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Mississippi Valley Type ore deposits, the Laisvall Pb-Zn deposit and origin of Pb-Zn-bearing sandstone glacial erratic from the Raahe area

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ABSTRACT FOR THESIS

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Abstract

The Geological Survey of Finland collected zinc-, lead- and copper-bearing glacial sandstone boulders in 1970's and 1980's south of Raahe, Finland. The origin of these sandstones remains inconclusive. The petrographic analysis shows sphalerite, galena, pyrite and chalcopyrite as the main ore-bearing minerals in the matrix of the sedimentary rocks, associated with quartz, feldspar and calcite. Signs of a carbonate-cemented sediment and metal-rich fluid interaction suggest that mineralization was formed as part of a Mississippi Valley type deposit system. The main hypotheses suggest that the boulders were derived from the Laisvall MVT deposit of Sweden or from an unknown mineralization in the Bothnia Bay. The objective of this study was to make a literature review of the Laisvall deposit and analyze the compositional range of sphalerite in a sample from Raahe and compare it to the chemical characteristics of the Laisvall MVT deposit in Norwegian Caledonides, to determine the origin of Raahe glacial erratic sample. The second objective of the study was to assess the dependency of the color on the iron content of the sphalerite. The study is completed by optical microscopy and electron microprobe analysis (EPMA).

Keywords: Glacial erratics, Mississippi Valley type Pb-Zn deposit, sphalerite, Caledonides, Laisvall, Raahe.

Additional Information		

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1 INTRODUCTION

In 1981, Geological Survey of Finland (GTK) studied the shore of the Bothnian Bay south of Raahe (Fig. 1) (Niemelä, 1983). In a shore line distance of 10 km from Raahe, several Pb-Zn-Cu-bearing sandstones were found. The origin of the samples was unknown and has become a point of interest to GTK. Similar Pb-Zn-Cu-bearing sandstones occur in hydrothermal Pb-Zn-Cu-enriched systems, such as sedimentary exhalative deposits (SEDEX), volcanogenic massive sulfide deposits (VMS) and Mississippi Valley type deposits (MVT). Niemelä (1983) compared the samples with the Muhos Formation, which is located northeast from Raahe, with the sandstones from Satakunta, in Western Finland Province, and with Pb-Zn-bearing sandstones in Sweden, including those occurring at Laisvall, considering them as a possible provenance of the Raahe sample. Another possible scenario is that samples were transported from the Bothnia Bay seafloor by a glacial ice flow, where an unknown mineralization potentially occurs (Nilsson, 2017).

In this study, the focus is on the Laisvall deposit in Swedish Caledonides, because the many mineralogical, textural and chemical characteristics of the Raahe boulders are similar with those of the Laisvall deposit. The aim of this work is to analyze the element content of the sphalerite in one of the Raahe samples and compare it to sphalerite from Laisvall. The study also deals with the iron content of sphalerite and the factors that cause its variation.

This study started by examining 4 thin section samples of sandstone from Raahe. One sample with sphalerite grains showing clear growth zoning was chosen for for electron microprobe analysis (EPMA) to examine its composition.

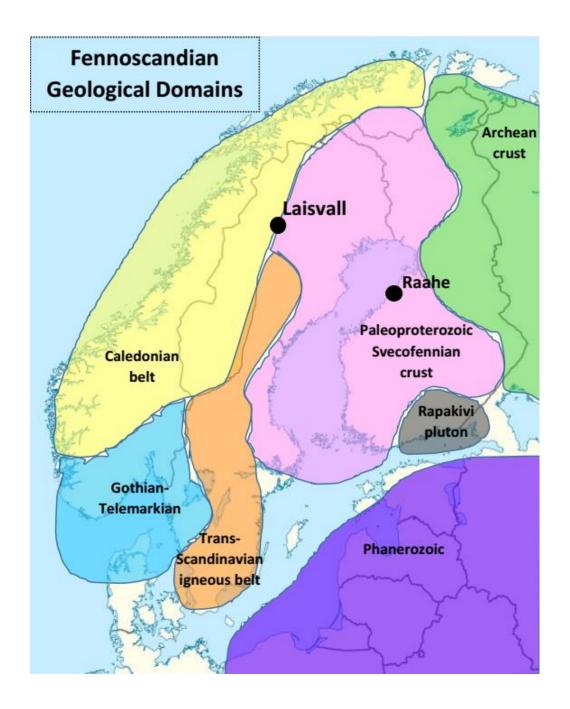


Figure 1. Main geological units in Fennoscandia and the location of Raahe and Laisvall. Based on Roberts and Slagstad (2015) and Scandinavia location map.svg under the GNU Free Documentation Licence and Creative Commons license.

2 TYPICAL CHARACTERISTICS OF THE MVT DEPOSITS

The Mississippi Valley type (MVT) deposits are epigenetic Pb-Zn sulfide deposits formed within large sedimentary basins. The age of the MVT deposits is mostly Devonian to Permian (400-250 Ma). They have characteristically a simple ore and gangue mineralogy: the main ore minerals are sphalerite and galena with chalcopyrite and other sulfide minerals, and the gangue minerals include calcite, dolomite, fluorite, and barite. Ore textures are usually matrix breccias or breccia clasts (Ridley, 2013). Median resource parameters for individual MVT deposits are 7.0 Mt ore with 1.9 wt% Pb, 6.0 wt% Zn, 0.23 wt% Cu and 32.5 g/t Ag.

2.1 Geological settings of the MVT deposits

Missisippi Valley type deposits usually occur in shallow sedimentary basins in carbonate rock environments (Ridley, 2013). Bjørlykke and Sangster (1981) proposed a sandstone-hosted deposit type as a distinct subtype of the MVT deposits. They are less numerous than their carbonate-hosted counterparts, with the most important and well-studied sandstone-hosted deposits being the Jinding deposit in China (Xue et al., 2007), the Mechernich and Maubach deposits in Germany (Bjørlykke and Sangster, 1981; Krahn and Baumann, 1996) and the Laisvall deposit in Sweden (Robb, 2005).

The evolution of the host basins has been influenced by tectonism after sedimentation. Radiometric age and palaeomagnetic data show that the majority of MVT deposits formed between ten and hundred million years later than deposition of the host sediments (Ridley, 2013). Several MVT deposits formed during the Devonian to Permian, during assimilation of Pangea and corresponded to a series of tectonic events. The second most important time interval for the formation was from the Cretaceous to Tertiary when microplate assimilation, associated with compressional tectonic activity, affected Africa-Eurasia and the western margin of North America (Leach et al., 2001). Tectonic events provide an important clue as a factor that caused hydrothermal activity involved in the formation of the MVT deposits (Robb, 2005).

2.2 Mineralogy and textures

The Mississippi Valley type ore deposits have characteristically a simple ore and gangue mineralogy, which is the main characteristic of the MVT deposits, but a simplicity usually appears only on a district scale, while a considering several MVT districts, the list of minerals can consist more than 30 minerals (Ohle, 1959). Lead and zinc are the most common economically valuable elements in the ore (Sangster, 1990). As ore minerals also marcasite, pyrite with minor chalcopyrite and other sulfide minerals occur (Ridley, 2013). The gangue mineralogy is mainly composed of dolomite or calcite, barite and fluorite (Ridley, 2013).

Ore textures in MVT deposits are variable but most diagnostic textures are those produced by open-space filling, i.e. ore textures are partly controlled by ore-bearing breccias. There are three major types of breccia: crackle breccia, mineralized breccia (ore matrix breccias, ore minerals grown between breccia clasts of the host rock) and barren breccia (rock-matrix breccias, where smaller host-rock fragments between breccia clasts are replaced by sulfide minerals). Ore minerals can also grow as replacement of carbonate and evaporite minerals (Sangster, 1988).

The textures of the sulfide minerals are complex and mixed with coarse, euhedral crystals, banded sulfides and, for example, dendritic galena. Textures indicate that open space represents secondary porosity that formed before deposition of the ore minerals. Progressive filling of the open space is complex and systematic, as indicated by growth of one gangue or ore mineral over earlier minerals and by sphalerite with different colored growth zones. Dolomite is the latest mineral to form in between the ore sulfides in many ores (Ridley, 2013).

2.3 Relations of ore to its host rock

Deposits are discordant on a deposit scale but stratabound on a district scale. Ores are hosted in carbonate units, most commonly in zones of highly brecciated dolomites and limestones (Sangster, 1990). An important host for the ore is the lowest carbonate unit above clastic sedimentary rocks, but in most cases, the ore body occurs in carbonate

units at different levels, in ore-hosting breccia bodies (Ridley, 2013). According to Sangster (1990) dolomite can form a large discordant halo around the entire ore or surround individual deposits. The most common alteration style in all MVT deposits is dissolution of the host carbonate inside and around ores, usually associated with brecciation. With such effects as dolomitization and silicification they constitute the major form of wall rock alteration (Sangster, 1990).

2.4 Nature of the ore fluid

Modern models of the origin of MVT deposits start with the idea that Pb and Zn were carried into the MVT region with a migrating, topographically driven fluid flow. Fluids are sodium-calcium-chloride brines with a high-salinity (\geq 15 wt% NaCl); and low temperature (100-150°C) (Ridley, 2013). Fluids also contain SO_4 , CO_2 and CH_4 , organic compounds and oil-like droplets, and its pH is 4-6 (Robb, 2005). The fluid originally might have been acidic or hydrogen ions were produced by precipitation of metal sulfides (Robb, 2005):

$$H_2S + Zn^{2+} \rightarrow ZnS + 2H^+$$

Hydrothermal dissolution of carbonate itself requires acidic solution (Robb, 2005) and occur by a reaction as:

$$CaMg(CO_3)_2 + 4H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2H_2O + 2CO_2$$

The composition of the saline ore fluids is similar to saline pore waters at few kilometers depth in many present-day sedimentary basins with evaporite units. Geochemical studies of the ore fluids show that the fluids were generally generated by evaporation of seawater or other surface water and less commonly by dissolution of halite into groundwater (Ridley, 2013).

2.5 Genesis of the MVT deposits

The understanding of the behavior and the origin of the hydrothermal fluids forming MVT deposits forming hydrothermal fluids has not been straightforward and simple since their discovery, but the lack of igneous rocks associated with MVT deposits demonstrates that igneous intrusions cannot represent the sources for ore fluids (Sangster, 1990).

First interpretations showed that major composition, high salinities and temperatures of the MVT ore forming fluids are quite similar to oilfield brines that can be found in present-day sedimentary basins (Sverjensky, 1986). According to Ohle (1980), White (1974) and Cathles and Smith (1983), ore-forming brines are produced by burial of sedimentary basins, when with increasing temperature, pore fluids started to heat up and rise along aquifers towards the surface forming the MVT ore deposit in carbonate host rocks. The theory of basin-generated origin for the MVT fluids, however, cannot explain the origin of metals in the ore (Sangster, 1990). Interpretations have been presented that fluid has acquired metals and other elements along the path (Anderson and Macqueen, 1982) and that solutions migrated through two different aquifers, quartz-sandstone and dolostone, react with sandstone and affect enrichment of Zn. In dolostone aquifers, the MVT deposit with a high content of Zn and Pb can form (Sverjensky, 1984).

The MVT deposits are related to orogenic activity. This provides a clue as to the causes of hydrothermal activity involved in the MVT formation. In this model, compression results faults and also drive heated acidic fluids travel towards the surface through brecciated fault zones and react with dolomite and sandstone, forming bedded-type Pb-Zn mineralization (Robb, 2005). Concerning metal transport and deposition, salty brines transport Pb and Zn in the form of chloride complexes. The solubility of these metals is controlled by pH, temperature and concentration of sulfide (Leach et al., 2005). There are several ways to achieve feasible solubilities of Pb and Zn: 1) fluids must be relatively oxidized (sulfur transported as SO_4^{2-} and not as H_2 S or HS_-) or at low pH (Anderson, 1975), 2) sulfate is reduced by organic matter to sulfide at the depositional site (Robb, 2005), or 3) fluid contains a sulfate-reducing agent itself (Robb, 2005).

3 LAISVALL PB-ZN DEPOSIT

One of the world's major and Europe's largest lead-zinc deposit is located at Laisvall in central Sweden. It is one of the numerous similar sandstone-hosted Pb-Zn deposits occurring at the eastern front of the Caledonides (Fig. 2). Despite challenging exploration conditions in a remote and sub-arctic area, the Laisvall ore deposit was discovered in 1939 using boulder tracing and following diamond drilling. Mining operations ran from 1942 to 2001, during which 64 Mt of ore was extracted (Colin, 1979).

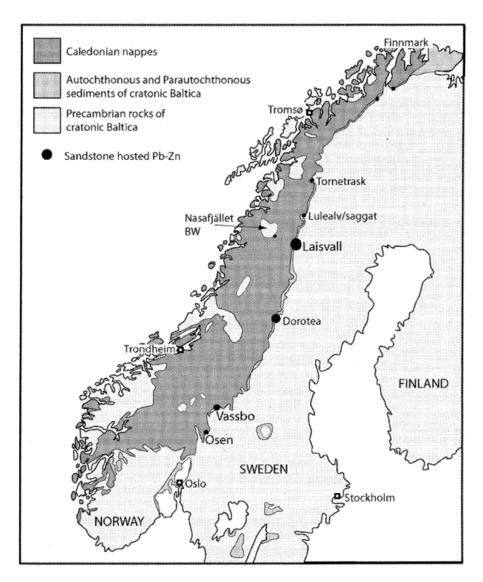


Figure 2. Map of Scandinavia showing sandstone- hosted Pb-Zn deposits (Kendrick et al., 2005). Published with permission from Elsevier and Copyright Clearance Center.

3.1 Geological setting of the area

In the central part of Sweden, the crystalline basement contains Archean and Paleoproterozoic rock, which were deformed in the Svecofennian orogeny at 1.8-2.0 Ga, and late Paleoproterozoic to early Neoproterozoic sedimentary, volcanic, and intrusive rocks dated at 0.9-1.7 Ga (Bergman et al., 2012). On the western stable platformal margin of the crystalline basement of the Baltica continent, a thin cover of Ediacaran to Lower Ordovician sedimentary siliciclastic rocks were deposited discontinuously (Bergman et al., 2012). As result of the collision of Baltica and island arc during the Caledonian orogeny, foreland basin developed followed by exhumation of high-pressure rocks (Dallmeyer and Gee 1986; Stephens 1988). The collision and development of a foreland basin preceded the closure of Iapetus Ocean and Laurentia-Baltica collision in late Ordovician (450 Ma) and continued through the Silirian and the Devonian with emplacement of the Caledonian thrust nappes. (Gee, 1975; Stephens, 1988). Laisvall deposit occurs within Ediacaran to Silurian platformal sediments beneath allochtonous Caledonian nappes (Rickard et al., 1979).

3.2 Geology of the Laisvall deposit

The mineralization at Laisvall is stratabound and located mainly in autochtonous sandstones (Fig. 3) having. Precambrian weathered granite forms the basement at Laisvall. It is overlain by sandstones, which are assigned to the Laisvall Group. The group is subdivided into 3 formations, the Ackerselet, Sävvovare and Grammajukku Formations. The glaciogenic Ackerselet Formation is attributed to the 630 Ma Varangerian glaciation when Baltica lay at southerly polar latitudes (Willdén, 1980; Torsvik and Rehnstorm, 2001). The Sävvovare Formation was deposited in a marine environment on the Balticoscandian margin and includes lagoonal phosporites and limestones. The Grammajukku Formation consists brachiopod- and trilobite-bearing limestones indicating an Early Cambrian age when Baltica lay at midlatitudes (Willdén, 1980; Torsvik and Rehnstorm, 2001). The Middle Cambrian pyritic and carbonaceous Alum Shale, which contains mainly of black- and gray laminated, organic-rich shale, acted as a plane of weakness for Caledonian thrusting (Gee et al., 1974).

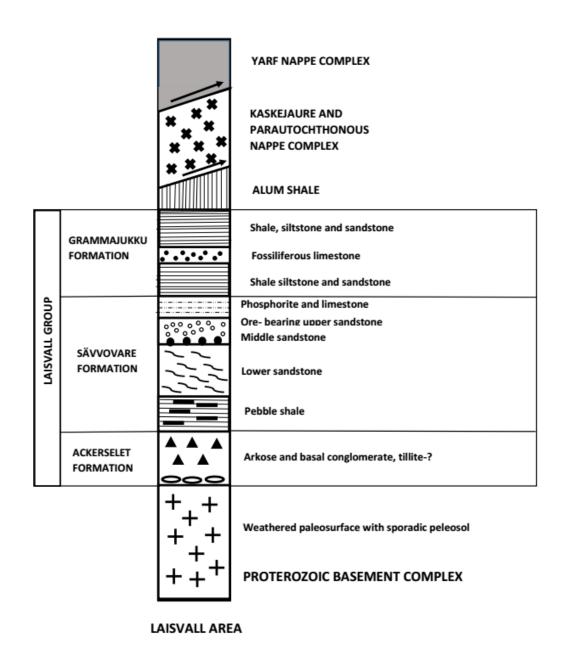


Figure 3. Stratigraphy of the Laisvall area (modified after Rickard et al., 1979).

3.3 Ore size and grade

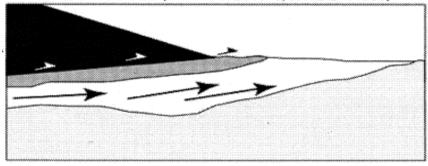
The Laisvall ore bodies are deposited in the Sävvovare Formation in the lowermost sandstones (Rickard et al., 1979) and in mineralized veins in the basement (Romer, 1992). In addition, some vein-type mineralization is reported in the Ackerselet

Formation (Romer, 1992). Sandstones have a high porosity (<25%) and in ore- rich layers, almost all the original intergranular space is filled with galena or sphalerite, the main minerals of the MVT deposits. The Laisvall ore bodies contain a total ore amount of 80 Mt averaging 4.3 wt% Pb, 0,6 wt% Zn, 9 g/t Ag and 30 g/t Cd (Colin, 1979). The ore-bearing strata can be divided into two economic stratabound orebodies: the Kautsky Member, which is mainly Pb- mineralized (4.62 wt% Pb, 0.24 wt% Zn, Pb/Zn= 19:1) and the Nadok Member, which has a higher zinc content (3.53 wt% Pb, 1.51 wt% Zn, Pb/Zn=2.3:1) (Lindblom, 1986). Even though only the mineralization in the Kautsky and the Nadok Members is economic, other mineralized occurrences are reported from the Saivatj Member and Tjalek Member (Rickard et al., 1979).

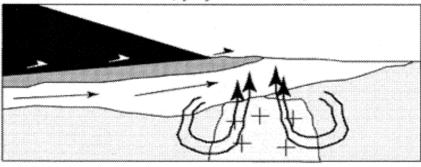
3.4 Genetic models of the Laisvall deposit

The origin source of the Laisvall mineralization is a subject to speculations. Sulfur isotope compositions of sulfides indicate a sea water source. The 3 proposed genetic models are summarized in Fig. 4. All of them agree that a fluid source from within the western Caledonian orogenic belt and fluid mixing are a substantial trigger for mineralization. According to the model of Rickard et al. (1979), fluids migrated to the site of mineralization through the sedimentary aquifers as a result of orogenic deformation and thrusting (Rickard et al., 1979; Lindblom, 1986). The single pass fluid flow model of Romer (1992) suggests that reactivated Caledonian basement fractures created zones with a higher permeability causing penetration of brines and fluid migration through the basement. Thus, structural faults may be important in localizing high grade ore zones and fluid mixing. Bjorlykke et al. (1991) argue that at Laisvall a multipass fluid flow took place; in this model, an average higher crustal heat flow caused fluid convection in the basement. Saintilan et al. (2016) provided the most recent genetic model for the Laisvall deposit, suggesting that slightly acidic brines residing in pre-Ediacaran rift sediments migrated through the same plumbing system and acquired metal on the way.

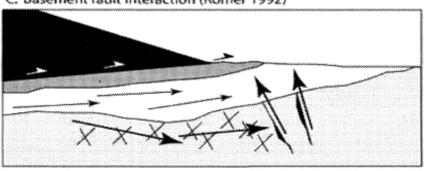
A. Basinal-brine model (Rickard et al. 1979, Lindblom 1986)



B. Convective circulation (Bjørlykke et al. 1991)



C. Basement fault interaction (Romer 1992)



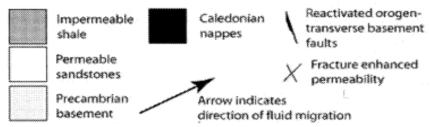


Figure 4. Schematic diagrams of 3 alternative genetic models for the Laisvall deposit, Sweden (Kendrick et al., 2005). A) Basinal brine migration through sedimentary aquifers (Rickard et al., 1979; Rickard, 1983; Lindblom, 1986; Duane and de Wit, 1988). B) Convective circulation of a basinal brine driven by underlying granites (Bjorlykke et al., 1991). C) Fluid migration through Caledonian reactivated orogen transverse basement faults and basement culminations (Romer, 1992). Published with permission from Elsevier and Copyright Clearance Center.

4 GEOLOGY OF THE RAAHE-LADOGA ZONE

Raahe is located in the Vihanti-Pyhäsalmi belt, which is part of the Raahe-Ladoga zone. The Vihanti-Pyhäsalmi belt is the most important host of the volcanogenic massive sulfide (VMS) deposits in Finland. The region is divided into two main units: the lower biomodal volcanic unit, the Pyhäsalmi Group, and the upper volcano-sedimentary association, the Vihanti Group. The ages of the two groups are similar, ca. 1.93-1.92 Ga (Mäki et al., 2015).

The Vihanti-Pyhäsalmi belt is bordered by the Central Finland Granitoid Complex and supracrustal formations (1.93-1.87 Ga) of the Svecofennian domain in the west and Archean basement complexes (3.1-2.6 Ga) in the east. The Raahe-Ladoga zone itself is the collisional border of Paleoproterozoic island arcs against Archean terranes (Fig.1). The metamorphic grade of the Vihanti-Pyhäsalmi belt area is mainly from lower to upper amphibolite facies (Korsman et al., 1997). Two main economically profitable deposits are Pyhäsalmi in the Pyhäsalmi Group and Vihanti in the Vihanti Group. Several other small deposits are also present, but they are not economic (Laine et al., 2015).

5 SCANDINAVIAN GLACIATION

During the Weichcelian glaciation (11 500-116 000 years before present), the whole Fennoscandia, including northern parts of Russia, Poland, German countries and Denmark was covered by the Scandinavian ice sheet. Glacial striae, such as scoured and scratched rocks, glacial erratics and deposition of till prove that the origin of the Weichcelian glaciation was in the mountains of Scandinavia (Gluckert, 1973). The increasing ice masses expanded into piedmont glaciers and spread over Fennoscandia. The variation of the directions of the striae indicates that the ice divided into several ice flows during the glaciation. However, the main trend of the ice flow movement over Scandinavia is from west to east. The divided ice flows are indicated on the map of Fig.5. Differences in the ice flow strongly depend on the local topography (Gluckert,

1973). The sample studied in this work is considered as a glacial erratic, which has been transported roughly from the west by the ice flows during the Weichcelian glaciation.



Figure 5. Glacial ice flow directions (modified after Gluckert, 1973) and the locations of Laisvall and Raahe.

6 SPHALERITE COMPOSITIONAL VARIATION

Sphalerite is a zinc sulfide mineral with a chemical composition of (Zn,Fe)S. It can be found in igneous, metamorphic and sedimentary rocks. Sphalerite is the major source of one of the world's most important metals, zinc.

The iron content of sphalerite depends on the equilibrium between sphalerite and iron sulfides approached during the deposition or metamorphism of the ore deposit (Craig et al., 1984). A small amount of iron is present when sphalerite equilibrated with pyrite

under conditions of a high sulfur activity and low temperature. If ore's sulfur activity was buffered by pyrrhotite and pyrite, the iron content of sphalerite is much higher and relatively constant (approximately 11.7 wt% Fe). If sphalerite was equilibrated only with pyrrhotite, it can contain up to 30.1 wt% of iron.

Craig et al. (1984) pointed out that the contents of cadmium and manganese in sphalerite in sulfide ores can range from 0.1 to 0.3 wt% and 0.0 to 0.5 wt%, respectively. The manganese and cadmium content of sphalerite tend to rise as the pyrrhotite/pyrite ratio increases; however, the controls on this distribution remain unknown.

Spectroscopic analyses suggest that the color of sphalerite can be associated with the presence of certain elements: green with Co and Fe, red with Sn, In, Ag and Mo, and yellow often with Ge, Ga, Cu, Hg and Cd (Nesse, 2003). The presence of minor element also affects the luminescence of sphalerite grains.

7 SAMPLES AND RESEARCH METHODS

7.1 Sample

The sample studied in this work was picked from the shore of the Bothnian Bay south of Raahe in 2015, where zinc-, lead- and copper-bearing glacial sandstone erratics have been found by GTK (Niemelä, 1983). According to Niemelä (1983), the abundance of the boulders pointed to a proximal source. In 1982, GTK accomplished sampling on the sea ice to the north from the previous discovery using a cobra-drill equipment, but no sandstone mineralization was found where the boulders might have come from (Niemelä, 1983).

The detrital grains in the sample are quartz and feldspar. Their size is 0.05-1 mm and they are well rounded, though often resorbed when in contact with sulfides. The sample does not show any orientation or signs of metamorphism. The matrix consists of galena, sphalerite, and calcite. Figure 6 displays a scanned figure of one of the sphalerite-rich sandstone samples.



Figure 6. Scanned thin section of sulfide-bearing sandstone, showing a typical clastic structure with matrix brown sphalerite. Sample 2-EAN-15. Figure width 2 cm.

7.2 Analytical methods

7.2.1 Microscopy

A transmitted- and reflected-light polarizing microscope was used in the petrographical study and the image of the zoned crystal of sphalerite was taken by a digital microscope camera.

7.2.2 Electron microprobe analyzer

The electron microprobe analyzer (EPMA) is an analytical tool used to determine the chemical composition of small volumes of solid material. The operation principle is similar to that of the scanning electron microscope where the sample is bombarded by an electron beam and x-rays are emitted from the surface, with each element being distinguished at its characteristic wavelength. In the Center of Microscopy and Nanotechnology of Oulu University, a Jeol JXA-8200 electron microprobe analyzer allowed to run chemical analyses of the sample.

8 RESULTS

8.1 Mineral chemistry

Pure sphalerites are colorless and transparent under the microscope, but in association with iron, copper and lead sulfides, the transparency decreases and the color of sphalerite changes. All seven electron microprobe analyses showed low amounts of Fe in sphalerite, ranging from less than one weight percent to five weight percent. This is consistent with sphalerite occurring together with pyrite (Craig et al., 1984).

Almost opaque bands of the analyzed sphalerite (Fig. 7) grain clearly have higher iron content, up to 4.4 wt%. The lowest iron content is in transparent sphalerite grains, decreasing down to 0.7-1.3 wt% (Table 1). Transparent grains also show changes of shade, which is probably affected by the presence of manganese (Fig. 8). The grains become darker with the increase in the manganese and iron contents.

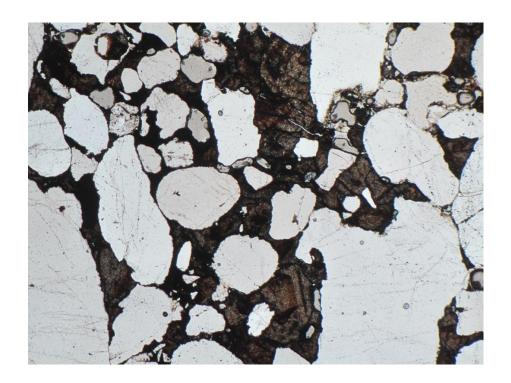


Figure 7. Photomicrograph of sphalerite-rich sandstone in transmitted light, showing growth zoning in the lower part of the figure. Width of view 3.4 mm. Sample 2-EAN-15. Photo taken by E. Hanski.

Small variations in abundances of the harmful minerals such as cadmium were also observed. According to Wen et al. (2016), in the low-temperature systems such as MVT deposits, Cd concentrations are usually high but variable. The results of this study show low Cd concentrations of 0.03- 0.13 wt%, with Zn/Cd ratio varying from 500 up to 2000.

Table 1. Electron microprobe analyses of sphalerite. For locations of the analytical points, see Fig. 6.

No.	Ga wt%	S wt%	Mn wt%	Bi wt%	As wt%	Pb wt%	Cu wt%	Ag wt%	Fe wt%	Cd wt%	Zn wt%	In wt%	Sb wt%	Total
1	0.024	33.433	0.051	0.000	0.000	0.000	0.009	0.009	1.254	0.094	65.662	0.019	0.022	100.577
2	0.064	33.570	0.022	0.000	0.132	0.000	0.116	0.006	2.473	0.029	64.401	0.051	0.043	100.907
3	0.000	33.394	0.022	0.000	0.003	0.000	0.026	0.012	0.670	0.076	65.790	0.016	0.013	100.022
4	0.076	33.697	0.000	0.000	0.000	0.000	0.020	0.012	0.748	0.130	66.282	0.000	0.013	100.987
5	0.063	33.188	0.027	0.000	0.048	0.000	0.000	0.023	4.224	0.121	61.275	0.000	0.019	98.988
6	0.000	33.990	0.000	0.015	0.000	0.000	0.118	0.017	1.746	0.052	64.272	0.000	0.000	100.210
7	0.000	34.428	0.000	0.000	0.000	0.000	0.100	0.000	4.378	0.105	61.567	0.000	0.000	100.578

Indium, which is nowadays used as an important component of touch screens and solar panels, was found in sphalerite of the studied sample, though its concentration is low, falling between 0.016 and 0.05 wt%; In Nilsson's (2017) project, the maximum concentration of indium is 0.07 wt%. According to Briskey (2015), the average content of indium in the MVT deposits is from 0.01 to 0.1 wt% and mineral deposits with the highest indium concentration have 0.1-1.25 wt%, meaning that there is no potential economic interest in extracting indium as a byproduct.

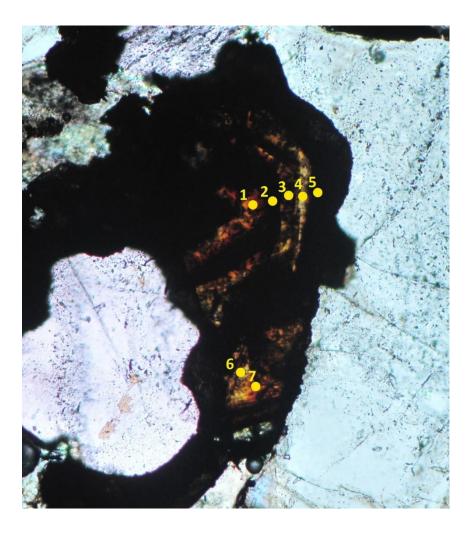


Figure 8. Photomicrograph of a sphalerite grain showing analytical points (numbers 1-7) of electron microscope analysis. Transmitted light, parallel polars, sample 2-EAN-15.

9 DISCUSSION

The origin of the Raahe glacial sandstones erratics has been point of interest for many geologists for decades. Niemelä (1983) discussed the possible origin from the Muhos Formation in the Bothnia Bay area and from the Swedish Caledonian belt, where the lead-zinc deposits of Vassbo, Dorotea, Laisvall, Luleälv, Saggat and Torneträsk are located.

The sample of this study and the Laisvall deposit are both rich in Pb and Zn, and their mineralogy is also similar, with quartz clusters and carbonate matrix replaced by sphalerite, galena and sulfides. No signs of metamorphism have been observed. Laisvall is also located on a movement direction of a Weichcelian glacier (Fig. 5), which could also have passed near Raahe and transported boulder to their discovery site. Several Nilsson's (2017) project samples contain galena ore only and others contain galena and sphalerite ore; similar segregation can be observed in the Laisvall deposit (Nilsson, 2017).

Lead isotope analysis shows that the Raahe samples and the Laisvall deposit have similar radiogenic Pb-Pb isotope compositions, produced by high time-integrated U/Pb ratios in the Pb source, but sulfur isotope data indicates much heavier sulfur in the Laisvall deposit than in the Raahe sandstone boulders (Nilsson, 2017).

Despite the fact the Raahe Pb-Zn-bearing sandstone boulder and the Laisvall deposit have many features in common, there are some factors that make Laisvall as a source for the Raahe boulders very unlikely. The most important among them are the difference in sulfur isotope composition and the long distance (350 km) from Laisvall to Raahe. As suggested by Niemelä (1983) and Nilsson (2017), a closer look at the Bothnia Bay seafloor could lead to a discovery of a new sandstone unit, which is correlative with the Ediacaran to Silurian platformal cover sedimentary rocks at the Caledonian front, representing a new metallogenic area in the Bothnian Bay region.

10 REFERENCES

Anderson, G.M., 1975. Precipitation of Mississippi Valley-type ores. *Economic Geology* **70**, 937-42.

Anderson, G.M. and Macqueen, R.W., 1982. Ore deposits models-6. Mississippi Valley-type lead-zinc deposits. *Geoscience Canada* **9**, 108-17.

Bergman, S., Stephens, M.B., Andersson, J., Kathol, B., Bergman, T., 2012. Geological Map of Sweden: Geological Survey of Sweden, scale 1:1 000 000.

Bjørlykke, A., Sangster, D.F., 1981. An overview of sandstone lead deposits and their relation to red-bed copper and carbonate-hosted lead-zinc deposits. *Economic Geology* **75**, 179–213.

Bjørlykke, A., Sangster, D.F. and Fehn, Y., 1991. Relationship between high heat - producing [Hhp] granites and stratabound lead - zinc deposits. In: Pagel, M., Leroy, M. (eds) Source, Transport, and Deposition of Metals. Balkema, Rotterdam, p. 257-260.

Briskey, J.A., 2005. Indium in zinc-lead and other mineral deposits- a reconnaissance survey of 1118 indium analyses published before 1985. U.S. Geological Survey, Open File Report 2005-1209, 8p.

Cathles, L.M. and Smith, A.T., 1983. Thermal constraints on the formation of mississippi valley-type lead-zinc deposits and their implications for episodic basin dewatering and deposit genesis. *Economic Geology* **78**, 983-1002.

Colin, D., 1979. *Atlas of Economic Mineral Deposits*. Chapman and Hall, London, 141 p.

Craig, J.R., Ljokjell, P. and Vokes, F.M., 1984. Sphalerite compositional variations in sulfide ores of the Norwegian Caledonides. *Economic Geology* **79**, 1727-1735.

Dallmeyer, R.D., Gee, D.J., 1986. 40Ar/39Ar mineral dates from retrogressed eclogites within the Baltoscandian miogeocline: implication for a polyphase Caledonian orogenic evolution. *Geological Society of America Bulletin* **97**, 26-34.

Duane, M.J. and de Wit, M.J., 1988. Pb-Zn ore deposits of the northern Caledonides: Products of continental-scale fluid mixing and tectonic expulsion during continental collision. *Geology* **16**, 999-1002.

Gee, D.J., Karis, L., Kumpulainen, R. and Thelander, T., 1974. A summary of Caledonian front stratigraphy, northen Jämtland/southern Västerbotten, central Swedish Caledonides. *Geologiska Föreningens I Stockholm Förhandlingar* **96**,389-397.

Gee, D.G., 1975. A tectonic model for the central part of the Scandinavian Caledonides. *American Journal of Science* **275**, 468-515.

Gluckert, G., 1973. Map of glacial striation of the Scandinavian ice sheet during the last (Weichsel) glaciation in northern Europe. *Bulletin of the Geological Society of Finland* 1-8.

Kendrick, M.A., Burgess, R., Harrison, D., and Bjørlykke, A., 2005. Noble gas and halogen evidence for the origin of Scandinavian sandstone-hosted Pb-Zn deposits. *Geockimica et Cosmochimica Acta* **69**, 109-129.

Korsman, K., Koistinen, T., Kohonen, J., Wennerström M., Ekdahl, E., Honkamo, M., Idman, H., Pekkala Y., 1997. *Suomen kallioperäkartta—Berggrundskarta över Finland—Bedrock map of Finland 1:1,000,000*. Geological Survey of Finland, Espoo.

Krahn, L., Baumann, A., 1996. Lead isotoope systematics of epigenetic lead-zinc mineralization of the western part of the Rheinisches Schiefergebirge, Germany. *Mineral Deposita* **31**, 225-237.

Laine, E., Luukas, J., Mäki, T., Kousa, J., Ruotsalainen, A., Suppala, I., Imana, M., Heinonen, S. and Häkkinen, T., 2015. The Vihanti-Pyhäsalmi area: 3D, 4D and 10 predictive modelling of major mineral belts in Europe. In: Weihed, P. (Ed.), 3D, 4D and 10 Predictive Modelling of Major Mineral Belts in Europe. Springer, Cham, p. 123-144.

Leach, D., Sangster, D., Kelley, K., Large, R.R., Garven, G., Allen, C., Gutzmer, J. and Walters, S., 2005. Sediment-hosted lead-zinc deposits: A global perspective. *Economic Geology* **100**, 561-607.

Leach, D., Bradley, D., Lewchuk, M., Symons, D., De Marsily, G. and Brannon, J., 2001. Mississippi Valley-type lead–zinc deposits through geological time: implications from recent age-dating research. *Mineralium Deposita* **36**, 711-740.

Lindblom, S., 1986. Textural and fluid inclusion evidence for ore deposition in the Pb-Zn deposit at Laisvall, Sweden. *Economic Geology* **81**, 46-64.

Mäki, T., Kousa, J., Luukas, J., 2015. The Vihanti-Pyhäsalmi VMS Belt. In Maier, W.D., Lahtinen, R. and O'brien, H., (Eds.) *Mineral Deposits of Finland*. Elsevier, USA. p. 507-527.

Nesse, W. D., 2012. *Introduction to Optical Mineralogy*. Oxford University Press, 384 p.

Niemelä, M., 1983. Investigations of zinc-, lead-, and copper-bearing sandstone boulders in the Raahe area in years 1981-1982. Unpublished Report M19/2441/-83/1/10. Geological Survey of Finland, 21 p. (in Finnish)

Nilsson, E.A., 2017. Zn-Pb-Cu sulfide-bearing sandstone glacial erratic near Raahe on the western coast of Finland and a discussion on their origin. Master's thesis, Oulu Mining School, University of Oulu, 55 p.

Ohle, E.L., 1980. Some considerations in determining the origin of ore deposits of the mississippi valley type; Part II. *Economic Geology* **75**, 161-72.

Ohle, E.L., 1959. Some considerations in determining the origin of ore deposits of the Mississippi Valley type. *Economic Geologists* **54**, 769-789.

Rickard, D.T., 1983. Precipitation and mixing mechanisms in Laisvall-type sandstone lead-zinc deposits. In: Kisvarsanyi, G. et al. (Eds.) *International Conference on Mississippi Valley- Type Lead-Zinc Deposits*, University of Missouri-Rolla, p. 449-458.

Rickard, D.T., Wallin, B., Selkman, S. and Christofferson, C.H., 1979. Mineralization controls in the sandstone lead-zinc deposits at Vassbo, Sweden. *Economic Geology* **74**, 1239-1249.

Ridley, J., 2013. Ore Deposit Geology. Cambridge University Press, Cambridge, 398 p.

Robb, L.J., 2005. *Introduction to Ore-Forming Processes*. Blackwell Publishing, Oxford, 373 p.

Roberts, N.M.W. and Slagstad, T., 2015. Continental growth and reworking on the edge of the Columbia and Rodinia supercontinents; 1.86-0.9 Ga accretionary orogeny in southwest Fennoscandia. *International Geology Review* **57**, 1582-1606.

Romer, R.L., 1992. Sandstone-hosted lead-zinc mineral deposits and their relation to the tectonic mobilization of the baltic shield during the Caledonian orogeny, a reinterpretation. *Mineralogy and Petrology* **47**, 67-85.

Sangster, D.F., 1990. Mississippi Valley-type and sedex lead-zinc deposits: a comparative examination. Transactions of the Institute of Mineralogy and Metallurgy, Section B99, B21-B42.

Sangster, D.F., 1988. Breccia-hosted lead-zinc deposits in carbonate rocks. In: James N.P., Choquette P.W. (Eds.) *Paleokarst*. Springer, New York, NY, p. 102-116.

Stephens, M.B., 1988. The Scandinavian Caledonides: a complexity of collusions. *Geology Today* **4**, 20-26.

Sverjensky, D.A., 1986. Genesis of Mississippi Valley-Type lead-zinc desposits. *Annual Review of Earth and Planetary Sciences* **14**, 177-199.

Sverjensky, D.A., 1984. Oil field brines as ore-forming solutions. *Economic Geology* **79**, 23-37.

Torsvik, T.H. and Rehnstorm, E.F., 2001. Cambrian palaeomagnetic data from Baltica: implications for true polar wander and Cambrian palaeogeography. *Journal of the Geological Society* **158**, 321-329.

Wen, H., Zhu, C., Zhang, Y., Cloquet, C., Fan, H. and Fu, S., 2016. Zn/Cd ration and cadmium isotope evidence for the classification of lead-zinc deposits. *Scientific Reports* **6**. 25273, doi:10.1038/srep25273.

Willdén, M.Y., 1980. *Paleoenvironment of the autochthonous sedimentary rock sequence at Laisvall, Swedish Caledonides*. Stockholm, Contribution in Geology **33**, 100 p.

Xue, C., Zeng, R., Liu, S., Chi, G., Quing, H., Chen, Y., Yang, J., Wang, D., 2007. Geologic, fluid inclusion and isotopic characteristics of the Jinding Zn-Pb deposit, western Yunnan, South China: a review. *Ore Geology* **31**, 337-359.