LITHOGEOCHEMICAL pXRF STUDY ON THE VIRTASALMI Cu DEPOSIT, EASTERN FINLAND

by

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Field-portable X-ray fluorescence (pXRF) analysers have become widely used tools, for example, in collecting primary exploration data and distinguishing different minerals. In brownfield exploration targets, where pre-existing drill-core data can be re-measured with a high density and in a relatively reliable manner using pXRF, it can help in improving the understanding of local geology and exploration targeting.

In this study, historical drill cores were re-examined to test the use of a pXRF analyser in detecting the geochemical halos around the Virtasalmi Cu deposit and to demonstrate that the analyser characterizes the mineralization intercepted in drill cores. A total of 304 in situ, non-destructive measurements from five drill holes were conducted to observe the elemental dispersion from distal to proximal zones. From the results, the main lithological units can be discriminated. The data display a gradual increase in CaO, and high concentrations of chalcophile elements, such as Cu, were detected with pXRF. pXRF data were shown to be reliable and can be used for different modelling purposes, as well as in mineral systems studies.

Electronic Appendix is available at: http://tupa.gtk.fi/julkaisu/liiteaineisto/bt_407_electronci_appendix.xlsx

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1 INTRODUCTION

Field-portable X-ray fluorescence analysers (pXRF) have clear benefits due to their portability and ease of use, real-time data acquisition with minimal processing, immediate availability and analysis of a reasonably large amount of elemental data in the field in a relatively reliable manner. All these aspects have made pXRF an essential tool in many geological environments.

In recent years, the number of scientific publications in mineral exploration related to pXRF has increased (e.g. Kalnicky & Singhvi 2001, Glanzman & Closs 2007, Goodale et al. 2012, Sarala et al. 2012, Somarin 2012, Sack & Lewis 2013, Durance et al. 2014, Ross et al. 2014a, Ross et al. 2014b, Hall et al. 2014, Sack & Lewis 2013, Durance et al. 2014, Hall et al. 2014, Ross et al. 2014a, Ross et al. 2014b, Sarala et al. 2015, Bourke & Ross 2016). pXRF studies have been conducted in a variety of geological environments and different deposit types. It has been shown that a portable XRF analyser provides an effective tool in exploration lithogeochemistry and chemostratigraphy and can assist in distinguishing between different volcanic units, especially in the pervasively hydrothermal altered lithologies related to volcanogenic massive sulphide deposits, where the primary protolith is visually unrecognizable (Peter et al. 2009, Sack & Lewis 2013, Ross et al. 2014b).

Recently, a 3D model of the historical Virtasalmi Cu deposit was constructed as part of an MSc thesis project (Virnes 2018) using pre-existing geological data. This has provided new insights into the local Virtasalmi geology and provides an attractive dataset for further exploration and ore research. Lawrie (1988) used immobile element geochemistry to subdivide volcanic rocks in the Virtasalmi region into chemostratigraphic groups according to their similar geochemical signature and spatial distribution. In the proximity of the Virtasalmi mine, mafic volcanic rocks were characterized as suite IIIa amphibolites, which mainly consist of massive flow units that were altered to massive calc-silicate lithologies in the proximity of mineralization. These altered calc-silicate skarn lithologies are interpreted to represent the widespread syn-volcanic hydrothermal alteration in the Virtasalmi volcanic suite, which is coeval with the Virtasalmi mineralization (Lawrie 1988 & Lawrie 1992).

Nevertheless, only a few samples have been collected from the Virtasalmi deposit to confirm the chemostratigraphic groups, and no systematic sampling has been conducted from the drill cores. In this study, non-destructive, in situ pXRF measurements were conducted using unprepared core samples to examine whether pXRF results can detect the mineralization-related geochemical signatures from distal to proximal zones in the Virtasalmi deposit. This could provide an effective exploration tool in the Virtasalmi volcanic suite.

2 GEOLOGICAL SETTING

Virtasalmi belongs to the Jäppilä–Virtasalmi block, which forms the southeast end point of the older Svecofennian magmatic rocks and is part of the supracrustal rocks of the Svecofennian Raahe–Ladoga zone (RLZ) (Kousa et al. 2018, Fig. 1).

This primitive arc complex is economically important due to several volcanogenic massive sulphide deposits, such as the Vihanti–Pyhäälä VMS belt (Mäki et al. 2015 and references therein). Supracrustal rocks of Virtasalmi region, 1.920–1.906 Ga in age (Huhma 1986, Vaasjoki & Sakko 1988, Korsman et al. 1997, Pekkarinen 2002, Kousa et al. 2018), are dominated by different amphibolites, which are mostly submarine subalkaline mafic volcanic rocks, mainly composed of medium-K tholeiitic basalts and andesites (Lawrie 1992, Pekkarinen 2002). All the lithologies have been cut by synkinematic intrusions, which are the most abundant lithology in the district (~60% of the rocks in the area are intrusive rocks) and which in Virtasalmi consists of a gabbro–diorite–quartz–di-orite–tonalite–trondhjemite suite of intrusive rocks (Lawrie 1988, Nironen 1989, Kähkönen 2005). The peak metamorphism occurred at Virtasalmi in granulite facies during D1 and went through subsequent retrogression during D2 to lower amphibolite facies conditions (Lawrie 1988). Incomplete retrogression has created a polymetamorphic mineral assemblage where the textures of the granulite facies minerals range from complete amphibolisation to corona textures (Lawrie 1988, Lawrie 1992).
Fig. 1. A) Location of the Jäppilä-Virtasalmi block in Eastern Finland. B) A simplified regional geological map of Eastern Finland showing the Virtasalmi study area. C) A simplified local geological map of the Virtasalmi area.
The Virtasalmi deposit (also known as the Hällinmäki mine) is a polydeformed, prominently lower amphibolite facies metamorphosed, strata-bound syn-volcanic hydrothermal exhalative deposit. The deposit is located within a ca. 1-km-wide and several-kilometres-long, large, northerly dipping F2 antiform structure (Lawrie 1992). The mineralized zone is ca. 650 m long and 16–30 m wide, and under the open pit it continues at least ca. 350 m below the surface (218 m below sea level). The Virtasalmi deposit is comprised of several 2– to 30-m-wide, steeply ~80° NE dipping (Fig. 2) disseminated and network textured chalcopyrite ore lenses within amphibolite and calc-silicate skarn lithologies, respectively (Hyvärinen 1969, Lawrie 1988 & Pekkarinen 2002). High-grade ore is located within unevenly distributed skarnified rocks (Fig. 3), which were formed through intense hydrothermal alteration of the amphibolites. The skarn alteration, which is present in the amphibolites, is most evident in a gradual increase in the proportion of calcic andradite garnet, which can locally form up to 90% of the rock. Typically, scapolite replaces plagioclase in more intensively altered rocks (Lawrie 1988). The main ore minerals in Virtasalmi are chalcopyrite, with minor cubanite as lamellae as well as pyrrhotite, pyrite and magnetite with minor bornite, mackinawite, pentlandite, bravoite, sphalerite, molybdenite, linneite minerals, gersdorffite and millerite (Hyvärinen 1966, 1969).

The Virtasalmi deposit was discovered by the Geological Survey of Finland in 1964. The Virtasalmi mine was operated by Outokumpu Oy during 1966–1983. A total of 4.2 Mt of ore was mined with an average grade of 0.73% Cu and total production reaching 31717.5 tonnes of copper (Puustinen 2003).
Fig. 3. The Virtasalmi ore types. A) The disseminated ore is of low to medium grade (0.2–0.7% Cu), and either homogeneously distributed or forming sulphide bands in diopside-rich amphibolite. The average grain size of the disseminated ore is between 0.1–0.4 mm. B) The network texture ore is of high grade (0.7–8% Cu). It commonly forms as network textures around skarn and amphibolite fragments, but sometimes as massive 5–10-cm-long and 1–3-cm-wide lenticular shapes. The average grain size of the main ore minerals is much greater than in the disseminated ore and the grain width can be up to 4 cm.
3 METHODS

3.1 Data collection

The study was conducted with a handheld Delta Premium analyser from Olympus Corporation. The instrument is owned by Geological Survey of Finland. The device is equipped with a 4 W optimized Ta X-ray tube with a maximum tube voltage of 40 kV and a silicon drift detector. The instrument was provided with a mining plus mode (2-beam) and a soil mode (3-beam). Only the mining mode was used in this study. In addition, KT-10 susceptibility measurements were taken from the same measurement points as pXRF readings.

The analyser was placed in a portable workstation with an integrated safety lock to prevent any movement during measurements. The pXRF analyser was set to the mining mode and the final result was an average of three spatially separate point measurements taken from the same depth interval. Due to time constraints, the measurement spacing was optimized according to the lithological units as follows: the mafic volcanic rocks were measured with ca. 1 m spacing, calc-silicate altered units with ca. 0.5 m spacing and the cross-cutting, barren, quartz diorite intrusive rocks with 3 m spacing. The integration time was 60 seconds, i.e. 30 seconds per beam.

The raw data were converted from elemental form to oxide form for the elements Mg, Al, Si, P, K, Ca, Mn, Ti and Fe, while the rest of the elements were left in elemental form. In addition, the alteration index (AI) and chlorite-carbonate-pyrite index (CCPI) after Ishikawa et al. (1976) and Large et al. (2001) were calculated using the modified formula of Sack & Lewis (2013). Moreover, the ratios of immobile elements Ti/Zr and Al/Zr were calculated.

A single point calibration was applied to level the data (Piercey & Devine 2014). A single point calibration was applied to level the data (Piercey & Devine 2014). The calibration standard used for this study was an basaltic andesite (N5122014R19 26.9–27.2). This standard were chosen as it has similar concentrations and matrix as the samples analyzed in this study. Correction was only applied to following elements: Al₂O₃, SiO₂, P₂O₅, CaO, TiO₂, MnO, Fe₂O₃, Cr, Ni and Zr having performed well in matrix-matched precision and accuracy test.

3.2 Data verification and quality control

At the beginning, the instrument was tested for short-term variations using a single NIST 2710A standard (Montana 1 Soil; https://www-s.nist.gov/srmors/view_cert.cfm?srm=2710A) for a one-hour continuous measurement time. This was conducted to test the instrumental drift for the pXRF analyser used in this study. One hour was selected to examine whether there was variation in the first 30–60 minutes of measurement after the instrument had been turned on. The results of the short-term one-hour drift test on a NIST standard for the selected elements showed some variation for all elements, but within the instrument precision for each element.

Instrumental performance was monitored throughout the measuring programme using an in-house field reference sample, which consisted of laboratory pulp (returns) from a fine-grained felsic volcanic rock placed in an XRF sampling cup with prolene (4 µm) thin film. The sample was previously determined by Labtium Oy, Rovaniemi, Northern Finland (WD-XRF, method code 175X). The verification procedure also included internal calibration and a quartz blank measured at a constant interval to check the contamination. The instrument’s internal calibration check was performed with a 316 stainless steel calibration check reference coin provided by the manufacturer.

A matrix-matched precision and accuracy test was conducted using a homogeneous basaltic andesite core slab (N5122014R19 26.9–27.2) that had previously been analysed by Labtium Oy from a pressed pellet and using an XRF analyser. The core slab was shot a total of 30 times to obtain measurements covering the whole cut surface. The test was performed using mining plus mode and the pXRF analyser was installed in the portable workstation during measurement. Measurements were then averaged for each sample, giving a representative pXRF composition, and compared with the whole-rock assay results determined by the laboratory.
The calculation was based on concentration data from multiple analyses \((n = 30)\) taken from the rock slab using Equation (1).

The same results were also used to determine the sample precision or reproducibility, which were reported as the relative standard deviation \((\text{RSD\%})\) after measuring the sample 30 times and comparing the results to determine the mineralogical heterogeneity of in situ pXRF measurements (Bourke & Ross 2016).

\[
\text{RSD\%} = \left( \frac{\text{stdv}_1}{\text{mean}_1} \right) \times 100 \tag{1}
\]

Accuracy was determined by assessing the degree to which the pXRF measurement of an element in a sample matched the reference value from the rock slab. The Labtium laboratory–based concentrations were used as reference values for this test. Differences between the data sets were assessed according to the relative percentage difference (equation (2)).

\[
\%\text{Difference} = \left( \frac{\text{Mean}_{\text{sample}} - \text{Certified}_{\text{sample}}}{\text{Certified}_{\text{sample}}} \right) \times 100 \tag{2}
\]

The mafic rock sample results indicated poor results for K\(_2\)O, while a few elements had precision values between 11% and 21%, including MgO, P\(_2\)O\(_5\) and V, and the rest had good to excellent precision. Generally, the accepted level for field–portable XRF is 20% RSD. When comparing the accuracy or bias value with the laboratory assay results, significant variability was observed, and the accuracy for most elements was poor \((> \pm 20\%)\). The most reliable elements were P\(_2\)O\(_5\), CaO, MnO, Fe\(_2\)O\(_3\), Cr and Zr, which all had good accuracy \((< \pm 6\%)\).

4 RESULTS

A total of 304 pXRF measurements, all listed in the Electronic Appendix, were conducted from five representative drill holes (R54, R3, R28, R34 and R44) from two sections, 5385 and 5200, respectively. The drill holes R3, R28, R44 are presented as the main results in this study (Figs 4, 5 and 6). It was demonstrated that pXRF measurements can discriminate the main lithological units of amphibolites, mineralized hedenbergite–garnet skarn and gabbro–diorite.

The pXRF results show the proximal ore zone as a gradual increase in CaO, representing the diopside amphibolite and calcic garnet–hedenbergite skarn altered lithologies, which are the predominant host rocks of Virtasalmi ore. The correlation with the Cu value is also distinctive (Fig. 7). Chalcophile elements such as Cu, Zn, Fe and Pb are mainly elevated in calc–silicate altered rocks, which indicates that they were introduced from an external hydrothermal fluid source. Pb values are high in the ore zone, but also in adjacent intrusive rocks. The ore typically contains magnetite, pyrite and pyrrhotite, which is seen as elevated Fe and S contents, as well as higher susceptibility readings. The CCPI displays relatively high values in these altered rock units (CCPI 60–90), whereas the AI values are low for all data points (AI 0–30).

The Virtasalmi pXRF dataset was also compared with previously published immobile element geochemistry published in Lawrie (1988). When comparing least–altered amphibolite units of pXRF data against type III amphibolites in the Zr–TiO\(_2\) diagram, a relatively similar trend can be seen with slightly more scatter (Fig. 7). When examining calc–silicate skarn altered lithologies, they plot with a different trend, having a lower TiO\(_2\) concentration and elevated Zr.
Fig. 4. Non-destructive measurements conducted on the drill core from distal to proximal zones of known mineralization from drill hole R3, together with the simplified original lithological log. The solid red line represents the original continuous sampling intervals. Only ≤1% Cu assay results are presented in this log. The portable XRF measurements clearly indicate the main lithological units of amphibolites, hedenbergite-garnet skarn and gabbro-diorite and sulphide ore.
Fig. 5. Non-destructive measurements conducted on the drill core from distal to proximal zones of known mineralization from drill hole R28, together with the simplified original log and Cu assay results.
Fig. 6. Non-destructive measurements conducted on the drill core from distal to proximal zones of known mineralization from drill hole R44, together with the simplified original log and Cu assay results.
Fig. 7. A) Comparison of least-altered amphibolite units from pXRF data with group III amphibolites in and around the Virtasalmi mine shows a similar trend in the Zr–TiO₂ plot. B) The red-coloured circles represent calc-silicate skarn altered lithologies measured with pXRF, which can be interpreted as alteration trends. The high CaO content is concentrated in calc-silicate skarn altered lithologies due to hedebergite and diopside minerals (red-coloured circles). C) A CaO–TiO₂ diagram in which calc-silicate skarn altered lithologies are plotted according to susceptibility readings. Most of the high readings are in altered sequences due to the presence of magnetite and pyrrhotite minerals. D) A CaO–TiO₂ diagram in which calc-silicate skarn altered lithologies are plotted according to Cu values, clearly showing the correlation between Cu and CaO values. E–F) The corrected values in Zr–TiO₂ plot show several co-genetic trends for amphibolites and calc-silicate skarn altered lithologies. This can be seen in both conventional whole rock (Lawrie 1988) and pXRF data.

5 DISCUSSION AND CONCLUSION

The portable XRF results correlate relatively well with previously analysed intervals and visual logging. However, the results should not be interpreted as true elemental concentrations, but rather as providing a tool for identifying trends. For example, the Pb results are extremely high across the lithologies in all measured drill cores (Figs 4, 5 and 6). Although sphalerite is widely distributed in the Virtasalmi deposit, it is always present at low concentrations, mainly as lamellae in chalcopyrite, pyrrhotite and cubanite (Hyvärinen 1966, 1969). The extremely high readings measured with pXRF could be caused by many different factors, such as the matrix effect, and high readings should always be interpreted carefully. This also emphasizes the importance of reference samples and background information on mineralogy.
The comparison with previously reported immobile element geochemistry published in Lawrie (1988) revealed a difference in the trend, with a lower TiO$_2$ concentration and elevated Zr (Figs 7A, B). This could be caused by the accuracy of the pXRF device, producing more spread out trends than the original laboratory whole-rock results. Nevertheless, after correction applied the pXRF results in the Zr-TiO$_2$ diagram also display different trend, which could be interpreted as different cogenetic trends between amphibolite and calc-silicate altered lithologies (Fig 7 E–F). According to Lawrie (1992), HFSE elements in the Virtasalmi amphibolite reflect the original magmatic processes, with limited secondary redistribution. Moreover, it is mentioned that in the Virtasalmi mine, the inter-element ratios of the HFSE elements change in a non-systematic manner in samples taken across the irregular and gradational contacts from amphibolite to calc-silicate rock. Nevertheless, in high metamorphic environments, TiO$_2$ can be mobile to some extent, and this needs to be taken into consideration and further investigated. Moreover, this could be interpreted as indication of strong mass change in altered lithologies. Also the carbonate rocks (Fig.5) show very similar trends in elemental concentrations compared to calc-silicate altered rocks related to the ore zone.

pXRF illustrates the alteration intensity and characterizes the base metal contents of mineralized intercepts in a drill core. In situ pXRF measurements enable unprepared rock samples to be examined with a high density in a relatively rapid manner and provide very detailed results for lithological units, making pXRF a powerful tool in volcanic geochemistry. Although pXRF cannot achieve the accuracy and precision of laboratory whole-rock analysis, it can be used to detect trends and populations critical to the ore zone. In the case of further study and drilling in the Virtasalmi area, pXRF data could confirm the ore sequence and help to make correct decisions in exploration drilling. It could also provide a low-cost data set for further modelling with, for example, multivariate analysis. This could be further used in understanding genetic aspects of the Virtasalmi mineral system.

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