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Snow in mineral exploration – examples and practices in glaciated terrain

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ABSTRACT

Although the origin of the snow is atmospheric, heat and gases coming from underlying soil affect the concentration of hydrocarbons and elements in snow. For testing the use of snow in geochemical exploration, a test campaign was carried out in three different mineralization types in northern Finland: Au-Co, P-REE and Cu mineralizations. The snow samples were collected from the bottom of snow cover in two consecutive years. Two methods for analysing geochemical signatures of mineralized bedrock were applied to these snow samples: Spatiotemporal Geochemical Hydrocarbons (SGH) and ultra-trace elements determination by single collector high resolution inductively coupled plasma mass spectrometry (SC-HR-ICP-MS). The SGH method is based on detection of the hydrocarbons that are decomposition products of bacteria that use specific mineralization in their growth phase. In the case of the inductively coupled mass spectrometry, the content of a wide range of elements was determined. The results of both methods showed that the traces inherited from the tested mineralization can be observed in snow. The SGH signature located the Au-Co mineralization using an Au template and the Cu mineralization using a Cu template, although low signal repeatability may be the weakness. The response to the P-REE mineralization with a Polymetallic template was unclear. An improvement was achieved by reinterpreting the result with a customized template for REE. In addition, the repeatability with reinterpreted results showed similarities in the results between the sampling rounds. In the case of the SC-HR-ICP-MS method, results for several elements (e.g. As, Cu, Fe) showed a clear response over the mineralized zones for all three mineralization types. Mineral exploration would benefit using of snow as sampling material: this activity leaves virtually no footprint. Further studies are needed to improve the confidence and reliability in the use of snow as a sampling medium in mineral exploration.

KEYWORDS

Snow, geochemistry, exploration, sampling, Spatiotemporal Geochemical Hydrocarbons, SC-HR-ICP-MS, mobile metal ions, Finland

1. INTRODUCTION

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Recently, the need for advanced geochemical exploration methods has arisen due to a demand of environmentally friendly mineral exploration in vulnerable areas and particularly, in sensitive northern areas (Sarala, 2015a). New sample media (including snow) and methods have been studied in several test projects in Finland (Sarala, 2015a, b; Sarala and Nykänen, 2014; Taivalkoski et al., 2016). In recent years, mobile metal ion techniques based on weak and selective leach methods have become common in mineral exploration (Heberlein, 2010). There are several techniques for the measurement of metal ion transport through the sediment cover to the top of the mineral soil (Cameron et al., 2004; Hamilton et al., 2004; Mann et al., 2005).

Some of the geochemical exploration methods are seasonal in the Northern Hemisphere due to a long cold period that restricts field and sampling work. However, during long winter season, snow regularly covers large areas. For example, in the southern parts of Finland the snow cover exists commonly from two to three months and in the northern parts up to seven months. The same situation occurs in large areas in the Northern Hemisphere, which increases interest in the use of snow as a sampling medium for mineral exploration.

Snow includes both locally derived and long-distance components such as dust, airborne vegetation particles, metal ions, hydrocarbons, and soil particles. Precipitation periods and the snow properties are constant on a regional scale, which gives a good foundation for large and comparable geochemical exploration surveys. The lowest part of snow cover potentially provides the most useful sampling medium because of the longest exposure to the flux of elements and hydrocarbons rising from the underlying soil and bedrock. Some good experiences of using the middle section of snow cover are also presented (Sutherland, 2014). The coverage of the upper snow layers provides protection from the additional deposition of atmospheric contaminants. However, sampling from the snow and soil contact should be avoided to prevent any disturbance caused by the mineral particles or vegetation. Snow sampling is easy and quick, and it causes minimum environmental impact. Access to some land areas, such as boggy ground, by snowmobile or snowshoes may be easier during winter than in other seasons.

Already in the early 1970’s, snow has been tested as a sampling medium in hydrogeochemical prospecting over sulphide ore deposits (Jonasson and Allan, 1973; Saastamoinen, 1974), but the analytical results contained only a few elements even though they were at ppb levels. Later in the 1980’s and 1990’s, environmental studies on the Barents region included snow sampling for monitoring the anthropogenic and atmospheric deposition of the elements (de Caritat et al., 1998; Gregurek et al., 1998). In those studies, melt water and filtered residue fractions were analysed separately using ICP-MS and ICP-AES techniques giving very characteristic patterns for the different industrial sources (Lindroos et al., 1995; Reimann et al., 1996) but not local metal ion responses from the underlying bedrock. Also, in Canada and Russia, snow has been exploited for environmental studies (Kliza et al., 2000; Zarina et al., 2011). Later on, some tests for the use of selective leach methods in snow analysis were done in Canada providing positive signals in mineral exploration (Yavorskaya and Gale, 2011). However, the use of snow in mineral exploration using modern analytical techniques (*i.e.* single collector high resolution inductively coupled plasma mass spectrometry SC-HR-ICP-MS and high-resolution gas chromatography coupled with mass spectrometry HRGC/MS for Spatiotemporal Geochemical Hydrocarbon SGH) has not been reported.

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McCarthy ad Reimer (1986) have compiled advances in soil gas geochemical exploration. In their paper, for example, it is presented that there are two processes, diffusion and mass transport, how gasses migrate to overburden. In their studies they have also found methane and other light hydrocarbons in soil gas over porphyry copper deposits and disseminated gold deposits. Particular soil hydrocarbons have shown to be specific decomposition products of micro-organisms and that have used the mineralized target in their growth processes (Sutherland, 2011a; Taivalkoski and Sarala 2015a, b). In soils, groundwater and rock, autotrophic organisms thrive at the redox boundaries because they gain metabolic energy from the transfer of electrons from reducing agents to oxidizing agents. In many cases, such organisms include iron and sulphur oxidizing bacteria, which oxidize Fe^{2+} to Fe^{3+} and S^{2-} to S^{6+}, respectively (Hamilton, 2007). In the death phase some of the decomposition products released as hydrocarbon compounds migrate through bedrock and overburden and presumably, into snow pack (Sutherland, 2011a).

Hydrocarbons can be determined using the SGH method, which is based on a classification of the large number of hydrocarbon compounds into indicative groups or signatures known as pathfinder classes. The empirical results of the previous research shows that specific hydrocarbons are associated with certain mineralization types (Sutherland, 2011a). These hydrocarbons are detected by SGH in the sub-ppt (parts-per-trillion) concentration range and determined by HRGC/MS (Sutherland, 2011b). In areas with thick cover, SGH method has been used to measure hydrocarbons and it has yielded responses over deeply buried mineralization (Sutherland, 2011a, b). Sample material used for SGH analysis is collected from the upper part of the soil profile from the same places that are typically used for selective or weak leach methods. However, other material, such as sand, till, submerged sediments humus, and snow can also be used.

The other tested method is direct determination of element concentrations in snow with SC-HR-ICP-MS without pre-processing or leaching techniques. It has been reported that gasses can transport elements and/or metal ions with them and these elements can provide a signature of underlying buried mineralization (Aspandiar et al., 2006). The concentration levels are very low and only the modern analytical methods such as SC-HR-ICP-MS can detect ions at concentrations down to the ppt levels where the responses can be detected.

This paper describes the procedures for of snow sampling and the geochemical results for three test sites in northern Finland: Au-Co, Cu and P-REE . The questions addressed by this study were: a) is it possible to detect the signatures of soil geochemical hydrocarbons and elements in snow and if so: b) are they related to mineralization below? It was also assumed that the optimal sampling depth would be the lowest part of snow pack and that airborne dust would not affect much as the air in the northern Finland is the cleanest in Europe (Anttila, 2014). Repeatability and reliability were assessed by repeating the sampling in two consecutive winters: 2014 and 2015. Using of two very different methods on small surveys, a comparison is shown to provide some insight into use of snow as a sampling media. This study is a contribution to the project ´Ultra low-impact exploration methods in the subarctic’ funded by the Finnish Funding Agency for Technology and Innovation (Tekes) and operated by the Geological Survey of Finland (GTK) and the University of Oulu. The results of the UltraLIM project are presented in Sarala and Nykänen (2014), Sarala and Taivalkoski (2016) and Taivalkoski et al. (2016) and in the project final report (2018 in prep.).

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2. STUDY AREA

Three different types of mineralization, none of them under commercial production, were selected as sampling sites: the Juomasuo Au-Co deposit in Kuusamo, the Kyörtesselkä P-REE occurrence in Savukoski and the Saivel Cu target in Sodankylä. All of the sites are located in northern Finland (Fig. 1).

2.1 Geological settings

The Juomasuo Au-Co deposit belongs to the Kuusamo volcano-sedimentary belt of an Early Proterozoic rift system of the Fennoscandian Shield (Pankka and Vanhanen, 1992). The deposit is hosted by the sericite quartzite formation and is controlled by a NW-SE trending shear zone which has controlled hydrothermal alteration and mineralization (Pankka and Vanhanen, 1992; Fig. 2). Juomasuo is the largest of the known gold deposits in the area and it comprises one major and a number of smaller lodes (Vanhanen, 2001). According to Vanhanen (2001), Au with sporadic Bi is enriched in pyrite within the ore zone. Visible Au is rare. Several elements, e.g. Cu, REEs, U and Ni, are also enriched in this deposit (Pankka and Vanhanen, 1992; Vanhanen, 2001).

The Kyörtesselkä P-REE occurrence is situated in the southern part of the Sokli carbonatite complex in north-eastern Finland. The Sokli complex is about 7 km in diameter and consists of fenite aureole and a three-part carbonatite massif; a transition zone of metasomatites, a metacarbonatite area and a magmatic core (Vartiainen, 1980). The seismic soundings have shown that the complex reaches the depth of six kilometres (Paarma et al., 1981). The latest studies by GTK in the Kyörtesselkä area have proved that weathered, magnetite-rich carbonatite ring dykes are enriched in apatite and have potential for P-REE occurrences and that the apatite-rich carbonatite dykes include weathered apatite near surface and fresh apatite mineralization below (Sarapää et al., 2013, 2015; Fig. 3). . The average P_2O_5 content is 7 wt%.. New trenching results also show that the total REE contents are up to 10.9 wt% at Kyörtesselkä (Sarapää et al., 2015). The REE-carbonatites, ferrocarbonatites and calcium carbonatites have the richest concentrations of Nb (Pynttäri, 2015). Uranium, Th and Zn are also present (Sarapää et al., 2015).

FQM FinnEx Oy has performed mineral exploration of the Saivel Cu mineralization. The target is located close to the Kevitsa Ni-Cu-PGE Mine in northern part of Sodankylä. The bedrock in the Saivel target area consists of gabbros of the Kevitsa intrusion (Mutanen, 1997), carbonaceous schist, phyllites and mafic volcanic rocks. The gabbro unit, which has intruded into these Matarakoski metasediments, is highly fractured and weathered. Biotite-amphibole alteration is common and thin zones of altered mafic volcanic rocks have broken up the unit. The upper portion of the metasediments surrounding the gabbro is best described as carbonaceous phyllite. The amount of graphite increases with depth and rocks become pyrrhotite rich. The Saivel target is thought to comprise a thin shallowly NE dipping copper mineralized zone (Fig. 4) hosted solely within the gabbroic unit. Levels of Cu and other base metals are very low in the black schist. (T. Lehtilä, personal communication, November 2015).

3. MATERIALS AND METHODS

3.1 Sampling

Activation Laboratories (Supplementary reports Taivalkoski and Sarala, 2015a, b) recommends that the snow collected for the SGH analysis should be at least three weeks old to form clear signals. Due to this, the snow sampling was conducted over two years in late winter: in March-April 2014 and in March 2015. The numbers of sampling points were as follows: 38 points in Juomasuo (Fig. 2a) and Saivel (Fig. 4), and 51 at Kyörtesselkä (Fig. 3). The spacing between the sampling points varied from ten meters over mineralization to a maximum of about 200 meters over inferred background. In 2015, the sampling was repeated at all three sites: however, at Kyörtesselkä the sampling was repeated only on the western line. Two to six field duplicate samples were taken from all sampling areas. The samples were analysed by the SGH method at Activation Laboratories Ltd., Canada, and in 2015 samples were also collected for SC-HR-ICP-MS analysis, that were conducted in the Research Laboratory of GTK, Finland.

The snow sampling was done using a modified acrylic tube (50 mm in diameter; one meter in length) sampler, which enables taking the samples from the bottom of a snow layer, about 10 to 20 cm above the soil surface. All visible minerogenic or organic material was avoided during the sampling as snow samples must not have any sediment or foreign material present in the survey samples. The sample was dropped from the tube into a 120 ml sized polypropylene jar. Similar jars were used for the samples for SC-HR-ICP-MS analysis, but before sampling they were acid cleaned as follows: The jars and caps were washed with DI-water three times. After washing, they were soaked in Suprapur nitric acid (7 mol/l) for three days and washed again with DI-water for five times. After treatment, the jars and caps were dried and sealed in plastic bags.

The samples were kept frozen before analysis and were sent in cool boxes to the laboratories. The samples melted during the transport to Activation Laboratories Ltd, Canada and arrived in liquid form at the laboratory. The samples sent for SC-HR-ICP-MS analysis, arrived still frozen at the laboratory.

The daily observations of snow depth and minimum and maximum temperatures in three observatories (Lokka in Sodankylä, Kiutaköngäs in Kuusamo and Ruuvaoja in Savukoski; Finnish Meteorological Institute, n.d.) show that in the early winter 2013 temperature has risen above 0°C causing thinning of the snowpack; likewise in the early winter 2014. Similar warm periods have been observed in February-March 2014 and 2015. However, during sampling in late winter 2014 the depth of snow varied between 59 cm and 71 cm and in 2015 between 66 cm to 84 cm. Based on the observations during the sampling, the snow depth varied between 45 and 92 cm in Saivel; 34 to70 cm in Juomasuo and 40 to73 cm in Kyörtesselkä. Mean monthly temperature (1985-2014) in Sodankylä region stays below 0°C at least from November to April (Vikhamar-Schuler, et al. 2016).

3.2 Sample preparation and analyses

3.2.1 Spatiotemporal Geochemical Hydrocarbons (SGH)

The 120 ml snow sample provides approximately 50 ml of water. A particulate free sample of about 8 ml was taken and an aliquot of this was used for analysis; the rest is stored. The analysis consists

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of an extraction, separation of the hydrocarbons compounds by high resolution capillary column gas chromatography and detection by mass spectrometry. The 162 hydrocarbon compounds are grouped into 19 SGH subclasses, for example specific alkanes or polyaromatic compounds. The combination of multiple SGH subclasses that have been associated with presence of specific mineralization are called SGH pathfinder classes, and they are used to detect signals of different types of mineralization. A set of hydrocarbon subclasses that together form a geochemical signature and has been associated with the presence of particular type of mineralization, is called template. To conduct the interpretation in a timely fashion the type of mineralization of exploration interest is noted and that template is used. Multiple interpretations can be made from the same data for extra cost. (Supplementary report Taivalkoski and Sarala, 2015a, b). The SGH method is proprietary, it is not possible to describe the method in full detail.

In the case of Juomasuo, interpretation based on the Au template was requested. A Ni template was requested for the Saivel target due to its' location next to Boliden Kevitsa Ni-Cu-Au-Pd-Pt mine and it was complemented with the Cu template. Kyörtesselkä is a potential P-REE mineralization and the laboratory was initially requested to interpret it as a polymetallic target since there was no template available for P-REE mineralization type. However, this signature had previously been developed for Cu, Pb and Zn deposits. In 2016, it was realized that the P-REE mineralization at Kyörtesselkä was very complex and the interpretation using an SGH polymetallic template was not appropriate. This resulted in a development of a customized REE template for reinterpretation of the SGH data in 2016.

3.2.2 Single collector high resolution mass spectrometry (SC-HR-ICP-MS)

The snow samples were melted for the inorganic analysis and 10 ml of samples were filtered into 15 ml plastic tubes using a disposable, sterile 0.8/0.2 µm filter and syringe. Normal parameters of operation of the ICP-MS include the use of an auto sampler, a peristaltic pump and a Disolvator nebulizer which improve the sensitivity by a factor of 5 in comparison with a traditional Meinhard nebulizer. A pair of Cu-Ni sampler and skimmer cones from Precision Glassblowing was used. As a consequence, the detection limits for these two elements was improved. Analyses were performed in a peak jumping mode using 500 sweeps of 10 ms in five cycles. The used element menu consists of 92 isotopes from 59 elements. Several non-isobaric isotopes of the same elements were used in order to correct for potential interferences. Washing time was about 3 min, and a further 90 s of sample uptake was allowed before measurement started. Two percent nitric acid was produced from double-distilled (sub-boiling) concentrated acids and deionised Milli-Q water (resistivity of ≥18.2 MΩ•cm). This acid was used for flushing the instrument in between the samples and standards. Blank values were used to blank-subtract the standard and sample data to remove any carryover effect from previous samples. The samples were split into five sequences of about 20 samples each. The limits of detection (LOD) were calculated as three times the standard deviation and averaged over the sequences. Element concentrations are reported in part per trillion (ppt) units.

3.3 Quality control

All the quality control procedures and the overall precisions of the SGH analysis for each sampling sites are presented in laboratory reports of Activation Laboratories Ltd. (Supplementary reports Taivalkoski and Sarala 2015a, b). Activation Laboratories Ltd. uses laboratory replicate analysis

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and laboratory materials blank (LMB-QA) as a measure of SGH data quality within the laboratory. For the laboratory replicates, an equal aliquot of a sample is analysed and the estimate for method variability is reported as a percent coefficient of variation (%CV, Table 1), which is calculated from pairs of replicate samples that have hydrocarbon values ≥ 0.2 ppt as twice the value of the reporting limit. The reporting limit for the snow SGH results is 0.1 ppt. The same method is used for reporting the variability of field duplicate samples.

A 10 ppt standard solution has been used as a quality control for the trace element analysis by SC-HR-ICP-MS. The quality control sample was measured twice at each run of 20 to 24 samples: at the beginning, middle or at the end of the analysis sequence. This standard solution covers most of the periodic table. It was prepared from single and multi-elemental solutions and diluted down to 2% with concentrated (65%) double distilled nitric acid and MQ water. Blank nitric acid aliquots have been measured before every batch of samples and standards. The blank values were used to blank-subtract the standard and sample data. Eleven field duplicate samples were analysed in the same batch together with other samples.

The %CV were calculated for SC-HR-ICP-MS results using field duplicates from two of the three sites (Table 2). The %CV values are high in both groups, because the concentrations in the snow are very low, close to our clean room acid blanks. The blank contribution on the total signal could be up to 85%. The reproducibility on the measured concentrations is strongly dependant on the reproducibility of the acid blanks, which is sensitive to parameters such as unpredictable long term carry over contamination.

3.4 Data Analysis

Activation Laboratories Ltd. delivers the results of SGH analysis in Excel files and as standard reports with separate SGH class maps for each study area (see supplementary reports Taivalkoski and Sarala, 2015a, b). A Kriging algorithm in the Geosoft Oasis Montaj mapping software was used to trend the data on the maps. The objective with SGH is to identify zones where the agreement between specific SGH classes identifies the presence of the type of mineralization of interest. Activation Laboratories did not know the position of the mineralization at these study sites prior to issuing a report. SGH predictions of mineralization were only based on SGH results.

In this study, the sampling was conducted as lines and thus the interpolated SGH class maps do not necessarily provide a realistic impression of the results: the Kriging interpolation of SGH may produce values in areas without sampling points and depending on the Kriging blanking distance used, the area where the interpolation extends around sampling lines may be unrealistically wide. Therefore, in this paper, the results are presented as scatter plots conducted from the different pathfinder class data delivered in Excel files by Activation Laboratories. It should be noted that the use and evaluation with single sample lines does not allow a proper spatial interpretation of anomalies using the interpretation method of 3D-SGH.

The SC-HR-ICP-MS results (see electronic appendix) of snow samples were viewed in two different ways. The results were compared with the mineralized zones as summed concentrations where the elements in each mineralization style were summed for each sample. Pathfinder element associations for each styles of mineralization (e.g. Koljonen, 1992) are presented in Table 3.

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Response ratio (RR; Mann et al., 2005) values were used on the scatter plots to highlight elevated concentrations. The response ratio is a ratio of an element concentration in a sample to the background value of each element and was calculated with a following formula:

RR= an element X concentration in a sample / (mean (1st quartile of an element X concentration in a test area))

The RR value was calculated separately for each element and separately on all three test areas. A concentration is considered to be elevated, if the response ratio value is more than five (Sarala et al., 2008). The RR values were compared simply by observing the magnitude of the values over the known mineralization.

4. RESULTS

4.1 SGH results

Two SGH pathfinder class maps are presented for the Juomasuo target (Supplementary report Taivalkoski and Sarala, 2015a). The pattern of the elevated values is quite similar in both of the maps, they show a response over the Au mineralization that is located in depth of 150-200 meters (Fig. 5a-b). The zone having the SGH Au signature was depicted over this mineralization target (Supplementary report Taivalkoski and Sarala, 2015a). The concentrations become elevated over the subcropping mineralization only in one data set, and hence the subcropping mineralization area has probably not been interpreted as a potential Au anomaly. However, the use of a single sampling line neither allows the more detailed 3D-SGH interpretation procedure.

Only one SGH class map was initially produced for Kyörtesselkä using the Polymetallic template. According to the laboratory (Supplementary report Taivalkoski and Sarala, 2015a), it was complex to interpret due to a lack of suitable P-REE template. The interpreted SGH response is of a polymetallic signature over the silicate-apatite mineralization on the western line. The same zone with the similar glacial overburden on the eastern line does not show a corresponding response in the results. (Supplementary report Taivalkoski and Sarala, 2015a; Figs. 5c-d: Polymetallic class data). A 2016 reinterpretation of the SGH results, using a customized REE template shows weakly elevated concentrations over both mineralization types on the both sampling lines (Figs. 5c-d: REE class data) The high concentrations on the northernmost sampling point on the western line maybe due to location on the carbonatite bedrock (Fig. 5c: REE class data). However, no SGH REE response was delineated. This is the possibly due to the use of the new SGH template developed for this site that had not been previously tested.

Two SGH pathfinder class maps and data produced two different interpretations from the Saivel target (Taivalkoski and Sarala, 2015a). The Ni template returned an extremely weak signal (Fig. 5e).The Cu template shows relatively elevated concentrations over the Cu mineralization (Taivalkoski and Sarala, 2015a; Fig. 5f). Note that the SGH interpretation does not rely on any one class map as SGH signatures are made up of multiple class maps. Not all the class maps are shown in this paper.

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4.2 Repeatability of SGH Signature

At Juomasuo, the 2015 results, show that the SGH Au responses occur in markedly different places on the two class maps (Taivalkoski and Sarala, 2015b) than those presented in 2014. However, they are located over the Au mineralization at a depth of 40-60 m and the subcropping mineralization, but equally high values occur also in the area without any known mineralization underneath (Figs. 6a-b). The hydrocarbon concentrations (ppt) are in different level (Figs. 6a-b) compared to the 2014 results.

On the initial interpretation at Kyörtesselkä, using a Polymetallic template, response was defined in the middle of the sampling line partly over the silicate-apatite zone (Taivalkoski and Sarala, 2015b). Scatter plot show very little variation in results (Fig. 6c: Polymetallic class data). The re-analysis using the customized REE template revealed some elevated SGH concentrations over the mineralized zones (Fig. 6c: REE class data), but no SGH response was delineated in the standard report delivered by the laboratory.

The SGH interpretation of Saivel using the Ni template shows a very low contrast signal and no repeatable patterns between the 2014 and 2015 surveys (Fig. 6d, Supplementary report Taivalkoski and Sarala, 2015b). The second interpretation using the Cu template delineates the known Cu mineralization with a higher contrast signal (Fig. 6e). The response appears to have a rabbit-ear form.

4.3 Metal concentrations in snow

The summed concentrations (see Section 3.4) of elements (ppt) characteristic of P-REE deposits do not show a clear difference between the P-REE and Cu deposits (Fig. 7a) and presumably, are low in the Au deposit. The Saivel target has evidently higher concentrations characteristic for a Cu deposit (Fig. 7b). The concentrations related to Au mineralization are the lowest at Juomasuo (Fig. 7c), but still they show a single peak anomaly over the subcropping Au mineralization (Fig. 7d).

The RR values (see Section 3.4) for Cu show a strong positive anomaly over the Cu anomaly at Saivel. Also at Juomasuo, a spiky Cu anomaly is formed close to the deep mineralized zones (Fig. 8a), which include up to 0.7 % Cu based on the drilling. The subcropping mineralization in Juomasuo stands out as high As, U, Pb and Fe RR values (Fig. 8b-c). Although the concentrations of Pb, U, Ni, Cu, Ce and Fe in Juomasuo are mostly below the detection limit, they do show detectable concentrations over the mineralized zones.

Iron has elevated RR values at Kyörtesselkä over the silicate-apatite soft ore zones as well as over the carbonatite dyke (Fig. 9). Iron is ubiquitous and thus not a good pathfinder element, but in this case the elevated response ratio values of Fe are over the soft silicate-apatite zones enriched in magnetite and thus appear to reflect the bedrock below. The high Fe concentrations occur also sporadically over carbonatite dykes (O. Sarapää, pers.comm., January 2016). Cerium was one of REEs with concentrations above the detection limit and the elevated RR values can be observed in Kyörtesselkä over the silicate-apatite ore contact and over the northern zone of silicate–apatite soft ore (Fig. 9).

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5. DISCUSSION

The sampling of snow has a negligible impact on the environment. The collection of snow samples is quick and convenient: an acrylic tube is light to carry as are the snow samples themselves. No machinery is needed. Therefore, sampling can be implemented in sensitive areas. Snowmobiles can be used for access to sites, but it is advisable to leave them at some distance from sampling points to avoid the contamination of samples. In sensitive areas, sampling sites can be approached without motor vehicles. As a down side, its use is possible only in the areas where snow covers landscape for a long enough time to allow metal ions and soil hydrocarbons to accumulate. In northern Finland, snow stays on the ground for at least three months, which makes the methodological testing optimal and ensures that signals have enough time to form if the sampling is done in late winter or early spring before the thaw. In large areas of the northern hemisphere, the winter season is long enough to make snow sampling feasible, but over the past few years the winters have been milder in southern Finland with unpredictable snow conditions which can complicate sampling. The guideline of three-week-old snow applies to snow sampling in the areas where the snow pack does not last several months.

It is promoted that SGH method is a deep penetrating geochemical method (Taivalkoski & Sarala 2015a, b). In the case of Juomasuo, the elevated SGH results in 2014 have a response with gold mineralization at about 200 m below the surface (Fig. 2a). In Kyörtesselkä, the overburden overlying the weathered bedrock is widely contaminated with weathered material and it is possible that the sampling lines were not long enough to reach true background and thus clear differences between the background and the mineralized zones are not observed. In advance it was known that the Polymetallic template used was not appropriate to locate REE targets. In addition, the mineralization is subcropping and according to Sutherland (Taivalkoski & Sarala 2015a, b) shallow targets typically have a reduced SGH signal. The REE template was an improvement but still needs more work. At Saivel the requested Ni and Cu templates give different results: SGH did not show any Ni mineralization but did show the elevated SGH concentrations above the Cu mineralization. SGH can be used as a general exploration tool as several different templates may be used in the interpretation of the same data. However, many mining companies are specifically interested in locating a particular type of mineralization based on their knowledge of the geology of the area.

In the repeat sampling results, the location of the mineralization in the 2014 survey was not replicated in 2015: the responses were in different places. In Juomasuo the subjective interpretation located the gold mineralization, but the deep mineralized structure was not shown in the second sampling campaign. At Saivel, the Ni zones were defined on different sides of the known Cu mineralization (Taivalkoski & Sarala 2015a, b). The SGH zones in Kyörtesselkä were overlapping, but the zone interpreted from the repetition samples did not have any known bedrock response. One reason for unsuccessful repeatability in Kyörtesselkä and Saivel is that at first the SGH template used was not the most suitable for those targets. In the case of Saivel, the better results were achieved when the reinterpretation was done using the Cu template better reflecting the targets' mineralization style. The customized REE template used in Kyörtesselkä returned higher concentration compared to Polymetallic template.

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The interpolated maps (Taivalkoski and Sarala 2015 a, b) show the elevated SGH values clear. The scatter plots (Figs. 5-6) give more realistic image of the results: all of the SGH results do not show much of a variation. Detecting the SGH zones for different types of mineralization from the scatter plots would probably result in a different results.

The originator of SGH at Activation Laboratories Ltd. recommends grid sampling or a series of transects for the SGH method to be used effectively. This enables a review of the results from a 3D-SGH perspective to observe the symmetrical anomalies which also adds confidence to the interpretations (Taivalkoski and Sarala, 2015b). On the other hand, grid sampling would not explain the variation, i.e. the difference of the hydrocarbon concentrations at the same sampling points between the years. As SGH is a semi-quantitative technique and not an assay method, variation in individual concentrations is acceptable since the more important result for exploration is the repeatability of patterns over the mineralization. It should be noted that the SGH interpretation conducted by Activation Laboratories for Juomasuo was conducted without any knowledge of the location of the mineralization. In this study it was not possible to test grid sampling, but it is recommended for future surveys to test whether repeatability would be better in that case.

The tested SGH method differs from conventional geochemistry in two ways: instead of element concentrations the concentrations of soil hydrocarbons are measured, and the Excel files including the concentrations are delivered to a client together with interpolated (Plan and 3D view) maps. Results also include an interpretation with a subjective confidence rating (1.0 (poor) – 6.0 (the best)) in the possible occurrence of the mineralization requested for interpretation and the illustration of the estimated location of the target as a vertical projection. The interpretation compares several SGH classes together to produce a mineralization signature and uses empirical experience of the use of certain hydrocarbon classes typical for different types of mineralization. The SGH rating includes the confidence obtained from the multi-measurement and multiple chemical class signatures as well as the assessment of the sampling survey, i.e. a small single sampling line survey will result in lower confidence result than a larger multiple transect or grid survey. Although the SGH report is detailed, for customers it can be difficult to review the results and make conclusions of their own.

Promising results were achieved with the SC-HR-ICP-MS method. The aim of the testing was to find out if the mineralization in each of the test areas is reflected in the elemental composition of snow. Using a specific set of pathfinder elements for each type of deposit we have shown that the overall abundances of these pathfinder elements were at their highest concentration in the Kyörtesselkä and Saivel (Fig. 7a-b). Although the Au deposit has the lowest concentrations of pathfinder elements (Fig. 7c), they show a well define spike above the mineralisation (Fig. 7d). However, further studies are needed to improve the selection of these pathfinder elements for specific types of mineralization, based on their regional geology settings. A limitation to the obtained results was that most of the concentrations of REEs among some other elements are below the method detection limit. In addition, due to isobaric interferences inherent to the analytical technique, critical elements such as P and S could not be measured at sufficiently low concentration. Although the samples were filtered before analysis, based on this test, it is not possible to estimate if airborne dust affects the results. Based on the studies of Jonasson and Allan (1973), airborne particulates contribute an insignificant amount of metals to snow strata. However,

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air pollution does not discriminate between mineralised and non-mineralised environment and introduce a systematic bias to the overall dataset, which will not modify the calculated response ratio. Only samples collected in 2015 were analysed with SC-HR-ICP-MS, the repeatability of the method was not tested.

Both of the tested methods showed elevated values also in the areas where there is no information about mineralizations. It would increase reliability of the methods if there would be an explanation for them. Drilling data from the whole testing area would help to understand the result better, but often they are not available.

The combination of using snow as a sampling medium and analysing it with SC-HR-ICP-MS can be considered as a potential method for exploration purposes in the near future. Sampling quality is the main key to achieving interpretable results. As the element concentrations in snow are at ppt levels, any contamination during sampling needs to be avoided. Further testing and improvement need to be done to enhance the results by lowering blanks levels and detection limits and by improving the quality of acids and the cleaning protocols of the equipment used. Preconcentration by evaporation should be also tested. Focusing on some specific elements at the expense of other less sensitive elements during the analysis could also enhanced the sensitivity of the technique.

In both sampling years the mild periods, when the temperature rose above 0°C, occurred several times during winter. This has caused thinning of the snowpack for few centimetres (Finnish Meteorological Institute, 3.7.2018) at the beginning of the snow seasons and during winter causing thickening of snow pack, but at the sampling time the thickness of snow pack was approximately the same in both years. Based on the observations made during sampling, thin layers of ice or icy snow have existed. Also gravel snow at the base of the snowpack has been observed. Instead, observations have not been made from ice layers between soil and base of the snowpack. It is suggested (van Bochove et al., 2001) that in certain conditions basal ice layer, formed at the soil and snow interference, can be impermeable to gas diffusion. This may also affect the migration of soil hydrocarbons and metal ions from soil to snowpack and thus in future sampling campaigns gathering up information of different ice layers and lenses should be done.

In this study it was not possible to test different snow layers to find out the most suitable sampling depth for both analytical methods. By testing different layers, the effect of airborne dust could be better estimated. In addition, more studies are needed to increase knowledge of the processes behind the mobile metal and hydrocarbon migration through the overburden into surface and accumulation into snow.

Similar glaciated terrains with snowy winter conditions exist in large areas of the northern hemisphere, which increases the potential interest in the use snow as a sampling media for mineral exploration.

6. CONCLUSIONS

In the UltraLIM project, snow was tested as one ultra-low impact method for exploration. The collected samples were analysed by two methods: Spatiotemporal Geochemical Hydrocarbons

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(SGH), created by Activation Laboratories Ltd., which measures hydrocarbons in samples and SC-HR-ICP-MS, performed at GTK´s Research Laboratory, for elemental analysis. The first sampling round was conducted in 2014 and it was repeated in 2015.

The SGH method produced encouraging results at the Juomasuo and Saivel test areas for both years, however the concentrations differed between campaigns (as the technique is semi-quantitative). Nevertheless, the SGH signatures for Au at Juomasuo and for Cu at Saivel were generally repeatable. In the original SGH results of Kyörtesselkä a Polymetallic template was used with poor results. When a more customized REE template was developed and used, reinterpretation of the results defined positive responses over the mineralization. Use of the requested SGH template for Ni at Saivel resulted in uncertain results which were repeated in the 2015 survey. As SGH does not typically review all of the available signatures of identification, it is important to request an interpretation using an SGH signature that reflects the mineralization sought. SGH is a targeted technique as most mining companies explore for a specific type of commodity based on their knowledge of the geology. SGH includes the provision of a mandatory interpretation that is to say that an interpretation of the analytical results is delivered to a customer together with analytical data. This study illustrates that multiple interpretations can be made on the results without reanalysis. Still, more studies are needed to define the capability of locating different types of mineralization with the SGH method. The weaknesses of this method are that results were not repeatable and that the method is proprietary: a more open demonstrations of how interpretations are created, would make this method more attractive as an exploration tool.

The SC-HR-ICP-MS method can be used for detecting direct element concentrations in snow. Instead of absolute values, response ratio (RR) values were calculated to observe the changes in the elemental concentrations over the mineralized zones. E levated RR values related to mineralization were observed at all sites: As, U and Cu in Juomasuo; Cu in Saivel; Fe and Ce in Kyörtesselkä. The SC-HR-ICP-MS method was tested only for the samples taken in 2015, hence the repeatability of this method could not be tested. In addition, to achieve the best practices for analysing snow with this method, further method development is needed.

In mineral exploration, snow sampling should be a supporting method together with other geological, geophysical or geochemical approaches. To merit a reliable status for snow in mineral exploration, not only the analytical methods should be open and reliable but also additional studies are needed to understand the different factors affecting to final results: the interaction between snow and soil surface and underlying bedrock, accumulation processes of hydrocarbons and ions, the effect of ice layers and lenses and to define the optimum sampling depth.

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FIGURE CAPTIONS

Figure 1. The locations of Juomasuo, Kyörtesselkä and Saivel targets in northern Finland.

Figure 2. The snow sampling locations at Juomasuo (a) on the top of the surface projection of the lithological map and (b) on the top of the cross section of the lithology (y-axis shows depth in m). Figures by Olli Pajula and Pentti Grönholm (Dragon Mining), Maarit Middleton and Viena Arvola (GTK). Coordinate system: Finnish KKJ.

Figure 3. (a) Surface projection of the lithological map and the location of the snow sampling lines in Kyörtesselkä. The position of silicate-apatite ores and silicate-apatite soft ore in ring dikes is estimated from diamond and percussion drilling of weathered rock and chemical analyses. (b) Cross section of the lithology under the sampling line at western sampling line and (c) at eastern sampling line in Kyörtesselkä. Coordinate system: EUREFFIN. Bedrock map: O. Sarapää, GTK.

Figure 4. The lithological map and the location of the snow sampling points in Saivel. The original bedrock map of the Saivel target is part of Bedrock of Finland – DigiKP that has been modified by T. Lehtilä, FQM FinnEx Oy. Coordinate system: EUREFFIN.

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Figure 5. SGH pathfinder class data for different mineralization in 2014 plotted as scatter plots against distance: (a-b) two different Au class data at Juomasuo; (c) the western sampling line and (d) the eastern sampling line at Kyörtesselkä with logarithmic Y axis; (e) two different Ni different class data and (f) Cu class data at Saivel.

Figure 6. SGH pathfinder class data for different mineralizations in 2015 plotted as scatter plots against distance: (a-b) two different Au class data at Juomasuo; (c) the western sampling line at Kyörtesselkä; (d) two Ni class data and (e) Cu class data at Saivel. Legend of the mineralized zones for each site as in the figure 5.

Figure 7. The summed up overall concentrations (ppt) of elements related to (a) P-REE, (b) Cu and (c) Au deposits presented as Tukey's boxplots (Tukey, 1977). (d) Summed up overall concentrations (ppt) of elements related to Au mineralization in Juomasuo, presented on scatter plot.

Figure 8. The RR values (Y axis) of Cu, As and U in Juomasuo. Legend for the mineralization zones as in Fig 5b.

Figure 9. The RR values (Y axis) of Fe and Ce in Kyörtesselkä. Legend for the mineralization zones as in Fig 5d.

TABLE CAPTIONS

Table 1. The percent coefficient of variation (%CV) of laboratory replicate (LR) results and field duplicates (FD) in both years, n = number of field duplicates. The SGH results.

Table 2. The percent coefficient of variation (%VC) of some elements of the field duplicates in Saivel and Kyörtesselkä. The SC-HR-ICP-MS results.

Table 3. Pathfinder element associations for each styles of mineralization (e.g. Koljonen, 1992).

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Table 1

Test area	2014			2015		
	LR	**FD**	**n**	**LR**	**FD**	**n**
Juomasuo	5.1	5.5	6	3.5	12.9	6
Kyörtesselkä	5.8	4.8	5	6.4	6.8	2
Saivel	3.6	4.4	6	3.3	12.7	4

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Table 2

	Fe	Ni	Cu	As	U
Saivel	73.7	139.4	67.3	45.3	57.8
Kyörtesselkä	52.3	96.3	101.0	57.8	71.4

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Table 3

	Mineralization type		
	P-REE	**Au**	**Cu**
Elements	Sc, Sr, Y, Zr, Nb, Ba, Lu, Hf, Ta, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb	As, Se, Ag, Au, Sb, Te, Bi	V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Os, Ir, Pt

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Highlights

- This study provides snow as a potential new sampling media for mineral exploration.
- The SGH and SC-HR-ICP-MS methods can observe the traces of mineralization in snow.
- The use of snow geochemistry have a negligible impact on the environment.

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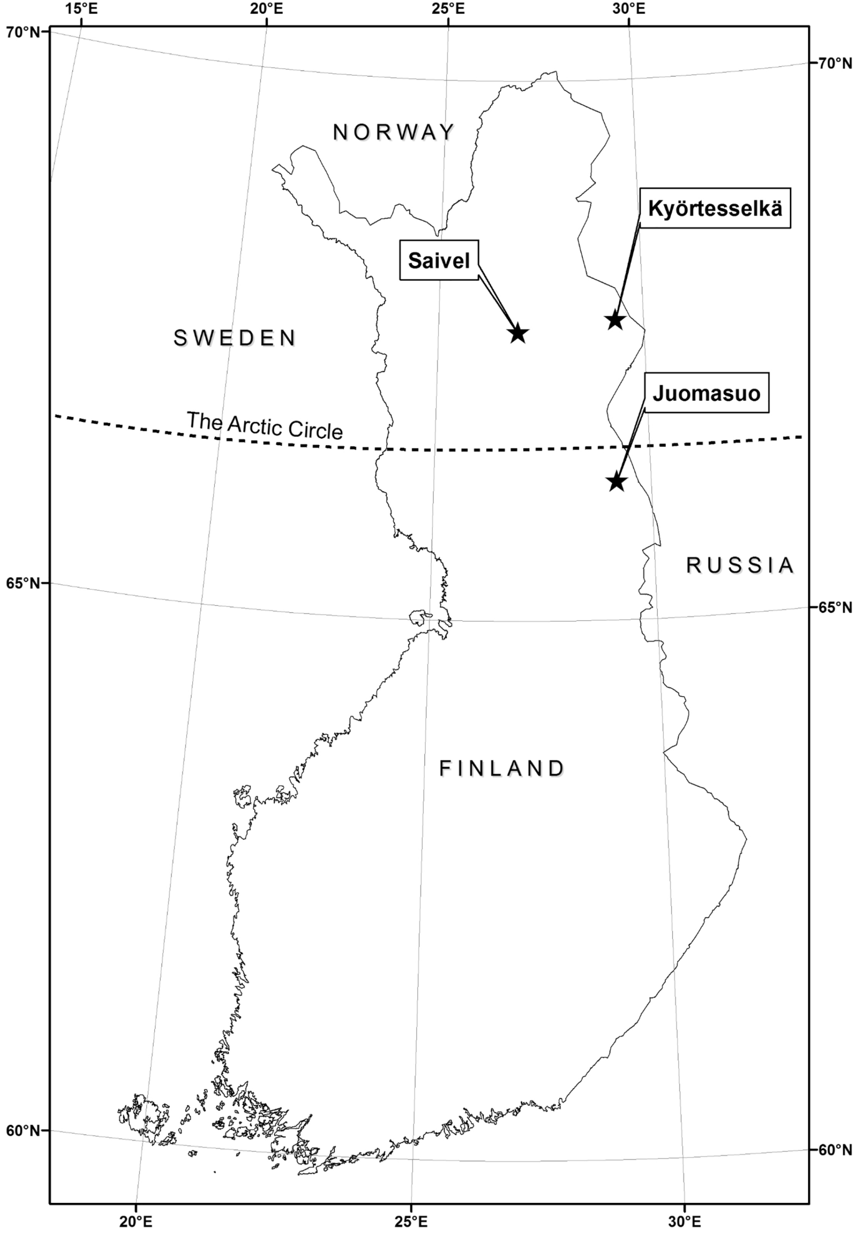
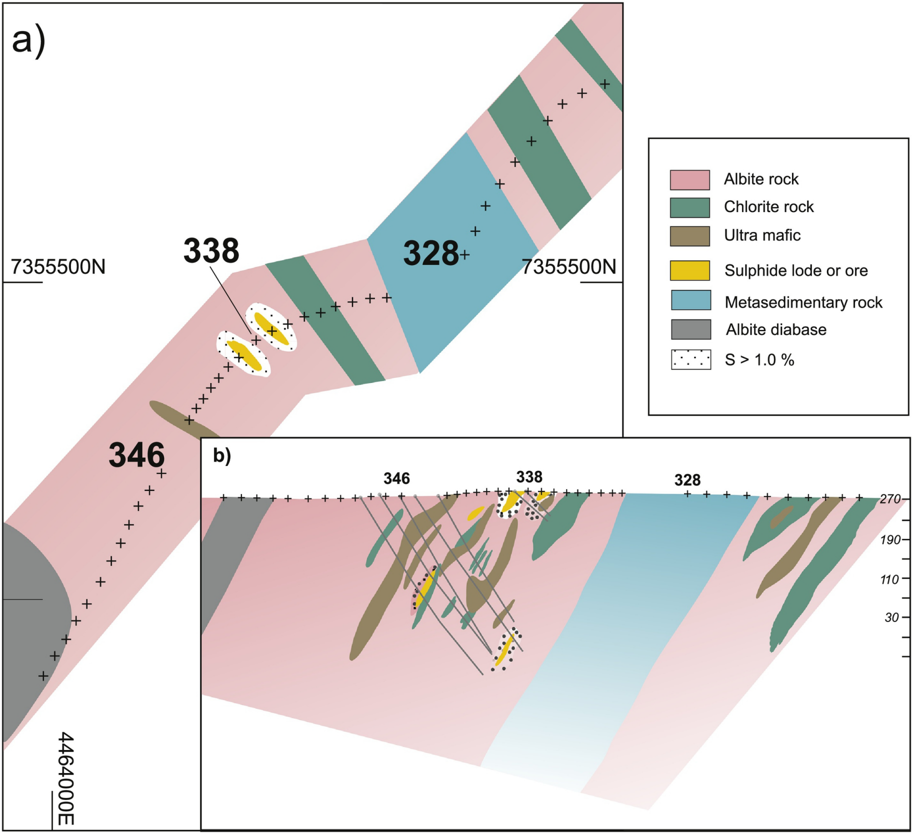

15°E
20°E
25°E
30°E
70°N
70°N
NORWAY
Kyörtesselkä
Saivel
SWEDEN
Juomasuo
The Arctic Circle
RUSSIA
65°N
65°N
FINLAND
60°N
60°N
20°E
25°E
30°E

Figure 1


a)
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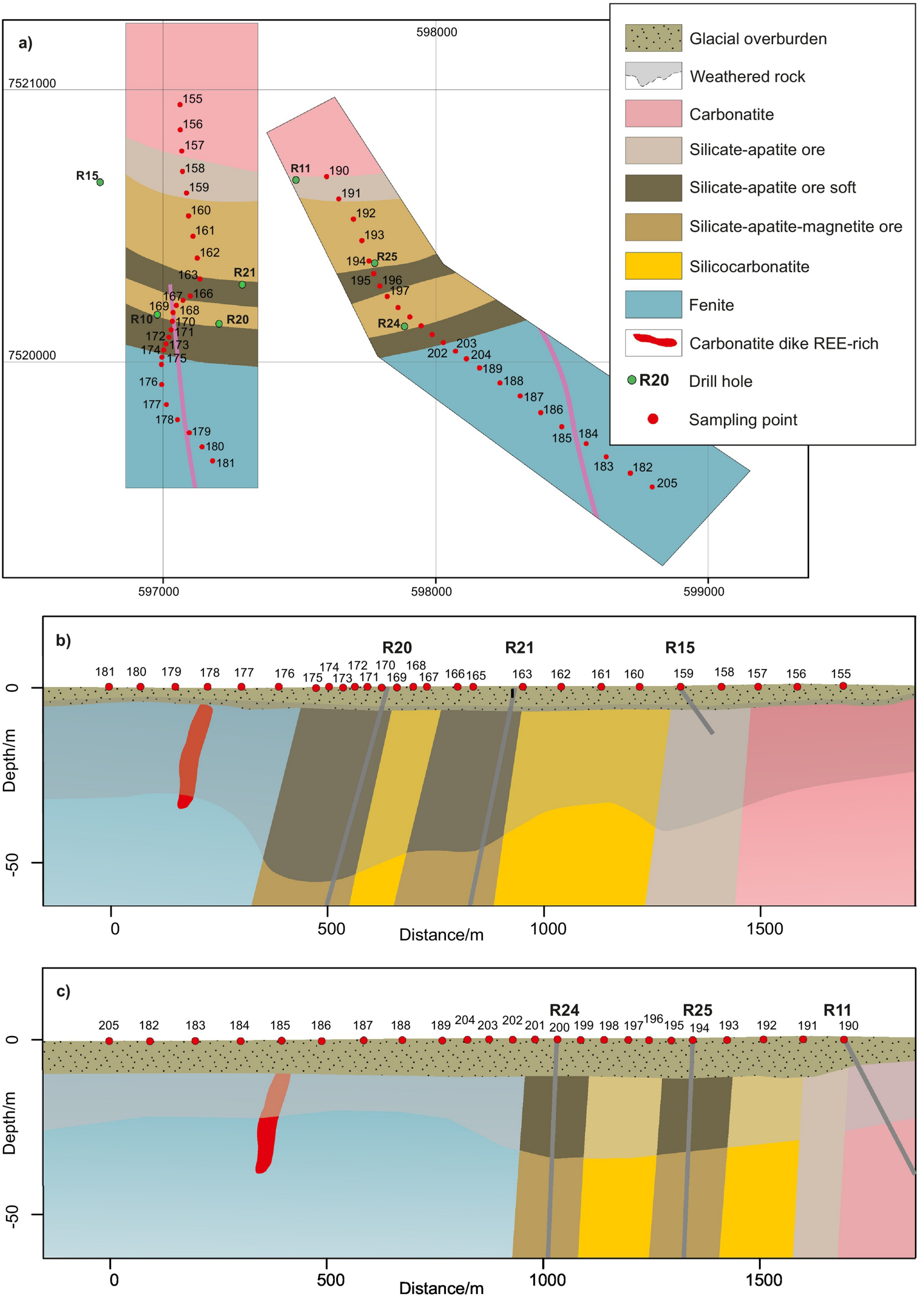
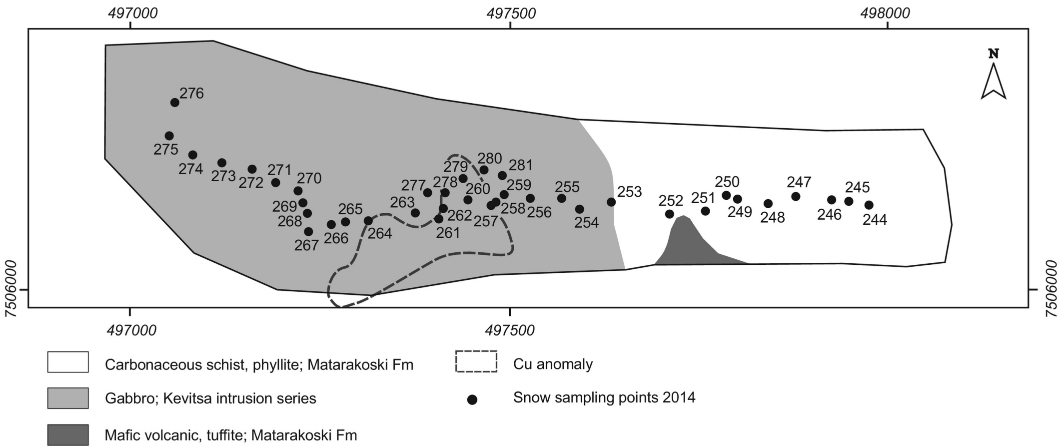
328
346
7355500N
7355500N
4464000E
Albite rock
Chlorite rock
Ultra mafic
Sulphide lode or ore
Metasedimentary rock
Albite diabase
S > 1.0 %
b)
346
338
328
270
190
110
30

Figure 2



a)
598000
7521000
7520000
597000
598000
599000
R15
R21
R10
R20
R11
R25
R24
Glacial overburden
Weathered rock
Carbonatite
Silicate-apatite ore
Silicate-apatite ore soft
Silicate-apatite-magnetite ore
Silicocarbonatite
Fenite
Carbonatite dike REE-rich
R20 Drill hole
Sampling point
b)
R20
R21
R15
Depth/m
Distance/m
0
-50
0
500
1000
1500
c)
R24
R25
R11
Depth/m
Distance/m
0
-50
0
500
1000
1500

Figure 3


497000
497500
498000
N
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245
244
7506000
Carbonaceous schist, phyllite; Matarakoski Fm
Gabbro; Kevitsa intrusion series
Mafic volcanic, tuffite; Matarakoski Fm
Cu anomaly
Snow sampling points 2014

Figure 4

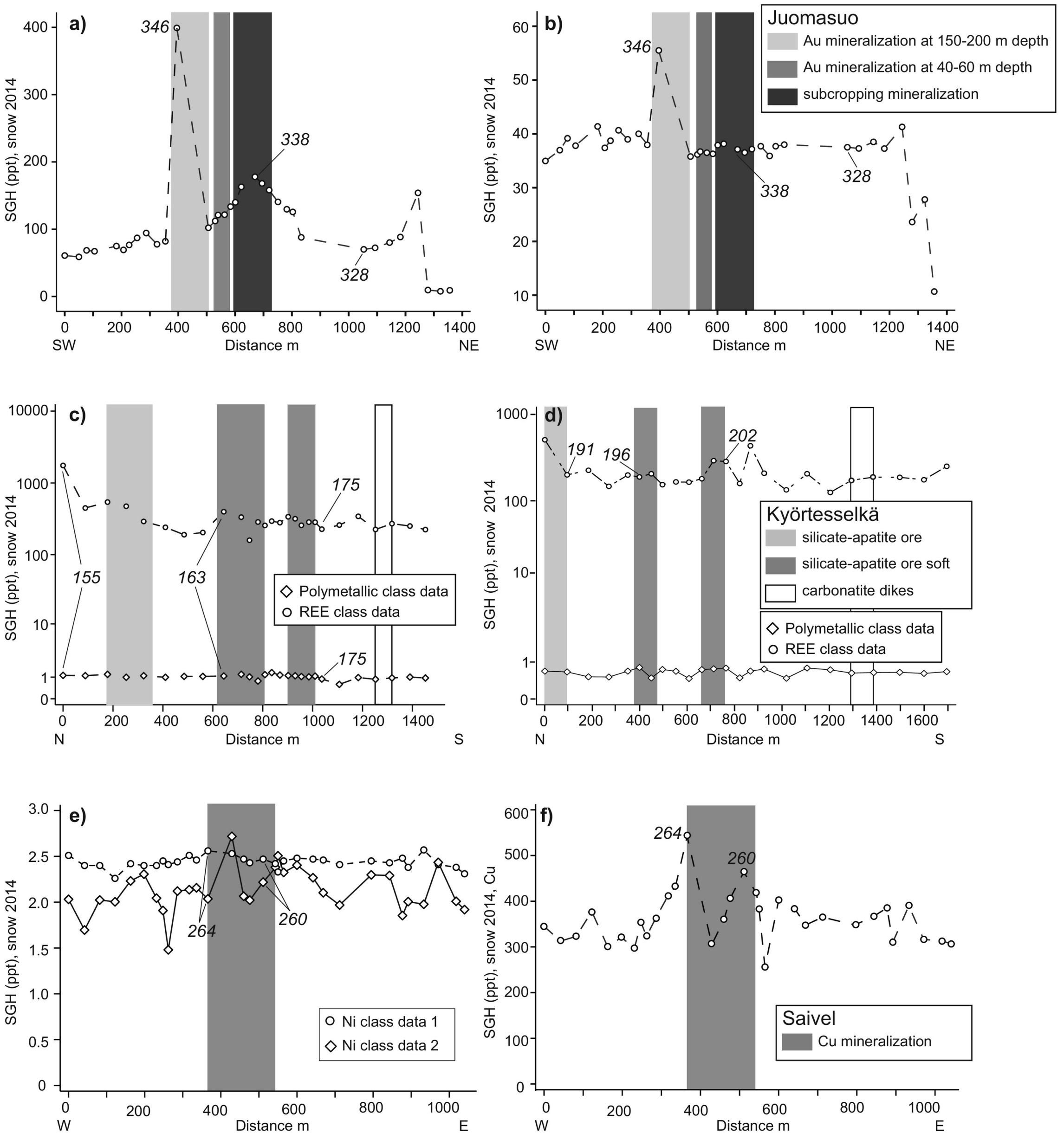
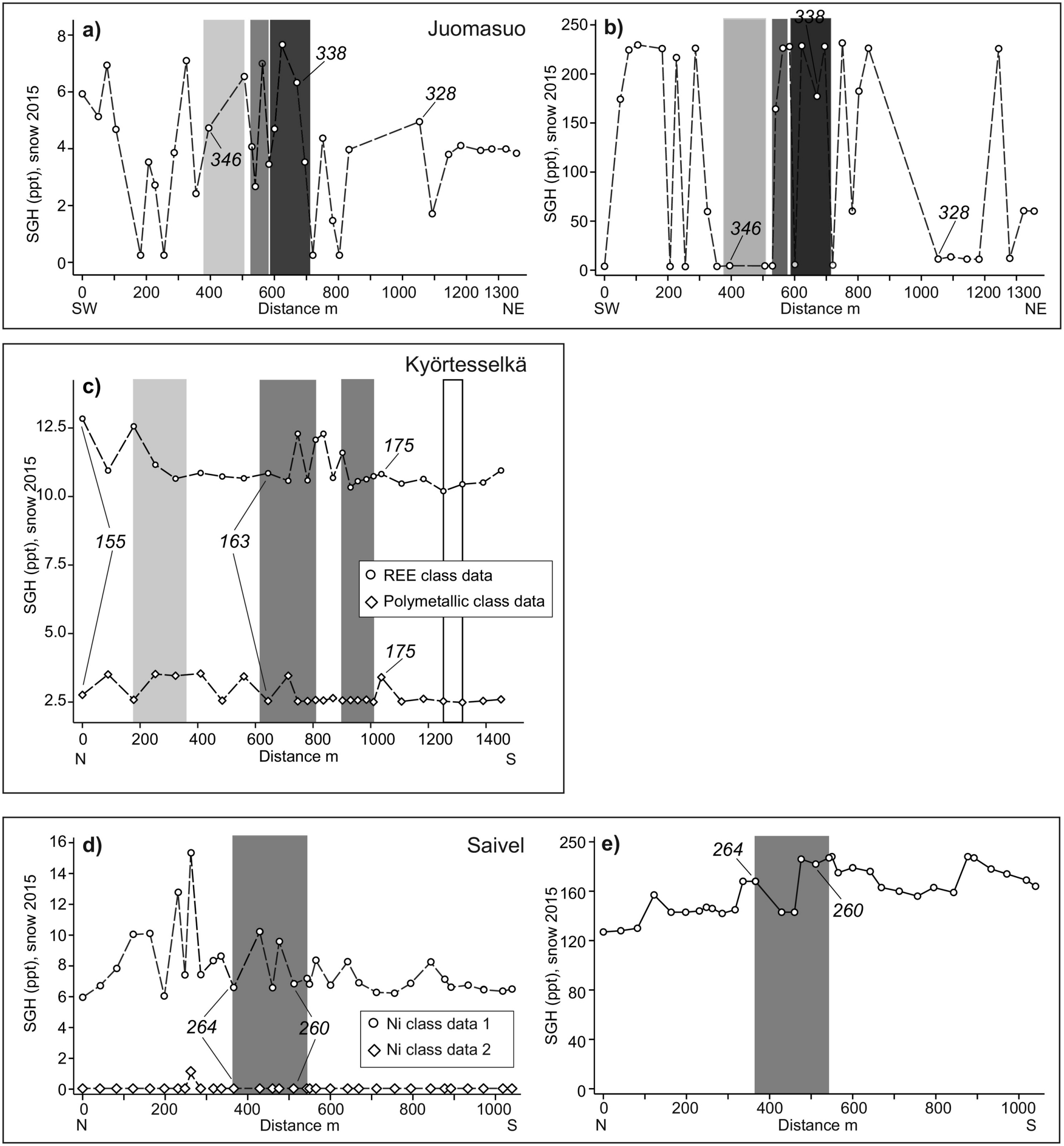
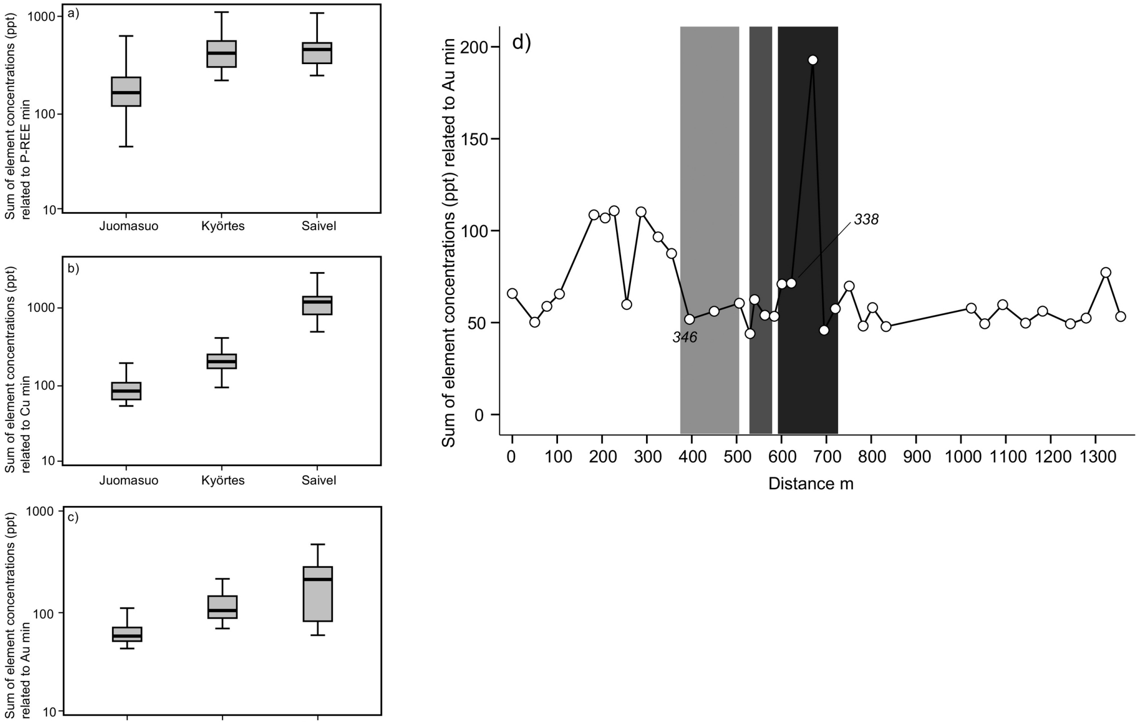

a)
b)
c)
d)
e)
f)
Juomasuo
Au mineralization at 150-200 m depth
Au mineralization at 40-60 m depth
subcropping mineralization
Kyörtesselkä
silicate-apatite ore
silicate-apatite ore soft
carbonatite dikes
Polymetallic class data
REE class data
Saivel
Cu mineralization
Ni class data 1
Ni class data 2
SGH (ppt), snow 2014
SGH (ppt), snow 2014, Cu
Distance m
SW
NE
N
S
W
E
346
338
328
155
163
175
191
196
202
264
260

Figure 5



a)
Juomasuo
SGH (ppt), snow 2015
346
338
328
0
200
400
600
800
1000
1200
1300
SW
Distance m
NE
b)
338
346
328
c)
Kyörtesselkä
155
163
175
REE class data
Polymetallic class data
N
S
d)
Saivel
264
260
Ni class data 1
Ni class data 2
e)

Figure 6



a)
Sum of element concentrations (ppt) related to P-REE min
1000
100
10
Juomasuo
Kyörtes
Saivel
b)
Sum of element concentrations (ppt) related to Cu min
1000
100
10
Juomasuo
Kyörtes
Saivel
c)
Sum of element concentrations (ppt) related to Au min
1000
100
10
Juomasuo
Kyörtes
Saivel
d)
Sum of element concentrations (ppt) related to Au min
200
150
100
50
0
338
346
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
Distance m

Figure 7

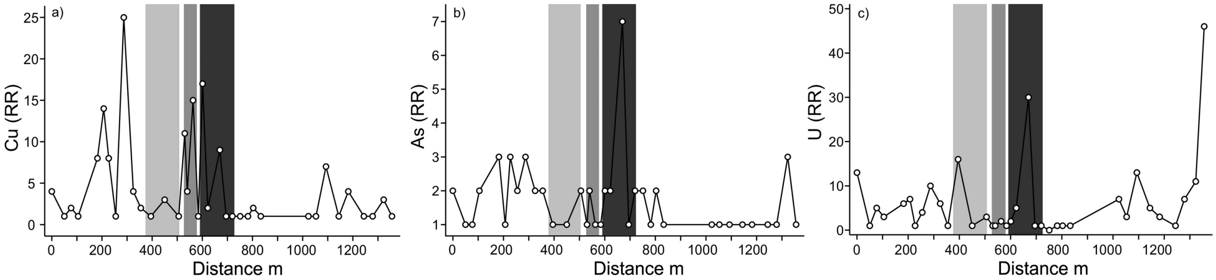
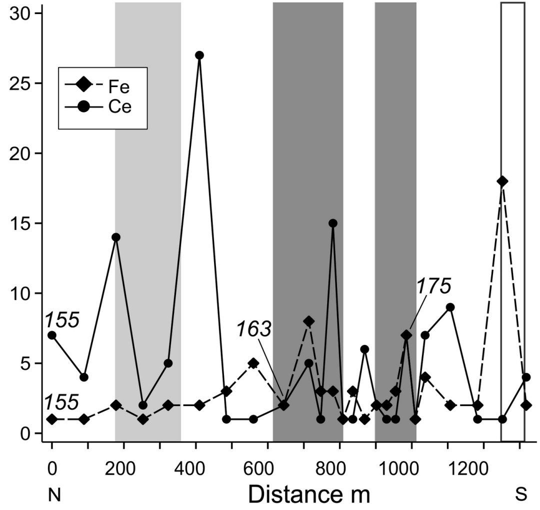

a)
Cu (RR)
0
5
10
15
20
25
0
200
400
600
800
1000
1200
Distance m
b)
As (RR)
1
2
3
4
5
6
7
0
200
400
600
800
1000
1200
Distance m
c)
U (RR)
0
10
20
30
40
50
0
200
400
600
800
1000
1200
Distance m

Figure 8



30
25
20
15
10
5
0
Fe
Ce
155
155
163
175
0
200
400
600
800
1000
1200
N
Distance m
S

Figure 9