The samples were selected on the basis of their magnetic susceptibility measured in the field. Structural features such as the strike of schistosity, bedding and cleavage planes were compared to the interpreted magnetic structural features. Two main strikes of schistosity were observed: a more N-S trending related to the weakly magnetic schists in the basin area, and a NW-SE related to the Mulo schists. These directions correspond to the main magnetic anomaly strike of the same formations.

Petrophysical properties, petrophysical laboratory, GTK. Density, magnetic susceptibility and intensity of remanent magnetization of the collected block samples were measured in the petrophysical laboratory. Their properties were compared to those of drill core samples taken from the hanging-wall black schist of the Hammashlahti ore deposit and black schists exposed in the area. The scatter diagrams of magnetic susceptibility against density and remanent magnetization showed that petrophysically the collected block samples correspond to the average Finnish graphite-bearing and black schist type described by Airo (1997).

Curie points, paleomagnetic laboratory, GTK. The temperature dependence of the magnetic susceptibility of the samples were measured in the paleomagnetic laboratory by using the CS-2 Apparatus and KLY-2 Kappabridge. This variation is monitored as a thermomagnetic curve and it is used to identify the ferrimagnetic mineral composition on the basis of the characteristic Curie temperature (= Curie point) of each ferrimagnetic mineral. At this temperature the magnetization of the ferrimagnetic substance decreases to the value which corresponds to its paramagnetic state. Two of the samples (of magmatic type) primarily contained magnetite, while the schist samples contained pyrrhotite. Two of the schist sam-
Fig. 2. Aeromagnetic image of Hammaslahti and Mulo regions.

Fig. 3. Horizontal derivative of magnetic field combined with electrical conductors.

Fig. 4. Magnetic horizontal image and the interpreted thrust fault trend.

Fig. 5. Ternary image of gamma-radiation.
samples contained only monoclinic pyrrhotite, while the rest contained two-phase pyrrhotite: hexagonal pyrrhotite together with the monoclinic type. The hexagonal pyrrhotite switched to monoclinic at ~220-280 °C. Since this change is not reversible, it can be proposed that the hexagonal pyrrhotite was formed after the temperature peak of the regional metamorphism, e.g. during a post-metamorphic mineralising process. Further temperature increase in laboratory tests resulted in production of magnetite above ~400 °C. During heating of graphite-bearing schists carbon consumes oxygen, which is required in the process of developing magnetite. Two of the samples that contain monoclinic pyrrhotite have greater values of total carbon (3.30% and 2.13%, respectively). In these samples only a very small amount of magnetite was produced during heating. Other samples with less carbon developed more magnetite during heating.

Chemical analysis, chemical laboratory, GTK. Twelve block samples were analysed chemically. Analytical methods used were: inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence (XRF). Total carbon and total sulphur were determined with carbon and sulphur analysers while C_carb and C_non-carb were analysed with Leco analyser. Results show that S and C contents of samples from the Mulo region are higher than the rest. Of the 12 samples 11 contained more than 1% S and four contained more than 1% C. According to Loukola-Ruskeeniemi (1991), 1% S and 1% C are considered a minimum for black schist classification. In comparison, the average C, S and base metal values of the collected block samples are lower than the median values (%) of total carbon, sulphur and base metals in the hanging-wall black schist of the Hammaslahti sediment-hosted massive sulphide ore deposit, the black schists from the Outokumpu or Talvivaara area or the black schists associated with the Jormua ophiolite complex.

Airborne radiometric data: comparison of Hammaslahti and Mulo schists

The gamma-ray data for the structurally outlined Hammaslahti unit and three neighbouring units are discussed in more detail in the pro-graduate study by Karell (2001). The radioelement statistics for those units which contain the Hammaslahti and Mulo schists are compared here in Figures 6-8. Comparison of the radioelement distributions between individual geological and/or structural units improves the understanding of airborne radiometric data. The K, Th and U histograms show higher median values for Mulo ("alue_1") in comparison to Hammaslahti ("alue_3"). The Mulo
schists are particularly characterized by high U, which is also verified by chemical analysis. The histograms for Hammaslahti show lower median values for all three radioelements and the relative enhancement of the low values for K and Th. The Mulo schists are composed of mainly two magnetically different formations, with magnetic anomalies aligned with the strike of bedding. The northeastern anomaly is of lower-amplitude and associated with higher U than the southwestern high-amplitude anomaly. There is no such difference in K or Th. The difference in U may be explained by the role of oxidizing fluids at some stage of the geological history of the schists. The oxidized six-valent state of U is soluble in many hydrothermal fluids and it preferentially leaves the metasediment thus raising Th relative to U.

Discussion

Pyrrhotite is the characteristic mineral for almost every rock type associated with the Hammaslahti sulphide mineralisation, and from the geophysical point of view it is the main mineral of interest in the Pyhäselkä region. The great decrease in magnetization of black schists surrounding the sulphide deposit can be explained by, e.g. the following two theories.

Firstly, the occurrence of two-phase pyrrhotite, particularly the low-temperature hexagonal phase, may be explained by its origin from the time of mineralisation. At Hammaslahti, the mineralisation post-dates the regional metamorphism. Conditions of lower amphibolite facies at the time of regional metamorphism are indicated by the accessory hornblende grown on the chlorite + quartz mass (Loukola-Ruskeeniemi et al. 1991) and these conditions favour formation of (monoclinic) pyrrhotite from pyrite. Hexagonal pyrrhotite would have changed to the monoclinic form under the high temperatures of the regional metamorphism. The other explanation is that the amount of pyrrhotite has decreased relative to pyrite. Oliveira and Leonardos (1990) have shown that local retrogressive mineralogical changes within tectonized and deformed zones of bedrock result in pyrrhotite converting to pyrite. Such conditions may occur within transtensional fault zones where fluid pressure exceeds that of lithostatic pressure.

High U and Th gamma-radiation is typical of bedrock units containing graphite-bearing metasedimentary rocks, also black schists. The radioelement statistics for the Hammaslahti tectonic unit, however, show typically low overall K, Th and U radiation, with a local increase in K due to the brecciated and sericitized host rocks. Comparisons between Mulo and Hammaslahti black schists suggest that generally a higher U radiation appears together with reduced magnetic anomaly signature and lower monoclinic pyrrhotite content, whereas the stronger magnetic anomalies are combined with lower U content. Dickson and Scott (1997) have discussed the behaviour of radioelements during metamorphic and deformational processes. Of the three radioelements, K is most often influenced both by metamorphic processes and by most alteration and mineralising processes. U and Th are not much affected by metamorphic processes, but they may be either enriched or depleted due to mineralisation. The mobilisation of Th results in elevated U/Th ratios and is known for many massive sulphide deposits worldwide. Also the Hammaslahti and Mulo schists are marked by generally high U related to low Th and low K.

Integration of aerogeophysical data with geological information of bedrock requires field checking and correlation with digital elevation data. Most important is to know the hydrothermal alteration history of the study area. This is because different radioelement distributions - Th, U and K concentration - may reflect variation caused by several reasons: variation of lithology and alteration geochemistry; variation in exposure or the influence of the surficial cover. These are affected by different environmental conditions, either during the primary sedimentation and diagenesis, or during the later deformational stages. In summary, the results of the project confirm that the high-resolution airborne data are in most cases comparable in sensitivity with ground geophysical measurements, particularly when analyzing individual flight-line data. In addition to the detailed information, the airborne data gives knowledge of the structural control and the regional background level for magnetic and electromagnetic properties and the radioelement distribution.

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CHARACTERISTICS OF PROTEROZOIC LATE-/ POST-COLLISIONAL INTRUSIVES IN ARCHAEOAN CRUST IN IISALMI – LAPINLAHTI AREA, CENTRAL FINLAND

by

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Key words (GeoRef Thesaurus, AGI): intrusions, granites, quartz diorites, geochemistry, geophysics, plate collision, absolute age, U/Pb, Proterozoic, Archean, Iisalmi, Lapinlahti, Finland

Introduction

The Iisalmi - Lapinlahti area in central Finland is located in the western margin of Archaean craton against the Svecofennian collision zone from the west (Fig. 1). The Archaean bedrock in the area is predominantly composed of amphibolite-banded tonalitic-trondhjemitic migmatites. The zircon U-Pb ages of the migmatite components vary from 3.2 Ga of the palaeosome to 2.63 Ga of the late metamorphism (Mänttäri et al. 1998; Hölttä et al. 2000). The study area is characterized by well-preserved Archaean granulite facies blocks with fresh mineral parageneses (Paavola 1984; Hölttä & Paavola 2000) despite strong Palaeoproterozoic overprint 1.9 – 1.8 Ga ago (Kontinen et al. 1992). The area is cut by numerous Palaeoproterozoic fractures, some of them bordering the granulite blocks.

In addition to numerous 2.3–2.1 Ga old diabase dykes (Hölttä et al. 2000; Toivola et al. 1991), a significant amount of later Palaeoproterozoic magmatism is also characteristic of the Archaean craton margin. The magmatism comprises intrusions of varying size, chemical composition varying from basic to acid. The very variable bimodal appearances between gabbro – diorite material together with younger granite – granodiorite material are most characteristic of the area (Paavola 1987, 1990, 2001; Lukkarinen 2000; Äikäs 2000). Intermediate intrusions are common, too. Also so-called microtonalite dykes (Huhma 1981; Rautiainen 2000) occur in the zone. According to the existing conventional zircon datings the age of the Palaeoproterozoic magmatism is distributed around 1.90 – 1.85 Ga (e.g. Paavola 1988).

This paper concentrates on the characteristics of some late- to post-collisional granitoids in the Iisalmi - Lapinlahti area. They are compared to a larger background material from a sample profile NW from the study area (Figs. 2 – 4) called ‘Ladoga-Bothnian Bay’ (LBZ) profile in the following.

From the regional magnetic and gravity maps in Figures 2–3 it can be seen that the Archaean-Proterozoic (AP-) border in the western part of the Iisalmi - Lapinlahti area is characterized by a strong magnetic and gravity minimum zone reflecting the loss of magnetite and density in the shearing associated with the collision processes.

In the low-altitude magnetic map in Figure 4 are shown in more detail the location of the samples considered in this paper. From the map it can be seen that the area is characterized by roundish magnetic anomalies, sometimes cut by numerous younger fractures, such as the anomaly between samples 1-3 and 11.
Fig. 1. A simplified geological map of Finland after Korsman et al. 1997. The location of the geophysical maps in Figures 2–4 are shown by black and red rectangles.
Fig. 2. The magnetic map of the study area. Compiled from high- and low-altitude magnetic data by Geological Survey of Finland. The red line borders the the Iisalmi - Lapinlahti area shown in more detail in Figure 4. The location of the study samples are shown as red and blue circles and red squares in the figure. The location of background ‘Ladoga-Bothnian bay’ profile samples are shown as white circles. Black line shows the approximate course of the Archaean-Proterozoic (AP-) border. The gray line gives the western border of the Ladoga-Bothnian zone (LBZ, eastern edge being roughly the AP-border).

Fig. 3. The regional gravity map of the survey area. Compiled from data by Geodetic Institute of Finland. For definitions, see caption of Figure 2.

Fig. 4. The detailed low-altitude magnetic map of the Iisalmi - Lapinlahti area and location of the samples described below. The red dots and squares show the location of the samples ILa 1 - 11. The blue dots refer to samples (ILb) collected separately from the Kaarakkala intrusion. The map is compiled from low-altitude magnetic data of the Geological Survey of Finland.

Description of the samples

This work concentrates on sample groups ILa 1-11 and ILb, collected separately. The background material from felsic to mafic granitoids from the profile crossing the Ladoga-Bothnian Bay zone, is divided to Proterozoic and Archaean samples on basis of their geographical location. In the following is given a short description of the sample groups ILa and ILb.

The Palomäki quartz diorite (samples ILa 1-3) is a homogeneous and massive intrusion covering a large area and it contains commonly fine-grained dark fragments. The main minerals are plagioclase, quartz, biotite and hornblende. Epidote, titanite, apatite and opaques are conspicuously abundant. The Ohenmäki granite (sample ILa 11) cuts the Palomäki quartz diorite.

The Palosvuori granite – granodiorite (sample ILa 4) is homogeneous, grey and massive. The mineral composition is quartz, plagioclase, potassium feldspar and biotite. Epidote, titanite, carbonate, chlorite and opaques are the main accessory minerals.

The Ryhälänmäki granite (samples ILa 5-6) is reddish, massive and generally homogeneous, but includes diorite and quartz dioritic xenoliths in certain areas. The granite is reddish or reddish grey and mainly medium grained. It is massive or very weakly foliated. The main minerals are quartz, plagioclase,
potassium feldspar and biotite. Hornblende is rare. Varying amounts of epidote, muscovite, chlorite, titanite, apatite and opaque occur.

The Kaarakkala (leuco-) gabbroic ring intrusion (samples ILa) causes a strong zonal magnetic anomaly (Fig. 4). Excluding the contact zones it is undeformed and fresh. The rock is quite homogeneous but compositional banding is common. The main minerals are plagioclase, hornblende and biotite. Quartz is occasionally present. Titanite, apatite and magnetite are relatively abundant. The most basic inner part of the intrusion is nearly hornblenditic. Red medium grained homogeneous leucogranite crosscut the intrusion. It follows conformly the ring structure being an essential part of the appearance of the Kaarakkala intrusion. The Nieminen sample (ILa 7) represents the granite. The Ahvenlampi sample (ILa 8) is from a typical, homogeneous leucogabbroic zone of the main Kaarakkala intrusion.

Palosenni granite - granodiorite is a roundish intrusion causing a negative anomaly on the magnetic map (Fig. 4). The rock is relatively coarse-grained, reddish white and very homogeneous consisting of plagioclase, quartz, potassium feldspar and biotite. Plagioclase is distinguished in the texture as larger, subhedral and zoned crystals. The Pirttimäki sample (ILa 9) is from the southern border zone of the intrusion representing an anomalous, porphyric contact type while the Hallamäki sample (ILa 10) is most typical representative of the intrusion.

The Kiikkerinvuori granite (sample ILa 11) is reddish, massive and homogenous. It is a part of the Ohenmäki multistage granitic intrusion.

Petrophysical characteristics of the ILa samples

The major geophysical features of the study area are already evident from Figures 2–4. In Figure 5 is given a summary of the density and susceptibility of the ILa 1-11 sample groups. From the figure it can be seen that the Palomäki samples 1-3 have distinctly higher 'mafic' density compared to all other groups having lower densities characteristic of felsic intrusives. The susceptibility varies from ferri- to paramagnetic in both groups.

Isotopic characteristics of the samples

Conventional U-Pb dating

The decomposition of zircons and extraction of U and Pb for conventional isotopic age determination follows mainly the procedure described by Krogh (1973). Zircon fractions were ≤0.65 mg in weight (see Table 1), and the total procedural blank was ≤50 pg. $^{235}$U-$^{208}$Pb-spiked and non-spiked isotopic ratios were measured using a VG Sector 54 thermal ionization multicollector mass spectrometer. The measured lead and uranium isotopic ratios were normalized according to accepted ratios of SRM 981 and U500 standards. The U-Pb age calculations were done using the PbDat-program (Ludwig 1991) and the fitting of
Table 1. Conventional U-Pb age data on zircons from samples A1512 Ahvenlampi diorite, A1516 Palomäki quartz diorite, A1517 Palosvuori quartz diorite, and A1518 Kikkerinvuori granite.

<table>
<thead>
<tr>
<th>Sample information</th>
<th>Sample</th>
<th>U</th>
<th>Pb</th>
<th>206Pb/204Pb</th>
<th>207Pb/204Pb</th>
<th>208Pb/204Pb</th>
<th>Radiogenic</th>
<th>206Pb/238U</th>
<th>2σ</th>
<th>207Pb/238U</th>
<th>2SE</th>
<th>208Pb/238U</th>
<th>2SE</th>
<th>206Pb/207Pb</th>
<th>2σ</th>
<th>207Pb/206Pb</th>
<th>2σ</th>
<th>208Pb/206Pb</th>
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<tr>
<td>Analysed mineral and fraction</td>
<td>weight/mg</td>
<td>ppm</td>
<td>measure</td>
<td></td>
<td></td>
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<tr>
<td>ILb (A1512 Ahvenlampi, Kaarakkala)</td>
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<td>A) d=4.3, abraded 20h</td>
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<td>757</td>
<td>284</td>
<td>11553</td>
<td>0.21</td>
<td>0.3282</td>
<td>0.60</td>
<td>5.157</td>
<td>0.60</td>
<td>0.1140</td>
<td>0.15</td>
<td>0.97</td>
<td>1830</td>
<td>1846</td>
<td>1864±1</td>
<td></td>
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</tr>
<tr>
<td>B) d=3.6-4.0</td>
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<td>315</td>
<td>1696</td>
<td>0.27</td>
<td>0.3112</td>
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<td>4.886</td>
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<td>0.1139</td>
<td>0.15</td>
<td>0.97</td>
<td>1747</td>
<td>1800</td>
<td>1863±2</td>
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<tr>
<td>C) d=4.3</td>
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<td>485</td>
<td>179</td>
<td>1743</td>
<td>0.19</td>
<td>0.3200</td>
<td>0.60</td>
<td>5.017</td>
<td>0.60</td>
<td>0.1137</td>
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<td>0.97</td>
<td>1790</td>
<td>1822</td>
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<td>543</td>
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<td>1112</td>
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<td>0.3190</td>
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<td>5.002</td>
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<td>1129</td>
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<td>817</td>
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<td>5006</td>
<td>0.08</td>
<td>0.3234</td>
<td>0.38</td>
<td>5.066</td>
<td>0.39</td>
<td>0.1136</td>
<td>0.06</td>
<td>0.99</td>
<td>1806</td>
<td>1830</td>
<td>1858±1</td>
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<tr>
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<td>0.99</td>
<td>1774</td>
<td>1812</td>
<td>1857±2</td>
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<tr>
<td>ILa 4 (A1517 Palosvuori)</td>
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<tr>
<td>A) d=4.3, +200mesh, abraded 15h</td>
<td>0.34</td>
<td>320</td>
<td>110</td>
<td>5065</td>
<td>0.11</td>
<td>0.3233</td>
<td>0.60</td>
<td>5.109</td>
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<td>0.1146</td>
<td>0.19</td>
<td>0.97</td>
<td>1806</td>
<td>1838</td>
<td>1874±4</td>
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<tr>
<td>B) d=4.3, +200mesh</td>
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<td>324</td>
<td>102</td>
<td>5021</td>
<td>0.10</td>
<td>0.3000</td>
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<td>0.97</td>
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<td>1875±1</td>
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<tr>
<td>ILa 11 (A1518 Kikkerinvuori)</td>
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<tr>
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<td>408</td>
<td>129</td>
<td>1077</td>
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<td>1843±2</td>
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<tr>
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<td>1734</td>
<td>1849±1</td>
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</table>

1) Isotopic ratios corrected for fractionation, blank (50 pg), and age related common lead (Stacey and Kramers 1975).
2) Correlation between 207Pb/206U and 206Pb/207U errors.
the discordia lines using the Isoplot/Ex program (Ludwig 1998).

**Results**

**ILb group sample, Ahvenlampi, Kaarakkala intrusion:** Zircons are mainly long prismatic, brownish and dull. Typically zircons contain inclusions of unknown dark mineral. Brown and more rounded zircons most probably represent inherited material. Six analysed zircon fractions plot on a discordia line with intercept ages of 1864±8 and 76±330 Ma (MSWD=5.3; n=6) (Table 1, Fig. 6). The slightly high MSWD value indicates minor heterogeneity in zircon material and is caused mainly by zircon fractions F and B which plot slightly on the older side of the other four data points. However, the $^{207}$Pb/$^{206}$Pb ages of 1863±1 and 1864±1 Ma from the two nearly concordant fractions F and B determine the emplacement age of the Ahvenlampi diorite independently.

**ILa sample 3, Palomäki quartz diorite:** Zircons from the Palomäki quartz diorite show extreme homogeneity. These morphologically typical magmatic zircons have long prisms and are translucent to transpar-
ent and light brown in colour. Four analysed zircon fractions plot well on a same discordia line (Table 1, Fig. 7). The upper intercept age of 1861±1 Ma determines the age for the Palomäki quartz diorite.

**ILa sample 4 Palosvuori, granite – granodiorite:** In the Palosvuori sample the amount of the zircon was quite small and the zircon material quite heterogeneous. However, some zircons contain dark mineral inclusions. Among the clearly magmatic type, there are brown and dull zircon grains and fragments with varying morphologies.

Four of the five analysed zircon fractions plot on the same line. The most discordant analysis point D plots on the older side of this discordia (Table 1 and Fig. 8). These highly discordant data points are normally not very reliable, and can be rejected from the calculations. Although the slightly high MSWD value of 5.1 indicates some heterogeneity in the sample material, the upper intercept age 1879±11 Ma gives a good age estimate for the Palosvuori granite – granodiorite intrusion. This age, with the 207/206Pb ages of 1874 and 1875 Ma for the most concordant data points (A and E) indicate that the Palosvuori granite – granodiorite belongs into the 1.88 Ga age group and not into the 1.86 Ga group represented by the Palomäki quartz diorite and Kaarikkala intrusion.

**IIa sample 11, Kiikkerinvuori granite:** This sample yielded a very small amount of prismatic, brownish, dull zircon. Among these, there are also some irregular shaped grains of zircons.

The analysed five zircon fractions indicate that the zircon material was heterogeneous, as the MSWD value for the five point discordia line would be as high as 28 (Fig. 9.). Rough age approximation can be done using the four data point discordia line. However, to reject the data point C an assumption that it contains clearly older zircon material is needed. Then the discordia line plotted through data points A, B, D, and E gives an upper intercept age of 1851±20 Ma with the MSWD value of 8.2. Although the age error and MSWD value are high, it is considered that the Kiikkerinvuori granite do not belong to the syn-collisional age group. To ascertain this, few additional analysis should be done.

**Sm-Nd-analyses**

Hannu Huhma (Geological Survey of Finland) has analyzed Sm/Nd-ratios from the samples ILa 3, 4 and 11 and calculated their eNd values and model ages (Table 2). The analytical procedures are described e.g. in Huhma (1986). From the eNd values it can be seen that the Archaean crustal component is strongest (lowest eNd) in Kiikkerinvuori (-6.5) increasing from Palosvuori (-3.4) to Palomäki (-2.2).

**Geochemical characteristics of the samples**

In Figure 10 is given the classification of the rocks on the diagram of Cox et al. (1979). From the figure it can be seen that the Palomäki (=ILa 1-3) and ILb samples from Kaarikkala are close to each other in the low-SiO₂ alkaline gabbroic fields. The other ILa samples (ILa 4-11) and LBZ-Archaean samples plot in the sub-alkaline granite-quartz-diorite fields. The Proterozoic LBZ-samples have a wider spectrum from mainly sub-alkaline gabbros to diorite and granites.

In the Classification diagram by de la Roche et al. (1980, Fig. 11) and Batchelor and Bowden (1985) the ILb and ILa samples 1-3 plot mainly in the fields of ‘post-collision uplift’ monzonites and syeno-gabbros. The Archaean LBZ and ILa samples 4-11 cluster mainly in the syn-collisional granodiorites and monzonite-syeno-granites. However, it is clear from tectonic and isotopic consideration above that ILa samples 4-11 are also late- to post-collisional. Their characteristics are possibly distorted by the strong Archaean crustal component which is evident from their isotopic and chemical compositions. The Proterozoic LBZ samples plot in a wide range of rock type fields having tectonic characteristics from pre-plate collision to syn-collision and post-collision uplift, which is reasonable for these rocks.

The diagram introduced by Pearce and Peate (1995, Fig. 12) originally for volcanic arc magmas gives in a compact form a wide spectrum of elements in order of their increasing compatibility. From the diagram it is evident that there is a close correlation between Archaean LBZ samples and felsic ILa samples 4-11. Moreover, the similarity between mafic rocks ILb (Kaarikkala) and ILa samples 1-3 (Palomäki) is striking. When considering the REE compositions it can be seen that the Archaean LBZ and ILa samples 4-11 are clearly depleted compared to the more mafic ILb and ILa 1-3 rock groups, which means that these rocks cannot be derivatives from each other. However, it is clear that the ILa 4-11 rocks can be derivatives of Archaean LBZ rocks. Moreover, ILb and ILa 1-3 rocks have apparently a similar or the same source.

The Proterozoic LBZ samples are more enriched compared to the Archaean LBZ and ILa samples 4-11 but has a flatter REE pattern (i.e. lower LREE and higher HREE) compared to the ILb and ILa samples 1-3. This means that the ILb and ILa 1-3 rocks could be contaminated by the Proterozoic LBZ component but they are probably not directly their derivatives.

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Fig. 10. Classification of the rocks on the diagram of Cox et al. (1979). The alkaline - sub-alkaline boundary lines (in gray) are adopted from Rickwood (1989). The area between them can be considered ‘uncertain’. The nomenclature of igneous rocks is adopted from Wilson (1993).

Fig. 11. Classification of the rocks by multicational diagram of de la Roche et al. (1980). The tectonomagmatic classification border lines have been adopted from Batchelor and Bowden (1985).
because of their lower $\text{SiO}_2$ content.

**Conclusions and evolution model**

From the consideration above it can be seen that both, felsic and mafic rocks give ages from ca 1.88 – 1.86 indicating late- and post-collisional processes. From their chemical composition it can also be concluded that they have clearly a different source of origin. The ILa 4-11 rocks are less enriched in incompatible elements. Moreover, the $\varepsilon_{Nd}$ value measured from the ILa 1-3 rocks is highest referring to the smallest component of Archaean crustal contamination. From this it can be concluded that they have a strong component from the enriched upper mantle below the Archaean crust. The enrichment has apparently happened during and after the Svecofennian collision while no signs of such enrichment was observed in the older rocks (or their derivatives) as is evident from the Archaean LBZ and ILa 4-11 samples in Figure 12.

The observed features of the Iisalmi - Lapinlahti area rocks can be explained by a schematic model shown in Figure 13. adopted from Ruotoistenmäki (1996) which depicts the collision of Svecofennian crust against the Archaean craton. In the collision process, ca. 1.9–1.885 Ga ago, the Proterozoic (Pielavesi) crust and possibly wet sediments carried by subducting slab are thrust against the Archaean (Iisalni) block. In the collision the Archaean crust is broken into blocks, some of which still contain well-preserved granulite facies mineral assemblages. The block margins are evident as fracture zones in the geophysical maps shown above. The overthrust tectonics on the Archaean-Proterozoic boundary has been described in e.g. Pietikäinen and Vaasjoki (1999). Indications of fossilized subducting slab behind the Central Finland granite have been observed in the reflection seismic profile ‘Babel’ (Babel Working Group 1990).

After the Svecofennian collision the erosion of the Archaean crust has been close to 15-20 km (e.g. Kontinen et al. 1992; Pajunen, 1999) which means that after the collision the crust was possibly up to 80 km thick at its maximum. The lower parts of the thickened crust and mantle below were thus thrust to depths where temperature and pressure are higher.

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**Figure 12**: Morb-normalized patterns of the average of the elements using diagram introduced by Pearce and Peate (1995). For sake of clarity the Archaean LBZ and ILa 4-11 values have been plotted with bars. The REE-elements have been emphasized by D:s in the horizontal axis.
Moreover, they were intruded and contaminated by fluids and melts from the subducting slab and sedimentary wedge. As a result, the lower crust and upper mantle were slowly heated and melted which resulted in late-/post-collisional magmatism observed in the Iisalmi-Lapinlahti area. The ILa 1-3 and ILb rocks have higher component from the upper mantle and sedimentary Proterozoic material, while the ILa 4-11 rocks represent components having higher proportion of the old Archaean crust. The increased component from the high density upper mantle raised the average density of the crust in the area making it possible to sustain the isostatic balance and a very thick crust even today.

Acknowledgements

In this connection we want to thank Anita Niemelä for handpicking and zircon chemistry, Hannu Huhma for Sm-Nd analysis and Pentti Hölttä for inspiring comments during the work.

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**THE MAGNETIC ANOMALY MAPS OF CENTRAL FINLAND - RUSSIAN KARELIA AND NORTH FINLAND - KOLA 1 : 1,000,000**

by

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Key words (GeoRef Thesaurus, AGI): geophysical surveys, airborne methods, magnetic methods, geophysical maps, aeromagnetic maps, magnetic anomalies, Finland, Russian Federation

**Introduction**

Magnetic method has been used in mining for centuries, by observing deviations of mining compass and interpreting anomalous readings in terms of forces caused by magnetic ore minerals. A natural consequence of this tradition was development of magnetic mapping for prospecting. Until the 1940's magnetic ground surveys were made e.g. in Orijärv, Jussarö, Misi, Outokumpu, Pitkäranta, Pirkonen-Pahtavaara and Pechenga areas. At that time airborne magnetic method was already tested in Sweden and Russia, and in the next decade it became a major geological tool for prospecting and geological mapping in Precambrian areas worldwide. Due to flux gate instrumentation these measurements originally represented relative magnetic intensities, good for displaying local anomalies only. (Ketola 1986 and references therein)

In 1960's the new proton magnetometer allowed airborne registration of total field, and together with use of base stations and geomagnetic observatories made it possible to reduce the observations to a common epoch and - consequently - to compile wide regional coverages simultaneously presenting sharp and smoothly varying anomaly components. These new techniques together with more detailed survey layouts led to the second generation of magnetic mapping programs. Magnetic gradiometer techniques, both vertical and horizontal, were tested and used in routine work. Helicopter surveys were carried out in rough terrain, and to obtain high resolution at a very low altitude. By end of the Millennium, major areas of the Eastern Fennoscandian Shield were covered by new sets of digitally registered and processed measurements. New fields of application extended towards other modern geological uses such as groundwater exploration, engineering geology, crustal scale research, planning of land use and environmental studies.

The possibilities of the use of magnetic data sets are not yet exhausted. They will have permanent value that will even increase in time with the accumulation of petrophysical and other geological information and by development of more sophisticated data processing and interpretation techniques. Hence we are still at the beginning of a long road.

**Finnish magnetic grid**

In 1951 the Geological Survey of Finland initiated the Finnish airborne surveys. The altitude was 150 m above the ground and the line spacing 400 m. The main goals were indicating magnetic iron ores and Ni-Cu deposits in mafic and ultramafic intrusions, finding
Fig. 1. Aeromagnetic map of Central Finland - Karelia. Map reduced from Korhonen et al. 2001a.
Fig. 2. Aeromagnetic map of North Finland - Kola. Map reduced from Korhonen et al. 2001b.
sources of magnetic erratic ore boulders and assisting in bedrock mapping. (Puranen & Kahma 1949)

At first one third of the country was aimed to be surveyed in detail, but finally it was preferred to cover the whole of Finland with a more coarse net of lines. The compiled relative magnetic total field maps were presented in a scale of 1 to 20,000. The survey was completed in 1972, covering all mainland Finland, coastal waters and economic zone in the Baltic Sea area.

In 1968-69 absolute tie lines were measured with 40 km line spacing, and reduced to 1965.0 to prepare coloured IGRF-65 anomaly maps in a scale of 1 to 100,000. The maps were further digitized on a 1 km x 1 km grid to produce the Magnetic Anomaly Map of Finland 1 to 2,000,000 (Korhonen 1980). The estimated standard error of magnetic anomaly grid was 20 nT as compared to later absolute total field measurements.

A data gap from 3 to 10 km was left in the measurements in the eastern border until 1993 when it was filled. New tie lines, with a base station array of the BEAR-project were measured in 1998 to check the previous magnetic levels and to indicate a possible drift of magnetic anomalies in time.

In 1972, a new detailed mapping program was initiated with a flight altitude of 40 m and a line spacing of 200 m. So far 85% of the mainland Finland has been covered by these surveys.

**Russian magnetic grid**

In 1955 North West Russian airborne magnetic surveys were initiated for the same geological purposes as in Finland. The scale was 1 to 200,000 originally, and 1 to 25,000 later in the 1960's. The nominal flight altitude changed from 250 m to 100 m - 60 m and the nominal line separation from 2000 m to 250 m respectively. The White Sea was covered at an altitude of 300 m by a line spacing of 10,000 m in a scale of 1 to 1,000,000.

Tie lines measured in 1963 and 1965 were used to reduce the data to a common anomaly level in reference to the normal field of IZMIRAN 1965.0. Maps of anomalous magnetic field 1 to 200,000 and 1 to 500,000 were further edited from the original maps in 1973 and 1975 (Sokol 1975), and further digitized on a 1 km x 1 km grid to provide a numerical magnetic anomaly field set. The estimated error of the Russian grid was estimated to be 20 nT.

New digital magnetic measurements have been made since 1991. The existing gaps in data in the border area were filled by measurements in 1993, 1994 and 1998. In 1999 two new tie lines were measured to check the baseline levels of magnetic anomalies by using Russian and Finnish magnetic observatory and observation station networks as base stations. The normal fields of IAGA (DGRF-65) and IZMIRAN were locally correlated for international co-operation.

**Joint magnetic maps**

Magnetic maps can be reliably referenced to each other over large areas. They reflect Precambrian geological structures well and are commonly used in spatial geological correlation. Hence it was proposed to compile a magnetic map of the Eastern Fennoscandian Shield in the framework of a technical and scientific co-operation between Finland and the Soviet Union in 1979. However, it was 1991 until the project really commenced between the Geological Survey of Finland and the Petersburg Geophysical Expedition.

The map was made in a scale of 1 to 1,000,000 and divided in two sheets, Central Finland - Karelia and North Finland - Kola (Figs. 1 and 2). The maps represent DGRF-65 total field anomalies on a 1 km x 1 km grid that extends for the southern sheet over an area 600 km wide and 600 km high, centered at Lat = 64°N and Long = 30°E, and for the northern sheet 1000 km wide and 500 km high, centered at Lat = 68°N and Long = 30°E. The maps overlap for 100 km. Map datum is WGS84 and projection Gauss-Krueger with central meridian 30°E.

The southern sheet covers the main part of a deformed Neoarchaean basement area, the former Jatulian Continent called Karelian Terrain as well, and some Palaeoproterozoic formations at its margins, eg. intra- and epicontinental rocks and arc supracrustals and plutonics. In addition the northern sheet covers the Archaean Kola Terrain and its tectonic contact zone with the Karelian Terrain plus younger Phanerozoic formations, like the Kandalaksha rift zone and alkaline intrusions on its both sides.

The limits and areal distribution of major geological formations and structural units are clearly discernible on the map due to their contrasting magnetic patterns and intensities of magnetization. Part of the smooth magnetic anomalies are of deep origin and, hence, do not correlate to the surficial geology.

Besides providing an overall picture, the maps assist in making better crustal scale geophysical and geological interpretations of formations crossing the Finnish - Russian border. Specifically, the major apparent level difference in magnetic total intensity across the former data gap of 20 - 30 km along Finnish-Russian
state border (Simonenko & Pashkevich 1990), stands out to be of geological origin, the Russian part representing higher regional magnetic levels in general. The regional magnetic high in Ilomantsi, in the south east associated with greenstone belt which hosts several Au occurrences, has a major continuation in Russia. On the other hand, the magnetic anomalies of the prospective layered intrusions of Koillismaa and that of the iron formations of Kostamuksha do not continue to the opposite side of the state border. The bulls eye type anomaly family associated with Phanerozoic alkaline intrusions of Russia has a lone counterpart in the west (Sokli). The anomalies of Petchenga formation die out near the Finnish border. The structural continuity of the Lapland granulite belt is indicated to extend to the southern shore of Kola.

Recently the results of the study have been included in the work for Magnetic Map of the Fennoscandian Shield (Korhonen et al 1999). Together with gravity anomaly and petrophysical data, the magnetic anomaly map offers a geophysical reference to the area for developing models of its structure and evolution, and planning more specific work.

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APPLYING PALAEO MAGNETIC METHOD FOR DATING YOUNG GEOLOGICAL EVENTS

by
S. Mertanen, M. Pajunen and T. Elminen

Introduction

A new application of the palaeomagnetic method was tested for shear and fracture zones in southern Finland. In this preliminary study the unique property of remanent magnetization, its ability to reflect the time of acquisition of magnetization, is used as a tool for dating processes that have occurred during polyphase shearing and fracturing. The palaeomagnetic method has been shown to be effective in detecting and dating metamorphic overprints, like the Svecofennian overprint on Archaean-Palaeoproterozoic rocks in the eastern Fennoscandian Shield (e.g. Mertanen 1995, Mertanen et al. 1999). In many cases those studies have shown how the primary remanent magnetization has been overprinted by a secondary younger magnetization owing to formation or reactivation of magnetic minerals in later geological processes. In this study our main purpose was particularly to test this method in dating the younger ‘secondary’ geological events. Isotopic dating of shear zones has in many cases proven to be difficult. Because of different mobilities of radioactive and radiogenic elements, isotopic methods often give ages that cannot be connected to any tectonic or magmatic processes, and obtaining suitable sample materials is often difficult.

We show here the results of oriented test samples from the Porkkala-Mäntsälä shear zone in southern Finland (Elminen 1999). The properties of the rocks in the zones, especially their microstructures, differ according to their age (Pajunen 1986, Heeremans & Wijbrans 1999, Elminen 1999). The palaeomagnetic method was employed in order to examine its usefulness in correlating and predicting zones of similar age of crustal weakness. The study forms part of a larger project of the Geological Survey of Finland where the bedrock of southern Finland is studied in order to develop a bedrock model of weakness zones for the use of urban planning and building (Pajunen et al. 2000).

Palaeomagnetic method

The two principal mechanisms for acquisition of remanent magnetization in crystalline rocks are thermoremanent magnetization (TRM) and chemical remanent magnetization (CRM) or the combination of the two, thermo-chemical remanent magnetization (TCRM) (e.g. Butler 1992). TRM is formed when the rock cools trough the Curie point of the rock forming magnetic minerals and the direction of the external magnetic field of the Earth is blocked in the minerals. For example, the Curie point of magnetite is 580°C and that of hematite 680°C. The mechanism of acquisition of CRM is different. CRM may be formed in much lower temperatures, even as low as 200-300°C due to growth of totally new magnetic minerals derived from pre-existing silicates or due to alteration of pre-existing magnetic minerals. The controlling factor in both cases is the oxidation state and excess of fluids. The shear zones act as channels for fluid flow which allows new magnetic minerals to be formed and

Key words (GeoRef Thesaurus, AGI): palaeomagnetism, shear zones, amphibolites, physical properties, magnetization, geochronology, Proterozoic, Muurala, Espoo, Finland

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remanent magnetization to be blocked in the minerals. The direction of the remanent magnetization is compared to the directions of known isotopically dated rocks and it is thus possible to constrain the age for magnetization.

**Description of the study site**

The study area (Fig. 1) is located in the Svecofennian granite-migmatite belt in southern Finland (Korsman et al. 1999). The NE-SW-trending Porkkala-Mäntsälä shear zone bends and cuts the EW-trending lithologies and structures characterising the bedrock of southern Finland (Elminen 1999). The shear zone has been repeatedly active. According to structural observations, the 1645 Ma old Subjotnian rapakivi granites (Vaasjoki 1977), Bodom and Obbnäs, were intruded into tectonically active crust and they were deformed...

![Geological map around the Porkkala-Mäntsälä shear zone](image1)

**Fig. 1.** Geological map around the Porkkala-Mäntsälä shear zone (marked with dashed line). The studied site in Muurala, Espoo, is marked with M.

![Part of the study site at Muurala](image2)

**Fig. 2.** Part of the study site at Muurala (map sheet 20 3212, \(x = 6678.63, y = 253538\)) which shows a variety of rock types. From left to right: albite-quartz rock, amphibolite and pegmatitic granite. The contacts are tectonic and characterised by slickenside surfaces. Photo from Elminen (1999).
still later along the Porkkala-Mäntsälä shear zone (Pajunen et al. 2001).

This preliminary study was carried out on one outcrop in Muurala, Espoo, which shows well the structural complexity of the Porkkala-Mäntsälä shear zone. The main part of the outcrop (Fig. 2) where eight oriented samples were taken, consists mainly of foliated amphibolite and altered albite-quartz rock and to a lesser extent of pegmatitic granite. The contacts between the rock types are mostly tectonic. Foliation in fine-grained amphibolite varies from moderate (sample 3) to strong (sample 5). The microstructure of the samples is mostly granoblastic with narrow microshear bands. A narrow ultramylonitic zone, which was deformed later in cataclastic brecciation, cuts the amphibolite (sample 4). The medium-grained albite-quartz rock is originally a felsic intrusive rock that has experienced protomylonitic deformation (sample 7). Hydrothermal alteration took place during or soon after the mylonitization causing new mineral growth. The albite-quartz rock was deformed by narrow shear bands, in which idioblastic epidote is concentrated (samples 1, 2 and 6).

Sampling and laboratory methods

In the first preliminary test, unoriented samples from four sites in the Porkkala-Mäntsälä shear zone were studied for their stability of remanence directions. Part of the samples showed very stable directions although some of them were too weakly magnetized with no permanent remanence. The eight new oriented samples from Muurala (Figs. 1 and 2) showed the highest remanence stability. The purpose was to see whether the remanence has meaningful directions that can be correlated to known geological events and whether further palaeomagnetic sampling should be carried out. The samples were taken as hand samples and oriented in the field by magnetic compass. Three specimens from each sample were measured. The specimens were demagnetized by alternating field (AF) in 16 steps from zero to 160 mA/m. After each demagnetization step the remanence was measured with SQUID magnetometer. The remanence directions were separated by using principal component analysis (Kirschvink 1980) and Tubefind program (Leino 1991) and inspected visually by Zijverveld diagrams (Zijverveld 1967). Statistical means were calculated according to Fisher (1953). In addition to palaeomagnetic measurements, the petrophysical properties (susceptibility and density and the calculated Q value) were determined from each specimen.

Results and interpretation

Petrophysical properties of the test samples show that the rocks are mainly weakly magnetized (Table 1). The Q value (ratio between induced and remanent magnetization) ranges from 0.03 to 1.70. Although the Q values are very low in part of the samples, they show extremely high coercivities and stable remanence directions. This may be due to the fact that the Q value may be significantly lower in the case of chemical remanence when the original thermoremanence has been destroyed (e.g. Kletetschka et al. 2000).

Palaeomagnetic results are shown in Table 2. The NRM directions of all samples deviate from the present Earth's field direction. By AF demagnetization three remanence components, named A, S and J were separated. Each component occurs as a single direction, so that no superimposed components occur within a specimen. Component A (Table 2, Fig. 3) was isolated in two even grained red albite-quartz rocks. Both samples carry a SE pointing negative inclination direction with rather large scatter of directions during demagnetization. The direction is of opposite polarity to the direction that is typically found in Svecofennian rocks. Sample 6 also carries a direction that is close to the normal polarity Svecofennian direction. By comp-

Table 1. Petrophysical properties of rocks in Muurala, Espoo.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Rock type</th>
<th>J (NRM) (mA/m)</th>
<th>K (10^-6)</th>
<th>Q</th>
<th>D (g/cm^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Albite-quartz rock</td>
<td>661.7</td>
<td>44126</td>
<td>0.38</td>
<td>2.734</td>
</tr>
<tr>
<td>2</td>
<td>Albite-quartz rock</td>
<td>61.7</td>
<td>5928</td>
<td>0.22</td>
<td>2.789</td>
</tr>
<tr>
<td>3</td>
<td>Amphibolite</td>
<td>103.9</td>
<td>2036</td>
<td>1.30</td>
<td>2.897</td>
</tr>
<tr>
<td>4</td>
<td>Ultramylonite</td>
<td>0.8</td>
<td>630</td>
<td>0.03</td>
<td>2.918</td>
</tr>
<tr>
<td>5</td>
<td>Foliated amphibolite</td>
<td>3776.7</td>
<td>56875</td>
<td>1.68</td>
<td>2.800</td>
</tr>
<tr>
<td>6</td>
<td>Red albite-quartz rock</td>
<td>5.1</td>
<td>550</td>
<td>0.25</td>
<td>2.687</td>
</tr>
<tr>
<td>7</td>
<td>Red albite-quartz rock</td>
<td>9.9</td>
<td>594</td>
<td>0.39</td>
<td>2.647</td>
</tr>
<tr>
<td>8</td>
<td>Red albite-quartz rock</td>
<td>7.0</td>
<td>401</td>
<td>0.43</td>
<td>2.642</td>
</tr>
</tbody>
</table>

Note: J (NRM) is remanence intensity, K is susceptibility. Q is Königsberger ratio. D is density.
reversed polarities. Figure 4 shows the demagnetization behaviour of specimen MU3-1B which is weakly preparing the pole of component A to the key poles (Fig. 6) of the Fennoscandian Shield (Buchan et al. 2000, Mertanen & Pesonen 1997), it is interpreted that the direction represents the primary Svecofennian age remanent magnetization that has been weakly preserved from later geological events.

Component S was isolated in one sample (sample 3, Tables 1 and 2) which was taken from a fine grained amphibolite. Component S yields both normal and reversed polarities. Figure 4 shows the demagnetization behaviour of specimen MU3-1B which is palaeomagnetically a fine example of a stable occurrence of a dual polarity remanence within one specimen. Similar direction and pole (Fig. 6) as of component S has typically been isolated in Subjotnian rapakivi granites and associated dykes in the Fennoscandian Shield. In addition, dual polarity is a characteristic feature for Subjotnian formations. Based on these observations, it is interpreted that component S was acquired ca. 1630-1570 Ma ago as a result of newly formed magnetic material which, based on comparatively high susceptibility and remanence intensity val-

<table>
<thead>
<tr>
<th>Component A</th>
<th>No.</th>
<th>N/n</th>
<th>D (°)</th>
<th>I (°)</th>
<th>α 95 (°)</th>
<th>k</th>
<th>Pol</th>
<th>Plat (°N)</th>
<th>Plong (°E)</th>
<th>A95 (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red albite-quartz rock</td>
<td>6</td>
<td>1</td>
<td>135.3</td>
<td>-38.5</td>
<td>-</td>
<td>-</td>
<td>R</td>
<td>40.5</td>
<td>263.8</td>
<td>-</td>
</tr>
<tr>
<td>Red albite-quartz rock</td>
<td>7</td>
<td>1</td>
<td>145.2</td>
<td>-37.2</td>
<td>-</td>
<td>-</td>
<td>R</td>
<td>43.6</td>
<td>72.1</td>
<td>-</td>
</tr>
<tr>
<td>Mean A</td>
<td>*/2/2</td>
<td>140.3</td>
<td>-38.0</td>
<td>-</td>
<td>-</td>
<td>R</td>
<td>42.2</td>
<td>258.0</td>
<td>-</td>
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<table>
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<tr>
<th>Component S</th>
<th>No.</th>
<th>N/n</th>
<th>D (°)</th>
<th>I (°)</th>
<th>α 95 (°)</th>
<th>k</th>
<th>Pol</th>
<th>Plat (°N)</th>
<th>Plong (°E)</th>
<th>A95 (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amphibolite</td>
<td>3</td>
<td>3</td>
<td>23.0</td>
<td>-27.1</td>
<td>5.2</td>
<td>574</td>
<td>N</td>
<td>13.2</td>
<td>181.7</td>
<td>-</td>
</tr>
<tr>
<td>Amphibolite</td>
<td>3</td>
<td>3</td>
<td>188.4</td>
<td>29.0</td>
<td>3.4</td>
<td>1004</td>
<td>R</td>
<td>14.0</td>
<td>196.2</td>
<td>-</td>
</tr>
<tr>
<td>Mean S</td>
<td>*/2/3</td>
<td>15.8</td>
<td>-28.2</td>
<td>-</td>
<td>-</td>
<td>C</td>
<td>13.7</td>
<td>188.9</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component J</th>
<th>No.</th>
<th>N/n</th>
<th>D (°)</th>
<th>I (°)</th>
<th>α 95 (°)</th>
<th>k</th>
<th>Pol</th>
<th>Plat (°N)</th>
<th>Plong (°E)</th>
<th>A95 (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albite-quartz rock</td>
<td>1</td>
<td>1</td>
<td>43.8</td>
<td>-26.9</td>
<td>-</td>
<td>-</td>
<td>N</td>
<td>7.7</td>
<td>161.9</td>
<td>-</td>
</tr>
<tr>
<td>Albite-quartz rock</td>
<td>2</td>
<td>2</td>
<td>41.2</td>
<td>-3.8</td>
<td>-</td>
<td>-</td>
<td>N</td>
<td>20.2</td>
<td>160.1</td>
<td>-</td>
</tr>
<tr>
<td>Albite-quartz rock</td>
<td>2</td>
<td>1</td>
<td>231.6</td>
<td>-0.3</td>
<td>-</td>
<td>-</td>
<td>N</td>
<td>18.1</td>
<td>149.1</td>
<td>-</td>
</tr>
<tr>
<td>Mean of sample 2</td>
<td>*/2/3</td>
<td>46.4</td>
<td>-1.8</td>
<td>-</td>
<td>-</td>
<td>C</td>
<td>19.2</td>
<td>154.5</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ultramylonite</td>
<td>4</td>
<td>3</td>
<td>242.6</td>
<td>43.1</td>
<td>16.4</td>
<td>58</td>
<td>R</td>
<td>-9.2</td>
<td>150.1</td>
<td>-</td>
</tr>
<tr>
<td>Foliated amphibolite</td>
<td>5</td>
<td>3</td>
<td>61.7</td>
<td>2.2</td>
<td>3.3</td>
<td>1364</td>
<td>N</td>
<td>14.6</td>
<td>139.1</td>
<td>-</td>
</tr>
<tr>
<td>Mean J</td>
<td>*/4/10</td>
<td>53.3</td>
<td>-17.5</td>
<td>27.4</td>
<td>12</td>
<td>C</td>
<td>8.2</td>
<td>151.5</td>
<td>18.0</td>
<td></td>
</tr>
</tbody>
</table>

Note: No. is the sample number. N/n is the number of samples/specimens used for mean calculations. * denotes the statistical level used for mean calculation. D and I are the mean declination and inclination, respectively. α95 is the radius of the circle of 95% confidence and k is the Fisher's (1953) precision parameter ($a95$ and $k$ are indicated only when the minimum of three samples/specimens are used). Pol denotes the normal (N), reversed (R) or combined (C) polarity. Plat and Plong are the palaeolatitude and palaeolongitude for the Virtual Geomagnetic Poles. A95 is the radius of the circle of 95% confidence of the mean pole.

Fig. 3. An example of demagnetization behaviour of albite-quartz rock (MU7-2B) that carries component $A*$. The remanence direction is similar, but of opposite polarity to the direction typically obtained in Svecofennian rocks. a) stereographic projection where closed (open) symbols indicate downward (upward) pointing remanence direction, b) relative NRM intensity decay curves upon AF demagnetization, c) orthogonal vector projections where dots (crosses) denote projections onto horizontal (vertical) planes. Numbers at demagnetization steps denote peak alternating field (mT). The Present Earth's magnetic Field (PEF) at the sampling locality is shown as a cross.
ues, is probably magnetite. The source for the magnetization is presumably hydrothermal fluids expelled from the rapakivi granites (Pajunen et al. 2001).

Component J represents the most typical remanence direction of the site at Muurala where it was isolated in four samples of different rock types (Table 2). Component J has dual polarity and the directions are quite scattered between samples.Specimen MU1-1A (Fig. 5) from an albite-quartz rock represents a typical behaviour of normal polarity component J. Specimen MU4-1A (Fig. 5) from the center of the zone of ultramylonitized amphibolite shows a very stable direction, although the NRM intensity and Q value are very low (Table 1). However, the NRM intensity is still well above the noise level of the SQUID magnetometer which, combined with the hard coercivity and stable direction, suggest that the direction can be regarded reliable and to have geological meaning. The mean direction of component J is close to the direction that has been obtained in Post-Jotnian dykes in the Fennoscandian Shield although dual polarity has not been observed in those formations. Based on the mean pole position (Fig. 6) it is interpreted that component J represents a magnetization acquired about 1265 Ma ago. When looking at separate samples, the direction of J could in some cases be grouped together with the Subjotnian direction. Therefore, it is also possible that it was acquired some earlier time between Subjotnian and Post-Jotnian times between ca. 1.65-1.25 Ga. The probable mechanism of magnetization is chemical precipitation of magnetic material, probably hematite or pyrrhotite (indicated by low remanence intensities and hard coercivities), which took place due to hydrothermal fluids circulating in the fracture zone. The geological implication of this observation suggests that Jotnian or Post-Jotnian geological
events, which were tectonically active in Satakunta area in western Finland, also had an imprint in the study area.

Based on the palaeomagnetic results it is evident that at the studied site the shear zone has been reactivated at least two times after the cooling of the Svecofennian basement. First, during the emplacement of the rapakivi granites at ca. 1.63 Ga ago and later during Jotnian-Post-Jotnian times at ca. 1.26 Ma ago. The data from three other sites where the first unoriented test samples were taken showed very similar remanence and demagnetization behaviour implying that comparable palaeomagnetic results can be obtained invariably from the shear zones in southern Finland.

Conclusions

The preliminary results from southern Finland are promising and show that it is worth continuing this type of palaeomagnetic application. Palaeomagnetic studies, integrated with geological, petrophysical and aeromagnetic data facilitate classification and correlation of different shear systems. According to our results, hydrothermal fluids that are active in the late stages of geological processes are the source for formation of new magnetic minerals which can be dated palaeomagnetically. Thus palaeomagnetic results from known type localities will be helpful in the assessment of structurally corresponding fault or shear zones.

Acknowledgements

Reijo Niemelä is thanked for taking the samples in Muurala and Markku Küäriä for making the palaeomagnetic measurements. Dr. Matti Vaasjoki is acknowledged for comments and for revising the language of the manuscript. Financial support for the project was provided by National Technology Agency (Tekes), Rockplan LTD, SCC Viatek and the cities of Espoo, Helsinki and Vantaa.
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DEVELOPMENT OF CHEMICAL RESPONSE METHODS FOR FIRE AND RESCUE SERVICES

by

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Introduction

General

The purpose of this survey was to ascertain how fire and rescue services could, in their emergency response work, take into consideration environmental aspects better than previously when recovering chemicals spilled into the soil. The most common type of accident is a liquid spill on the ground, which, depending on amount, the chemical involved, and the site of a spill chemical, can cause serious pollution of soil and groundwater. In the acute response phase to a chemical spill accident the availability of geological information is essential. Therefore, it is important that Geological Survey of Finland is involved in a project that is assessing the chemical spill response methods.

Most of the chemical accidents responded to by the emergency and rescue services are accidents during the transportation of hazardous materials. Because in Finland about 75 percent of the hazardous materials transported by road and railway are flammable liquids, it is vitally important that we develop response methods for the spills of these chemicals. In particular, methods have to be developed for an effective recovery of volatile organic compounds (VOC) from the soil.

The current response measures of emergency and rescue services are restricted mainly to preventing the spread of chemicals on the ground or on water, and to recovering the spilt chemicals. When a chemical has seeped into the soil, at the moment there are not many methods of retrieval—most common methods used are pumping from ground pits, excavation and transportation of contaminated soil for a treatment on landfills. Because fire and rescue services usually come to the site of an accident first, by taking a rapid action, they can prevent spreading of chemicals into the soil and prevent the contamination of the groundwater with soil vapor extraction methods.

Soil Vapor Extraction (SVE) is a method of remediation for contaminated soils and can be used for recovery of chemicals from the soil. By starting the simplified soil vapor extraction immediately after a chemical spill, the remediation costs can be reduced to only a tenth of what it would cost to clean the soil that has been contaminated for a longer time. The recovery capacity of SVE is about 5 – 8 times more effective for a fresh spill than for a spill that has been in the soil for a longer time (Johnson et al. 1990). The emergency response actions taken by fire and rescue services do not, however, reduce the importance of remediation actions to be taken by soil experts after emergency response measures, but they make the follow-up remediation work considerably more effective and quicker.

SVE response equipment costs about 100 000 FIM (16 700 euros), and its main components include a vacuum pump and extraction pipes to be sunk into soil. If the transfer of contaminants from soil to atmosphere...
is to be prevented, the system must be completed with a burner for hydrocarbons, which will increase costs to about 200 000 FIM (33 300 euros). Equipment costs can be divided by arrangements that fire and rescue services and environmental organizations supply the response equipment as joint purchases. In addition, a common strategy should be planned to link the response actions of the fire and rescue services seamlessly to the follow-up remediation measures of the environmental organizations.

Most vulnerable areas are those with permeable soils and shallow ground waters. Special maps prepared by the Geological Survey of Finland help the fire and rescue services and environmental organizations to concentrate their response resources where risks are highest. To reduce the remediation costs in the future, even more closer co-operation will be needed between the fire and rescue services and soil experts when responding to chemical spills.

The operational model of Soil Vapor Extraction can

Fig. 1. A unifying framework for multidisciplinary research (Suk et al. 1999).

Fig. 2. A typical chemical spill after an overturn of a tanker transporting flammable liquids.
be practised by the fire and rescue services, but practical experiments are still needed to design and determine the dimensions of response equipment that is suitable for a typical fresh leakage. Such experiments will be conducted during the so-called SVE - project that has been started in November 2000.

Many disciplines are interrelated, even within the environmental sciences. The framework for this thesis can be seen in Figure 1, the focus of which is remediation technology as both an effective and economical site remediation. The work included in this thesis will be continued as demonstration research for a doctoral dissertation.

Chemical accidents in Finland

Based on previous work, most of the accidents that have an environmental effect take place in industry (47%) but the second most common type of environmentally important accidents occur during the road and railway transportation (20%). (Väätäinen & Seppälä 1995)

In 1997, a total of 53.6 million tons of hazardous materials were transported in Finland. This amount is divided among the different types of transportation as follows: on roads 9.6 million tons, by rail 8.4 million tons, by sea 34.2 million tons and by air 1.4 million tons. The part of flammable liquids from the transported chemicals was 75% (Liikenneministeriö 1999).

Typical transportation accidents are overturns of a tanker on a road or railway, and the leakages caused by such accidents. Most common chemicals spilt are oil products, such as heavy fuel oil, diesel oil or petrol. In addition, there have been accidents to vehicles transporting corrosives or gases (Liikenneministeriö 1997).

Figure 2 shows a typical situation on chemical accident to be responded by fire and rescue services.

The Ministry of Transportation investigated 105 chemical accidents that took place during 1990 - 1996; 80 of these were cases in which a chemical was spilt on the ground, the amount varying from a few liters to 40 m³ (Liikenneministeriö 1997).

Consequences of chemical spills

The consequences of spilt flammable liquids can be grouped as follows:
- toxic and irritating gases evaporate from a leakage pool
- flammable gases evaporate from a leakage pool
- spilt liquid seeps into the soil, but does not reach the groundwater
- spilt liquid seeps into the soil and reaches the groundwater
- the liquid spills into a watercourse.

Typical flammable liquids and harmful solvents evaporate easily, but because of their high flammability, fire is a greater risk than their toxicity. Most flammable liquids become toxic at large concentrations (Pipatti et al. 1985).

In permeable soils, mineral oil seeps easily into the ground. The depth and width of spreading depend on the quality of the soil, the level of the groundwater, the quality and amount of spilt oil, the atmospheric temperature and the slope of the ground (Verio 1990). Viscous liquids, like heavy fuel oil, do not penetrate deep into the soil and do not spread widely. Petrol-like liquids, having a low viscosity, easily penetrate deep into the ground. Because the groundwater level in Finland is, in general, only 2 - 4 meters below the surface of the ground, it is rather easy for petrol to reach the groundwater (Airaksinen 1978). Table 1 gives approximate retention capacities of sorted soil types for common fuels.

It can be seen from Table 1, for a given contaminant, retention by soil increases as the grain size of the soil becomes finer.

The pollution danger of a chemical reaching the groundwater depends largely on its water solubility. For example modern unleaded petrols can contain 10 - 15% methyl-tert-butylether (MTBE), a poisonous additive with a water solubility of 5%. One liter of MTBE is able to pollute million liters of groundwater, making it undrinkable.

With rapid and correct action taken by the fire and rescue services at the chemical spill site during the first minutes, the environmental consequences of chemical accidents can be minimized. Therefore it is very important to find new methods that fire and rescue services can use to prevent the spread of a pollutant and save the groundwater from contamination. This is also the goal of this summary.

Table 1. Retention capacities of typical soil types for common fuels (Oy Vesi-Hydro Ab 1992, Nikkarinen 1995).

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Retention capacity (l/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Petrol</td>
</tr>
<tr>
<td>Coarse gravel</td>
<td>2.5</td>
</tr>
<tr>
<td>Gravel, coarse sand</td>
<td>4</td>
</tr>
<tr>
<td>Coarse sand, sand</td>
<td>8</td>
</tr>
<tr>
<td>Sand, fine sand</td>
<td>13</td>
</tr>
<tr>
<td>Fine sand, silt</td>
<td>20</td>
</tr>
</tbody>
</table>

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**Geological information**

The soil environment significantly affects the transport and fate of released polluting products and the likelihood of success with SVE. Highly permeable soils are most vulnerable, but they are also best suited to SVE. In clayey and silty soils penetration and spreading of fuels is much slower.

At the moment, fire and rescue services have not enough geological information on soils. Geological Survey of Finland (GTK) has prepared special theme maps, where vulnerable areas have been marked. (Nikkarinen 1995, Viatek 2000). These maps can be very easily interpreted by fire and rescue services when planning their response guides for chemical accidents that can take place on the roads or railways. Since the beginning of year 2002 geological information on the areas vulnerable to chemical spills in Finland is planned to be available on an Internet map server of GTK. Figure 3 shows how the main roads and railways commonly follow sandy and gravelly soils which are important groundwater formation areas. Figure 3 has been provided with typical weekly transportation amounts of flammable liquids on the roads and railways based on the statistics held by Liikenneministeriö.

**Fig. 3.** Main roads and railways on the sandy and gravelly soils of eastern Finland (Niemelä et al. 1993, Liikenneministeriö 1999).
Research material and methods

The following data sources and research methods have been utilized in this study:
- internet searches
- library searches
- use of computer programs
- interviews of experts
- visits to the sites where remediation is in progress
- study of the literature on remediation
- use of accident statistics.

The main focus is on the response to flammable liquid spills, because, based on the statistics on the incidents concerning hazardous materials released by the Ministry of Transportation, the most common chemicals spilt in the transportation accidents are flammable liquids. Descriptions of these accidents can be found in the newspapers and in the accident reports.

Response actions that are in use abroad (The Handbook of the National Fire Protection Association) were compared with those used in Finland (Tokeva Instructions). Tokeva Instructions include Nordic – chiefly Finnish and Swedish – response knowhow, but the German and English guidelines have also been used. The plant safety engineer, Jyrki Karppala (Fortum, the ex-fire chief of the Neste refinery), also provided useful information about the use of remediation techniques in the response methods of fire and rescue services. (Tokle 1992, Emergency Services College 1996).

Information about remediation methods used throughout the world can be found by searching the home page of The Environmental Protection Agency (EPA) on the internet. The keywords used were soil remediation and soil vapor extraction. In the EPA's web pages there is an exhaustive description of the different remediation methods with their advantages and disadvantages (EPA 1995). Under EPA there is also the VISITT -database (VISITT 1997), which includes both firms and the cleaning techniques they use, complete with the cost information. In addition to the EPA material, Finnish publications on the environmental technology have been used. These also included useful information on remediation methods and their costs.

After the different methods of remediation were analysed, soil vapor extraction appears to be a suitable response method for fire and rescue services.

There is available a special computer program (Hyper Ventilate) for evaluation of the suitability of SVE. The usefulness of SVE as a response method can be shown by an example. The spreading of a chemical in soil has been evaluated by the Swedish program RIB (RIB 1999).

Response methods of fire and rescue services

There are two basic types of methods for the mitigation of hazardous materials incidents, both physical and chemical. The following methods are in use abroad, especially in the USA.

Physical methods

Physical methods of control may involve several processes or procedures to reduce the area of the spill. The most common physical methods are (Tokle 1992):

Absorption. A process in which absorbents bind liquid.
Covering. By using plastic, it is possible to prevent the evaporation of volatile chemicals.
Dikes, dams, diversions, and retention. These refer to the use of physical barriers to prevent or reduce the quantity of liquid flowing into the environment.
Dilution. Refers to the application of water to water-soluble hazardous materials in order to reduce their concentrations.
Overpacking. The most common form of overpacking is that in which an oversized container is used.
Plug and patch. These are used to stop leaks in tanks or containers.
Transfer. Refers to moving a liquid, gas, or solid, either manually, by pump or by pressure transfer, from a leaking or damaged container or tank.
Vacuuming. Refers to vacuum removal of chemicals.
Vapor dispersion. Vapors from certain materials can be dispersed or moved by spraying with water.
Vapor suppression (blanketing). For example a layer of extinguishing foam is used on the surface of volatile liquid to prevent spreading of vapors.
Venting. A method for removing flammable or toxic gases from indoor areas.

Chemical methods

Chemical methods of control involve the application of chemicals to treat spills of hazardous materials. The most common chemical methods are (Tokle 1992):

Adsorption. A process in which a sorbate (hazardous material) interacts with a solid sorbent surface.
Controlled burning. Risks can be reduced by burning, in particular, burning an environmentally hazardous chemical to non-hazardous products.
Dispersion, surface active agents, and biological additives. Certain chemical and biological agents are used
Flaring. Refers to a safe way to destroy flammable vapors or gases.

Gelation. A hazardous material is bound to a gel.

Neutralization. Spills of acids or bases are neutralized to form a neutral salt.

Polymerization. A hazardous material reacts in the presence of a catalyst to form a polymeric substance. Solidification. A hazardous liquid is treated chemically to form a solid material.

Vapor suppression. Solid activated materials are used to treat hazardous materials and cause off-gassing.

Venting and burning. Refers to venting and controlled burning of a chemical with a high vapor pressure.

Response methods of Finnish Fire and Rescue Services

The response methods used in Finland are documented in the Tokeva Instructions (Tactical and Technical Guides for the response to chemical accidents). According to these instructions, which are suitable for acute mitigation of chemical accidents, the response methods used are (Emergency Services College 1996):

- reconnaissance of the accident site
- reconnaissance of the leak
- determination of an ignition hazard
- determination of the hazard area of a toxic gas
- removing ignition sources and ventilating
- cooling a tank
- covering the spray jet of a toxic liquid gas
- diking a spill, plugging a drain
- diluting and scrubbing a gas cloud
- controlling spill evaporation
- closing or plugging a leak
- pumping
- using sorbents
- neutralization
- decontamination of clothing and equipment
- discharge and lifting of road tankers
- controlled burning.

If we compare the response methods used in Finland to those used in the USA, we see that most of the Finnish methods are based on physical methods. Among the chemical methods, only controlled burning and neutralization are used. When it comes to the environmental effects and their reduction, internationally, fire and rescue services do not have effective methods for recovering chemicals from the soil or ground.

Remediation methods

Remediation methods can be grouped into four classes: chemical, physical, thermal and biological. Chemical methods include technologies such as washing and extraction, dechlorination, oxidation and reduction, electrochemical separation, stabilization (VISITT 6.0, 1997).

Physical methods include technologies such as soil vapor extraction, air sparging and dual-phase extraction (EPA 1995).

Thermal methods include technologies such as low or high temperature thermal desorption (EPA 1995), burning, vitrification (Jeltsch 1990) and steamstripping (Hilberts et al. 1986).

Biological methods include many different technologies such as bioventing, biopiles, landfarming, biosparging, natural attenuation and in situ bioremediation of groundwater (EPA 1995).

Methods suitable for fire and rescue services

There are some special terms for the methods that can be utilized by fire and rescue services. Preconditions for this kind of acute response work could be:

- the response equipment must be easily available
- the method and the equipment must be easy and fast to use
- the response has to be suitable for an acute spill
- the response method must be carried out as an "in situ" method
- the response method has to be suitable for a case where there is a lot of chemical on the ground, part as a pool on a ground surface, part absorbed into the soil.

Biological methods are too slow to be used by fire and rescue services and, therefore, not suitable for them. On the other hand, so-called ex situ methods cannot be used, because the response work has to be carried out "in situ" (e.g. without excavation or removal of polluted soils). Thus, only in situ methods can be accepted.

Use of chemical methods are restricted as most fire and rescue response teams do not have enough knowledge about chemical reactions. Moreover, fire and rescue services do not have the special chemicals or equipment needed for applying chemical technologies.

Among the thermal methods, the only useful technology for fire and rescue services is controlled burning of the soil polluted with flammable or combustible materials. Again, burning must be carried out as an in situ method.

Possible physical methods could be SVE, air sparging and dual-phase extraction. When air sparging is used, there is a risk of the chemical spreading, and
it is therefore not recommended for use if there is a free product on the ground. A disadvantage of using the traditional dual-phase extraction is that the equipment is too complicated. Still, the simplified idea of dual-phase extraction is useful. But the most useful physical method seems to be SVE.

Soil vapor extraction (SVE), also known as soil venting or vacuum extraction, is an in situ remedial method that reduces concentrations of volatile constituents in petroleum products adsorbed into the soils in the unsaturated (vadose) zone. In this method, a vacuum is applied through wells near the source of contamination in the soil. Volatile constituents of the contaminant mass “evaporate” and the vapors are drawn towards the extraction wells. Extracted vapor is then treated as required (commonly with carbon adsorption) before being released into the atmosphere. In Figure 4 a simplified system is presented for SVE.

The use of soil vapor extraction (SVE) in chemical spills

Because the structure of a spilt chemical changes over time, it is quite different to use SVE for a chemical that has been on the ground a longer time than in a case where the spilt chemical can be recovered as a fresh product. When SVE is applied, the yield of fresh petrol is 5 – 8 times greater than that of weathered petrol (Johnson et al. 1990).

There are many other factors that affect the effectiveness of SVE. Vapor pressure depends on the atmospheric temperature; the higher the temperature, the higher the vapor pressure and the easier it is to recover chemicals. SVE is not suitable for chemicals with low vapor pressures (e.g. non-volatile compounds).

Vapor flow is highest in permeable soils like sand and gravel. The vapor flow can be increased by using

Table 2. Yield of petrol when one extraction well is used (Johnson et al. 1990).

<table>
<thead>
<tr>
<th>Yield of petrol vapors (kg/h)</th>
<th>Soil</th>
<th>Vapor flow 1/min</th>
<th>Temperature °C</th>
<th>Darcy</th>
<th>Fresh Old</th>
<th>Fresh Old</th>
<th>Fresh Old</th>
<th>Fresh Old</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soils</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sand 0-100</td>
<td>Fine sand 1-10</td>
<td>Silty 0.1-1</td>
<td>Clayey silty 0.01-0.1</td>
</tr>
<tr>
<td>4069</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>407</td>
<td>41</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>407</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>41</td>
<td>4</td>
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<td>41</td>
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<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

- diameter of the extraction well 8 cm, radius of influence 12 m, vacuum of the extraction well 89 kPa
a strong vacuum. In emergency use the strongest possible vacuum should be utilized.

Table 2 shows the yield of petrol during the use of SVE in different soils and for both fresh spills and old spills.

An example

Typical transportation accidents are overturns of a tanker on a road. If we take an example of a tanker with about 20 m$^3$ of petrol (15 ton), and it leaks totally on the ground, we get a pool with an area of 50 m$^2$. The soil is sandy and the groundwater is 3 meters below the ground surface. The atmospheric temperature is 20 degrees Celsius.

After 15 minutes the spilt petrol has seeped down to 0.9 meter, and after an hour it has reached the groundwater. In this case the soil is able to hold only few cubic meters of petrol, but the remaining will be mixed with the groundwater. Water-soluble components of petrol, like MTBE and alcohols, will dissolve in the groundwater and the oily components will spread on the surface of the groundwater (RIB 1999).

Fire and rescue services normally arrive to the site of an accident in less than 15 minutes. So they have time to start response actions before the groundwater is contaminated. In this example, it is vitally important to recover quickly that part of petrol that could not be held by the soil. The fire and rescue services will first recover the liquid of the petrol pool by using a special turbine pump. After that, they could start soil vapor extraction from a hole made with a crowbar or a spade. A strong vacuum pump will be used to maximize the vapor flow. The effect of SVE can be increased by covering the spilt area with plastic. In this case the groundwater could be saved by the rapid actions of the fire and rescue services.

Conclusions

Because nowadays fire and rescue services have the readiness and equipment to pump flammable liquids, it is not a problem to pump these liquids from pools. On the other hand, fire and rescue services have no an effective method for recovering flammable liquids from the soil. With strong vacuum pumps, it is possible also to recover hydrocarbons from the soil. Even a simplified soil vapor extraction (or slurping) method can prevent the contamination of groundwater, and it will also minimize the environmental effects of leakage by preventing the spreading of oil products.

Fire and rescue services can easily learn to use SVE in their response work, but it will take years before they are well trained for this job. The biggest problem is the lack of special equipment and the lack of money to buy it. The cost of this equipment including a burner is about 200 000 FIM (33 000 euros) per unit. These costs could, however, be divided by co-operating with the environmental organizations in the same way as the oil accident response costs on watercourses are shared. Soil experts can help the fire and rescue services both in making response plans in advance for vulnerable areas, and providing expert advice on the soils of accident sites during the emergency response work.

Further study has already been started to tailor the dual-phase extraction or slurping based equipment for the emergency work. This so-called SVE-project will take two years and will be participated by rescue and environmental organizations. To our knowledge vapor extraction based techniques have not been utilized in Finland or other countries before in an accident response to recover chemicals from the soil.

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