Pyrite composition as an exploration tool for volcanogenic massive sulfide deposits

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1. Abstract

Pyrite is a ubiquitous sulfide mineral in all volcanogenic massive sulfide deposits of the Bathurst Mining Camp (BMC), northern New Brunswick, Canada. In particular, the quantity of pyrite within host rocks associated with massive sulfide deposits of the BMC incrementally increases towards the sulfide horizons in both hanging wall and footwall samples. Pyrite shows variety of textures classified as pre-deformation, syn-deformation, and post deformation, having subtle but detectable correlation with geochemical signatures observed. For example, the framboidal pyrite and spongy core pyrite show the highest concentration of trace-elements compared to recrystallized pyrite. Therefore, the evolution history of the mineralization systems can be postulated based on textures and chemistry of pyrite. Also, this study demonstrated the variation and magnitude of geochemical signatures within pyrite in the host rocks surrounding the massive sulfide horizons, which can be used as a micro-chemical exploration tool.

2. Introduction

Volcanogenic massive sulfides are among the most divers mineralization systems in terms of metal tenor and host lithology in geological time and space (see Piercy, 2011 and references therein). So, what makes research and exploration of VMS systems challenging is that each VMS-type should be understood individually. Besides, wide geochemical variations are observed exclusive to each type. More puzzling is to find signature of mineralization in higher depth as a current demand in the industry (see Peter and Mercier-Langevin, 2015 and references therein). Therefore, new tools are necessitated to assist filling the knowledge gaps for a better understanding of VMS types and potentially integrating modern approaches with the current exploration techniques. In particular, as exploration increasingly focusses on deeper targets and moves inevitably into areas of post-mineral cover, the geochemical approaches in exploration programs are being more focused. This is achieved by significant advancements in analytical technologies in the last decades. Geochemical advances with a focus of micro-analytical techniques have been and continue to be favorable methods of use in Earth Sciences research in the last decades (i.e., Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA–ICP–MS), see Cook et al., 2016 and references therein). In particular, great developments have been achieved for sample preparation, analysis speed, multi-element analysis capability, resolution and sensitivity, and by the availability of reliable reference materials. In addition to conventional LA–ICP–MS data request, the application of LA–ICP–MS is examined in the exploration of several mineral deposits to introduce vectoring and fertility tools towards mineralization systems (porphyry systems: Wilkinson et al., 2015; VMS systems: Soltani Dehnavi, 2017 and references therein). Mineral chemistry can offer a wealth of new information on texturally complex and fine-grained samples of VMS systems.

This synapsis presents the results of LA-ICP-MS analysis of pyrite from representative VMS deposits of the Bathurst Mining Camp. The extended geochemical data of texturally-distinct pyrite is presented. The magnitude and variation of pyrite chemistry around the massive sulfides is introduced as vectoring tool.

3. Summary Geology of the BMC

3.1. Regional Geology

The VMS deposits of the BMC are part of *Central Mobile Belt* of New Brunswick and Newfoundland are related to extensional arcs and early phase continental back-arcs setting (Rogers et al., 2007). The Middle Ordovician bimodal-siliciclastic Zn-Pb-Cu (Au-Ag) VMS systems of the BMC contains 45

known deposits. Closure of the Tetagouche-Exploits back-arc basin from the Late Ordovician to Early Silurian resulted in the incorporation of the Miramichi Group and Bathurst Supergroup rocks into the Brunswick subduction complex. The Bathurst Supergroup formed within an intra-crustal (continental) proto-back-arc basin (similar to the Japan Sea) and is referred to as the Tetagouche-Exploits Basin. The BMC can be divided into five groups, namely: Miramichi, Tetagouche, California Lake, Sheephouse Brook, and Fournier groups (Fig. 1; van Staal et al., 2003 and references therein). The Cambro-Ordovician Miramichi Group (490–478 Ma) occurs at the base of the sequence and consists of a passive-margin continentally derived turbidite sequence of quartz wacke, quartzite, siltstone, and shale deposited on the Gondwana margin. The Miramichi Group was succeeded by Bathurst Supergroup that constitutes the Sheephouse Brook, Tetagouche, California Lake, and Fournier groups. The first three groups mainly include ensialic
volcanic and sedimentary rocks, which are dominated by two distinct cycles of felsic volcanism that give way up section to mafic rocks. The Fournier Group is the youngest group (~ 465 Ma); it is defined by ocean-floor mafic volcanic and related sedimentary rocks.

Fig. 1

3.2. Mineralization

Most deposits of the BMC show some or all of five distinct hydrothermal facies typical to VMS deposits, namely: 1) sulfide stringer, 2) vent complex (basal Cu zone, or basal sulfide), 3) bedded sulfide (or banded sulfide), 4) bedded pyrite, and 5) carbonate-oxide-silicate exhalite (iron formation). Also, hydrothermal events have been recognized in the BMC, including Caribou (472–470 Ma), Brunswick and Chester (469–468 Ma), and Stratmat (467–465 Ma) horizons. The Stratmat and Brunswick horizons both occur in the Tetagouche Group, whereas the Caribou and Chester horizons occur in the California Lake and Sheephouse Brook groups, respectively.

4. Methodology

4.1. LA-ICP-MS analysis

Over 3000 LA-ICP-MS spot analysis is performed on representative polished thin sections of major VMS deposits of the BMC. Dataset is carefully handled and any analysis showing the sub-surface inclusions of other minerals is excluded (*n = 1561* spot analysis presented here). The LA-ICP-MS system in the Department of Earth Sciences, University of New Brunswick includes an Australian Scientific Instruments (formerly Resonetics Llc.) Resolutione M-50 193 nm ArF (excimer) laser connected to an Agilent 7700x quadrupole inductively coupled plasma-mass spectrometer (Q-ICP-MS) equipped with dual external rotary pumps. The ICP-MS was operated at 1450–1550 W and a torch depth of 4.5–5.0 mm. It was tuned during ablation of a raster line across NIST610 glass to achieve $ThO^+/Th^+ < 0.3\%$ (monitor of oxide production), $^{238}U^+/^{232}Th^+ \sim 1.0$ (monitor of plasma robustness), and $^{44}Ca^{++}/^{44}Ca^+ < 0.3\%$ (monitor of double-charged production). Raw counts were collected with the ICP-MS in peak-hopping mode (total quadrupole sweep time about 1 s) and displayed in time-resolved format. Analyte dwell times were set individually, with the longest dwell times set for elements with the lowest concentrations or elements of interest. Concentrations in unknowns were standardized against external standard USGS MASS-1 and internal standardization was achieved using the stoichiometric value of iron in the pyrite. The LA-ICP-MS technique was also used to generate element maps of various pyrite type. Further details of the methodology and raster-mapping approach can be found in Soltani Dehnavi, 2017.

5. Results

5.1. Textural variability of pyrite

Pyrite in the massive sulfide deposits of the BMC occurs in association with three principal sulfide facies, including the: 1) vent complex, 2) bedded sulfide, and 3) bedded barren pyrite. Also, finely laminated sulfide lenses hosted by iron formation near the hanging wall of some of the deposits contain various amounts of pyrite. Additionally, host rocks associated with massive sulfide deposits contain pyrite from 0.5 to over 25% in volume (Fig. 2).

Fig. 2

Textural criteria and grain size were used to categorize pyrite in to: 1) pre-deformation (primary pyrite) that is divided into 4 sub-types (Py1a-d), and

2) deformation related (metamorphic) types. The latter is further divided into syn-deformation (Type 2a) and post-deformation (Type 2b) (see Soltani Dehnavi et al., 2018). According to this classification, LA-ICP-MS analysis was performed, which shows subtle but related geochemical signatures.

5.2. Composition of pyrite

The majority of pyrite analyzed are arsenian type (up to 3.31 wt%, belong to pyrite from Louvicourt, followed by Caribou and Brunswick No. 12 deposits), in which Sb, Tl, Au, Bi, Sn, and Hg contents are elevated as well. In addition, over half of the analyzed pyrite grains contain more than 100 ppm Co and Ni within their structure. Intra-deposit geochemical variations suggest different physico-chemical condition of ore formation (see Soltani Dehnavi et al., 2018) and subsequent events.

6. Implications

6.1. Evolution history of VMS systems via pyrite textures and composition

Pyrite refrectory nature demonestrates resistance to diagenesis and/or metamorphism events via remobilization and recrystallization processes by which softer sulfides commonly being affected (Cook et al. 1993). Therefore, pyrite primary and pseudo-primary textures can be representative of its crystalization from hydrothermal fluids. The seconday and tertiary textures can be formed by syn- to post-deformation processes. According to the results of this study metamorphism results in depletion of trace-element (except Se) in recrystalized textures (See Soltani Dehnavi et al., 2018). As it is previously presnted, the BMC has undergone several phases of deformation and subsequent metamorphism which is reflected in the pyrite chemistry presented here. The question is if trace-element lost happened from the sulfide horizons, is there any signature of these elements can be traced in surrounding host rocks ? And how far from the sulfide horizons these signatures can be detected? Finally, what are the main mineral phases being able to accomodate these trace-elements? Answering these question is the foundation of micro-chemical vectoring tool.

6.2. Pyrite vectoring tool

The host rocks associated with massive sulfide deposits of the BMC contain pyrite from 0.5 to over 25% in volume that can be detected in several hundred meters outboard of sulfide horizons in both hanging wall and footwall samples (see Soltani Dehnavi et al., 2018).

Conclusions

Composition and texture of pyrite from the BMC demonestrate the robustness of a simple and ubiquitous sulfide phase within sulfide horizons and host rocks as a tool for interpretation of evolution history and formation of massive sulfides as well as potential exploration tool.

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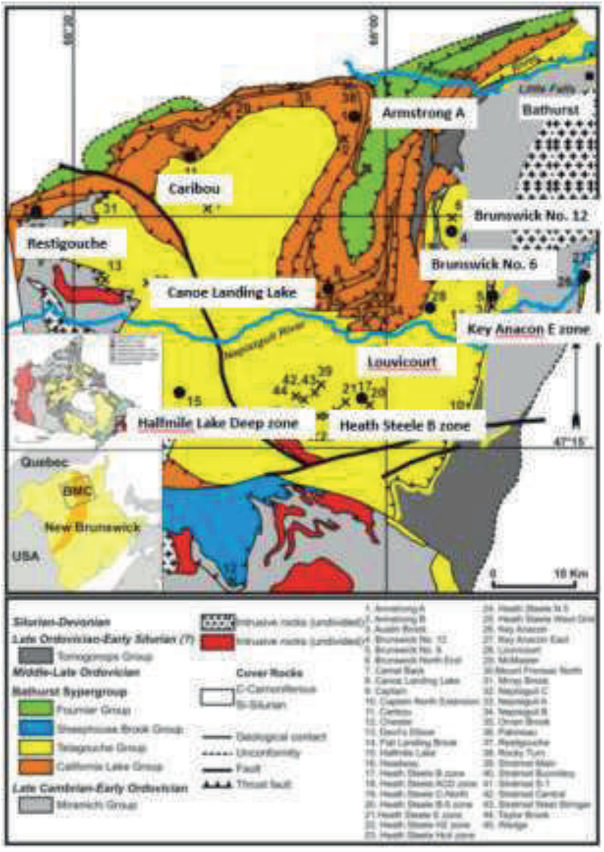

Fig. 1. Simplified geological map of the Bathurst Mining Camp, northeastern New Brunswick, showing the location of massive sulfide deposits examined during this study (modified from Walker and McCutcheon, 2011).

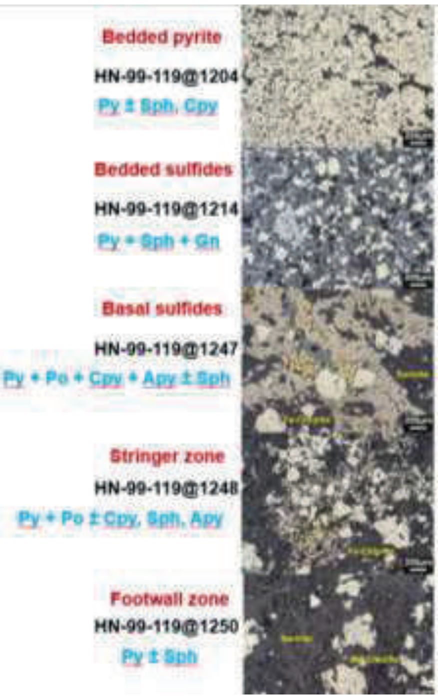

Fig. 2. Pyrite occurrence in various zones of Halfmile Lake Deep zone deposit, BMC.