



VUORIMIESYHDISTYS-
BERGSMANNAFÖRENINGEN r.y.



12. Geokemian Päivät 2016 – 12th Finnish Geochemistry Days 2016

21.-22.4.2016
Åbo Akademi, Turku
Finland



Tiivistelmät - Abstracts

Toimittaneet – Edited by
Pertti Sarala ja Pasi Eilu



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12. Geokemian Päivät 2016 – 12th Finnish Geochemical Meeting 2016

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SEMINAARIOHJELMA – SEMINAR PROGRAMME

Torstai - Thursday 21.4.

8.30-9.00 Ilmoittautuminen ja kahvit – Registration and coffee

Sessio 1, Kaivosympäristöjen geokemiallinen tutkimus – Geochemical research in mine districts

Puheenjohtaja - Chair Pertti Sarala

klo 9.00-9.05	Pertti Sarala	Avaus - Opening
klo 9.05-9.45	Ruth Warrender	Keynote talk; Navigating the jungle of best practices in mine waste characterisation
klo 9.45-10.05	Päivi Kauppila	Mineral resource potential of tailings from closed sulphide mine sites in Finland
klo 10.05-10.25	Leena Tarri	Aggregate quarries - potential sources of explosive residues in groundwater
klo 10.25-10.45	Soili Solismaa	Novel synthesis methods for advanced porous ceramics from mine tailings (CeraTail)

klo 10.45-11.00 Tauko - Break

Puheenjohtaja - Chair Päivi Kauppila

klo 11.00-11.20	Raija Pietilä	Development, evaluation and optimization of measures to reduce the impact on the environment from mining activities in northern regions
klo 11.20-11.40	Irma Puttonen	Estimating the internal loading for a water quality model using chemical characterization of sediment phosphorus
klo 11.40-12.00	Tiina Nieminen	The effect of bedrock on drainage water quality at forested peatland catchments

klo 12.00-13.00 Lounas – Lunch

Sessio 2, Luontaisen ja rakennetun ympäristön geokemia – Geochemistry of natural and urban environment

Puheenjohtaja – Chair Tiina Nieminen

klo 13.00-13.20	Jaana Jarva	Preliminary risk assessment of soil parent material with elevated element concentrations
klo 13.20-13.40	Tarja Hatakka	Applying pXRF analyzer to the geochemical baseline studies
klo 13.40-14.00	Timo Tarvainen	The geochemical correlation between coarse and fine fractions of urban soil in Finland
klo 14.00-14.20	Pauliina Liwata-Kenttälä	Geogenic and anthropogenic effects on stream water in Kittilä, Finnish Lapland
klo 14.20-14.40	Gerhard Hakkarainen	Biogeochemical exploration for limestone
klo 14.40-15.10	Kahvitauko – Coffee break	

Sessio 2, Luontaisen ja rakennetun ympäristön geokemia – Geochemistry of natural and urban environment

Puheenjohtaja - Chair Timo Tarvainen

klo 15.10-15.30	Pertti Sarala	Application of the weak leach methods in sustainable mineral exploration
klo 15.30-15.50	Maarit Middleton	Learned lessons in biogeochemistry by targeting known mineralizations in the UltraLIM orientation survey in northern Finland

klo 15.50-16.10	Anne Taivalkoski	Snow in mineral exploration - examples from the UltraLIM project
klo 16.10-16.30	Keijo Nenonen	Soil geochemical response in glaciated terrain: examples from till- and peat-covered mineralizations in Finland
klo 16.30-17.45	Posterit ja virvokkeita – Posters and refreshments	
klo 18.00-20.00	Geologisen seuran kuukausikokous – Meeting of the Geological Society of Finland	

Perjantai - Friday 22.4.

Sessio 3, Geokemian sovellukset geologisessa tutkimuksessa – Geochemical applications in geological study

Puheenjohtaja - Chair Pasi Eilu		
klo 8.30-8.50	Krister Sundblad	300 million years of indium-forming processes in A-type igneous environments in the central parts of the Fennoscandian Shield
klo 8.50-9.10	Sari Romppanen	Laser spectroscopic methods in analysis of REE-bearing minerals
klo 9.10-9.30	Heikki Papunen	Fractionation of nickel converter slag – a comparison to sulphide-bearing komatiitic flows
klo 9.30-9.50	Ilona Romu	Deciphering the geological environment for rock samples of unknown origin
klo 9.50-10.10	Kahvitauko – Coffee break	
Puheenjohtaja - Chair Kirsti Korkka-Niemi		
klo 10.10-10.30	Raimo Sutinen	Vertical soil zonation - a constraint for treeline Norway
klo 10.30-10.50	Jussi Aarnisalo	Use of PCA in calculation of residual abundance values of various elements in geochemical till survey data
klo 10.50-11.00	Keskustelua ja kysymyksiä - Discussion and questions	
klo 11.00-12.15	Lounas – Lunch	

Sessio 4, Geologit työelämässä – Working as a geologist - experiences of different duties and organizations

Puheenjohtaja - Chair Timo Kilpeläinen		
klo 12.15-12.35	Päivi Kauppila	GTK
klo 12.35-12.55	Sami Saraperä	TSV
klo 12.55-13.15	Petri Peltonen	Itsenäinen konsultti
klo 13.15-13.35	Henri Annila	YKL-puheenvuoro
klo 13.35-14.00	Kahvitauko – Coffee break	
Puheenjohtaja - Chair Timo Kilpeläinen		
klo 14.00-14.20	Kaisa Nikkilä	Jatko-opiskelija
klo 14.20-14.40	Håkan Pihl	Nordkalk
klo 14.40-15.00	Jyrki Korteniemi	Agnico Eagle
klo 15.00-15.20	Ismo Aaltonen	Posiva
klo 15.20-15.30	Yhteenveto ja tilaisuuden päättäminen – Conclusions and closing	

Posterit – Posters

Peter Johansson and Raija Pietilä: The evaluation and management project of the cumulative environmental effects of the mining cluster in Lapland

Päivi M. Kauppila, Teemu Karlsson, Tero Korhonen, Marja Lehtonen, Antti Taskinen, Anna Tornivaara and Neea Heino: Mining waste management methods (KaiHaMe)

Jussi Kinnunen: Geochemical comparison between the medieval building dimension stones and potential quarry outcrops with pXRF

Tatu Lahtinen, Kirsti Korkka-Niemi, Anne Rautio and Veli-Pekka Salonen:
Hydrogeochemical characterization of the Sakatti mine prospecting area, Sodankylä, Finnish Lapland

Sonja Lavikko and Olav Eklund:
Recycling mine waste through mineral carbonation

Krista Mönkäre, Marjaana Ahven, Perttu Mikkola and Markku Väisänen:
Geochemistry of the volcanic rocks from the southeast of the Central Finland Granitoid Complex

Olli-Pekka Siira: Original partial serial extraction method for soil nutrient analysis

Marianne Valkama, Pertti Sarala and Anne Taivalkoski:
Geochemical baseline mapping in Rovaniemi, northern Finland

Julkaisu - Publication

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Use of PCA in calculation of residual abundance values of various elements in geochemical till survey data

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It is well known that the abundance levels of different elements in till vary according to the mineralogy of assayed till materials related to bedrock geology and glacial history, depending on the level of weathering processes of both bedrock and till. Moreover, dissolution rates of different minerals of the fine fraction of till affect the abundance levels of elements in the data received when hot *aqua regia* dissolution is used (e.g. Aarnisalo 1990, Lahtinen 1991, Mäkinen 1991, Vallius 1991, Räsänen et al. 1992, Salminen 1995, Kontas et al. 1995). Thus, the assay data contain, at least to some extent, a bias (here called “minerogenic effect”), which should be removed, obtaining residual abundance values for elements under study, before the assay data is used in more advanced geological and exploration studies.

Different statistical and mathematical methods can be used in modeling the minerogenic effect, either with an individual element or with a matrix of several elements selected to represent the minerogenic effect (e.g. Aarnisalo 1990, Lahtinen 1991). This presentation aims at demonstrating the use of principal component analysis (PCA) in this purpose, using examples from two till sampling surveys.

The process involves several steps. First, the original data has to be checked and all samples including missing values in any of the analyzed elements have to be discarded. Then, a decision on the treatment of concentration values below confidence and/or detection limits has to be made. The third step involves the standardization of the original values and checking of the normality or, at least, the symmetry of the distribution of each element. In case of skewed distribution, a transformation method – e.g. LOG transformation – has to be applied for bringing the data distribution closer to normal or at least to a symmetric shape. In the fourth step, the possible outliers for each element to be used have to be checked and outlier limits defined.

The actual PCA procedure starts with selection of elements considered to represent best the dissolution bias of silicates. Consequently, they are selected for the calculation of the model of “minerogenic effect”, which is carried out using principal component analysis (PCA) of the selected, preprocessed abundance values (outlier limits in use). Here, the principal component explaining most of the total variance of the selected model elements represents the “minerogenic effect”; most commonly this is PC-1. Then, the model formula for “minerogenic effect” is created using its eigenvector loadings. This formula is used in calculating the model values (MINERO) for each sample without outlier restrictions. Next, outlier limits for MINERO and the preprocessed abundance values of each element are defined separately and PCA on MINERO vs. each element is run using these outlier limits. The PC-2s of these PCAs represent the residuals of each element’s abundance values from the common model. Finally, the residual values for each element in each sample are calculated using element abundance values and MINERO values, both weighted with respective PC-2 eigenvector loadings. Success of the removal of the “minerogenic effect” from each processed concentration value can be perceived by calculating the correlations of the obtained residual values of the elements and comparing scatterplots of MINERO vs. original values and MINERO vs. corresponding residual values.

Some examples of the residual results from two study areas are shown together with comparisons to the original results:

- 1) GTK regional till survey data from western Finland
- 2) Local, systematic deep sampling till survey data from Liittoperä

A third example data set involves old till sampling data from surroundings of the Hallaperä Zn-Cu occurrence. Only four base metal elements have been analyzed there, so that model for the minerogenic effect could not be calculated. However, PCA can be used to enhance the weak anomalies by processing first a model for the common base metal matrix and then using it when calculating how abundance values of each metal differ from it for each sample.

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Applying pXRF analyzer to the geochemical baseline studies

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The Geological Survey of Finland (GTK) has carried out several geochemical soil baseline mapping projects in the natural areas as well as in the urban areas in Finland (e.g. Tarvainen et al. 2006, Hatakka et al. 2010 and Tarvainen et al. 2013). Applicability of Innov-X Systems' Olympus Delta 6000 Premium portable XRF analyzer (pXRF) to the geochemical baseline mapping and environmental studies has also been tested. In this presentation, we have compared different soil and rock powder sample treatment methods affecting the pXRF measuring results in contrast to the results of laboratory *aqua regia* analysis and/or laboratory XRF analysis of the same samples. Also the pXRF measuring modes, Soil or Mining+, have been studied.

We measured and analyzed soil samples taken from natural and urban soils as well as rock powder and rock aggregate samples of bedrock related to several geochemical baseline mapping projects in Finland and in the ASROCKS project (http://projects.gtk.fi/ASROCKS_ENG/index.html). The pXRF measurements were performed from fresh, untreated samples, and/or from dried and sieved (< 2 mm) or pulverized samples with the Soil and/or Mining+ modes of pXRF. Duplicate measurements and duplicate samples were also tested. The total number of samples in this study is 1134 and the total number of measurements is about 1600. Each sample was measured three times with pXRF and the calculated mean concentration of those three single measurements was used. The concentrations below the detection limit were divided by two for the statistical and graphical analysis. In this presentation, we introduce the results of those trace elements prescribed in the Appendix 1 of the soil contamination-related Government Decree (214/2007).

The repeatability of the pXRF measurements was good for most metals. For example, the variation of the Zn concentrations was small in the original measurement versus the duplicate measurement, as well as in the original sample versus the duplicate sample (Fig. 1). For Cr, the repeatability was also good, although, the Cr concentrations measured with the Mining+ mode differed in most cases of those analyzed with the other methods (Fig. 1). The concentrations for As in the soil samples were on an average lower in the pXRF results than the As concentrations analyzed in the laboratory (Fig. 2).

Chromium, Cu, Pb, V and Zn concentrations were usually above the analyzer's detection limits with both modes. According to this study, the pXRF is feasible to determine the geochemical baseline for Co, Cr, Cu, Pb, V and Zn. Nickel baseline concentrations were measurable with the Mining+ mode. On the other hand, the Mining+ mode of pXRF did not provide any detectable values for Co, but with the Soil mode the baseline concentration can be detected. In this study, the detection limit of pXRF for As varied 1.1–4.4 mg/kg in the Soil mode and 26–58 mg/kg in the Mining+ mode. Thus, pXRF is usable for geochemical baseline studies only for areas where the natural As concentrations are elevated in the soil and bedrock, like in the Pirkanmaa area. For determining Sb, Hg and Cd baseline concentrations the pXRF is not feasible.

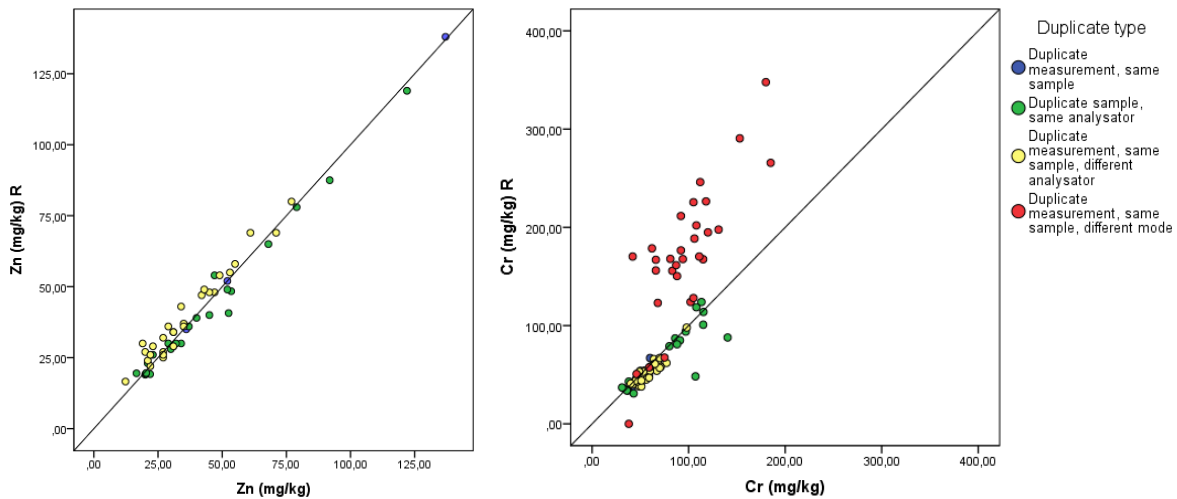


Fig. 1. The repeatability of the portable XRF analyzer measurements of Zn and Cr for different duplicate sample and measurement types and different measurement modes (Soil, Mining +) in soil and rock aggregate samples.

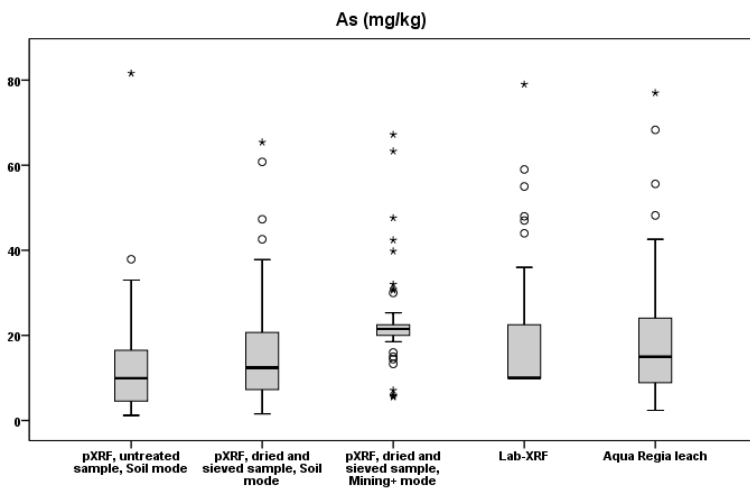


Fig. 2. Arsenic concentrations in the soil samples of the Pirkanmaa region classified by different pretreatment and analysis methods. pXRF= portable XRF analyzer.

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Biogeochemical exploration for limestone

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The main purpose of this development project was to improve and test prospecting method for limestone by studying the biogeochemical response of vegetation to a carbonate mineralization below. The study was done using Norway spruce (*Picea abies*) samples in known dolomite deposit area verified by diamond drillings. The use of Norway spruce in mineral exploration in the Finnish conditions was reported earlier by Närhi et al. (2013, 2014) and the study was conducted in co-operation with the Geological Survey of Finland. Biogeochemical exploration is based on chemical analysis of organic matter where chemical signature (anomalous concentrations of certain elements) corresponds to mineralization of the bedrock below. For example, in trees, metals exceeding the metabolic needs are transported to bark, leaves and twigs.

The sampling was planned to go linearly 800 m across the known deposit area; Spruce samples were collected every 20 m. Total of 40 samples (excluding 5 duplicates and 4 reference samples) were taken consisting of small spruce twigs and branches. Afterwards the samples were dried and twigs and needles separated. All samples were ashed, dissolved by aqua regia digestion and analyzed in AcmeLabs laboratory in Vancouver, Canada. Element concentrations of both sample types were tested separately by using ICP-MS analytics. The results were evaluated visually by interpreting concentration profiles and using self-organizing (SOM) maps by T. Kohonen (2001). The geological map of the deposit was used as background information. The anomalies from the twig samples were especially clear and the concentrations were high compared to the needle samples; for example, Ca and Sr concentrations were elevated comparing to background values of the surrounding bedrock in the southern part of the study area (Fig. 1). Furthermore, elements like Ba and Mg were interpreted as possible positive indicators of carbonate mineralization. Ni, Fe, Al, Ti and La were interpreted as negative indicators because of their especially low concentrations over the carbonate deposit. The results of the study showed also indications for a possible deposit extension to the north of the known deposit.

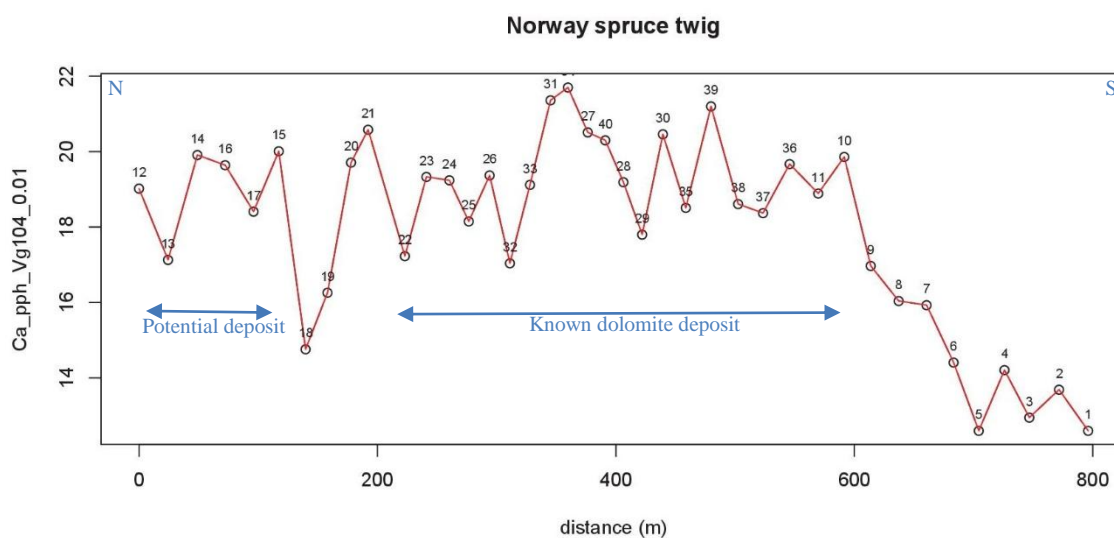


Fig. 1. Variation of Ca -concentration in the sampling points.

The biogeochemical exploration method is extensively used in Canada, Russia, and Australia mainly for prospecting precious metals. According to this project, the results show promising opportunities for applying the method also in carbonate rocks but so far the results are still only indicative. In future, sampling should be planned so that sampling line or sample point grid is reaching the background areas in both side of the mineralization or mineralized structure in the bedrock. Interpretations should be improved by comparing and combining the results to other methods such as litho- and soil geochemistry.

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Preliminary risk assessment of soil parent material with elevated element concentrations

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In Finland, new guidelines on the exploitation of excavated land (Ministry of the Environment 2015) designate the classification of excavated land as a waste or exploitative material. In principle, aggregates with elevated background concentrations, i.e. where the concentration is higher than the threshold value given in the Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007) are not considered contaminated if there is a plan for future use of the material. This material can be exploited or placed in the areas with similar or higher regional geochemical baseline concentrations.

The re-use and utilization of excavated land with elevated concentrations may pose concern on their potential environmental impacts and especially potential migration of the harmful substances to groundwater. Thus, at the Geological Survey of Finland (GTK), preliminary studies have been conducted in order to answer questions: How can we separate the site-specific metal contamination from the elevated geochemical baseline concentrations? Is the mobility of potential harmful elements same in the areas with naturally high concentrations than in the areas with a heavy anthropogenic input?

The chemical characterization of metal contaminated soil was assessed in a study area in Finland (Jarva et al. 2009). Different leaching methods were used to characterize the potential mobility of trace elements and to determine the origin of the elements. The median concentrations of selected elements within the study area were first compared with those from various geochemical baseline studies. Based on this comparison, the studied elements were divided into two groups: elements displaying general enrichment in the study area and those with median concentrations within the range of baseline levels. Study area represented an area with less than 1 m anthropogenic soil covering undisturbed glaciofluvial sediments. The potential leachability of the selected elements in contaminated, mainly man-made soil was examined. Some elements had elevated leachability to ammonium acetate and even to de-ionised water and were considered more mobile. They could therefore pose a risk to the environment and groundwater. Finally, hierarchical cluster analysis was used to observe suggestive grouping of selected elements according to their potential mobility and hypothetical origin, i.e. anthropogenic, natural or mixed soils. Similar grouping of elements was found in factor analysis. Cluster analysis as well as factor analysis was found to be feasible for the chemical characterization of contaminated, mainly man-made soil and elevated baselines, provided that a sufficient number of samples with appropriate analysis are available (Fig. 1).

Series of leaching methods were used to recognize the easily mobile elements, often related to anthropogenic sources and the less mobile elements of geogenic origin. However, more precise parameter for mobility is needed for site specific risk analysis. Soil solid -solution partition coefficients (K_d values) can provide a numeric estimate of the mobility of potentially harmful elements. GTK has determined local K_d values for areas with naturally high metal or arsenic concentrations and for areas with a heavy anthropogenic input of metals or arsenic (Tarvainen & Jarva 2009, Tarvainen et al. 2011). The studies showed that elements of anthropogenic origin were often more weakly sorbed than elements of natural origin. However, local studies are essential while K_d value greatly depends on soil characteristics, such as pH, organic matter, fine-fraction content and abundance of oxyhydroxides of iron, aluminium and manganese.

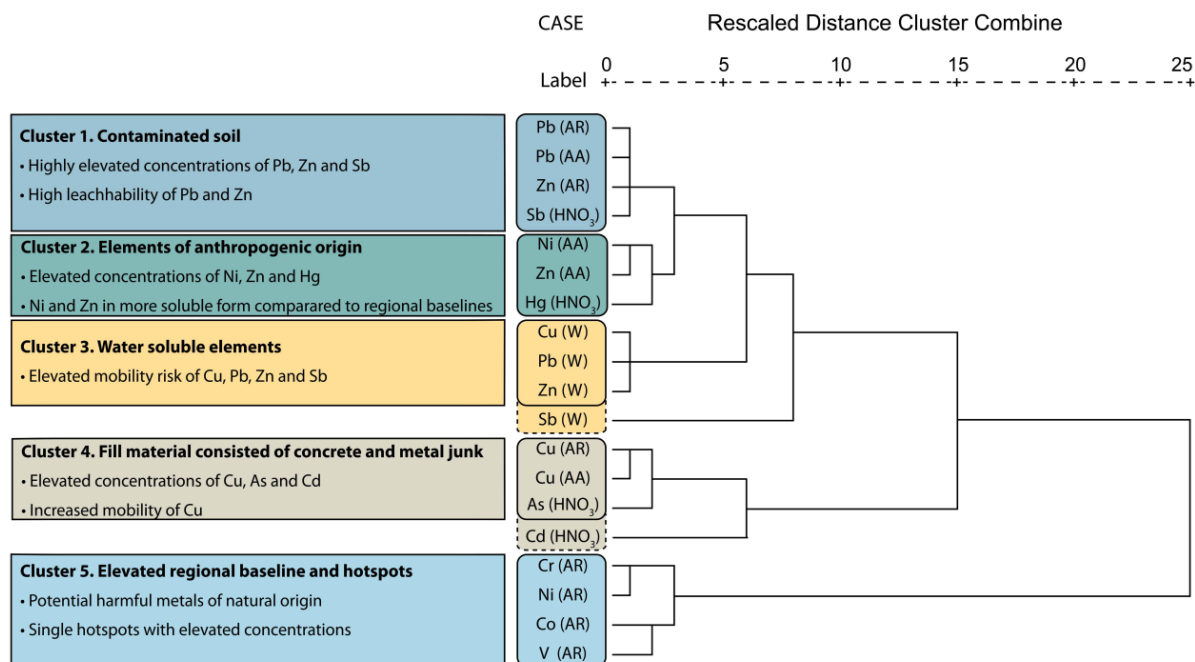


Fig. 1. Hierarchical clustering results (dendrogram) of the element concentrations in a study area with less than 1 m anthropogenic, partly contaminated soil covering undisturbed glaciofluvial sediment. AR = *aqua regia* extraction, HNO₃ = concentrated nitric acid, AA = ammonium acetate extraction, W = distilled, de-ionised water extraction.

Potential harmful elements may have higher leachability if they are anthropogenic of their origin. Combination of strong acid leach and weak leaching methods can be used to group the elements according to their potential mobility and origin. Measurements of K_d values is recommended especially for those elements showing higher leachability with weak leaching methods. K_d values can be used to estimate the present mobility of the elements. However, slow geochemical processes such as oxidation of sulphides can cause increasing leachability. This should be also taken into account in risk assessment.

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The evaluation and management project of the cumulative environmental effects of the mining cluster in Lapland

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The evaluation and management project of the cumulative environmental effects of the mining cluster in Lapland, Lapin Kaiku, is a cooperation research project with Geological Survey of Finland (GTK) and the Finnish Environment Institute (SYKE). The project is planned to take three years and financed by the European Regional Development Fund. Lapin Kaiku entails the systematic analysis of environmental effects surpassing the evaluation target and principle of single projects.

The aim is to study the overall effects of mineral potential areas in Northern Finland (Lapland and Taivalkoski) from the perspective of sustainable development and regional well-being and to add knowledge about the basic condition of the environment in the northern region. The purpose is to develop monitoring methods and systems to a more comprehensive and cost-efficient direction and achieve results which serve society and companies in their decision making and planning, while promoting the responsibility of the mining industry and obtaining of social license. The project aims to evaluate the adequacy, accuracy, good and weak points of the current data collection and monitoring and to pay attention to development targets.

The project has three operational work packages which will be produce regional geological evidence-based predictions of Lapland's ore potential, in order to create a more accurate estimate where the potential mining areas in the future most likely to be centralise. This study can also be used particularly in provincial determination of different forms of land use, as well as background material of environmental risk assessment. The objectives of the work packages 3 and 4 are to investigate geochemical characters of soil and ground water in Lapland area using existing geochemical data. Through regional geochemical variations will be produced a general impression of possible geochemical provinces and special characteristics of the mining and mineral potential areas. The aim is also to chart regional geological properties which effect on typology and classification of the water bodies, and to study cumulative impacts of the mining activity on stream and lake water geochemistry, different organisms (aquatic macrophytes, benthic invertebrates, algae, microbes), and chemical properties and bioavailability of the heavy metals using ultra filtration, transplanted aquatic bryophytes and passive samplers (DGT), and the existing geochemical and biological data.

Mining Waste Management Methods (KaiHaMe)

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Management of mining wastes is one of the primary challenges of sustainable mining due to their large amounts and potential long-term generation of low quality mine drainage. Only a small part of excavated metal ores can usually be utilized and the rest of the material is disposed as a waste, i.e. as waste rocks or tailings. The uncontrolled drainage from sulphide mine tailings and waste rocks may deteriorate downstream water bodies and cause harm to aquatic biota and human health. During the last twenty years, notable research has focused on understanding the reactions leading to the generation of mining influenced waters and how to prevent or mitigate the negative impacts. The primary cause for the low quality mine drainage is the oxidation of sulphide minerals in the wastes when they are exposed to atmospheric oxygen and water. The strategies to control this reaction include removal of one of the agents that promote oxidation that is water, oxygen, ferric iron, bacteria or the sulphides themselves (e.g. Lottermoser 2010). However, despite the research efforts, the management of mining wastes faces challenges even today and the amounts of wastes are expected to further increase with the exploitation of lower grade ores in the future. Therefore, new research and technologies are needed to secure the long-term management of extractive wastes.

The project “Mining waste management methods” aims at decreasing the negative impacts of mining waste disposal and promoting sustainable mining by enhancing material ecoefficiency already from the beginning of the mining operations. Ultimate goal of the project is to increase raw material value of excavated ores and to decrease the amount of disposed hazardous wastes. To reach these objectives utilization and raw material potential of waste materials are evaluated through mineralogical and geochemical characterization, and waste processing and optimization are used to increase usage level of wastes. During the project, beneficiation tests to decrease As and sulphide content of tailings materials are carried out, and applicability of the generated tailings as a waste cover material will be assessed using filled in lysimeter tests. An operational model for the optimal use of waste will be developed to enhance material ecoefficiency. The developed procedure will combine raw material aspects and environmental properties of waste materials.

The project also seeks new options for the characterization and use of waste rocks. Waste rocks are typically used at mine sites in earth construction, such as in roads or in dams or basal structures of tailings facilities. However, only small part of waste rocks fulfil the environmental criteria set for the use at mine site construction, namely those rocks that are classified as inert or with low sulphide content, whereas elevated contents of environmentally harmful elements and sulphide minerals limit their usage. To increase the usage level of these types of rocks and to validate common characterization methods, field lysimeter tests are used to test weathering behaviour of waste rocks and applicability of the rocks in structures where oxygen ingress is limited (Fig. 1).

As a result of the KaiHaMe project, sustainability and viability of mining activities will increase through enhanced use of materials and a decrease in the environmental footprint of operations. The results will benefit mining industry, environmental consultancies, technology providers, environmental and permitting authorities, societal decision making,

research organizations and people living within the sphere of influence of mines. The project is funded by European Regional Development Fund, Geological Survey of Finland (GTK), FQM Kevitsa Mining Oy, Kemira Oyj and Endomines Oy.



Fig. 1. Filled in lysimeters to study leaching behaviour of waste rocks in varying conditions. Photo © Teemu Karlsson, GTK.

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Mineral resource potential of tailings from closed sulphide mine sites in Finland

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With the ever accelerating technological and economic growth in the world, there is a continuously increasing need for raw materials. Due to the long mining history in Europe, majority of easily accessible high grade ore deposits have already been mined out or are currently being exploited. New ore deposits are likely to be of lower grade or locate deeper in the ground, which complicates their mining and increases the costs. Therefore there is an increasing demand to locate new raw material resources. As a result, interest on the recovering of, for example, metals from their secondary sources, such as scrap metal, electronic scrap and mining wastes has grown. During the last century, more than 50 metal mines have operated in Finland leaving behind variable amounts of waste rocks and/or mine tailings (Puustinen 2003). The efficiency of ore processing has varied throughout the decades and the focus of exploitation has mainly been the base metals. Therefore, the old tailings in Finland may be a potential mineral resource not only for the base metals that maybe left in the waste but also for the metals which have been recognized critical only during the last decades, such as rare earth elements (REEs) and platinum group elements (PGEs). The aim of this study is to make a preliminary assessment of the mineral resource potential of Finnish sulphide mine tailings with a special focus on the previously unexploited metals in the deposits.

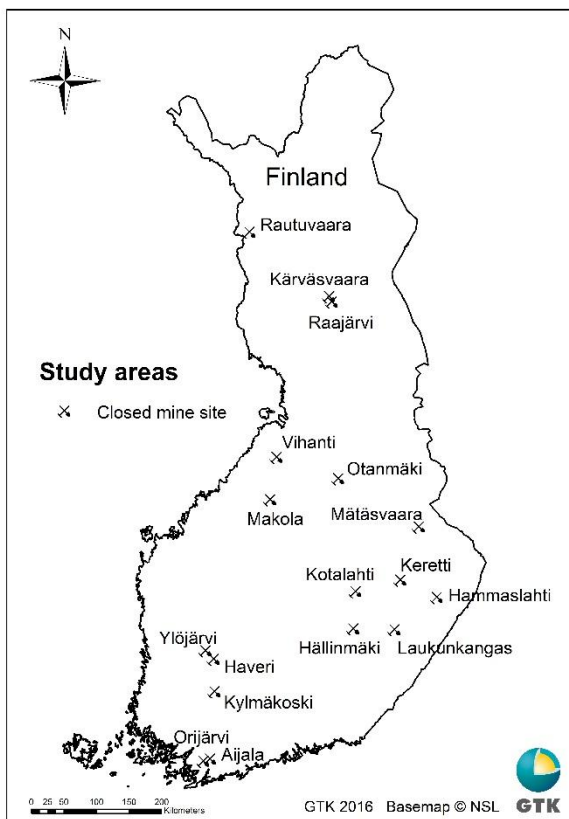


Fig. 1. Locations of the studied mine sites. (Contains data from the National Land Survey of Finland)

The assessment was made from 18 closed sulphide mine sites in which ores had been processed by flotation in the 20th century (Fig. 1). The ore deposits of the studied sites represented genetically 9 different ore types: volcanogenic massive sulphide deposits, sedimentary exhalative type, magmatic nickel deposits, polygenetic type, mafic intrusion-hosted Ti-Fe-V, porphyry copper deposits, carbonatite associated deposit, skarn and iron oxide ore types (Eilu et al. 2012). The tailings at these sites may, however, originate from several ore deposits mined close to the processing plant. The amounts of tailings vary from 0.3 Mt up to 13.7 Mt (Räsänen et al. 2015). Tailings samples were collected from shovel dug sampling pits on top of the tailings piles. The pits were dug as deep as possible to reach the unweathered tailings. The samples were freeze-dried and pulverized in a carbon steel bowl before analyses. Total concentrations of base metals and REEs were measured using HF-HClO₄ digestion and ICP-OES/MS, and those for Au and PGEs with NiS fire assay and ICP-MS (Juvonen et al. 1994).

Based on the data, the studied sulphide mine tailings contain mainly variable amounts of base metals with only minor indications of Au, REEs and PGEs. For example, the Vihanti and Aijala tailings contain notable amounts of Zn (1.3% and 0.6%, respectively) and Pb (0.6% and 0.3%, respectively), and Orijärvi Zn (0.4%), Cu (0.3%), and Pb (0.17%). Makola tailings contained 0.3% Ni and 0.1 % Cu. Korsnäs tailings were the only one with elevated concentrations of REEs (sum of REEs 0.5%), whereas the Käräväsaara tailings contained minor Pt (0.1 ppm). Significant amounts of Au were measured in the tailings of Aijala (0.7 ppm), Haveri (0.7 ppm) and Vihanti (1.0 ppm).

The results show that the Finnish sulphide mine tailings have potential for secondary sources for metals. Based on the study, further research should be focused particularly on the Vihanti, Orijärvi, Aijala, Makola and Korsnäs tailings to assess their metal potential in more detail and to evaluate if the valuable metals are feasible to recover from the tailings.

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Geochemical comparison between the medieval building dimension stones and potential quarry outcrops with pXRF

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There are several medieval (mainly 14–15th century) city building remains in the Aboa Vetus museum (Turku, Finland) consisting mainly of plaster-walled masonry, quarried dimension stones, and natural loose stones and bricks (Sartes 2003, Uotila 2003). An aim of this research is to find out the origin of the quarried dimension stones. Even in a broad sense, previous research on the subject does not exist in Finland.

Research methods are:

- Comparison between obviously quarried and sculpted (boreholes, chisel marks, cut surfaces) dimension stones, bedrock outcrops and quarries.
- Geochemical comparison between the medieval building dimension stones and potential quarry outcrops by using handheld, i.e. portable XRF analyser (pXRF).

Close mesoscale photography, examination, identifying and naming of the building stones in the museum and bedrock outcrops in the field is important base for the research. Sampling in the museum is understandably prohibited. Research process will be managed as a GIS project. Investigation of old quarries will be carried out using literature, old maps and GIS analysing. Geochemical rock analyses of all chosen stones will be made with a pXRF device. Plotting of geochemical data will be done with GCDKit (Janousek et al. 2006) for visual and statistical correspondence analysis.

This cross-disciplinary graduate research is performed at Department of Archaeology, University of Turku, under the supervision of Docent Liisa Seppänen and Professor Jussi-Pekka Taavitsainen. Preliminary research was carried out in May 2015. However, it was later found out that calibration of the pXRF was ruined just before the 2015 field work. A new sequence of analyses will be accomplished in May–June 2016. So this work is unfinished and the currently provided information and the results are preliminary only.

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Hydrogeochemical characterization of the Sakatti mine prospecting area, Sodankylä, Finnish Lapland

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The study area is located approximately 15 kilometers north-east of the municipality of Sodankylä in the Finnish Lapland, and consists of the both sides of river Kitinen and the western parts of Viiankiaapa mire. The western parts of the mire are included in the Natura 2000 reserve. Under the nature protection area, a rich Cu-Ni-PGE ore deposit is located. In order to understand the potential environmental impacts of the ore prospecting and possible future mining activities, the complicated groundwater conditions at the site must be well understood.

Variance in the chemical composition of water can be utilized in depicting and classifying the different water types present at the research area. For this purpose, 53 stable isotope (δD and $\delta^{18}O$) 38 dissolved silica, 39 main ion and 39 trace element samples were collected from the site during a field campaign (5.8.2015–19.8.2015) and analyzed at the Department of Geosciences and Geography, University of Helsinki in October 2015. Water isotope samples were analyzed at the Department of Water Resources and Environmental Engineering, University of Oulu. Statistical methods including hierarchical cluster analysis and principal component analysis are used to further understand the variance among the hydrogeochemical variables.

Groundwater from the study site mostly represent the natural Finnish groundwater composition (water type Ca-HCO₃), but on three locations Na-HCO₃ type waters were detected (Fig. 1). The source for the large amounts of sodium and potassium in these locations is yet unknown, but the mafic volcanic rocks present at the area might provide a lithological source. In many cases groundwater samples show signs of evaporation (Fig. 2), which indicates re-infiltration of surface waters into the groundwater system. The median value for $\delta^{18}O$ in groundwater samples is -12.87, which can be considered high since the natural background value for $\delta^{18}O$ should be closer to -15 on the area (Kortelainen & Karhu 2004). Groundwater and surface water interactions seem to be common in the area, since many samples contain clear chemical characteristics of both groundwater and surface water. Out of the hydrogeochemical variables sodium, potassium, $\delta^{18}O$, δD and DSi can be used to identify the groundwater at the area. For river Kitinen higher Al, Li and Cu contents are common and can be used to distinguish the river water from the groundwater.

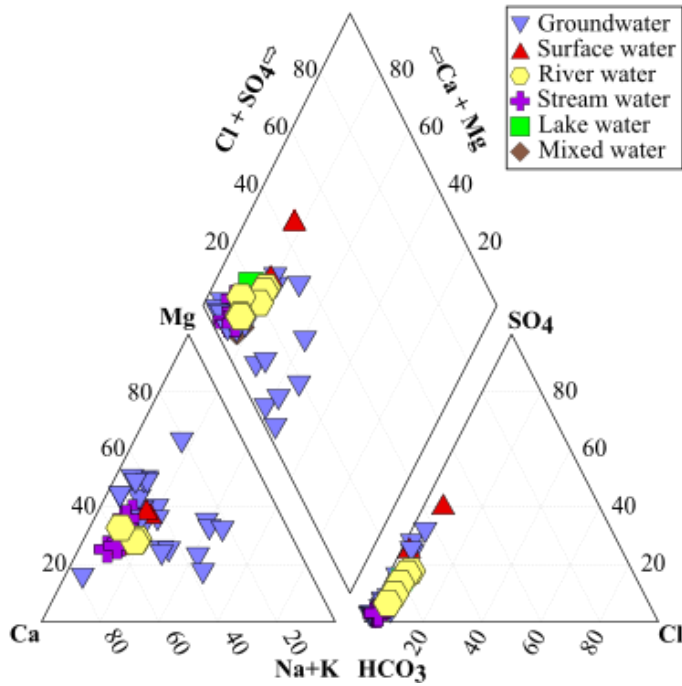


Fig. 1. A piper diagram containing the water samples taken in August 2015.

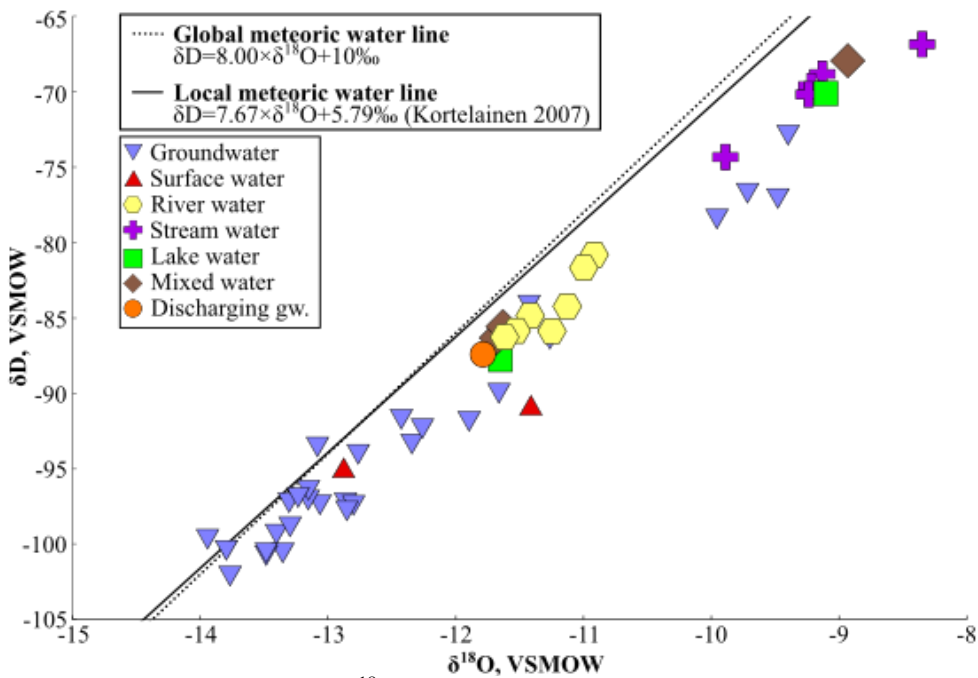


Fig. 2. Plot of δD against $\delta^{18}O$. Clear signs of evaporation can be seen in some groundwater samples, as well.

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Recycling mine waste through mineral carbonation

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Mining produces a lot of rock material that is not profitable ore but unavoidable waste material (Fig. 1). The barren rock needs to be mined in order to get to the rich ore and therefore mines are often surrounded by large waste rock piles that modify the terrain (Fig. 1). These piles can be used to fill open pits as the mine is closed and the area landscaped, but often the piles are landscaped as they are. Mining of these rocks costs the mine so their interest would be the exploitation of these rocks as much as possible. One option of using them could be as raw material for mineral carbonation purposes, depending on the rocks chemical composition. Rocks that do not release harmful compounds, such as sulfides, due to the treating during carbonation process, may be exploited in this manner. From mine waste rocks it is possible to extract Mg, Fe and Ca, and bind them into another problematic waste - anthropogenic CO₂ (Nduagu et al. 2012a, 2012b, Romão 2015). The product that follows is a carbonate rock that a mine can sell as a building material for the construction industry. Common building blocks are most often produced with methods that produce CO₂ instead of consuming it (Gunning et. al 2009). Therefore the mine waste rock combined with CO₂-emissions provides the industry a profitable and environmental alternative. Depending on the Mg/Fe/Ca-content of a rock, waste would be cut back significantly as theoretically up to 60 % of the waste rock could be carbonated (Sjöblom & Eklund 2014, Nduagu et al. 2012b).



Fig. 1. The unavoidable mine waste includes waste rocks and mine tailings. Unless they are reused or recycled, they are stored as rock piles on the outskirts of the pit (left, marked with red) and as tailing basins (right). Photos: Hitura by S. Lavikko

The waste rocks are not the only mine waste that requires caretaking, also the mine tailings left after ore enrichment processes may become a possible source for mineral carbonation. Some tailings contain highly reactive compounds such as chemical residue from enrichment process and explosive residue from blasting, and thus, cannot be used for carbonation as they are (Sjöblom & Eklund 2014). Depending on the original rock, tailings may also produce reactive compounds due to the changes in their chemical composition

during ore extraction. However, treating tailings correctly may enable even their exploitation. The tailings are usually stored in monitored basins, which requires longtime input from the mining company as the required monitoring time in general is around 30 years after the mine has been closed. Cutting back the amount of tailings also cuts back these monitoring costs.

Exploitation of ultramafic mine waste materials can be done with “The ÅA Route”-method, developed at Åbo Akademi University. The method works through production of $Mg(OH)_2$ from waste rock material and its subsequent reaction with CO_2 in an exothermic reaction that produces a magnesium carbonate, magnesite ($MgCO_3$) (Sjöblom & Eklund 2014). The end product is an enduring, stable and natural carbonate rock.

All waste rocks do not function as required and the research considering the properties of different rocks and minerals has been under close studying. The results suggest that a suitable waste material would consist of an ultramafic rock containing phyllosilicates that contains at least 17 % MgO and more than 12.5 % crystalline H_2O (Sjöblom & Eklund 2014). The crystal structure and the location of Mg in the lattice also play an important role in the successfulness of the extraction process (Lavikko & Eklund 2016b). The composition of the parental rock also has an influence on the ability to extract Mg, Ca or Fe for carbonation (Lavikko & Eklund 2016a). Based on the results, it can be stated that in Finland there are several mines (e.g. Hitura, Horsmanaho, Kylylahti) that have waste materials suitable for mineral carbonation.

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Geogenic and anthropogenic effects on stream water in Kittilä, Finnish Lapland

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Stream water quality is a matter of great concern today. Nutrients and other elements can cause eutrophication or toxic contamination of watersheds, hence leading to depletion of dissolved oxygen, increase in phytoplankton, and changes in species compositions (Närhi et al. 2012). Especially metals constitute a threat to ecosystems because they can be toxic even at low concentrations and can bioaccumulate.

Potential anthropogenic and geogenic impacts on stream water were studied in Kittilä municipality (8000 km², population 6000), the area known of currently active gold exploration in Finnish Lapland (Fig. 1). The active Kittilä Gold Mine, the largest in Europe, is composed of arsenopyrite-gold deposits. Also tailings of former Saattopora Gold Mine (1988-1995) are a potential source of water contamination. The infrastructure, including Levi ski resort, Kittilä airport, Kittilä town, as well as forestry (mechanical site preparation and drainage; Sutinen et al. 2006) may have impact on water quality, whereas the role of agriculture is minor. River water was analyzed for As, Ca, S, and SO₄ at 45 sites using ICP-AES, ICP-MS, and ion chromatography. In addition, electrical conductivity (EC) was point-wise measured at 54 sites and with continuous logging along Ounasjoki river (30 km distance with 3500 measurements) using CS547 conductivity probe with Cambell logger. We focused on these elements since As is known to be a strong pathfinder for gold and Ca, S and SO₄ correlate strongly with EC.

Tailings of the former Saattopora mine were the source of S (up to 4.6 mg l⁻¹) and SO₄ (13.8 mg l⁻¹), whereas in other areas the concentrations were 0.75-2.5 mg l⁻¹ and 2.2-7.3 mg l⁻¹, respectively. The Iso-Kuotko arsenopyrite-gold deposit produced natural downstream As concentration of 18.7 µg l⁻¹ (Närhi et al. 2013). Other gold deposits/mines formed As up to 4.8 µg l⁻¹, whereas in uncontaminated areas As concentrations varied from 0.06 to 2 µg l⁻¹. The EC and Ca downstream from the gold deposits/mines were up to 12.4 mS m⁻¹ and 19.7 mg l⁻¹, whereas the rest of the measured values were 3.2-10.4 mS m⁻¹ and 4.1-15 mg l⁻¹, respectively. Continuous EC measurements in Ounasjoki River showed values up to 7.5 mS m⁻¹ in Kittilä town and associated with major forest drainage areas, whereas upstream values varied between 4.9 and 5.3 mS m⁻¹. With regard to high concentrations of As in springs, up to 36.2 µg l⁻¹ (Tanskanen et al. 2004) and up to 50.1 µg l⁻¹ (Närhi et al. 2013), the present results on stream water As are spatially coincidental in Kittilä, hence suggesting significant geogenic input (Fig. 1a). The mobile surveillance (in 2009) revealed a significant anthropogenic impact of forest management (ploughings) on water quality (EC in Fig. 1b).

In conclusion, gold deposits and especially the tailings of the former Saattopora mine substantially increased watershed S, SO₄, As, Ca, and EC, whereas forestry resulted increase in the stream water EC. Tailings can release substantial amounts of metals and nutrients for a long period of time, and the present results emphasize the importance of efficient stabilization of tailings to protect aquatic ecosystems. These results emphasize the need of monitoring the watershed scale river water quality. Resampling is scheduled in August 2016 to see if effects of the former Saattopora mine are still visible. Ala-Kuusanjoki River will be studied for forestry impacts and also the effects of the Suasselkä

postglacial fault on Nuutijoki river water quality will be examined within the postglacial faults project by the Geological Survey of Finland in 2016.

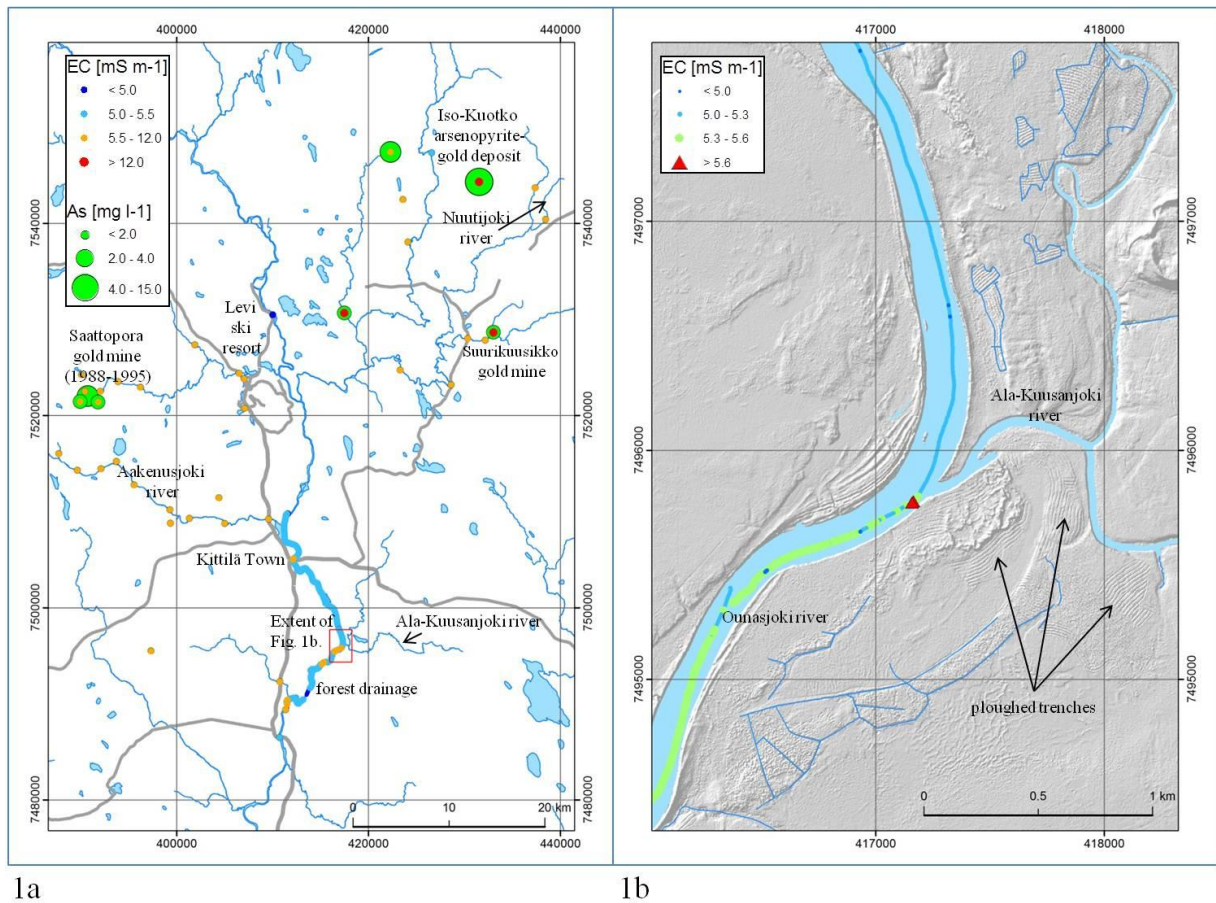


Fig. 1a. Stream water chemistry (As) in 2009. Fig. 1b. Stream water conductivity in Ounasjoki river in 2009 and ploughed trenches on LiDAR image. Basemaps: © National Land Survey of Finland. Coordinate system: ETRS-TM35FIN.

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Learned lessons in biogeochemistry by targeting known mineralizations in the UltraLIM orientation survey in northern Finland

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Biogeochemical exploration involves sampling of living plants (i.e. phytogeochemistry), decomposed soil organic horizons or peat. In phytogeochemical exploration the selected plant species and organs are first collected, foliage samples are prepared by drying and sorting into needles/leaves and twigs/stems, optionally ashed, leached, and finally, the element concentrations are analytically quantified. In 2013 and 2014 an orientation survey was conducted by gathering samples of a variety of species along sampling transects over six known mineralizations in northern Finland, i.e. Juomasuo Au-Co deposit in Kuusamo, Vähäjoki Fe-Cu-Au deposit in Tervola, the Kersilö Ni-PGE-Cu deposit in Sodankylä, Hakokodanmaa Au occurrence in Kittilä, Saivel Cu occurrence in Sodankylä and Kyörteselkä P-REE occurrence in Savukoski. The objectives were 1) to create practical guidelines for plant sampling and data analysis applicable to northern Finland, and 2) to gain confidence in the analysis of biogeochemical data in order to use it for prospecting of blind mineralizations in the future.

The Juomasuo Au-Co deposit had the strongest biogeochemical response of all sites. The horizontal extent of the subcropping and deeply buried (>200 m) lodes were clearly defined with increased concentrations of a large number of elements in crowberry (*Empetrum nigrum*), Labrador tea (*Rhododendron tomentosum*) and common juniper (*Juniperus communis*), and the anomalies were also repeatable in two consecutive years. Another Au mineralization, the arsenopyrite hosted Hakokodanmaa occurrence, showed a weaker multielement response to subcropping mineralizations in Norway spruce (*Picea abies*) needles but the deeper mineralizations exhibited a stronger response as correlated concentrations of Au, As, Fe and S in Scots pine (*Pinus sylvestris*) bark. Over the Vähäjoki IOCG deposit, the minor elements in plants (Cu, Fe, S, Zn), characteristic for the Fe-Cu-Au type deposits, exhibited only weak anomalies and the anomaly-background-contrast was low. Instead, Co and trace elements (Ba, Na, Cr) in Norway spruce and Labrador tea were much more effective in delineating the mineralized magnetite lenses. Norway spruce twigs and Scots pine bark showed the location of the Kersilö Ni-PGE-Cu deposit. The Kersilö case demonstrated a spatial relationship between the base of till geochemistry and plant biogeochemistry. Saivel Cu and Kyörteselkä P-REE occurrences gave very weak signatures in the overlying plant chemistry.

The element concentrations in plant tissues, determined with commercial chemical analysis of ICP-MS, suffer from under the lower detection limit (LDL) values and uncertainties related to populations being close to the LDLs. Consequently, quality of biogeochemical data varies: data may be noisy, single peak anomalies may be significant, apical anomalies formed from several sample points are often observed, and negative anomalies may also be significant. Biogeochemical signatures were found not to be as strong as soil weak and selective leach anomalies (see Middleton et al. 2016). Even then, plant chemistry indicated several significant deposits and most importantly also blind mineralizations. However, lithogeochemical contrast is needed for the plant chemistry anomalies. Plant chemistry was observed to be associated to subcropping lithogeochemistry but structural pathways, deeply seated mineralized zones and

pedogeochemistry also have an effect on the plant chemistry. This means that we are interpreting overlaid geochemical imprints of several phenomena in biogeochemical work. Thus interpretation requires confidence and experience. To locate a mineralizations 'blind folded', the interpreter needs to pay attention to association of elements, unconventional pathfinder elements, elements related to alteration and recognition of coincidental spatial patterns.

We conclude that greenfield exploration in northern Finland may be conducted successfully with biogeochemistry but the risk of false negative minor occurrences has to be accepted. In order to increase the acceptance of biogeochemistry in mineral exploration future work should concentrate on answering some fundamental questions: the transport mechanisms of ions from bedrock to root zone, what is the impact of lithogeochemistry vs. root zone soil chemistry on plant chemistry, what is the effect of soil pH and moisture on element uptake, and what causes some element correlations that are often observed (e.g. Fe, Al and REEs).

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Geochemistry of the volcanic rocks from the southeast of the Central Finland Granitoid Complex

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Introduction

The Master Thesis study is part of the Central Finland mineral potential estimation project of Geological Survey of Finland (GTK). The GTK project began in 2012. The approximately 60 by 80 km study area is situated in the south-eastern corner of the Paleoproterozoic Central Finland Granitoid Complex. The whole research area had been poorly investigated, thus the first objective of the project was to improve the basic geological knowledge of the area. In connection to new bedrock mapping, geochemical and isotope data were accumulated.

The research area consists mainly of various plutonic rocks, whereas the supracrustal and subvolcanic rocks form a discontinuous, scattered, NE-oriented belt in the middle of the area. Part of the volcanic belt consists of recrystallized tuffaceous, occasionally pyroclastic rocks, which are crosscut by uraltite and plagioclase porphyrites, whereas other parts consist almost completely of deformed subvolcanic rocks. The aim of the study was to characterize the volcanic rocks in the area and interpret whether they resemble other Svecofennian volcanic rocks in southern Finland.

The material consisted of bedrock observations, whole-rock geochemical analyses, thin sections and aeromagnetic maps. Due to scattered occurrence of the volcanic rocks as well as extensive Quaternary coverage in the study area, a geochemical approach was chosen. Altogether 184 whole-rock analyses were used in the study.

Results

On the basis of field relationships and lithological differences, the volcanic rocks were divided into five different belts (Makkola, Kauppila, Halttula, Leivonmäki, Korospohja) which were compared with each other. Apart from a few exceptions (e.g., altered rocks), all the volcanic rocks have similar geochemical features. All of the belts are characterized by a compositional range from basalts to rhyolites. However, intermediate rocks are the most abundant. The volcanic rocks range from tholeiitic to shoshonitic, but calc-alkaline and high-K calc-alkaline series are the most common in all belts.

All of the volcanic rocks are enriched in LILE and LREE relative to HFSE and characterized by low Ti and Nb contents. Their trace element geochemistry is more strongly correlated with the SiO₂ content than the location of the sample, as the felsic rocks are more enriched in the LILE relative to the HFSE compared to the mafic rocks. The Makkola and Korospohja belts are slightly more felsic and evolved, on average, whereas the Kauppila, Halttula and Leivonmäki belts have more mafic compositions.

Discussion & conclusions

Based on available data, it seems that all the volcanic belts investigated are part of the same system as no significant compositional differences between them exist. The results revealed that both the major and trace element geochemistry of the volcanic rocks indicate

a mature, Andean-type continental arc setting (Fig. 1). Some of the studied volcanic rocks also exhibit adakite-like geochemical features such as high Sr/Y and La/Yb ratios.

A wide compositional range suggests quite complex source areas for the magmas. Almost all of the volcanic rocks are interpreted to have derived mainly from amphibolite melts. It is evident that all the studied rocks have evolved through processes such as fractional crystallization and crustal contamination, and possibly magma mixing. The abundance of evolved, intermediate and felsic volcanic rocks indicates a strong role for the continental crust which has induced assimilation and fractionation of the magmas resulting in the typical geochemical composition of continental arcs.

The geochemical features of the volcanic rocks resemble in many ways the volcanic rocks from the Tampere and Häme belts (Fig. 1).

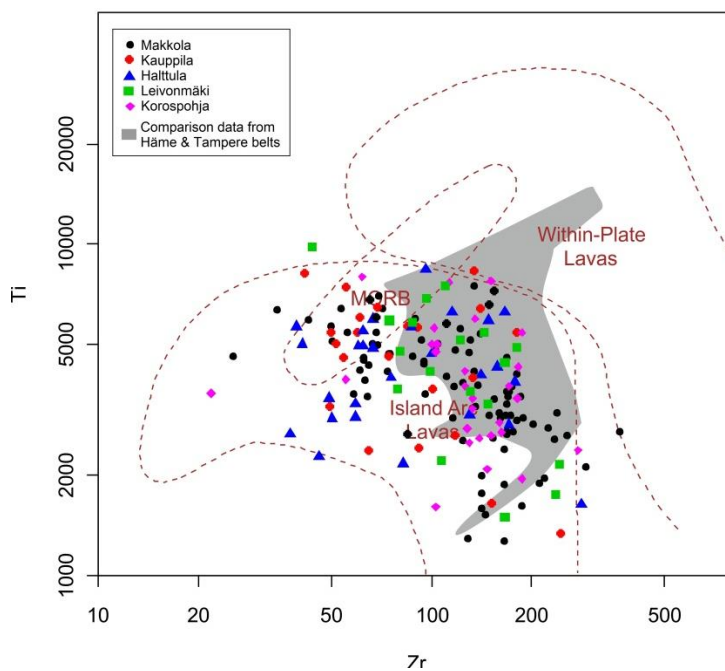


Fig. 1. Zr vs. Ti discriminant diagram (Pearce 1982) of the volcanic rocks from the study area and the comparison data (Kähkönen 1989, Lahtinen 1996, Sipilä & Kujala 2014).

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The effect of bedrock on drainage water quality at forested peatland catchments

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Forest management practices, such as intensive harvesting, site preparation and ditch network maintenance, tend to increase leaching of nutrients and suspended solids to recipient water courses. Much less attention has been paid on the effect of forest management on leaching of heavy metals. However, especially on sites containing high sulphide concentrations in bedrock, overburden or peat, forest management can lead to enhanced leaching of acidity and heavy metals. It has been shown that peat underlain by black schist contained elevated concentrations of sulphur and heavy metals (Mäkilä et al. 2015), while another paper showed that methylmercury concentrations in ditch water were higher at catchments on black schist than at those on felsic bedrock (Ukonmaanaho et al. 2015).

The aim of this study was to monitor the chemical composition of drainage water from forested peatland catchments, focusing on sulphate (SO_4), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni) and zinc (Zn). Ditch water from the outlet ditch of each catchment was sampled biweekly or monthly during snow-free period at peatlands overlying either dark-coloured black schist or felsic bedrock consisting mainly of igneous rock types in eastern Finland. Black schist is enriched in heavy metals, sulphur and graphitic carbon, and therefore it is also susceptible to weathering, whereas felsic rock types in the study region are more resistant and contain only negligible amounts of heavy metals, sulphur and carbon. The concentrations of all elements under study tended to be higher at catchment underlain by black schist compared to those on felsic bedrock during the study period 2008-2013, especially the SO_4 (Fig. 1), Fe and Ni concentrations.

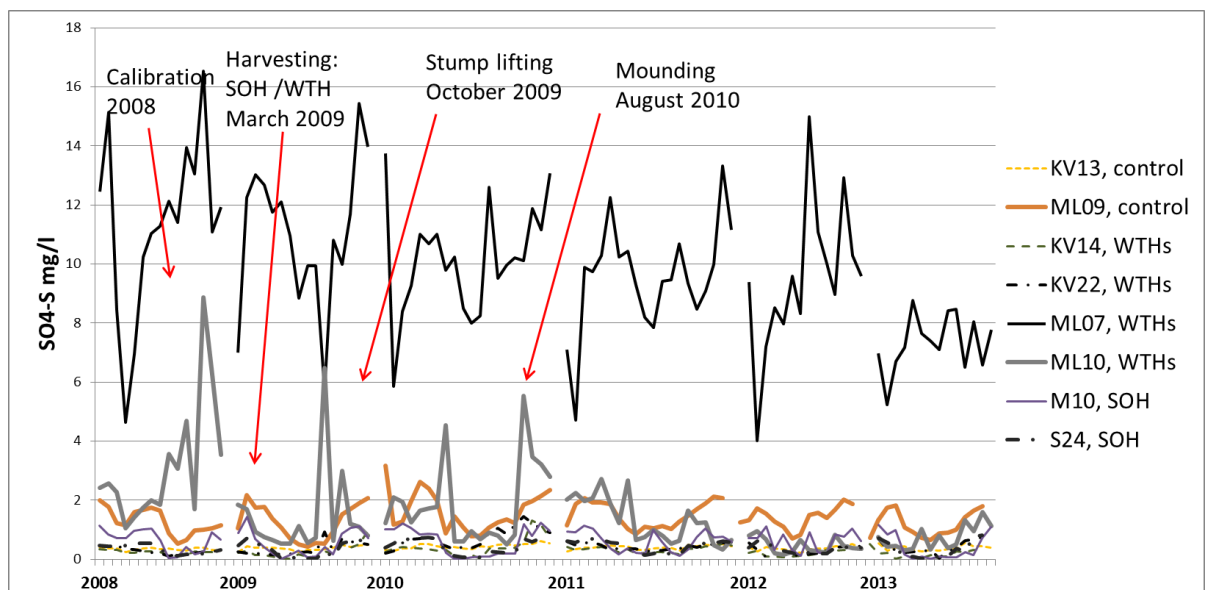


Fig. 1. The SO_4 concentrations in drainage water from forested catchments underlain by black schist (solid line) or felsic bedrock (dashed line).

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Soil geochemical response in glaciated terrain: examples from till- and peat-covered mineralizations in Finland

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In Finland, most of the bedrock is covered with glacial sediments, usually till, and approximately one-third of the soil consists of peat. Only some 3% of the bedrock is outcropping in Finland, and a glacial till is consequently the most frequently used sampling material in geochemical exploration studies. The loose overburden has an average depth of 8.5 m and can be penetrated and sampled to greater depths only by powerful percussion drilling or using excavators. This is costly and causes environmental impacts due to machinery tracks and excavations. Because of the increasing environmental regulations and restrictions set by authorities, it is time consuming and sometimes even impossible to obtain a license for machinery driven geochemical sampling for exploration purposes in the vast natural areas of northern and eastern Finland.

Here, the natural conditions in the tightly packed, consolidated glacial till and a well-humified organic peat material come to the aid of the geochemical explorer. The Finnish glacial till typically contains abundant fine-grained silt material and the clay content is usually 5%, but sometimes even up to 20% (Nenonen 1995). The granulometric composition of Finnish till makes it susceptible to frost heaving and the capillary rise of water in the small till pores and vents. Simultaneously, the capillary forces also push pore water horizontally with even greater pressure. According to capillary measurements and observations, the capillary rise of pore water is in most cases more than 10 m in average glacial tills and fine-grained sediments, and even greater in the clay and fines-rich tills that are typical in western and eastern parts of Finland (cf. Jääskeläinen 2013). Well-humified peat overlying till has a considerable capacity to fix metal ions (Virtanen 1991). This means that pore water and water-soluble chemical elements dissolved in it have a pathway from a mineralization outcropping in the bedrock up to the surface soil layers or peat, even through a thick layer of glacial overburden. By sampling the soil horizons and peat, one can detect anomalies and obtain information on the underlying mineralization, and even pinpoint hidden covered outcrops under sediments. The capillary forces are the largest when the temperature difference between soil and air is the greatest, such as during hot summer days in June to August and the coldest winter periods in December to March.

Peat deposits also most frequently cover till and other sediments in western, eastern and northern parts of the country. Metal concentrations in peat are generally quite low in comparison with the general concentrations in the surface materials of the earth's crust (Virtanen 2005). Peat is formed from plant remains, which contain naturally the low concentrations of metals.

The dissolved metal ions released during the weathering are horizontally transported through the till by acidic groundwater and rise by the capillary forcing (Fig. 1). On the surface of the till, or in other words, in bottom peat, the metal ions easily bind to the humified peat substances under different pH and redox conditions. Organic substances that readily bind metal ions are chemically humus complexes, e.g. humus acids, fulvic acids and humins. Humus complexes form chemical compounds such as chelates and ligands, or they fix metallic compounds with an ion change mechanism and adsorption to the surface of humus particles. In peat, one element usually binds directly to another element, e.g. iron

binds to arsenic (Virtanen 1990) and aluminium binds to titanium (Virtanen & Lerssi 2008).

Metallic ore formations and some rock types, e.g. sulphide-rich black schists (Virtanen & Lerssi 2008) and calcareous rocks (Virtanen 1993) have been recognised to strongly influence the element content of peat. The influence is clearly observed in some high element concentrations compared with normal concentrations, despite the covering Quaternary layer between the peat deposit on the surface and the metal source in bedrock metallic ore and black schist (Fig. 2). The metal anomaly in a peat deposit may form directly above the metal source (Figs 1 & 2) as has been proven in several cases.

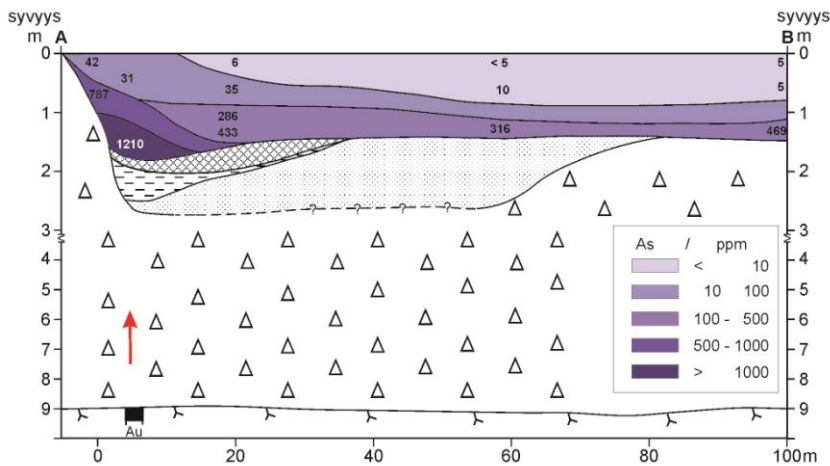


Fig 1. The Pampalo gold deposit in Iломantsi. Many elements, such as As, Cu, Ni and Te, have been transported close to 10 m upwards in the till to the peat layer by capillary forcing. Gold mineralization is indicated in black (Virtanen et al. 1997).

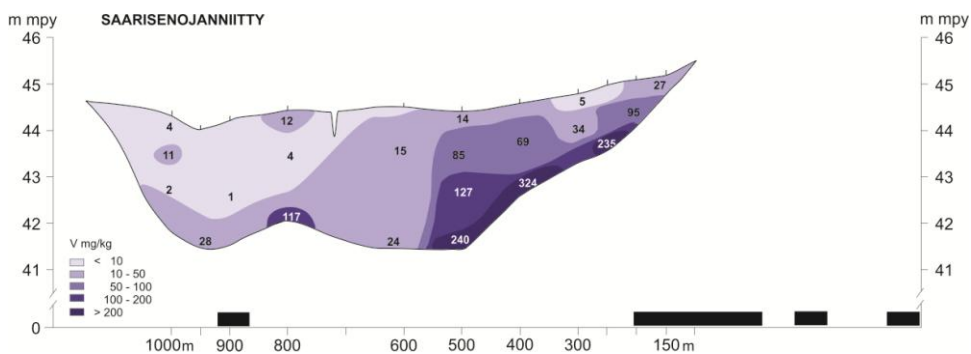


Fig. 2. The vanadium content in peat (Saarisenojanniitty, Kiiminki) forms an anomaly over a black schist metal source. Black schist is indicated in black (Virtanen & Lerssi 2008).

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Fractionation of nickel converter slag – a comparison to sulphide-bearing komatiitic flows

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Crystallization and fractionation of nickel converter slag was tested at the Harjavalta nickel smelter in 1968. A molten slag was poured in a chill mould 60 x 60 x 60 cm in size to test the fractionation of sulphide-bearing iron-rich ultramafic melt. After a few days of cooling and crystallization, a core was drilled through the mould. It indicated that dense immiscible sulphide droplets were settled down in the slag melt to form a sulphide-rich layer at the bottom. The iron silicate-oxide slag was crystallized as ferroan olivine (fayalite) and iron oxides. Minor amount of silicate glass existed between the crystals. A layer just below the chilled top consisted of cm-size fayalite crystals. The rest of the slag mould composed skeletal crystals of fine-grained fayalite and magnetite. Minor amount of sulphides were as very small 0.1 mm droplets throughout the mould. The lowermost 10 cm of the mould contained more abundant spherical sulphide grains ranging from 0.5 to 2 mm in size. The sulphide drops were zoned with Fe-Ni sulphides as outer shell and Cu sulphides as the core. Chalcopyrite, chalcocite, covellite and bornite were the copper sulphides, whereas pyrrhotite and pentlandite were the observed crystalline phases of the Fe-Ni sulphides. The crystallization order of the Fe-Ni-Cu sulphides corresponds to experimentally indicated fractionation, where the heavy Fe-Ni monosulphide (mss) crystallizes and fractionates first leaving a residual melt with Cu-rich intermediate composition (iss). The early crystallized mss locates at the margin of the droplet, and the Cu-rich iss at the core.

Although the slag composition is iron-rich compared with Mg-rich ultramafic komatiitic melt, the distribution of Ni, Cu and minor chalcophile metals in the chill mould corresponds to that of sulphide-bearing komatiitic flows. Accordingly, the large fayalite crystals at the top of the mould correspond to spinifex crystals of komatiitic flows.

Analyses of the sulphide fraction prove that the sulphides at the base of the mould are enriched in Ni compared to Cu and Co, and also Cu is slightly enriched compared to Co. The distribution of the chalcophile elements in the sulphide fraction can be explained as the result of heavy mss fractionation and accumulation at the base, and the residual Cu-rich sulphide melt with iss remained as fine dissemination among the crystallizing fayalite and oxide grains. The distribution of Co is interesting since it does not correlate well with mss (Ni) or iss (Cu), and the iron-rich silicate and oxide phases seem to affect the anomalous distribution of Co.

Development, evaluation and optimization of measures to reduce the impact on the environment from mining activities in northern regions

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MIN-NORTH (Development, Evaluation and Optimization of Measures to Reduce the Impact on the Environment from Mining Activities in Northern Regions) is a cross-border cooperation project between the Geological Survey of Finland (GTK), the University of Oulu (UO), the Arctic University of Norway (UiT) and Luleå University of Technology (LTU, coordinator) to study and reduce the environmental impacts of mining in the northern regions. Three-year project started in January 2016 and is financed by the Interreg Nord program.

Project contains four operational work packages (Fig. 1) and has four main tasks: 1) research of the construction and behavior of cover system to seal hazardous mine wastes 2) develop and test methodology for tracing pollution transport in the mine waste, mine area and in the surrounding by integrating geophysical and geochemical methods 3) study wetlands construction for reduction of nitrogen and metals by using bio-sorbent materials and 4) study of capping technology for marine deposition of tailings.

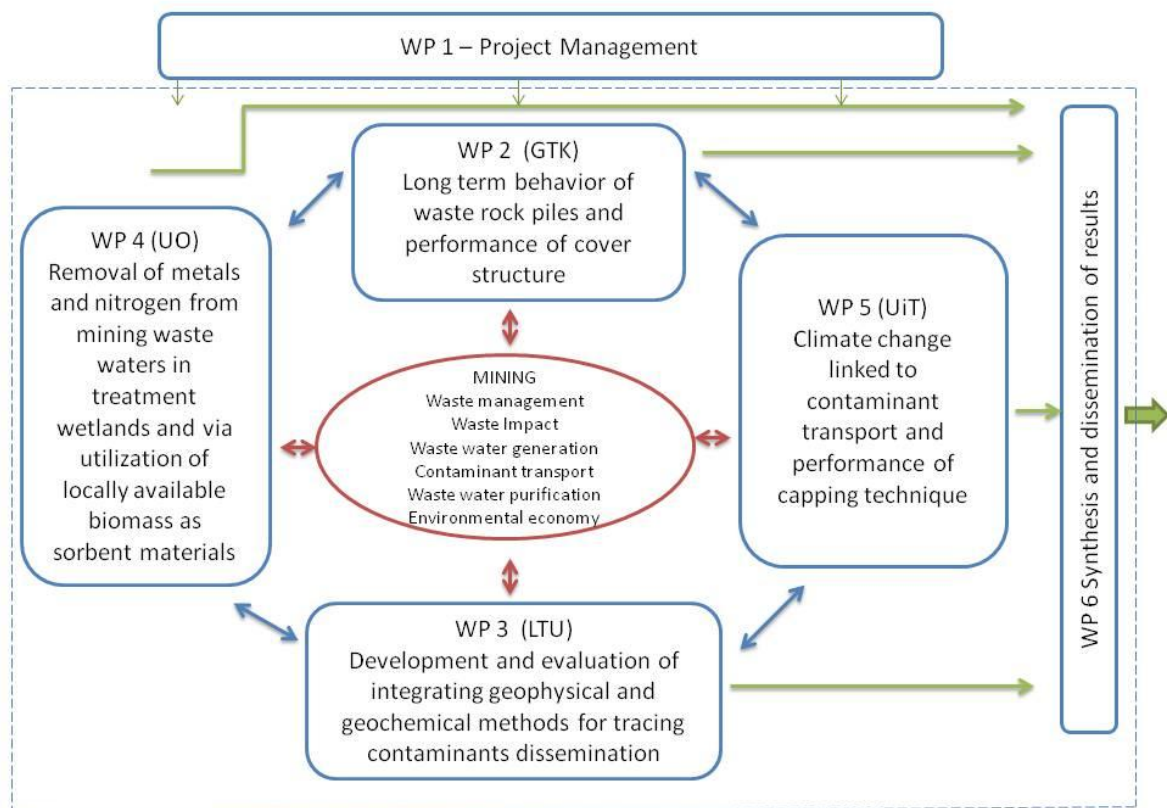


Fig. 1. The structure of the management and work packages in Min-North project

In GTK's work package (WP 2) the long term behaviour of waste rock piles and performance of cover structure will be studied in two mine sites in Finland. Waste rock, which typically contains varying amounts of sulphide minerals, is commonly deposited in large, heterogeneous piles at the mine site. When the sulphide minerals are exposed to water and oxygen, acid rock drainage (ARD) develops as bacterially-mediated oxidation processes release acidity and dissolved elements. These processes may continue for hundreds of years (Nordström and Alpers 1999) and are mainly controlled by the geochemical characteristics of the waste rock, physical properties of the waste rock pile and the climate conditions (e.g. Lefebvre et al. 2001). Previously, waste rocks were left unremediated, but today it is recommended to use various dry cover structures to prevent sulphide oxidation and formation of acid mine drainage in the waste piles. However, data on the long-term performance of dry cover structures in Northern climate is limited.

The main objective of this work package is to study the management of waste rock areas in Lapland. This will be carried out by covering experimental pilot-scale waste rock piles at the active Kevitsa mine, and by monitoring stability and permeability of the structures, and quality of the effluent waters year-round. Various large lysimeters will be installed at the basal structures of the pilot piles, to investigate the amounts and qualities of the effluent waters, and to evaluate the performance of different cover structures. As a comparison, ARD generation and element release from waste rock piles without a cover will also be monitored at Kevitsa and also at a closed mine site, Saattopora.

At the Saattopora and additionally at the Rautuvaara closed mines the investigations will be concentrated on evaluating the suitability and developing geophysical methods to determine the water flow within waste rock pile and the pathways of effluent waters by using also geochemical methods and data. At Kevitsa, geochemical tools such as isotopes (O, H, S and Pb, Mg or Sr) will be used for tracking the performance of cover structure of a waste rock pile and transport of contaminants from the pile.

The chemical and mineralogical properties of the waste rock materials and effluent waters will be analysed by novel methods and wide elemental spectrum, including different forms of nitrogen. The environmental impacts of mine waste are commonly assessed by preliminary laboratory testing programs including different kinds of solubility tests (e.g. Lapakko 2002). However, physical and geochemical properties and heterogeneities in large scale waste rock piles in Nordic climate conditions are complex and may not be adequately represented by laboratory scale experiments. The field scale experiments conducted during this project will therefore be essential to evaluate the accuracy and applicability of commonly used laboratory scale characterisation methods.

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Estimating the internal loading for a water quality model using chemical characterization of sediment phosphorus

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The Archipelago Sea of Finland has long been subject to intensive loading of phosphorus (P) which has led to high P concentrations in the sediments. Part of the Archipelago Sea suffers from seasonal hypoxia and internal loading has been assumed to play an important role in the P budget. Because of the mosaic topography of the sea floor and the complexity of biogeochemical processes that affect P release from the sediment to the water, modelling of the magnitude of the internal P loading in this sea area is challenging. In this study, approximations of potentially mobile pools of sediment P determined by chemical characterization were used to estimate the net release of P from the sediments to the overlying water. A new water quality model was developed for evaluating the impact of nutrient reductions in the catchment to the water quality of the sea area, and the estimated P release was entered as a separate input in the model. By this approach, the total quantity of the annual net release of P from the Archipelago Sea sediments was estimated to amount to 1800–3680 tonnes from the 12 700 km² model area, depending on variability in the oxygen conditions.

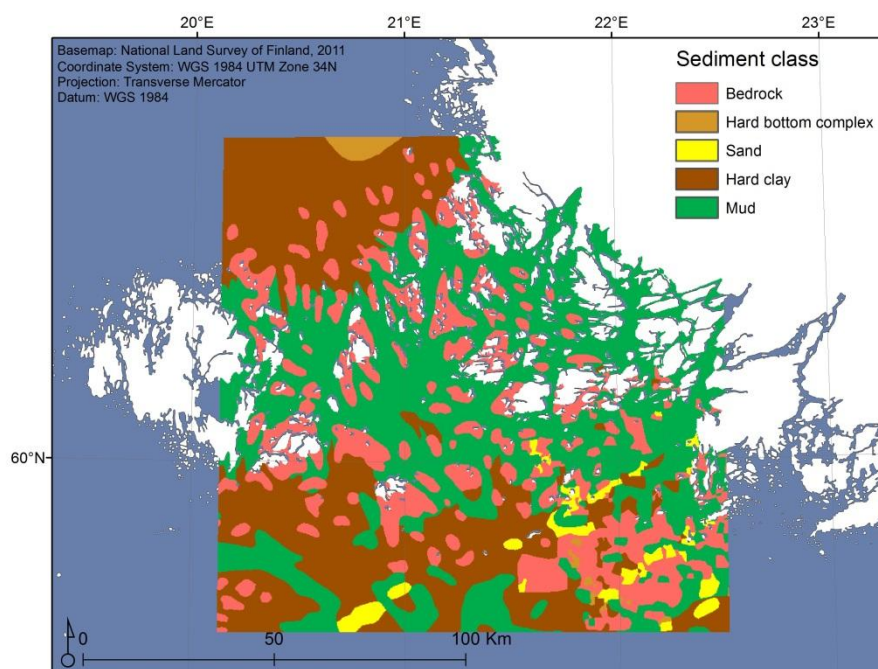


Fig. 1. The seabed sediments in the model area as classified in Al-Hamdani and Reker (2007). The model area covers 12 700 km².

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Laser spectroscopic methods in analysis of REE-bearing minerals

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Rare earth elements (REEs) consist of 17 transition metals, including lanthanoids as well as scandium (Sc) and yttrium (Y). REEs typically exist in oxidation stage +3 and they naturally occur in silicate minerals (~43 %), carbonates (23 %), oxides (14 %) and oxysalts like phosphates (14 %). In minerals, REEs can also substitute other cations with comparable charge and radius. In the modern technology and society, REEs are valued for their special chemical and physical properties. Nowadays, rare earth elements are also acknowledged as critical metals due to their economic importance and high supply risk (Chakhmouradian & Wall 2012).

Analysis of REEs from rock samples is quite challenging. Instrumental techniques ICP-MS, ICP-OES, XRF and NAA are most commonly used for the task. However, the equipment are expensive and these methods operate usually only in laboratory environment. In addition, the techniques are often not directly applicable to solid samples which mean long and rigorous sample preparation (Zawisza et al. 2011).

Our LaseREE project is currently focusing on finding the parameters for the optimized and rapid analysis of REE-bearing minerals using laser spectroscopy. With time-resolved photoluminescence (PL), it is possible to determine elements based on their emission spectrum. With time-resolved photoluminescence, different decay times of luminescence centres can be recognized and separated from each other (Gaft et al. 2001). By this method, e.g., short-lived Ce^{3+} luminescence can be separated from long-lived and dominating Mn^{2+} luminescence from calcite samples (Fig. 1).

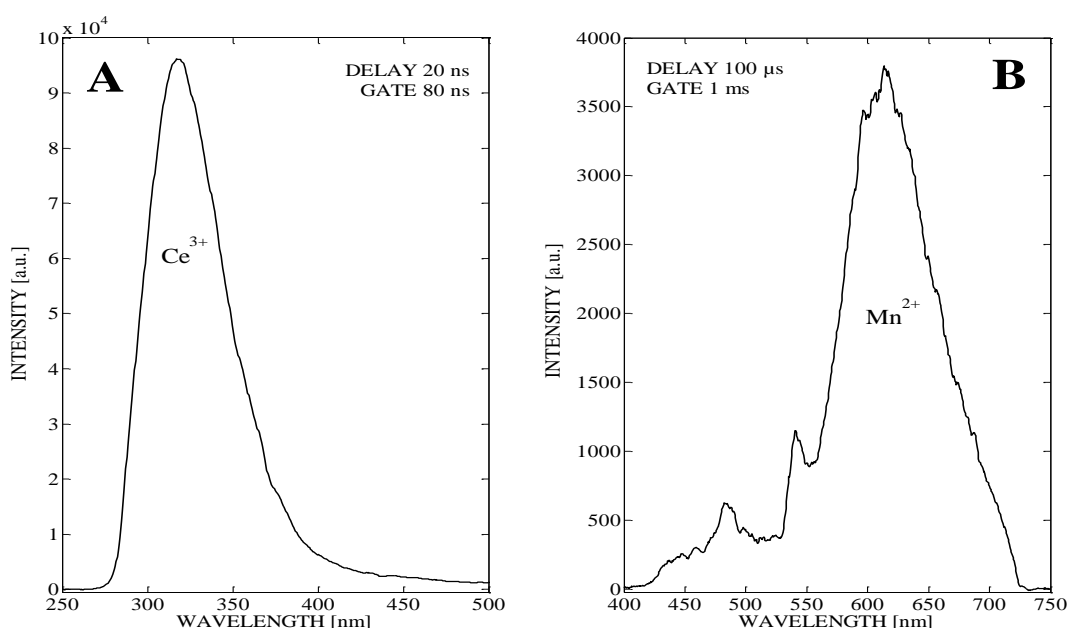


Fig. 1. The time-resolved photoluminescence spectra of REE-bearing calcite. Calcite sample has red luminescence under 254 nm UV light. With different delay times (= time when measurement starts after excitation) different luminescence centres can be detected. With long delay time, also

different REE luminescence centres can be detected beside a wide Mn^{2+} band (narrow peaks on Fig. 1B).

The elemental composition of a mineral can be analysed with laser-induced breakdown spectroscopy (LIBS). The technique is also able to detect light elements like phosphorus (P), lithium (Li), sulphur (S), and beryllium (Be). For example, mineral distributions of sulphide ore samples from the Pyhäsalmi mine have been estimated from LIBS measurements (Kaski et al. 2003).

The combination of the elemental distribution (LIBS) and the occurrence of luminescent REE-centres (PL) give versatile information of the composition from the REE-bearing rock sample. Figure 2 represents the spectra measured from REE-bearing apatite using LIBS (A) and time-resolved photoluminescence (B). By adding the data together with mineralogical data obtained by Raman spectroscopy, a holistic picture of the investigated rock sample can be constructed.

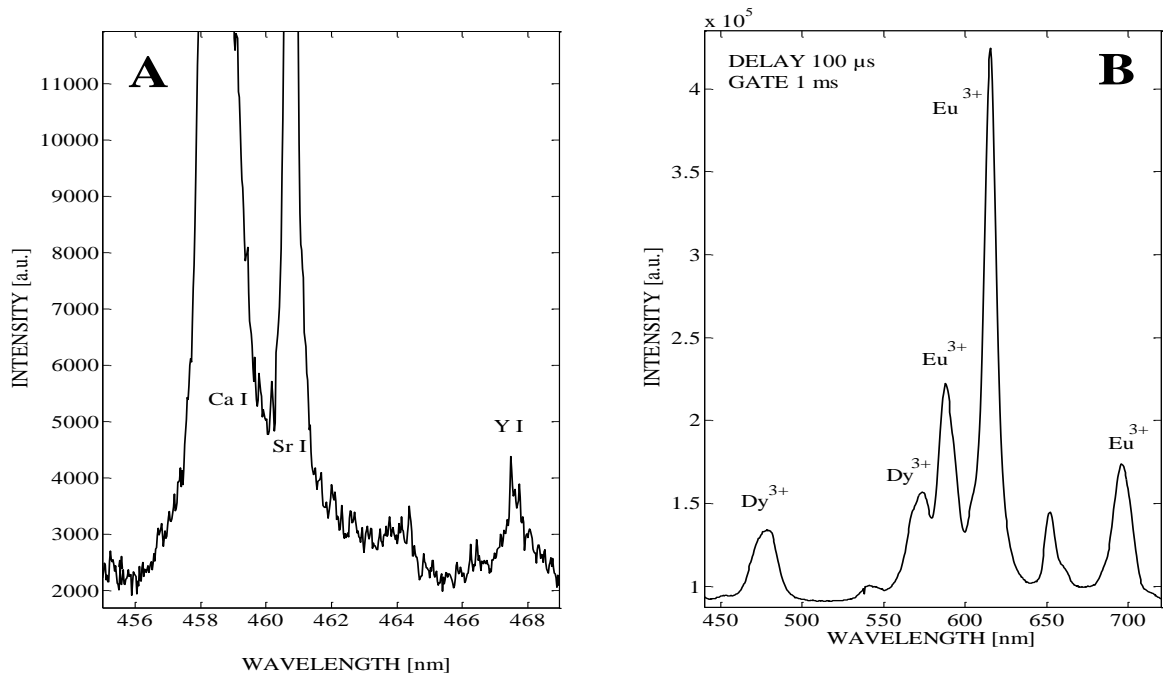


Fig. 2. Emission peaks of LIBS spectrum (A) and recognized luminescence centres from time-resolved photoluminescence spectrum (B) measured from a REE-bearing apatite sample.

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Deciphering the geological environment for rock samples of unknown origin

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There is a plethora of different geological samples for geochemical studies. In an ideal world, the source of the samples is well documented and the related geological environment (bedrock, soil, surface and ground water, deposition environment, the age of geological events, and dominating processes, etc.) comprehensively studied. There are, however, many circumstances where the essential task is to trace the source rock type or the source area of the samples. The provenance studies of sediments and sedimentary rocks, boulder tracing and indicator mineral studies in mineral exploration, hydrogeological modeling, and diverse drilling projects of the unexposed bedrock bear a long tradition for this. The well-documented geochemical methods of these applications provide advanced tools in solving the source area of different geomaterials. The importance of the source area is more than identifying the geographical setting: The knowledge of the geological environment such as tectonic setting, metamorphic grade, weathering, and mineralogical characteristics can also be used for preliminary assessments of mineral potential as well as in assessment of potential environmental risks related to industrial activities such as mining and quarrying.

Xenoliths are a type of geological samples with uncertain origin. Generally, the xenoliths represent foreign rock fragments entrained into host magma. The xenoliths entrained into alkaline dyke magmas, such as lamproites, kimberlites, and ultramafic lamprophyres, may represent rock fragments from mantle depths to upper crustal levels. A suite of lamproite-hosted crustal xenoliths from Western Dronning Maud Land, Antarctica, provided me with an extraordinary opportunity to learn the variety of geochemical methods and combine those with petrographical and geochronological observations. The xenoliths showed the mineralogical and geochemical evidence of partial melting, metamorphism, and metasomatism. Though the xenoliths bear no evidence on low-grade metamorphism common in xenoliths hosted by lamproites and kimberlites, also the high-grade reactions have their effect on the whole rock and mineral geochemistry. These factors had to be considered while deciphering the protoliths and the original geological environment for the xenoliths. The methods used in the study were standard petrographical examination, mineral mode determination, mineral separation, SEM-EDS and EMPA mineral chemical analyses, whole-rock major and trace elements analysis (XRF, ICP-MS), Sm-Nd and Rb-Sr isotope analyses, and SIMS/SHRIMP single zircon U-Pb isotope geochronology.

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Application of the weak leach methods in sustainable mineral exploration

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Field working and sampling for mineral exploration in the sensitive nature areas requires low-impact sampling techniques. Surficial sampling materials like upper soil horizons, humus, plants and snow provide a good solution for that. Mobile metal ion processes for migrating ions from the bedrock surface direct to the upper soil supported by the weak leach techniques provide new, environmentally friendly way to do mineral exploration.

In the UltraLIM Project, carried out in the Green Mining Programme of the Finnish Funding Agency for Innovation (Tekes) in 2013-2015, the goal was the methodological development work in finding the best possible sampling media and analyses methods for the top soil mineral sediments (analyses are based on selective and/or weak leaching), biogeochemistry and snow geochemistry. Six target areas located on a variety of mineralisation types in northern Finland were chosen for testing and comparing surficial and/or shallow sampling depths and leaching methods. The thickness of the glaciogenic overburden and boreal vegetation types varied between the sites. In this presentation, the focus is in soil sediment samples and weak leach methods.

Seven selective and weak leaching methods were chosen: Mobile metal ion (MMI-M), ionic leach, ammonium acetate, bioleach, enzyme leach, Ah-horizon with modified aqua regia leach and Soil Gas Hydrogen (SGH) methods. The samples were also analyzed using traditional analysis methods like aqua regia leaching and XRF analysis to compare results and get background concentrations both from the upper soil and fresh till material. Seven different laboratories were used for analyses. Selected weak leach analysis packages and traditional geochemical methods are all commercially available and thus broadly useful to exploration and consultant companies.

A comparative study made in the project showed that most of the methods are useful in several ore/mineralization types. The methods worked the best in cases where the mineral deposit or mineralization is distinct, and stands out from the surrounding rock types. For example, most of the Au, IOCG and Ni-Cu-PGE deposits (Fig. 1) which have strong structural control were well suitable mineralizations. In addition, sulphide ore types had a distinct geochemical response as a result of the strong electrochemical charge difference between the ore and parent rock. Sulphide ores also caused low pH values to the surficial soil samples and clear positive response to the self-potential results. In cases, where lithological contrast was missing or mineralization and alteration are wide-spread, low-extraction methods are not the most appropriate methods.

True comparison of methods was problematic because all elements cannot be analysed with all leaches. For example, with the ionic, enzyme and bio leaching methods, it was not possible to analyse phosphorus which is the main ore element in the P-REE occurrences, important for example, in critical mineral exploration. Also, gold is difficult to determine by some methods because the detection limit was too high. Instead, by looking at the concentrations of pathfinder elements, the absence or low detectability of the main ore elements can be replaced. In the case of weak leach method results, relative values and trends instead of absolute concentrations should be look at.

The test of weak leach methods showed that glaciogenic till and stratified sediments are usable materials for mobile (metal) ion tracing. The thickness of overburden is not an

essential factor in detection of the mobile ion concentrations in the upper soil horizon. However, the influence of complex till stratigraphy still remains one of the factors causing uncertainty for ion mobilization. For example, could the till layer with mineralized material act as a source for positive response instead of the bedrock source? The large number of trace elements available in weak leach analytical packages makes them effective for exploration of many types of ores. When surveying for the known Au, Cu, Cu-Ni-PGE and P-REE deposits, many anomalies gave positive responses in samples collected from soil horizons.

The use of surficial soil sampling and the weak leach analysis provides easy and quick, and particularly, environmental low-impact geochemical research methods. This decreases traces of mineral exploration and gives a possibility to do sampling in vulnerable nature areas without heavy sampling machines. Furthermore, it increases cost-efficiency and diminishes environmental strain in a raw material production chain. An ideology of migration of mobile metal ions together with weak leach methods is also important part of geo-bio interaction and would have significant further research opportunities for example in the environmental research applications and natural geochemical background or risk mapping.

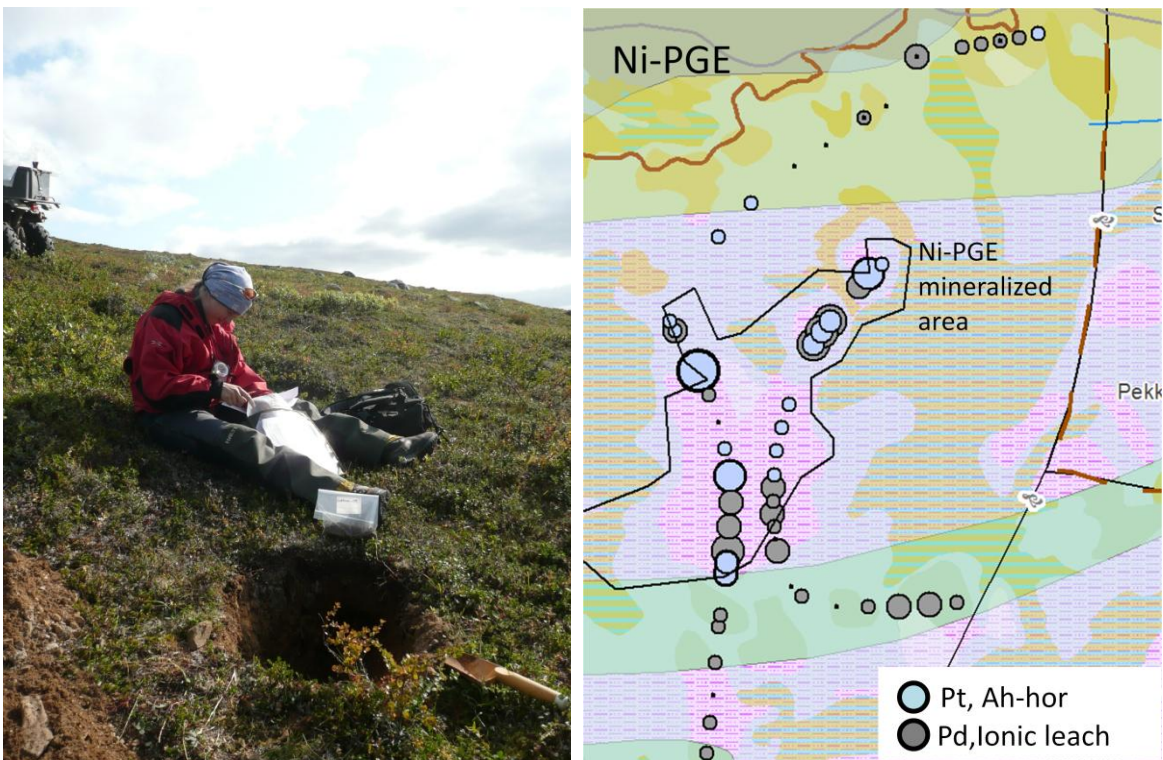


Fig. 1. Surfacial soil sampling in the fell area and an example of the results of two different weak leach methods in detecting Ni-PGE mineralization as a part of mineral exploration. Photo by M. Mäkikyrö. Bedrock map based on DigiKP of GTK.

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Original partial serial extraction method for soil nutrient analysis

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This study presents a new method for soil nutrient analysis. The principle of the serial extraction method is to dilute extractable elements of a soil sample by stepwise procedure. A seven-step procedure (Fig. 1) was performed. In each step the supernatant was analyzed and the remains were removed to the next step. This method (OPSEM) included new implications of the traditional soil chemical methods of analysis. The method presented included also cation exchange capacity (CEC) analyses by a new method. This study comprised also comparative investigations of the traditional methods for soil nutrient analyses. Advances of serial extraction method in comparison to traditional partial extraction methods, which are widely used in soil science, were obvious: The OPSEM gives all-inclusive concept of the nutrient element fractionation of soil. All elements can be detected in the same solution. Stepwise procedure reveals specific features of the extractant used for soil nutrient analyses. The OPSEM is less laborious, and less time (money) consuming than traditional simple partial extraction methods. OPSEM is a precise and specific method to distinguish different fractions of the soluble elements of soil samples.

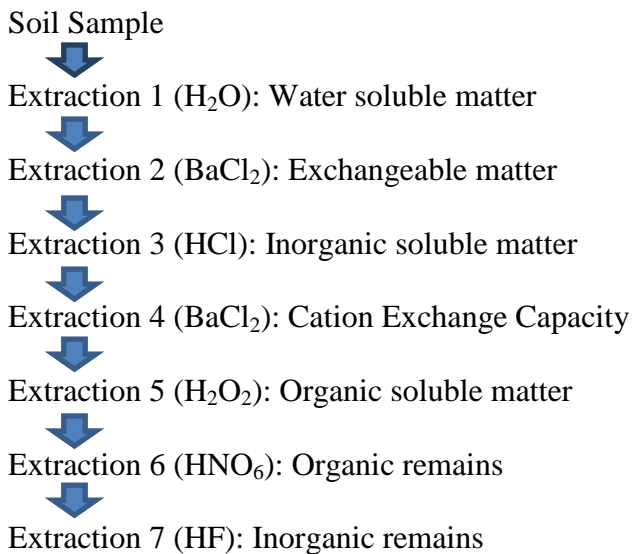


Fig. 1. Procedure of the OPSEM.

This comprehensive soil nutrient analysis method is applicable especially in forestry and agriculture. The method presented is useful also in environmental monitoring, and in that way, it can be related to the issues of material research in circular economy and clean technology.

Laboratory manual is available (in Finnish) from the author.

Novel synthesis methods for advanced porous ceramics from mine tailings (CeraTail)

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The utilization of mining waste as a source for secondary raw materials has been acknowledged as an essential objective by the European Commission. Therefore, the utilization of mine tailings to produce low-cost construction and building materials has been widely investigated (e.g. Lemeshev et al. 2004, Shao et al. 2005). However, the application of mine tailings in technical ceramics has been rare because the raw material requirements for producing pure ceramic phases tend to be very demanding. The purity requirements for porous ceramics tend to be lower, which makes mine tailings a good candidate for raw material. Porous ceramics are frequently used as filters, catalyst supports, insulators and absorbents. Within this Academy of Finland funded project, Novel synthesis methods for advanced porous ceramics from mine tailings (CeraTail), robust processes for utilizing mine tailings as raw material for porous ceramics will be developed (Fig. 1).

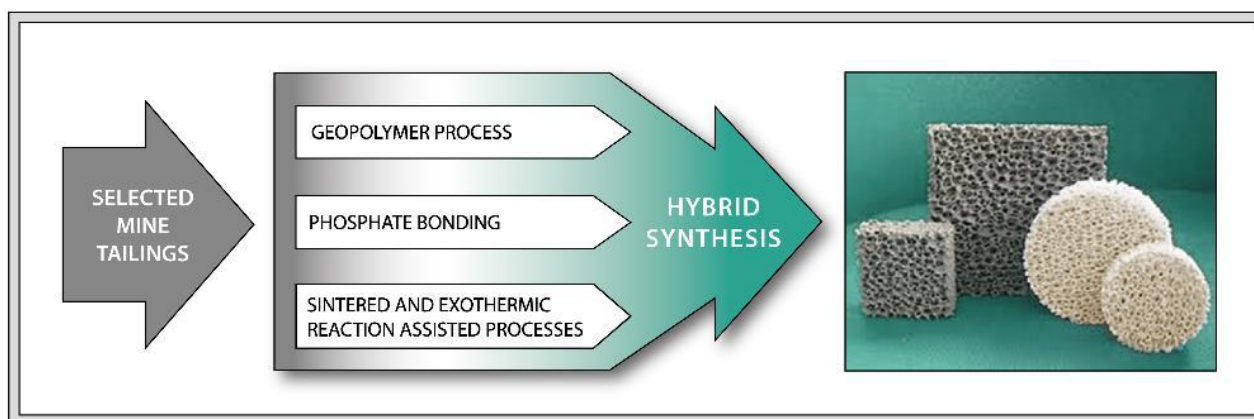


Fig. 1. Porous ceramics from selected mine tailings by suitable low-energy processes and process combinations

The aim of the CeraTail project is to make porous ceramics from selected tailings with the help of geopolymerisation, phosphate bonding and heat producing reactions. Low-energy methods to introduce porosity into ceramics are direct foaming by agitation or gas formation, freeze drying/freeze casting, or through the creation of residual voids formed by incomplete reaction.

The key difference between geopolymers (GP) and chemically bonded phosphate ceramics (CBPC) lies in the chemical reactions and conditions required to form solid matter. Geopolymer reactions require alkali activation, whereas phosphate formation occurs in slightly acidic conditions. Aluminosilicate tailings can be used as precursor materials for geopolymerization (Xu and Van Deventer 2000). Previous investigations on

the use of tailings to produce chemically bonded phosphate ceramics were not found, though naturally occurring minerals such as wollastonite are known to be suitable raw materials (Colorado et al. 2011). An important thing to notice is that the formation of phosphate ceramics does not completely deplete the raw material. Instead, a significant portion of the primary source is encapsulated into the ceramic structure as filler. The phosphate content of apatite rich tailings will be utilized in the production of phosphate bonded ceramics in the CeraTail project.

Viera et al. (2005) produced fully densified mullite rich material from muscovite rich slate rock wastes combined with Al-sludge. Mullite gives good physical properties to ceramics and is a very attractive compound for dense and porous material applications. One aim of the CeraTail project is to synthesize the mullite phase from mine tailings with the help of heat producing reactions.

The responsibilities of the Geological Survey of Finland (GTK) in the CeraTail project include screening and selection of the potential raw materials, e.g. Al-silicate, phosphate, and Mg carbonate (magnesite) based tailings. Tailings characterization is made by novel mineralogical and chemical analyses. The first analytical results from five different tailings sources in Finland show great potential for finding adequate material for producing porous ceramics. The most suitable materials are being selected and unwanted components are being extracted with the help of particle size estimation. Additional support in processing selected materials will be provided by GTK's Mineral Processing and Materials Research unit.

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300 million years of indium-forming processes in A-type igneous environments in the central parts of the Fennoscandian Shield

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Introduction

Indium has an increasing demand for liquid crystal displays, high-definition televisions and other products of modern electronic industry. Most of the indium on the global market is a by-product of zinc mining from a number of ore types. However, even if many mines in Sweden and Finland (VMS ores in the Bergslagen, Skellefte and Pyhäsalmi regions) currently are major Zn producers, they are not indium producers. Instead, since the first indium discovery in the Fennoscandian Shield, at Pitkäranta in the Ladoga region (Vernadsky 1910), almost all indium discoveries in the Fennoscandian Shield have been made in vein and skarn occurrences in close association with 1.85–1.54 Ga anorogenic granites. A review of the most important indium-bearing environments in the central parts of the Fennoscandian Shield follows.

1.85-1.67 Ga TIB environments in south-central Sweden

Moderate indium grades have been recorded in Sn-Cu-Zn-Pb-bearing greisen veins in A-type granites in the Transscandinavian Igneous Belt (TIB) and in skarn and vein ores in the adjacent supracrustal rocks in the Bergslagen region. The oldest ore-forming system is in the 1.85 Ga Kamptjärn granite (Ahl & Sundblad 2007), belonging to the TIB 0 generation, which is host for polymetallic greisen veins at Gillerdrågen and Tyfors (with up to 52 ppm In). A younger system (the 1.67–1.70 Ga Siljan granite in the Dala region, belonging to TIB II generation), is host for Sn-Cu-Zn-Pb-bearing greisen veins at Van and Norra Hålen with up to 83 ppm In. The 1.85 Ga anorogenic granites are also considered to be responsible (Sundblad 1991) for the metal supply to the polymetallic skarn/vein ores in Svecofennian supracrustal formations in the Filipstad region, westernmost Bergslagen (e.g. Getön, Hällefors, Gruvåsen and Långban), where up to 100 ppm In has been recorded.

The 1.64 Ga Wiborg batholith, SE Finland

A number of In-bearing polymetallic occurrences have been detected in the western parts of the 1.64 Ga Wiborg batholith, SE Finland. High indium grades are recorded in a Zn-Pb-Ag-rich greisen vein at Jungfrubergen (up to 600 ppm In) and in the Cu-As-Sn-rich Korsvik veins at Sarvlaxviken (up to 1500 ppm), the latter with indium in roquesite, sphalerite and chalcopyrite (Cook et al. 2011, Valkama et al. 2016a). Indium grades of about 40 ppm are also recorded in compact magnetite-sphalerite bodies at Getmossmalmen and Pahasaari. The highly evolved Marviken granite played a major role in the formation of polymetallic occurrences in the Sarvlaxviken area.

1.57 Ga Eurajoki stock, SW Finland

Although numerous Sn-Cu-Zn-Pb-bearing greisen veins were recorded in the 1.57 Ga Eurajoki stock in SW Finland by Haapala (1977), the indium-grades in these veins are very low (< 20 ppm). However, a discovery of a quartz vein with polymetallic mineralisation at Onkamo, 5 km west of the Eurajoki stock, has revealed indium grades at the level of 570 ppm (Pere 2009), suggesting an underlying granitic stock with unknown economic potential under the nuclear power plant of Olkiluoto.

1.54 Ga Salmi batholith

Indium is abundant (up to 600 ppm) in the Fe-Cu-Zn-Pb-Sn-Ag-rich skarn ores at Pitkäranta, which were subject to intense mining in the 19th century. The Pitkäranta indium is usually sphalerite-hosted but tiny roquesite grains have been observed in the Hopunvaara deposit (Valkama et al. 2016b). The ores are hosted by metamorphosed Jatulian and Kalevian supracrustal rocks along the western margin of the 1.54 Ga Salmi batholith. The Salmi batholith is dominated by coarse-grained rapakivi granites with a matching lead-isotopic pattern to the ores (Sundblad 1991) but lacks concrete evidence of hydrothermal activity. Instead, several smaller satellite rapakivi granite plutons, with evolved geochemical composition, along the western margin of the Salmi Batholith, e.g., at Torppusuo and Lupikko, show significant hydrothermal alteration and are more likely the metal sources for the Pitkäranta ores (Sundblad et al. 2011).

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Vertical soil zonality - a constraint for treeline Norway spruce

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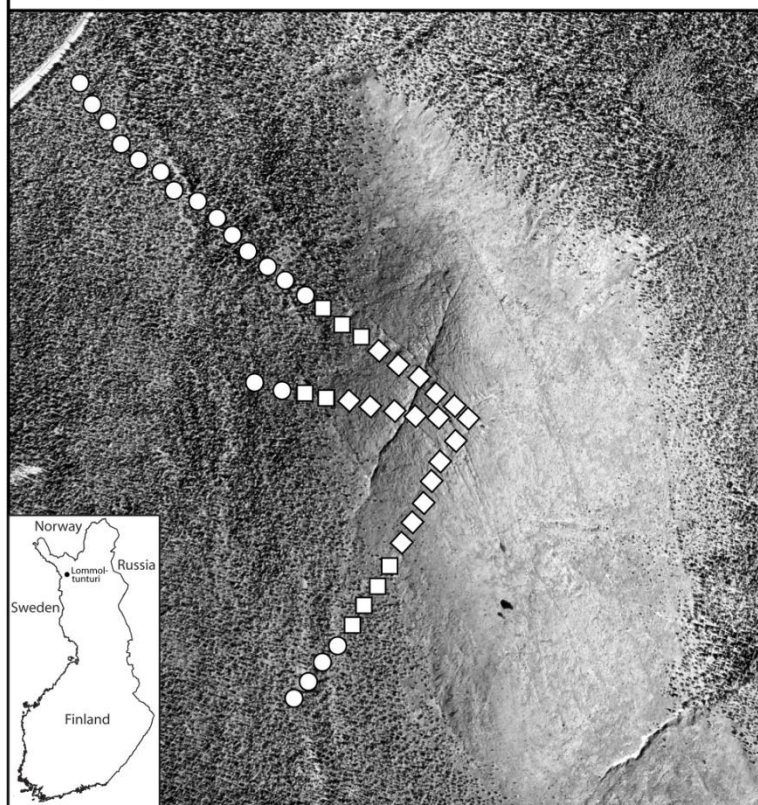
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Soil chemical properties tend to be associated with the underlying rock types, yet those also exhibit variations with respect to elevation. This concept of vertical soil zonality, first introduced by Dokuchaev in the late 1890's, implies that soil nutrient content tends to decrease along with increasing elevation. This feature will eventually restrict the spread of spruce, known to be particularly tied to elevated concentrations of soil Ca and Mg, onto higher fell elevations.

The soil zonality hypothesis was tested along the forest-tundra gradient of Lommoltunturi fell, located 30 km south of the Norway spruce (*Picea abies* (L.) Karst.) forest line (Fig. 1; Middleton et al. 2008; Sutinen et al. 2012) The Paleoproterozoic fell is composed of mafic Mg-tholeiitic metavolcanite rocks and covered by a thin veneer of glacial till. Bedrock outcrops are common at the top of the fell reaching 557 m (a.s.l.). Mineral topsoil was sampled at 46 plots (Fig. 1) with a cylindrical "topsoiler" sampler. The samples were measured in field for pH and soil electrical conductivity (EC) was measured using conductivity fork. Soil samples were analyzed for concentrations of Al, As, Ba, Be, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, P, K, Na, S, Sr, Ti, V, and Zn, extractable with 1 M ammonium acetate (NH₄OAc) at pH 4.5 using ICP-AES. Total carbon (C_{TOT}) and nitrogen (N_{TOT}) were analyzed on a dry-weight percentage basis using a Vario MAX CN analyser.

68°00'30"N, 24°07'56"E



67°59'35"N, 24°10'16"E

Fig. 1. The elevational gradients along Lommoltunturi fell as follows: diamond=tundra; square=transition zone and circle=forest. Air photo 2003 by Blom-Kartta Oy©.

The soil EC, exchangeable Ca:Al molar ratio, and exchangeable concentrations of the soil Mg and Na were higher in forest, whereas concentrations of the soil exchangeable Al and total N were higher in tundra ($p \leq 0.01$). With regard to soil chemical properties the transition zone was intermediate, except for concentration of the soil N_{TOT} , which was lower both in forest and transition zone compared to tundra. The soil variables, correlative with elevation ($p \leq 0.01$) were as follows: EC ($r_s = -0.58$), soil water content θ ($r_s = 0.43$), $Ca_{exch}:Al_{exch}$ ratio ($r_s = -0.46$), Al_{exch} ($r_s = 0.58$), Mg_{exch} ($r_s = -0.39$), total N ($r_s = 0.49$), S_{exch} ($r_s = 0.39$).

A positive correlation was observed between the field measured soil EC and exchangeable concentrations of the soil Ca ($r_s = 0.32$, $p = 0.031$), Mg ($r_s = 0.44$, $p = 0.002$) and Na ($r_s = 0.38$, $p = 0.009$), whereas negative correlation with Al ($r_s = -0.57$, $p < 0.001$). The soil EC negatively correlated with N_{TOT} ($r_s = -0.38$, $p = 0.010$) and C_{TOT} ($r_s = -0.31$, $p = 0.034$), as well as elevation ($r_s = -0.58$, $p < 0.001$). Even though the soil N_{TOT} ($r_s = 0.49$, $p = 0.001$) and C_{TOT} ($r_s = 0.37$, $p = 0.011$) increased with elevation, $C_{TOT}:N_{TOT}$ ratio did not show elevation dependency. In addition, neither the soil pH ($p = 0.11$) nor extractable concentration of soil P ($p = 0.23$) correlated with elevation.

Our data on soil zonality suggest that constraint for spruce in tundra is low $Ca_{exch}:Al_{exch}$ ratio. It is known that distribution of spruce species, particularly white spruce (*Picea glauca* (Moench) Voss) and Norway spruce, is associated with elevated concentrations of Ca and Mg in parent tills. The excess of Al on the root uptake of Mg may be an inhibitor to spruce, and Ca availability could be impacted by the displacement of Ca on the exchange complex by Al in the soil solution. According to Cronan & Grigal (1995) the soil solution Ca:Al molar ratio less than 1 may indicate harmful soil acidity and Al phyto-toxicity, hence posing a risk of adverse impacts on tree growth. Even in the forest, soil $Ca_{exch}:Al_{exch}$ molar ratio of 0.23 (median) pose a considerable Al-stress for spruce. The maximum concentrations of the soil Mg_{exch} and Ca_{exch} , and the soil $Ca_{exch}:Al_{exch}$ ratio of 2.2 was found at 420 m a.s.l, where the pioneer establishment of Norway spruce occurred in 1840's and 1860's. With regard to increasing elevation, we found an increase in soil N_{TOT} , C_{TOT} and Al_{exch} , but a decrease in soil Ca_{exch} , Mg_{exch} , $Ca_{exch}:Al_{exch}$ ratio as well as electrical conductivity (EC). The treeline of Norway spruce has shifted 55 m in elevation within 60 years, yet poor soil $Ca_{exch}:Al_{exch}$ ratio of 0.02 and winter wind climate on tundra apparently are constraints for spruce (Middleton et al. 2008; Sutinen et al. 2012).

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Snow in mineral exploration- examples from the UltraLIM project

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The Ultra low impact geochemical exploration methods in the sub-arctic (UltraLIM) project was carried out in 2013-2015 and was funded by the Green Mining Programme of the Finnish Funding Agency for Innovation (Tekes). In this project, different geochemical methods and different sampling media (plants, mineral soil and snow) were tested for mineral exploration purposes in northern vulnerable areas. This presentation exposes some practical information and results gained from this study. Finally the suitability of snow in mineral exploration will be evaluated.

Snow has been commonly used as sampling media in environmental studies, but has been rarely used in mineral exploration. The earliest tests are presented in 1970's in Canada and in Finland. Development in ICP-MS instrumentation over the last two decades allowed the determination of various trace elements down the PPQ level. Snow sampling is also an environmentally friendly method; it does not require heavy machinery, the environmental impact during sampling is negligible, the material is light and easy to sample and in addition no disposal remainders are left after analysis. The main disadvantage is that snow can be sampled only in the areas where it stays in the ground long enough and the snow cover is thick enough for sampling. Also, the requirement that samples must be kept in a frozen state before analysis has to take into consideration.

In this study, snow samples over six known mineralized areas, representing Au, Au-Co, Fe-Cu-Co-Au, Cu, P-REE and Ni-Cu-PGE types of deposits, were analysed to test their ability to fingerprint these mineralization environments. The snow samples were collected from the bottom of the snow layer, about 10-20 cm above organic soil surface, where the hydrocarbons and trace elements derived from the bedrock have accumulated (Fig. 1). The first sampling round was conducted in all six test sites in 2014 and it was repeated in the three of them (Au-Co, Cu and P-REE deposits) in 2015.

Two different methods were tested for analyzing the snow samples: Soil gas hydrocarbons (SGH) method and trace element concentration by single collector high resolution inductively coupled plasma mass spectrometry (SC-HR-ICP-MS). The SGH method is developed by Activation Laboratories Ltd. Canada while the trace element analyses were performed at the Research Laboratory, Geological Survey of Finland.

Both tested analysis methods returned positive results. The SGH results are interpreted by the researchers from Activation Laboratories Ltd. The zones having the special SGH signatures have been located over the known mineralized areas in Au, Au-Co, Fe-Cu-Co-Au and Ni-Cu-PGE targets. However, in Cu and P-REE targets the requested interpretation was not perfect for the target type and thus the results had no response over the mineralizations. The repeatability of the SGH method showed differences in all the test sites between the two sampling rounds.

The positive trace element signatures were detected using the SC-HR-ICP-MS method. The method was tested only in 2015 in the same three test sites as the SGH method. The snow samples were melted and filtered before analysis. In all these three test sites elements related to the mineralization gave good response showing elevated response ratio values over the known mineralizations (Fig. 2).

Based on these results, possibilities for using snow in mineral exploration show great potentials, but more testing and studies are needed. The repeatability test on SGH results

has failed and the factors causing these differences need to be sort out if possible. The sample preparation for the trace element analysis of the snow samples could be improved as well as the data acquisition protocol, which will enhance the sensitivity of the SC-HR-ICP-MS method. In addition, the possible influence of the airborne fall-out should be taken into account in the concentrations of elements in future.

Snow as a sampling medium in mineral exploration provides an environmental friendly method for vulnerable northern areas in near future.

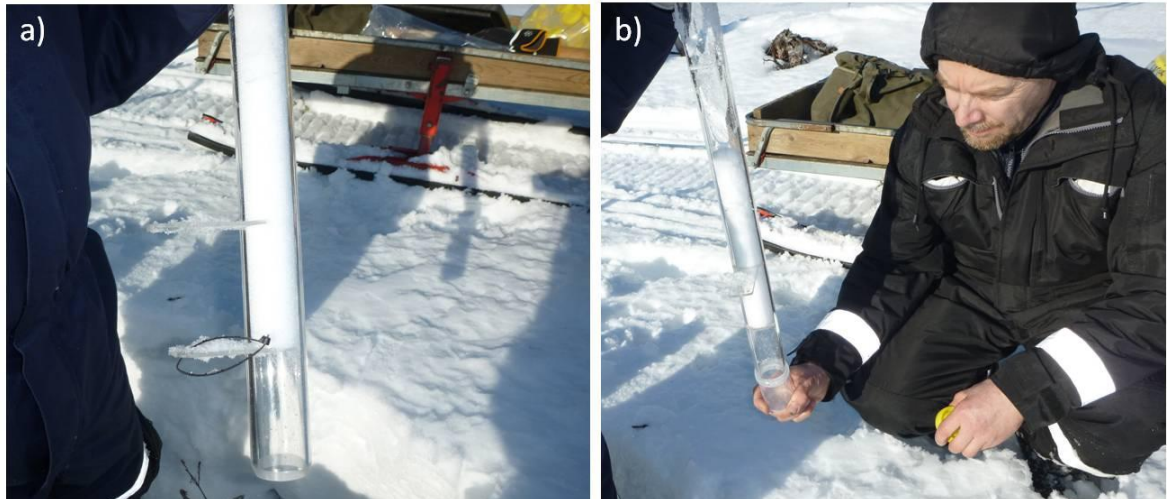


Fig. 1. A plastic tube generated for snow sampling. The transversal valves keep the sample in the tube and let the lowest part of the snowpack fallout from the tube (a). The snow sample was dropped from the sampling tube directly to the sampling jar (b). Photos: Jens Rönqvist

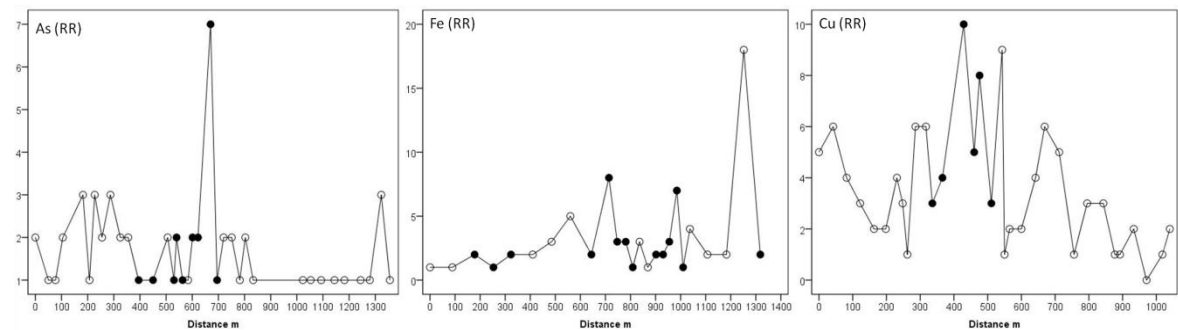


Fig. 2. The response ratio (RR) values of As in Au-Co target, Fe in P-REE target and Cu in Cu target in snow samples. The samples were analysed by SC-HR-ICP-MS. The sampling points over the known mineralization are marked with black dots. The elevated RR values show response over the mineralizations. The distance (m) on x-axis is the distance between the first and the other sampling points.

The geochemical correlation between coarse and fine fractions of urban soil in Finland

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Geochemical mapping of till in a reconnaissance scale (Koljonen 1992) and in a regional scale (Salminen 1995) in Finland was based on analyses of the fine fraction (<0.06 mm) of till samples. The fine fraction has also been successfully employed since the 1950s for detailed geochemical exploration in Finland. Soil scientists and environmental researchers have often preferred a coarser (<2 mm) fraction in soil geochemical studies. The Geological Survey of Finland has recently applied <2 mm size fraction in baseline geochemical mapping in urban areas and in natural soils.

Tarvainen (1995) compared *aqua regia* extractable trace element concentrations in <0.06 mm size fraction and in <2 mm size fraction for over 600 till samples from southern Finland. There was a good linear correlation between the *aqua regia* results for the two size fractions. The concentration in the coarse fraction could be estimated as a function of concentration in fine fraction. Parameters for the linear functional relationships have been published for many elements. The levels of heavy metals were lower in the coarse fraction probably due to higher proportion of quartz, feldspar and rock fragments in the coarse fraction.

The Geological Survey of Finland carried out an urban soil baseline geochemical mapping in the city of Hämeenlinna in 2010 (Tarvainen 2011). The urban soil samples were taken from 400 locations. The sampling depth was 0 - 10 cm. Samples were dried and sieved to <2 mm size fraction and analysed by ICP-MS after *aqua regia* extraction. A subset of samples (231 samples) were sieved also to finer <0.177 mm (-80 mesh) size fraction before *aqua regia* extraction. The concentrations of Co, Cu, Cr, Ni, V, and Zn in the two size fractions were compared using Spearman's rank correlation coefficient and scatter diagrams. The samples were classified according to the soil type.

The concentrations of the studied elements correlated positively (Spearman's ρ 0.844 – 0.902) between the two size fractions. The concentrations in the two fractions were almost similar for clay soils and fine-grained man-made soils. Concentrations of the studied trace elements were often lower in the coarse fraction compared to the fine fraction in coarser soil types. The linear functional relationships based on Finnish till samples (Tarvainen 1995) could be applied to till, sand and coarse-grained man-made soil samples (Fig. 1).

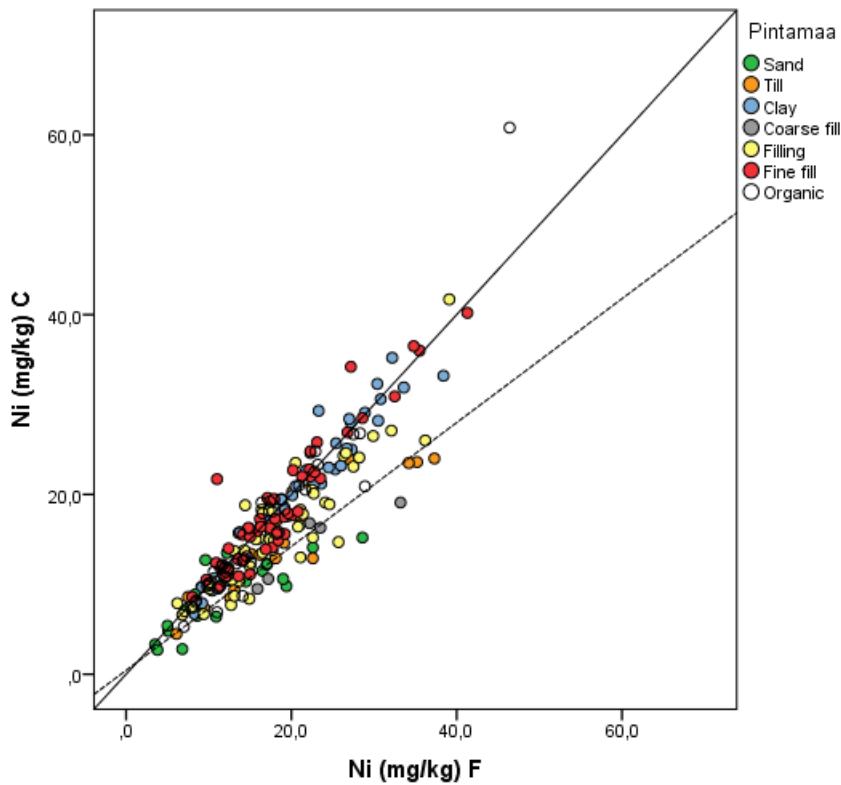


Fig. 1. Scatter diagram of *aqua regia* soluble Ni concentrations in the fine fraction (<0.177 mm, x axis) and the coarse fraction (< 2 mm, y axis) of urban soil samples from Hämeenlinna (sampling depth 0 – 10 cm). Dashed line = The linear functional relationships based on Finnish till samples (Tarvainen 1995).

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Aggregate quarries - potential sources of explosive residues in groundwater

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One of the key issues related to the circular economy in Finland is the need to develop common practices for sustainable excavation, use and recycling of the construction aggregates needed in the future. Construction aggregates include natural sand and gravel, crushed rock that fulfil certain quality specifications as well as recycled mineral material. Since the early days the aggregate production in Finland has been based on natural sand and gravel excavation. However, today the natural sand and gravel excavation is often considered problematic in the environmental aspect, because of the contamination risk in groundwater reserves and because of their negative effect on the biodiversity in esker sites. Especially in densely populated areas in Southern Finland where the amount of sand and gravel sources is getting lower the major part of the aggregate production in the future will be based on bedrock quarrying.

Since the amount of bedrock quarries will increase in the future we will need to understand the challenges related to explosive originated nitrogen compounds and other residues ending up to surface and ground waters. The majority of the explosives used in the aggregate quarries contain significant amounts of nitrogen (20-33% by weight). The main sources for nitrogen emissions in quarrying are 1) the explosive residues due to incomplete detonation, 2) leaching of nitrogen in wet conditions and 3) loss of explosives during the handling and loading processes (Forcitt 2010). The potential of nitrogen to release into the water system depends on the type of explosives used, local water conditions, explosives management and efficiency of the blasting operations (Forsyth et al. 1995).

The aggregate quarries are often located in rural areas where residents are dependent on their own private drinking water wells. Sometimes soil and bedrock excavation is combined, and the quarry may be located in protected groundwater area. Nitrogen concentrations exceeding drinking water quality criteria in groundwater may have extensive economic impacts and also social and health influences. It is not unusual that the elevated concentrations in groundwater are not notified until the plume is already widespread.

One approach to manage the risks related to explosive residues is the use of different types of explosives. Traditionally ANFO type of explosive that is basically composed of ammonium nitrate and fuel oil is used in aggregate quarries. It has been shown that in the other types of explosives such as slurries and emulsions, the amount of nitrogen is lower and they are more resistant to the water (Forsyth et al. 1995, Paalumäki et al. 2015). In addition, the total amount of the explosive needed is lower. However, this is not a sufficient method solely to manage the risks, since the nitrogen from the emulsion type explosives is leached to the water over time even if the leaching does take more time.

Following challenges have been identified related to the explosive residues in aggregate quarries:

- The range of enterprises operating in aggregate production industry is wide and their environmental awareness and knowledge is variable. Bigger operators often use subcontractors that may likewise have variable practices. Concordant training and practices are needed for explosive handling, blasting operations and risk management.

- Documentation of explosion operations may be incomplete or missing. The documentation and data management is a key to understand the origin of possible elevated concentrations in groundwater.
- Groundwater monitoring needs to be comprehensive and well documented. The enterprises and their consults should be aware of the risks and react quickly to possible changes in water quality.
- The explosive residues are migrated into the groundwater not only during blasting operations but also by leaching from the stock piles. Top soil recovery and location of the stock piles shall be designed and implemented effectively.
- Guidance and training for regulators, operators and designers is needed in order to understand the risks and recognize the problems.
- It is obvious that the blasting techniques and explosives could still be improved towards more environmentally better direction.

All in all, more conversation about this topic is needed in order to create reliable risk management methods and practices for groundwater protection in aggregate quarries. Similar risks are faced in all the quarrying operations including e.g. mining and underground construction.

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Geochemical baseline mapping in Rovaniemi, northern Finland

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Concentrations of the elements in natural and urban soils are important to know for directing land-use and detecting harmful soil areas in the constructed areas. By geochemical baseline studies it is possible to define natural background levels of the elements in different soil types, to calculate upper recommended limit of soil baseline variation, and to estimate the need of acts for the safe use of land areas. In this research, the geochemical baseline study was carried out in the centre of Rovaniemi town in northern Finland. Soil samples (104) were collected from upper soil (depth 0-10 cm) in 2013-2014 and the sieved < 2 mm fractions were analysed using multielemental analysis package (ICP-OES/-MS) after aqua regia digestion. Furthermore, ten samples were analysed for PAH concentrations.

Soil geochemical baselines include both natural geological background concentrations and the diffuse anthropogenic input of substances. In Finland, Government Decree on the Assessment of Soil Contamination and Remediation Needs 214/2007 (Ministry of the Environment, 2007) obligates to take into account geochemical baselines in the assessment of soil contamination and remediation needs. According to the Decree, the amount of contamination and a remediation plan have to be estimated if one or more harmful elements show higher values than the threshold values given in the Decree (Ministry of the Environment, 2007). However, if the local baseline concentration of a contaminant is higher than the threshold value given in the regulation, the baseline is used as a trigger value. Information on soil geochemical baselines is available from the national geochemical baseline database, Tapir (www.geo.fi/tapir). The database is hosted by the Geological Survey of Finland (GTK). The public user interface of the Tapir system includes statistical summary information from several pre-defined geochemical provinces within Finland, but it is also possible to count statistical values of natural soil data using free spatial selection. In addition, Tapir includes also data from some main cities in Finland, such as the Helsinki Metropolitan Area and the Tampere city centre.

The results from Rovaniemi show that practically all the concentrations of elements listed in the Government Decree are under recommended values. Only arsenic concentrations were higher (up to 8.7 ppm) than recommended value (5 ppm) in couple of the sampling points. PAH concentrations were all under detection limits in the ten analysed samples. The final results from the Rovaniemi case study will be published in a master's thesis by M. Valkama later in 2016. The data will be also available via the national geochemical baseline database, Tapir after that.

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Navigating the jungle of best practices in mine waste characterisation

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Geochemical characterisation of mine materials, including waste rock, marginal ore, tailings and cover material, is an important component of developing an environmentally and socially sustainable mining operation. Geochemical characterisation programmes should ideally be implemented during the early stages of mine planning to inform waste rock management strategies and ensure that appropriate engineered controls are put in place to minimise future impacts. The identification and characterisation of risks at this stage can minimise the requirement for overly conservative mitigation designs that can be costly. In addition, a well-planned characterisation programme enables early identification of waste material properties that may affect its use in project development and construction. Where possible, opportunities for waste prevention and waste recycling should be addressed in the waste management plans for mining waste.

The requirement for mine waste characterisation is recognised in a number of key international and national guidance/policy documents relating to mine waste management. For example an assessment of the potential for Acid Rock Drainage and Metal Leaching (ARDML) is a key requirement of the Equator Principles governing Environmental and Social Impact Assessment and permitting on projects funded by the World Bank. It is also a requirement of the European Directive 2006/21/EC on the Management of Waste from Extractive Industries.

Despite geochemical characterisation being recognised as a key aspect of effective mine waste management, there are different levels of guidance and the requirements may differ. Guidance ranges from international documentation such as the International Cyanide Management Code (ICMI, 2014; www.cyanidecode.org), to regional guidance such as the EU Mine Waste Directive (2006/21/EC). These are guidance documents are then used as a basis for developing national legislative policy such as the Finnish Government Decree on Waste from Extractive Industries (190/2013), the Finnish Waste Act (646/2011) and Decree (179/2012). These various international, regional and national guidance documents have different purposes, but the common aims are generally analogous.

From a waste recycling perspective, there are also standards and regulations relating to the use of mine waste materials in construction, for example the European Construction Products Regulation (305/2011).

In Nordic countries, the geochemical assessment of mining waste is typically undertaken as part of the mine permitting process in accordance with adopted European Directives. This allows waste to be characterised as either inert or non-inert materials. Every mine operation is unique in terms of its geochemical characteristics, yet the management of the waste rock is often dictated by generic solutions prescribed in the permitting processes. As such, site-specific geochemical characterisation is important to understand how the unique geological, climatic and hydrogeochemical conditions will influence mine waste behaviour in order to drive effective waste management practices.

This presentation will navigate the jungle of mine waste characterisation policy and will discuss how early incorporation of geochemical characterisation into project development can benefit material recycling, reduce long term costs and prevent environmental and health impacts. A series of short case studies will be presented that demonstrate how early-

stage geochemical characterisation has driven the development of different engineering solutions for effective mine waste management.