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Forward/Context

Targeted Geoscience Initiative Phase 6 (TGI-6) is a five-year (2020-25) research program of Natural Resources Canada to conduct national, collaborative research, with the aim to provide the Canadian mineral industry with the next generation of geoscience knowledge, innovative techniques, and predictive models that will result in more effective targeting of buried mineral deposits. Specific program objectives are: 1) generate geoscience knowledge to enhance the understanding of the processes that formed Canada's mineral deposits, including critical minerals, and identify and develop novel indicators and parameters to guide exploration in emerging and existing mining areas; and 2) improve mineral exploration effectiveness by developing next-generation geological knowledge, as well as leading edge tools, innovative techniques, and predictive models.

The former objective aims to clarify the processes that formed various mineral deposits with a focus on elements that are critical to Canada's transition to a green and digital economy. Volcanogenic massive sulfide (VMS) and other massive sulfide deposits (e.g., magmatic sulfide, skarns, Mississippi Valley-type, and clastic-dominated lead-zinc) host several metals important to this transition, grouped under the term "critical minerals" (such as, but not limited to, copper, nickel, zinc, cobalt, antimony, gallium, germanium, and indium). In many cases, however, the specific sulfide minerals hosting these metals are not well known. Such metal deportment information may be essential for accurate resource assessment, including assessment of downstream impacts for mineral processing. Furthermore, the effect of deformation and metamorphism on the (re)distribution of these metals is generally poorly constrained. The results presented here form part of TGI-6 research on the primary distribution of critical minerals, such as cobalt, copper, zinc, and germanium, in VMS deposits, and on how deformation and metamorphism affect this.

Summary

This report presents 19 in-situ, quantitative, multi-element compositional maps of sulfides from the Windy Craggy VMS deposit, located in the Alexander Terrane in NW British Columbia, Canada. The samples were collected in 1988 and 1989 by Jan Peter during his Ph.D. research on the Windy Craggy deposit (Peter, 1992). Additional information about this deposit can be found in Peter and Scott (1999). Quantitative compositional mapping was conducted on select thin sections by Tarryn Cawood, Duane Petts, and Janina Czas in 2022-2023, with funding from the TGI-6 program. The purpose of these compositional maps is to determine which minerals host various critical-, precious- and other trace elements; and (together with petrographic observations, and microstructural maps reported in Cawood et al., 2024, Open File 9075) to investigate the compositional variations associated with different sulfide textures, microstructures, and degrees of deformation in this specific deposit. In addition, pyrite and pyrrhotite were divided into groups based on morphological- and compositional characteristics (Cawood et al., submitted to Economic Geology), and the composition signature of each group was extracted from the respective LA-ICP-MS maps using multivariate statistical methods and manual filtering (see below for details).

This open file .zip package includes: the processed map data (as one .csv file for each of the 19 mapped regions); images of all maps generated (as one .pptx file for each mapped region, containing a photomicrograph of the mapped region and the compositional maps of all the mapped elements); photomicrographs of the samples showing the location of the mapped regions, along with images showing the different groups of pyrite and pyrrhotite in each map, and principal component analysis biplots showing the distinct compositional characteristics of each group (Figs. 1-18, in a single .pdf file); the extracted compositional data for each pyrite- and pyrrhotite group (as two .xlsx files: one each for pyrite and pyrrhotite, respectively); Pearson product-moment correlations between the elements in these groups of pyrite and pyrrhotite, illustrated using tables and select plots (in two .docx files: one each for pyrite and pyrrhotite, respectively); and this report summarizing analytical methods and results.

Analytical Methods

For this study, >400 hand samples (along with ~200 associated thin sections) were examined to identify mineralization styles and sulfide textures. From these, 11 samples were selected that display representative sulfide textures. Thin sections of these were made and investigated with standard petrographic methods and microstructural mapping by electron backscatter diffraction (EBSD, see Cawood et al., 2024, Open File 9075).

Quantitative trace element mapping of the Windy Craggy sulfides was undertaken at the Geological Survey of Canada (Ottawa) using an Applied Spectra RESOlution-SE 193 nm laser ablation (LA) system, with a two-volume S155 ablation cell, coupled to an Agilent 8900 or Agilent 7700 inductively coupled plasma mass spectrometer (ICP-MS). The mapping procedure closely follows the analytical method described in Lawley et al. (2020) and Smith et al. (2022; 2023), with details about the analytical sessions listed in Table S1. Element compositional maps were constructed using a series of parallel laser line scans, with laser conditions of 5 to 12 µm beam diameter, a scan speed of 5 to 24 µm/second, 20 to 40 Hz repetition rate, and a fluence of 4 to 4.5 J/cm2. The total sweep time to measure all elements on the ICP-MS was 250 ms (Table S1), which was synchronized with the laser scan speed so that every 0.5 or 1 second of data acquisition (i.e., one full beam diameter) included 2 or 4 measurements of each mass, which was subsequently averaged to form one map pixel. The line scan data was calibrated against USGS glass reference material GSE-1G (Guillong et al., 2005), normalizing the total element, or element oxide, abundances to 100%, via Lamtrace data processing software (Jackson, 2008). Compositional maps presented in the .pptx files were generated using an in-house Python script. Detailed plotting and interrogation of the calibrated map data was undertaken using XMapTools 4.2 (Lanari et al., 2014; 2019) and the Reflex ioGAS software, version 8.1 (reflexnow.com/product/ioGAS/).

Pyrite and pyrrhotite were each divided into several distinct groups, based on morphological and compositional characteristics, as described in Cawood et al. (submitted to Economic Geology). In short, Group 1 contains only pyrite (Py1), which comprises pyrite framboids, polyframboids, and colloform textures, along with fine-grained spongy masses. Group 2 is dominated by pyrite (Py2), along with minor interstitial sphalerite, galena, chalcopyrite, and pyrrhotite. Py2 occurs as medium- to coarse euhedral grains that overgrew earlier Py1. Group 3 is dominated by pyrrhotite (Po3) and chalcopyrite, with lesser but locally significant pyrite (Py3). Po3 is typically coarse grained and anhedral, whereas Py3 occurs as euhedral crystals, euhedral overgrowths on pre-existing pyrite, fine-grained masses, and radial polycrystalline aggregates. Group 4 includes any sulfides that grew or were significantly modified during deformation and metamorphism. It includes Po3 that was mechanically remobilized to form Po3(4); pyrrhotite that was remobilized in a fluid phase and re-precipitated as Po4; Py3 that was dynamically recrystallized to form Py3(4); and rims of new metamorphic pyrite, called Py4, that overgrow pre-existing Py3 and Py3(4).

IoGAS was used to extract the compositional data for each of these groups, using a combination of compositional filtering, multivariate statistics including principal component analysis (PCA) and K-means clustering following published approaches (Jansson et al., 2022; Lee et al., 2022; Smith et al., 2022), and manual selection of specific data points. For each map, the data were first filtered using major element compositions to extract one sulfide phase at a time (e.g., S > 200,000 ppm, Fe > 450,000 ppm, and Cu < 200,000 ppm to isolate pyrrhotite from chalcopyrite and non-sulfide gangue minerals). Data points below the lower limit of detection were replaced with half the detection limit value. For each sulfide, only those elements for which <30% of the data are below the lower limit of detection were used for PCA and K-means clustering. These elements were first normalized with a centered logarithmic-ratio (CLR) transformation to overcome closure issues in the data (Aitchison, 1982), followed by a Z-score transformation (e.g., Lee et al., 2022). The centered, normalized data were used as input for classical PCA (e.g., Smith et al., 2022). The resulting principal components are illustrated in PCA biplots in Figures 1-18 (e.g., Fig. 1C). Note that these plots have been produced using RQ-mode PCA (Zhou et al., 1983), which allows the principal components to be illustrated along with the data points on a single diagram. In these plots, "RQ1" therefore refers to the first principal component, and so on.

The principal components were then subjected to K-means clustering. The results were viewed in 2D as maps showing the spatial distribution of each cluster (representing a geochemical group, see Figs. 1-18), and were validated against photomicrographs and the original LA-ICP-MS raster maps (e.g., Lee et al., 2022). The number of principal components and clusters were adjusted until the identified clusters captured the observed mineralogy and geochemical variations (e.g., Smith et al., 2022). In some cases, sulfide groups with different textures or

habits nevertheless display similar compositions, such that PCA was unable to separate them. In these cases, the data corresponding to a specific group (characterized by a specific texture or microstructure) were manually selected by outlining on the map (e.g., Fig. 15C). Finally, the composition of each pyrite- or pyrrhotite group was extracted, and these compositions are provided in the two accompanying .xlsx files.

Results

The resulting calibrated LA-ICP-MS data for each mapped region are provided as a single .csv file for each region, which can be visualized and interrogated with a variety of software options (e.g., ioGAS, XMapTools, or ArcGIS) using the provided spatial information (x- and y- coordinates) to display the data as maps. Images of all the compositional maps generated for each region are also provided in .pptx files. The locations of each mapped region are shown on the photomicrographs in Figures 1-18 in the accompanying .pdf file.

Images showing the compositional groups of pyrite and pyrrhotite are also provided in Figures 1-18. The extracted compositional data for each of the pyrite and pyrrhotite groups are provided in two .xlsx files, and the Pearson product-moment correlations between elements within each of these groups are shown with tables and select plots in two .docx files. In the correlation matrix tables, highly positive or negative correlated pairs of data are coloured red or pink, with a deeper colour indicating a stronger correlation. N is given in the top left cell of each matrix.

Table S1. LA-ICP-MS operating conditions for elemental mapping

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LA

Model	Applied Spectra RESOlution-SE with S155 two-volume cell
Wavelength	193 nm
Map type	Series of parallel line scans
Spot diameter	5 to 12 μm
Scan speed	5 to 24 μm/s
Fluence	4 to 4.5 J/cm^2
Repetition rate	20 to 40 Hz
Cleaning step	Line scan @ 50 Hz, ~2 shots/spot diameter
Primary calibration standard	GSE-1G – doped basalt glass (USGS) (Guillong et al., 2005)
Calibration standard (S)	In-house pyrrhotite
Calibration standard (C)	In-house calcite

ICP-MS

Model	Agilent 8900 and Agilent 7700
Forward power	1550 kW
Sample depth	5.3 to 5.5 mm (8900) and 6.5 mm (7700)
Gas flows	
He (cell)	0.53 to 0.55 l/min
Argon (cup)	0.98 to 1.10 l/min
ThO$^+$/Th$^+$	<0.2 %
U/Th signal intensity ratio (NIST-612)	1.04 to 1.10
Sensitivity ^{175}Lu (NIST-612)	Agilent 8900: 30,000 cps/ppm (38 μm @ 5 μm/s, 5 J/cm^2, 20 Hz)
	Agilent 7700: 12,000 cps/ppm (50 μm @ 5 μm/s, 7 J/cm^2, 10 Hz)

Data acquisition and processing parameters

Data acquisition protocol	Time Resolved Analysis
Scanning mode	Peak hopping, 1 point per peak
Isotopes determined	^{13}C, ^{23}Na, ^{25}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{34}S, ^{39}K, ^{42}Ca, ^{47}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{67}Zn, ^{71}Ga, ^{73}Ge, ^{75}As, ^{77}Se, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{95}Mo, ^{107}Ag, ^{111}Cd, ^{115}In, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{137}Ba, ^{140}Ce, ^{157}Gd, ^{173}Yb, ^{181}Ta, ^{182}W, ^{185}Re, ^{197}Au, ^{205}Tl, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{209}Bi ^{232}Th, ^{238}U
Dwell time per isotope	2–4 ms (major and monitor), 4–10 ms (minor and trace elements)
Total acquisition time	250 ms
Sweeps/spot diameter	2 and 4 (88-41_151.0 M1 only)
Background measurement	20 s
Data processing software	Lamtrace (Jackson, 2008) and in-house Python script
Calibration	Fe internal standardization with 100% normalization (see Halicz and Günther, 2004)
Reference values	'GEOREM preferred values' (GSE-1G)
Map plotting/interrogation	XMapTools 4.2 (Lanari et al. 2014; 2019)
	Reflex ioGAS 8.1

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