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Tiivistelmä

Indium on olennaisen tärkeä raaka-aine maailman elektroniikkateollisuudelle. Indiumia käytetään nestekide-, plasma- ja OLED-näytöissä, televisioissa, matkapuhelimissa sekä kannettavissa tietokoneissa. Tämän hetkinen kysynnän ja tarjonnan suhde on maailmanlaajuisesti lisännyt kiinnostusta indiumin etsintään. Tämä väitöskirja kuvailee kaksi Fennoskandian kaakkoisosassa sijaitsevaa, rapakivigraniitteihin liittyvää indiumpitoista esiintymää; Kaakkois-Suomessa sijaitsevat Loviisan Sarvlaxvikenin monimetallijuonet sekä Venäjällä Laatokan Karjalan Pitkärannassa olevan karsimalmin.

Sarvlaxvikenin monimetallijuonet esiintyvät kahdessa eri rapakivigraniitityypissä ja ne voidaan jakaa viiteen eri ryhmään; viborgiitissa esiintyvät Li-As-W-Zn-Mn, Pb-Zn sekä Cu-As-In ja tasarakeisessa graniitissa esiintyvät As-Sn-Cu sekä Mo-Bi-Be. Juonet muodostavat monimutkaisen järjestelmän, jossa esiintyy useita juonigeneraatioita. Viborgiitissa esiintyvissä juonet ovat NNN -suuntaisia ja ne ovat kehittyneet kahdessa eri vaiheessa (generaatiot 1 ja 2). Tasarakeisen Marvikenin graniitin muuttumisvyöhykkeellä esiintyviä juonia on tavattu ainoastaan jään kuljettamissa lohkareissa, minkä vuoksi niiden ikäsuhde edellisiin on epäselvä (generaatio x). Viborgiitissa esiintyvien juonten syntyolosuhteet ovat fluidisulkeumatutkimusten perusteella olleet lähes identtiset generaatiosta riippumatta. Fluidin kloori- ja rikkipitoisuudet ovat vaikuttaneet metallien rikastumiseen. Metalleja rikastanut fluoripitoinen fluidi on todennäköisesti peräisin Marviken graniitista.

Pitkärannan historiallisen kaivosalueen karsimalmi sisältää neljä päämalmityyppiä; rauta-, kupari-, tina-, ja sinkkityypit. Samassa kaivoksessa tavataan useita eri malmityyppejä, joiden välillä on havaittavissa mahdollisesti syntyolosuhteiden vaihteluista johtuvaa asteittaista vaihettumista. Tietyt metallit ovat kuitenkin yleisempiä tietyillä alueilla ja esiintyvät yhdessä erityisten hivenaineiden, esim. Ag, Bi, In ja Li, kanssa.

Molemmilla tutkimusalueilla indium esiintyy pääsääntöisesti sinkkipitoisessa malmissa, jossa se on useimmiten sinkkivälkkeessä. Tutkimusalueilla on kuitenkin havaittu myös indium-mineraalia nimeltä roquesiitti. Indium-mineraalien esiintymistä voidaan ennustaa laskemalla In (ppm) / Zn (%) suhde. Jos tämä suhde on suurempi kuin 50, on todennäköistä, että näyte sisältää indium-mineraaleja.

Sarvlaxvikenin alueelta on kerätty 100 tai 20 metrin näytevälein yli 2000 maaperänäytettä geokemiallisia analyysejä varten. Lukuisat anomaaliset näytteet viittaavat useaan eri metallilähteeseen. Havaittujen anomalioiden sekä tunnettujen metallipitoisten juonten välillä ei kuitenkaan voitu havaita selkeää yhteyttä. Siitä syystä anomaliat vahvasti viittaavat löytymättömiin, maaperäkerroksen alla oleviin, metallijuoniin.

Tämä väitöskirja antaa tärkeää tietoa Fennoskandian kilven rapakivien yhteydessä esiintyvistä indiumpitoisista esiintymistä. Väitöskirja sisältää yksityiskohtaisen alueellisen kallioperäkartoituksen sekä mineralogisia, geokemiallisia ja fluidisulkeumatutkimuksia. Nämä kaikki yhdistettynä tarjoavat apuvälineen rapakivialueiden metallinetsintään.

Avainsanat: indium, rapakivigraniitti, Fennoskandia, roquesiitti, Sarvlaxviken, Pitkäranta

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Abstract

Indium is a critical metal for the world's electronic industry due to its use in flat panel devices such as liquid crystal displays, plasma display panels and OLED displays. Thus, indium is used in televisions, mobile phones, laptops and notebooks. The current supply and demand has led to an increased interest for indium exploration globally. This thesis describes features of two different rapakivi-related In-rich mineralisations in southeastern Fennoscandia; polymetallic veins in Sarvlaxviken, Lovisa, southeastern Finland and skarn ore in Pitkäranta, Ladoga-Karelia, westernmost Russia.

The polymetallic veins in Sarvlaxviken occur in two rapakivi granite varieties and can be divided into five metal associations: Li-As-W-Zn-Mn, Pb-Zn and Cu-As-In in wiborgite bedrock and As-Sn-Cu and Mo-Bi-Be in even-grained granite. These veins form complex systems, with multiple vein generations. The first three associations are strongly controlled by NNW-trending structures and evolved in two main stages (generation 1 and 2). The two latter associations exist in alteration zones of the Marviken granite but have only been observed in glacier transported boulders and thus, the timing of these are uncertain (generation x). The fluid inclusion data indicate that the depositional conditions of the wiborgite hosted veins were almost identical in all generations. The chlorine and sulphur contents in the fluids affected the formation of metals. The F-rich ore forming fluids emanated most likely from the Marviken granite.

The skarn ore in the historic mining district of Pitkäranta is composed of four end member ore types, dominated by the metals Fe, Cu, Sn and Zn. However, several ore types exist in one and the same mine with gradational borders between each ore type, most likely reflecting variations in the depositional conditions. Some metals are, however, more common in certain areas and associated with certain trace elements, e.g. Ag, Bi, In and Li.

Indium is in both study areas commonly associated with Zn –rich ores with sphalerite as the main carrier. Yet, the indium mineral roquesite has been observed in both study areas. The presence of indium minerals can be predicted by calculating the ppm In / % Zn ratios. If the ppm In / % Zn ratio exceeds 50, it is likely that the sample contains indium minerals.

Over 2000 till samples were collected at 100-m or 20-m intervals for geochemical investigations in the Sarvlaxviken area. Numerous anomalous samples indicate several metal sources. The clear connection between anomalies and the already discovered polymetallic veins were not detected. These anomalies strongly suggest undiscovered veins under the soil cover.

This thesis provides important information about rapakivi-related In-rich mineralisations in the Fennoscandian Shield. It includes mineralogical, geochemical and fluid inclusion studies, as well as detailed mapping of the bedrock and the till anomaly patterns, and thus provides a tool for exploration of metals in the rapakivi areas.

Keywords: indium, rapakivi granite, Fennoscandia, roquesite, Sarvlaxviken, Pitkäranta

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"I am not what happened to me, I am what I choose to become."
– C.G. Jung

2.4.2019
Mira Valkama

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List of original publications

This thesis is based on the following five original publications listed below, referred to with respect to their Roman numerals (I-V) in the text:

I Cook, N.J., Sundblad, K., Valkama, M., Nygård, R., Ciobanu, C. and Danyushevsky, L., 2011. Indium mineralisation in A-type granites in southeastern Finland: Insights into mineralogy and partitioning between coexisting minerals. Chemical Geology 284, 62-73. Reprinted with permission from Elsevier.

II Valkama, M., Sundblad, K., Cook, N.J. and Ivashchenko, V.I, 2016. Geochemistry and Petrology of the Indium –bearing Polymetallic Skarn Ores at Pitkäranta, Ladoga, Karelia, Russia. Mineralium Deposita 51, 823-839. Reprinted with permission from Springer Nature.

III Valkama, M., Sundblad, K. Nygård, R. and Cook, N.J., 2016. Mineralogy and geochemistry of Indium –bearing polymetallic veins in the Sarvlaxviken area, Lovisa, Finland. Ore Geology Reviews 75, 206-219. Reprinted with permission from Elsevier.

IV Broman, C., Sundblad, K., Valkama, M. and Villar, A., 2018. Deposition conditions for the Indium-bearing Polymetallic Quartz Veins at Sarvlaxviken, South-Eastern Finland. Mineralogical Magazine 82, S43-S59. Reprinted with permission from Cambridge University Press.

V Valkama, M., Sundblad, K. and Korkka-Niemi, K., 2018. Metal Anomalies in Till in the Sarvlaxviken area, Lovisa, Finland. Manuscript.

1. Introduction

1.1. Indium

Indium is one of the metals that society needs to maintain the present lifestyle. Indium is most commonly used in the form of indium-tin oxide (ITO) in flat panel devices such as liquid crystal displays (LCDs), plasma display panels (PDPs) and OLED displays (U.S. Geological Survey, 2017). Thus, indium is widely used in televisions, mobile phones, laptops and notebooks. Other applications of indium are in solders, solar cells, thermal interface material (TIMs), batteries etc. The principal source of indium is as a by-product of residues generated during zinc ore processing (Schwarz-Schampera, 2014). Smaller amounts of indium are also recovered from lead, tin and copper ores. The leading refinery producer of indium is China (57 %) followed by the South Korea (15 %), Japan (10 %) and Canada (9 %) (Schwarz-Schampera, 2014; European commission, 2017). However, it should be noticed, that not all producer countries have significant indium bearing ore deposits. Generally, the metal-rich residues are sold to secondary producers which have better ability to use electrolytic refining and the treatment of zinc-refinery slimes which are needed to recover indium. The clearly dominating role of China as an indium producer is complicated because China also regulates its indium production industry (European Commission, 2016; U.S. Geological Survey, 2017). In order to export indium, producers and traders are required to apply for and receive an export license from the Ministry of Commerce of China, which also regulates the total export quota. These circumstances are unfavourable to all other countries that need indium for the industry. This is a main reason why the European Commission has classified indium as a critical high-tech metal (European Commission, 2017) and also the main reason for increased indium exploration in globally (Bowles et al. 2018).

Indium was originally discovered in 1863 in a Zn-rich sample from the Erzgebirge mining district, Germany (Schwarz-Schampera, 2014). After this discovery, the next mention of indium is in Wladimir Vernadsky's (1910) report where he noted the presence of indium in sphalerite, at several sites in Russia including the abandoned Pitkäranta mining district. Since indium was found to have valuable for the industry in 1924 and especially after the 1950s when production of indium-containing semi-conductors started (Schwarz-Schampera, 2014), it became an economical metal which was worth to prospect for. Current knowledge (Sundblad and Ahl, 2008; papers II and III) indicates, that northern Europe has the highest potential for economic indium discoveries in Europe.

Indium occurs in several types of ore deposits with a wide range of geological ages. The most common ore deposit types where indium is present are volcanic- and sediment-hosted exhalative massive sulphide deposits, epithermal deposits, granite-related tin-base metal deposits, skarn deposits and porphyry copper deposits (Schwarz-Schampera, 2014). The most important indium-bearing mineral and source of most of the indium is sphalerite. However, indium also occurs as a major component in several other minerals, all rare in natural systems. The most common of these is roquesite ($CuInS_2$), which usually is associated with principal ore forming minerals like bornite, chalcopyrite and sphalerite (Schwarz-Schampera, 2014). Indium minerals have been recognized at several sites globally, roquesite was first discovered in France (Picot and Pierrot, 1963) while indite ($FeIn_2S$) and dzhalindite ($In(OH)_3$) were identified in the Far East of Russia (Genkin and Murav'eva, 1963). Roquesite was also discovered in e.g. Japan (Kato, 1965), Russia (Kachalovskaya et al., 1973) and Canada (Sutherland and Boorman, 1969; Sinclair et al., 2006; Thorpe et al., 1976) as well as in the Fe-Mn ores of Långban and Gåsborn in westernmost Bergslagen, Sweden (Burke and Kieft, 1980; Kieft and Damman, 1990) and in the Erzgebirge mining district in Germany (Seifert and Sandmann, 2006).

1.2. Indium occurrences in a global and Fennoscandian perspective

Granite-related indium occurrences are recognized in several deposits across the globe, including the giant Olympic Dam Cu-U-Au-Ag deposits, South Australia (e.g., Roberts and Hudson, 1983), the Sn-bearing polymetallic deposits in Rondônia and Amazonas, Brazil (e.g., Bettencourt and Dall'Agnol, 1987), Mount Pleasant, New Brunswick, Canada (Sinclair et al., 2006), SW England (Andersen et al., 2016) and at St. Francois Mountain, Missouri, USA (Kisvarsanyi and Kisvarsanyi, 1991).

The Fennoscandian Shield extends from southern Norway, through Sweden and Finland into north-western Russia. Precambrian indium occurrences have been reported from all these countries. All of them are associated with granites, in most cases with anorogenic rapakivi granites, which mainly occur in southern Finland and in the Ladoga region (Fig. 1) in Russia. Indium was first discovered in the historic mining district in Pitkäranta, Russia (Vernadsky, 1910; Erämetsä, 1938), where it occurs in skarn ores, formed from hydrothermal fluids from the Salmi rapakivi granite. More detailed investigations of the Pitkäranta ore (paper II) have revealed high (up to 605 ppm) indium concentrations in several locations as well as a roquesite discovery in the western part of Russia. Most of the recent indium discoveries have been made in the western parts of the Wiborg rapakivi batholith in southeastern Finland. These targets can either be classified as compact In-bearing magnetite-sphalerite ore (Pahasaari and Getmossmalmen), Zn-Cu-Pb-Ag-In-bearing greisen veins (Jungfrubergen) or In-bearing polymetallic veins (Sarvlaxviken) (paper I). Indium-rich polymetallic veins have also been found in Svecofennian rocks outside the Eurajoki stock, close to the Laitila rapakivi batholith in SW Finland (Pere, 2009).

1.3. Objectives of the thesis

This study aims to understand the character of the rapakivi-related indium mineralisations in southeastern Finland and in Ladoga-Karelia in Russia by using different investigation methods. The thesis describes the petrological, mineralogical and geochemical features of the mineralisations (papers I-III). Detailed field relationships and bedrock descriptions are presented and discussed in papers III. The depositional conditions of the mineralisations are discussed with the aid of the fluid inclusion data in paper IV. A study of till geochemistry of the surrounding area is presented and tested for potential exploration of the indium-bearing mineralisations in paper V.

The main question has been what kind of ore forming conditions, in terms of geology and temperature, are needed to create indium-rich mineralisation from the rapakivi granites. The research questions of this thesis are the following

1) What kind of mineralogical and geochemical features do the rapakivi-related indium-rich mineralisations have?

2) What kind of depositional conditions have formed the mineralisations?

3) Can till geochemistry provide an exploration tool for the distribution of hitherto undiscovered veins in this region?

With the results presented in this thesis, critical knowledge and exploration models are provided for this new type of mineralisation.

2. Study area

This thesis is focused on In-mineralisations in two main areas; Sarvlaxviken, Lovisa, southeastern Finland and Ladoga-Karelia, westernmost Russia. Both areas are located in the southeastern part of the Fennoscandian Shield where the Archaean and Paleoproterozoic metamorphosed bedrock was intruded by Mesoproterozoic rapakivi granites.

The Archaean Domain represents the oldest crustal unit with ages of 3.1−2.6 Ga. It can be divided into the Karelian, Belomorian and Kola Peninsula provinces, which formed during the Saamian (~3.1-2.9 Ga) and Lopian (~2.9-2.6 Ga) orogenies (Gaál and Gorbatschev, 1987). The Karelian Province occupies the main part of the Archaean Domain and consists of greenstone belts, enveloping gneisses and granitoids. At 2.5-2.0 Ga, several volcano-sedimentary successions were deposited on top of the Archaean units. These successions are distinguished as Sumian-Sariolan, Kainuan-Lapponian, Jatulian and Kaleva, of which the latter two occur in the Pitkäranta area. After a long period of weathering of the Archaean Domain, the bedrock was mostly covered by quartz sand, limestone and pillow lava which later formed Jatulian quartzites, marbles and amphibolites (Laajoki, 2005). The Kaleva successions overlie the Jatulian tectofacies or, locally, the Archaean basement. The Kaleva succession can be subdivided into the Lower and Upper Kaleva. The Lower Kaleva represents heterogeneous autochthonous-parautochthonous sequences of turbidites, greywackes and shales, deposited in conjunction with a continental rift phase. The Upper Kaleva represents an allochthonous marine basin and consists of meta-sandstones, greywackes and mica schists. These supracrustal successions were all folded, metamorphosed and locally thrusted on to the Archaean continent during the Svecofennian orogeny at 1.9-1.8 Ga (Laajoki, 2005). The amalgamation of the Archaean and the Proterozoic supracrustal successions created allochthonous root-less fragments that consist of Archaean cores and envelopes of Jatulian and Kaleva successions (Park, 1985; 1991). These fragments are common in the Kuopio, Joensuu and north Ladoga regions.

The Palaeoproterozoic Svecofennian Domain consists of c. 1.9 Ga juvenile crust that includes remnants of magmatic and sedimentary components of ophiolites, island arcs, and active continental margins which all were amalgamated and accreted to the Archaean crust during the Svecofennian orogeny (Korsman et al., 1997). As the bedrock cooled after the orogeny, fissures opened and magmas intruded to the upper crust (Vaasjoki et al., 2005).

The rapakivi granites in the Fennoscandian Shield are known in Sweden, southern Finland and the Ladoga region in Russia where several batholiths and intrusions of different sizes have been recognized (Fig. 1 and 2). The largest of them is the Wiborgite batholith (surface over about 18,000 km^2) which mainly is located in southeastern Finland (Fig. 1). The Wiborg batholith intruded in several phases between 1.65 and 1.63 Ga (Vaasjoki et al., 1991). The most common rock type (80 %) is wiborgite which is characterized by large rounded alkali feldspar phenocrysts, surrounded by a rim of plagioclase. Minor rock types in the Wiborg batholith comprises pyterlite, dark even-grained rapakivi granite, porphyritic rapakivi granite and various biotite granites.

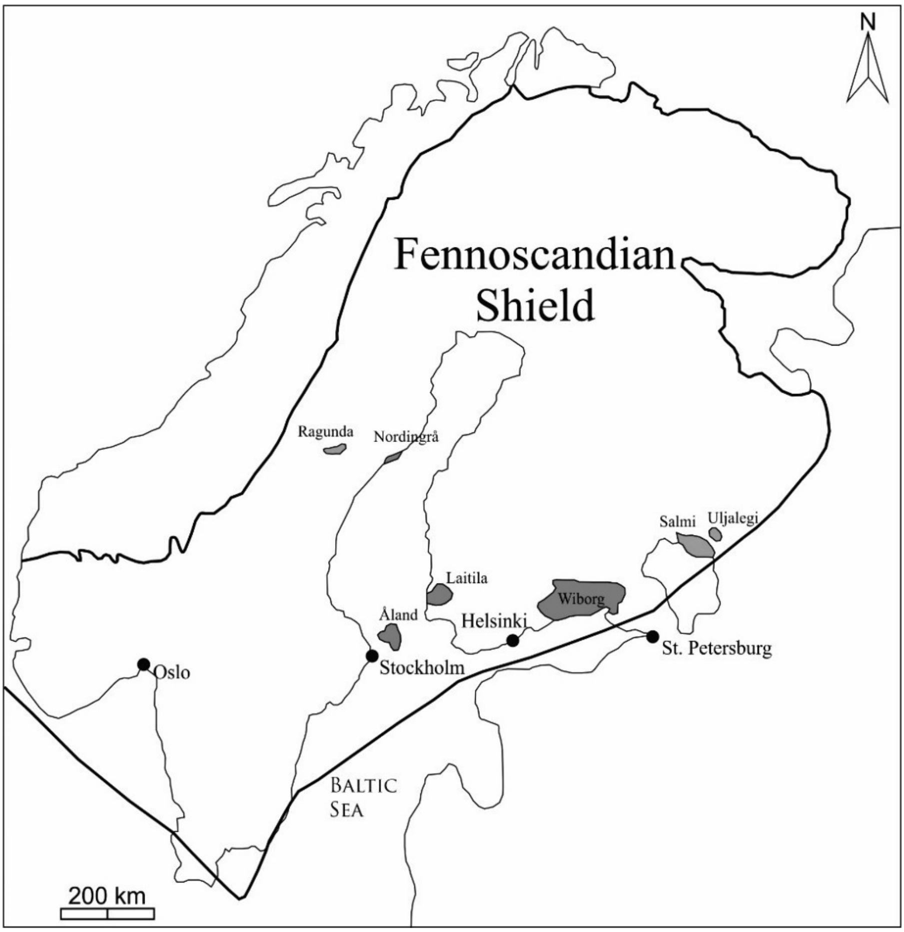

Fig 1. Location of the main Rapakivi Batholiths in the Fennoscandian Shield.

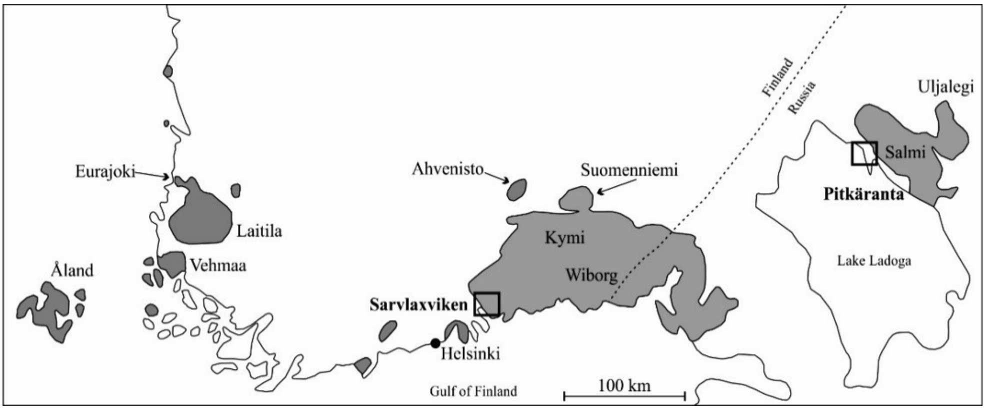

Fig 2. Location of the main Rapakivi Batholiths in southern Finland and Ladoga

The Salmi batholith is the second largest (4,000 km^2) batholith in the Fennoscandian Shield and is located on the northeastern side of Lake Ladoga, Karelia, Russia. The Salmi batholith formed in several phases from 1547 Ma to 1530 Ma (Amelin et al., 1997) and consists of an anorthosite-rapakivi granite complex including gabbronorite, monzonite, syenogranite, wiborgite, pyterlite, biotite granite, olivine gabbro and biotite-amphibole granites.

The rapakivi granites are anorogenic with a typical within-plate (WPG) geochemical pattern. Compared to other granitic rocks, the rapakivi granites contain more Si, K, F, Rb, Ga, Zr, Hf, Th, U, Zn and REE but less Ca, Mg, Al, P, and Sr (Rämö and Haapala, 1995). The rapakivi granites are especially enriched in LREE and have a negative Eu anomaly. In late rapakivi phases (e.g. topaz-bearing units), Sn, F, Ga, Rb, and Nb are notably abundant, while Ba, Sr, and Zr are depleted. In addition, late stage intrusive phases have flat chondrite-normalized REE fractionation patterns as well as pronounced negative Eu anomalies (Rämö and Haapala, 1995).

Continental ice sheets covered Finland during the Holocene (Koljonen and Tanskanen, 1992) until c. 13 100 years ago when the coastal areas of southern Finland were free from ice (Saarnisto and Saarinen, 2001). The main direction of the ice-movements in the Lovisa area at that time was 320º-330º (Punakivi et al., 1977).

2.1. Sarvlaxviken, Lovisa, Finland (papers I, III, IV and V)

Recently, a number of In-bearing exploration targets were identified in the westernmost part of the Wiborg batholith (Sundblad and Ahl, 2008; paper I). Paper

I provides an introduction to these ore types, but has the main focus on the polymetallic veins in the Sarvlaxviken area. The results of more detailed investigations of the Sarvlaxviken veins are presented in papers III and IV.

Paper I describes also briefly two other occurrences, located 10-12 km NNW of Sarvlaxviken. The Jungfrubergen vein is a Pb-Zn-Ag-In-bearing greisen vein which can be followed for 10 m along strike and is hosted by a wiborgitic rapakivi granite. A compact body of magnetite and In-bearing sphalerite is found at Getmossmalmen, 2 km south of Jungfrubergen. The Getmossmalmen body is 1-2 m thick and c. 50 long and is one of several magnetite-sphalerite lenses that extend for about 1 km (Penttinen, 2009), close to the contact between rapakivi granites and ignimbrites.

2.2. Pitkäranta, Ladoga Karelia, Russia (paper II)

Pitkäranta is a historic mining district where more than 50 mines and prospects were exploited between 1810 and 1904 (Trüstedt, 1907; 1908). It consists of five mining areas: the Old Mine Field, Herberz, Winberg, Hopunvaara and Lupikko as well as several smaller mines and prospects such as Kelivaara (Kitilä), Heposelkä and Uuksu.

The ores occur as a skarn type in two marble layers in the Jatulian succession. Early theories about the origin of the Pitkäranta ores were presented by Jossa (1834), Breithaupt (1849) and Groddeck (1879). Törnebohm (1891) was the first to propose a hydrothermal origin for the ores and subsequently, the Pitkäranta mineralisations were considered to form in multi stages in conjunction with the intrusion of the rapakivi granites (Trüstedt, 1907; Saksela, 1951; Larin et al., 1990; Amelin et al., 1991; Sundblad, 1991).

3. Material and methods

3.1. Rock sampling and sample preparation

More than 100 rock samples were collected for the purpose of petrographic, geochemical and fluid inclusion studies. Most of the samples were collected with a hammer from the exposed bedrock or from the ore piles (adjacent to the Pitkäranta mines). The polymetallic veins in the Sarvlaxviken area were sampled with diamond saw along the strike direction of the veins which created 25-40 cm-long rock slabs. All locations were positioned with GPS and plotted on modern MML maps for the Sarvlaxviken area and by using Trüstedt's (1907) map and topographic maps of Finland from 1920-1930 for the Pitkäranta mines.

All samples were cut to smaller pieces with a diamond saw. One part of the sample was used to produce polished sections, polished thin and thick sections while the remains was crushed with jaw crusher and furthermore ground with a swing-grinder to rock powder. The rock powders were analysed by Activation laboratory, Ancaster, Canada with the Ultratrace-3 analytical package (ActLab Ltd., 2018a). The element concentrations of the rock powders were determined by a combination of instrumental neutron activation analysis (INAA), multi-acid digestion inductively coupled plasma (ICP) and inductively coupled plasma emission mass spectrometry (ICP-MS) techniques. The ICP-MS equipment used for the Ultratrace-3 package was a Perkin Elmer-SCIEX ELAN 6000.

3.2. Till sampling and sample preparation

Nearly 2000 till samples were collected from a 20 km^2 area in the Sarvlaxviken area between 2009 and 2014. The samples were taken either with 20 m or 100 m intervals. The samples collected in 100 m grids consist of three sub-samples; a main sample and two satellite samples. The main sample was taken from a point where the coordinates were recorded while the satellite samples were taken 20 m south-west and north-east from the main sample point. Since the local ice-movement direction has been from the northwest (Punakivi et al., 1977), the satellite samples were placed so that the possible till anomaly were best detected. The samples in the 20 m grids were taken in areas where the 100 m grid samples had indicated an anomaly. The 20 m samples were taken only from one point without any satellite samples. Most till samples were collected from the non-weathered C-horizon. A few samples were also collected from the B and C horizons to compare if there is any differences between the horizons.

The sample pits were dug as deep as possible (normally 2-5 dm) with a metal spade after which each sample was collected with a plastic spade from the fresh pit wall and put into a low density polyethylene (LDPE) bag. The samples were dried for 24 hours at 70-80ºC and sieved with a plastic sieve with sieve opening 0.25 mm. The fine fraction till (usually 20-30 g) was analysed by Activation laboratory, Ancaster, Canada, with the Ultratrace 4 analytical package (ActLab Ltd., 2018b). The metal contents were determined by inductively coupled plasma emission mass spectrometry (ICP-MS) technique with Perkin Elmer-SCIEX ELAN 6000, 6100 or 9000 equipment.

The geochemical data were classified into groups with the K-means clustering algorithm. K-means clustering analysis (SPSS) was used for the whole dataset for Fe, Mn, Sn, W, Mo, Cu, Zn, Pb, Ag, In, As, Bi, Co, Cd, Ba, Be, Ga, Li, Ni, Te and U. The obtained clusters were investigated to determine the geochemical differences between groups and the spatial distribution of clusters. The results were presented in proportional and cluster maps.

3.3. Petrographic descriptions

The basic identification of minerals, mineral paragenesis and rock textures were studied with reflected and transmitted light microscope. The transmitted light microscope was used to study wall rock alteration and to identify minerals in the host rocks. The transmitted light microscopy transmits a light beam upwards from a source below, towards and through the specimen into an objective lens. The reflected light microscope is used to study opaque minerals such as native metals, sulphides, oxides etc. The reflected light microscope is basically the same as the transmitted light microscope but the light source is above the sample which allows the examination of light waves that have reflected off the polished surfaces. In addition, the smallest grains were studied with oil immersion microscope objective lenses.

Scanning Electron Microscope (SEM) technique with Energy Dispersive X-Ray Spectroscopy (EDS) and Back-Scattered Electron detector (BSE), were used to confirm the identities of minerals and to investigate smaller mineral grains and textures, as well as compositional differences. The scanning electron microscope focus a high-energy electron beam to generate a variety of signals at the surface of the sample (Reed, 2005). The EDS-spectrometer and the BSE-detector evaluate the signals that derive from the electron-sample interactions and reveal information about the sub-microscopic features and texture of the sample as well as relative chemical composition of the minerals. Two different SEM instruments were used: HITACHI S-3600 N equipped with an EDS-spectrometer and a BSE-detector, and a JEOL JSM 5900 LV instrument with an Oxford EDS-spectrometer and a BSE-detector.

Visible and near infrared (VNIR) and shortwave infrared (SWIR) reflectance spectroscopy was used to confirm the identification of some of the alteration minerals. The VNIR-SWIR technique creates wavelengths between 350 and 2500 nm which can be measured by the spectrometer. The spectroscopic data were measured with an ADS TerraSpec® spectrometer. Spectral processing and mineral identification were performed with the TSG (The Spectral Geologist) software. Spectroscopic data were gathered from the flat surface of the cut sample piece.

3.4. Sulphide chemistry

The composition of the ore minerals (paper I) as well as an unnamed Cu-Ag-Fe-S phase and the Ag-contents in chalcopyrite (paper II) were studied with a Cameca SX100 electron microprobe. The electron microprobe bombs a micro area of the sample with a focused electron beam and collect the X-ray photons emitted by the various elemental species (Reed, 2005). The emitting species creates characteristic wavelengths of X-rays from where the sample composition can be identified with a WDS spectrometer.

Spot analyses of sphalerite, chalcopyrite, bornite and roquesite were made with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The instruments used were an Agilent HP4500 and a 7700 Quadripole ICPMS. In the LA-ICP-MS technique, a laser beam is focused on the sample surface and fine particles ablate from it (Liu et al., 2013). These particles are transported for elemental and isotopic analysis. This method is especially good for chemical analyses of minor and trace elements because of the low detection limits (sub-ppm).

3.5. Fluid inclusion micro-thermometry

Fluid inclusions are microscopic droplets of liquid and/or vapour that are trapped in the growing mineral crystal (Bodnar, 2003). Fluid inclusions are common in all minerals, but are mainly studied in hydrothermal transparent minerals such as quartz and calcite. Fluid inclusion studies provide information about the conditions existing during the formation of the enclosing mineral. A basic petrographic microscope was used to study common features and the distribution of the fluid inclusion in doubly-polished 150 µm thick sections. Micro-thermometric analyses were performed with a Linkam THM 600 heating/freezing stage (working range -196 to +600 ºC) adapted for a Nikon microscope. Commercial SynFlinc® synthetic fluid inclusion standards were used for calibration.

4. Results and discussion

4.1. Mineralogical and geochemical features

This study has focused on two ore types: polymetallic veins and skarn. Both types formed from hydrothermal fluids that was generated by the intrusion of rapakivi granites.

4.1.1. Polymetallic veins

Several examples of polymetallic veins have been recognized in the Sarvlaxviken area. These veins are divided into five groups based on the dominant metal associations (papers III and IV); Li-As-W-Zn-Mn, Pb-Zn and Cu-As-In as well as As-Sn-Cu and Mo-Bi-Be. The first three of these are hosted by wiborgite and are strongly controlled by a NNW-trending structural pattern that evolved in two main stages (generation 1 and 2). The two latter are hosted by alteration zones in the Marviken granite, but the timing of these veins is uncertain and are therefore referred to as generation x.

The Li-As-W-Zn-Mn association (Högberget group) is the oldest mineralisation event (generation 1) and consists of cm-wide quartz veins surrounded by cm-wide alteration zones in the wiborgitic rapakivi granite. In addition to Li, As, W, Zn and Mn, these veins are locally enriched in Fe, Ga, Pb and Sn. The ore minerals are mainly composed of arsenopyrite, sphalerite, chalcopyrite and bornite as well as traces of other copper minerals. The ore minerals are hosted by dark mica, chamosite, fluorite and quartz. The greisen style of alteration is distinctly present in all wiborgite hosted veins. The Högberget group displays a geochemically more complex alteration process, in which B, F and Li also were involved, thus confirming an early stage of vein formation.

The Pb-Zn association is suggested to belong to the same generation (1) as the Li-As-W-Zn-Mn association, based on the field observations and structural pattern. However, the metal signature is very different with high contents of Pb and Zn, Mn and low contents of As, Bi, Co, Cu, Fe, In, Li and S. The vein is dominated by quartz with less chlorite, magnetite and galena.

The Cu-As-In association (generation 2) formed slightly later under more brittle conditions and represents a more evolved stage of greisenization accompanied by silicification. This generation can be subdivided into generations 2a and 2b based on structural observations. The strike direction of the generation 2a veins is NE-NNE, while the generation 2b veins are oriented in a NW-NNW direction. However, the paragenetic and geochemical patterns of these sub-generations are so similar that they are considered to represent the same vein-forming event with a very small time difference between them.

Even if the two sub-generations are considered to have formed in a very close in time, the mineralogical and geochemical features are used to subdivide the Cu-As-In association. The Virbäcken vein (generation 2a) is enriched in Cu, Bi, Ag, In, Be and Li. The ore minerals (chalcopyrite, arsenopyrite, sphalerite, pyrite, cassiterite, bornite, galena and several Bi-minerals) are hosted by quartz, dark mica, chlorite, beryl and fluorite. The Korsvik vein group (generation 2b) is enriched in Fe, Cu, In, As, Bi and locally W and is dominated by large grains of chalcopyrite and arsenopyrite together with accessory sphalerite, roquesite, cassiterite, pyrite, native bismuth, wittichenite and wolframite. In addition, stannoidite, bornite and emplectite exist locally. The sulphides are mainly hosted by quartz, dark mica and chlorite. The Korsvikberget vein is characterized by a very high As content, mainly in form of arsenopyrite, which together with small amounts of chalcopyrite, bornite, pyrite, sphalerite and ilmenite are hosted by quartz, plagioclase, fluorite, chlorite and epidote.

The As-Cu-Sn and Mo-Bi-Be associations have only been found in glacial transported boulders, but are safely tied to the Marviken granite located immediately NW of the boulders. These boulders include veins with ore-bearing alteration zones. The origin of the boulders can be traced based on the main glacial transport direction from NNW (Punakivi et al. 1977), short transportation distance, soil geochemistry data (paper IV) as well as matching granitic lithology in the boulders vs. the bedrock. Thus, the source area is suggested to be located in the north-eastern part of the Marviken granite. The veins are of a different type than the wiborgite-hosted veins, with dm-wide alteration zones and with no hydrothermal quartz in the alteration assemblage.

The As-Cu-Sn association veins are enriched in As, Cu, Zn, Li, Pb, Ag, In and U. A major part of the veins consists of the same minerals, and with the same textures, as in the Marviken granite, i.e. quartz, plagioclase, orthoclase and accessory amphiboles, fluorite, beryl, zircons and apatite. In addition, the veins contain chlorite and mica which represent alteration process as well as scattered arsenopyrite, chalcopyrite and sphalerite that formed during the hydrothermal process. The Mo-Bi-Be association consists of up to 5 mm large molybdenite grains in a light green alteration zone with beryl, fluorite, epidote, chalcopyrite and unidentified, sub-microscopic Bi-bearing minerals. The ore paragenesis in one of the boulders represents a mixture of the As-Cu-Sn and Mo-Bi-Be associations, and thus represents a link between these two associations.

4.1.2 Skarn

Numerous examples of the skarn type is found in the Pitkäranta district, where four end members ore types have been distinguished based on the dominating metal (Fe, Cu, Sn and Zn). However, almost all samples are mixtures of these end members, reflecting local zoning between the ore types. The results from this study were compared with investigations by Palmunen (1939), Larin (1980) and Amelin et al. (1991), but are only partly consistent with them. The most abundant metals in the main ore types in the district are Fe, Cu, Sn and Zn. These ore types are not restricted to individual mines or mining districts. Thus, each mine cannot be classified based on these ore types because in one and the same mine, several ore types can occur with gradational borders between each other. However, some metals are more common in certain areas and associated with certain trace elements, e.g. Ag, Bi, In and Li.

4.1.3 Presence of Indium

A common feature for the ore types in the Pitkäranta district and the Sarvlaxviken area is that indium mainly occurs in Zn-rich ores. In the Pitkäranta district, the indium grades are hundreds of ppm and sphalerite is the most important indium carrier. Yet, in the Korsvik veins in the Sarvlaxviken area, the indium grades are significantly higher (up to 1490 ppm) while the zinc grades are unusually low (< 0.5 %), which has allowed for large amounts of indium minerals to form.

Zinc-rich hydrothermal fluids are able to form large amounts of sphalerite, with a large capacity to host indium. When a Zn-rich fluid is sufficiently In-rich, the sphalerite will become oversaturated with indium and proper indium minerals are formed (such as roquesite). The presence of such indium minerals can be predicted from the geochemical data of In and Zn in an ore sample; if the ratio ppm In / % Zn exceeds 50, it is very likely that the sample contains proper indium minerals. However, the indium grade must also be high enough for the mineral grains to be detected visibly in a microscope. Only one sample in Pitkäranta fulfils these criteria (having an In/Zn ratio of 51 and a In content of 291 ppm). Most of the In in that sample crystallized in chalcopyrite and sphalerite, but a minute roquesite grain was also detected. For the Korsvik veins in the Sarvlaxviken area, the extremely high indium contents (>1000 ppm) and low zinc contents (< 0.4 wt.%) yielded In/Zn ratios up to 8600 and consequently abundant roquesite was detected. The roquesite in the Korsvik veins is accompanied with sphalerite, chalcopyrite and bornite or stannoidite. This paragenesis implies formation via cooling of the hydrothermal fluids and sequential exsolution of a high-temperature Cu-Zn-(Fe)-In-sulphide. The In/Zn ratios in the Korsvikberget and Virbäcken veins are also high (c. 2000), but the In grades are not high enough (< 146 ppm) to form visible In-minerals.

4.2. The ore forming conditions in the Sarvlaxviken area

The fluid inclusion data unveiled the deposition conditions for the Sarvlaxviken veins. The inclusions contain low to moderate saline aqueous fluids with some CO_2. The fluids also carried F and S, which explains why fluorite and sulphides precipitated. The high temperature aqueous fluids exsolved in the last stage of magma crystallization. The decreasing pressure formed fractures and created the separation of a liquid/vapour phase. The steam was highly concentrated by metals and started to rise upwards in the fractures. The steam temperature decreased near the fracture walls and droplets of the higher density liquid phase separated. Some of the droplets were first carried in the ascending dispersed vapour flow until a descending liquid layer was formed due to the decreasing temperature. The salt concentration increased along the granite wall when the droplets fell down in the fracture where the water was reheated and salt-free water boiled off and passed upwards as a steam again. During this process, the liquid layer became metal saturated and started to precipitate. The vapour flow continued until the fracture was filled and sealed by quartz. This formation model may also explain the irregular metal concentrations in the polymetallic veins. Depending on the metal, it concentrates either in the liquid or in the vapour phase (Heinrich et al., 1999).

The fluid inclusion data indicate that the same fluid created generations 1, 2a and 2b. The origin of generation x remains unsolved due to absence of hydrothermal quartz in the veins hosted by the Marviken granite. Barren quartz veins in the Lillträsket area are considered to have formed from late stage granite activity from low temperature and low-salinity aqueous fluids (generation 3). However, the structural setting of the generation 3 veins is in many ways very similar to generations 1 and 2, but yet cannot be considered to represent the same main ore mineralising system.

Detailed field investigations in this area has revealed several intrusive phases, of which the wiborgite is the oldest. However, the Marviken granite is most likely co-magmatic with the wiborgite, thus probably formed during cooling of the wiborgite via filter pressing (Nygård, 2016) and resembles geochemically the late stage topaz-bearing granites described by Rämö and Haapala (2005). It is the most F-rich granite in the area and is considered as the source of the F-rich ore forming fluids.

4.3. Prospecting with the aid of till geochemistry

Till geochemistry was used to explore for possible metal anomalies in the till in the Sarvlaxviken area. Over 2000 samples were collected from nearly 20 km^2 wide area. According to Drake (1983), Dreimanis (1956), Hirvas et al. (1977) and McClenaghan et al. (2000), a till anomaly represents a local metal source if the samples are collected adjacent to the bedrock. The soil cover in the Sarvlaxviken is thin (around 0-1 m) and the samples were taken from the C-horizon, which commonly contains material from underlying bedrock. It can, therefore, be concluded that the transportation distance in Sarvlaxviken must have been very short and thus the anomalies represent local sources.

The geochemical data was processed with the K-means clustering algorithms which revealed two clusters. The samples in cluster 1 represent the local background concentrations of selected metals and include 92% of the samples. However, 8% of the samples form cluster 2, which corresponds to anomalous concentrations of Mn, In, Fe, U, Sn, W, Zn, Mo, Cu, Pb, Ag, As, Bi, Co, Cd, Be, Ga, Li, Ni and Te.

The eastern side of Sarvlaxviken includes several As, Ag, Be, Bi, Cd, Cu, Fe, In, Sn and Zn-rich till samples which are located at the Högberget. Many of these samples were also detected in the K-means cluster plot. These anomalous samples do not however represent any previously discovered polymetallic veins, because the local ice-movement would have transported the metals in a different direction. Thus, these anomalous samples indicate numerous undiscovered veins under the soil cover.

The western side of the Sarvlaxviken area includes two anomalous areas; Marviken and Lillträsket. At least two source areas are recognized in the Marviken area. Large amount of anomalous till samples and precision magnetometric measurements indicate c. 50 m long Fe, Zn, In, Cd and Sn-rich, ENE-trending mineralisation in the wiborgite while 200 m to the north, a large set of anomalous samples and the glacial transported metal-enrich boulders of the Marviken granite indicate As, Sn, Cu, Pb, Mo and Bi-rich mineralisation hosted by the Marviken granite. In the Lillträsket area, the anomalous samples exist in the Late Svecofennian granite, but the enriched metals are more or less the same. A granite boulder with Zn-rich alteration found in the Lillträsket area, support the idea of a similar type of vein forming environment in the area as for the rapakivi-hosted veins.

Till geochemistry is an efficient tool for prospecting undiscovered mineralisations. The till geochemical results indicate numerous hidden polymetallic veins on both sides of the Sarvlaxviken bay and thus the area is potential for exploration.

5. Conclusion

The overall aim of this study was to understand the character and origin of rapakivi granite-related indium mineralisations by using several different methods. As a general conclusion, it can be stated that hydrothermal environments, related to the formation of rapakivi granites, can produce a variety of indium-rich metal deposits. This thesis provides important knowledge for exploration of metals in the rapakivi areas. The thesis discuss two indium-rich ore types in southeastern Fennoscandia; polymetallic veins and skarn.

1. Polymetallic veins exist in the Sarvlaxviken area and form five groups based on the dominant metal associations. The Li–As–W–Zn–Mn, Pb–Zn and Cu–As–In associations are hosted by wiborgite, and are strongly controlled by NNW-trending structures that evolved in two main stages. The Li–As–W–Zn–Mn association (generation 1) formed in a typical greisen environment with Li-bearing mica in significant alteration halos around a narrow quartz vein. The Pb–Zn association occurs in a similar vein generation, but without typical high-temperature minerals and is considered to have formed at a higher crustal level. The Cu–As–In association (generations 2a and 2b) formed under more brittle conditions leading to fracturing, quartz veining and metal precipitation of ore minerals. The As-Sn-Cu and Mo-Bi-Be associations (generation x) are hosted by alteration zones in the Marviken granite, but has only been recognized in glacier transported boulders of Marviken granite.

2. Four end member skarn ore types, represented by the dominating metal (Fe, Cu, Sn and Zn) have been recognised in Pitkäranta. These end members form mixtures that are reflecting local zoning between the ore types. Several ore types can exist in one and the same mine with gradational borders between each other. However, some metals are more common in certain areas and associated with specific trace elements (e.g. Ag, Bi, In, Li).

3. Indium occurs mainly in Zn-rich ores with sphalerite as the main carrier, both in the Pitkäranta ore district and the Savlaxviken area. However, high (> 50) ppm In/% Zn ratios leads to the formation of proper indium minerals, e.g. roquesite. Roquesite was observed in one sample from the Pitkäranta district and in several samples from the Korsvik veins in the Sarvlaxviken area.

4. The fluid inclusion data indicate that the depositional conditions for the wiborgite hosted polymetallic veins were similar regardless of vein generation. Formation of specific metal were related to the abundance of chlorine in the liquid-dominated phase and sulphur in the vapour-rich phase. The fluids emanated most likely from the F-rich Marviken granite.

5. Till geochemistry is an good method to study geochemical signatures of the till around the polymetallic veins in the Sarvlaxviken area. Numerous metal anomalies were recognized, which could not be connected to the already discovered veins. Therefore, these till anomalies are interpreted to indicate numerous undiscovered veins in the area.

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