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The publication contains 9 articles outlining the current research at the Geological Survey of Finland (GTK). The articles are divided into four categories. Petrological investigations, economicgeology and mineral exploration, Environmental studies, Geophysical applications and Analytical methods. At the end of the publication there is a list of publications by GTK staff in 2003 and 2004. From now on the current research of the GTK will be published in electronic form at the GTK’s internet pages, so this issue will be the last printed version on this subject so far.

An article in alvikite vein-dykes presents a new carbonatite in southwestern Finland. The vein-dykes intrude Palaeoproterozoic (1.88 Ga) pyroxene tonalite. The *Svecofennian orogeny in Finland produced a series of 1.9 Ga nickel bearing mafic and ultramafic intrusions mainly found within migmatisic mica gneisses. An intrusion model is presented for these in different tectonic conditions produced intrusions with pronounced variation in size, shape and lithology. An article on gold prospectivity of highly metamorphosed gneisses and migmatised southwestern Finland is presented. The mineralization is characterized by rusty, strongly foliated sillimanite-cordierite gneisses and mica schists. Ore prospecting in the ribbed moraine area of Misi, northern Finland has carried out as a part of the detailed investigation of the iron oxide-copper-gold deposits. Observations made have shown the area to be potential for ore prospecting. In the search for abundant and high quality kaolin resources more than 20 kaolin deposits has been investigated in northern Finland. This research has focussed on Palaeoproterozoic metasedimentary rocks using a variety of airborne and ground geophysical techniques supplemented by drilling.

In the Ostrobothnian region of western Finland extensive parts are covered by sulphide rich clay and silt sediments which alter to harmful sulphate soils when exposed to the air. A geophysical characterizing of the fine-grained sediments has been made and the results gathered are not directly applicable to another area without new reference drilling, sampling and chemical analysis. The preliminary results of a project to test and develop geophysical techniques for mapping sulphide tailings impoundments. The study site Hammaslahti Cu-Zn mine has a tailings area of 30 hectares with average height of 9 metres. Four different field-based portable fluorescence (OXRF) instruments for the determination of heavy-metal contents in contaminated soils were evaluated. The results were compared with results obtained by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and X-ray fluorescence spectrometry (XRF).

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

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THE NAANTALI ALVIKITE VEIN-DYKES: A NEW CARBONATITE IN SOUTHWESTERN FINLAND

by
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Key words (GeoRef Thesaurus, AGI): carbonatites, alvikite, dikes, geochemistry, host rocks, alteration, fenite, Naantali, Finland

Introduction

A small swarm of carbonate vein-dykes has been identified in the town of Naantali in southwest Finland. The vein-dykes range in width from 1-60 centimetres, with the majority between 3-20 cm. The vein-dykes intrude Svecofennian pyroxene tonalite. The vein-dykes are surrounded by a narrow band of fenitic alteration characterised chemically by removal of silicon and addition of potassium. In a wide area around the vein-dykes, the host rocks show signs of hydrothermal alteration, including widespread randomly oriented calcite + epidote + prehnite veinlets as well as pervasive staining from iron oxides. Chemical and textural evidence suggest that the carbonate vein-dykes are of magmatic origin.

Geological setting

The study area is extending for approximately two kilometres in length and one kilometre in width in the town centre area of Naantali. The majority of the vein-dykes follow the same general NW-SE trend and dip to the northeast at an average angle of 45°. The vein-dykes cut the existing schistosity of the surrounding rocks, the difference in strike being 60-90° and in dip 45–50°. Figure 1 is a map of the study area, showing the zones of alteration. Good quality outcrops are found along the steep western slopes of the Kuparivuori hill and along shorelines. Elsewhere, outcrops are limited to occasional roadcuts. Extreme sensitivity to weathering, soil or water cover, and the presence of man-made structures inhibits the search for additional vein-dykes.

Carbonate rocks are light grey to pink in colour, and often show a banded or layered texture. The vein-dykes are composed of medium to fine grained calcite, with repetitions of grain size variation parallel to the margins. Accordingly, the rock type could be called alvikite. Iron oxides are common as an interstitial dusting in streaks also parallel to the strike. Similar texture from the Wasaki complex of Kenya is taken as evidence by Le Bas (1977) of flow parallel to the margins and crystallisation from molten magma. Figure 2 shows the appearance of the vein-dykes in outcrop. In addition to the iron oxides, dark red-brownapatite is also easily visible in hand specimen. Other accessory minerals occasionally visible include quartz, allanite, and chlorite. Andersen (1984) describes a similar paragenesis from the Rødberg portion of the Fen complex. In one outcrop, fragments of the wall rock appear within the vein-dyke and appear to have been plucked from the sides. Given the low viscosity of carbonate melts (e.g. Dobson et al. 1996), this would require a forceful intrusion and rapid cooling.

The vein-dykes intrude dark grey Palaeoproterozoic (1.88 Ga, Väisälänen et al. 2002) Svecofennian pyroxene tonalite. A petrography of these rocks is given by Helenius (2003). Alteration surrounding the vein-dykes can be divided into three zones. Zone
I is in immediate contact with the vein-dykes and rarely exceeds 30 cm in width. It is a potassic contact fenite, dark red in colour, with a normative syenite composition.

Zones II and III are aureole fenites showing a gradation in alteration intensity. Randomly oriented calcite + epidote + prehnite veinlets are abundant in both zones. Zone II is approximately 200–300 metres in width, pink to red in colour, and has a normative granodiorite composition. Zone III extends an additional 200–300 metres from the vein-dykes, and is a pyroxene bearing grey granodiorite, with narrow bands (≤1 cm) of Zone II type alterations around the veinlets. The border between Zones II and III is arbitrarily placed at the limit of grey rocks. The original foliation of the rocks is preserved in Zone III, but is no longer evident in Zone II. Grain size is noticeably increased to 3–5 mm in the Zone I contact fenites, compared to 0.5–1.5 mm in the aureole fenites, Zones II and III.

**Petrography**

Thin section study reveals that the texture of the carbonate rock (alvikite) is hypidiomorphic. Calcite is subhedral and comprises approximately 90% of the rock. Quartz occurs as fine-grained aggregates and appears limited to areas near the contact. Fine grains of apatite, allanite, chlorite, fluorite, and titanite occur as
accessory minerals. In some samples calcite has been altered to prehnite at the contact. Opaque minerals occur generally in bands, and some mineral grains, particularly apatite, are stained with iron oxides. SEM examination has revealed monazite and members of the bastnäsite series as inclusions in apatite.

Allanite is non-metamict, strongly pleochroic, and commonly forms haloes around aggregates of apatite and quartz. Woolley et al. (1991) describe this texture from extrusive carbonatites in the Uuyanah area of the United Arab Emirates. Allanite is not a common mineral in carbonatites, but it has been reported from various locations including Bayan Obo, China (Yang & Le Bas 2004), Mountain Pass, California and Uuyanah, UAE (Woolley et al. 1991).

Zone I altered rocks one I contain K-feldspar, plagioclase, chlorite, and actinolite. Some samples have a thin (>5mm) band of actinolite + diopside at the contact. Silica in the form of free quartz has been almost completely removed from the rock. Feldspars are heavily altered and pervasively stained with iron oxides. Chessboard albite, as described by Kresten and Morogon (1986) from the Fen complex also occurs. Calcite, apatite, clinopyroxene, epidote and opaques occur as accessory phases.

Zone II rocks are similar, however, plagioclase is more abundant than K-feldspar. Zone II rocks also contain more quartz and less actinolite than Zone I. Alteration is less pronounced in feldspars, but iron oxide staining is still present throughout. Epidote, clinopyroxene and opaque minerals also occur as accessories. Apatite is no longer an important phase, and calcite only occurs in the calcite + epidote + prehnite veinlets.

In Zone III, alteration of the same type as in Zone II occurs only in bands (≤1cm) around veinlets. Biotite can be seen reacting to chlorite in the outer areas of these bands. Outside of these bands, the rock contains plagioclase, quartz, K-feldspar, biotite, and orthopyroxene. It should be noted that although the grey rocks of this zone appear unaltered, K-feldspar is present, while it is not present in the unaltered rocks examined by Helenius (2003). Microscopic-scale quartz veinlets also occur in this zone.

**Geochemistry**

Whole-rock geochemical analysis was conducted at the Geological Survey of Finland (GTK). Major and trace elements were determined using X-ray Fluorescence (XRF) and rare earth elements were determined using ICP-MS. Table 1 shows the analytical results as average concentrations of selected elements for the vein-dykes and each of the alteration zones. Average continental alvikite values are from Le Bas (1999). Pyroxene tonalite analyses represent unaltered host rocks and are taken from Helenius (2003).

Samples from Naantalni plot on the CaO-MgO-FeO diagram of Le Maitre et al. (1989) in the calcio-carbonatite field (Fig. 3). Both sövite and alvikite are calciocarbonatites, sövite being coarse grained and alvikite medium to fine grained. The Naantalni carbonatites fall into the latter category. Le Bas (1999) proposed a chemical distinction between sövite and alvikite based on trace element chemistry. On average, alvikites are less enriched in Sr and more enriched in REE than sövites. The Naantalni alvikite is enriched in Sr, REE and Y. Trace element concentrations from Naantalni are very close to the average for alvikite.

The carbonatite magma was enriched in K, Sr, Ba, P, REE, and to some extent Na and Y. Rollinson (1993) describes elements including K, Sr, Rb, and Ba as mobile, while P, REE, V, Y, Ti and Zr are immobile during hydrothermal alteration. Mobile element enrichment, particularly Sr, is disseminated throughout all the alteration zones. Immobile elements from the carbonatite magma, such as Y and REE, were only able to enter the Zone I fenesites. Immobile elements not present in the magma, but present in the host rocks, including V, Ti, and Zr, remain at constant levels in all the alteration zones. This shows that Zone I fenesites are the product of contact metasomatism while the Zone II and III aureole fenesitization was caused by a hydrous fluid. Whether the fluid source was degassing of the carbonatite or a later event is not known.

Figure 4 shows chondrite normalized REE abundances for the Naantalni rocks. LREE is heavily enriched relative to HREE, a pattern common to partial

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**Fig. 3. Naantalni alvikites plotted on the CaO-MgO-FeO diagram of Le Maitre et al. (1989).**
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<th>JWL0432 alivikite</th>
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<th>JWL0436 Zone I</th>
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Melting in mantle sources (e.g. Rollinson 1993). A high LREE/HREE ratio is typical to carbonatites (e.g. Woolley et al. 1991), while Ekambaram et al. (1986) have shown that hydrothermal carbonates will have low LREE concentrations and relative enrichment in MREE and HREE.

Three samples were analysed for stable carbon and oxygen isotopes. Sample JW0404 is alvikite and was analysed at the University of Helsinki; samples PSH-04–01.1 (alvikite) and PSH-04–01.2 (Zone II calcite + epidote + prehnite veinlet) were analysed at the Geological Survey of Finland. Results are given in Table 2. $\delta^{18}O$ values from alvikite samples fall within the normal range for carbonatites, while the value from the veinlet is only slightly heavier. Combined with the $\delta^{13}C$ values, the alvikite samples fall just below (lighter C) the field for carbonatites given by Deines and Gold (1973) whereas values from the veinlets fall to the right (heavier O).

### Discussion

Carbonatites are igneous rocks comprised of greater than 50% carbonate minerals (e.g. Le Bas 1977). Many different criteria have been proposed for the identification of carbonatites, unfortunately no single piece of evidence is truly diagnostic. Evidence from multiple sources including textures, mineral assemblages, geochemistry, alteration, and stable isotopes must be considered.

Carbonatites are characterised by high levels of Sr, Ba, REE and Y (e.g. Puustinen & Karhu 1999). The vein-dykes in Naantali are enriched in Sr, Y, and REE, particularly LREE. Ba, though virtually absent in the vein-dykes, is highly enriched in altered rocks, particularly in Zone I. Although carbonatite melts are typically high in K and Na, this is not universally true. For example, Barker and Nixon (1989) report K- and Na-poor carbonatite magma at Fort Portal, Uganda. The Naantali vein-dykes lack alkalis, but the enrichment pattern in the fenites suggests that the carbonatite magma was rich in K but relatively poor in Na.

Fenitization is a metasomatic process occurring around carbonatite and alkaline igneous intrusions typically involving the removal of silica and the addition of alkali elements (e.g. Le Bas 1977). Fenites show a great deal of variation in chemical composition, based on variations in the compositions of the fenitizing fluid, degree of fenitization, and original composition of the rock. Vartiainen and Woolley (1976) distinguish between sodic and potassic fenitization, while Kresten (1988) makes divisions of contact, aureole, and vein-type fenites. In Naantali, addition of K and removal of Si corresponds to potassic fenitization. Zone I alteration in Naantali represents contact fenitization; Zones II and III are aureole fenites of decreasing intensity.

A $\delta^{13}C$–$\delta^{18}O$ isotope comparison is often used to trace the origins of limestones. Isotope values are within the range of -2 to -12 $\delta^{13}C$ PDB and +10 to +26 $\delta^{18}O$ SMOW given by Barker and Nixon (1989) for the Fort Portal carbonatite in Uganda. Values are also close to those given by Puustinen and Karhu (1999) for the Halpanen carbonatite in southeastern Finland. The $\delta^{13}C$ values also differ markedly from the range of -3 to 3 $\delta^{13}C$ given by Karhu (1993) for sedimentary carbonates in the Svecofennian domain.

Carbonate vein-dykes in Naantali show magmatic textures including flow banding and incorporation of wall-rock fragments on an outcrop scale. Chemical evidence is consistent with established normal values for carbonatite. Isotopic evidence is also consistent with other carbonatites. Chemical and isotopic data also differ from normal sedimentary and hydrothermal carbonates. The combined body of evidence shows that the carbonate vein-dykes in Naantali formed by the intrusion of carbonatite magma.

### Table 2. Carbon and Oxygen isotope ratios. Samples are described in text.

<table>
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<th>JW0404</th>
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<td>$\delta^{13}C$ PDB</td>
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<tr>
<td>$\delta^{18}O$ SMOW</td>
<td>9.96</td>
<td>11.76</td>
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REFERENCES


INTRUSION MODEL FOR SVECOFENNIAN (1.9 GA) MAFIC-ULTRAMAFIC INTRUSIONS IN FINLAND

by
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Key words (GeoRef Thesaurus, AGI): intrusions, models, magmatism, shear zones, Paleoproterozoic, Svecofennian, Finland

Introduction

The Svecofennian orogeny in Finland produced a series of 1.9 Ga mafic-ultramafic intrusions in which, according to Nironen (1997) and Peltonen (2005), the mafic magma intruded in tensional structures above the subduction zone. Most of the nickel bearing intrusions occur within the Kotalahti and Vammala Nickel Belts around the Central Finland Granitoid Complex (Fig. 1). The country rocks surrounding the intrusions were in most cases extensively metamorphosed and deformed during the early stage of the Svecofennian orogeny (Gaál 1980, Kilpeläinen 1998, Koistinen 1981, Mäkinen & Makkonen 2004). Metamorphic conditions reached upper amphibolite facies, and overthrusting and faulting resulted in fragmentation of both the intrusions and the country rocks. Different tectonic conditions produced intrusions with pronounced variations in size, shape and lithology (cf. Papunen & Gorbunov 1985). Owing to the synorogenic timing of the magmatism the related intrusions have very complicated tectonomagmatic history. This makes the Svecofennian intrusions quite different when compared to anorogenic nickel sulphide bearing intrusions like Sudbury, Voisey’s Bay and Norilsk (Mäkinen & Makkonen 2004).

The Svecofennian nickel bearing mafic and ultramafic intrusions are mainly found within migmatitic mica gneisses, although in the Kotalahti Nickel Belt...
some occur within or at the contact of the Archaean gneisses. In the surface section they often form oval shaped bodies of varying dimensions, the largest ones up to 10 km. The intrusion bodies include gabbro-only, peridotite-only and gabbro-peridotite types. According to Mäkinen (1987), two types can be separated mineralogically: 1) Vammala type with abundant clinopyroxene and 2) Kotalahti type with abundant orthopyroxene, the former occurring mainly in the Vammala Nickel Belt and the latter in the Kotalahti Nickel Belt. The mineralogical differences are largely due to differences in country rock contamination (Makkonen 1996).

In Finnish nickel mining history the Svecofennian deposits have played a major role. Altogether nine deposits have been mined beginning in 1941 at Makola (Puustinen et al. 1995) and mining still at Hitura, which has become the largest nickel mine in Finland (12.4 Mt at 0.60 % Ni and 0.22 % Cu, Isomäki 2004). The total production of the Svecofennian nickel mines is at present about 41 Mt at 0.6 % Ni.

**Intrusion Model**

The 1.9 Ga tholeiitic magma has been described forming both extrusions and intrusions in Finland. In the Juva area extrusions are represented by the mafic and ultramafic volcanics (Makkonen 1996) and in the Tampere-Vammala area by the Takamaa-type mafic volcanics (Kilpeläinen 1998). In both areas it is proposed that intrusion bodies were formed at different levels during magma ascent, as also suggested by Peltonen (1995) in the Vammala area.

Some important facts for an intrusion model are available: 1) intrusion took place near the maximum intensity of $D_2$ and peak of the metamorphism (Kilpeläinen 1998, Koistinen et al. 1996, Mäkinen & Makkonen 2004, Marshall et al. 1995, Peltonen 1995, 2005), 2) most of the intrusions occur within a highly deformed/high metamorphic zone but there are intrusions also at higher levels within lower metamorphic grade rocks, and 3) comagmatic volcanics usually occur within lower metamorphic grade areas relative to the intrusions, but in some places they are in contact with an intrusion.

$D_2$ deformation phase is characterised by recumbent folds and overthrusting due to compression from south to north (Koistinen 1981, Koistinen et al. 1996). This is indicated by the Proterozoic sequences overthrusted onto the Archaean craton. Overthrusting also caused fragmentation of the Archaean/Proterozoic boundary and thus blocks of Archaean gneiss are enclosed within Proterozoic supracrustals. $D_3$ tectonic activity generated variable migmatite structures in supracrustals including stromatic, schollen, schlieren and nebulitic structures. The neosomes composition is tonalitic and a wide range of mafic-ultramafic rock fragments is found within migmatites (Mäkinen & Makkonen 2004). The occurrence of these migmatite zones together with the intrusion bodies and fragments has been described by many researchers (e.g. Gaál & Rauhämäki 1971, Gaál 1972, Gaál 1985, Grundström 1980, Häkli et al. 1979, Mäkinen 1987, Pupunen 1980), but the genetic link between the migmatite zones and the intrusions has remained in many cases indistinct. Korsman et al. (1999), however, proposed that the low-P/high-T metamorphism and the generation of tonalite-trondhjemitic migmatites in the Svecofennian crust were caused by extensive magma under/intraplating during and soon after subduction and crustal thickening (1885 Ma). Mafic magmatic underplating after tectonic thickening of the Svecofennian crust has also been proposed by Korja et al. (1993), Lahtinen (1994) and Lahtinen and Huhma (1997).

Figure 2 shows a model, in which magma is intruding during $D_2$ within the Svecofennian collision zone. The basic idea in the model is the generation of a high temperature shear zone (HTSZ) between a large midcrustal mantle magma reservoir and an imbrication zone of thrust folds, probably above the subduction (after rifting in a collision zone). The shear zone developed at the level of 15 – 20 km as indicated by the PT-calculations from spinel-bearing symplectites and reaction rims formed between cumulus olivine and intercumulus plagioclase during cooling of the intrusion (Tuisku & Makkonen 1999). Similar shear zones have been described, e.g., in the southern Alps (Ivrea-Verbano zone, Snoke et al. 1999). HTSZ corresponds to the Svecofennian nickel belt migmatites described earlier (especially to the schollen migmatites). When the mafic magma intruded the mobile shear zone, it formed bodies of various shape and size. The bodies were not deformed strongly and only in rare cases $S_2$ schistosity was formed within. Because many intrusion bodies are found in $F_3$ folds, magma possibly favoured such an extensional place in the shorter limb of a sheared $F_2$ fold (Mäkinen & Makkonen 2004). After crystallisation, the competent intrusion bodies also controlled fold formation (1 in Fig. 2a). Some of the bodies were overturned after crystallisation due to continuous thrusting and many of them fragmented. In larger intrusion bodies thrusting is represented by faults separating the intrusion body into blocks (3 in Fig. 2a). More sill-like bodies were folded.

Most of the magma intruded into the HTSZ, but because of local extension caused by the uplift of imbrication blocks, as described similarly e.g. in the eastern Alps by Ratschbacher (1989), some intrusion
bodies (2 in Fig. 2a) were formed above the HTSZ within the lower metamorphic grade rocks (e.g. metaturbidites showing primary structures).

The heat of the mafic magma, together with the latent heat produced by the crystallisation of the magma, enabled migmatite neosome formation. In extensional places neosome formation was promoted by pressure release and the melt concentrated as tonalitic bodies.

The true thickness of the HTSZ is difficult to estimate. Probably it varied along the zone being largest in places where magmatic activity was strong. In the Kotalahti Nickel Belt schollen migmatite zones are up to 2 km wide (Gaál 1985), although the total width of the migmatite zone is wider. The Ivrea-Verbano zone with stromatic migmatites in the southern Alps is 1 to 1.5 km thick (Snøke et al. 1999). From above, it can be assumed that the thickness of the HTSZ was less than 5 km.

The mafic magma probably reached the surface slightly before the main intrusion event. This volcanic event thus took place during the rifting stage in the collision zone. The volcanic rocks are now represented within the Finnish Svecofennian by the 1.9 Ga amphibolites and picrites (cf. Gaál & Rauhanäki 1971, Häkli et al. 1979, Kousa 1985, Lahtinen 1996 and references therein, Makkonen 1996, Peltonen 1990, Schreurs et al. 1986). Because of the subsequent thrust folding the volcanic rocks were buried down to the same levels where comagmatic intrusion took place. This, together with the possibility that the intrusion bodies are lifted up during thrusting (3 in Fig. 2a), may explain the close spatial association of the volcanic and comagmatic intrusive rocks seen in places within the Svecofennian. In addition, later, during the D3 phase (Fig. 2b) the earlier sub-horizontal rock units were folded in many places sub-vertical to vertical, which brought rock units to the present erosion level from various levels (Gaál 1980, Koistinen et al. 1996, Kilpeläinen 1998, Makkonen 2002, Mäkinen & Makkonen 2004). It is important to note that, according to the model the volcanics do not necessarily occur just above their plutonic counterparts. Rather, it is more probable that there is always a degree of lateral movement between them. This makes the correlation difficult at a local scale.

Fig. 2. Intrusion of Svecofennian 1.9 Ga mafic magma and related structural history. A) Intrusion took place during the maximum intensity of D2, when the high temperature shear zone (HTSZ, marked by broken line) was active. Above the HTSZ continuous thrusting formed an imbrication zone in which the primary stratigraphy was obscured. B) During D3 sub horizontal rock units were folded vertical to sub-vertical. For more explanation see text.
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THE HALIKKO KULTANUMMI PROSPECT – A NEW TYPE OF GOLD MINERALIZATION IN THE HIGH-GRADE GNEISS TERRAIN OF SOUTHWESTERN FINLAND

by

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Key words (GeoRef Thesaurus, AGI): mineral exploration, gold ores, gneisses, sulfides, hydrothermal alteration, Proterozoic, Kultanummi, Halikko, Finland

Introduction

In this article we consider the gold prospectivity of the highly metamorphosed gneisses and migmatites of southwestern Finland, using the Kultanummi occurrence at Halikko as a potentially representative example of the type of mineralization to expect in this terrain. In recent years a number of gold occurrences have been found in the region between Paimio and Halikko in southwestern Finland, largely due to the efforts of amateur prospectors, who have submitted both outcrop samples and mineralized glacial boulders to the Geological Survey of Finland (GTK) for further evaluation. The first discovery was the Korvenala-Kaleva occurrence near Paimio but further incentive was given in 2001 when Veli-Matti Koi-vula recovered gold while panning oxidized regolith material at Kultanummi, near Halikko. Three short holes were drilled at this site, with the best intercept yielding gold grades of 0.5–6 ppm over intervals of 1–6 m. Follow-up exploration during the next field season delineated a gold-critical sulfide-bearing zone over a distance of 600 m, and with a maximum width of 150 m, to the south of Isorahkaneva mineralized zone (Figs. 1 and 2). The anomalous area was then sampled for heavy mineral fractions, and systematically covered by ground magnetic and IP surveys, and finally drilled; the results of these investigations are reported below.

Geological setting

The bedrock at Kultanummi consists of upper amphibolite facies mica gneisses and metavolcanics, intruded by granitic veins. The Korvenala-Kaleva prospect, which was studied earlier by GTK, is situated some 10 km west of Kultanummi (Fig. 1). Interpretations based on both bedrock maps and airborne magnetic data indicate that both prospects lie within a discrete structural domain bounded by shear zones and granitoids (Fig. 3). Regional structural trends tend to be nearly E-W, with tight folding. Kultanummi is located within a magnetic anomaly zone that is stronger in the southern part. The area immediately to the north of Kultanummi is reminiscent of the structural block defined at Paimio. The Korvenala-Kaleva prospect at Paimio was located by heavy mineral studies following discovery of a mineralized boulder, and it is also well expressed in till geochemistry and has a distinct IP response (Rosenberg 2000). Drill cores analyzed from the from Korvenala-Kaleva show anomalous gold values over a relatively wide area, with a mean of 310 ppb for 252 samples. However, in the most anomalous intervals, grades are usually 0.1–1 ppm,
with only a few exceptional intersections of 5.4 ppm over 1 meter and 1 ppm over 5.45 m (Rosenberg 2000). Arsenopyrite is also present, but there is the degree of correlation between Au and As is not high (Rosenberg 2000).

Geological setting at Kultanummi

Mica schists and gneisses intruded by granitic and pegmatitic veins predominate at Kultanummi, with minor intercalations of amphibolites and plagioclase porphyry. However, the most prospective lithology appears to be a relatively quartz-rich gneiss, occurring as discrete units 10–30 m thick within the more typical mica gneisses. They typically contain disseminated sulfides and are characterized by aggregates of sillimanite and sporadic cordierite, alternating with bands of calc-silicate rock.

Mica schists locally display distinct banding, as a result of systematic variations in mica abundance as well as concentrations of presumably metamorphic, idioblastic magnetite grains (Figs. 4 and 5). Principal minerals are quartz, plagioclase, potassium feldspar and biotite, with smaller amounts of red garnet, apatite, zircon, carbonate and tourmaline. Mica schists occasionally grade into coarser-grained gneisses and may even display a more granitic appearance or show extensive epidote alteration. Occasional quartzo-feldspathic intercalations also occur, with distinctly less biotite, forming discrete aggregates, and correspondingly more potassium feldspar than in the mica schists.

Quartz-rich sillimanite gneisses and sillimanite-cordierite gneisses tend to pale greenish gray on weathered surfaces and are somewhat rusty, with complex, tightly folded quartz veins (Fig. 6). These rocks are also readily distinguishable in drill core because of their pale colour and textural heterogeneity. Sillimanite is fibrous, indeed fibrolitic (Fig. 7), while cordierite occurs as pale blebs 1–5 mm in size; microscopic inspection shows that they are extensively pinitized. In addition to sillimanite and cordierite, the gneisses consist principally of quartz, plagioclase, potassium feldspar and biotite. Compositional variation between layers is defined by variations in the proportions of sillimanite and cordierite. Accessory minerals include muscovite, garnet, tourmaline and a range of sulfides, notably chalcopyrite, pyrite, pyrrhotite; arsenopyrite is also present, and galena has been found in fracture fillings.

During drilling, a dark green plagioclase porphyry unit about 10 m thick was intersected. The rock is foliated, with some silicification and alteration of hornblende to biotite and also contains angular fragments of mafic composition several cm in diameter. Reddish or grey pegmatite dykes, usually less than 5 m

Fig. 1. Locations of the Korvenala-Kaleva and Kultanummi gold occurrences on the bedrock geological maps sheets 2021 (Lehijärvi, 1955) and 2022 (Huhma, 1957).
Fig. 2. Detailed map of the Kultanummi prospect (Wiik, 2004), showing drill hole locations. Area of map is approximately 8 km². Gold-critical rusty outcrops are indicated with pale brown colour.

Fig. 3. Korvenala-Kaleva (Paimio) and Kultanummi (Halikko) occurrences shown on airborne magnetic image. Tapio Ruotoistenmäki (2004) has indicated inferred tight fold hinges with E-W trending axial surfaces by yellow crosses. Yellow lines indicate trends of proposed Au-critical zones, subparallel to fold limbs.
thick, are common and contain, in addition to quartz, feldspar and mica, black tourmaline, magnetite and occasionally sillimanite. Medium-grained reddish granitic dykes are also present, sometimes containing garnet and magnetite.

**Gold mineralization**

Pyrite is the most typical sulfide phase at Kultanummi, imparting a rusty aspect to outcrops, and occurring as disseminations, as solitary grains and aggregates.
Fig. 6. Rusty sillimanite-cordierite gneiss; light-coloured, elongate knobby aggregates of both sillimanite and cordierite stand out in relief on weathered surfaces. Note also intense folding of reddish feldspathic quartz vein. Photo: Sari Grönholm

Fig. 7. Photomicrograph of sillimanite gneiss. Si = sillimanite, Qz = quartz. Photo: Jari Väätäinen

and along joint planes. Disseminated chalcopyrite and pyrrhotite also occur, and isolated arsenopyrite grains or grain aggregates are present, particularly near quartz vein margins. Galena has also been found in a few narrow veins. Tourmaline is also a characteristic phase in mineralized rock. Chemical data reveal a reasonable correlation between Au and S, but only a weak relation between Au and As (Fig. 8).

Gold at Kultanummi appears to be closely associated with the relatively silicic, or silicified sillimanite
gneisses, the highest abundances of 6490 ppb and 2100 ppb having been recorded from sillimanite mica gneiss and sillimanite-cordierite gneiss respectively. However, this correlation is not so obvious from the geochemical data, in that results appear to indicate that other lithologies can be anomalous with respect to Au. It is likely however, that the gold in the more typical mica gneisses is associated principally with quartzofeldspathic veins. Altered lithologies (Groups 2 and 3 in Fig. 9) also contain relatively high S, compared of the generally low background values in other rock types at Kultanummi.

**Alteration**

Hydrothermal alteration in the gold-anomalous zone at Kultanummi is typically evident from increased sulfide abundances (pyrite, pyrrhotite, chalcopyrite and more rarely arsenopyrite), presence of sillimanite-cordierite rocks, silicification and locally from abundant magnetite in adjacent mica schists. Silicified rock almost invariably contains black, fine-grained tourmaline, accompanied by sillimanite, cordierite, sulfides and gold. Carbonate minerals are occasionally present in Au-enriched rocks. Intensely foliated lay-

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**Fig. 8.** Correlation diagrams for Au and S and Au and As; data from the first three holes drilled at Kultanummi (R379-R381) are not included.

**Fig. 9.** Variation in Au (left) and S (right) for different rock types at Kultanummi: 1 = mica schist and gneiss, 2 = sillimanite-quartz rock, 3 = sillimanite-cordierite gneiss, 4 = pegmatite, 5 = plagioclase porphyry, 6 = amphibolite, 7 = quartzofeldspathic schist. Lithologies determined from drill core logging.
Fig. 10. Selected major element abundances for various rock types at Kultanummi: 1= mica schist and gneiss, 2= sillimanite-quartz rock and sillimanite-cordierite gneiss, 3= plagioclase porphyry, 4= amphibolite 5= quartzofeldspathic schist 6= pegmatite. Rock types defined from drill core logging.

MgO
ROCKTYPE

0 1 2 3 4 5 6 7 8
-2 -1 0 1 2 3 4 5 6

Al2O3
ROCKTYPE

0 1 2 3 4 5 6 7 8
-10 -8 -6 -4 -2 0 2 4 6 8

K2O
ROCKTYPE

0 1 2 3 4 5 6 7 8
-1 -0.5 0 0.5 1 1.5 2 2.5

Fe2O3
ROCKTYPE

0 1 2 3 4 5 6 7 8
-2 -1 0 1 2 3 4 5 6

ers also display late metamorphic retrograde mineral assemblages, notably biotite replacement of other minerals, in particular hornblende, biotite replacement by chlorite and sericitization of plagioclase. Within the zone of hydrothermal alteration, even the plagioclase porphyry contains more elevated gold concentrations (106 ppb over 1 m) compared to values of below 5 ppb when it is associated with unaltered amphibolites.

Major element abundances in altered rocks broadly mirror those of mica schists and mica gneisses; magnesium, aluminum, potassium, and iron contents in particular suggest that the sillimanite and cordierite gneisses were originally typical pelitic gneisses in composition (Fig. 10).

Magnetite is a characteristic accessory mineral throughout the study area. Nevertheless, the Au-mineralized sillimanite-cordierite gneisses are generally only weakly magnetic. Susceptibilities are higher in associated mica schist intercalations. Magnetite also occurs as large discrete crystals at the margins of the sillimanite-cordierite gneiss layers, and within cross-cutting granitic and pegmatic dykes, particularly within the hydrothermally altered zone. Magnetite can also be found in the mica schists as isolated idioblastic grains, or forming narrow bands.

Susceptibility measurements indicate some systematic relationships between magnetite, sulfides and gold, and these correlation may be related to mineralization process. For example, in drill core from R391 and R394, Au and S abundances correlate well (Fig. 11).
Fig. 11. Variations in gold concentration (red), susceptibility (black) ja sulfur (blue) for selected drill core intervals from Kultanummi. Note the strong positive correlation between Au and S and high susceptibility values, due to the presence of magnetite, at the margins of the mineralized zone.
Whilst in general Au and S abundances fall markedly as magnetite content – and hence susceptibility – increase, in some cases (R388), a positive association between S abundance and susceptibility is observed, related to the presence of pyrrhotite.

**Discussion**

GTK has been studying the Paimio Korvenala-Kaleva and Halikko Kultanummi gold occurrences sporadically since 1995. The geological environment of these prospects differs from that of the Tampere and Häme schist belts, which are at lower metamorphic grade and have been the main focus of GTK activity for many years (Kärkkäinen et al. 2003). The Korvenala-Kaleva and Halikko prospects both occur within similar rock types, within a distinct structural zone bounded by shear zones and relatively late orogenic granitoids. The mineralization at the Halikko Kultanummi occurrence is characterized by rusty, strongly foliated sillimanite-cordierite gneisses and mica schists.

This Au-critical association of sillimanite- and cordierite-bearing gneisses is considered to represent hydrothermal alteration accompanying the gold mineralization, and the sillimanite and cordierite is attributed to a younger prograde metamorphic event superimposed on pre-existing sericitic and chlorite schists. On the basis of currently available data it is, however, difficult to determine whether or not the sericitic/chloritic alteration would have been formed within a shear zone developed during early stages of the regional metamorphic event, rather than predating the metamorphism. Geochemical data suggest that the protoliths to the altered rocks were mica schists and the unaltered mica gneisses adjacent to the mineralized zone also appear to represent the more strongly recrystallized derivatives of mica schists.

The Kultanummi gold mineralization is characterized by strong geochemical correlation between gold and sulfur, the relatively low As and a prominent enrichment of magnetite in wall rocks. Sulfidation reactions are suggested as a mechanism for gold precipitation, because the highly sulfidized zone and elevated Au abundances occur within a restricted part of the hydrothermal alteration zone, while the cordierite-sillimanite rocks in the western part of the Kultanummi zone are less mineralized when compared to the main zone. The altered rocks and accompanying quartz veins are also tightly folded, indicated that gold mineralization predates at least some of the deformation.

According to Rosenberg (2000), the predominant rock type at the Korvenala-Kaleva prospect is plagioclase porphyry, which has somewhat higher As abundances than at Halikko. At both prospects however, free gold must be present, as deduced from gold grains in heavy mineral separates recovered from till and weathered bedrock. A third Au occurrence in relatively high grade terrain is at Stenno, near Kemiö, where gold is present in sillimanite gneisses within a metavolcanic sequence (Nordbäck 2003).

**Summary**

Recent studies in the relatively high grade metamorphic terrain of southwestern Finland have delineated several gold occurrences, including the Halikko Kultanummi prospect. Mineralization at Halikko is associated with silicic alteration in sillimanite-cordierite gneisses and a strong association between silicification, sulfidation and gold has been recognized. In addition, rocks surrounding the mineralized zone show a prominent enrichment in magnetite. The alteration zone and associated quartz veins carrying anomalous gold values (>10 ppb) are also strongly folded. The distribution of gold is relatively well constrained by drilling within the alteration zone and correlates well with sulfide abundance.

Both the Halikko Kultanummi prospect and the Paimio Korvenala-Kaleva occurrence previously discovered by GTK attest to the mineralization potential of this previously neglected metamorphic terrain in southwestern Finland.

**REFERENCES**


ORE PROSPECTING IN THE RIBBED MORaine AREA OF MISI, NORTHERN FINLAND

by
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Key words (GeoRef Thesaurus, AGI): mineral exploration, moraines, ribbed moraines, till, boulders, glacial transport, Misi, Kemi-järvi, Finland

Introduction

Geological Survey of Finland (GTK) has carried out intensive ore prospecting in the area of Misi since the 1990s. The studies have been a part of the detailed investigation of the iron oxide-copper-gold deposits in northern Finland. At the same time, bedrock mapping has been undertaken in the area and the map sheet of Vikajärvi (map sheet 3614) at a scale 1:100 000 was published at the end of 2002 (Hanski 2002). The area is known for its iron formations, of which the occurrences of Kärväsvaara, Raajärvi and Leveäselkä were mined during 1959-1975. The total volume of the quarried ore is over 8 million tons, of which 3.5 million tons is Fe concentrate. Observations made by local people and geologists during mapping have shown the Misi area to be once again potential for ore prospecting.

The village of Misi is situated about 50 km NE of the city of Rovaniemi, in the direction of Kemijärvi (Fig. 1). The area lies in the middle of the ribbed moraine area of Peräpohjola, northern Finland. Ore boulder observations made of the different landform types have focused on the areas of Köyry, Tuorevaara and Venejärvi (Fig. 2). The boulders are mainly composed of hydrothermally altered amphibolites with anomalous contents of Zn (ca. 5% in Köyry and ca. 3% in other areas), Cu and Au. In the present study, carried out in 2004, the transport distances and the most potential source areas of the boulders have been estimated. The methods we have used have been field studies and tractor excavations together with interpretation of glacial morphology. Glacial flow directions, till structures and stratigraphy, pebble lithology, heavy mineral composition and geochemical features have been studied in the 23 test pits, of which the mean depth was about 3.5 m. Till samples have been left at the GTK’s laboratory in Rovaniemi for chemical analysis (ICP-AES method).

Geological setting

Bedrock of the study area is composed of the rocks of the Peräpohja Schist Belt (2.0-2.3 Ga) and the Central Lapland Granites (1.8 Ga) (Fig. 2). The southern part of the area consists of mica gneiss while the central area consists of the large NW-SE-oriented zone of arkosic gneiss. A narrow zone of mafic tuffites and mica schists cuts the whole area in the same direction as the arkosic gneiss. By contrast, the assemblage of mafic metalavas and basalt magmas (gabbros) is dominant on the eastern side of the village of Misi. The schist belt is bordered by granites in the north. The massive Fe-ore occurrences are closely related to the dolomite-skarn rock-serpentinite assemblage in the east. The schists with hydrothermal alteration in the
Fig. 1. A location of the study area in the village of Misi, NE of the city of Rovaniemi. The area is located in the middle of the ribbed moraine area in Peräpohjola, southern Lapland.

Fig. 2. Generalized bedrock map of the study area and the location of the most potential ore boulders in the case study areas.
volcanic environment seem to be the most critical for a new type of ore occurrences in the central area.

The proportion of bedrock outcrops is estimated to be only 1% of the land area. The outcrops occur mainly as groups near the high hill areas. The surface of the bedrock is mostly covered by the glaciogenic deposits, which include different types of active-ice formations and one esker-system (Fig. 3). In topographic expression and lowland areas, ribbed moraines are the most common formation type. The ribbed moraine is a group of moraine formations that have the same kind of morphology and similar subglacial origin (cf. Hätterstrand 1997). They are formed of ridges perpendicular to the most recent glacial flow direction, which is, according to striae and fabric analyses from the direction about $270^\circ-290^\circ$ in the Misi area. The transition to the longitudinal formations is seen as a streamline element related to the unique ribbed moraine ridges and as a transitional series from ribbed moraines to drumlins and flutings (cf. Aario 1990). For that reason, these moraine ridges can also be called Rogen moraines, according to Lundqvist (1969).

The ridges are composed of two till units representing different glacial phases (Fig. 4). The lower unit is compact and homogenous in its structure and sandy in its matrix. It formed subglacially during the advancing stage of the glacier under lodgement processes. Glacial flow direction was from NW to SE. By contrast, the upper till unit consists partly of re-deposited material due to the quarrying activity during the formation of the ridges and also melt-out till deposited at the latest stage of deglaciation, while the edge of the glacier melted away after the movement stopped. The structures are sandy lenses and layers together with fine-grain laminae in the former case and homogeneity and occasional flow or consolidation structures in the latter case. The uppermost part of the ridges was washed during the later stages of the Ancylus Lake, after which the water level decreased due to isostatic uplift of the ground.

The ribbed moraine ridges in the Misi area are characteristically strewn with boulders. The abundance of boulders at the surface is mainly due to the depositional processes occurring during the formation of ridges, but partly in consequence of the post-glacial washing. The rock types of the boulders correlate well with the rock types found in the underlying bedrock, and this is a typical feature for the ribbed moraines in other parts of the Peräpohjola area, too (cf. Aario & Peuraniemi 1992, Sarala & Rossi 1998, 2000). The transport distances
are estimated to be only from some tens of metres to a few hundreds of metres for local rock material but several kilometres for granites. The same feature is also reflected in the geochemistry of the upper till (cf. Sarala & Rossi 1998). Field observations have proven this phenomenon is of use in prospecting. In the case of drumlins and flutings, transport distances are many times greater and the direct control between till material or surficial boulders and bedrock is hard to determine.

**Conclusion**

The ore potentiality of the Misi area, northern Finland seems to be high, because of the great number of ore boulders found at the surface of different moraine formations in the area. The transitional series of active-ice moraine formations from transversal ribbed moraines to longitudinal drumlins and flutings have been observed. Ribbed moraine ridges are composed of Rogen moraine and hummocky ribbed moraine types in the area. Formation of the ridges seems to be a result of a two-step process (Fig. 5), where frozen subglacial sediments were fragmented and moved under compressive glacial flow in the first stage. Secondly, the dominant freezing conditions caused the freeze-thaw process to prevail under the moving ice leading to the quarrying activity that reached the bedrock surface between the newly born ridges. These kinds of conditions seem to have existed under the ice sheet in the transition zone between frozen and thawed beds during deglaciation (cf. Hättestrand 1997).

Ribbed moraines are ideal for prospecting work, because of the short transport distance of rock material in the uppermost till. Particularly, boulders within the till and at the surface reflect the variation of local bedrock composition. This phenomenon is common for all ribbed moraine types if the pre-existing sediments have been thin enough for the quarrying to have reached the bedrock surface. Due to formation processes, prospecting work differs quite a lot in the areas of ribbed moraines compared to areas of drumlins and flutings. For example, the boulders in the uppermost parts of ridges must be taken account when choosing the equipment for geochemical sampling. The observations and the results presented here will be clarified in the near future when the chemical analyses of till samples and some planned deep drillings have been done.

**Acknowledgements**

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REFERENCES


EXPLORATION RESULTS AND MINERALOGICAL STUDIES ON THE LUMIKANGAS APATITE-ILMENITE GABBRO, KAUHAJOKI, WESTERN FINLAND

by

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Key words (GeoRef Thesaurus, AGI): mineral exploration, titanium ores, ilmenite, magnetite, apatite, gabbros, geochemistry, Proterozoic, Lumikangas, Finland

Introduction

Geological Survey of Finland (GTK) has explored the Lumikangas gabbro since 2002 as a potential source for titanium and phosphorous. Lumikangas is situated 15 km south of the town of Kauhajoki in South Pohjanmaa (Fig. 1). The landscape is a flat divide area, 170 m above sea level, consisting of eskers bordered by marshes. According to previous seismic measurements, the overburden is 30-70 m thick. Recent drillings intersected a 35-50 m soil cover composed of sand-silt-gravel layers with a till interbed.

The Lumikangas area was selected as a target for exploration on the basis of an outstanding regional geophysical anomaly (Fig. 2). There are magnetic and gravity highs on the low-altitude aeromagnetic and on the regional gravity maps, respectively. The economic interest of Lumikangas is in titanium and phosphorous because this geophysical anomaly belongs to the Kauhajoki gabbro province, which is generally characterised by high content of ilmenite, magnetite and apatite (Kärkkäinen et al. 1997).

The first exploration stage, carried out in 2002, was related to GTK’s bedrock mapping and ore exploration at Pohjanmaa. The first drill hole (R396) was focused on the magnetic and gravity maxima, where the overburden is the lowest, according to seismic profile across the Lumikangas regional anomaly (Lehtimäki 1984). This drill hole penetrated a layered gabbro containing 15-20 wt% of magnetite, apatite and ilmenite in total. The Lumikangas gabbro was found to be a potential exploration target on the basis of chemical analyses and mineralogical studies.

In the second stage, carried out in 2004, systematic ground magnetic and gravity measurements were made for the area of 5 km². After geophysical interpretation five drill holes in two profiles were drilled, totalling 1308 m (R396-401), and geophysically logged. Material for this study includes 446 XRF-analyses, mass susceptibility measurements (magnetite wt %) along the drill core samples, microprobe analyses from polished thin sections and ICP-MS analysis from apatite concentrate. This paper presents the results of preliminary exploration and mineralogical studies on the Lumikangas apatite-ilmenite gabbro.

Regional geology

The Kauhajoki gabbro province is situated in the western part of Central Finland Granitoid Complex (1870-1890 Ma), between the synorogenic granitoids and the late orogenic Lauhanvuori granite (Fig. 1). The mafic-ultramafic intrusions at Honkajoki (Pääkkönen 1962, Pakarinen 1984, Rämö 1986), Kauhajarvi (Kärkkäinen & Appelqvist 1999), Hyppää (Huuskonen & Kärkkäinen 1994) and Lumikangas are layered, mainly gabbroic in composition, and are variably differentiated from peridotite to anorthosite. They all
Fig. 1. Location of Lumikangas at Kauhajoki on a road map and a generalised geological map.

Fig. 2. Aeromagnetic and residual gravity high (curves) indicating potential ilmenite targets.
contain considerable amounts of ilmenite, apatite and magnetite, averaging 18–22 wt% together.

**Exploration geophysics**

All known ilmenite gabbros of the Kauhajoki province are visible as magnetic and gravity highs on the predicted map compiled from aeromagnetic and residual gravity data (4–6 points/km², Fig. 2.). The Lumikangas gabbro is situated in an areal gravity gradient, where the regional level increases 3 mGal over a distance of 1.5 km. The maximum gravity anomaly caused by the Lumikangas intrusion is 3.5 mGal as measured from the estimated base level of the regional gravity field.

The area of 5 km² was studied by using magnetic, gravity and horizontal loop EM measurements over the Lumikangas gabbro. According to the seismic profile, the overburden is 30–70 m thick over the intrusion. The magnetic anomaly, at its highest 4 000 nT, is caused by magnetite and remanent magnetism (Fig. 3). Magnetic and gravity interpretations indicate that the deposit extends to a depth of 300–500 m.

**Lumikangas apatite-ilmenite gabbro**

**General description, stratigraphy and resources**

This study focuses on the southern part of the Lumikangas positive magnetic anomaly, where, according to the ground geophysics, the gabbro body is 1.5 km long and a half kilometre wide, while the total length of the magnetic anomaly is five kilometres (Figs. 2 and 3). Drilling results show that the apatite-ilmenite gabbro dips to the east at an angle of 30 degrees (Fig. 4). Based on the drilling, the thickness of this oxide
gabbro, with a total amount of ilmenite and magnetite over 10%, is at least 200 m and, according to the geophysics, reaches 500 m. The gabbro is dissected into two blocks by reverse faulting, so that the western block (hanging wall) (R396 and R401) has been uplifted and the eastern block (footwall) (R400, R399) has descended (Fig. 4). As a result of this movement, the oxide content decreases downwards in the western block and increases in the eastern block.

The structure of the intrusion is clearly layered and the compositional variation ranges from Fe-Ti-rich dark gabbros toapatite-rich leucogabbros. The intrusion can be divided into two main sections. The basal part is composed of dark medium-grained gabbro or gabbronorite, hornblende gabbro and olivine gabbro, and the upper part is medium to coarse-grained leucogabbro or monzogabbro within a few metres thick layers of gabbro-pegmatoid and metadiabase dikes.

The inferred and possible resources based on geophysics and two drilling sections include 230 million tons of oxide gabbro, which are 1200 m long, 300 m wide and 200 m thick. Almost the whole drilling section is composed of oxide gabbro, which contains an average of 19% ore minerals: 8.7% (max. 21%) ilmenite, 4.8% (max. 17%) magnetite and 5.4% (max. 17%) apatite (Table 1).

**Petrography**

The alternate layering of the various rock types in drill hole R400 is as follows: subhedral medium-grained monzogabbro, olivine monzogabbro, gabbronorite, hornblende gabbro, olivine gabbronorite and gabbro. The primary texture of the rock generally is subophitic, which is still preserved. The rock-forming minerals are pyroxenes, uralite and hornblende, cummingtonite, albite and K-feldspar, plagioclase, biotite, Fe-Ti oxides, apatite, olivine, chlorite, quartz and rarely sphene. Silicate minerals constitute 75–95 vol% of the rock.

Igneous clinopyroxene, orthopyroxene and olivine are partially metamorphosed and replaced mainly by uralites and biotite (Fig. 5a). Prismatic to granular plagioclase and alkali feldspar are the major rock-forming minerals (Fig. 5b, 6f) up to 2 mm in length and commonly affected by sericitization. Plagioclase

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Composition is mainly labradorite (Table 2) and occasionally ranges from oligoclase to labradorite. In places, plagioclase is partially transformed into albite (analysis no.7, Table 2). Alkali feldspar is represented by the typical texture of microperthite exsolution intergrowth of sodium-rich and potassium rich feldspar, and amphibole intergrowth of potassium-rich feldspar in sodium-rich (albite) matrix. Equal proportions of albite and K-feldspar intergrowth (mesoperthite) and microcline feldspar with crossed hatched twinning structure are also observed. Biotite (both primary and secondary) is another common silicate mineral that together with uralite often rim ilmenite and magnetite (Fig. 5a).

Table 2. Selected electron microprobe (Cameca Camebax SX100) analyses of ilmenite, magnetite, apatite and some silicate minerals (operating conditions: 15-20KeV, 10-15nA, 1-10μm beam diameter; analysed by Bo Johanson and Lassi Pakkanen)

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</table>
| SO₃ | 0.01 | 0.01 | Total | 98.31 | 98.80 | 93.11 | 94.12 | 99.14 | 99.00 | 99.06 | 99.39 | 98.85 | 98.21 | 98.87 | 98.71 | 97.37 | 35

Note: Ilmenite (1,2), magnetite (3,4), apatite (5,6), albite (7), k-feldspar (8), Ba-feldspar (9), plagioclase (10,11), augite (12), cummingtonite (13)


Fig 5a. Pyroxene, uralite and mica; ilmenite rimmed by biotite and uralite (R398/57.5m)

Fig 5b. Alkali-feldspar and plagioclase as major rock forming minerals (R400/81m)

Fig 5c. Free ilmenite grain; large pyrrhotite grain associated with ilmenite and magnetite (R400/149.2m)

Fig 5d. Ilmenite commonly occurs as a separate anhedral to subhedral grains (R400/192m)

Fig 5e. Ilmenite lamellae in magnetite, up to 40microns thick and 300 microns long; note spinel granules along the border of the lamellae (R400/149.2m)

Fig 5f. Magnified exsolved structure of fine ilmenite and spinel in magnetite (R398/57.5m)

Geochemistry

The mafic rocks of the Lumikangas intrusion are characterised by uniformly high P₂O₅ and TiO₂ contents, rather high K₂O, variable but usually high Fe₂O₃ and rather low Cr content (Table 1). There is very small variation in the Fe/Mg ratio as shown in the AFM diagram (Fig. 7), and the distribution falls within the tholeiitic field. Because of high Fe-Ti oxide and apatite contents the Lumikangas gabbroic rocks are not classified in the subalkaline field. In fact, many samples from Lumikangas show increased alumina saturation
and the whole rock was metaluminous (\( \text{Al}_2\text{O}_3 > \text{Na}_2\text{O} + \text{K}_2\text{O} < \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O} \)) (Table 1). This is partly related to the high \( \text{K}_2\text{O} > 1\% \) content of the gabbro. Based on chemical analyses the normative orthoclase content is 5 – 10 %, and may be up to 25% in gabbropegmatoids. In the Streckeisen-type triangular classification diagram most samples group within the monzogabbro field, which means that they contain at least 10% alkali feldspar component (Fig. 8).

The special feature of the Lumikangas gabbro is that Ti, P and Mg correlate very closely as shown in drill hole R400 (Fig. 9). This could be explained by
a simultaneous crystallisation of iron-oxide, apatite and Mg-rich silicates (see Fig. 5 and Fig. 6).

**Ore mineralogy**

*Ilmenite and magnetite*

Based on microscope observation the rocks contain about 3–20 vol% ilmenite and magnetite. They occur as separate crystals, anhedral to subhedral granular aggregates and range in size from 0.1 to 1.5 mm. Ilmenite occurs as well-developed single crystals (Figs. 5c, 5d), and as latticed oxyexsolution textures in and along the boundaries of magnetite grains (Fig. 5e), where the boundaries are often delineated by spinel granules. The ilmenite grains are commonly monomineralic, except for occasional magnetite lamellae, rare rutile inclusions and spinel needles.

Fig. 7. Distribution of Lumikangas gabbro in AFM-diagram.

Fig. 8. Lumikangas samples in normative (quartz-orthoclase-plagioclase) triangular diagram. Most samples contain more than 10 % normative orthoclase and have the composition of monzogabbro.

Fig. 9. Variation of magnesium, titanium and phosphorous in two drill holes R400 and R399 from Lumikangas.
Magnetite contains both ilmenite and spinel as exsolved inclusions (Figs. 5e, 5f), where the magnetite here can be referred to as ilmenomagnetite. The ilmenite exsolution might represent two generations, with oriented long lamellae and fine needle-like structures ranging from submicroscopic to 100μm across, and up to 1.2 mm in length. The fine oriented ilmenite needles are distributed evenly throughout the magnetite grains along with very fine spinel microcrystals (Fig. 5f). Ilmenite and magnetite show myrmekitic intergrowth with silicate minerals, mainly pyroxene, uralite and apatite (Fig. 6a), which indicate simultaneous crystallisation of the ore and the silicate minerals. Pyrite and pyrrhotite are the common sulphides observed, occurring mainly as separate grains associated with the ore and gangue minerals. Fine grains of chalcopyrite occur often associated with pyrrhotite and pyrite as inclusions. Inclusions of pentlandite in pyrrhotite and secondary hematite with pyrrhotite were observed. Magnetite is less common within the sections where pyrrhotite is abundant.

Apatite

The Lumikangas gabbroic rock consists of about 1–6 vol% of apatite (Figs. 6b–6f). Locally elevated amounts of apatite covering nearly 25 vol% the rock are observed in R400/141.6m, which corresponds to the highest phosphorus content (5.5% P₂O₅, R400/140–142m). The apatite crystals occur either as single crystals or in small clusters associated with feldspars, pyroxene and Fe-Ti oxides (Figs. 6c, 6f). Inclusions of apatite in the ore minerals (Fig. 6b) and in silicates (Figs. 6c, 6f) are the most typical textures. Apatite occurs in various forms: euhedral (Fig. 6c), subhedral (Fig. 6d) and ranges in size from about 50μm to 4–5mm long. Apatite chadacrysts (inclusions in oikocrysts) occurring as fine subrounded and elongated structure are enclosed by feldspar oikocrysts, which is typical of poikilohitic texture (Fig. 6f).

Pure apatite concentrate was made using heavy liquid separations. The concentrate was analysed by ICP-MS for rare elements. The chondrite normalised REE-array of apatite is rather plain and only gently decreasing (Fig. 10). A special feature of the Lumikangas apatite is that there is no Eu minimum as compared to neighbouring elements, which is typical for apatite in the Kauhajärvi gabbro. This indicates that plagioclase has not been extracted during magmatic differentiation. The similar shape of the REE-arrays of both Lumikangas and Kauhajärvi apatite may indicate the same magmatic source for both gabbros.

Electron microprobe analyses

The TiO₂ content of ilmenite (49.3–51.2) is very close to the theoretical ilmenite composition (TiO₂=52.65 %) indicating no significant alteration (Table 2). The MgO and Cr₂O₃ contents of ilmenite are low as is V₂O₅, that hardly exceeds 0.15 % in Lumikangas ilmenite. The MnO content of both ilmenite grains and lamellae in magnetite is constant but relatively high (0.8–1.3 %).

The TiO₂ content in the magnetite lattice is considerably low (0.0–1.8 wt%) having been taken up by the two generations of exsolved ilmenite lamellae. The magnetite lamellae in ilmenite, however, contains up to 3.2 wt% TiO₂. Interestingly, the Cr₂O₃ content of magnetite is insignificant, ranging from 0.03 to 0.22 wt%. Vanadium in magnetite, on the other hand, is relatively high (V₂O₅=0.5–2.35 wt%), and varies from sample to sample, 0.95–1.4 % V₂O₅ in R398/57.5m and 2.1–3.25 wt% V₂O₅ in R400/63.9m. The vanadium content in the Lumikangas magnetite (0.34–1.6 wt% V) is within the range of Koivusaarenneva (0.7 wt% V; Kärkkäinen et al. 2003), Mustavaara (0.83 wt% V; Juopperi 1977) and Otanmäki (0.64 wt% V; Kerkkonen 1979) but relatively higher than that of Kauhajärvi (0.1–0.4 wt% V; Kärkkäinen & Appelqvist 1999).

In spite of grain morphology and size differences, the apatite composition is relatively uniform but contains small amounts of SiO₂, MnO, FeO and SrO, as these minerals are known to substitute Ca in apatite (Table 2). The fluorine content of apatite (2.0–4.3 wt%) is indicative of fluorapatite composition.

Potassium feldspar is occasionally found to contain extremely high barium content giving a composition of Ba-feldspar (Table 2). The clinopyroxene has a ferro-augite composition, characterised by low Al₂O₃ and TiO₂ contents. The clinopyroxene is associated with primary plagioclase, and according to chemical analyses and microscope observation, plagioclase is in part transformed into albite.

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*P*  
Fig. 10. Apatite REE arrays of Lumikangas and Kauhajärvi.  

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Discussion

In almost all igneous rocks, apatite is known as an accessory mineral. However, apatite enrichment with ilmenite and magnetite are recorded in a number of deposits, for example in mafic intrusions as in Bushveld (Von Gruenewaldt 1993), in Sept-Iles (Nabil et al. 2003), Kauhajärvi (Kärkkäinen 1999), and in anorthosite complexes as in Bjerkreim-Sokndal (Duchesne 1972, Korneliussen et al. 2000) and Lac Mirepoix (Morisset 2003).

Apatite-bearing ilmenite-magnetite deposits and prospects generally contain ilmenite with low MgO and Cr2O3, and ilmenite poor in hematite (Schillirup et al. 2003). One interesting feature at Lumikangas is the early crystallisation of apatite and coeval crystallisation of apatite, Fe-Ti oxides and mafic silicates (Fig. 9). In practice this means that the parent mafic magma was abnormally rich in P and also Fe and Ti. This kind of Ti-P enriched mafic rocks in crustal environments are often called jotunites (Norway), oxide apatite gabbronorites (Canada) or ferrogabbros (USA) and they are more or less closely related to the anorthosite massifs or rapakivi granite-anorthosite suite. These kinds of rocks have lately been studied as a possible source of Ti and P, for instance in Norway (Korneliussen et al. 2000).

Conclusion

Lumikangas area was selected as a target for Ti-P exploration on the basis of a high magnetic and gravity anomaly and its location in the Kauhajoki apatite-ilmenite gabbro province. The Lumikangas apatite ilmenite monzogabbro may be a potential ore resource in the future, containing an average of 19% ore minerals: 8.7% (max. 21%) ilmenite, 4.8% (max. 17%) magnetite and 5.4% (max. 17%) apatite. Apatite, ilmenite and magnetite were crystallised at the same time at a very early stage of magmatic differentiation, because they have a good correlation with magnesite. The drilling profiles did not intersect pyroxenites, in which the highest ore contents could be hiding.

REFERENCES


THE VITTAJÄNKÄ KAOLIN DEPOSIT, SALLA, FINNISH LAPLAND

by

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Introduction

In the search for abundant and high quality kaolin resources to satisfy the growing demands of the Finnish paper industry, the Geological Survey of Finland (GTK) has, over the period 1998–2004, investigated more than 20 kaolin deposits in the pre-glacial regolith of northern Finland. Research has focussed on Paleoproterozoic metasedimentary rocks in central Lapland, particularly in areas of relatively low metamorphic grade, using a variety of airborne and ground geophysical techniques, supplemented by drilling. Airborne geophysical data are particularly useful in identifying weathered bedrock, while drilling or excavation during earlier bedrock exploration activities has commonly provided direct confirmation of the presence of kaolin and deeply weathered regolith beneath Quaternary till. In contrast, there is a paucity of prior indications of kaolin from terrain dominated by granitoids and gneisses of higher metamorphic grade.

During the course of investigations, research has gradually focussed on two specific regions, namely the eastern parts of the Sudankylä municipality and the areas to the east and northeast of the tonwhisp of Salla. The presence of kaolin in the Sudankylä district, at Siurunmaa, has been known since 1976

(Rask & Lintinen 2001, Pekkala & Sarapää 1989), while the Suolakaarko deposit was discovered more recently, in 1998 (Lintinen 2000). The first investigations in the Salla region were undertaken in 1999, as a result of which white kaolin was found at Vittajänkä. By the end of 2004 three separate drilling programs had been carried out at Vittajänkä, with a total length of 2000 m. At the same time, exploratory drilling has been undertaken in surrounding terrain, in the search for analogous occurrences.

Assessment of the quality of kaolin at Vittajänkä has also been carried out concurrently with delineation of reserves, with particular emphasis on its suitability as a paper pigment. Preliminary enrichment tests simulating industrial processing have been conducted at GTK and also at the former VTT mineral processing laboratories (now GTK Mineral Processing Laboratories) and results of studies completed prior to 2004 have been reported by Al-Ani et al. (2004).

Geological setting

The Vittajänkä kaolin deposit is located within the southeastern extension of the Paleoproterozoic Central Lapland greenstone belt (Fig. 1). In this area however, quartz-rich metasediments dominate, bounded to the east by the extensive metavolcanics of the Salla greenstone area, which continues across the national
border into adjacent Russia. The central Lapland granitic complex occurs to the south and southwest of Vittajärvi, whereas Archean granitic and supracrustal terrain lies to the north.

Regional geological investigations have been carried out during the Lapland Volcanite Project (LVP), by Manninen (1991), on the basis of which the metasedimentary Matovaara Formation is considered to be the protolith from which the Vittajärvi kaolin was derived. Although the area is covered by extensive wetlands, with very few bedrock exposures, the metasediments appear to have been calcareous siltstones, with calcilicate and laminated orthoquartzite intercalations.

Geophysical investigations

The Vittajärvi kaolin deposit can be distinguished in regional airborne geophysical data as an electromagnetic anomaly with an intense imaginary component and a considerably reduced real component. The Matovaara Formation metasedimentary host rocks are non-magnetic, although they are surrounded by a narrow, conspicuously magnetic zone of tholeiitic volcanics belonging to the Tahkoselkä Formation.

The area delineated by the airborne EM anomaly was surveyed on the ground as well, firstly along widely spaced profiles and then on a systematic grid covering 3.6 km². Both EM VLF-R measurements and gravity surveys were made. In addition, a regional scale gravimetric survey was carried out over 300 km² in the Salla district during 2000–2001, with a site density of 8 measurements per km². On the basis of these gravity surveys, the Vittajärvi kaolin deposit appears to coincide with a northerly trending elongate 2 mGal gravity minimum, approximately 1.75 km² (2.5x0.8 km) in extent (Fig. 2). The shape of the gravity anomaly is controlled by both degree of weathering and the structurally defined bedrock geology, with mafic volcanics surrounding the metasediments.

Sampling strategy

The Vittajärvi deposit was drilled in three stages in 1999, 2001 and 2003, using different equipment and core recovery techniques. Drilling has been both technically challenging and required careful sampling in order to maximize the research value of recovered material.
The gravity anomaly has been drilled along two E-W profiles 700 m apart (Figs. 2 and 3). The more northerly profile intersected white or yellowish kaolin over a distance of 300 m, while the total width of the weathered zone was about 400 m. In the southern profile the weathered zone was about 150 m across, with 75 m of light-coloured kaolin. White to yellowish kaolin tend to occur in the central parts of the weathered zone, while marginal parts were considerably darker. Overburden thickness varied from 10–25 m, with a mean depth of 15 m. The thickest kaolin intersections were nearly 30 m although the average was around 20 m. Sporadic quartz-rich horizons, or weathered accumulations of quartz sand were sporadically found within the kaolin.

Some diamond drill core was recovered from the quartz-rich intercalations, and from the bedrock beneath the kaolin deposit, despite their being intensely...
weathered. Thus, significantly weathered regolith occurs at depths considerably greater than the main kaolin deposit.

**Laboratory analyses and enrichment trials**

**Methods**

A total of 96 samples of kaolin, both white and coloured, were taken for systematic analysis at GTK, with an average sample length of 3.8 m. Samples were classified according to grain size distributions using a combination of sieving and sedigraph analysis. Sample fractions <20 µm were separated and measured for whiteness and yellowness with an L&W Elrepho-spectrophotometer, according to ISO 2496 specifications. In addition, the mineralogy and chemical compositions of the original samples, prior to sieving, as well as the <20 µm fractions were analyzed by XRD and XRF respectively.

The best samples of white kaolin were then evaluated with a trial industrial enrichment process at the VTT (now GTK) Mineral Processing Laboratories at Outokumpu. The process consisted of sieving and centrifuging, followed by magnetic separation and chemical bleaching with sodium dithionite. The centrifuging was intended to recover the size fraction finer than 2 µm. Magnetic separation was performed with a Sala HGMS (High Gradient Magnetic Separation) separator. After bleaching, the samples were filtered, dried and again measured for whiteness and yellowness according to ISOR457-specifications with an Elrepho 2000-colour meter. The final purified samples were then analyzed with both XRD and XRF at the GTK laboratories.

**Whiteness and yellowness**

Kaolin samples were classified according to the ISO brightness index, for which 'white' refers to a brightness >60 % and coloured to values <60 %. This approach to classification was also used by Sarapiä (1996) for the kaolin deposits at Virtasalmi, where the 20 µm size fraction was also used as a cut-off threshold; therefore, results from the two studies are in principle comparable.

Brightness values for kaolin from the <20µm size fraction were, for the samples classified as white, as high as 80–85 %. Such a result can be considered particularly good for kaolin that has not been treated to magnetic or chemical purification. The yellowness of these whitest samples was on average 7–8 %. Pale yel-

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low samples had brightness values between 70–78% and corresponding yellowness values of 15–10%.

Magnetically and chemically refined processed kaolin in the <2 µm size range had brightness values only a few percent higher. For example, the brightness index for the <20µm fraction increased from 80% to around 83%. On the other hand, yellowness values fell significantly by about half, to values around 3.5–5%. Because kaolin products suitable for paper pigment require a brightness index of at least 87% and yellowness below 3%, these results indicate that the Vittajärkä kaolin would be suitable as a filler only.

**Mineralogical composition**

Table 1 shows mineralogical and chemical data for selected elements for white and coloured kaolin at various size fractions. Original untreated white kaolin samples contain, on the basis of XRD analyses, an average of 30% kaolinite, 49% quartz, 8% muscovite, 6% feldspar and trace amounts of hematite and pyroxene. The abundance of kaolinite increases to an average of 66% for the <20µm size fractions, but still contains significant amounts of quartz and muscovite. The refined <2µm kaolin product contains 85–95% kaolinite, the remainder comprising from 5–10% quartz and 0–5% muscovite.

Coloured kaolin contains similar proportions of, or slightly less kaolinite than white kaolin. On the other hand, quartz contents are comparatively lower and feldspar abundances somewhat greater. The eastern parts of the drilling profiles tend to contain more plagioclase, up to 40% in untreated primary samples and as much as 55% in the <20µm size fraction. In the central parts of the profiles, inclusions or intercalations of coloured kaolin within the white kaolin contain significant amounts of hematite, in places up to 20%.

The refined kaolin products were studied under the scanning electron microscope (SEM), as a result of which illite was identified amongst kaolinite and muscovite. XRD analysis of the settled clay fractions of white kaolin samples also showed a characteristic illite peak, while coloured kaolinite samples were also found to contain mixed layer illite-smectite phyllosilicates. XRD data were used to determine Hinckley crystallinity indices (Hinckley 1963, Aparicio & Galan 1999), with values in the range 0.59–0.88 indicating a relatively high degree of crystallinity for the kaolin lattice, in places moderately crystalline. The SEM images (Fig. 4) also revealed that kaolin crystals were nearly euhedral, with a rather uniform grain size distribution and a tendency for small flaky particles to remain in isolation from one another, rather than aggregate into larger phyllosilicate booklets.
Chemical composition

White Vittajärvi kaolin tends to have relatively high SiO$_2$- and K$_2$O- abundances and low Al$_2$O$_3$- irrespective of grain size. After refining, the <2μm size fraction contained on average 51.6 % SiO$_2$, 27.9 % Al$_2$O$_3$ and 2.9 % K$_2$O. The abundance of silica and low alumina can be understood in terms of residual quartz, while the retention of muscovite and illite can explain the high potassium and Fe$_2$O$_3$, which attains 1.5 % in some samples. By way of comparison, the ideal theoretical kaolinite composition is 46.5 % SiO$_2$ and 39.5 % Al$_2$O$_3$. As a general rule, kaolin products of commercial quality are very close to this ideal composition, although K$_2$O abundances may commonly exceed 2 %, providing that Fe$_2$O$_3$-abundances remain below 1 %.

Coloured kaolin in the eastern parts of the profiles show elevated Na$_2$O abundances (mean = 1.5–2 %, maximum = 9.7 %), which corresponds to relatively high amounts of albic plagioclase. In the <20μm size fraction both Na$_2$O abundances and plagioclase contents determined by XRD are even higher, which indicates further that the albite is particularly fine-grained. It is therefore possible that the protoliths for the regolith in the eastern part of the profile were tholeiitic volcanics of the Tahkospelkä Formation. However, to the west of the volcanic contact, the coloured kaolin has a chemical composition consistent with derivation from metapelitic rocks or even calc-silicates of the Matovaara Formation, given the relatively high abundances of Mg, Fe and K, and locally high Mg+Fe with low K and Na. Locally dark pigmentation within the white kaolin is usually caused by hematite, which is clearly reflected in Fe$_2$O$_3$ concentrations.

Conclusions

Protoliths for the kaolin

The white kaolin is evidently derived from weathering of sericitic quartzites and sericitic schists. Local intercalations of quartzite have weathered to kaolinitic quartz sand. Thin section studies show that the host rocks were exceedingly fine-grained, massive to weakly laminated and generally only weakly foliated, with quartz occurring amongst fine-grained phyllosilicates. Accessory minerals include albic plagioclase, potassium feldspar, tourmaline and porphyroblasts of scapolite.

The most likely protoliths for the coloured kaolin are phyllic metasediments and mafic metavolcanics. Weathered volcanics in the eastern part of the drilling profiles contain abundant albic plagioclase and exhibit relatively high Na$_2$O, Fe$_2$O$_3$- and MgO-abundances. In contrast, weathered metapelites have higher K$_2$O abundances, with very low Na$_2$O. Thin section studies reveal that the mafic volcanics are fine-grained and massive, with mineralogy dominated by albite and actinolite, the latter locally replaced by talc. Phyllitic rocks resemble sericite schists, except that in addition they contain biotite.

The kaolinization process

The mineralogical and chemical attributes of the Vittajärvi kaolin deposit, together with its overall geometry indicate that the kaolin formed by in situ weathering of silicate minerals. The high degree of crystallinity and euhedral habit of the kaolin is also consistent with a primary weathering origin. The presence of muscovite and illite indicate that the process had not proceeded to completion, at least at the present erosion level. It is probably that most of the kaolin formed during decomposition of feldspar and muscovite.

Preservation of kaolin

At least the lower part of the regolith profile at Vittajärvi has survived, despite repeated glaciation and deglaciation events. In general, pre-glacial regolith is more extensively preserved in eastern and northeastern Lapland than elsewhere in the country. At Vittajärvi the following factors contributed to the preservation of kaolin:

1) Primary compositional variations in the protoliths to the kaolin occurrences, in particular more resistant quartz-rich intercalations have protected adjacent weathered material from the effects of erosion.

2) The general topographic depression in the area, inherited from bedrock geology, with highly weathered metasediments surrounded by a ring of more resistant, massive and fine-grained tholeiitic metavolcanics (Fig. 1).

Beneficiation and exploitation of kaolin

At present it is only possible to provide a provisional and speculative estimate of the potential kaolin resource at Vittajärvi, using the dimensions of the gravity anomaly and information from the drilling profiles. Given that the gravity minimum is nearly 2 km in length and that the mean width and depth of the weathered zone are 275 m and 20 m respectively, and assuming a regolith density of 2000 kg/m$^3$, a total mass of around 22 million tonnes is obtained. Samples
analyzed to date have on average 60 % white kaolin, of which the average proportion of kaolinite is about 30 %. Accordingly, the deposit would contain about 13 Mt of white kaolin, which could yield about 4 Mt of kaolin concentrate. It should also be noted that although the mean depth of the kaolin regolith is only 20 m, kaolinization is extensive to much greater depths.

After refinement, the Vittajärkä kaolin product still contained considerable amounts of quartz and muscovite, which is reflected in the higher SiO₂ and lower Al₂O₃ abundances than in commercially available kaolin products. Despite all of the refining processes used, the brightness remained below the acceptable levels for kaolin pigment. One of the main reasons for this is the fine grain size of the protoliths, particularly quartz and muscovite, as a result of which mechanical purification is difficult. Further processing using flotation is planned, which will hopefully be effective in removing not only quartz, but also at least some of the mica, resulting in a product with improved brightness values.

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GEOPHYSICAL CHARACTERIZING OF TAILINGS IMPOUNDMENT – A CASE FROM THE CLOSED HAMMASLAHTI CU-ZN MINE, EASTERN FINLAND

by
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Introduction

We present here preliminary results of a project in which we test and develop geophysical techniques for mapping sulphide tailings impoundments. Our study site, the small Hammaslahti Cu-Zn mine, worked in 1973–1986. The tailings impoundment having an area of 30 hectares and an average height of 9 metres, has been established on a bog. The interest in developing geophysical techniques for studying tailings impoundments arises from the need of high-resolution 3D structural, chemical and hydrological data for modelling and understanding the tailings impoundment systems.

Rehabilitation of tailings impoundment for final closure, as well as assessing the risk of old impoundments require relevant data about the structure and composition of the tailings material and the water table and its temporal and spatial variation inside the impoundment. In Finland, tailings impoundments of several metal sulphide mines have been engineered in bog basins or the depressions of small lakes. In both cases, the substrata are organic rich sediments underlying glaciolacustrine silt sediments, which are compressing under load (Sipilä & Salminen 1995, Räisänen 2003). In general, the stratigraphy and characteristics of the impoundment are investigated by drilling, including the profile sampling throughout the tailings and underlying parent sediments. The fact that dense drilling, needed for detailed characterising and 3D modelling of an impoundment, is expensive, led us to start a project to test and develop geophysical techniques for mapping tailings impoundments. Our test site is the closed Hammaslahti mine (Fig. 1).

The mine tailings typically exhibit a low electrical resistivity (i.e., high electrical conductivity). Therefore, electrical and electromagnetic (EM) methods are the most commonly used in mine tailings studies (Campbell et al. 1999, Campbell & Fitterman 2000, Watson et al. 2001). At the Geological Survey of Finland, airborne geophysics has been for few years successfully applied to mapping both regional and site-scale environmental impacts of mining in different kind of geological environments. Beamish and Kurimo (2000) used airborne electrical conductivity data to detect acid leaks from active and closed coal mines in the United Kingdom, while Lahti et al. (2000) used airborne radiometric, magnetic and EM (electromagnetic) and ground geophysical data for mapping environmental issues related to uranium mining activities in eastern Germany. Vanhala et al. (2002) studied the environmental, hydrogeological and geological issues around an oil shale mining area in northeast Estonia. Electrical resistivity sounding
results from the Hitura Ni mine tailings have been presented by Heikkinen et al. (2002).

The first geophysical tests at the closed Hammaslahti Cu-Zn mine were made in 2000 when a few electrical resistivity soundings (ERT), aimed at locating subsurface leakage pathways through the impoundment dam, were measured (Vanhala & Lahti 2001). More ERT data were collected in 2001 – 2004, but most of the geophysical measurements (refraction seismic, gravity, EM and ERT) are from 2003. Drillings and sampling for chemical analysis were made in 2000, 2003 and 2004. Petrophysical results are from 2004 (Table 1).

The general objective of the ongoing study is to develop ground geophysical methods, gravity, refraction seismic, EM and ERT, for mapping and monitoring tailings impoundment and dam constructions and bedrock and sediment structures under and around the impoundment. Petrophysical properties (electrical conductivity and induced polarization (IP), seismic velocity and density) of the tailing material have been only poorly known and one of the key tasks is to define them. Especially the relationship between the electrical conductivity and IP and the properties of the tailing material is of great importance. The structural features presumed to be suitable for geophysical mapping are the follows:

(a) water table and the oxidised zone,
(b) variation of grain size, mineralogy and chemistry inside the impoundment
(c) thickness of the tailings bed and the underlying sediments,
(d) bedrock relief and fracture zones
(e) internal structures (dams, cavities)

In this paper we present the preliminary results of the geophysical studies. Furthermore, we discuss on the relationship between the geochemistry and the geophysical data of tailings and underlying sediments at some reference sites.

Description of the study site

The Hammaslahti Cu deposit is located at the eastern margin of the Early Proterozoic Svecofennian Orogen (2.0–1.75 Ga), 12 km west of the exposed Archaean-Proterozoic boundary (Fig. 1). The country rocks are composed of low-grade metamorphosed epiclastic sediments dominated by graded-beded feldspathic graywackes intercalated with black schist layers and phyllites. Three orebodies (S, N and Z) are located in hydrothermally altered rocks. Major sulphides are pyrrhotite, chalcopyrite and pyrite in the S and N orebodies, and sphalerite in the zinc ore body.

The Hammaslahti Cu-Zn Mine operated in 1973–1986. Outokumpu Oy mined 7 million tons of ore grading 1.16 % Cu and minor amounts of Zn and Au.

The tailings impoundment is situated north of the flotation plant. Its surface area is about 30 hectares.
The tailings impoundment is dammed on the bog (Fig 2). The tailings embankment consists of local glacial till strengthened by country rock stones from the open pits (Pelkonen et al. 1973). The average height of the heap is 9 metres above the surface of the bog. The impoundment is recovered by a thin basal meltout till layer (10–60 cm). At present, plants typical for wild meadows (mainly wild grass), and young birches and planted pines grow more or less successfully (Fig. 3, Räisänen et al. 2003).

**Investigation methods of the tailings impoundment**

**Profile drilling and sampling**

The basement and layer structure of the facility, and its hydrological conditions were studied by drilling with a non-rotated percussion drill equipped with a soil core sampler at 22 sites (Fig. 4). Drilling work was done firstly in November 2000, then in May 2003.
and May 2004. In 2000, profile samples from tailings materials and underlying Quaternary sediments were continuously collected into non-contaminated plastic (high dense polyethylene, HDPE) tubes with a piston and in 2003 with a special soil core sampler during the drilling. The sampling technique is developed by the GTK. In 2004, the tube sampling was used, since it allows the making of petrophysical core sample measurements. The sampling was done in a set of 1 m sample per tube. After the measurements, sample tubes were half opened, and sample layers for chemical analysis were separated on the basis of the oxidation degree of the tailings and physical characteristics of the underlying sediments. In all cases, samples for chemical analysis were frozen in the field or immediately after transporting to the Geolaboratory of the GTK.

For chemical analysis tailings and underlying peat and silt sediment samples were freeze-dried and then sieved to <2.0 mm fraction. Ammonium acetate (1 M) solution buffered to pH 4.5 for chemically adsorbed elements (exchangeable, surface complexes) and hot (90 °C) *aqua regia* for mica and clay mineral fraction (including sulphides) (Niskavaara 1995, Räisänen & Carlson 2003, Räisänen et al. 2003). In contrast to mineral sediment samples, the nitric acid leach assisted with microwave (EPA 3051) was used for peat samples (Niskavaara 1995). The ICP-AES technique was used for measurements of the element concentrations in the above extracts.

The total sulphur was determined using with the Leco-S technique and total concentration of carbon and nitrogen with a CN analyser. The extractions and ICP-AES, S, C and N determinations were made at the FINAS accredited Geolaboratory of the Geological Survey of Finland (GTK) in Kuopio.

**Geophysical measurements and interpretation tools**

The geophysical data used in this study is presented in Table 1. Location of the ground geophysical lines and profile sampling sites are in Figure 4.

Two refraction seismic profiles were measured across the impoundment. The seismic measurements enable the interpretation of dry overburden (tailings + natural sediments), saturated overburden and the depth to bedrock. The method also gave information about the type of overburden and the bedrock. The fracture zones in the bedrock can be detected from the low seismic velocity of broken rock. In certain circumstances, layers cannot be detected by seismic refraction. This is usually due to the insufficient thickness or velocity contrast between the layers. If the “hidden” layer is not taken into account in the interpretation the calculated total thickness of the overburden is too small. In Hammaslahti, the thick pile of dry and saturated tailings covers underlying Quaternary sediments. The underlying natural sediment layer is in most cases undetectable by refraction.
seismic survey. It can only be seen in the middle of upper seismic line (Fig. 4). The second problem in refraction interpretation is called the “reversal velocity case” – the velocity in a layer is lower than in the overlying layer. The low velocity cannot be detected by refraction survey. If there is no information of the low velocity layer the calculated total thickness of overburden is overestimated. A typical reversal velocity case is a sand layer under gravel.

Six gravity profiles were measured across the impoundment. Seismic results and the water table interpreted from the seismic data were used as reference data in gravity interpretation. The interpretation of the gravity data was made using a three-layer model – bedrock, saturated sediment layer and dry sediment layer. For the sediment material, densities of 1500 kg/m$^3$ (dry) and 1950 kg/m$^3$ (saturated) were used. Possible sources of error were the density variation of bedrock and the water table.

Ground slingram measurements were carried out using a multi-frequency horizontal loop EM method (HLEM), (APEX MaxMin 1+8S system). Eight frequencies (440, 880, 1760, 3520, 7040, 14080, 28160 and 56320 Hz) were measured.

1D inversion was used to interpret the EM data. First the quality of the HLEM data was assessed with 1D multi-layer inversion using a few layers with varying thickness and conductivity, in order to examine the effects caused by 3D conductivity structures and misalignment of the loops. Then the layered-earth interpretation was made with model norm-based inversion. In the 1D model, the earth is composed of a stack of layers, each having a uniform conductivity. The 1D conductivity structure, i.e., the conductivities of each layer, is sought by the regularised inversion. The goal is to find for every measuring point a minimum-structure model, which can fit the measurement data sufficiently well. The minimisation of the objective function \( \text{data misfit} + \beta \times \text{model norm} \) has been carried out with a damped Gauss-Newton algorithm.

In HLEM measurements 20 metre and 40 metre coil spacing were used. The wider coil spacing means deeper effective depth of investigation. The EM system with the shorter coil spacing has a higher spatial resolution. Because here the conductivity of the tailings bed is high enough the multi-frequency slingram system has frequency-dependent sensitivity to the conductivity variations in that layer. Inversion results of HLEM data measured with coil separation of 20 m and 40 m delineate similar conductivity structures. However in the results measured with wider coil separation more 3D effects could be seen, probably caused by the bedrock conductors.

Inaccuracy in loop spacing and alignment of the loops are likely to be the largest sources of error in the horizontal loop EM measurements. A reference cable connects the transmitter and receiver loops and with the help of the cable the keeping of the coil

<table>
<thead>
<tr>
<th>METHOD</th>
<th>Time</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Airborne data</td>
<td>1991</td>
<td>radiometric, magnetic &amp; EM (3.1 kHz), 200 m line spacing, 30 m nominal flight altitude</td>
</tr>
<tr>
<td>Gravity</td>
<td>2003, June</td>
<td>6 lines</td>
</tr>
<tr>
<td>Refraction seismic</td>
<td>2003, June</td>
<td>2 lines (&amp; one short line across PP72)</td>
</tr>
<tr>
<td>HLEM</td>
<td>2003, June</td>
<td>slingram (horizontal loop EM) (8 frequencies, 440, 880, 1760, 3520, 7040, 14080 and 28160 Hz), 10m/reading: 4 lines, coil spacing 20 m 2 lines, coil spacing 20 m &amp; 40 m</td>
</tr>
<tr>
<td>TEM</td>
<td>2003, July</td>
<td>single loop (50x50 m$^2$), 7 soundings</td>
</tr>
<tr>
<td>ERT</td>
<td>2000 – 2004</td>
<td>wener &amp; dipole-dipole, a=1,2,3 or 5 m, automatic multielectrode system, 28,42 or 56 electrode groundings, most of the drilling sites.</td>
</tr>
<tr>
<td>IP</td>
<td>2001</td>
<td>1D wener, a=2 m, 6 soundings</td>
</tr>
<tr>
<td>Laboratory resistivity and IP</td>
<td>2004, May</td>
<td>Drilling sites N17, N18, N19, N20, N21, N22 (240 samples)</td>
</tr>
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</table>
separation is attempted at the constant value (in this study 20 or 40 m). The error in coil separation is most evidently seen in the in-phase component caused by the incompletely compensated primary magnetic field (e.g. Frischnecht et al. 1991). We have also considered the true coil spacing as an unknown parameter and estimated it carefully from the field data. At least in the case of 1D conductivity structure the used model for the layered ground and for measuring system works better than the inversion assuming constant coil spacing.

The first resistivity soundings (ERT, electrical resistivity tomography) at Hammaslahti were made in 2000 (Vanhalta & Lahti 2000) and continued annually until 2004. All the soundings have been made using AGI/Sting multielectrode system, Wenner or dipole-dipole configuration and electrode spacings of 1, 2, 3 or 5 metres. 2D inversion of the 2D field data has been made using RES2DINV software (Loke & Parker 1996). Presumably because of the dry and high-resistivity top-layer and a low-resistivity deeper sub-surface, the resistivity data were partly too noisy for reliable interpretation.

240 samples for laboratory resistivity and IP measurements were collected in May 2004 from six drilling sites (N17, N18, N19, N20, N21, N22). The laboratory measurements were made within a few hours after the drilling, directly from the original (nearly undisturbed samples) in one-metre long plastic sample tubes by a spectral IP system described by Vanhalta and Soininen (1995). Small holes were drilled for platinum stick electrodes at both ends and in the middle of the tube so that (for each sample) three resistivity-IP spectra could be measured.

**Chemical analysis**

For chemical analysis tailings and underlying peat and silt sediment samples were freeze-dried and then sieved to <2.0 mm fraction. The hot (90 °C) *aqua regia* digestion method was used to determine element concentrations in sulphides and mica and clay mineral fractions of the tailings (Niskavaara 1995, Räisänen & Carlson 2003, Räisänen et al. 2003). Peat samples were digested with the concentrated nitric acid in the microwave (EPA 3051, Niskavaara 1995). The ICP-AES technique was used for measurements of the element concentrations in both extracts. In this context, chemical data is only presented from the reference profiles at site N19 and N20.

Total sulphur was determined using with the Leco-S technique and total concentration of carbon and nitrogen with a CN analyser. The extractions and ICP-AES, S, C and N determinations were made at the FINAS accredited Geolaboratory of the Geological Survey of Finland in Kuopio.
Results and discussion

The structure of the tailings impoundment

Originally, the tailings impoundment was divided into two ponds by a dam, which cannot be visually distinguished from the surface topography (Fig. 2, aerial photo on the right). The shallow depression is mainly located in the central part of the eastern pond. There the elevation of the surface increases about 2 m towards the dike in the north and northeast, whereas it does not change much toward the south. By contrast, the surface elevation of the western pond varies a lot. The difference in the surface topography between the southern and central parts is about 4.5 m and between the central and northern parts about 1.5 m. Similarly, the base of the eastern pond is more or less flat, whereas in the western pond it descends about 6 m from south to north (Räisänen et al. 2003).

According to the drilling data, tailings in both ponds can be divided into dry oxidised and weakly oxidised layers, and underlying water-saturated and non-oxidised layer. In the eastern pond, the water table (water-saturation zone) has stayed quite close to the surface, varying at the depth of 0.1–3 metres from the surface (lowest at the edges). In spring and rainy autumns, the depression of the eastern pond is water covered. In the western pond, the base gradient slants toward the north, and therefore the water table is more changeable than in the eastern pond. The water table dropped in the mid 1990s when the northern dike was fractured. In 2000, the water-saturation zone was at a depth of 5 m below the surface and in May 2004, at about 3 m from surface. Similarly to the eastern pond, the thickness of oxidised layer is thin, being about 0.7 cm thick. Fortunately, the accident had only minor consequences. Only a small amount of tailings flowed out to the bog. Presumably, the water leakage was moderate, since no deterioration was detected downstream in the Iksejoki River.

The variation in the base gradient between the western and eastern ponds results from the compression capacity of bottom sediments and underlying bedrock topography. The basement close to the southern dike of the western pond lies partially on outcrops of crystalline Archean bedrock and partially on the sandy till overlain by a thin peat layer. The central and northern parts of the western pond lie on thick peat sediments, which are underlain by silt and clayey silt sediments. The eastern pond lies entirely on peat and silt sediments. According to drilling data, the peat layer and partially the underlying silt have been compressed. The groundwater table in the bottom sediments lies variably 0.5–1.5 m below the tailings. This indicates that the basement of the tailings is watertight.

Geophysical results

The airborne data is from 1991. The tailings impoundment can be seen as a low-resistivity anomaly in the quadrature (out-of-phase) component map. Today the GTK’s airborne system has a dual-frequency (3.1 kHz and 14.4 kHz) EM-data acquisition and a high accuracy GPS positioning, giving rise to inversion of subsurface conductivity distribution (see for example Suppala et al. 2003, Lintinen et al. 2003). The 1991 EM, radiometric and magnetic data can be used for regional scale mapping of rock units, major fracture zones, overburden thickness and quality estimates, but not for detailed mapping of targets like the Hammaslahti tailings impoundment.

Refraction seismic interpretation from line 1 is illustrated in Figure 5 (see also Fig. 4). Dry and saturated overburden as well as the bedrock with fracture zones can be detected from the model. The measured seismic velocity for the dry tailings in the profile was 300–480 m/s (Fig. 5). For natural sand and gravel formations the seismic velocity is typically 400–800 m/s depending on the grain size. The measured seismic

![Fig. 5. Seismic interpretation, line L_1.](image-url)
velocity of water-saturated tailings was 800 – 1100 m/s. It is clearly lower than the seismic velocity of natural sediments of 1400 – 1700 m/s. The measured seismic velocities of the bedrock under the tailing bed showed that the rock is commonly more or less fractured (< 4500 m/s). The seismic velocity for fresh rock is typically > 5000 m/s.

The interpretation results of the six gravity lines together with the seismic results were integrated to a 3D bedrock relief model shown in Figure 6. Together with the seismic results, which indicate the fracture zones, the 3D bedrock relief model (or the depth-to-bedrock map) is of great importance in modelling the hydrogeology of the area.

Figure 7, which present EM interpretation from line 5, shows that the inverted results are in agreement with the drill core resistivity data. Constraining with the minimum structure model, i.e., minimal spatial derivatives with respect to conductivity, can make the inverted conductivity sections also too smooth. Results from multi-layer inversion using 4 or 5 layers are for the most part equally useful. The smooth inversion is just more robust if we do not know the number of layers.

Figure 9 shows two examples of resistivity sections (ERT) and their relationship to the drilling results. The upper section also includes a comparison between laboratory and ground resistivity (2004). The electrical layering seen in the sections reflect the structure and composition of the tailings material and the water table.

Figure 10 shows the relationships between the electrical conductivity and chemistry of tailings profiles at drilling site N6 (eastern pond). The chemical data is from samples taken in November 2000 and the electrical resistivity measurement from field data in

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**Fig. 6.** 3D bedrock relief model under the tailings impoundment. The model is based on gravity and seismic data.

**Fig. 7.** Line 5, drill core resistivity data (N19 and N20) embedded to electrical resistivity section based on HiEM, i.e., multi-frequency slingram data (1D inversion, 20m coil spacing). Here slingram measurements with the wider coil spacing bring more frequency-dependent information from the conductivity of the formation. Possibly due the bedrock conductors, the 1D model explains slightly better the results with coil spacing of 20 m than with the coil spacing of 40 m. Since the inversion results with both coil separations seem to be consistent with each other, the resolution of the inverted results could be improved using joint inversion of both measurements.
July 2001. The whole resistivity section (July 2001) is presented in Figure 9. The distributions show similarities, especially above the water tables. Obviously, the actual water table was deeper during the measurements in July 2001 than during drilling in November 2000. Figure 11 reveals a significant relationship between the electrical conductivity and distribution of Cu and Zn concentrations at drilling sites N19 (western pond) and N20 (eastern pond). A similar trend can also be seen for sulphur. The IP data do not show as detectable a relationship as the conductivity.

The electrical resistivity values measured for the tailings in the laboratory and inverted from the field data, 5–20 Ohmm (200–50 mS/m), are lower than the resistivity values of the natural soils and sediments in Finland. In earlier papers (Campbell et al. 1998, Campbell & Fitterman 2000, Campbell & Beanland 2001, Campbell 2001, Anderson et al. 2001) IP has been found to be a promising method of characterising the tailings. The first results in this study (Fig. 11) are not, however, promising. The IP values are low and no evident relationship to the chemistry is visible.

Fig. 8. Line 5, electrical resistivity (HELM, 1D inversion, 20m coil spacing), embedded to gravity, seismic and drilling results. The tailings bed can be seen as a low-resistivity layer. The higher-resistivity top-layer refers to dry tailings. Note that the elevation is exaggerated.

Fig. 9. Electrical resistivity (ERT) sections from drilling sites N6 and N20. Note the different distance and depth scales. In both sections resistivity reflects the structure of tailings. In the upper section core resistivity data (N20) is also presented. It is very similar to the ERT result.
Discussion and conclusions

Up to present the geophysical results have seemed promising. Although the tailings impoundment is a very complicated target consisting of material not having a natural origin, the conventional techniques, gravity and seismic, provided accurate results of the bedrock relief and fracture zones. Seismic velocities differ from those of natural sediments and more work has to done to connect the data to the properties of the tailings material.

Electrical conductivity seems to provide information not only on the thickness of the tailings bed and the moisture content and water table in the impoundment, but also on the chemical composition (metal sulphide content) of the tailings as seen in Figure 11. The fact that the field conductivity data (both the ERT and EM results) are very similar to that of the core sample conductivities, suggests that geophysics will be an effective tool for versatile characterising of tailings impoundments.

In general, the geophysical methods provided relevant information on the main structural elements of the tailings impoundment – relief and structure zones of the underlying bedrock, thickness of the tailings bed, internal embankments and water table. Electrical conductivity and refraction seismic data refer to lateral and vertical variation in the properties and/or composition of the tailings. Comparison between the chemical and electrical data suggests that at least part of the electrical conductivity variations can be related to the chemical composition of the tailings, especially to variation of metal sulphide content.

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Fig. 11. Comparison between drill-core electrical conductivity and IP with chemical data of the tailings (Zn, Cu and S). N19 (11a) and N20 (11b). Figure 11b also shows a resistivity sounding (ERT) result from Figure 9.


GEOPHYSICAL CHARACTERISING OF SULPHIDE RICH FINE-GRAINED SEDIMENTS IN SEINÄJOKI AREA, WESTERN FINLAND

by
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Key words (GeoRef Thesaurus, AGI): sediments, acid sulphate soils, geophysical methods, airborne methods, ground methods, electromagnetic methods, resistivity, electrical conductivity, Seinäjoki, Finland

Introduction

In the Ostrobothnian region of western Finland extensive parts are covered by sulphide rich clay and silt sediments, which were deposited during a more extensive phase of the Baltic Sea, mainly during the Litorina Sea period 7500–1500 years BC. During the deposition of organic rich Litorina sediments in shallow sea anoxic conditions prevailed resulting in sulphate reduction to sulphide. The sulphide-bearing sediments alter to harmful sulphate soils when exposed to the air. In central Ostrobothnia the present rate of land uplift is 8–9 mm / year (Donner 1995) leading to continuous exposure of new dry land. In addition to natural processes, human activities related to cultivation increase the natural oxidation process. Soils developed on sulphide rich sediments are characterised by pH values as low as 3–4 and they are often called acid sulphate soils (ASS). Steady oxidation of sulphides annually releases significant amounts of Al and other harmful elements, such as Ni and Cd, into river water (Palko & Weppling 1994).

Palko (1994) has estimated that in coastal areas of Finland the total extent of ASS is some 3300 km². In Sweden the total extent of ASS is approximately 1400 km² (Öborn 1994). Previous studies related to ASS soils have mainly focused on the surficial soil layers to some 3 m in depth, where oxidising and leaching process operates.

The sulphide clays are characterised by an exceptionally high electric conductivity (100–500 mS/m (10−2 Ωm)) compared to other glacial sediments, which makes them especially suitable for EM methods. Peltoniemi (1982) made the first tests of using AEM measurements for the mapping of conductive overburden in the Kyrönjoki river valley. He used apparent resistivities and depths and conductive horizontal thin-layer (1D) models calculated from one-frequency (3 kHz) AEM data. These results were compared with ground geophysics and ground truth. Åström (1996) used AEM maps (the amplitude of response and the ratio of in-phase to quadrature component) to delineate the fine-grained sulphidic sediments in the Petalax å catchment area.

Puranen et al. (1999a, b) demonstrated how one-frequency airborne EM data can be used for mapping the thickness and lateral distribution of the western Finland sulphide clays. These papers also presented new in-situ conductivity probing measurements, which were made in different fine-grained sediment areas.
in Finland. Puranen et al. (1999a, b) also pointed out that AEM data should be combined with ground-truth data to get a reliable tool for overburden mapping. In interpretation they used AEM maps of apparent resistivities and the in-phase/quadrate values. Puranen et al. (1999a, 1999b) emphasised the role of soluble chloride as an important component causing the high electrical conductivity of sulphide-bearing fine-grained sediments.

In Australia Bell (2003) tested ground EM to predict acidification risk, but found only poor correlation between the sulphide content and the inverted electrical conductivity. In that test area saline porewaters are probably the main factor controlling the electrical conductivity. His conclusion was that EM is not an effective tool for directly mapping the acid sulphate soil hazard of saline (and conducting) Australian soils.

The present study started in 2002 and the main objective was to develop airborne EM method for mapping and delineating the sulphide clay – sulphate soil areas (Lintinen et al. 2003, Suppala et al. 2003, Vanhala et al. 2004). As reference data and for detailed studies and development of integrated interpretation, airborne magnetic and radiometric, ground EM and resistivity, gravity and refraction seismic measurements were also made. Results are compared to chemical and physical properties analysed from reference profile drilled through clay and silt sediments.

Geology of the study area

The study area is situated in the Kyrönjoki-Seinäjoki river valley plain in the municipalities of Seinäjoki and Ilmajoki (Fig.1). The landscape is typical of southern Ostrobothnian with low-lying river valleys filled with clay and silt sediments often reaching thickness of 20 m. Bedrock outcrops, partly covered by till, delineate the river valleys. Fine-grained sediments in the river valleys are mainly cultivated and they are situated at an altitude of 40 m a.s.l, whereas the adjacent gently undulating hills often reach an altitude of 60–90 m a.s.l. The surface relief of Kyrönjoki river valley is relatively flat with minor topographical differences mainly caused by recent human activities related to ditching and the prevention of spring flooding. The bedrock in the study area is mostly composed of mica schists (Mäkitie & Lahti 1991, Mäkitie et al. 1991).

Previous drilling results show that the glacioaquatic and postglacial organic rich clay and silt sediments in the Kyrönjoki river valley are typically about 20 m in total thickness (Kukkonen 1990a,b) and they were deposited during the earlier, more extensive stages of the Baltic Sea. According to Kukkonen (1983), the lowermost 1–2 m of fine-grained sediment was deposited during the Yoldia Sea period, the middle part during the Ancylus Lake period and the upper part during the Litorina Sea period. The highest shoreline of the Litorina Sea lies at 60 m a.s.l. The uppermost sedimentary unit, usually less than 1 m in thickness, is only found near the Kyrönjoki river, where annual spring flooding has maintained wetland areas.

Based on 30 studied soil profiles Osterholm (1998) estimated that two-thirds of the soils in the Rintala reclamation area, situated within the survey area of this study, are very acid, having a minimum pH value in the oxidised layer of around 3.5. In soils with very

Fig. 1. Location map of the survey area in the Seinäjoki region of Ostrobothnia, western Finland. The highest shoreline, which delineates subaquatic and supraquatic land (3), the isobases (4) of the highest shoreline, and the shoreline of Litorina Sea (2) and the present coast line (1) is marked (after Alalamm 1992).
low pH values the sulphur concentration was typically 0.25–0.8 % in the reduced layer and the carbon content 1–3% in the oxidised layer. Whereas in the rest of the soil profiles the minimum pH was seldom less than 5, the sulphur content in the reduced layer was typically <0.1 % and the carbon content in the oxidised layer >4 %.

**Sampling and laboratory analyses**

Drilling was conducted by GM 100 drilling rig applying a piston sampler with a sampling tube 2 m in length and a 45 mm inner diameter. The drilling locations are shown in Figure 4. Standard sedimentological procedures were applied for the logging of drilled samples. Continuous piston core samples of soft sediments, i.e., clay, silt or fine sand were opened in the laboratory. Coarse-grained sediments difficult to penetrate with the piston corer were sampled by flow-through-bit and only studied in 1 m intervals or in intervals related to the changes of the penetration rate indicating consistency differences of the sediment. Flow-through-bit samples were studied in the field and they reveal only scattered information on major sediment units.

Resistivity and pH values of core samples were immediately performed after piston cores have been opened in the laboratory. The measurements were performed through the surface as quickly as possible in order to obtain measurement from unoxidised sediment. The laboratory system consists of HP 35665A Signal Analyser and a Wenner-type electrode array with 1 cm long steel electrodes and 1 cm electrode spacing. Measurements were conducted at an interval of 10 cm in drilled cores. The pH of the samples was determined by a portable analyser.

After logging, resistivity and pH measurements piston cores were sampled at approximately 0.5–1 m intervals. Samples consisted of about 0.1 m sequence of piston core. In all, 75 soil samples were chemically analysed at the Geolaboratory of GTK. Prior chemical analyses the soil samples were lyophilised. Fluoride, chloride, bromide, nitrate and sulphate concentrations were determined from the water leached samples by ion chromatography ( Dionex DX120). Total sulphur concentration was analysed with LECO equipment.

**Geophysical data and interpretation**

The airborne data was acquired using the GTK’s (Geological Survey of Finland) Twin Otter aircraft equipped with magnetic (horizontal gradiometer
— two magnetometers at the wingtips), radiometric (earth’s gamma radiation – total count, Th, K, U channels), and dual-frequency EM system (3125 Hz and 14368 Hz). The vertical coplanar coils, mounted on the wingtips, have a separation of 21.36 metres. A detailed description of the EM system is given by Poikonen et al. (1998). The nominal flight altitude was 30 m and the line spacing 100 m. Altogether, 89 lines were measured.

Ground EM measurements were carried out using the multi-frequency horizontal loop slingram method (APEX MaxMin I+8S system). Six frequencies (880, 1760, 3520, 7040, 14080 and 28160 Hz) were measured. Nominal coil spacing of 40 m was used in all ground EM profiles. Also measurements with terrain conductivity metres (EM-31 & GEM-300) have been made along the slingram profiles.

Airborne magnetics is most useful for mapping bedrock geology (Fig. 3, upper left). Anomalies are caused by magnetic remanence and magnetic susceptibility. Magnetic susceptibility affects the EM responses, but in this study are there are no signs of that. Conductive overburden dampens the possible contribution of anomalous susceptibility of bedrock.

Fig. 3. Airborne geophysical maps of the Seinäjoki study area – magnetic map (upper left), Total radiation (upper right), Electromagnetic in-phase component, 3.1 kHz (lower left) and the apparent depth, 14.4 kHz (lower right).
The Earth’s measured gamma radiation, through airborne radiometrics, is highlighted in the uppermost surface material. Values of K, U and Th channels and their ratios have also been used to assist mapping soil deposits in Finland (Hyvönen et al. 2003). Radiometrics gives a measure of the radioactive mineral content of the surface, but the intensity of radiation is also affected by the moisture/water content of the uppermost part of the surface. Figure 3 (upper right) shows the map of the total count channel. The strongest signal reflects the exposed bedrock. The lowest values show the wetlands and mires. Variation in water or moisture content of surface soils is also observable in areas of fine-grained sediments.

AEM and EM expose the sub-surface conductivity structure. Here we are interested in conductive overburden and that conductivity which is related to sulphide-bearing fine-grained sediments. Some of the magnetic anomaly zones are also conductive (Fig. 3 left, magnetic and EM in-phase at 3125 Hz).

In AEM interpretation the contribution these zones make could only be seen in areas without conductive overburden. Variation in moisture and water content of surface soils has an effect on the conductivity of the uppermost part of the sediments. This could be seen in ground EM measurement, e.g. in the results of the terrain conductivity metres.

The maps of apparent resistivity and depth are useful for first-pass interpretation. These maps are provided together with the measuring quantities. Apparent resistivity and apparent distance mean that the resistivity of a homogeneous half-space and that distance of that half-space from the sensor system, which explain measured in-phase and quadrature responses (Fraser 1978; Peltoniemi 1982). Apparent depth is then apparent distance minus measured flight altitude. This transformation is the simplest 1D interpretation method.

Resistivity mapping is a proper display method for AEM data, at least in these low resistive clay areas. Here the conducting homogeneous half-space can be quite a valid model to explain the measured responses. The skin depth is one measure of electrical attenuation (e.g. Peltoniemi 1982). Assuming a resistivity of 7 Ωm, the skin depths are 23.8 and 11.1 m for the low and high frequency, respectively. In the deeper parts of this clay area the apparent resistivities (at high frequency at least) are near the spatial average resistivity of these fine-grained sediments.

In this study, 1D layered-earth interpretation of the EM data was made with model norm -based inversion. In the 1D model, the earth is composed of a stack of layers, each having a uniform conductivity. The 1D conductivity structure, i.e., the conductivities of each layer, is sought by the regularized inversion. The goal is to find for every measuring point a minimum-structure model, which can fit the measurement data sufficiently well. The 1D responses and sensitivity matrices have been calculated by the Airbeo program (Chen & Raiche 1998). The minimization of objective function \( \text{data misfit} + \beta \times \text{model norm} \) has been carried out with Haber’s (1997) damped Gauss-Newton algorithm.

The EM system of Twin Otter (at 3125 and 14368 Hz) is most sensitive to the conductivity of a half-space in conductivity aperture of \( \sim 0.02 - 1 \, \text{S/m} \) (50 – 1 Ωm). A change in conductivity will cause clearly noticeable changes in at least 3 measured responses (in both in-phase components and at least in one quadrature component). So with two-frequency AEM data we can also get reasonable results, and the interpreted variations in conductivity and thickness of the overlying conducting sediments depict the true conductivity structure of the sediments.

The volume of the earth contributing to the response of an AEM system is said to be the illumination footprint of the system. There are different definitions of the footprint; originally Liu and Becker (1990) defined it as a side length of a square surface, centred directly below the transmitter coil that contains the induced currents which accounts for 90% of the observed secondary field. Beamish (2003) has defined a transmitter footprint using only induced current. We have visualized the illumination footprints of used EM systems by using 3D sensitivity functions (distributions) of these coil systems (Suppala et al. 2003). Considering the footprint of the ground EM systems the electromagnetic coupling between the induced current system and the receiver should be taken into account, as in the Liu-Becker footprint (Reid & Vrbancich 2004) or in the 3D sensitivity functions approach. The footprint of the EM system is only one qualitative measure of its lateral resolution, and usually these estimates have been calculated using a homogeneous half-space.

For the AEM system of the Twin Otter the most sensitive region is below the coil system and elongated perpendicular to the flight direction. Vertical coils whose axes are oriented parallel to the flight line means a good spatial resolution along the flight line and an adequate lateral coverage perpendicular to the flight line. For the ground horizontal loop system, the most sensitive region is elongated along the profile between the coils. For the AEM system the footprint is larger than for the APEX MaxMin ground EM system with the coil spacing of 40 m. The footprint of the terrain conductivity metres EM-31 with the coil separations of 3.66 m is less than 10 m.
Results

Figure 3 (lower right) shows the map of apparent depth and Figure 4 shows the map of apparent resistivity, transformed from the AEM measurements at 14368 kHz. With the apparent depths the validity of the 1D homogeneous half-space model can be assessed. In areas where the apparent depth is negative, the cause of the AEM response is most probably a thin low resistive overburden and the apparent resistivity value overestimates the average resistivity of the overburden. In Figure 3 these negative apparent depths are shown the bluish colours.

The apparent resistivity and depth maps show that the main part of the low resistive clay and silt sediment area seems to be thick enough for this kind of interpretation when the AEM data at 14368 Hz is used. There the apparent resistivities are spatial averages of true resistivity of these sediments. Small positive apparent depths indicate that the uppermost part of the sediment is more resistive than the deeper part.

The apparent depth map delineates the Kyrönjoki riverbank (see the topography in Figure 5), so that there the uppermost more resistive layer seems to be thicker than elsewhere in the cultivated area.

One 4 km long gravity profile (L-5) and three short refraction seismic lines (on L-5) were measured in order to get reference data (i.e., the thickness of the Quaternary sediments) for EM interpretation (Fig. 5). Seismics provides information also on the water table as well as the quality of the sediments.

Figure 6 shows the inversion result from the profile L-2 (shown in Fig. 4). The slingram profile runs over the low-resistivity sediments and the buried ice-marginal deposits (at D-2) (Lintinen et al. 2003). D-1 and D-2 are drilling sites. In Figure 6 resistivity data from the drilling site D-1 is presented in the separate box. Also shown is the measured and modeled slingram data. Excluding the 3D effect caused by the buried ice-marginal deposits, the 1D model explains the measurements well. In the 1D interpretation also the true coil spacing has been considered as an unknown...
parameter. It has been estimated carefully from the field data. The inverted and measured resistivities are consistent with each other.

Figure 7 shows the electrical conductivity of drill-core samples from the drilling site D-1 (the same data as in the box in Figure 6) and the inversion results from the AEM data and from electrical resistivity tomography (ERT). The ERT data is 80 m to SE of the drilling site (along the line L-2). The inversion results are in good agreement with the drill-core samples, as well as the results in Figure 6. According to the inverted ERT results, the resistivity of the uppermost surface is lower when moving to SE along the line L-2. This resistivity decrease in the uppermost layer could be seen approximately in Figure 6 and from the inverted AEM results.

Figure 8 shows a comparison between airborne and ground EM inversion results. The ground geophysical
measurements along the line L-5 were carried out in 2003 and the flight in 2002. The AEM lines 42, 43 and 44 (Fig. 4) cross the ground EM line L-5. The slingram inversion results are fairly consistent with the gravity and seismic interpretation but also show “higher-resistivity” layers between the low-resistivity fine-grained sediments and the high-resistivity bedrock. The AEM system cannot detect the contact between the possible coarse (high-resistivity) sediments and the bedrock, but resolves only the biggest resistivity contrast (i.e., between the low-resistivity fine-grained sediments and the material below it).

The inversion results of the AEM and slingram data (e.g. from Figs. 6,8,10) show that here the slingram system operating at 6 frequencies has a better depth resolution with a slightly deeper exploration depth than the AEM dual-frequency system.

Drilling at D-1 terminated at a depth of 20.1 m. Neither bedrock nor till was detected. The whole drilled sequence consists of soft clay, silt and sand-sized sediments, which are divided into three lithostratigraphical units. The lowermost unit from a depth of 20.1 m to 17 m is composed of laminated clay and silt/fine sand. In each rhythmite coarser layers are from 2 to 10 cm in thickness and finer layers are from 0.3 to 1.0 cm in thickness. Dropstone structures with pebble-size clasts were observed in this unit. This unit is also characterised by low sulphate, total sulphur and chloride concentration (Fig. 9). The lamina thickness gradually decreases and dark sulphide rich laminated clay and silt with 1–3 mm lamina thickness overlies the lowermost unit. In this unit chloride concentration is distinctively elevated compared to the unit below. At a depth of 12–11 m the laminated sediment unit

Fig. 7. Comparison between the electrical conductivity of drill-core samples and the inversion results of the AEM data and ground resistivity data. The ground resistivity data is 80 m to SE from the drilling site.

Fig. 8. Comparison between AEM and ground EM inversion results (see Figure 4). Note that AEM lines 42, 43 and 44 crosses line L-5 and the gravity and seismic data (the inverted bedrock surface) is from line 5.
gradually changes to the upper weakly laminated or massive sulphide clay and silt unit. This unit is characterised by total sulphur concentrations of 0.3–1.0%.

The Cl₂ concentrations do not correlate with the total S concentrations. The result was expected because both results indicate different geochemical regime in a water body. The overall decrease of chloride from deeper layers to the surficial layers possibly indicates the natural decrease of salinity during the Litorina Sea period. Subaerial leaching can not totally be excluded, but its effect may be minimal. This view is supported by the fact that the Rintala area was artificially drained for agricultural purposes by ditching and pumping only few decades ago. Also the low permeability of fine-grained sediment, and the groundwater table at the depth of about 2 m support the view that the leaching effect has had a minimal effect on the chloride content of the profile studied.

Discussion and concluding remarks

Peltoniemi (1982) validated one-frequency low altitude AEM data, which was measured by DC-3 aircraft with a vertical coaxial coils system and showed the usefulness of the simple 1D models in area of low-resistivity fine-grained sediments. He made his test at a distance of less than 10 km from the Rintala area along the lower course of the Kyrońjoki river. The typical layer-structure of the overburden is, according to the results of Peltoniemi (1982): organic soil in the surface (45–120 Ωm), sulphide clay and gyttja (7–21 Ωm), and till (> 340 Ωm). A similar resistivity structure is obtained in the Rintala area, where the resistivity of the fine-grained sediment can be still less than 5 Ωm.

Puranen et al. (1999a, b) and Åström (1996) showed that by using one-frequency airborne EM data, the occurrence of low-resistivity sulphide-bearing sediments can be delineated. With two-frequency AEM data we can also interpret variations in the resistivity and thickness of the overlying low resistive sediments.

The slingram system operating at 6 frequencies has a better depth resolution with slightly deeper exploration depth than the AEM dual-frequency system. The ground EM has a better spatial resolution too. To increase the depth resolution of the AEM system it should be upgraded to operate at more than two frequencies. A frequency higher than 14368 Hz would help to resolve subtle resistivity variations near the surface, while a frequency lower than 3125 Hz would increase the exploration depth. To gain the best possible resolution from an EM system the calibration and levelling should be done properly.

The thicknesses of the fine-grained deposit, inverted from the AEM data, were in good agreement with other available data. Furthermore, the resistivity distributions based on AEM data were very similar to the drill-core, resistivity soundings and ground EM results. The high electrical conductivity of the sulphide clay arises from the salinity and sulphate of the pore water. However, the salinity originates from the same depositional environment as the sulphides, and the results strongly suggest that the AEM data can be an economic tool for regional scale sulphide clay maps.
and acidification predictions. The other geophysical data played invaluable role not only as reference and calibration data for AEM interpretation, but also in characterisation of soil types.

The need to resolve conductivity variation near the surface and at depth over a large area suggested an airborne EM system as most appropriate. Here we have used AEM data to complement other information (with higher resolution), ground EM measurements and in-situ conductivities, to delineate the conductivity structure in the area (Fig. 10). We have not constrained one inversion using in-situ or inverted conductivities from other data sets. By comparing the different results we can validate e.g. the calibration of the AEM measurement.

Due to topography controlled deposition and erosion processes, as well as differences in redox conditions prevailing in the water body and sediment, the results gathered from one area are not directly applicable to another research area without new reference drilling, sampling and chemical analyses. However, when the basin-related relationship between chemistry and EM-results are carefully worked out the applied integrated methodology shows great potential characterising potentially problematic sulphur-rich clay and silt deposits.

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EVALUATION OF PORTABLE X-RAY FLUORESCENCE (PXRF) SAMPLE PREPARATION METHODS

by
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Introduction

The performance of four different field-based portable X-ray fluorescence (PXRF) instruments for the determination of heavy-metal contents in contaminated soils were evaluated. Instead of inter-comparison of the instruments, this investigation focused on testing of several different sample preparation methods for the assessment of contaminated soil. The results obtained by PXRF methods were compared with results obtained by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and X-ray fluorescence spectrometry (XRF).

In this study, the soil moisture and the particle size of the samples were the two factors, which mostly affected the trueness of the results. These effects were observed with all of the tested PXRF instruments.

The work highlighted the importance of sample preparation when analysing soil samples at contaminated sites by PXRF instruments. As a conclusion of the study, a list of recommendations was produced for sampling and measurement of contaminated soil samples by PXRF.

It is desirable for the PXRF measuring method to be simple, inexpensive and fast, but at the same time capable of producing analytical data of low detection limits and high reliability. This puts several demands on quality control and sample preparation procedures. On the other hand, the greater the requirement for accuracy and precision required, the more difficult the procedure will be to run.

Field-based portable X-ray fluorescence analysers operate on the principle of energy dispersive X-ray fluorescence spectrometry, whereby the characteristic X-ray excited spectra are analysed directly taking into account their energy proportional response in an X-ray detector. Traditionally PXRF analysers have used sealed radioisotope sources to excite samples with gamma rays and X-rays of the appropriate energy. During the last two years, however, a few manufacturers have introduced analysers that utilise a rugged X-ray tube instead of radioactive isotopes.

In situations where the precision, accuracy, and detection limits of the XRF technology are consistent with the data quality objectives of a site characterisation project, PXRF provides a fast, powerful, non-destructive, and cost effective technology for multielemental analysis. In recent years, the PXRF analysers have been applied increasingly to environmental characterisation and remediation measurements, particularly in the analysis of heavy metal contaminants in soils.

In 1995, the U.S. Environmental Protection Agency (EPA) supported a study of innovative PXRF technology at two Superfund sites to characterise the
performance of the latest models of commercially available PXRF analysers. This study found that the PXRF analysers were effective tools for field-based analysis of soil samples for metal contamination. The data from these trials provided background material for the creation of a draft method (EPA 1998). This method provides guidance to users of PXRF for environmental characterisation.

It is well known that accuracy of the XRF technique is dependant on the homogeneity of the samples. PXRF should, therefore, be defined as a screening method used together with confirmatory analysis of laboratory methods. Furthermore, the quality and precision of PXRF results are strongly dependent on sample collection and sample preparation methods (including sieving and drying) and calibration of instruments. XRF emission of a particular element is usually strongly dependent on the nature of the sample matrix and interfering elements that might be present. Site-specific reference samples that have similar matrix characteristics to the samples to be analysed, are used in some procedures to optimise calibrations.

Several approaches can be used for calibrating XRF analysers (Kalnicky and Singhvi 2001). One method is based on the fundamental parameter method, another method is to perform an empirical calibration based on site-specific calibration standards analysed by an appropriate reference method.

Measuring soil samples by XRF-based techniques usually requires multi-step sample preparation procedures in order to obtain accurate and precise results. Elements in geological samples are usually determined by XRF using loose powder samples that have been fused as a glass disk or pressed as powder pellets (Potts 1987).

Currently PXRF instruments are used to an increasing extent to provide immediate results at lower costs, than conventional laboratory techniques, in particular in connection with the investigation and remediation of contaminated soil and groundwater. On-site analysis is thus performed by the field staff using simple equipment and non-standardised methods and without costly and time-consuming quality assurance (QA) schemes. The major disadvantage of any scheme that does not incorporate an appropriate QA procedure is that the analytical quality of the data is not then known, i.e.: it is not possible to know the precision and the bias associated with the data, or even if the equipment is functioning properly.

The primary aim of this study is to recognise and minimise systematic errors related to in homogeneity and matrix effects of the sample, which may be associated with measurements when analysing soil samples contaminated with heavy metals by PXRF and to improve the reliability of results, without creating procedures that are too complicated for routine use.

**Site Descriptions**

The sites selected for field study represent typical sites contaminated with heavy metals in southern Finland (Table 1).

Site A: The first site was a fallow field at the outskirts of the city of Lohja about 50 km northwest of Helsinki. A wood impregnation plant had operated at this site, causing slightly raised As, Cu, and Cr concentrations (typically 50-1000 mg kg⁻¹). Investigations of this site were focused on an area of 200 m² in order to find the “hot spots” of the site.

Site B: An industrial area of about 40,000 m² located in the city of Vantaa near Helsinki. Here, the heavy metal pollution derives from Pb smelting in the 20th century. Recent ICP-AES analyses (Laiho 2003) revealed Pb concentrations between 100 and 80,000 mg kg⁻¹ in the top 0 – 400 mm soil layer.

Site C: A shooting range in central Finland. Several sand samples were found to be contaminated with Pb. Samples from this area was primarily used for inter-comparison of the four PXRF instruments.

**Experimental**

**Sampling**

Several persons from different organisations collected soil samples, using different techniques. The uncertainty due to variation in sampling practices is not taken into consideration, and therefore the term sample is used here to note for an untreated fresh sample.

**Materials**

Samples were collected by traditional methods using hand auger (drill) and shovel, after removing the surface vegetation from the sampling point. Washing all the equipments by water between the samples eliminated gross contamination. Table 1 describes the sample material used for these investigations. Samples were homogenised manually and stored in thin polypropylene bags (Minigrip, PE-LD04). Non contaminated plastic Nylon sieves (<0.5 and <2.0 mm) were used for sieving tests and the sieves were cleaned with compressed air and ethanol between the samples. HNO₃ (65%, Baker, Pro Analysis) and HCl (37%, Baker, Pro Analysis) were used for acid extraction of ICP-AES analyses in the laboratory.
Table 1. Sample materials used for the investigations.

<table>
<thead>
<tr>
<th>Sample(s)</th>
<th>Sampling site</th>
<th>Soil type</th>
<th>Used for following investigations</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>Un-known</td>
<td>Sand</td>
<td>Control of PXRF instruments</td>
<td>Uncontaminated, analysed by ICP-AES</td>
</tr>
<tr>
<td>Reference sample, GTKREF1</td>
<td>Un-known</td>
<td>Sand</td>
<td>Control of PXRF instruments</td>
<td>Analysed by ICP-AES</td>
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<tr>
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<td>Site B</td>
<td>Sand</td>
<td>Control of PXRF instruments</td>
<td></td>
</tr>
<tr>
<td>Sample A</td>
<td>Site A</td>
<td>Clay</td>
<td>Limit of detection, sample preparation tests</td>
<td>Total amount of samples: 29 from site A</td>
</tr>
<tr>
<td>Sample B</td>
<td>Site B</td>
<td>Sand</td>
<td>Precision of PXRF on high level concentration of Pb</td>
<td>Total amount of samples: 21 from site B</td>
</tr>
<tr>
<td>Eleven C samples (Fig. 5)</td>
<td>Site C</td>
<td>Sand</td>
<td>Inter-comparison of PXRF instruments (Fig. 5)</td>
<td>Total amount of samples: 33 from site C</td>
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<tr>
<td>NIST CRM 2710</td>
<td>Montana soil</td>
<td></td>
<td>Validation</td>
<td></td>
</tr>
<tr>
<td>NIST CRM 2711</td>
<td>Montana Soil</td>
<td></td>
<td>Validation</td>
<td></td>
</tr>
</tbody>
</table>

**Sample preparation methods**

The typical size of samples was 500-1000 g. The samples were split into sub-samples of about 100 g. These were used for testing varying parameters, such as grain size (0.5 mm and 2.0 mm), humidity, count time of the measurement (from 30 s to 240 s), and temperature (between –5 °C and +25 °C).

In the study mentioned above, the simplest field-based sample preparation method consisted of removing vegetation and other organic material, as well as particles larger than 10 mm. The sample (samples A and B) was homogenised manually in a plastic bag. Samples were neither dried nor sieved, and the measurement was taken directly through the bag on a small wooden table without replicate measurements, using a 30 s count time.

The most complicated of the tested field-based sample preparation procedures was similar to the sample preparation preceding ICP-AES determination in the laboratory (International Organization of Standardization 1994). In this method, the soil samples (sub-samples from sites A and B) were dried at a temperature < 70 °C for 24 hours and sieved to < 2.0 mm or <0.5 mm fraction. Several tests, with samples prepared as pressed powder pellets, were also performed. Pellet preparation procedure is rather time consuming and requires skilled personnel, which makes it less attractive for quick field-type measurements. Count time for measurement was typically 120 s.

The following sampling protocol (GTK protocol) was developed for sampling and measuring contaminated soil samples by PXRF:

- Remove stones and plant fragments from the sampling point
- Choose a sample for sample preparation (500–1000 g)
- Pre-homogenise the sample manually (in plastic bag)
- Dry the sample (water content must be less than 20 % before measuring)
- Sieve the sample to a pre-defined particle size (grain size < 2.0 mm)
- Place the sample into a plastic bag
- Use at least 10 mm thickness of sample for measuring (100–500 g)
- Use the same background plate or strong table under the sample, in order to avoid different background effects between the measurements
- Flatten the plastic bag containing the sample evenly on the surface
• Use 120 seconds count time
• Perform a minimum of three replicate measurements
• Report all three results, calculate the average
• Record observations and decisions
• Confirm at least 5% of the results by alternative, preferably accredited, analytical methods
• Measure control samples, a blank sample and a reference sample, before and after every sample set (also after every ten samples or after service of instrument)
• Clean and/or service the instrument if control sample measurement fall outside approval range
• Service the instrument if drift control measurement fall outside approval range (if provided by manufacturer)

To obtain more reliable PXRF measurements, following should also be considered:
• Compare in situ results to confirmatory laboratory results to obtain a correlation curve and/or prepare several calibration samples to determine correlation curve
• Extend the count time to up to 300 seconds
• Use up to 10 replicate measurements instead of three
• Prepare duplicate samples
• Carry out measurements on samples prepared as pressed powder pellets

Instrumental analysis

XRF

All the laboratory XRF analyses and measurements were carried out at the Geolaboratory of Geological Survey of Finland in Espoo. The in-house reference material was analysed by Philips PW 1480 XRF spectrometer in the laboratory using pressed powder pellets. Pellets were prepared by weighting dried and sieved soil samples from site B (Table 1) in to a pulverising swing-mill (Herzog HSM 100P) and pulverised in a carbon steel bowl. For preparation of the pressed pellet, 7.0 g of pulverised (< 75 μm) sample was mixed with 0.4 g of organic binder and pulverised in a tungsten carbide bowl to obtain a grain size of 95% < 10 μm. The pulverised pulp was pressed into a pellet at 20 tons, using a steel piston press. Pellets were stored in a closed polypropylene bag at room temperature, in order to avoid contamination.

ICP-AES

All the laboratory ICP-AES analyses and measurements were carried out at the Geolaboratory of Geological Survey of Finland in Espoo. An ICP-AES Thermo Jarrel Ash IRIS Advantage instrument was used for obtaining reference data to compare with the PXRF results. Sieved soil samples (from sites A, B and C) were analysed by ICP-AES using an internationally accepted method for soil analysis, the ISO standard method 11464. The acid leach was performed as follows: 2.00 (±0.10) g of soil sample were digested with 12 ml of aqua regia (9.0 ml HCl + 3.0 ml HNO3) at 90 °C for 8 hours. After addition of 50 ml H2O, samples were centrifuged for 20 minutes at 3000 rpm (Jouan C 412). The clear solution was used for (further) analysis. An in-house reference material of pulverised soil was used as a control sample.

PXRF

Four PXRF analysers were used for the sample preparation study for inter-comparison of Pb-contaminated sand samples (Table 2).

The preliminary analyses of the study samples were carried out both in the laboratory and under field conditions for comparing the PXRF instruments. Samples for the inter-comparison study were collected from site C. The minimum amount of sample for measurement was about 10 g, which formed a layer of about 10 mm in the plastic bag used in the procedure. Further field measurements and tests on sample preparation methods were undertaken with the INNOV-X analyser.

Calibration and quality control (QC) and quality assurance (QA) of PXRF’s

PXRF instruments can be used for several purposes, each requiring different QC and QA procedures. Typically, PXRF instruments have been used for locating contaminated areas, in particular hotspots, when absolute values are not as important as finding a variation of high and low values.

In this study internal calibration, using fundamental parameters software chosen by individual, was used. PXRF instruments also require user to make drift correction, for example with a stainless steel plate, before starting the measurements.

As a compromise between idea quality assurance and ease of operation, two control samples, one reference sample and one blank sample of uncontaminated sand
Table 2. Technical specifications of the PXRF-analysers used for the investigations.

<table>
<thead>
<tr>
<th>MODEL:</th>
<th>INNOV-X</th>
<th>X-MET 2000</th>
<th>NITON XLi 700</th>
<th>NITON XLi 700</th>
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<tbody>
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<td>Innov-X-Systems, USA</td>
<td>Metorex Inc., Finland</td>
<td>Niton Corp., USA</td>
<td>Niton Corp., USA</td>
</tr>
<tr>
<td>Operation principle</td>
<td>EDXRF</td>
<td>EDXRF</td>
<td>EDXRF</td>
<td>EDXRF</td>
</tr>
<tr>
<td>X-ray source</td>
<td>X-ray tube, silver anode</td>
<td>$^{55}$Fe, $^{109}$Cd, $^{241}$Am-isotopes</td>
<td>$^{55}$Fe, $^{109}$Cd, $^{241}$Am-isotopes</td>
<td>X-ray tube, silver anode</td>
</tr>
<tr>
<td>Detector</td>
<td>High resolution Si-PIN</td>
<td>High resolution Si-PIN</td>
<td>High performance Si-PIN</td>
<td>High Performance Si-PIN</td>
</tr>
<tr>
<td>Cooling system</td>
<td>Thermo electrical</td>
<td>Thermo electrical</td>
<td>Thermo electrical</td>
<td>Thermo electrical</td>
</tr>
<tr>
<td>Main components</td>
<td>Single unit with integrated PC</td>
<td>SIPS-probe and PC-unit</td>
<td>Single unit with VGA touch screen</td>
<td>Single unit with VGA touch screen</td>
</tr>
<tr>
<td>Weight</td>
<td>1.8 kg</td>
<td>1.6 kg (5.8 kg with PC)</td>
<td>0.72 kg</td>
<td>1.4 kg</td>
</tr>
</tbody>
</table>

Table 3. Results of the reference samples analysed by INNOV-X PXRF instrument and reference values by well-established laboratory methods using the XRF and ICP-AES techniques (mg kg⁻¹).

<table>
<thead>
<tr>
<th>Sample name:</th>
<th>Elements</th>
<th>PXRF (ppm ± SD)</th>
<th>XRF</th>
<th>ICP-AES</th>
<th>Certified Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>GTKREF 1</td>
<td>Mn</td>
<td>500±93 *</td>
<td>400</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>GTKREF 1</td>
<td>Cu</td>
<td>550±41 *</td>
<td>170</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>GTKREF 1</td>
<td>Zn</td>
<td>570±67</td>
<td>41</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>GTKREF 1</td>
<td>As</td>
<td>54±16 *</td>
<td>46</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>GTKREF 1</td>
<td>Pb</td>
<td>&lt;LOD (±21)</td>
<td>99</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>GTKREF 2</td>
<td>Zn</td>
<td>450±19 *</td>
<td>166</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>GTKREF 2</td>
<td>Pb</td>
<td>170±18 *</td>
<td>340</td>
<td>280</td>
<td></td>
</tr>
<tr>
<td>NIST CRM 2710</td>
<td>Mn</td>
<td>14700±360</td>
<td>7780</td>
<td>10100±400</td>
<td></td>
</tr>
<tr>
<td>NIST CRM 2710</td>
<td>Cu</td>
<td>3450±78</td>
<td>2900</td>
<td>2950±130</td>
<td></td>
</tr>
<tr>
<td>NIST CRM 2710</td>
<td>Zn</td>
<td>8200±120</td>
<td>6250</td>
<td>6950±91</td>
<td></td>
</tr>
<tr>
<td>NIST CRM 2710</td>
<td>As</td>
<td>910±53</td>
<td>598</td>
<td>626±38</td>
<td></td>
</tr>
<tr>
<td>NIST CRM 2710</td>
<td>Pb</td>
<td>6200±86</td>
<td>5300</td>
<td>5532±80</td>
<td></td>
</tr>
<tr>
<td>NIST CRM 2711</td>
<td>Mn</td>
<td>1260±210 *</td>
<td>501</td>
<td>638±28</td>
<td></td>
</tr>
<tr>
<td>NIST CRM 2711</td>
<td>Cu</td>
<td>145±38 *</td>
<td>102</td>
<td>114±2</td>
<td></td>
</tr>
<tr>
<td>NIST CRM 2711</td>
<td>Zn</td>
<td>400±29 *</td>
<td>325</td>
<td>350.4±4.8</td>
<td></td>
</tr>
<tr>
<td>NIST CRM 2711</td>
<td>As</td>
<td>138±29 *</td>
<td>99</td>
<td>105±8</td>
<td></td>
</tr>
<tr>
<td>NIST CRM 2711</td>
<td>Pb</td>
<td>1360±37 *</td>
<td>1095</td>
<td>1162±31</td>
<td></td>
</tr>
</tbody>
</table>

*) These values were followed during the investigations.
(Table 1), were measured after each ten samples, as well as at the beginning and in the end of each sample set. The reference materials used in this study were also analysed in the laboratory by XRF using pressed powder pellets and by ICP-AES after acid extraction (Table 3).

An average of 25 replicate measurements by PXRF were used on field to control the sampling and measuring conditions, precision and the bias associated with the data. Only elements described above were determined from the samples (site A and site B). The reference sample and blank sample were chosen to represent the soil type and elements at the site, even if some of the measurements were close to detection limits.

There can be several reasons for low detection limits; probably a silver anode tube does not effectively excite Mn, Cu and Zn. Also the standard deviation (SD) was varying between the different soil types. The low Mn result analysed by ICP-AES is thought to be due to some minerals not completely soluble to acid.

Preliminary tests on different (site-characteristic) empirical calibration procedures were run with NIST standard reference materials (Table 3), but those were found to be too complicated for routine use under field conditions. However, site characteristic calibration can be recommended for minimising the systematic error observed between different analytical methods.

Results and discussion

Preliminary tests were carried out under field conditions (sites A, B and C) in order to test the simplest sample preparation method described above. Untreated samples (size 500 - 1000 g) were put in plastic bags and measured by one PXRF analyser from different side of the sample. Relative difference between the highest and the lowest result rose up to 1000% with inhomogeneous samples containing particles of various sizes. Similar results were observed for all PXRF analyzers when the test was repeated with the same sample. The relative difference was found the most significant when analysing wet samples, or inhomogeneous samples such as waste material.

Another preliminary test, an inter-comparison test between different PXRF analysers, was run on site C. Eleven air dried sand samples were homogenised manually in plastic bags and analysed by four different PXRF analysers (Fig. 5). The yield of the PXRF analysers (ICP-AES = 100%) was measured to be between 65 % and 160 %. Accordingly it was judged that this test showed that PXRF analysers are suitable for analysing Pb from sand samples, as in this case the differences between results from different analysers was not significant.

These preliminary tests showed clearly that soil type can strongly effect the repeatability of PXRF measurements as well as the comparability of PXRF results to the laboratory analyses. Hence, it was essential to start developing PXRF measurements by evaluation of sample preparation methods.

The first investigation, dealing with soil sample preparation procedures, was to evaluate the effect of sieving on the subsequently analysed elemental concentration, since particle size is known to affect the results of XRF analyses (Clark et al.1999). It is clear that the type of sample and the concentration levels also affect the results. The sample chosen for the first sieving investigations was a sandy clay sample (sample A from site A, Table 1), containing a concentration
of heavy metals near the background values found in Finland (Puolanne et al. 1994). The sample was very homogeneous and air-dried.

Sieving had an effect on the mean concentration measured by PXRF. Figure 1 shows that almost without exception, the highest values (average of 10 replicates) were obtained for the smaller particle size fractions (<0.5 mm or <2.0 mm). This was expected due to enrichment of elements in the smallest particles and the different mineralogy of samples.

More significant differences between replicate measurements were observed, for all fractions, when analysing either relatively high concentrations (<1000 mg kg\(^{-1}\)) or concentration near the detection limit of PXRF measurement (Fig. 3). For example, a variation in the low concentration of Zn in different particle size fractions is substantial, when comparing the different grain size fractions, and could lead to errors in decision-making on field (Table 4), if for example remediation level for Zn is based on lower guideline value (150 mg kg\(^{-1}\)).

The study indicated that for the best results, at least three replicate measurements should be made with the PXRF instrument and that the samples should be sieved before the measurements.

Relative standard deviation was calculated for ten replicate measurements of a dried sand sample (sample A), after different sample preparation procedures: (1) without sieving, (2) sieving to > 2.0 mm, (3) sieving to < 2.0 mm, and (4) sieving to < 0.5 mm. The results can be seen in Figure 2. The repeatability of the PXRF measurement was generally better for samples of smaller particle size: this effect was observed for all the elements measured.

At the second stage of the investigation the effect of sample preparation on the sensitivity of the PXRF measurements was studied. Detection limits were determined by taking ten replicate measurements on soil samples. Based on these measurements, the standard deviation was calculated. The detection limits presented in the Figure 3 are defined as 3 times the standard deviation for each analyte.

In this study the detection limits of 9 environmentally important elements were determined by four different sample preparation methods. Two EPA methods (EPA 1998) were compared with two of our own sample preparation protocols, of which one is a field method and the other is the GTK protocol outlined above. EPA1 uses quartz (SiO\(_2\)) to determine interference-free detection limits and EPA2 is a field-based method applied to dried soil samples. Sample A (Table 1) was the selected study sample, because it was relatively homogeneous, it did not contain particles larger than 2 mm, which could cause physical interferences in the measurement. It was also observed, that the limit of detection for Cr, Cu and Zn rose considerably when measured after sample preparation by field protocol (EPA2 and GTK1), using relatively dry soil material (moisture content 5 % – 10 %). This should be consid-

Table 4. Comparison of Zn concentrations (mg kg\(^{-1}\)) in Finnish soil by particle size fraction as determined by PXRF during the sieving tests (n=10).

<table>
<thead>
<tr>
<th>Particle size</th>
<th>Mean</th>
<th>Lowest</th>
<th>Highest</th>
<th>Highest / lowest, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>81</td>
<td>48</td>
<td>115</td>
<td>240</td>
</tr>
<tr>
<td>&gt;2.0 mm</td>
<td>81</td>
<td>39</td>
<td>135</td>
<td>346</td>
</tr>
<tr>
<td>&lt;2.0 mm</td>
<td>88</td>
<td>64</td>
<td>115</td>
<td>180</td>
</tr>
<tr>
<td>&lt;0.5 mm</td>
<td>80</td>
<td>54</td>
<td>109</td>
<td>202</td>
</tr>
</tbody>
</table>

Fig. 2. The effect of sieving on precision of the PXRF measurement (Other elements were not detected in the sample)
When analysing soil samples by PXRF analysers from relatively unpolluted sites.

In Figure 4 the detection limits of 9 environmentally important elements are compared with Finnish guideline values for contaminant concentrations in soil (Puolanne et al. 1994). It was observed that PXRF instruments could easily be applied for determination of low concentration levels of Pb and Zn, whereas there were some problems to detect even relatively high concentrations of Cr or Cd. Similar results were observed with all of the PXRF instruments tested.

The effect of moisture content on the accuracy of PXRF measurement was investigated by adding 5 % - 40 % of distilled water to the dried and sieved sample. Water content of the soil sample was determined gravimetrically. The results showed clearly that overall error was minor when moisture content was small (5 %–15 %), and sample moisture contents above 20 % was leading to significant errors in PXRF measurements of the tested types of materials. Moisture alters the matrix and therefore the penetration depth of the radiation. For example, the concentration of Pb and Zn in a dry sample was about 2.0 times higher than the concentration obtained for samples with moisture contents of 30 %. These results were similar to results of previous investigations (Kalnicky et al. 1992, Laine-Ylijoki et al. 2002).

Conclusions

In this study it was observed that both different techniques and sample preparation affected the final results. According the results, it can be presumed that sample preparation can lead to more significant errors than the differences between PXRF instruments. Furthermore, errors due to sample preparation can easily be minimised by proper sample preparation techniques. These studies pointed out that soil moisture and particle size of the samples were the two factors, which mostly affected the trueness of the results. As a conclusion of the study, a list of recommendations was produced for sampling and measurement of contaminated soil samples by PXRF.

However, not all the errors can be avoided by more accurate sample preparation, and differences between the PXRF instruments increased dramatically when soil samples of high concentration levels (>1000 mg kg⁻¹) were analysed without soil-characteristic calibration. This is suspected to be due to different fundamental calibration given by the instrument manufacturers. Therefore, it is always recommended to compare in situ results to confirmatory laboratory results to obtain a correlation curve and/or prepare several calibration samples to determine correlation curve before starting any big projects.

During the study it was also observed that further work is needed for the improvement and harmonisation of the PXRF methods as well as quality control of in situ analyses. Various field methods are being developed, to an increasing extent, in order to optimise investigation and remediation of soil and ground water pollution. There is an urgent need to establish a common methodology for assessing the analytical quality of the data obtained, i.e. a set of practical QA schemes. The QA schemes should be a compromise between the laboratory QA (EN ISO/IEC 17025:2000) and the currently very limited QA used for most field methods. A guide for environmental administrators should be provided to enable them to evaluate data obtained by these field methods properly. Harmonisa-
tion of methodologies would provide not only more reliable results of field measurements, but also more comparable results between all users.

Good planning of the survey is needed before using PXRF for in situ field-based analysis, in order to gain as much information as possible on estimates of both concentration values and uncertainties, and to permit a realistic interpretation of the extent of contamination at the site.

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