

Critical metals in volcanogenic massive sulphide (VMS) deposits in British Columbia: A progress report



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Recommended citation: Piercey, S.J., Pietruszka, D., and Goudie, D., 2025. Critical metals in volcanogenic massive sulphide (VMS) deposits in British Columbia: A progress report. In: Geological Fieldwork 2024, British Columbia Ministry of Mining and Critical Minerals, British Columbia Geological Survey Paper 2025-01, pp. 189-201.

Abstract

Probability plots and principal component analysis derived from bulk-rock geochemistry, reflected light microscopy, and scanning electron microscopy (SEM) on archival samples from across British Columbia indicate that provincial volcanogenic massive sulphide (VMS) deposits contain diverse elements on the 2024 Canadian critical minerals list; most contain Cu and Zn as primary commodities with varying concentrations of Co, In, Sb, Sn, and Te. Felsic-hosted deposits have greater enrichments in Zn, Pb, As, Ag, Au, Cd, Ga, and Sb relative to mafic-hosted deposits, which have enrichments in Cu, Co, Fe, In, Mn, Mo, Se, Sn, and Te, similar to global VMS deposits described in the literature. The Zn-Pb-element associations likely reflect deposition from low-temperature (<300°C) VMS fluids, whereas the Cu-rich assemblages represent deposition from higher temperature (>300°C) VMS fluids. Reflected light microscopy and scanning electron microscopy indicate that the main mineral hosts for critical minerals are chalcopyrite (Cu) and sphalerite (Zn) and to a lesser extent bornite (Cu), covellite (Cu), and tetrahedrite (Cu, Zn, Sb). Suites of relatively minor phases occur as small grains in different mineral groups including: 1) sulphides-stannite (Cu, Sn, In?), bismuthinite, and Ag-bearing bismuthinite (Bi); 2) arsenides and antimonides-berthierite (Sb), cobaltite (Co), Ni-bearing cobaltite (Co, Ni), stibnite (Sb), jamesonite (Sb), and ullmannite (Sb, Ni); 3) tellurides-hessite and empressite (Te); and 4) native elements and oxides-native bismuth (Bi) and cassiterite (Sn). The next phase of work will involve quantitative mineral compositions and determination of major, minor, and trace metal concentrations in various mineral phases using electron probe microanalysis (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

Keywords: Volcanogenic massive sulphide, VMS, critical minerals, mineral liberation analysis, MLA, bulk-rock geochemistry, reflected light microscopy, scanning electron microscopy, SEM, sulphide mineralogy, metal residence

1. Introduction

Volcanogenic massive sulphide (VMS) deposits are important global sources of base (Cu, Zn, Pb) and precious metals (Au, Ag) and are important contributors to the Canadian economy (e.g., Galley et al., 2007). British Columbia hosts VMS systems (see review by Northcote, 2022) that are endowed in metals that are on the 2024 version of the national critical minerals list (NRCAN, 2024) including Cu (e.g., Windy Craggy, Peter and Scott, 1999; Anyox, Sherlock and Domville, 2007) and Zn (e.g., Myra Falls, Barrett and Sherlock, 1996; Marshall et al., 2018; McNulty et al., 2018). Beyond primary commodity Cu and Zn, some British Columbia VMS deposits also contain metals that are on the Canadian critical metals list (Bi, Co, In, Sb, Sn, Te). Despite previous studies (e.g., Grammatikopoulos et al., 2005; Marshall et al., 2018; Roth, 2002; Roth et al., 1999; Sinclair, 2023) the abundance, mineralogy, and siting of these metals and the controls on their origins are not well understood.

To remedy this knowledge gap, we initiated a study to better understand the concentrations of metals, the sulphide mineralogy, and metal residence in British Columbia VMS

deposits. In this progress report we focus on results from initial geochemistry, petrographic, and scanning electron microscopy (SEM) work from a suite of archived samples previously collected from across the province (Fig. 1).

2. Methods

2.1. Sampling

Samples from various VMS deposits (Fig. 1; Table 1) were obtained from the archives of the British Columbia Geological Survey (BCGS) and the Mineral Deposit Research Unit (MDRU) at the University of British Columbia (UBC). Samples were originally collected during studies by BCGS geologists (e.g., Höy, 1991; Höy et al., 1984) and as part of the VMS project of MDRU undertaken in the 1990s (Barrett and Sherlock, 1996; MacDonald et al., 1996; McKinley et al., 1996; Sherlock et al., 1996).

Although we classified VMS deposit sub-types based on lithostratigraphy and host rocks (see Barrie and Hannington, 1999; Franklin et al., 2005; Galley et al., 2007; Piercey et al., 2015), we include reference to BCGS deposit profile terminology as partly updated by Lefebure and

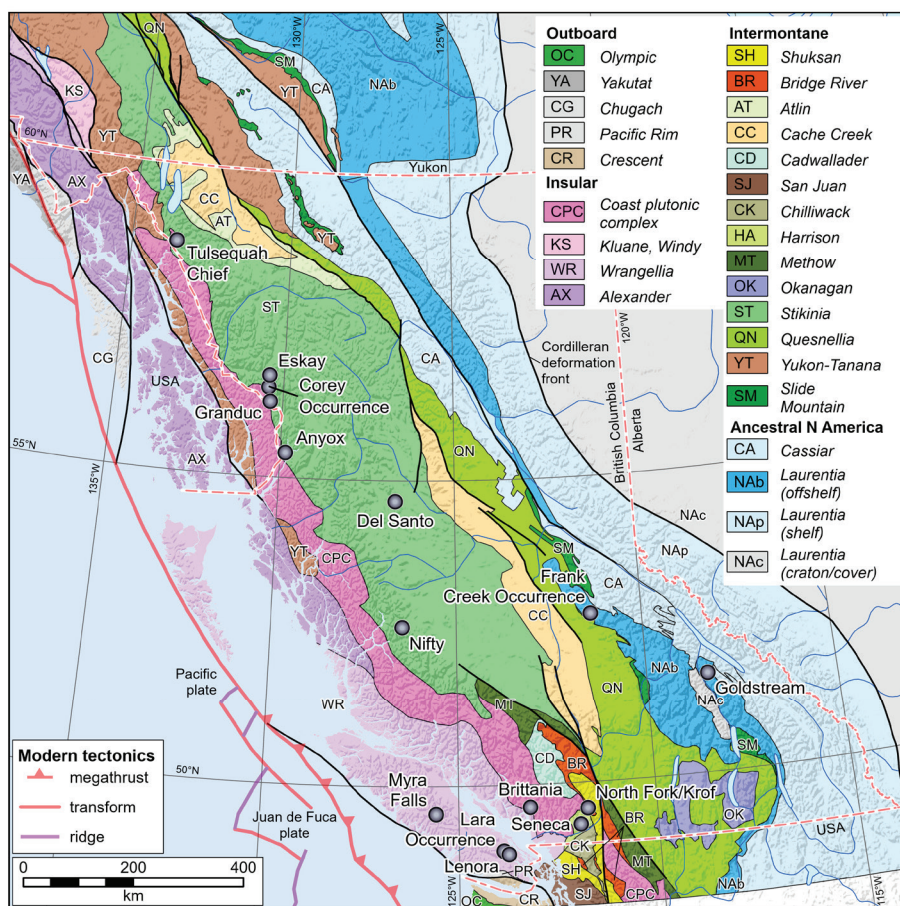


Fig. 1. Location of volcanogenic massive sulphide (VMS) occurrences sample. Terranes after Colpron (2020).

Jones (2022; see Northcote 2022 for discussion). Samples presented herein reflect three VMS sub-types, including: 1) bimodal felsic (i.e., Kuroko-type) deposits, which are hosted in predominantly felsic volcanic host rocks and sequences; 2) hybrid bimodal felsic (i.e., Eskay Creek-type) deposits, which are hosted in felsic volcanic sequences but have evidence for both VMS and epithermal/magmatic-hydrothermal mineralization; and 3) mafic siliciclastic deposits, which are hosted in sequences that contain both basaltic flows and intrusions and siliciclastic rocks.

Samples acquired from the archives at the BCGS have unique identification codes that link them to previous projects, the geologists who collected them, and specific MINFILE occurrences. Samples from the MDRU archives have codes that reflect the original samplers, mostly linked to previous thesis projects at UBC. Each sample was described, photographed, and cut to provide sufficient material for a bulk rock geochemical analysis and multiple thin sections and mounts for petrographic and scanning electron microscope work (Fig. 2). Most of the sample material remains in the BCGS and MDRU archives.

2.2. Geochemical analysis

All samples were submitted for multi-elements at ALS Minerals in Vancouver, BC. The samples were crushed in

a steel jaw crusher, riffle split, and an aliquot was pulverized in mild steel to generate a powder that was used for all analyses. Sample powders were digested via two methods then analyzed by inductively coupled plasma mass spectrometry (ICP-MS). The aqua regia digestion is less aggressive and was assumed to provide better results for relatively volatile trace elements in sulphides (e.g., As, Bi, Hg, Sb, Se, Te). The 4-acid digestion is more aggressive and is the standard used in the mineral industry for elements like Cu, Zn, Pb, Ag, Co, Ni, and Fe. Samples above the detection limit by ICP-MS (overlimit values) were further analyzed using ‘ore grade methods’ that included analysis by inductively coupled plasma emission spectroscopy (ICP-ES) or atomic absorption spectroscopy (AAS) for all elements except Au, for which overlimit values were determined by either ICP-ES or gravimetric methods depending on grade.

2.3. Petrography and scanning electron microscopy (SEM)

Polished thin sections (60 μm thick) were prepared at Vancouver Petrographics and examined by standard reflected light petrography using a Nikon LV100 polarizing microscope at the Metallogeny of Orogenic Belts Laboratory, Memorial University. The thin sections were also examined using backscatter electron (BSE) images, semi-quantitative energy dispersive spectrometry (EDS) maps, and quantitative mineral

Table 1. Archival samples that were examined in this study. Samples were collected during previous studies of VMS deposits across British Columbia (see Figure 1).

Deposit	Terrane	Host unit	Age	Sub-type	BCGS profile	n	Notes
Frank Creek	Barkerville	Snowshoe Gp.	530 Ma	Mafic siliciclastic	G04 - Besshi	2	Age based on regional correlations in Ferri and Schiarizza (2006).
North Fork/Krof	Bridge River	Cogburn schist	Late Permian to Early Jurassic	Mafic siliciclastic	G04 - Besshi	1	Possibly hosted in equivalents of the Bridge River complex. Assumed age range as per Monger (1986).
Seneca	Harrison	Harrison Lake Fm.	166 Ma	Felsic siliciclastic	G06 - Kuroko or G07 - Subaqueous hot spring	4	Age: Childe (pers. comm.) cited in McKinley et al. (1996).
Goldstream	Kootenay	Lardeau Gp.	550 Ma	Mafic siliciclastic	G04 - Besshi	4	Age inferred from host stratigraphy (Galley et al., 2007).
Nifty	Stikinia	Hazelton Gp., Telkwa Fm.	164 Ma	Bimodal felsic	G06 - Kuroko	3	Age based on Ray et al. (1998) interpretations; host rocks cut by 164 Ma porphyry dikes, potentially older.
Del Santo	Stikinia	Hazelton Gp., Telkwa Fm.	164 Ma	Mafic siliciclastic	G04 - Besshi	4	Age uncertain; based on Ray et al. (1998) and regional correlations. Possible similar stratigraphic setting to Granduc and/or Anyox.
Eskay Creek	Stikinia	Hazelton Gp.	174 Ma	Hybrid bimodal felsic	G07 - Subaqueous hot spring	10	Age from Childe (1996) on host rhyolite.
Anyox-Hidden Creek	Stikinia	Hazelton Gp.	174 Ma	Mafic siliciclastic	G04 - Besshi	4	Assumed ca. 174 Ma; at upper part of Hazelton Group and base of Bowser Lake Group (Bajocian to Bathonian) as per Evenchick and McNicoll (2002) and stratigraphy of MacDonald et al. (1996).
Corey	Stikinia	Hazelton Gp.	174 Ma	Hybrid bimodal felsic	G06 - Kuroko or G07 - Subaqueous hot spring	2	Assumed to correlate with units at Eskay Creek. Age from Childe (1996).
Granduc	Stikinia	Stuhini Gp.	208 Ma	Mafic siliciclastic	G04 - Besshi	2	Age is minimum; based on Mihalynuk et al. (2019).
Tulsequah Chief	Stikinia	Mount Eaton suite	330 Ma	Bimodal felsic	G06 - Kuroko	10	U-Pb zircon maximum age from Childe (1997).
Britannia	Wrangellia	Gambier Gp.	130 Ma	Bimodal felsic	G06 - Kuroko	3	Minimum age based on Hauterivian fossils in Gambier Group (136-130 Ma); from Arthur et al. (1993).
Myra Falls	Wrangellia	Sicker Gp., Myra Fm.	365 Ma	Bimodal felsic	G06 - Kuroko	12	U-Pb zircon ages of host rhyolite (Barrett and Sherlock, 1996).
Lara	Wrangellia	Sicker Gp., McLaughlin Ridge Fm.	365 Ma	Bimodal felsic	G06 - Kuroko	1	Ages based on Ruks (2015), McLaughlin Ridge Formation.
Lenora	Wrangellia	Sicker Gp., McLaughlin Ridge Fm.	365 Ma	Bimodal felsic	G06 - Kuroko	1	Ages based on Ruks (2015), McLaughlin Ridge Formation.

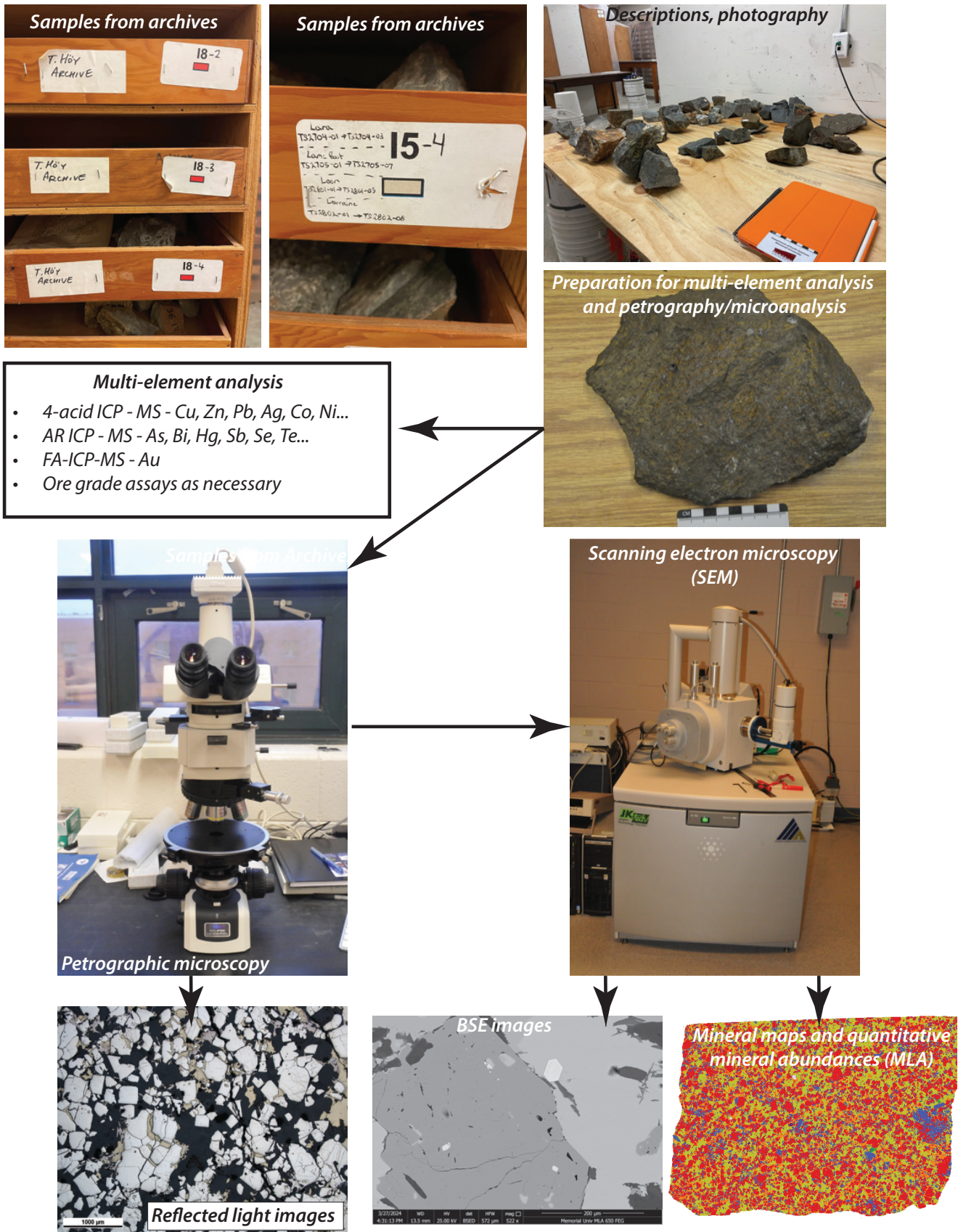


Fig. 2. Workflow: retrieval from BCGS and MDRU archives; photography and documentation of the samples; preparation of samples for both multi-element analysis and microscopic work; petrography and scanning electron microscopy-mineral liberation analysis (SEM-MLA).

abundance maps and determinations by mineral liberation analysis (MLA). The SEM work was undertaken at the CREAT Microanalysis Facility (MAF), Memorial University, using a FEI MLA 650 field emission gun SEM equipped with two Bruker silicon drift EDS detectors. Operating conditions included 25kV accelerating voltage for BSE images and EDS maps. The EDS maps were obtained using Bruker Espirit version 1.9 for acquisition and version 2.5 for offline post-processing. Operating conditions for MLA included a 25kV accelerating voltage, 10nA current, and a 5.85 electron beam spot size. Thin sections were measured in GXMAP (grain-based X-ray mapping) mode where X-ray analyses were triggered for a BSE range of 40 to 255. Each X-ray measurement was acquired for 12 ms on a 1.5 by 1.5 mm frame with a resolution of 500 pixels per frame and an imaging scan speed of 16 μ sec. Data reduction was performed on MLA Data View (FEI) software version 3.1.4.683.

3. Preliminary assay results

The following summary is based on a full multi-element dataset, which is available in Piercey (2025). We summarize these data here using probability plots (Fig. 3) and principal component analysis (Fig. 4), which were generated using ioGAS version 8.2. Data for Cu, Zn, Pb, Ag, and Au are from 4-acid digestion + ICP-MS finish or fire assay + ICP-MS finish except for values above ICP-MS detection limits, which were re-analyzed using the ore grade methods referred to above. For the latter, Cu, Zn, Pb, Ag, and Au are presented as the highest values. For elements that were close to detection limits, half the detection limit was chosen, and only data that had >50% original values were included in our data analysis (i.e., elements that were consistently close to detection limits or had quantized values were not used).

3.1.1. Probability plots

The probability plots (Fig. 3) include primary commodities from VMS such as Cu and Zn, and elements such as Co, In, Sb, and Te, which can be byproducts of VMS mining (Galley et al., 2007). Concentrations of Zn (Fig. 3a) vary with deposit type, but generally Zn is enriched in the bimodal felsic and hybrid bimodal felsic deposit sub-types, as is expected for deposits associated with felsic volcanism and continental crust (Piercey et al., 2015). Although Cu concentrations are also variable, Cu is enriched in all VMS deposit sub-types without preference (Fig. 3b). With rare exceptions, Co is enriched in mafic siliciclastic VMS deposits, consistent with global work (Peter and Scott, 1999; Galley et al., 2007). Indium is enriched across all deposit sub-types (Fig. 3d) but mainly in samples from Tulsequah, Myra Falls, Del Santo, and a few samples from Eskay Creek, Seneca, and Hidden Creek (Anyox). Tin enrichment is only significant at the Frank Creek occurrence, with lesser enrichments in the Goldstream and Eskay Creek deposits (Fig. 3e). Tellurium is enriched primarily in bimodal felsic deposits, particularly at Myra Falls and Tulsequah, with a few enriched samples from Del Santo, Goldstream, and Eskay Creek (Fig. 3f).

3.1.2. Principal component analysis

Principal component analysis (PCA) was undertaken on a selected suite of metals from the assay data to evaluate element correlations and associations to specific VMS deposit sub-types and deposits (Fig. 4; Table 2). Principal component analysis is a dimensionality reduction tool that uses multiple variables and creates linear combinations of these variables (the principle components) that help explain the distribution of the data, including correlations between different variables, in this case elements (Grunsky, 2010). Four-acid digestion data with an ICP-MS or overlimit finish (e.g., AAS, ICP-ES) were used for the PCA and included traditional commodity elements found in VMS deposits, such as Cu, Zn, Pb, Ag, and Au (fire assay pre-preparation), as well as trace element and/or byproduct elements found in VMS deposits, including As, Cd, Co, Fe, In, Mn, Mo, Ga, Sb, Se, Sn, and Te. Given that the concentrations of most elements in natural geological materials are not normally distributed (e.g., Aitchison, 1982), it violates an assumption of PCA, which assumes variable populations are normally distributed. To remedy this, all analytes used were pre-treated using a centre log ratio (CLR) transformation for each element; this process results in improving the normality of distribution of the data and removes the effects of closure (Aitchison, 1982; Grunsky, 2010). All CLR transformations were undertaken in ioGAS.

The PCA results are shown in Figure 4 with eigenvalue and variance data presented in Table 2. Notably, the first four principal components (PC) explain ~70% of the variance in the dataset with each of the first four explaining ~34%, 14%, 11%, and 10% respectively (Table 2; also shown in eigenvalue form in the scree plot Fig. 4a). Thus, the first two components are the most significant and will be focused upon. The elements with positive loadings on PC1 include, in decreasing order of weighting, Zn, Cd, Pb, Sb, Au, Ag, Ga, As, and Mo (Figs. 4b-c), which are consistent with elements associated with low-temperature (<300°C fluids), Zn-Pb-rich sulphide and sulphosalt mineralization (e.g., Lydon, 1988; Large, 1992; Ohmoto, 1996). Higher PC1 values are also present in samples from Eskay Creek, Seneca, Myra Falls, a cluster of samples from Tulsequah, and one sample each from Hidden Creek and Britannia (Fig. 4b). However, most samples with positive PC1 loadings are bimodal felsic and hybrid bimodal felsic. The elements with negative loadings on PC1 include, in decreasing order of weighting, Fe, Co, Mn, Se, In, Sn, Cu, and Te, which are consistent with elements derived from high-temperature Cu-rich mineralization (e.g., Lydon, 1988; Large, 1992; Ohmoto, 1996). More negative PC1 loadings are associated mainly with mafic siliciclastic deposits (e.g., Granduc, Hidden Creek, Goldstream), and some samples from Britannia, Myra Falls, Seneca, and Tulsequah, consistent with Cu-rich mineralization at these deposits. The elements with positive loadings on PC2 include, in decreasing order of weighting, As, Sb, Sn, Ag, Au, Co, Fe, and Mn, which likely reflect sulphosalts, oxides and native elements, or arsenide minerals (Figs. 4b, d). The elements with the most negative loadings

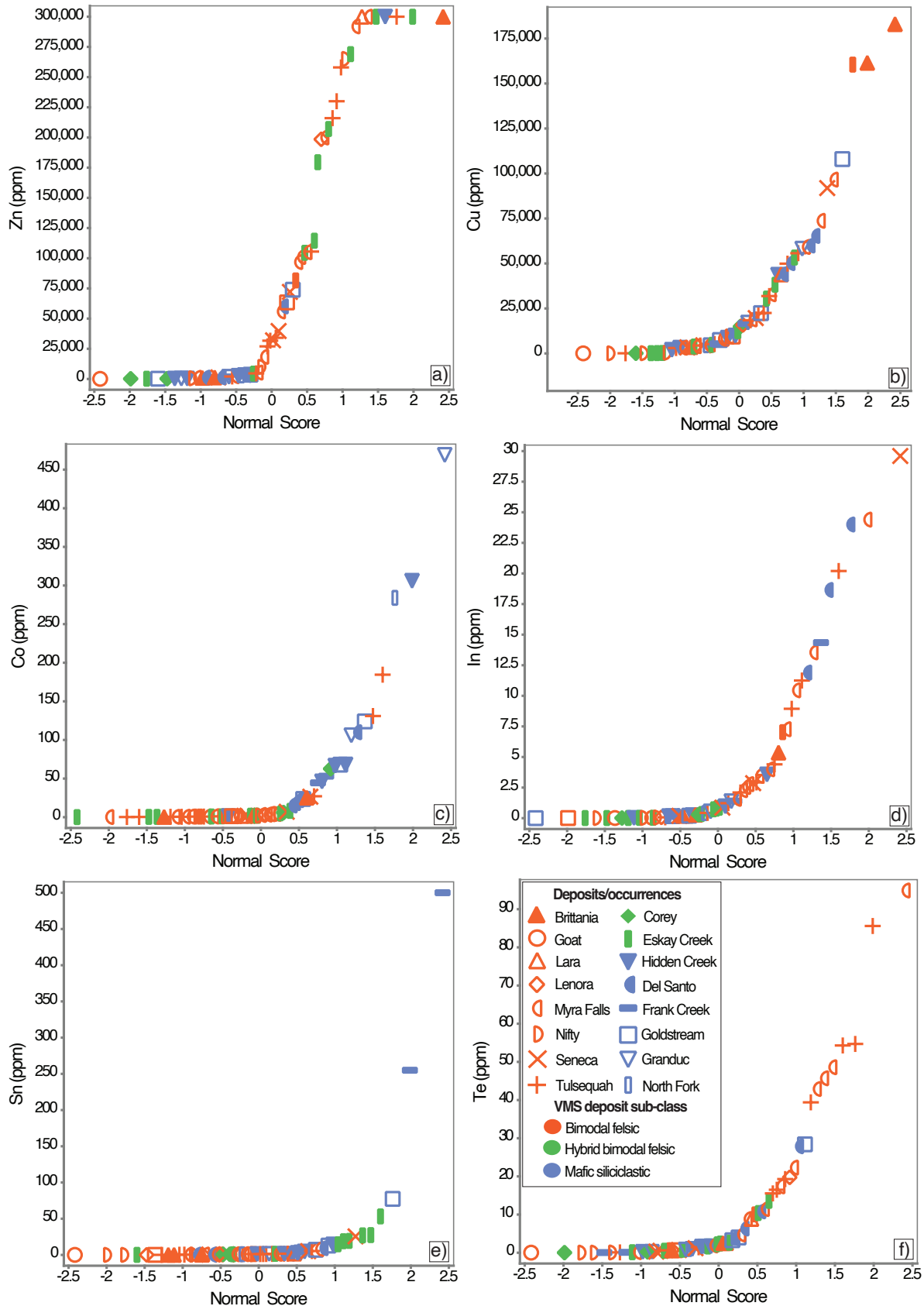


Fig. 3. Cumulative probability plots for selected metals from VMS occurrences. a) Zn, b) Cu, c) Co, d) In, e) Sn, f) Te. X-axis is the N-score, which is the z-scores from a standard normal distribution where the mean is 0 and the standard deviation is 1. More positive (and more negative) values indicate more anomalous values relative to the mean.

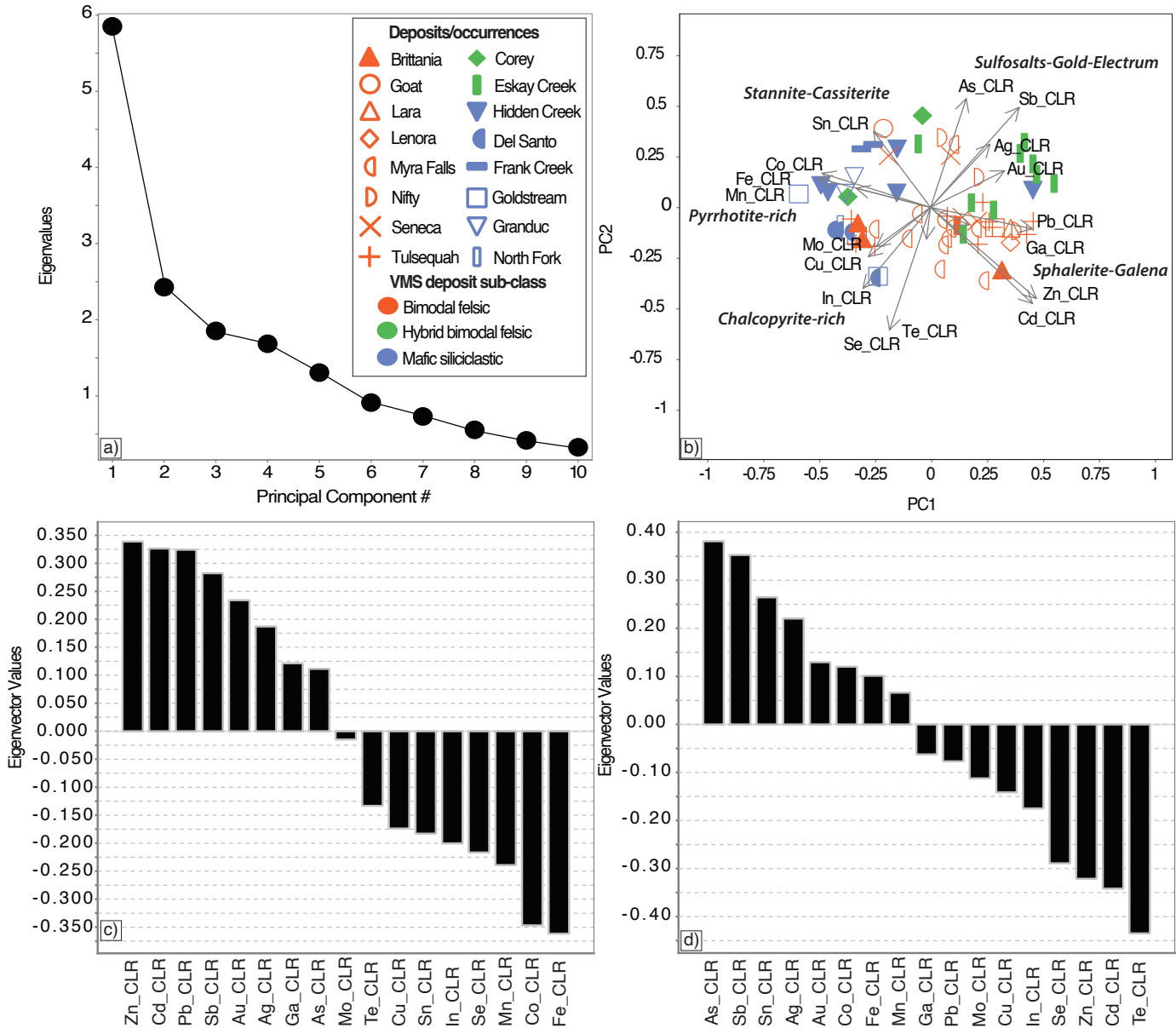


Fig. 4. Results from principal component analysis. **a)** Screen plot for the eigenvectors illustrating that most of the variance is explained by the first principal component and the slopes flatten dramatically thereafter. **b)** Principal component plot with the first two principal components. The lengths of the vectors from the origin reflect their weightings and clusters of elements reflect those with the strongest correlations. **c)** and **d)** Eigenvalue plots with loadings of various elements within the first (PC1) and second (PC2) principal component; the larger the bar from the origin the more significant the elements are in generating positive and negative principal component values and reflect their greater significance in the principal component.

for PC2 include, in decreasing order of weighting, Te, Cd, Zn, Se, In, Cu, Mo, Pb, and Ga, reflecting tellurides, selenides, and Cu-Mo-associated phases (Figs. 4b, d). Within PC1-PC2 space are also clusters of elements that likely reflect various mineral assemblages: sphalerite-galena; sulfosalts-gold-electrum; stannite-cassiterite; pyrrhotite-rich; and chalcopyrite-rich (Fig. 4b).

4. Preliminary mineralogical results

The elemental data provide insights into the potential

types of minerals that may be present in the samples, whereas petrography and SEM-based data provide mineral identifications that reflect the residence of potential elements (Figs. 5-7; Table 3; mineral abbreviations from the Mineralogical Association of Canada, 2019).

The main critical mineral-bearing phases present in nearly all the VMS deposits are chalcopyrite and sphalerite, along with varying abundances of pyrite, pyrrhotite, and other phases (Fig. 5). In some cases, Cu and Zn are hosted in other phases, including tetrahedrite (Cu, Zn), bornite (Cu), and covellite (Cu),

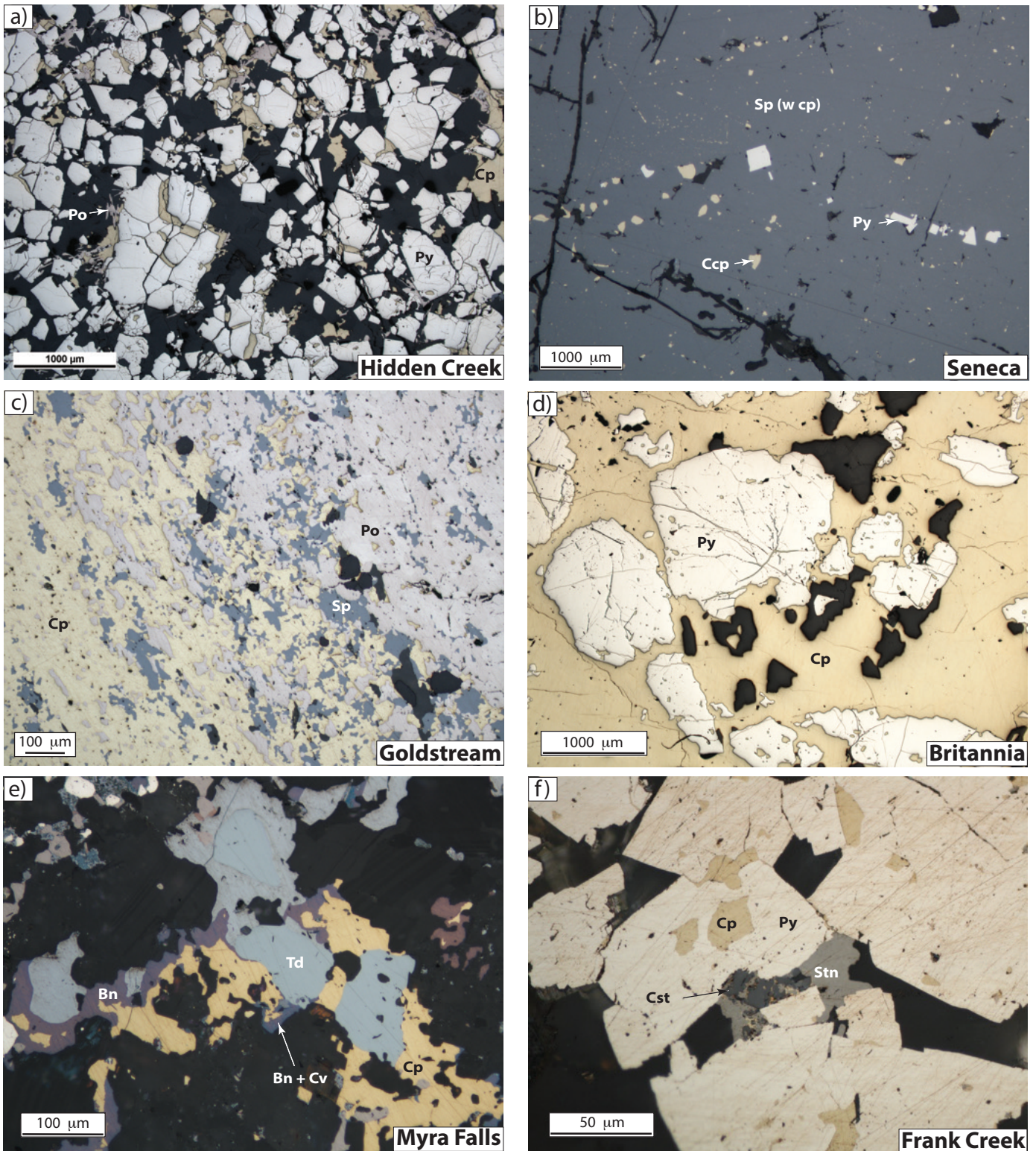


Fig. 5. Reflected light microscope images from selected deposits. **a)** Euhedral pyrite grains that are locally cracked, with interstitial chalcopyrite and lesser pyrrhotite (Hidden Creek deposit, Anyox Camp). **b)** Sphalerite-rich mineralization with chalcopyrite disease (Barton and Bethke, 1987) and blebs of chalcopyrite and euhedral pyrite grains (Seneca). **c)** Foliated massive sulphide with intergrown chalcopyrite, sphalerite, and pyrrhotite (Goldstream). **d)** Chalcopyrite-rich mineralization with rounded and cracked pyrite grains in massive sulphide (Britannia). **e)** Copper-rich assemblages with chalcopyrite, bornite (purple) with intergrown covellite (blue), and tetrahedrite (Myra Falls). **f)** Euhedral pyrite, chalcopyrite, stannite, and cassiterite (Frank Creek).

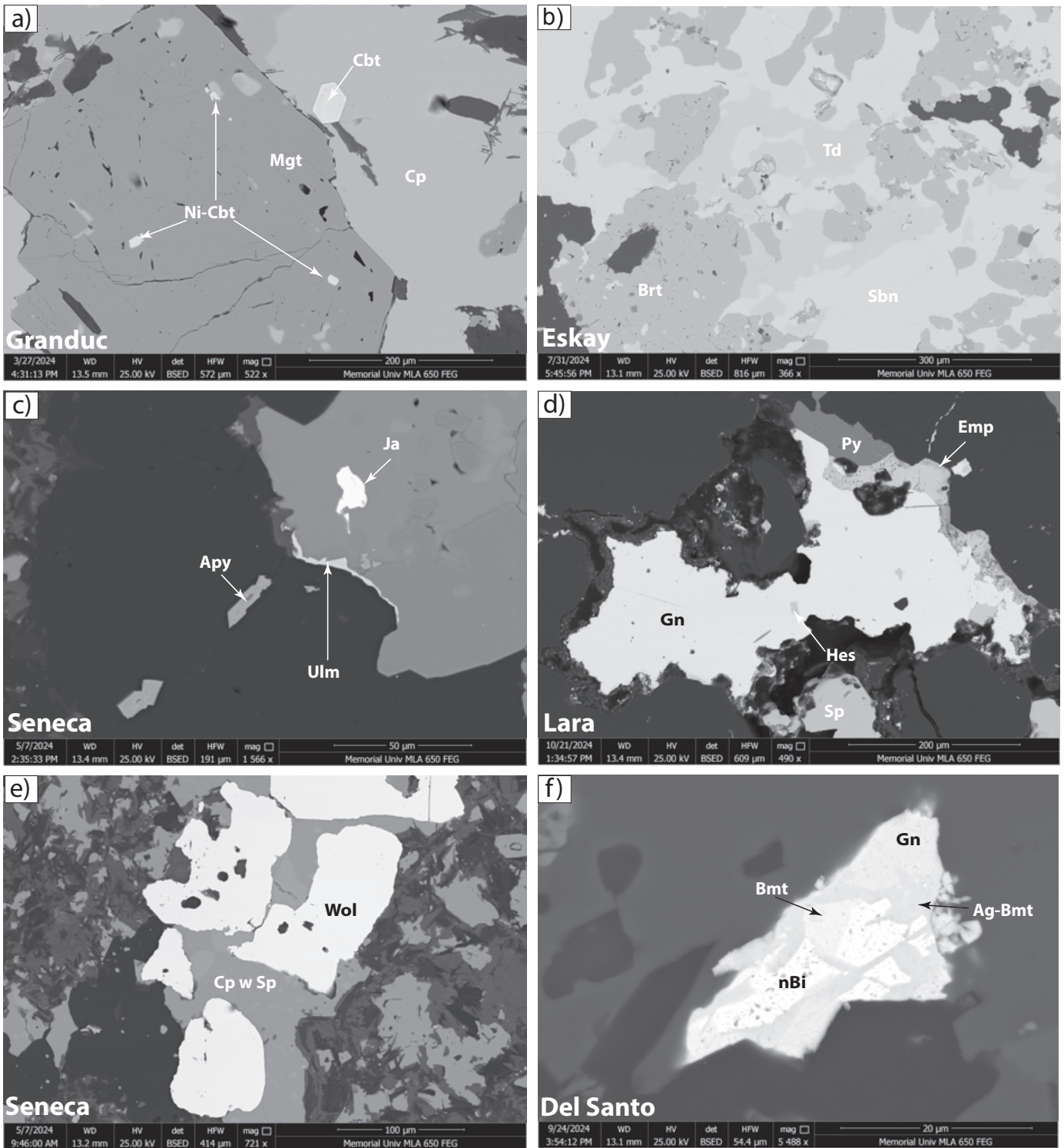


Fig. 6. Backscatter electron scanning electron microscopy images (BSE) from selected deposits. **a)** Euhedral cobaltite and Ni-bearing cobaltite associated with chalcopyrite and magnetite (Granduc). **b)** Intergrown barite, tetrahedrite, and stibnite in massive sulphide-sulphate (Eskay Creek). **c)** Jamesonite, ullmannite, and arsenopyrite (Seneca). **d)** Empressite and hessite associated with galena, pyrite, and sphalerite (Lara). **e)** Wolframite intergrown with chalcopyrite that has sphalerite blebs (sphalerite disease?; Seneca). **f)** Close up of intergrown galena, bismuthinite, Ag-bearing bismuthinite, and native bismuth (Del Santo).

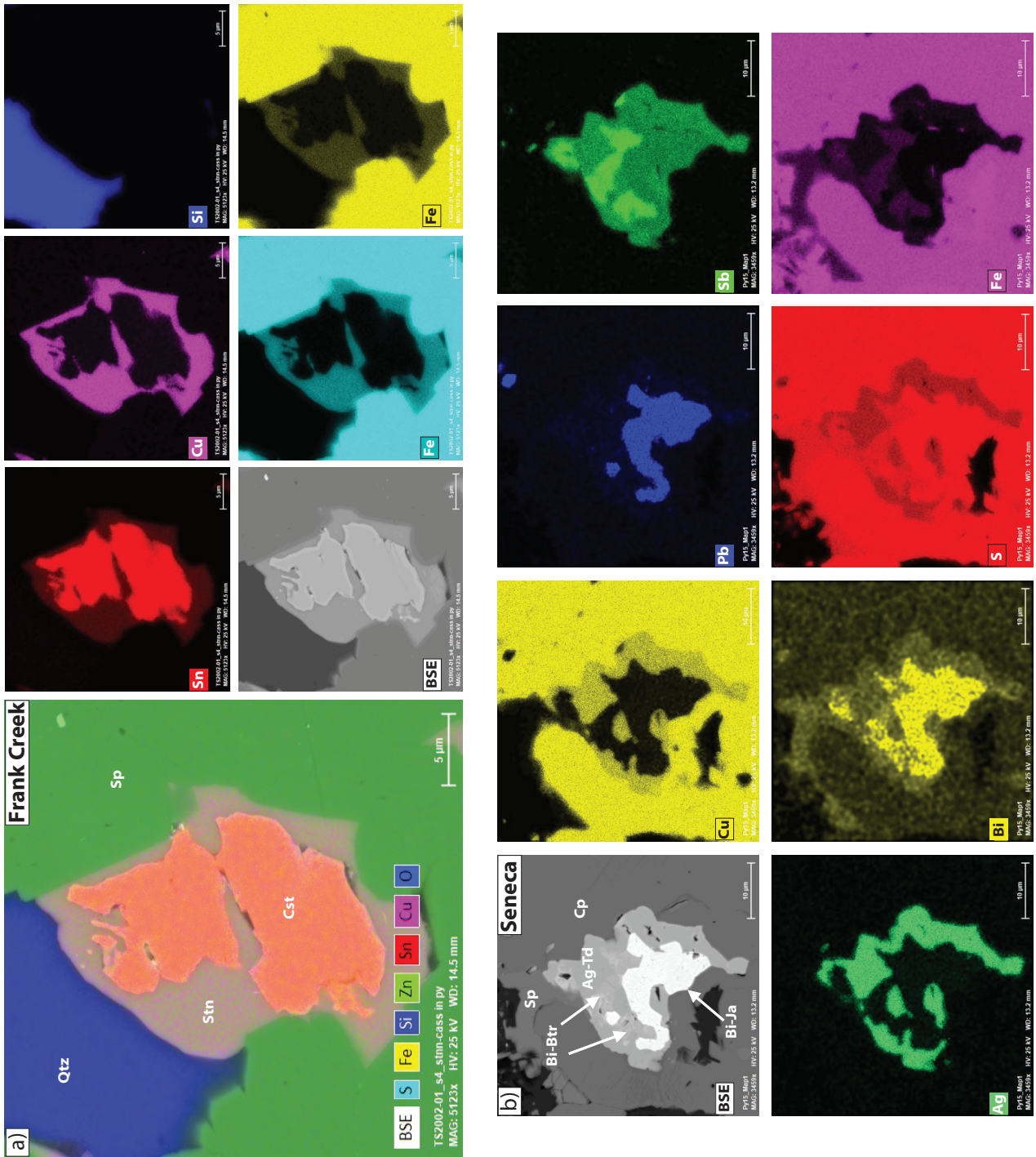


Fig. 7. Scanning electron microscopy-energy dispersive spectroscopy (EDS) maps for selected deposits. **a)** Map of complex intergrowth of cassiterite and stannite associated with sphalerite and quartz from the Frank Creek deposit with different panels illustrating the distribution of elements and mineral phases. **b)** Map of complex intergrowth of Bi-bearing jamesonite with Ag-bearing tetrahedrite, Bi-bearing berthierite, and sphalerite from the Seneca deposit with different panels illustrating the distribution of elements and mineral phases.

Table 2. Eigenvalues, per cent variance, and cumulative variance from principal component analysis of metals from VMS samples in this study.

	Eigenvalues	%	Cumulative %
PC1	5.85	34.42	34.42
PC2	2.43	14.28	48.70
PC3	1.85	10.90	59.61
PC4	1.68	9.91	69.52
PC5	1.31	7.68	77.20
PC6	0.91	5.37	82.57
PC7	0.73	4.30	86.87
PC8	0.55	3.26	90.13
PC9	0.42	2.45	92.58
PC10	0.33	1.92	94.49

and Sn is present as cassiterite and stannite in the Frank Creek occurrence (Fig. 5). Many critical mineral phases are only found at the microscopic to sub-microscopic scale, including arsenides and antimonides including berthierite, cobaltite, Ni-bearing cobaltite, stibnite, jamesonite, and ullmannite (Figs. 6a-d, 7). Tellurides are present in many samples, including minerals like hessite and empressite, whereas W is associated with wolframite, and Bi is associated with bismuthinite, Ag-bearing bismuthinite, and native bismuth, (Figs. 6d-f). These small mineral phases commonly exhibit complex intergrowth textures and associations with other phases (Fig. 7).

5. Summary

The archival samples examined in the present study indicate that volcanogenic massive sulphide deposits in British Columbia contain diverse elements that are on the current Canadian critical minerals list (NRCan, 2024); most contain Cu and Zn as primary commodities with varying concentrations of Co, In, Sb, Sn, Te, and other metals. Felsic hosted-deposits (i.e., bimodal felsic and hybrid bimodal felsic) have greater enrichments in Zn, Pb, As, Ag, Au, Cd, Ga, and Sb relative to mafic-hosted deposits (i.e., mafic-siliciclastic), which have enrichments in Cu, Co, Fe, In, Mn, Mo, Se, Sn, and Te.

The main mineral hosts for metals are chalcopyrite (Cu) and sphalerite (Zn) and, to a lesser extent, bornite (Cu), covellite (Cu), and tetrahedrite (Cu, Zn, Sb). Chalcopyrite and sphalerite are in most deposits, tetrahedrite is common, and bornite and covellite are rare. Suites of relatively minor phases occur as trace phases and in different mineral groups including: 1) sulphides-stannite (Cu, Sn, In?), bismuthinite, and Ag-bearing bismuthinite (Bi); 2) arsenides and antimonides-berthierite (Sb), cobaltite (Co), Ni-bearing cobaltite (Co, Ni), stibnite (Sb), jamesonite (Sb), and ullmannite (Sb, Ni); 3) tellurides-hessite and empressite

Table 3. Mineral formulae and critical metals present in given minerals described in the text and figures.

Mineral	Mineral formula	Main critical metal
Berthierite	FeSb ₂ S ₄	Bi
Bismuthinite	Bi ₂ S ₃	Bi
Bornite	Cu ₅ FeS ₄	Cu
Cassiterite	SnO ₂	Sn
Chalcopyrite	CuFeS ₂	Cu
Cobaltite	CoAsS	Co, trace Ni
Covellite	CuS	Cu
Empressite	AgTe	Te
Hessite	Ag ₂ Te	Te
Jamesonite	Pb ₄ FeSb ₆ S ₁₄	Sb, trace Bi
Native Bismuth	Bi	Bi
Sphalerite	ZnS	Zn
Stannite	Cu ₂ FeSnS ₄	Cu, Sn
Stibnite	Sb ₂ S ₃	Sb
Tetrahedrite	[(Cu,Fe,Zn,Ag) ₁₂ Sb ₄ S ₁₃]	Cu, Zn, Sb
Ullmannite	NiSbS	Ni, Sb
Wolframite	(Fe,Mn)WO ₃	W

(Te); and 4) native elements and oxides-native bismuth (Bi) and cassiterite (Sn).

Continued work in this project will involve quantitative determinations of mineral compositions for major and minor elements by electron probe microanalysis (EPMA), and trace elements by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

Acknowledgments

This work is supported by the British Columbia Geological Survey, and we thank Adrian Hickin, Luke Ootes, Alexei Rukhlov, and Frei de Wall for their collaboration. We also thank colleagues at MRDU, including Shaun Barker, Nikola Denisova, and Brian McNulty, for hosting Piercey and assisting with sample acquisition and preparation from the MDRU archives. Additional funding for this project was provided by an NSERC Alliance Missions Critical Minerals grant awarded to Piercey. Bruce Northcote (BCGS) and Patrick Sack (Yukon Geological Survey) provided constructive reviews.

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