

**Secondary enrichment processes of silver in five-element veins, Cobalt Embayment,  
ON, Canada**

by

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## **Abstract**

The Cobalt Embayment, eastern Ontario, Canada, is a prominent historic silver mining district known for its five-element veins (Ag-Co-Bi-Ni-As), which are abundant in native silver and various (sulph-)-arsenides and antimonides. Previous studies have focused either on the genesis of the five-element veins or on the environmental impacts of toxic elements; however, no study has investigated the role of supergene processes in secondary native silver formation by integrating micro- and nanoscale observations. This study utilizes microscopy (reflected light microscopy, scanning electron microscopy, transmission electron microscopy) and compositional data (electron probe micro-analyses, laser ablation inductively coupled plasma mass spectrometry) from ore phases, host carbonates and secondary metal oxides to highlight both the role of hypogene phases in supergene processes and silver nanoparticles (Ag NPs) in the formation of secondary native silver.

The hypogene ore assemblage predominantly comprises native silver enriched in Sb and Hg, breithauptite, safflorite with minor skutterudite, nickeline, cobaltite and trace allargentum, maucherite, eugenite, loellingite, matiltide, and native bismuth hosted in carbonates. Metal oxides stibioclaudetite, Sb-rich annabergite, arsenian valentinite and erythrite occur locally around massive native silver in the vicinity of breithauptite and cobaltite, on contacts of native silver rosettes with safflorite, within skutterudite, on contacts of native silver veins with carbonate gangue, and within carbonate gangue as mm-thin veinlets or patches. These metal oxides host abundant disseminated, anhedral native silver visible either as Ag NPs on the nanoscale or as minute grains on the microscale. Ag NPs are associated (1) with oxidized ore phases (arsenates/antimonates), (2) within the carbonates, and (3) with Fe-rich clay and organic matter. The oxidation of hypogene safflorite, skutterudite, breithauptite, and cobaltite by acidic to weakly

alkaline, oxidized meteoric fluids led to the oxidation of (sulph-)arsenides and the release of  $\text{Ag}^+$  as a common trace component in these hypogene phases. The released  $\text{Ag}^+$  formed Ag NP either in situ (coupled pathway) or was transported to reactive chemical traps (e.g., clay minerals and organic matter; decoupled pathway). Independent of the pathway, NP aggregation occurred via crystal growth by particle attachment, producing nano- to micrometre-sized silver particles and nano-silver wires.

The entrapment of silver in (sulph-)arsenides, breithauptite, and host carbonates during hypogene vein mineralization is key to releasing  $\text{Ag}^+$  during oxidation under supergene conditions, resulting in the formation of secondary, high-purity native silver via aggregation and attachment of Ag NPs. The processes described in this study define new ways native silver can form and contribute to Ag refinement in five-element veins.

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## List of Abbreviations and Symbols

### General terms

AGB – Abitibi Greenstone Belt

CMN – Canadian Museum of Nature in  
Ottawa

CPA – crystal growth by particle attachment

EDL – Electrical double layer

Eh – Reduction Potential

ENP – engineered nanoparticles

Five elements – Ag-Bi-Co-Ni-As

FA – Fluvic acids

HA – Humic acid

MIM – Manitoba Institute of Materials

NP – Nanoparticles

NMs – Nanomaterials

OA – Oriented Attachment

OM – Organic Material/matter

PGE – Platinum group element

PZC – Point of Zero Charge

ROM – Royal Ontario Museum

Silver nanoparticle – Ag NPs

SOM – Soil Organic Matter

Sample ID – Sample Identification

UBC – University of British Columbia

UNB – University of New-Brunswick

UoM – University of Manitoba

### Units

Å – Angstrom (unit of length, equal to  
10<sup>-10</sup> metre)

at% – Atomic percentage

a.p.f.u./apfu – Atom(s) per formula unit

cm – Centimeter

cps – Counts per second

eV – Electronvolt

Ga – Billion years

g/t – Gram(s) per ton

Hz – Hertz

J/cm<sup>2</sup> – Joule per square centimeter

K – Kelvin

keV – Kilo electronvolt

kV – Kilo volt

m – Meter

Ma – Million years

mL/min – Millilitres per minute

mm – Millimeter

ms – Milliseconds

nA – Nanoampere

ns – Nanoseconds

Pa – Pascal

ppb – parts per billions

wt% – weight percentage

## **Mineralogy**

All – allargentum

Anb – annabergite

Arg – native silver

Bhp – breithauptite

Cbt – cobaltite

Cbt-Gdf ss – cobaltite-gersdorffite *solid solution*

Dol – dolomite

Ery – erythrite

Fe-Dol – Fe dolomite

FeMg Sil – FeMg silicate (clay)

Muc – maucherite

Nc – nickeline

Saf – safflorite

Scld – stibioclaudeite

Skt – skutterudite

s.s – solid solution

Vln – valentinite

## **Methods**

ATM – Atomic Force Microscopy

BSE – Back-scattered electron

EPMA – Electron probe micro-analysis

EDAX detector – Energy dispersive X-ray analysis detector

EDS – Electron Dispersive X-Ray

Spectroscopy

FFT – Fast Fourier Transformations

d – d-spacing

LA-ICP-MS – Laser Ablation Inductively

Coupled-Plasma Mass Spectrometry

LOD – Limit of detection

MS- Mass Spectrometry

RLM – Reflected light Microscopy

RRUFF – American Mineralogist Crystal

Structure Database

SAED – Selected Area Electron Diffraction

SEM – Scanning Electron Microscopy

STEM – Scanning-Transmission Electron

Microscopy

TEAM – Texture & Elemental Analytical

Microscopy

TEM – Transmission Electron Microscopy

WDS- Wavelength dispersive spectrometry

## Results

$1\sigma$  – 1 sigma/ 1 standard deviation (68%

confidence level)

ASI – Applied Spectr Inc.

Av – Average

Eq – Equation

$E^0$  – Redox potential

Max – Maximum value

Min – Minimum value

n – Number of analyses

nd – Not detected

Stdev – Standard deviation

Vs/vs – Versu

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## Chapter 1

### 1.1 Introduction

#### 1.1.1 Silver

The element silver (Ag) is a precious metal with the atomic number 47, an atomic mass of 107.87 g/mol, a relatively high density of 10.5 g/cm<sup>3</sup> (@ 20 °C), and a moderately high melting point of 960.8°C (Speight, 2005). Due to its electron shell configuration of [Kr] 4d<sup>10</sup>5s<sup>1</sup>, its primary valence state is +1; however, higher oxidation states (i.e., +2, +3) have been reported for fluorides (Bailar, 1944). Silver commonly forms metallic and/or covalent bonds due to its electronegativity of 1.9 (Pauling & Castro, 1960; Speight, 2005). When bonding to oxygen in tetrahedral to cubic coordination, the most prevalent cation, Ag<sup>+</sup>, has an ionic radius ranging from 1.00 to 1.28 Å (Shannon, 1976). Silver has been widely used for jewellery and coinage throughout human history (Boyle, 1968). Modern technologies involving electronics, photography, and medicine use silver for its metallic, malleable, acid-resistant properties and its highest electrical and thermal conductivities of any metal (Boyle, 1968; Klein & Dutrow, 2007).

Silver has low crustal abundance (53 ppb; Rudnick & Gao, 2003, 2014), a chalcophile character and has similar chemical and physical behaviour to the precious metal gold (Boyle, 1968). Silver occurs predominantly as a minor to trace element in sulphides, sulfosalts, arsenides, and antimonides; substituting for Cu, Zn, Pb, Bi, Sb, Au, Hg, Ni, or Co (Boyle, 1968; Moëlo et al., 2008). Among minerals with silver as a major component, native silver [Ag], electrum [Au, Ag], and acanthite with its polymorph argentite [Ag<sub>2</sub>S] occur more commonly than Ag-antimonides (e.g., allargentum, dyscrasite, pyrargyrite, myrargyrite), Ag-sulfosalts (e.g., freibergite), Ag-bismuthinides (e.g., matildite) or AgHg phases (e.g., eugenite; Moëlo et al., 2008).

Silver forms in a wide range of mineral deposit types, including magmatic, hydrothermal, sedimentary, and supergene deposits (Andrews, Owsiacki, et al., 1986a; Bastin, 1939, 1950; Franklin et al., 1986; Kissin & Mango, 2014). However, it is only a main or by-product in selected hydrothermal vein deposits (i.e., orogenic gold, Zn-Pb-Ag, five-element veins) that are the major global source of today's silver production (Boyle, 1968; Kissin & Mango, 2014). Among the dominant silver vein deposit types, five-element veins (Ag-Bi-Co-Ni-As) have been one of the primary target for silver exploration due to their high silver grade and association with critical metals Co, Ni, and Bi (Kissin & Mango, 2014). Main districts include the Cobalt Embayment, Canada, Bou Azzer, Morocco, and the now-abandoned veins in southwest and eastern Germany (Burisch et al., 2017; Markl et al., 2016).

The geology and mineralogy of the deposit at the Cobalt Embayment have been studied and documented in detail (e.g., Bastin, 1950; Boyle & Dass, 1971; Marshall & Watkinson, 2001; Smyk & Watkinson, 1990) due to its economic relevance and complexity. The Cobalt district hosted more than 40 mines and has produced over 13 billion grams of silver from 1904 to 1988 (Nichols, 1988).

In the Cobalt district, the Ag-Co-Ni-As-Bi veins are classified as five-element deposits, characterized by native silver,  $\text{Ni}\pm\text{Co}\pm\text{Fe}$  (sulph-)arsenides, antimonides and minor sulphides within carbonate gangue (Jambor, 1971b, 1971a; Petruk, 1971b, 1971c, 1971a; Petruk, Harris, & Stewart, 1971; Petruk, Harris, Cabri, et al., 1971). Silver-bearing veins are spatially associated with the Nipissing Diabase, the Archean-Huronian unconformity, and major faults (Andrews, Owsiacki, et al., 1986b; Nichols, 1988). The diabase has been dated at  $2217 \pm 6$  Ma, providing a minimum age for mineralization (Andrews, Masliwec, et al., 1986).

Several genetic theories have been proposed for the five-element (Ag, Ni, Co, As, Bi) vein deposits of Cobalt, ON. Among these models, proposed to constrain the source of the metals and

required heat, are: (1) hydrothermal evolution from deep-seated granitic and or mafic intrusions (Bastin, 1939; Tyrell, 1907); (2) in situ hydrothermal evolution of the Nipissing Diabase, which acted as the direct metal and heat source (Jambor, 1971b; Van Hise, 1907); (3) multiple source model, where hydrothermal fluids leach metals from country rocks as a result of diabase-driven convection or regional geothermal gradient (Boyle & Dass, 1971; Goodz et al., 1986; Potter & Taylor, 2010; Smyk & Watkinson, 1990; Watkinson, 1986); (4) connate basin/rift model, where metals are leached from basin sediments and basement by evolving connate waters in a continental rift environment (Halls & Stumpfl, 1972; Kissin, 1988). Several theories have been proposed to constrain the deposition mechanism and are attributed to mechanisms including cooling, boiling, fluid mixing of different salinity content, and reduction by various reductants (Burisch et al., 2017; Kerrich et al., 1986; Kissin, 1992; Markl et al., 2016; Marshall et al., 1993; Robinson & Ohmoto, 1973; Scharrer et al., 2019). Potential reductants identified in the district include pre-existing sulfides, organic carbon, hydrocarbons, and Fe<sup>2+</sup>-bearing minerals in the Archean basement (Kissin, 1992; Marshall & Watkinson, 2001; Naumov et al., 1970; Potter & Taylor, 2010; Robinson & Ohmoto, 1973; Scharrer et al., 2019).

Several models assume that silver was transported as chloride complexes based on the presence of highly saline brines (15–40 wt% NaCl eq.), and the low sulphur fugacity in the veins (Kerrich et al., 1986; Marshall et al., 1993; Seward, 1976). However, silver veins at Cobalt reach grades exceeding 130,000 g/t native silver (Miller, 1913; Petruk, Jambor, et al., 1971), which is extraordinarily high and cannot be explained by any single known depositional process. Yet, these high-grade bonanza shoots occur unpredictably along veins that are otherwise nearly barren (Marshall et al., 1993; Marshall & Watkinson, 2000). The sheer volume of hydrothermal fluid that would have been required to deliver this much silver into such a small rock volume, at the near-

perfect precipitation efficiency implied by the grades, has no satisfactory explanation in any current model of how the deposit formed (Marshall et al., 1993; Kissin, 1993).

Compared with silver, gold presents comparable mobility constraints. Studies demonstrate that Au can be transported and concentrated as nanoparticles, thereby providing an explanation for bonanza-grade gold deposits (McLeish et al., 2021; Saunders, 1990). This raises the question of whether Ag nanoparticles (NPs) play an analogous role in silver enrichment. Ag NPs have been proposed as colloids transported as suspended particles in hydrothermal fluids (Chai et al., 2024; Hu & Cao, 2019; Moiseenko & Kuznetsova, 2010; Sillitoe, 2009), and their involvement in silver-enrichment settings has been documented, though the mechanisms remain incompletely understood.

### **1.1.2 Nanoparticles**

Nanoparticles (NPs) are defined as particles of matter that measure between 1 and 100 nm in at least one dimension (M. F. Hochella et al., 2008). In comparison, colloids refer to particles dispersed in an aqueous solution or medium, typically ranging in size from 1 to 1000 nm (Frimmel et al., 2007; Saunders, 2022). Due to their small size, NPs exhibit high mobility and chemical reactivity, a result of their large surface-area-to-mass ratio (M. F. Hochella et al., 2008). This gives them properties that differ significantly from those of their larger compositional equivalents (M. F. Hochella et al., 2008; Yu et al., 2013).

Nanoparticles in the environment originate from both natural and anthropogenic sources; natural sources include weathering, volcanic activity, earthquake-generating faults, and biological processes (Jr. Hochella et al., 2019; M. F. Hochella et al., 2008). Advances in technology have enabled visualization of NPs using techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) (Putnis & Ruiz-

Agudo, 2021; Saunders, 2022). Numerous elements have been identified as NPs within ore systems, including Au, Ag, Cu, As, Pb, Sb, Bi, and platinum-group elements, hosted primarily within pyrite and other sulphide minerals from hydrothermal and epithermal deposits (Deditius et al., 2011; Han et al., 2014; McLeish et al., 2021; Reich et al., 2010; Wang et al., 2017).

Silver NPs occur naturally in soils and water systems as a result of ore bodies close by, and secondary enrichment processes (e.g., oxidative weathering of sulfide minerals like acanthite and argentite, supergene remobilization during weathering of Ag-bearing ores, and dissolution and reprecipitation of Ag phases at the oxidation zone) and are most commonly noticed in areas associated with historical silver mining, such as mine tailings or soils near silver-containing mine and mill facilities (Cymes et al., 2017; Hu & Cao, 2019). Less recognized is that Ag NPs also occur within mineral deposits. Studies have identified nano-sized silver particles in various geological settings, including hydrothermal Carlin-type deposits, in supergene-enriched porphyry Cu deposits, black shale-hosted Ni-Mo-Platinum group element (PGE) polymetallic layers, and active seafloor hydrothermal sulphide systems, suggesting that colloidal or nanoparticulate silver may represent an important transport and deposition pathway for metals in geological settings (Deditius et al., 2011; Han et al., 2014; Reich et al., 2010; Wu et al., 2016). These studies indicate that Ag NPs can be locally significant contributors to silver enrichment in ore deposits, though aqueous Ag complexes remain the principal transport mechanism in most hydrothermal systems.

Like bulk silver, Ag NPs possess many of the same characteristics, along with additional properties that make them valuable across multiple disciplines (e.g. antimicrobial and electronic properties; (Purcell & Peters, 1998; Zhang et al., 2016). As a result, much of the current understanding of Ag NPs and silver colloids comes from nanomaterials science, nanotechnology, and medical research, with a focus on engineered Ag NPs. Synthesis and characterization of the

latter engineered nanoparticles have provided valuable insight into the behaviour of Ag NPs, which can also be applied to naturally occurring NPs in geological environments (Yu et al., 2013).

While colloidal transport has been invoked to explain gold mobility in a range of mineral deposit settings (Hastie et al., 2021; McLeish et al., 2021; Saunders, 1990), the role of colloids in transporting silver (particularly in vein-type environments) remains poorly understood. This is despite silver being the element most frequently alloyed with gold (Hough et al., 2009), and in many precious metal deposits, silver concentrations often exceed those of gold (Han et al., 2014). Experimental work has demonstrated that dendritic silver can crystallize from colloidal precursors (Fang et al., 2007), suggesting that colloidal transport may be a viable mechanism for silver mobilization. Yet while gold nanoparticles have received extensive research attention, helping to clarify longstanding questions about metallogenic processes and element mobility in systems such as Carlin-type deposits (Hough et al., 2011; Palenik et al., 2004; Reich et al., 2005), their silver counterparts remain comparatively understudied. The potential metallogenic significance of silver nanoparticles is therefore rarely addressed. These observations highlight the need for further work on the occurrence, behaviour, and implications of ore-derived silver NPs.

Recent studies suggest massive silver forms by nanoparticle aggregation. Chai et al. (2024) showed that, in China's Poshan deposit, silver sulphide nanoparticles aggregated into acanthite crystals, which were later replaced by native silver via desulphurization.

Chai et al. (2024) documented acanthite ( $\text{Ag}_2\text{S}$ ) and native silver mineralization at the Poshan Ag-Pb-Zn deposit, a polymetallic system in the eastern Qinling orogen, China. Using Transmission Electron Microscopy (TEM), the authors investigated silver sulphide mineralization, its temporal evolution, ore-forming temperatures, replacement reactions, and the subsequent formation of native silver. The work identified aggregates of silver sulphide NPs (AgS NPs),

supporting the hypothesis that oriented attachment of these NPs drives acanthite crystallization. Paragenetic evidence indicated that native silver formed by replacing acanthite rather than by direct hydrothermal deposition. Chai et al. (2024) proposed the reaction:  $2\text{Ag}_2\text{S} + 2\text{H}_2\text{O} \rightarrow 4\text{Ag} + 2\text{H}_2\text{S} + \text{O}_2$ , which also produced pyrite ( $\text{FeS}_2$ ), chalcopyrite ( $\text{CuFeS}_2$ ), and galena ( $\text{PbS}$ ) as byproducts. By integrating TEM data with reaction mechanisms, the study elucidated the genesis of acanthite and native silver, as well as the enrichment processes that produced the high-grade silver ores in the Poshan deposit.

#### **1.1.2.1 Classical and non-classical crystal growth, bottom-up and top-down**

This section first outlines the theoretical framework for mineral growth, distinguishing between classical and non-classical crystal growth, including crystal growth by particle attachment (CPA). It then examines the controls on the attachment mechanism. To understand the formation of secondary Ag resulting from the weathering of ore phases, a review of mineral growth mechanisms is required. Crystal growth in solution follows either classical or non-classical mechanisms. In classical growth, a solution becomes oversaturated with ions, triggering spontaneous nucleation followed by ion-by-ion addition to macroscopic dimensions. Non-classical growth encompasses crystal growth by particle attachment (CPA), in which NP aggregation drives crystal growth rather than ion addition (De Yoreo et al., 2015). CPA comprises two modes: oriented attachment (OA), in which assembling particles become crystallographically co-aligned to produce single-crystal or twin-bearing aggregates (Li et al., 2023; Penn & Banfield, 1998), and non-oriented attachment (NOA), in which NPs aggregate without crystallographic alignment, producing polycrystalline aggregates with random orientation of the grain boundaries (De Yoreo et al., 2015).

The boundary between classical and non-classical growth is not always distinct. The Ostwald step rule can obscure evidence of CPA by repeated dissolution and recrystallization of a metastable phase as a more stable phase nucleates within it or in the surrounding solution (Lifshitz & Slyozov, 1961; Threlfall, 2003).

Nanomaterials (NMs) form through either bottom-up or top-down processes. In the bottom-up approach, NPs grow from atomic and ionic species through classical or non-classical mechanisms. In the top-down approach, NPs originate from the mechanical release of particles from mineral surfaces through repulsive intergranular forces (Emmanuel et al., 2015; Levenson & Emmanuel, 2017) or from the chemical and mechanical liberation of NPs from a host matrix through dissolution (Schindler et al., 2024). Distinguishing between these two origins requires a combined assessment of NP texture, composition, and crystallography. Bottom-up NPs tend to be euhedral, rounded to spherical, and crystalline, whereas top-down NPs are typically angular, compositionally similar to their source phase, and spatially proximal to the bulk solid (Hochella et al., 2019; C. V. Putnis & Ruiz-Agudo, 2021).

#### **1.1.2.2 Driving forces and controls on the attachment mechanism of Ag NPs**

CPA reflects the interplay of solution structure, interparticle forces, and particle motion. Crystal surfaces impose structure on the near-surface solution, generating interparticle forces that depend on the composition and structure of the near-surface solution, which, in turn, is governed by pH, ionic strength, ionic species, surface ligands, particle size, temperature, and supersaturation (De Yoreo et al., 2015; Li et al., 2023; Penn & Banfield, 1998).

Solution pH governs the surface charge of Ag NPs, thereby controlling both their stability and aggregation mechanism (Badawy et al., 2010; Fernando & Zhou, 2019). Acidic conditions promote rapid, disordered aggregation via NOA; particle size increases, while NP concentration

and stability decrease as dissolved silver increases. Near neutral to alkaline conditions provide sufficient time for crystallographic alignment, thereby favouring OA (Badawy et al., 2010; Fernando & Zhou, 2019).

Ionic strength compresses the electrical double layer (EDL) surrounding each Ag NP, promoting particle contact (Badawy et al., 2010). Divalent cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are particularly effective at increasing ionic strength (Badawy et al., 2010; Levard et al., 2012; Yu et al., 2013). Carbonate-buffered environments, as observed at Cobalt, which are rich in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , are therefore especially prone to rapid, disordered NOA of Ag NPs (Levard et al., 2012).

Organic matter and surface ligands play a dual role in the behaviour of Ag NPs. The adsorption of humic acid and fulvic acid onto Ag NP inhibit aggregation and enhances colloidal mobility, thereby facilitating transport away from the formation site (Adrian et al., 2019; Aiken et al., 2011; Akaighe et al., 2011; Delay et al., 2011). Organic matter (OM) also counteracts the destabilizing effect of increasing ionic strength (Delay et al., 2011) and increases the driving force for dissolution and redistribution of metal and metal oxide NPs (Aiken et al., 2011). In the context of the Cobalt assemblage, OM acts both as a reductant that nucleates Ag NPs at its surface and, at lower concentrations, as a stabilizer that promotes their transport prior to aggregation.

Particle size governs the balance between surface energy-driven OA and diffusion-controlled NOA. Smaller Ag NPs (less than approximately 5 nm) exhibit proportionally larger surface areas and higher surface energies, thereby driving crystallographic alignment and OA (Hunyadi Murph et al., 2015; Penn & Banfield, 1998; Zhang et al., 2010)). As particle size increases, the relative contribution of surface energy declines and the probability of achieving lattice alignment before coalescence diminishes, shifting the dominant mechanism toward NOA (Liu et al., 2020; Zhang et al., 2010).

Temperature controls Ag NP nucleation kinetics, aggregation rates, and the dominant attachment mechanism. Higher temperatures increase thermal energy and Brownian motion, thereby increasing the particle collision frequency and the probability of crystallographic pre-alignment required for OA, while also accelerating Ostwald ripening and the oxidative dissolution of Ag NPs back to  $\text{Ag}^+$  (Liu et al., 2020; Zhang et al., 2010). Very high temperatures favour disordered NOA.

Supersaturation governs the rate of Ag NP nucleation and the dominant growth mechanism. At high supersaturation, rapid nucleation produces large numbers of small NPs simultaneously, driving frequent particle collisions that favour fast, disordered NOA before crystallographic alignment can occur (De Yoreo et al., 2015; Liu et al., 2020)

## **1.2 Objectives**

This study focuses on seven samples from the Cobalt embayment, ON, obtained from the Royal Ontario Museum, the Museum of Nature in Ottawa, and Dr. Frank Santaguida (now Errington Metals). The main objectives of the study are to determine (1) silver occurrence in these veins both texturally and compositionally; (2) if secondary native silver underwent secondary processes that involved Ag NP transport, and (3) processes that resulted in supergene silver formation.

These objectives are addressed using micro- and nanoscale techniques, including reflected-light microscopy, scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS), electron microprobe analysis (EPMA), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), and transmission electron microscopy (TEM). This multi-scale approach will improve our understanding of the processes that result in Ag

formation in five-element veins, with a focus on the role of silver NPs in silver enrichment during supergene processes.

In the thesis “silver” and “Ag” to refer to the mineral and chemical element, respectively. Otherwise, all mineral abbreviations use the symbols of Warr (2021).

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## **Chapter 2**

### **Secondary enrichment processes of native silver in five-element veins, Cobalt Embayment, ON, Canada**

## 2.1 Introduction

The precious metal silver is a sought-after commodity for jewellery, monetary value, and applications in various technologies, including medical, photographic, and electronic technologies (Boyle, 1968; Klein & Dutrow, 2007). As a commodity metal, silver is predominantly mined as a by-product of epithermal deposits (Boyle, 1968; Kissin & Mango, 2014), but when it occurs as a primary commodity, it is concentrated in vein deposits, of which five-element veins (As-Bi-Ag-Co-Ni±U) have historically been the most important Ag source.

Silver formation in five-element veins is strongly debated. Hydrothermal models invoke metamorphic, magmatic, or basinal brine fluids in which Ag is transported as a chloro-complex at temperatures < 300°C under acidic conditions (Seward, 1976; Stefánsson & Seward, 2003). A fundamental challenge to this model is that the abundance of silver in five-element veins systematically exceeds the solubility of Ag in hydrothermal fluids. The low solubility and rapid precipitation of silver also limit its capacity to form extensive enriched zones (Sillitoe, 2009; Anderson & Muntean, 2016), and although Ag can be remobilized over short distances (Seward, 1976; Stoffregen, 1986), it is generally not transported beyond the oxidized zone (Lakin et al., 1974; Mann, 1984; Sillitoe, 2009; Anderson & Muntean, 2016; Redwood, 2024). Gold presents comparable mobility constraints, and studies demonstrating that Au can be transported and concentrated as nanoparticles (NPs) have provided an explanation for bonanza-grade gold deposits (Saunders, 1990; McLeish et al., 2021). This raises the question of whether silver nanoparticles (Ag NPs) play an analogous role in silver enrichment. Silver NPs have been proposed as colloids transported as suspended particles in hydrothermal fluids (Chai et al., 2024; Hu & Cao, 2019; Moiseenko & Kuznetsova, 2010; Sillitoe, 2009), and their involvement in silver enrichment settings has been documented, though the mechanisms remain incompletely understood.

In five-element vein deposits, the formation of primary textures such as dendritic silver, massive aggregates, mm-scale veins, and rosettes surrounded by arsenides is widely discussed, whereas subsequent supergene processes that result in the occurrence of Ag NPs are less well understood (Chai et al., 2024). The former textures are well developed in the five-element veins of the Cobalt embayment, Ontario, one of the world's largest silver districts (Boyle, 1968; Kissin, 1992; D. Marshall & Watkinson, 2001). Beyond syngenetic formation processes, the role of Ag NPs in epigenetic, low-temperature processes, including supergene enrichment driven by meteoric-fluid interactions, remains largely unresolved.

Mineral deposits undergo a range of epigenetic processes, including remobilization driven by metamorphism and deformation (Dubosq et al., 2019; Fougereuse et al., 2016; B. Marshall & Gilligan, 1987; Tomkins & Mavrogenes, 2002), supergene upgrading through interaction with meteoric waters and chemical weathering (Boyle, 1968; Reich & Vasconcelos, 2015; Vasconcelos et al., 2015), and secondary dispersion of metals into overlying strata, soils, rivers, and vegetation, which redistributes metals beyond the original deposit (Kyser et al., 2015). In recent years, metal occurrence and formation at the nanoscale (NPs) have been widely reported in a variety of deposits and environments (Hastie et al., 2021; Schindler & Hochella, 2024; Schindler et al., 2025), establishing NP-mediated transport as a broadly relevant mechanism in low-temperature geochemical systems. Whether this mechanism operates during the supergene modification of five-element vein deposits, and specifically at Cobalt, remains uninvestigated.

To address this knowledge gap, this study presents one of the first systematic nanoscale investigations of Ag NP occurrence and formation linked to supergene enrichment in a five-element vein deposit, using a combination of microscopy (reflected light microscopy-RLM, scanning electron microscopy-SEM, transmission electron microscopy-TEM) and mineral

chemistry (electron probe micro-analyses-EPMA, laser ablation inductively coupled plasma mass spectrometry-LA-ICP-MS) on ore phases, host carbonates, and metal oxides. Together, these methods resolve the microscale and nanoscale record of silver formation at Cobalt, with emphasis on secondary, epigenetic modification. The objectives of this study are to: (1) use the compositional variations in primary ore phases, including (sulph-)arsenides, antimonides, and carbonates to determine trace Ag content in primary ore phases, to constrain the silver source during supergene processes; (2) document the occurrence of native silver with metal oxides/oxyalts and associated phases; (3) document the occurrence of Ag NPs and their associations with primary and secondary phases across a range of geochemical condition; and (4) identify and interpret mechanisms that govern Ag NP formation and aggregation, and assess their contribution to silver upgrading in the five-element vein deposits of the Cobalt embayment.

## **2.2 Geological setting**

The Cobalt embayment, a historically significant mining district spanning approximately 30,000 to 60,000 km<sup>2</sup> in northeastern Ontario, Canada, has been a focal point of silver exploration and geological research for over a century (Potter & Taylor, 2009; Fig. 1a-b). Following the discovery of the first silver veins in 1903, the region became the largest silver producer in North America, with historic production from 1904 to 1990 exceeding 507 million ounces of Ag, alongside significant by-products of Co, Ni, and Cu (Guindon et al., 2016; D. Marshall & Watkinson, 2001). Although silver production has ceased, the area remains an active exploration and research target due to the presence of critical metals such as Bi, Co, and Ni.

The geology of the Cobalt Embayment records a complex tectonic and sedimentary history. The district lies within the northeastern Southern Province of the Canadian Shield, along the southern margin of the Superior Province, and is underlain by the Abitibi Greenstone Belt (AGB),

a composite Archean volcanic-sedimentary terrane formed between approximately 2.75 and 2.69 Ga (Ayer et al., 2002; Heather, 2001; Kissin, 1992; B. S. Wilson, 1988). The AGB comprises steeply dipping mafic to felsic volcanic rocks, interflow sedimentary units (including chert, black shale, siltstone, greywacke, and banded iron formation), and syn-volcanic to post-tectonic intrusions (Jambor, 1971b; Petruk, 1971a, 1971b; M. C. Smyk, 1987; Fig. 1). In the Cobalt district specifically, the Archean basement consists of pillowed to massive basalts, intermediate to felsic calc-alkaline volcanic rocks dated at  $2.6874 \pm 0.0017$  Ga, and interflow sedimentary lenses (Jambor, 1971b; Petruk, 1971b). Notably, massive to semi-massive pyrite-pyrrhotite  $\pm$  sphalerite, galena, and chalcopyrite occur as nodules, stockworks, and lenses up to 3 m thick within these interflow sediments and are considered a potential source of metals for the five-element veins (Kissin, 1992; Nichols, 1988; Patterson, 1979). These rocks were later deformed and metamorphosed to greenschist facies during the Kenoran Orogeny (Dimroth et al., 1983; Monecke et al., 2017).

Unconformably overlying the Archean basement are the shallow dipping Paleoproterozoic sedimentary rocks of the Huronian Supergroup, which fill the Cobalt embayment basin (Andrews et al., 1986; Potter & Taylor, 2009; Fig. 1). Deposition of the Huronian Supergroup occurred between approximately 2.49 and 2.22 Ga, constrained by detrital zircon and intrusive ages (Krogh et al., 1984; Smith & Heaman, 1999). In the Cobalt district, only the upper Cobalt Group is exposed, which is subdivided into the Gowganda and Lorrain formations (Jambor, 1971b; Fig. 1). The Gowganda Formation comprises the Coleman and Firstbrook members, both of which host silver mineralization (Andrews et al., 1986; Bastin, 1950; Boyle & Dass, 1971; Marshall et al., 1993). The Coleman Member, up to 180 m thick, consists of diamictite, conglomerate, sandstone, siltstone, and greywacke, and contains detrital sulphide clasts derived from erosion of Archean

sulphide-bearing strata (Jambor, 1971b; Patterson, 1979; Rainbird, 1986; Scammel, 1984; M. C. , Smyk & Watkinson, 1990). The overlying Firstbrook Member, 210 to 610 m thick, is characterized by laminated sandstone, siltstone, and argillite, while the Lorrain Formation, up to 300 m thick, comprises granule-pebble conglomerate, arkose, and quartz arenite (Jambor, 1971b; Fig. 1). The Archean-Huronian unconformity, representing a hiatus of approximately 300 million years, is a sub-horizontal to gently dipping surface locally exposed in antiformal cores and exerts a first-order control on both Nipissing sill emplacement and vein localization (Andrews, Owsicki, et al., 1986; D. Marshall & Watkinson, 2001; Potter & Taylor, 2010).

The region was intruded by several generations of mafic dikes and sills (Fig. 1). The Matachewan quartz gabbro dikes, dated at approximately 2.485 Ga, represent an early intrusive event (Fahrig & Wanless, 1963; Jambor, 1971a). The most significant intrusive body in the district is the Nipissing diabase, an extensive, shallow-dipping sill complex of olivine tholeiite composition with mid-ocean ridge basalt (MORB)-like trace element signatures, which intruded both Archean and Huronian rocks at  $2.217 \pm 0.006$  Ga (Andrews et al., 1986). The youngest intrusions are Keweenaw diabase dikes, approximately 30 m thick, associated with the Midcontinent Rift system at approximately 1.1 to 1.2 Ga (Moore, 1956; Silver & Green, 1972).

Structurally, the district is characterized by regional and local fault systems that controlled fluid flow and mineralization. Regionally, north-northwest- and north-northeast-striking faults extend for hundreds of kilometres, forming horst-graben systems that were active during Huronian rifting and reactivated during and after the Nipissing intrusive event (Wilson, 1949; Thomson, 1967; Wilson, 1986; Doughty et al. 2013). Locally, three fault sets are recognized: southeast-trending faults (e.g., Montreal River, Cross Lake, Quinze Dam) are regionally significant but generally barren; northeast-trending faults offset Nipissing diabase but predate mineralization; and

east-southeast-trending steep normal faults, which are short, subvertical structures with displacements up to 7.5 m, locally host silver-arsenide veins (Thomson, 1967; Lovell & Caine, 1970; Wilson, 1986; Marshall, 2008). Vein structural styles include dilatant veins, shear-zone veins, and brecciated zones documented in Archean, Huronian, and Nipissing hosts, with microscale hydraulic fracturing indicating the presence of overpressured fluids (Andrews, Owsicki, et al., 1986; Bastin, 1950; D. Marshall, 2008). The veins formed at or shortly after intrusion of the diabase sills with a maximum lag of 8.1 million years based on the error associated with baddeleyite (a primary phase of the Nipissing Diabase) and rutile ages (a secondary phase related to Ag-sulpharsenide vein) that are respectively  $2.217 \pm 0.0016$  Ga and  $2.217 \pm 0.006$  Ga, and a minimum lag of 20,000 to 50,000 years inferred from paleomagnetic data (Andrews, Masliwec, et al., 1986). Paleomagnetic and Ar-Ar data also record later disturbance by younger tectonothermal events (Andrews, Masliwec, et al., 1986; Kissin, 1992).

The Cobalt district hosted more than 40 mines and has produced over 13 billion grams of silver from 1904 to 1988 (Nichols, 1988). Grades in silver veins at Cobalt exceeded 130,000 g/t native silver (Miller, 1913; Jambor, 1971a). Silver mineralization in the Cobalt district is not restricted to a single host lithology but occurs within the Gowganda Formation, the Nipissing diabase, and the Archean pillowed basalts and interflow sediments (Hriskevich, 1968; Jambor, 1971c, 1971b, 1971a; D. Marshall & Watkinson, 2001; Petruk, 1971b, 1971a; Rush, 2019). The mineralogy of the ore deposit is complex, where the host gangue includes carbonates (e.g., calcite, dolomite), the main ore phases are silver phases (e.g., native silver, allargentum, dycrassite), arsenides (e.g., safflorite, skutterudite, nickeline, loellingite), sulpharsenides (e.g., cobaltite, gerdosfite), antimonide (e.g., breithauptite, rammerlbergite), sulfides (e.g., pyrite, chalcopyrite,

galena, sphalerite; (Petruk, 1971c; Petruk et al., 1970; Petruk, Harris, & Stewart, 1971; Petruk, Harris, Cabri, et al., 1971)).

### 2.3 Mineralogy

The seven samples were examined using RLM and SEM to determine the ore assemblage and textures, with a focus on silver phases and their relationships to other phases (i.e., ore phases, carbonates, oxidized phases; Table 1).

The mineral assemblage comprises silver phases, arsenides, sulph-arsenides, antimonide, native bismuth and trace secondary oxide phases; hosted within carbonate veins (Figs. 3-5; Table 1, Appendix C-D). The silver phases present in the studied samples are native silver (Ag; Figs. 3 and 4), minor to trace allargentum ( $\text{Ag}_{1-x}\text{Sb}_x$ ; Figs. 3f, i, 4), trace eugenite ( $\text{Ag}_{11}\text{Hg}_2$ ) and matildite ( $\text{AgBiS}_2$ ). Native silver dominates and texturally occurs as: (1) massive, anhedral grains with irregular grain boundaries and varying grain size (i.e.,  $\approx 50\text{ }\mu\text{m}$  up to several millimeters) that contain inclusion of arsenides, (sulph-)arsenides, breithauptite (Fig. 3a-e), and locally exsolution lamellae of allargentum (Fig. 3f) ; (2) partially oxidized rosettes (i.e.  $250\text{ }\mu\text{m}$  to  $1\text{ mm}$  in diameter) with native silver and locally allargentum in the core rimmed by arsenides, breithauptite (Fig. 3g-i), and locally native silver; (3) veins of native silver with and without arsenides and breithauptite ranging in width (i.e.,  $< 10\text{ }\mu\text{m}$  to  $2000\text{ }\mu\text{m}$ ) and cross-cutting carbonate gangue (Fig. 3j, k); (4) disseminated native silver occurring as small (i.e.,  $< 50\text{ }\mu\text{m}$ ), irregular or round grains in carbonate matrix or oxidized metal phases, and commonly are in close vicinity to the other three native silver textures (Fig. 3a, c, e, i, k, l); and (5) native silver occurring either as inclusions within or interstitial between (sulph-)arsenides (Fig. 3d, e). These five native silver textures vary in abundance within each sample; however, several are commonly co-occurring.

Despite the textural variations of native silver, it has a close spatial association with arsenides safflorite ( $\text{CoAs}_2$ ), nickeline ( $\text{NiAs}$ ), skutterudite ( $\text{CoAs}_{2-3}$ ), loellingite ( $\text{FeAs}_2$ ), maucherite ( $\text{Ni}_{11}\text{As}_8$ ), sulph-arsenide cobaltite ( $\text{CoAsS}$ ), and the antimonide breithauptite ( $\text{NiSb}$ ; Figs. 3a-j; 4) (identified with EPMA). All these phases are anhedral, vary in size from less than 10  $\mu\text{m}$  to several hundred microns (Fig. 3a-j), are partially intergrown with or replaced by each other (Fig. 3b, c, e, f, i, j), replace native silver (Fig. 3d, e) or form rounded inclusions within native silver (Fig. 3a, b).

Although the aim of this study is not to constrain a detailed paragenesis of the different primary ore phases since detailed investigations on the subject have been done by Petruk (1971b,c) and more recently by Rush (2019), the paragenesis is complex, with native silver forming both pre-, syn- and post-arsenide formation. The paragenesis is constrained based on the textural variations showing early (e.g., core of rosettes, replacement by arsenides) and late (e.g., veins extruding from rosettes, silver rims) native silver deposition. Additionally, the occurrence of allargentum exsolution lamellae (Figs. 3f, i) and the symplectitic intergrowths of allargentum with safflorite and cobaltite in native silver (Figs. 4) indicates that native silver formation is also closely temporally linked to the formation of (sulph-)arsenides.

All these observations are the result of processes related to the original formation of ore phases within carbonate gangue and linked to the emplacement of the Nipissing diabase at approximately  $2.219 \pm 0.0036/-0.0035$  Ga (Andrews, Masliwec, et al., 1986) which is widely accepted as the heat source for hydrothermal activity (Boyle & Dass, 1971b; Goodz et al., 1986; Kerrich et al., 1986; Potter & Taylor, 2010; M. C., Smyk & Watkinson, 1990; Watkinson, 1986). However, in the studied samples, oxidized phases are minor components and are associated with all silver textures (Figs. 3g, h, k, 5). Most commonly, safflorite, nickeline and/or cobaltite are

(partially) oxidized to various metal oxides, including erythrite ( $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ ), stibioclaudeite ( $\text{AsSbO}_3$ ), valentinite ( $\text{Sb}_2\text{O}_3$ ), and annabergite ( $\text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) (all identified with SEM and EPMA), which surround massive and disseminated native silver (Fig. 5a,e). These oxidized areas are irregular in size ( $< 20 \mu\text{m}$  up to  $400 \mu\text{m}$ ) and can be monomineralic (e.g., stibioclaudeite; Fig. 5a-d) or are composed of numerous phases. The latter assemblages can be quite complex, depicting zonation, such as an association of hydrous Ni-arsenate (annabergite) rimmed alternatively by hydrous Co-arsenate (erythrite) and Sb-oxide (valentinite) (Fig. 5e-h). Disseminated, round or amoeboid native silver particles  $< 50 \mu\text{m}$  in size commonly occur on the rim or within the metal oxysalts/oxide (Fig. 5e).

Within native silver rosettes, oxidation of (sulph-)arsenides can occur both in the cores and rims of native silver (Fig. 3g, h). Oxidized cores (sulph-)arsenides are composed of anhedral Sb-oxide (valentinite), hydrous Ni-arsenate (annabergite) rimmed by hydrous Co-arsenate (erythrite); the latter is most common when in contact with safflorite (Fig. 3h). Anhedral native silver with irregular grain boundaries and varying in size ( $< 10 \mu\text{m}$  up to  $200 \mu\text{m}$ ) is the remnant ore phase. Inclusions of (sulph-)arsenides and breithauptite within native silver are commonly not oxidized (Fig. 3g-i).

Oxidation of skutterudite results in dendritic veinlets of hydrous Co-arsenate (erythrite) that contain minute ( $< 10 \mu\text{m}$ ) round grains of native silver (Fig. 5i-l). The oxidation of native silver veins that do not contain other ore phases is local and rarely occurs along their entire length. The result of this oxidation is an irregular halo of stibioclaudeite around native silver (Fig. 3k, 5m). Stibioclaudeite veinlets can also cross-cut carbonate gangue without forming haloes around native silver veins (Fig. 5q-t).

Metal oxysalts/oxides that do not occur with primary ore phases are common in the carbonate gangue, either as thin veinlets crosscutting carbonates (Figs. 3d, k, 5a, e, l, m, q) or as irregular patches along cracks or corroded surfaces (Fig. 3k, 5m). In both occurrences, these metal oxides/oxysalts occur near oxidized (sulph-)arsenides, partially oxidized rosettes or native silver veins.

Carbonates are the dominant gangue phase hosting both ore and oxidized phases. They are strongly corroded and partially altered (Fig. 3l, 5) which makes it difficult to determine grain boundaries and hence sizes of individual grains. They can occur brecciated when native silver veins crosscut them (Fig. 3j, k).

## **2.4 Methodology**

This study employs a suite of micro- to nanoscale analytical techniques, each critical for identifying the source of Ag and the pathways of silver formation. A total of seven (7) samples from the Cobalt embayment were provided by the Canadian Museum of Nature in Ottawa, Ontario, Canada (CMN), Frank Santaguida (from Errington Metals Inc) and the Royal Ontario Museum (ROM) (Fig. 1c; Table 1). The samples were selected based on the occurrence of silver, heterogeneity, and the complexity of the associations and assemblages.

Minerals were identified using a combination of spectrometry techniques in conjunction with SEM, TEM, EPMA and LA-ICP-MS such as energy-dispersive spectrometry (EDS), wavelength-dispersive spectrometry (WDS), and mass spectrometry (MS); databases such as the American Mineralogist Crystal Structure Database (RRUFF) were used to identify minerals identifications based on their d-spacing and stoichiometry (Downs & Hall-Wallace, 2003).

### **2.4.1 Scanning electron microscopy (SEM)**

Samples were analyzed using the FEI Quanta environmental SEM and the FEI Nano Nova SEM at the Manitoba Institute of Materials (MIM) located on the University of Manitoba. The samples were characterized in backscattered electron (BSE) mode using energy-dispersive X-ray spectrometry (EDS) under high vacuum ( $10^{-7}$  Pa). The microscopes were operated at an electron voltage of 10-20 kV, a spot size of 4 mm, and a working distance of 10 mm. As some of the samples were composed of altered dolomite (M39127, M39011, M39035, M8922, and M39076), SEM imaging was conducted at 10 kV rather than 20 kV. Elemental maps were collected at 512 x 400 resolution, with a 200  $\mu$ s dwell time and approximately 20 frames, yielding maps that took 20 to 40 min each. Semi-quantitative EDS measurements were done on grains of interest to confirm their composition. For EDS analyses, X-ray signals were collected for 10 s on 1- $\mu$ m spots and processed using Texture & Elemental Analytical Microscopy (TEAM) software for the elements of interest (Ag, As, Ca, Co, O, Ni, S, and Sb).

### **2.4.2 Transmission electron microscopy (TEM)**

TEM analysis was conducted on sections extracted from three samples, C31018a-b and M39127 (Table 1). From the former sample, three TEM sections were extracted from two silver vein associated with primary ore phases and carbonate, and silver Ag-Sb veinlets extending from a larger silver aggregate (Fig. S1a-d [Appendix A]). From the latter sample, a TEM section was extracted from areas composed of silver, dolomite, arsenide, sulfa-arsenide, and various antimonates and arsenates, with varying compositions and ratios (Fig. S1e-f [Appendix A]).

The TEM samples were extracted and prepared for TEM in the Environmental Nanogeoscience Facility at the University of Manitoba. The rock samples were reinforced with a temporary holding agent, Crystal Bound 509. They were later thinned to 1-2 mm thick and laterally

trimmed in all directions around the area of interest. Samples were thinned to 200  $\mu\text{m}$  and ground using different-grit SiC abrasive paper (320 and 600 grit). They were then mounted with the polished side down to two glass coverslips, with one of them slanted  $3^\circ$  to wedge it thin right by the area of interests (AOI). The glass and holding agent were passively removed via dissolution in acetone. Samples with the polished side up were affixed to a three (3) mm-diameter cutout copper TEM grid using epoxy. The final step in preparing the TEM samples involved thinning the samples at a  $5^\circ$  angle below the polished surface using the Fischione Model 1051 TEM ion mill at the Environmental Nanogeoscience Facility, set at 4-6 kV.

The sections were characterized using an FEI Talos F200x S/TEM, located at the Manitoba Institute of Materials (MIM). Compositional analysis and chemical mapping were performed in scanning-TEM (STEM)-EDS mode with 4 silicon-drift detectors, set at 200 kV with a spot size ranging 2-5 mm. Mineral identification was performed using a combination of selected-area electron diffraction (SAED), fast Fourier transform (FFT) patterns of lattice fringes visible in high-resolution TEM images, chemical distribution, semi-quantitative chemical analysis by STEM-EDS, and textural features of various phases.

#### **2.4.3 Electron probe micro-analysis (EPMA)**

Seven samples were sent to the Electron Microbeam/X-ray Diffraction Facility at the Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia to conduct EPMA on ore phases (i.e., silver phases, antimonide, (sulph-)-arsenides), carbonates, and metal oxide phases. The analyses were done using a JEOL JXA-iHP200F field emission electron microprobe with 5 wavelength-dispersive X-ray spectrometers (WDS) and dual Bruker XFlash6 30 mm<sup>2</sup> SDD-energy dispersive X-ray spectrometers (EDS). The WDS spectrometers are equipped with standard (TAP, PETJ, LIF), large-sized (TAPL, PETL, LIFL), and specialized light-element

(LDE1L, LDE6L) analytical crystals; the latter were used to analyze oxygen when carbonates were measured. The instrument is equipped with a W filament, a Be window, and a Faraday cup. For quantitative analyses of all phases, an acceleration voltage of 20 keV, a beam current of 20 nA, and a takeoff angle of 40° were used. Ore phase and oxides were analyzed using a beam diameter of 2 µm; carbonate analyses utilized a 10 µm beam. Peak counting times ranged from 20 to 40 s, with background counts collected on both sides of the peak. Unknown and standard intensities were corrected for dead time. Standard intensities were corrected for standard drift over time using internal software. For data acquisition and correction, Probe-for-EPMA and Probe Image software (Probe Software, Inc.) were used, enabling integrated EDS-WDS data collection and the application of ZAF or  $\phi\rho Z$  corrections. Correction factors for known interferences, such as S by Co, As by Pb, Au by Fe, Hg by Ag, Bi by Au, and Mn by Hg, were measured and applied to the data. Analyses were deemed successful if analytical totals ranged from  $100 \pm 1.5$  wt%, with compositions consistent with the accepted mineral chemistry of the analyzed phases. Further, a standard single substitution method was applied to impute values below the measurable threshold (i.e., limit of detection) to decrease statistical bias (Hornung & Reed, 1990):

$$\text{Imputed value} = \frac{LOD_{\text{measured}}}{\sqrt{2}} \quad \text{Eq. (1)}$$

where  $LOD_{\text{measured}}$  is the measured value of an element beneath the limit of detection which was measured at 99% ( $3\sigma$ ) confidence level.

A total of 251 ore phases were analyzed. To ensure quality control and quality assurance, a combination of synthetic and natural mineral reference materials was used for calibration. The analyzed elements with reference material, first order element line, and detection limit with standard variation in wt% are: Ag ( $Au_{20}Ag_{80}$  by SRM481,  $L\alpha$ ,  $0.04 \pm 0.00$  wt%), As (gallium

arsenide by SPI,  $L\alpha$ ,  $0.04 \pm 0.01$  wt%), Bi (bismuth selenide by SPI,  $M\alpha$ ,  $0.12 \pm 0.00$  wt%), Co (cobalt by Astimex and cobalt sulfide by Maclean,  $K\alpha$ ,  $0.02 \pm 0.00$  wt%), Fe (hematite by SPI,  $K\alpha$ ,  $0.01 \pm 0.00$  wt%), Hg (cinnabar by SPI,  $M\alpha$ ,  $0.10 \pm 0.01$  wt%), Ni (nickel silicide by SPI,  $K\alpha$ ,  $0.02 \pm 0.00$  wt%), Pb (galena by SPI,  $M\alpha$ ,  $0.08 \pm 0.01$  wt%), S (pyrite by SPI,  $K\alpha$ ,  $0.02 \pm 0.00$  wt%), and Sb (stibnite by SPI and antimony by Cominco,  $L\alpha$ ,  $0.03 \pm 0.00$  wt%).

Carbonate analyses were conducted on 43 grains. The analyzed elements with reference material, first order element line, and detection limit with standard variation in wt% are: Ca (dolomite by SPI,  $K\alpha$ ,  $0.01 \pm 0.00$  wt%), Fe (hematite by SPI,  $K\alpha$ ,  $0.01 \pm 0.00$  wt%), Mg (dolomite by SPI,  $K\alpha$ ,  $0.01 \pm 0.00$  wt%), Mn (rhodonite by SPI,  $K\alpha$ ,  $0.01 \pm 0.00$  wt%), S (hematite by SPI,  $K\alpha$ ,  $0.01 \pm 0.00$  wt%), and Si (rhodonite by SPI,  $K\alpha$ ,  $0.01 \pm 0.00$  wt%).

Metal oxides and oxysalts were analyzed on 25 grains. Many analyses had a weak overlap with host carbonate phases (on average  $< 1$  wt%). Oxygen was recalculated (i.e.,  $100$  wt% - sum of elements) due to the small size of the analyzed grains, weak polishing, and uneven surface. The analyzed elements with reference material, first order element line, and detection limit with standard variation in wt% are: Ag ( $Au_{20}Ag_{80}$  by SRM481,  $L\alpha$ ,  $0.07 \pm 0.19$  wt%), As (gallium arsenide by SPI,  $L\alpha$ ,  $0.13 \pm 0.33$  wt%), Bi (bismuth selenide by SPI,  $M\alpha$ ,  $0.07 \pm 0.06$  wt%), Ca (dolomite by SPI,  $K\alpha$ ,  $0.02 \pm 0.02$  wt%), Co (cobalt by Astimex and cobalt sulfide by Maclean,  $K\alpha$ ,  $0.08 \pm 0.20$  wt%), Fe (hematite by SPI,  $K\alpha$ ,  $0.05 \pm 0.16$  wt%), Hg (cinnabar by SPI,  $M\alpha$ ,  $0.06 \pm 0.04$  wt%), Mg (dolomite by SPI,  $K\alpha$ ,  $0.10 \pm 0.23$  wt%), Mn (rhodonite by SPI,  $K\alpha$ ,  $0.11 \pm 0.26$  wt%), Ni (nickel silicide by SPI,  $K\alpha$ ,  $0.05 \pm 0.09$  wt%), Pb (galena by SPI,  $M\alpha$ ,  $0.13 \pm 0.20$  wt%), S (pyrite by SPI,  $K\alpha$ ,  $0.03 \pm 0.04$  wt%), Sb (stibnite by SPI and antimony by Cominco,  $L\alpha$ ,  $0.03 \pm 0.00$  wt%), and Si (rhodonite by SPI,  $K\alpha$ ,  $0.02 \pm 0.00$  wt%).

One elemental map was run on allargentum-safflorite-cobaltite intergrowth in native silver by analyzing for elements Ag, As, Co, Ni, Hg and Sb using the same emission lines and reference materials as for ore phase analyses at 20 keV acceleration voltage 20 nA beam current, a 40° take-off angle, and 2 µm beam diameter. The mapping followed the procedure outlined in (Donovan et al., 2021).

#### **2.4.4 Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)**

Carbonates from seven samples that were previously analyzed for their major and minor composition using EPMA were analyzed for their trace element composition at the MANTIS lab at the Department of Earth Sciences, University of New Brunswick, using an Agilent 7700x quadrupole laser ablation inductively coupled plasma mass spectrometer equipped with an Applied Spectra Inc. (ASI) Resolution LR 193nm Excimer laser ablation system. Analyses were performed using both spot and line analyses to create maps of selected carbonate grains. Gas rates were the same for both spot and line analyses using 900 ml/min argon, 300 ml/min ultra-pure helium, and 2 ml/min ultra-pure nitrogen while running both roughing pumps to increase vacuum and sensitivity.

Spot analyses were performed on the same carbonate grains from which EPMA analyses were collected, when possible. Masses  $^{24}\text{Mg}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ,  $^{34}\text{S}$ ,  $^{43}\text{Ca}$ ,  $^{56}\text{Fe}$ ,  $^{59}\text{Co}$ ,  $^{60}\text{Ni}$ ,  $^{75}\text{As}$ ,  $^{78}\text{Se}$ ,  $^{107}\text{Ag}$ ,  $^{121}\text{Sb}$ ,  $^{125}\text{Te}$ , and  $^{209}\text{Bi}$  were analyzed using a spot size of 36 µm at a repetition rate of 4 Hz and fluence of 2 J/cm<sup>2</sup> and measuring 25 sec of background followed by 30 sec of ablation. The dwell time for isotopes was set to 0.02 sec with the exception of  $^{34}\text{S}$  (0.01),  $^{56}\text{Fe}$  (0.01),  $^{75}\text{As}$  (0.03),  $^{107}\text{Ag}$  (0.03), and  $^{125}\text{Te}$  (0.03), leading to a total sweep cycle time (i.e., the sum of all the individual isotope dwell and settling times; Chew et al., 2021) per analysis of 0.584 sec. For calibration, reference material NIST 610 (i.e., basaltic glass reference material issued by the National Institute

of Standards and Technology), basaltic glass GSD-1G from the United States Geological Survey, and a carbonate pellet MACS-3 (issued by the United States Geological Survey, S. A. Wilson et al., 2008) were used. Data reduction was performed using the Trace Element data reduction scheme in Iolite 4 data processing software (Paton et al., 2011; Paul et al., 2023; Woodhead et al., 2007). As an internal standard,  $^{43}\text{Ca}$  was used, with concentrations set at 40 wt% for calcite and 21.7 wt% for (ferroan) dolomite. The LOD was determined using the method of Pettke et al. (2012) based on the dwell times reported above. Using this method, average detection limits for the analyzed elements were calculated and are:  $^{24}\text{Mg}$  with  $0.38 \pm 0.20$  ppm,  $^{27}\text{Al}$  with  $0.87 \pm 0.44$  ppm,  $^{29}\text{Si}$  with  $303 \pm 163$  ppm,  $^{34}\text{S}$  with  $63 \pm 32.7$  ppm,  $^{43}\text{Ca}$  with  $585 \pm 284$  ppm,  $^{56}\text{Fe}$  with  $3.92 \pm 2.05$  ppm,  $^{59}\text{Co}$  with  $0.02 \pm 0.02$  ppm,  $^{60}\text{Ni}$  with  $0.37 \pm 0.21$  ppm,  $^{75}\text{As}$  with  $28.6 \pm 11.8$  ppm,  $^{78}\text{Se}$  with  $39.8 \pm 19.9$  ppm,  $^{107}\text{Ag}$  with  $\pm 0.09 \pm 0.08$  ppm,  $^{121}\text{Sb}$  with  $1.53 \pm 1.18$  ppm,  $^{125}\text{Te}$  with  $1.21 \pm 1.01$  ppm, and  $^{209}\text{Bi}$  with  $0.31 \pm 0.20$  ppm.

Reference materials were analyzed at the beginning and end of each session, as well as every 25 unknown samples. Figure 2, Appendix D, displays the relative differences of the analyzed elements from the accepted values for NIST 610 (i.e., accuracy after Abzalov, 2008), compiled from the GeoReM database (Jochum et al., 2005), which exceed 5% only for Mg, Al, Fe, Ag, and Sb. Precision (Jenner & Wyman, 1996) based on four analyses each of NIST 610, GSD-1G, and MACS-3 is better than 3% for all analyzed elements in NIST-610, better than 4% for all elements analyzed in GSD-1G, and better than 5 % for Mg, Co, and Ni in MACS-3. Elements Al, Si, S, Fe, As, Ag, Sb, and Bi have a precision of 8 (Fe) to 20 % (As) in MACS-3, whereas As, Se and Te did not result in analyses due to values below the limit of detection in GSD-1G (As, Se) and MACS-3 (Se, Te).

Maps of carbonate focused on metal occurrences (i.e., structurally incorporated, ore-phase inclusions, or metal oxides/oxy salts). Similar conditions to those for spot analyses were used with masses analyzed of  $^{24}\text{Mg}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ,  $^{34}\text{S}$ ,  $^{43}\text{Ca}$ ,  $^{56}\text{Fe}$ ,  $^{59}\text{Co}$ ,  $^{60}\text{Ni}$ ,  $^{75}\text{As}$ ,  $^{78}\text{Se}$ ,  $^{107}\text{Ag}$ ,  $^{121}\text{Sb}$ ,  $^{125}\text{Te}$ , and  $^{209}\text{Bi}$ . A spot size of 36  $\mu\text{m}$  was used for each line at a scan velocity of 20  $\mu\text{m}/\text{sec}$ . Lines were 35  $\mu\text{m}$  apart, allowing for a slight overlap of areas to avoid missing material. Fluence for the maps was 2.5  $\text{J}/\text{cm}^2$  at a repetition rate of 12 Hz. Backgrounds for maps were 15 s due to the absence of a signal smoothing device, resulting in faster washout times, followed by 15 s of background measurement. Reference material blocks of NIST-610 and GSD-1G were collected every 30 min, with precision similar to that reported for spot analyses.

## 2.5 Results

### 2.5.1 Mineral Chemistry (EPMA and LA-ICP-MS)

#### 2.5.1.1 EPMA

Ore phases, carbonates and metal oxides were analyzed for their major and minor element abundances using EPMA. The results are shown in Figures 6 and 7, Tables 2-6, and Appendices C-D.

*Silver phases.* Eugenite, allargentum and native silver are stoichiometrically heterogeneous, whereas the one analysis of matildite gave a composition of  $(\text{Ag}_{1.01}(\text{Bi}_{0.94}\text{Fe}_{0.01})_{\Sigma=0.95}\text{S}_{2.03}, n=1)$  (Fig. 6a, Tables 2 and 3, Appendices C and D). Eugenite ( $n=3$ ) has a mineral formula of  $(\text{Ag}_{10.95-11.13}\text{Bi}_{0.01})_{\Sigma=10.96-11.14}(\text{Hg}_{1.61-1.93}\text{Sb}_{0.00-0.10}\text{S}_{0.03-0.06})_{\Sigma=1.65-1.99}$  that reflects variation in both Ag ( $78 \pm 2.2$  wt%) and Hg ( $22.8 \pm 1.8$  wt%; Fig. 6a) and minor elements Sb, S and Bi which have maximum concentrations of 0.8 wt%, 0.1 wt% and 0.2 wt%, respectively. All other elements have concentrations near the detection limit (Table 2; Appendices C-D). Allargentum ( $n=32$ ) ranges in composition with a mineral formula of  $\text{Ag}_{0.84-0.92}\text{Sb}_{0.08-0.14}$  due to a wide range in the molecular

Ag/Sb ratio (5.8-13.7). Major element variations of Ag ( $84.7 \pm 2.9$  wt%) and Sb ( $14.5 \pm 2.8$  wt%) are common in this phase (Petruk et al., 1970; Petruk et al., 1971). Mercury and Bi can have elevated concentrations of up to 1.27 wt% and 0.67 wt%, respectively (Table 2, Appendices C-D).

Native silver (n=79) is compositionally complex (Fig. 6; Table 3, Appendices C-D) as expressed by the range in mineral formula ( $\text{Ag}_{0.91-0.97}\text{Sb}_{0.01-0.05}\text{Hg}_{0.00-0.03}$ ) $_{\Sigma=1.00}$ . To understand, if texture, assemblage and the occurrence of native silver adjacent to oxidation control composition, the analyzed grains have been sub-divided based on (1) grains that are and are not associated with metal oxides/oxy salts, (2) variation in native silver textures (i.e., massive, rosette, vein, disseminated, inclusions), and (3) the type of ore assemblage in which native silver occurs either with or without allargentum, (sulph-)arsenides and breithauptite.

Native silver in the absence of oxidized phases occurs as low-Sb (n=21) and high-Sb (n=34) varieties with mineral formulae of ( $\text{Ag}_{0.93-0.97}\text{Sb}_{0.01-0.02}\text{Hg}_{0.01}$ ) $_{\Sigma=0.95-1.00}$  and ( $\text{Ag}_{0.91-0.96}\text{Sb}_{0.03-0.04}\text{Hg}_{0.00-0.03}$ ) $_{\Sigma=0.94-1.03}$ , respectively (Figure 6a and b). Despite lower average Sb ( $1.83 \pm 0.33$  wt%) and Hg ( $1.67 \pm 0.22$  wt%) concentrations in low-Sb native silver, their average concentrations of As ( $0.07 \pm 0.08$  wt%), Co ( $0.09 \pm 0.09$  wt%), Ni ( $0.19 \pm 0.50$  wt%), Bi ( $0.19 \pm 0.07$  wt%), Fe ( $0.03 \pm 0.02$  wt%), and S ( $0.09 \pm 0.11$  wt%) are higher compared to high-Sb native silver (Fig. 6b, c, k, Table 3, Appendices C-D). Texturally, low-Sb varieties are either massive (n=16) or vein (n=5) native silver and occur with (sulph-)arsenides and breithauptite; the range in chemical composition is greatest in massive native silver occurring with (sulph-)arsenides and breithauptite (Fig. 6d-k; Appendices C-D). High-Sb native silver exhibits a wider range of textures (i.e., massive, vein, disseminated, and inclusion/interstitial). Massive, vein, and disseminated native silver occur either with allargentum or without any ore phase (sulph-arsenide, antimonide) identified in the studied

samples and show inverse trends of Ag with both Sb and Hg (Fig. 6d, e), suggesting substitution of Ag by either Hg or Sb. The average concentrations in As, Co, Ni, Fe, Bi, and S are lower in high-Sb native silver with commonly narrow 25<sup>th</sup> to 75<sup>th</sup> percentile ranges (Fig. 6c). However, many of these trace elements show statistical outliers (Fig. 6c; Table 3, Appendices C-D), emphasizing the heterogeneity not only in native silver but specifically among high-Sb native silver. These compositional ranges are independent of the textural occurrences reported for high-Sb native silver (Fig. 6d-k).

Texturally, native silver in association with metal oxides/oxy salts occurs either as vein (n=6), massive (n=10) or rosette (n=8; Fig. 5). Massive and rosettes of silver in association with oxidized phases have the composition  $[(\text{Ag}_{0.94-0.95}\text{Sb}_{0.04}\text{Hg}_{0.01})_{\Sigma=0.99-1.00}]$  and  $[(\text{Ag}_{0.94-0.95}\text{Sb}_{0.04-0.05}\text{Hg}_{0.01})_{\Sigma=0.99-1.01}]$  with average Sb concentrations of  $4.53 \pm 0.20$  wt% and  $4.73 \pm 0.30$  wt%, respectively; this is similar to high-Sb native silver not-associated with oxidized phases (Fig. 6b). Elemental concentrations of the other analyzed trace elements are similar for all three varieties (with and without the presence of oxidized phases) and close to detection limit (Fig. 6, Table 4, Appendices C-D)

Summarizing the compositional range in native silver, major (Ag), minor (Sb, Hg), and trace (As, Co, Ni, Bi, Fe, S) elements show similar ranges in native silver with and without oxidized phases. This emphasizes that oxidation around native silver is neither controlled by texture, associated ore assemblage, or composition.

*Antimonide, arsenides and (sulph-)arsenides.* Native silver occurs with different ore phases, which were analyzed to constrain their composition and minor-element content (Fig. 7, Table 4). Breithauptite is the only antimonide (n=34), with a homogeneous stoichiometry of  $\text{Ni}_{0.96-1.00}(\text{Sb}_{0.93-}$

$0.97\text{As}_{0.03-0.08}\Sigma=0.99-1.01$  (Fig. 7a, b). Among trace elements, As is most abundant ( $1.93 \pm 0.47$  wt%) and lesser concentrations of Co ( $0.11 \pm 0.20$  wt%), Bi ( $0.13 \pm 0.1$  wt%), Fe ( $0.06 \pm 0.02$  wt%), and Hg ( $0.11 \pm 0.01$  wt%) are common. Silver concentrations average  $0.06 \pm 0.02$  wt% and are locally up to 0.12 wt% (Fig. 7c; Table 4, Appendices C-D).

Arsenides are the most abundant ore phases and vary compositionally between Ni, Co and Fe end members (Fig. 7a, b). Nickel-arsenides maucherite (n=6) and nickeline (n=13) (identified with SEM and EPMA) have mineral formulae of  $(\text{Ni}_{10.03-10.19}\text{Co}_{0.90-0.97})\Sigma=7.87-7.97(\text{As}_{7.84-7.92}\text{Sb}_{0.03-0.06})\Sigma=11.00-11.10$  and  $(\text{Ni}_{0.91-0.98}\text{Co}_{0.02-0.10})\Sigma=0.98-1.02(\text{As}_{0.92-0.96}\text{Sb}_{0.03-0.06})\Sigma=0.98-1.00$ , respectively. Cobalt is a minor element with an average concentration of  $4.40 \pm 0.21$  wt% and  $2.97 \pm 1.07$  wt% in maucherite and nickeline, respectively, where it substitutes for Ni. Antimony, which substitutes for As, is more abundant in nickeline ( $4.03 \pm 1.13$  wt%) than in maucherite ( $0.45 \pm 0.15$  wt%). Both phases show trace concentrations of the other metals and S (Fig. 7b,d, f-i; Table 4, Appendices C-D) with higher concentrations of Ag in nickeline ( $0.14 \pm 0.30$  wt%) than maucherite ( $0.06 \pm 0.07$  wt%).

Cobalt arsenides are safflorite and skutterudite. Safflorite occurs as three sub-types: (1) safflorite  $[(\text{Co}_{0.97-1.01}\text{Ni}_{0.01-0.05})\Sigma=1.00-1.03(\text{As}_{1.94-1.98}\text{Sb}_{0.00-0.01})\Sigma=1.95-1.98$ ; n=25], (2) Ni-rich safflorite  $[(\text{Co}_{0.71-0.93}\text{Ni}_{0.08-0.24}\text{Fe}_{0.01-0.12})\Sigma=1.01-1.04(\text{As}_{1.94-1.98}\text{Sb}_{0.00-0.01})\Sigma=1.95-1.98$ ; n=5], and (3) Ni-S-rich safflorite  $[(\text{Co}_{0.72-0.83}\text{Ni}_{0.07-0.34}\text{Fe}_{0.01-0.15})\Sigma=1.02-1.10(\text{As}_{1.68-1.80}\text{S}_{0.12-0.18}\text{Sb}_{0.02-0.08})\Sigma=1.88-1.97$ ; n=6]. The first sub-type is the most common and contains, on average,  $0.72 \pm 0.27$  wt% Ni,  $0.42 \pm 0.19$  wt% Sb and  $0.11 \pm 0.07$  wt% Fe. The other two safflorite sub-types contain greater abundances of Ni, Sb, and Fe (Fig. 7d, f-g; Table 4, Appendices C-D). Nickel-sulphur-rich safflorite has an average S concentration of  $2.38 \pm 0.33$  wt%, in which S substitutes for As (Fig 7e, i). Despite

variations in minor elements Ni, Sb, Fe and S, the abundance of Ag is similar in safflorite, Ni-rich safflorite and Ni-S-rich safflorite with averages of  $0.05 \pm 0.04$  wt%,  $0.09 \pm 0.06$  wt% and  $0.20 \pm 0.38$  wt%, respectively (Fig. 7c-e, h; Table 4, Appendices C-D).

Four analyzed samples belong to the *solid solution* (*s.s.*) between safflorite and löllingite (Radcliffe & Berry, 1968) and have the formula of  $(\text{Co}_{0.24-0.59}\text{Fe}_{0.28-0.55}\text{Ni}_{0.01-0.23})_{\Sigma=1.01-1.03}(\text{As}_{1.93-1.97}\text{S}_{0.01-0.04})_{\Sigma=1.97-1.99}$ . Compared to the other arsenides, minor and trace elements, Ni ( $3.28 \pm 2.92$  wt%) and S ( $0.30 \pm 0.21$  wt%) concentrations are the highest, whereas the average Ag ( $0.03 \pm 0.01$  wt%) concentration. The only analyzed löllingite grain  $[(\text{Fe}_{0.94}\text{Co}_{0.06}\text{Ni}_{0.03})_{\Sigma=1.03}(\text{As}_{1.91}\text{S}_{0.05})_{\Sigma=1.96}]$  has 1.90 wt% Co, 1.00 wt% Ni and 0.76 wt% S, whereas Ag is close to the detection limit with 0.03 wt% (Table 4, Appendices C-D).

The second Co-arsenide phase, skutterudite [ $n=12$ ] with a mineral formula of  $(\text{Co}_{0.88-1.01}\text{Fe}_{0.01-0.08}\text{Ni}_{0.00-0.06})_{\Sigma=1.02-1.04}\text{As}_{2.95-2.97}$ , shows local enrichment in the minor elements Ni ( $0.61 \pm 0.41$  wt%) and Fe ( $0.70 \pm 0.51$  wt%); Ag concentration averages  $0.06 \pm 0.04$  wt%.

The sulph-arsenides are cobaltite  $[(\text{Co}_{0.89-01.00}\text{Ni}_{0.02-0.13}\text{Fe}_{0.00-0.04})_{\Sigma=0.97-1.03}\text{As}_{0.96-1.02}\text{S}_{0.95-1.03}; n=20]$  or cobaltite-gersdorffite *s.s.*  $[(\text{Co}_{0.73-0.89}\text{Ni}_{0.10-0.23}\text{Fe}_{0.00-0.05})_{\Sigma=1.00-1.02}\text{As}_{1.01-1.05}\text{S}_{0.92-0.98}; n=6]$  (Klemm, 1965; Hem, 2006). In both minerals, Ni (cobaltite:  $2.37 \pm 1.16$  wt%; cobaltite-gersdorffite *s.s.*:  $4.88 \pm 1.56$  wt%) and Fe (cobaltite:  $0.25 \pm 0.32$  wt%; cobaltite-gersdorffite *s.s.*:  $0.92 \pm 0.52$  wt%) substitute for Co (Fig. 7f, g). Most grains contain less than 0.1 wt% Sb and Ag (Fig. 7e; Appendices C-D). However, individual grains of cobaltite and cobaltite-gersdorffite *s.s.* have Sb and Ag concentrations exceeding 0.1 wt%; in cobaltite and cobaltite-gersdorffite *s.s.* Ag concentrations reach maximum values of 0.93 wt% and 1.44 wt%, respectively (Fig. 7c, Table 4, Appendices C-D). Both minerals are positively correlated (Appendices C-D).

*Carbonates.* Carbonates are the dominant gangue minerals (Figs. 3, 5). These are dolomite [n=9], ferroan dolomite [n=28], and calcite [n=5] (identified with SEM and EPMA Fig. 8a, Table 5, Appendices C-D). All three phases are stoichiometrically homogeneous with mineral formulae of  $\text{Ca}_{0.95-1.12}(\text{Mg}_{0.73-0.97}\text{Fe}_{0.05-0.16}\text{Mn}_{0.01-0.05})_{\Sigma=0.97-1.03}\text{C}_{2.00-2.02}\text{O}_6$ ,  $\text{Ca}_{0.99-1.08}(\text{Mg}_{0.51-0.75}\text{Fe}_{0.20-0.37}\text{Mn}_{0.04-0.11})_{\Sigma=0.92-0.99}\text{C}_{2.00-2.02}\text{O}_6$ , and  $\text{Ca}_{1.00-1.01}\text{C}_{2.00-2.02}\text{O}_3$  for dolomite, ferroan dolomite and calcite, respectively. Manganese oxide is the most common trace element in dolomite and ferroan dolomite with  $0.86 \pm 0.45$  wt% and  $2.69 \pm 0.60$  wt%, respectively.

*Oxides.* Metal oxide results are compiled in Table 6, Figure 9, and Appendices C-D. Three different metal oxides were identified using EPMA: (1) arsenian valentinite  $[(\text{Sb}_{1.44-1.79}\text{As}_{0.13-0.47})_{\Sigma=1.91-1.92}\text{O}_3; n=4]$ , (2) stibioclaudeite  $[\text{As}_{0.92-1.09}\text{Sb}_{10.84-1.01}\text{O}_3; n=10]$ , and (3) Sb-rich annabergite  $[(\text{Ni}_{3.15-3.60}\text{Co}_{0.02-0.23}\text{Fe}_{0.00-0.20})_{\Sigma=3.40-3.82}(\text{As}_{2.00-2.46}\text{Sb}_{0.08-0.51})_{\Sigma=2.37-2.62}\text{O}_8 \times 8\text{H}_2\text{O}; n=11]$ . All three phases are heterogeneous in their major element composition with Sb-rich annabergite showing excess on both metal sites (Fig. 9a). Arsenic and Sb are enriched in valentinite ( $2.59 \pm 3.63$  wt% As) and annabergite ( $4.14 \pm 2.69$  wt% Sb), respectively. Since X-ray diffraction was not performed, it cannot be excluded that all three phases are intergrown with other phases. Among trace elements, Ag is close to the detection limit in both arsenian valentinite and stibioclaudeite with averages of  $0.02 \pm 0.03$  wt% and  $0.03 \pm 0.03$  wt%, respectively. In contrast, Sb-rich annabergite has a relatively high Ag concentration with an average of  $0.64 \pm 1.21$  wt% (Table 6). The presence of Ca, Mg and Fe as trace components in the analyzed metal oxides is likely an overlap with host carbonates due to the small grain size and weak polishing (Fig. 9b, Table 6).

### 2.5.1.2 LA-ICP-MS

Trace-element composition of the three carbonates, with a focus on metal(loid)s, are plotted in Figures 8 and 10, summarized in Table 7, and detailed in Appendices C-D.

Images, concentration, and laser spectra suggest that metal(loid)s are either structurally incorporated, occur as micro-inclusions in various ore phases (i.e., metal inclusions), or result from oxidation of primary ore phases (i.e., metal oxidation) (Figs. 3d, k, 5, 10). These different types of occurrences are reported for all three carbonate phases (Fig. 8d-i). Elemental maps of dolomite (Fig. 10) highlight that all three metal(loid) occurrences are common and that Co, Ni, and Sb (Fig. 9c, e, g, j, l, n) occur together regardless of occurrence type. Both Ag and Bi can occur with Al (e.g., clays) along cracks in carbonates (Fig. 10a, b, d, f), as structurally incorporated metal(loid) (Fig. 10d, f, k, m) or with other metals in oxidized veinlets (Fig. 10h, k, m).

Concentration ranges of metal(loid)s among the different carbonate types can be plotted individually or as the sum (i.e., Co, Ni, As, Se, Ag, Sb, Te, Bi) with S but without Fe (i.e. Sum2 in Table 7, Appendices C-D). Among the three types, structurally incorporated metal(loid)s have the lowest average concentration ( $379 \pm 205$  ppm), whereas inclusions of ore metals (i.e., breithauptite, (sulph-)arsenides) have the highest average concentrations ( $46.3 \pm 65.6$  wt%; Fig. 8c, Table 7, Appendices C-D). This general trend is displayed in a positive correlation between Ag–Sb, Ag–Ni, Ag–As and Ag–Co (Fig. 7d-g); however, trends within the three metal occurrences are more ambiguous (e.g., Ag vs As, Fig. 7f). The positive correlations that occur between As–Sb, Sb–Ni, As–Co, and Sb–Co among all three carbonate minerals (Fig. 7h-k) reflect (1) the similar geochemical character of these elements, and (2) the presence of different ore phases as metal inclusions (e.g., (sulph-)arsenides, breithauptite) and their oxidized counterparts within carbonates. Within all three minerals the highest measured metal(loid) concentrations, other than

Fe, are As and Sb (Fig. 7c); this mirrors the occurrence of arsenides and breithauptite as predominant, non-silver ore phases (Fig. 3). Concentrations of Ag vary widely within each type of carbonate mineral with average values of  $23.31 \pm 43.74$  ppm,  $25.2 \pm 26.0$  wt%, and  $315 \pm 816$  ppm for structurally incorporated, metal inclusion and metal oxidation occurrences, respectively (Table 7, Appendices C-D).

### 2.5.2 Nanoscale (TEM)

Native silver occurs in five different host phases: dolomite, As-Sb oxide, erythrite, and Fe-rich clay and organic matter, as well as along four distinct mineral interfaces.

#### *Silver nanoparticles hosted dolomite*

Silver occurs in two distinct modes in dolomite: as crosscutting nano- to micrometre-sized veinlets and as finely distributed Ag NPs (Fig. S1a-d). The silver veinlets are commonly rimmed by stibioclaudeite ( $\text{AsSbO}_3$ ), which forms thin partial to complete rims along the silver-dolomite interface (Fig. S1c-d). The Ag NP are distributed throughout dolomite and range in size from 2 to 25 nm (Fig. 11a-d). Silver occurs predominantly as individual particles but also form aggregates in which the lattice fringes of (111) planes show variable orientations (Fig. 11c-d, 13c). In some areas, Ag NPs are concentrated along dolomite growth features, oriented parallel to its growth planes (red dashed line in Figure 11a).

#### *Silver nanoparticles in AsSb-Oxide*

Ag NPs also occur along breithauptite ( $\text{NiSb}$ ) and As-Sb oxide interfaces, and within the As-Sb oxide matrix (Fig. 11e-h, S3). Surface textures of the breithauptite and the porous character of the breithauptite-As-Sb oxide interface are consistent with the replacement of breithauptite by As-Sb oxide (Fig. 11e-f). The As-Sb oxide has a variable Sb:As ratio, indicating a solid solution between Sb-rich and As-rich end members. The phase occurs in either the monoclinic claudeite

structure ( $\text{As}_2\text{O}_3$ ), isostructural with stibioclaudeite ( $\text{AsSbO}_3$ ), or the isometric cubic arsenolite structure ( $\text{As}_2\text{O}_3$ ), isostructural with senarmontite ( $\text{Sb}_2\text{O}_3$ ). SAED pattern indicates a mixture of phases from different end members. Ag NPs occur predominantly within the As-Sb oxide matrix and are also present on the surface and along the edges of breithauptite (Fig. S3). The As-Sb oxide displays distinct chemical zones enriched in either Sb or Ni (inset of Fig. 11h-h1), and Ag NPs are more abundant in Sb-enriched zones.

#### *Silver nanoparticles in erythrite*

Ag NPs also occur within erythrite ( $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ ); Fig. 11i-j, S3). The spatial distribution of Ag NPs varies from randomly scattered within the matrix (Fig. 11i1) to aligned with the erythrite layering (Fig. 11i2-3). Individual Ag NPs range in size from 5 to 40 nm. Upon aggregation, Ag NPs form either rounded aggregates reaching up to 75 nm in diameter or layered features with colloform textures comparable to those observed in sphalerite and malachite (Fig. 11i4). The layered aggregates are enriched in antimony (Sb) and coated by sulphur (S) (Fig. S3).

#### *Silver nanoparticles in a clay mineral and organic matter matrix*

Ag NPs also occur within a matrix of Fe-rich 2:1 clay mineral and organic matter (OM) (Fig. 11-k-l, S3). Their average diameter, 2.5 to 7.5 nm, is smaller than that recorded for the other host phases. The d-spacing of the Fe-rich clay is approximately 11.25 Å, consistent with a TOT-layered (2:1) clay structure. The OM contains detectable concentrations of Ca, Fe, and As. Furthermore, a secondary mineral, Bi-Fe-bearing As-Sb oxide is present on the clay surface and also hosts Ag NPs.

#### *Silver nanoparticles at interfaces*

##### *Dolomite-silver NP-antimonate interface*

The interface between porous dolomite and As-Sb oxide (most likely stibioclaudeite,  $\text{AsSbO}_3$ ) is partially disrupted by material removal during ion milling (Figs. 9a,h, 12a-b, S3). Where the interface is preserved, trails of Ag NPs extend from the dolomite into the stibioclaudeite matrix, running parallel to the interface. The spacing and continuity of these trails decrease with increasing distance from the interface. Individual Ag NPs within the trails are closely spaced and form features less than 12 nm in diameter, consistent with the permeable character of both stibioclaudeite and dolomite.

#### *Silver-cobaltite interface*

Figure 11c-d shows a high-resolution STEM image and STEM-EDS elemental distribution maps of Ag NPs arranged in a trail and a sulpharsenide phase, with an intermediate phase at their contact (sample M39127). The sulpharsenide is most likely cobaltite ( $\text{CoAsS}$ ), which exhibits corrosion features and a gradational boundary with the intermediate phase marked by compositional mixing and heterogeneity (Fig. 12c, S3). The intermediate phase occupies the boundary between the silver-dominant and an Ag NP- and Sb-bearing sulpharsenide (Fig. 12d). A texturally similar antimony-bearing phase along the silver-cobaltite interface is also observed at the microscale (samples C31018b and M39127), where silver veinlets are rimmed by an antimonate phase (Fig. 5m-t); and silver specks are in contact with cobaltite in the oxidized zone (Fig. 5a-h).

#### *Sb Arsenide-silver NP-dolomite interface*

Ag NPs occur at the interface between Sb-arsenide (suggested to be stibarsen based on STEM\_EDS) and dolomite (Fig. 12e-f). The elemental maps show four compositional zones (labelled f1 through f4 in Figure 12f, S4). Cobalt-bearing Sb arsenide mineral ( $\text{SbAs}$ ) (f1) contains traces of Ni and S (less than 5 at%), and transitions to As-Sb oxide ( $\text{AsSbO}_{1/2}$ ) over 1 to 2  $\mu\text{m}$  (f2),

reflecting progressive oxidation. At the contact zone between slightly oxidized arsenide and dolomite (f3), there is a marked increase in Ag NP abundance; these areas are enriched in Sb relative to the surrounding zones, with a bulk composition trending toward  $\text{AsSb}_2\text{O}$ . Dolomite occupies the lower left of the field of view (f4).

#### *Annabergite-silver NPs-arsenide interface*

Figure 11g-h shows an interface between six compositionally distinct zones (labelled h1 - h6 in Figure 11h, with their EDS quantification in Fig. S4). A Ni-hydrous-arsenate mineral ( $\text{NiAsO}_2$  (h1) with minor Sb (~ 6 at%) is probably annabergite  $\text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$  (based on STEM\_EDS data, Fig. S4). A Co-arsenide phase (Co : As 1:1) with minor S (~ 8 at%) corresponding most likely to langisite  $[(\text{CoNi})(\text{AsSb})]$  (h2). Between the latter two phases occurs, a silver-enriched zone (~ 50 at% Ag; h3) containing a mixture of Co, Ni, Sb, As, and O. An Ag-rich CoAs phase forms at a 1:1:1 Ag:Co:As ratio (h4) and is referred as Ag-bearing langisite. The cracks and fractures present in the arsenide (~langisite) zones are enriched in Sb and exhibit a mixed alteration rim (h5) comprising intergrown Co-As 1:1 and Ni-Sb phases (1:1 ratio between the elements) that extend upward along structural openings; these zones contain trace to minor Ag. An As-Sb oxide phase of variable composition ( $\text{As}_x\text{Sb}_y\text{O}_z$ ) occupies zone h6 and contains trace to minor Fe, Ni, and Ag; this phase is compositionally similar to the antimonate-rich material observed in zone leading to h4.

## **2.6 Discussion**

The Cobalt deposit offers a rare opportunity to examine the complex distribution of Ag in a five-element vein system, from primary hydrothermal deposition to supergene weathering processes at the nanoscale. Silver NPs play a central role in secondary silver enrichment: their nucleation, transport, and aggregation through crystal growth by particle attachment (CPA)

produce the microscale silver textures that define the supergene areas. The results from this study (microscopy, geochemical data) provide information on: (1) the role of hypogene phases for secondary Ag NP formation based on ore assemblage, textures and composition; (2) the pathways resulting in Ag NP formation observed using TEM; and (3) the different nanoparticle attachment mechanisms of Ag NPs with respect to different associations.

### **2.6.1 Role of hypogene phases in supergene processes**

The mineralogy of the Cobalt embayment has been intensively studied with landmark papers on (sulph-)arsenide and antimonide phases (Petruk, Harris, Cabri, et al., 1971), silver phases (Petruk, Harris, & Stewart, 1971), and gangue minerals (Jambor, 1971a) detailed the complexity of the non-sulphide ore and gangue assemblage. This study highlights this complexity by detailing the major-, minor-, and trace-element composition of the identified ore phases. Though, the purpose of this study has not been to constrain paragenesis of ore and gangue phases or to provide an alternative genesis model to previous studies on five element veins (e.g., Burisch et al., 2017; Kissin, 1992; Markl et al., 2016; D. Marshall et al., 1993; Petruk, 1971a; Rush, 2019) it is clear the silver phases were deposited pre-, syn- and post-(sulph-)arsenides and antimonide. This is evident in the different native silver textures and assemblages, including massive native silver and native silver veins with (sulph-)arsenides and breithauptite, replacement of native silver by (sulph-)arsenides and/or breithauptite, or native silver in cores and rims of rosettes (Figs. 3 and 4). Native silver phases are compositionally complex and stoichiometrically heterogeneous (Fig. 6), and trace Ag is a common component of (sulph-)arsenides, antimonide and carbonate gangue (Figs. 7, 8). This, together with textural evidence, supports the conclusion that native silver deposition occurred during various stages of hypogene mineralization. Further, the occurrence of Ag, As, Co, Ni, and Sb within carbonates at different concentrations (Fig. 8) indicates that

carbonate gangue formed with metal-bearing fluids. Carbonates in other mineral systems in which carbonates are either a metal source (e.g., Mississippi Valley type) or hydrothermal in origin (e.g., Irish-type Zn-Pb sedimentary deposits) can have lattice-bound metal concentrations including Ag, As, Co and Ni of several ppm (e.g., Graybeal & Vikre, 2010; Leach et al., 2010; Paradis et al., 2007; Wilkinson, 2014). This is consistent with metal concentrations reported in this study and that higher metal concentrations (100's to 1000's ppm) are probably inclusions of ore phases such as native silver, breithauptite and arsenides as well as the oxidized products of arsenides (Figs. 8 and 10).

The occurrence of metal oxides such as erythrite, valentinite, stibioclaudeite or annabergite has been widely reported from the Cobalt embayment and often have been related to environmental challenges (e.g., (Boyle & Dass, 1971a; Ziwa et al., 2025)); however, their relation to the occurrence of secondary native silver has not yet been identified. This study shows that metal-oxides stibioclaudeite, arsenian valentinite, Sb-rich annabergite and/or erythrite are common adjacent to massive, vein and rosette native silver associated with and without (sulph-)arsenides and breithauptite as well as in partially oxidized skutterudite replacing massive native silver (Fig. 5). These metal oxides are stoichiometrically heterogeneous and contain relatively large quantities of Ag and Co and can be significantly enriched in As and Sb (Fig. 10). Within these metal oxides, nano- to micro-scale, anhedral, native silver without elevated metal content is common (Figs. 3, 5, 11c-j). This secondary native silver is compositionally different than the hypogene. Secondary native silver, without elevated Sb and Hg contents, forms via the oxidation of original (sulph-)arsenides and breithauptite under various pH conditions, resulting in the release of Ag. Studies of water chemistry from wells, springs, and diamond drill holes in the Precambrian rocks of the Cobalt area indicate pH values ranging from 4 to 8.8 (Boyle & Dass, 1971a), consistent

with a progression from acidic oxidizing conditions dissolving (sulph-)arsenide phases to weakly alkaline conditions buffered by carbonate gangue. Hence, oxidation of (sulph-)arsenides and mobilization and precipitation of Ag may have either occurred under acidic or weakly alkaline conditions. Under each condition, Ag NP formation follows either a coupled or decoupled pathway, as defined by Schindler et al. (2024), depending on whether Ag release is directly tied to the dissolution of the parent phase or occurs independently through fluid transport. Each proposed pathway is explained in detail below using TEM evidence.

Although oxidation dominantly affects safflorite and skutterudite and lesser breithauptite and cobaltite (Fig. 5), the oxidation of hypogene ore phases is less a function of trace element abundances and rather controlled by grain boundaries and porosity or permeability in carbonates that both provide pathways for oxidized acidic to alkaline meteoric fluids circulating at low water/rock ratios through the mineralized veins. Native silver, breithauptite and (sulph-) arsenides have uniform minor and trace element chemistry, including redox-sensitive elements (e.g., Fe), when oxidation occurs near minerals. Rather, the composition is similar in primary ore phases adjacent to oxidation and unrelated to oxidized areas (Fig. 6). However, oxidation is common where carbonates are porous or permeable or along contacts of native silver veins within/crosscutting carbonates (Fig. 5). Further, metal oxides are common as thin veinlets or irregular patches in carbonates (Fig. 10), which is the result of meteoric fluids oxidizing original ore phases and depositing metal oxides in cracks and open spaces within carbonates or *in situ* oxidation of original metal inclusion present in carbonates, respectively.

The hypogene phases studied at the Cobalt embayment are important precursors to both the formation of metal oxides and the release of  $\text{Ag}^+$  those forms disseminated, high-purity native silver on the nano- and micro-scale during supergene processes. Also, native silver may not

oxidize; the occurrence of Ag as a trace component in hypogene (sulph-)arsenides and carbonates is associated with the formation of native silver under hypogene conditions. Without trace Ag in these hypogene phases, the supergene processes would have been less effective at forming secondary native silver as Ag NPs.

### **2.6.2 Formation pathways of nanomaterials**

Nanomaterials (NMs) such as Ag nanoparticles can form through abiotic and biotic formation pathways (Schindler et al., 2024). The abiotic pathways can be divided into processes in which the formation of NMs is coupled to or decoupled from weathering/alteration of the parent materials. Whether a formation pathway of NMs is coupled or decoupled from a weathering process depends on the relative rates of dissolution and ionic diffusion away from the reacting surface (Ruiz-Agudo et al., 2014).

In the coupled pathway, dissolution of the parent phase is slow relative to the precipitation kinetics of the product, causing local supersaturation within the thin boundary layer at the mineral surface and triggering immediate precipitation of a new, more stable phase directly at the interface (A. Putnis & Putnis, 2007; C. V. Putnis & Ruiz-Agudo, 2021). Molar volume differences between parent and product phases generate porosity in the product layer, maintaining fluid access to the reaction front and sustaining continued replacement (Pollok et al., 2011; A. Putnis, 2002). A similar formation pathway of nanomaterials can occur during supergene enrichments of Au. Here, low-temperature alteration of Au-bearing pyrite or hydrothermal alteration of Au-bearing As-rich pyrite results in the formation Au NPs alongside hematite and polycrystalline pyrite-arsenopyrite matrices, respectively (Hastie et al., 2021; Palenik et al., 2004). This is also in accord with AFM studies, also suggest that coupled dissolution and Au NP precipitation occur in the presence of arsenate- and antimonate-bearing solutions (Renard et al., 2015, 2018). Porosity is a defining

feature in a coupled interfacial dissolution-precipitation process. It develops in the secondary phase to maintain fluid access to the reaction front and sustain continued replacement (Pollok et al., 2011; A. Putnis, 2002). This porosity provides nucleation sites for heterogeneous mineral growth, but pore geometry also exerts an independent control: a reduction in pore diameter promotes the formation of inner-sphere complexes on nanopore surfaces by lowering the surface acidity constants of functional groups, thereby facilitating the accumulation of mineral constituents within the pore (Wang et al., 2003). Conversely, decreasing pore size increases material solubility by constraining particle size within pore spaces, as described by the Pore Controlled Solubility model (Stack, 2015).

In the decoupled pathway, diffusion outpaces dissolution, dispersing ionic species into the bulk solution before local supersaturation is reached, thereby causing product precipitation to occur remotely from the dissolving surface along sharp geochemical gradients elsewhere in the system (A. Putnis, 2002; Ruiz-Agudo et al., 2014).

Coupled and decoupled pathways can occur under acidic and alkaline conditions. Under alkaline pH conditions, reactions can deviate significantly from bulk thermodynamic predictions because the physicochemical properties of the thin interfacial boundary layer, including its dielectric constant, differ from those of bulk water, altering ion solvation energies and reaction thermodynamics at the nanoscale (Fumagalli et al., 2018; Gonella et al., 2021). Under acidic oxidizing solution, the different elements are more mobile and thus are easily dispersed (Boyle & Dass, 1971a).

### 2.6.3 Pathways of nanomaterial formation during supergene processes in the Cobalt ore assemblage

In the Cobalt area, supergene processes in veins reflect the action of meteoric waters that carry dissolved oxygen and atmospheric CO<sub>2</sub> (Boyle & Dass, 1971b). The Eh and pH of the fluid, together with the abundance of carbonate in the ore and the resulting concentrations of Ca<sup>2+</sup> and Mg<sup>2+</sup> in solution, control the migration, concentration, and dispersion of ore and gangue elements (Boyle & Dass, 1971b). Each element's mobility is governed by its redox potential relative to that of the local environment, which in turn determines where and how Ag is released and reprecipitated.

In the Cobalt area Ag NPs occur: (1) with oxidized ore phases (arsenates/antimonates), (2) within carbonates, and (3) with Fe-rich clay and organic matter (OM) (Figs. 5, 11, 12). These occurrences indicate that Ag is released during supergene processes in the Cobalt ore assemblage, which involved the oxidation of hypogene Ag-bearing arsenide, sulph-arsenide, and antimonide phases by meteoric fluids (Fig. 5). Upon release, Ag can take either an ionic form (Ag<sup>+</sup>) or precipitate directly as Ag<sup>0</sup>, depending on whether the formation pathway is decoupled or coupled from the dissolution of the parent phase, respectively (Schindler et al., 2024).

The formation of Ag NPs during a coupled dissolution-precipitation process occurs directly at the interface between the dissolving hypogene parent phase and the secondary arsenate/antimonate daughters and does not require an intermediate ionic step. This process was favoured under weakly alkaline conditions, where the dissolution is commonly slower than under acidic conditions. These conditions most likely occur during the formation of Ag NPs at the contacts between arsenides and arsenates, and between antimonides and antimonates (Figs. 11e, i, 12e, g). During the decoupled pathway, Ag was most likely released as Ag<sup>+</sup> species into the bulk

fluid due to its high acidity and redox potential. The subsequent precipitation of Ag NPs occurs upon encountering sharp Eh or pH gradients, such as those associated with Fe-rich clay and OM elsewhere in the system. The formation of Ag NPs in carbonates could have followed both coupled and decoupled pathways. Arsenide- and antimonide-inclusions within the carbonates oxidized under alkaline conditions, leading to the precipitation of Ag NPs in the carbonates' pore spaces (see below). Acidic solutions transporting  $\text{Ag}^+$  ions were neutralized upon carbonate dissolution, leading to the precipitation of Ag NPs.

#### ***2.6.3.1 The formation of Ag NPs under weakly alkaline conditions via coupled dissolution***

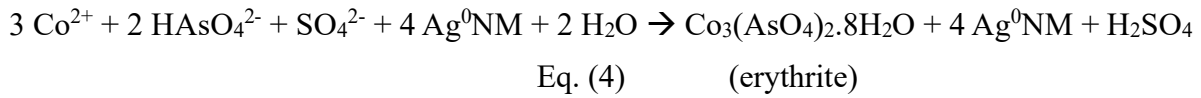
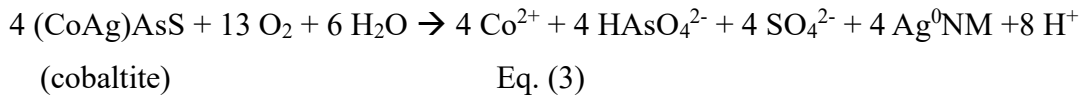
Lower redox potentials under weakly alkaline pH conditions (buffered by carbonate) favoured the formation of Ag NPs along the parent-daughter interfaces (Fig. 12e-h). The extent of this carbonate-buffered pathway depends on the available carbonate and degree of fluid-rock interaction (Ziwa et al., 2025). Here, carbonate dissolution produces a locally alkaline interfacial solution (Ca and Mg components can buffer the fluid to a pH of approximately 7–8.3) that destabilizes  $\text{Ag}^+$  complexes and lowers the reduction potential of the  $\text{Ag}^+/\text{Ag}^0$  couple according to the Nernst equation:

$$E = E^0 - (RT/nF)\ln[\text{Ag}^+] \quad \text{Eq. (2)}$$

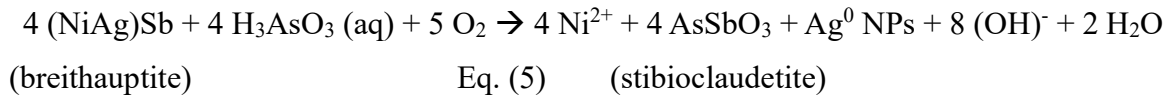
The destabilization and lower redox potential effectively shifts the system across the  $\text{Ag}^0$  stability field and promotes direct precipitation of  $\text{Ag}^0$  NPs (Sangameshwar & Barnes, 1983; Sato, 1992). An oxidizing fluid in equilibrium with Ca-carbonate at a pH of approximately 7.8 carries a redox potential of  $E^0 = 0.40$  V; and because the standard redox potential of Ag ( $E^0 = 0.80$  V) exceeds this value, carbonate-buffered, weakly alkaline conditions favour Ag NP formation (drives the precipitation of Ag NPs directly at the mineral-fluid interface).

The formation of Ag NPs via a coupled dissolution-precipitation process is documented at two scales. At the microscale, Ag aggregates where skutterudite and cobaltite weather to erythrite (Fig. 5i-l). At the nanoscale, Ag NPs in erythrite occur in close proximity to cobaltite (Fig. 11i-j, S3), Ag NPs within As-Sb oxide occur in contact with or very close to breithauptite (Fig. 11e-g), and Ag nanomaterials (NMs) are present at the interface between hypogene phases (arsenides, compositionally similar to langisite, and stibarsen based on STEM-EDS analysis) and their oxidized counterparts (annabergite and dolomite) (Fig. 12e-h).

Under oxidizing conditions at a pH of approximately 7.6-8.8, the dominant arsenic aqueous species is  $\text{HAsO}_4^{2-}$  (Charykova & Krivovichev, 2020). Hence, the oxidation of (sulph-)arsenide and the formation of arsenates under these Eh-pH conditions may be formulated as:



The oxidation of breithauptite to As-Sb oxide (stibioclaudeite), with  $\text{H}_3\text{AsO}_3$  as the  $\text{As}^{3+}$  source at neutral to weakly alkaline pH, may be formulated as:



The composition of the daughter phase depends on the amount of  $\text{As}^{3+}$  available: where  $\text{As}^{3+}$  is limited, the product becomes chemically similar to senarmontite or valentinite. Diffraction analysis of the daughter phase shows mixing of multiple elements consistent with intermediate oxidation products (Fig. 11g-h, S3). TEM observations show abundant Ag NPs in the As-Sb oxide proximal to the breithauptite, consistent with coupled NP formation during oxide precipitation. A

comparable process governs the oxidation of Ni-, Co-arsenides (compositionally similar to stibarsen and langisite as seen in Fig. S4 [Appendix A]), where Ag NMs formed at their interface with carbonate (Fig. 12e-f) and a phase with a 1:1:1 Ag:Co:As ratio (Figs. 12g-h, h5).

The occurrence of Ag NPs in carbonate reflects carbonate buffering of the fluid and the redox behaviour of Ag. EMPA analysis and LA-ICP-MS mapping of the carbonate reveals compositional heterogeneity of Mg and Fe (Figs. 8, 10). Ag is structurally bound in the dolomite, as shown by its consistent trace concentrations and abundant Ag particles that are associated with AsSb-oxides (Figs. 8–9, 12a-b; Appendices C-D). The latter is based on how at the microscale, low-detection-limit imaging (LA-ICP-MS) and elemental correlation plots (Sb vs. As, As vs. Ag, and Sb vs. Ag) show a positive covariation among Ag, As, and Sb. This links the Ag NPs to AsSb-oxide formed during the oxidation (weathering) of the hypogene phase constrained in the carbonate (Figs. 8–9; Appendices A, C-D). Further reinforcing our understanding of the association of Ag NPs and AsSb-oxides. TEM imaging in Figure 12a-b shows Ag NP trails at the contact between As-Sb oxide and dolomite, providing strong evidence for the association of Ag NPs, As-Sb oxide, and carbonate. Here, carbonate buffering lowered the redox potential below the  $\text{Ag}^+/\text{Ag}^0$  stability boundary, promoting Ag NP formation upon either oxidation of the hypogene phase inclusions or influx of  $\text{Ag}^+$ -bearing solutions.

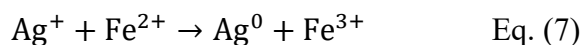
#### ***2.6.3.2 The reduction of $\text{Ag}^+$ species released under acidic conditions***

Acidic-oxidizing pH conditions most likely favoured the release and mobilization of  $\text{Ag}^+$  species in the system. This pathway is less common than the coupled counterpart but is suggested by the presence of Ag NPs, albeit to a lesser degree, on clays, OM and perhaps within and along the carbonates grain boundaries.

The oxidation of (sulph-)arsenide generates acidity (Eq. 3). Where little to no carbonate is available to buffer the fluid, pH can drop below 4 (Boyle, 1971), raising the redox potential to approximately  $E_0 = 1.23$  V. At this potential, As, Fe, Co, and Ni become highly mobile and are easily removed from the oxidized zone (Boyle, 1971). Ag can also remain oxidized upon release from the parent phases ( $E_0 = +0.80$  V, which means that  $\text{Ag}^0$  is stable only under sufficiently reducing conditions; Levard et al., 2012; Sillitoe, 2009).



The formation of Ag NPs along sharp redox gradients may have occurred, for example, at the surface of  $\text{Fe}^{2+}$ -bearing clay minerals and reduced functional groups in organic matter (OM). Field and experimental studies show that the high standard redox potential of Ag limits its ability to form laterally extensive or volumetrically significant supergene enrichment zones (Cooke, 1913; Ravicz, 1915; Sillitoe, 2009; Anderson, 2016). Secondary silver is thought to remain spatially restricted, becoming immobilized through interaction with Fe-bearing clays (Anderson, 2016), consistent with abiotic reduction of  $\text{Ag}^+$  by structural  $\text{Fe}^{2+}$ :



The high surface area and constant negative charge of clay minerals promote  $\text{Ag}^+$  adsorption and intercalation from solution (Boyle & Dass, 1971a; Fig. 11k-l, S3). Clay has been previously documented in the Cobalt ore deposit, and field observations at the Keeley Mine record clay-rich assemblages containing wire, platy, spongy, and stalactitic silver, chlorite, argentite, and disintegrated arsenides (Bell, 1923; Walker, 1924). These macroscale silver textures represent an aggregated product of Ag NPs formed on clay surfaces, consistent with the observed nanoscale associations.

A comparable process explains the association of Ag NPs with OM:  $\text{Ag}^+$ -bearing species diffuse into OM and are reduced by organic functional groups, producing Ag NPs, as demonstrated for both Ag and Cu systems (Akbari Alavijeh et al., 2023; Fulda et al., 2013; Lovering, 1927; Mantha et al., 2019).

Organic matter (OM) reported from the Cobalt embayment and in this study may originate from Huronian sediment (Jambor, 1971b). The  $\delta^{13}\text{C}$  values in the veins range from 2.78‰ to 16.78‰, reflecting variable interactions between hydrothermal fluids and OM across the Cobalt embayment (Potter & Taylor, 2010). Fluid inclusion studies further indicate a mixed carbonic fluid of  $\text{H}_2\text{O}-\text{CO}_2$  and  $\text{CH}_4-\text{CO}_2 \pm \text{N}_2$  (Rush, 2019), consistent with the presence of OM in the system.

The linear arrangement of Ag NPs in dolomite (Figs. 12a-b, 13c) compared to antimonide and arsenide inclusions do not exhibit this feature clearly indicate that the Ag NPs formed via a decoupled pathway. However, it is unknown whether the Ag originates from within the dolomite or was initially transported by acidic solutions.

In summary, the evidence shows that Ag enrichment at the Cobalt deposit operates through multiple concurrent pathways, all driven by the oxidation of hypogene arsenide and antimonide phases by meteoric fluids (Fig. 14, Table. 8). Under weakly alkaline, carbonate-buffered conditions, Ag is released directly as  $\text{Ag}^0$  NPs through a coupled pathway at the dissolution front (weathering of the ore phases) and constitutes the dominant process responsible for Ag NPs formation (Fig. 14, Table. 8). Minor processes occur under acidic conditions, in which Ag is mobilized as  $\text{Ag}^+$  via a decoupled pathway, with Fe-bearing clay minerals, OM, and perhaps carbonates serving as reactive surfaces that capture and immobilize Ag NPs regardless of proximity to the parent phase (Fig. 14, Table. 8). In all cases, Ag NP aggregation due to CPA produces submicron-scale, disseminated silver particles and nanowires in AsSb-oxide, carbonates,

or associated with clay/OM, which characterize the supergene processes resulting in oxidation in some samples (Fig. 14, Table. 8). The spatial restriction (occurrence in the oxidized zone, and association) governed by local Eh, pH, and substrate availability accounts for the patchy nature of secondary silver at Cobalt, highlights the critical role of induced liberation of Ag originally bound as trace phase in (sulph-)arsenide, and the importance of nanoscale processes in their characterization.

#### **2.6.4 Ag NPs characteristics at the nanoscale**

The size distributions, morphologies, and crystallographic orientations of the Ag NPs, and their associations with different host phases, provide insight into the mechanisms by which they nucleated, grew, and aggregated.

##### ***2.6.4.1 Characteristic and size distribution of Ag NPs by association***

The study of the characteristics of the Ag NPs comprises determining the size distribution of the NPs and applying CPA models (OA, NOA), which provide information on their formation and aggregation conditions. Size distribution constrains the nucleation history: a narrow, unimodal distribution indicates a single nucleation event and controlled growth, consistent with OA under stable interfacial conditions, while a broad or bimodal distribution points to multiple nucleation events, variable growth environments, or a mix of coupled and decoupled formation pathways (Thanh et al., 2014). OA is identified in the samples by continuous lattice fringes across particle boundaries, twin planes at contact zones, single-crystal electron diffraction patterns from multi-particle aggregates, and elongated wire or chain morphologies (De Yoreo et al., 2015; Penn & Banfield, 1998). NOA is identified by misoriented lattice fringes at grain boundaries, polycrystalline diffraction rings, and equant or irregular aggregate morphologies (De Yoreo et al., 2015).

Ag NPs are abundant in As-Sb oxide phases (Figs. 11a-d, 13a-b). They range from 2 to 6 nm in size, show a slightly seriate size distribution, and have shapes ranging from ellipsoidal to circular. A unimodal, uniform-size distribution is observed in the daughter phase in direct contact with the parent phase (Fig. 11e-f), where all NPs are no larger than 3 nm, consistent with a single nucleation event under controlled interfacial conditions. The Ag NPs form trails within the matrix (Fig. 13a) that, upon sufficient accumulation, develop into silver wires, recording the progressive aggregation of NPs through CPA. Within stibioclaudeite, Ag NPs aggregates range from individual particles to dendritic forms (Fig. 13b), including polycrystalline aggregates with varied lattice orientations indicative of NOA (Fig. 13b-b) and monocrystalline aggregates with uniform lattice planes indicative of OA (Fig. 13b-a). The d-spacing of the Ag NPs ranges from 2.42 to 2.22 Å, which is not consistent with the cubic close-packed structure of native silver but is better described by the  $P6_3/mmc$  space group. This is attributed to slight Sb substitution into the Ag structure, analogous to but distinct from allargentum, and accounts for the observed range in d-spacing values. The occurrence of both OA and NOA within the same phase reflects the variable geochemical conditions across the As-Sb oxide, where differences in local  $Ag^+$  availability, supersaturation, and pH govern which attachment mechanism dominates at a given site.

Ag NPs also occur in dolomite (Figs. 11a-d, 13c). High-resolution TEM imaging reveals variations in lattice plane orientation within individual Ag NPs and across aggregates, indicating growth through NOA upon trail formation and subsequent aggregation. The size distribution of Ag NPs in dolomite varies widely across measurement locations, reflecting the heterogeneous influence of  $Ca^{2+}$  on ionic strength and aggregation dynamics. In Figure 13c, two main size populations are present: smaller, more isolated Ag NPs at 1-2 nm and larger aggregating NPs forming trails at 4-7 nm. In Figures 11a-b, three populations can be identified within a 13 nm

window: 2-3 nm, 8-11 nm, and 15-17 nm. In Figure S3 A-B', NPs range overall from 5 to 10 nm, with large NOA aggregates reaching up to 25 nm. A wide range of d-spacing values recorded in Fig. 13c and the associated FFT patterns (insets ca and cb) is consistent with variable Sb incorporation and the disordered nature of the NOA aggregates. The variable size distribution and the suite of NOA aggregates, trails, and accumulation features in carbonate are consistent with the influence of  $\text{Ca}^{2+}$  on ionic strength, which promotes rapid disordered aggregation and suppresses the crystallographic alignment required for OA.

TEM imaging shows Ag NPs intercalated between the layers of Fe-bearing clay minerals and within OM (Figs. 11k-l, 13d), with NPs along clay layers spatially associated with adjacent OM. The size distribution in both phases is unimodal, ranging from 1 to 5 nm. The d-spacing of the Ag NPs varies slightly across measurement locations (Fig. 13d), likely reflecting minor compositional variations associated with local substrate chemistry. The unimodal size distribution and the spacing of individual NPs, consistent with a well-developed diffuse double layer that reduces particle-particle interaction, indicate a single main nucleation event from sufficient  $\text{Ag}^+$  precursor, with subsequent limited aggregation due to the stabilizing effect of OM on surface charge.

Ag NPs in erythrite show variable sizes (1 to 10 nm) and characteristics (Fig. 13e). They occur as monocrystalline particles with uniform atomic plane orientation (Fig. 13ea) or as disordered aggregates consistent with NOA (Fig. 13eb). As in other host phases, Ag NPs in erythrite accumulate in trails that develop into wire-like features (Fig. 13f); these NPs are uniformly oriented and elongated perpendicular to the trail direction. At lower magnification, NPs adopt a colloform texture and reach up to 70 nm in size (Fig. 11i-j). STEM-EDS shows larger layered NPs contains sulphur. The variable characteristics of Ag NPs in erythrite reflect the

complex and evolving chemical conditions during arsenide oxidation: S coating promotes further aggregation into larger particles, while the trail and wire morphologies record the sequential attachment of NPs following each other along preferred pathways through the porous secondary phase.

#### ***2.6.4.2 Bottom-up vs top-down implications (evidence at the microscale and nanoscale)***

The Ag NPs documented at Cobalt are interpreted as products of bottom-up formation, based on their association with geochemical interfaces, including oxidized arsenide and antimonide surfaces, Fe-rich clays, OM, and carbonate, rather than as fragments of a pre-existing bulk Ag phase. Their compositions reflect newly precipitated phases controlled by local Eh and pH conditions, not direct inheritance from hypogene Ag minerals. TEM imaging reveals rounded to wire-like morphologies consistent with nucleation from solution and subsequent aggregation through OA and NOA, rather than the angular, fracture-controlled forms expected of top-down fragmentation. For example, Ag NPs associated with various oxide phases can be detached from massive silver, indicating Ag NPs aggregated via CPA (Fig. 5a-h). Their occurrence at the dissolution interface suggests that they form via a coupled dissolution-precipitation process (Fig. 12c-h).

However, the top-down scenario cannot be entirely excluded for Ag-As-Sb oxide veins in dolomite (Fig. 5m-t, S1c-d). Within the native silver veins network in carbonates, the Ag NPs associated with As-Sb oxide in that sample could alternatively reflect mechanical and subsequent chemical reworking of massive Ag by the late oxidizing fluid. In this scenario, the top-down fragmentation of a pre-existing silver phase would produce angular Ag NPs that are subsequently chemically modified during oxidation, potentially obscuring the original fragmentation textures. Distinguishing between these two processes responsible for the Ag-As-Sb oxide veins remains an

open question and would benefit from additional crystallographic analysis of the Ag NPs shapes and grain-boundary characteristics.

The microscale observations above confirm that silver veins show no spatial association with arsenide or sulpharsenide phases, and that the As-Sb oxide rims are present regardless of vein width. The vein network follows carbonate cleavage planes and is occasionally connected to primary silver-arsenide or silver-arsenate assemblages, where the veins appear to extend from or nucleate at pre-existing hypogene features. BSE imaging and EDS-SEM mapping (Fig. 5m-t) reveal four consistent relationships: silver veins of any width occur within or surrounded by As-Sb oxide; the Ag veins are discontinuous relative to the oxide, which forms a more continuous network; Ag is invariably associated with the oxide at the microscale (Fig. 9); and EDS-SEM maps show discrete Ag particles within the oxide that are not resolvable at lower magnification, corresponding to Ag NPs confirmed at the nanoscale. Furthermore, the deformational and metamorphic textures in native silver, including squiggly, mylonitic, and gently folded veins, suggest that at least parts of the silver vein network may have experienced solid-state deformation prior to or during oxidation.

In contrast, TEM analyses of the veins confirm the presence of Ag NPs (Figs. 11e-f, 12a-b; S1), consistent with the colloidal transport of Ag, but confusing in terms of bottom-up or top-down process. Textural relationships support a post-depositional timing for the Ag NPs as they crosscut both As-Sb oxide and dolomite (Fig. 12a-b). Additionally, Fe-rich clay can occur at the contact between the silver veins and the As-Sb oxide phase; the presence of this clay suggests that the Ag NPs -bearing fluid was acidic, providing a link between the conditions that generated the As-Sb oxides and those that mobilized the Ag NPs. Associated oxides have compositional variability from location to location, particularly in the As:Sb ratio, which may reflect local variations in

oxidation state across the oxide. The degree of Ag NPs abundance correlates with the degree of oxide development, consistent with their precipitation from similar fluids.

To conclude, textural features at multiple scales are consistent with both models, and the available evidence does not exclude either. The “bottoms-up” model has difficulty explaining why only a small trail of the oxide phase is invariably associated with the silver wide veins. The “top-down” model must account for the porous nature of the contact between silver veins and carbonate, as well as the presence of Ag NPs at interfaces between hypogene and supergene phases, far from the primary silver, and for the fact that carbonate, which is abundant in the host, promotes coagulation and immobilization of Ag NPs, raising the question of how NPs remain mobile over the distances implied by the vein geometry.

Regardless of whether secondary silver formed through bottom-up or top-down mechanisms, the association of Ag NPs with As-Sb oxide, carbonate, clay and OM at both the nanoscale (TEM) and microscale (reflected light and SEM) indicates that Ag NPs mobility extends throughout the oxide network and is not spatially restricted to the immediate vicinity of the hypogene phase. The compositional and textural evidence, of the Ag-As-Sb-oxide veins suggests Ag mobilization by oxidizing meteoric fluids, as evidenced by Ag NPs exclusive association with As-Sb oxide and the presence of Ag NPs in both the oxide and the carbonate host.

## **2.7 Conclusion**

This study met the following objectives: (1) determining the compositional variation in primary ore phases and their trace Ag concentrations; (2) determining the occurrence of native silver and Ag NPs with metal oxides and associated oxidized primary phases; and (3) identifying and interpreting the secondary mobilization mechanisms that govern Ag NP formation and aggregation and assessing their contribution to silver upgrading in the five-element vein deposits

of the Cobalt embayment. These objectives are addressed using micro- and nanoscale techniques on seven samples from the Cobalt embayment, including RLM, SEM-EDS, EPMA, LA-ICP-MS, and TEM. This multi-scale approach improves our understanding of the processes governing Ag formation in five-element veins, with a focus on the role of Ag NPs in Ag enrichment during supergene processes.

A key finding of this study is the identification of trace Ag within (sulph-)arsenide and antimonide host phases, a component that was previously unidentified at Cobalt due to the limitations of earlier methods (e.g., SEM-EDS, EPMA). The ore assemblage consists of silver phases, arsenides, sulpharsenides, antimonides, native bismuth, and trace secondary oxide phases, all hosted within carbonate veins. The primary silver minerals identified are native silver, minor to trace allargentum, trace eugenite, and matildite. Native silver is the most abundant phase; it is enriched in Sb and Hg and occurs as massive to semi-massive anhedral grains, as cores and rims of rosettes, as veins and veinlets with and without arsenides and breithauptite, disseminated in the carbonate matrix or in oxidized phases, and as small inclusions in (sulph-)arsenides. Native silver is closely associated with arsenides including safflorite, nickeline, skutterudite, loellingite, and maucherite, sulpharsenide cobaltite, and antimonide breithauptite. These primary (sulph-)arsenide and antimonide ore phases are oxidized to erythrite, annabergite, stibioclaudeite, and valentinite and remain closely associated with silver.

Trace Ag in (sulph-) arsenide and antimonide minerals, and the textural associations of native silver with primary phases, establishes the hypogene mineralogical baseline against which supergene modifications can be assessed. The liberation of trace Ag during oxidation of (sulph-)arsenides and breithauptite explains the association of Ag NPs with As-Sb (hydrous-)oxides and

host carbonates, linking primary ore mineralogy to nanoscale weathering products formed during low-temperature dissolution-precipitation processes.

This study demonstrates that supergene silver enrichment at the Cobalt deposit operates through multiple concurrent molecular and nanoscale dissolution-precipitation pathways, all driven by the oxidation of hypogene arsenide, sulpharsenide, and antimonide phases by meteoric fluids (Fig. 14, Table. 8). Under acidic conditions, Ag is mobilized as  $\text{Ag}^+$  via a decoupled pathway, with Fe-bearing clay minerals and organic matter serving as reactive surfaces that capture and immobilize Ag NPs regardless of their proximity to the parent phase. Under weakly alkaline, carbonate-buffered conditions, Ag is released directly as  $\text{Ag}^0$  NPs through a coupled pathway at the dissolution front, where precipitation tracks the advancing redox front. The coupled weakly alkaline pathway is the most prevalent, reflecting the dominance of carbonate gangue and the buffering capacity of dolomite, the principal host. The spatial restriction of these enrichment features, governed by local Eh, pH, and the availability of reactive substrates such as As-Sb oxide, clay minerals, organic matter, and carbonate, accounts for the patchy but pure (homogeneous) nature of secondary silver at Cobalt and establishes molecular and nanoscale processes as contributors to silver enrichment at the deposit scale.

Under both acidic and weakly alkaline conditions, Ag NP aggregation through CPA produces nano- to micrometre-sized silver particles and nanowires, characteristic of the supergene enrichment processes. The dominant attachment mode, either OA or NOA, is controlled by pH, ionic strength, ionic species, particle size, temperature, and supersaturation at the time of formation. Critically, these controls are the same variables that define the local geochemical environment, meaning that OA and NOA textures constitute a direct fingerprint of the conditions under which Ag NPs formed and aggregated. NP occurrence is directly linked to hypogene ore

phases, and the oxidation of these phases, with subsequent release of Ag and secondary Ag NP formation, may represent a mechanism for Ag upgrading in the Cobalt embayment, the scale of which requires further investigation.

This study presents one of the first direct nanoscale characterizations of Ag NP formation linked to supergene enrichment in the five-element vein deposit of the Cobalt embayment, establishing a framework for the nanoscale investigation of secondary silver processes in similar systems worldwide.

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## Tables.

**Table 1:** Information on the selected samples, including their locations, the ore and gangue assemblages present in each sample (in order of decreasing abundance: **major**, minor, and trace). Analytical techniques used on each sample are given as superscript numbers beside the sample ID. In the text, the samples are referred by abbreviated names, CMNM-C and ROMESM-M, and numbers.

| Sample ID                           | Original location            | Ore and gangue assemblage                                                                                                                                                                                |
|-------------------------------------|------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>CMNM31018</b> <sup>1,2,3</sup>   | Cobalt, from glacial boulder | <b>Fe-Dolomite, dolomite</b> > <b>native silver</b> > <b>breithauptite</b> > <b>safflorite</b> > <b>nickeline</b> > <u>maucherite</u> > <u>stibioclaudeite</u> > <u>cobaltite</u> > native Bi= matildite |
| <b>Cob-3b</b> <sup>1,2</sup>        | Rock dump, Kerr Lake Mill    | <b>Fe-dolomite</b> > <b>native silver</b> > <b>skutterudite</b> > <b>erythrite</b> > calcite > cobaltite-gerdsorfite ss                                                                                  |
| <b>ROMESM39127</b> <sup>1,2,3</sup> | Hudson Bay Mine              | <b>Native Silver</b> > <b>dolomite</b> > <b>Sb-bearing annabergite</b> > <b>breithauptite</b> > <u>stibioclaudeite</u> > <u>cobaltite</u> > allargentum                                                  |
| <b>ROMESM39011</b> <sup>1,2</sup>   | O'Brien Mine                 | <b>Dolomite</b> > <b>native silver</b> > <b>safflorite</b> > <b>cobaltite</b> > <u>breithauptite</u> > <u>arsenian valentinite</u> > allargentum=stibioclaudeite                                         |
| <b>ROMESM39035</b> <sup>1,2</sup>   | La Rose Mine                 | <b>Fe-Dolomite</b> > <b>native silver</b> > <b>nickeline</b> = <b>safflorite</b> > <u>allargentum</u> > <u>cobaltite</u>                                                                                 |
| <b>ROMESM8922</b> <sup>1,2</sup>    | Seneca Superior Mine         | <b>Nickeline</b> > <b>breithauptite</b> > <b>Dolomite</b> > <b>safflorite</b> > native silver > cobaltite > Maucherite                                                                                   |
| <b>ROMESM39076</b> <sup>1,2</sup>   | Silver Center                | <b>Skutterudite</b> > <b>native silver</b> > <b>calcite</b> > <b>cobaltite-gersdorffite</b> > <u>breithauptite</u> > <u>allargentum</u> > <u>cobaltite-gersdorffite ss</u> > eugenite                    |

Footnote: <sup>1</sup>EPMA, <sup>2</sup>LAICPMS, <sup>3</sup>TEM, **major (>5%)-bold**, minor (1-5%)-underlined, trace (<1%)-normal.

**Table 2.** Summary statistics for analyzed matildite, eugenite and allargentum. Abbreviations: 25<sup>th</sup> – 25<sup>th</sup> percentile, 75<sup>th</sup> – 75<sup>th</sup> percentile, apfu – atoms per formula unit, at% - atomic percentage, Av – average, Med – median, Min – minimum, Max – maximum, Stdev – standard deviation, wt% - weight percentage, n – number of analyses.

| Elements             | Matildite<br>[n=1] | Eugenite [n=3]                                 |       |        |        |        |                  |                  |
|----------------------|--------------------|------------------------------------------------|-------|--------|--------|--------|------------------|------------------|
|                      |                    | Av                                             | Stdev | Med    | Min    | Max    | 25 <sup>th</sup> | 75 <sup>th</sup> |
| Ag [wt%]             | 29.28              | 77.98                                          | 2.19  | 78.14  | 75.72  | 80.09  | 75.72            | 80.09            |
| As                   | 0.03               | 0.04                                           | 0.01  | 0.03   | 0.03   | 0.05   | 0.03             | 0.05             |
| Co                   | 0.01               | 0.05                                           | 0.03  | 0.04   | 0.02   | 0.08   | 0.02             | 0.08             |
| Ni                   | 0.01               | 0.02                                           | 0.00  | 0.02   | 0.02   | 0.02   | 0.02             | 0.02             |
| Sb                   | 0.02               | 0.29                                           | 0.42  | 0.07   | 0.02   | 0.77   | 0.02             | 0.77             |
| Hg                   | 0.07               | 22.81                                          | 1.80  | 22.37  | 21.27  | 24.79  | 21.27            | 24.79            |
| Bi                   | 52.89              | 0.14                                           | 0.06  | 0.13   | 0.08   | 0.20   | 0.08             | 0.20             |
| Pb                   | 0.06               | 0.06                                           | 0.00  | 0.06   | 0.06   | 0.06   | 0.06             | 0.06             |
| Fe                   | 0.14               | 0.02                                           | 0.00  | 0.02   | 0.02   | 0.02   | 0.02             | 0.02             |
| S                    | 17.51              | 0.09                                           | 0.03  | 0.08   | 0.06   | 0.12   | 0.06             | 0.12             |
| <b>Total</b>         | 100.01             | 101.48                                         | 0.37  | 101.60 | 101.07 | 101.78 | 101.07           | 101.78           |
| Ag [at%]             | 25.37              | 85.71                                          | 1.37  | 85.73  | 84.33  | 87.07  | 84.33            | 87.07            |
| As                   | 0.00               | 0.01                                           | 0.07  | 0.00   | 0.00   | 0.08   | 0.00             | 0.08             |
| Co                   | 0.01               | 0.10                                           | 0.06  | 0.07   | 0.04   | 0.17   | 0.04             | 0.17             |
| Ni                   | 0.02               | 0.01                                           | 0.02  | 0.01   | 0.00   | 0.03   | 0.00             | 0.03             |
| Sb                   | 0.00               | 0.26                                           | 0.43  | 0.07   | 0.00   | 0.75   | 0.00             | 0.75             |
| Hg                   | 0.02               | 13.49                                          | 1.24  | 13.20  | 12.43  | 14.85  | 12.43            | 14.85            |
| Bi                   | 23.65              | 0.07                                           | 0.06  | 0.08   | 0.00   | 0.12   | 0.00             | 0.12             |
| Pb                   | 0.00               | 0.03                                           | 0.01  | 0.03   | 0.02   | 0.03   | 0.02             | 0.03             |
| Fe                   | 0.23               | 0.00                                           | 0.00  | 0.00   | 0.00   | 0.00   | 0.00             | 0.00             |
| S                    | 51.02              | 0.33                                           | 0.10  | 0.30   | 0.24   | 0.44   | 0.24             | 0.44             |
| <b>Total</b>         | 100.00             | 100.00                                         | 0.00  | 100.00 | 100.00 | 100.00 | 100.00           | 100.00           |
| <b>4 total atoms</b> |                    | <b>Mineral formula based on 13 total atoms</b> |       |        |        |        |                  |                  |
| Ag [apfu]            | 1.01               | 11.13                                          | 0.18  | 11.12  | 10.95  | 11.31  | 10.95            | 11.31            |
| As                   | 0.00               | 0.01                                           | 0.00  | 0.01   | 0.01   | 0.01   | 0.01             | 0.01             |
| Co                   | 0.00               | 0.01                                           | 0.01  | 0.01   | 0.01   | 0.02   | 0.01             | 0.02             |
| Ni                   | 0.00               | 0.01                                           | 0.00  | 0.01   | 0.01   | 0.01   | 0.01             | 0.01             |
| Sb                   | 0.00               | 0.04                                           | 0.05  | 0.01   | 0.00   | 0.10   | 0.00             | 0.10             |
| Hg                   | 0.00               | 1.75                                           | 0.16  | 1.71   | 1.61   | 1.93   | 1.61             | 1.93             |
| Bi                   | 0.94               | 0.01                                           | 0.00  | 0.01   | 0.01   | 0.01   | 0.01             | 0.01             |
| Pb                   | 0.00               | 0.00                                           | 0.00  | 0.00   | 0.00   | 0.00   | 0.00             | 0.00             |
| Fe                   | 0.01               | 0.00                                           | 0.00  | 0.00   | 0.00   | 0.00   | 0.00             | 0.00             |
| S                    | 2.03               | 0.04                                           | 0.01  | 0.04   | 0.03   | 0.06   | 0.03             | 0.06             |
| <b>Total</b>         | 4.00               | 13.00                                          | 0.00  | 13.00  | 13.00  | 13.00  | 13.00            | 13.00            |



Table 2. *continued*

| Elements                                     | Allargentum [n=32] |             |               |               |               |                  |                  |
|----------------------------------------------|--------------------|-------------|---------------|---------------|---------------|------------------|------------------|
|                                              | Av                 | Stdev       | Med           | Min           | Max           | 25 <sup>th</sup> | 75 <sup>th</sup> |
| Ag [wt%]                                     | 84.66              | 2.88        | 84.00         | 81.54         | 91.31         | 82.20            | 85.50            |
| As                                           | 0.03               | 0.00        | 0.03          | 0.03          | 0.03          | 0.03             | 0.03             |
| Co                                           | 0.04               | 0.08        | 0.01          | 0.01          | 0.39          | 0.01             | 0.05             |
| Ni                                           | 0.02               | 0.02        | 0.01          | 0.01          | 0.12          | 0.01             | 0.02             |
| Sb                                           | 14.48              | 2.85        | 15.93         | 7.51          | 16.42         | 12.88            | 16.23            |
| Hg                                           | 0.36               | 0.34        | 0.22          | 0.07          | 1.27          | 0.14             | 0.50             |
| Bi                                           | 0.31               | 0.19        | 0.25          | 0.08          | 0.67          | 0.14             | 0.49             |
| Pb                                           | 0.06               | 0.01        | 0.06          | 0.06          | 0.11          | 0.06             | 0.06             |
| Fe                                           | 0.05               | 0.15        | 0.01          | 0.00          | 0.72          | 0.01             | 0.01             |
| S                                            | 0.02               | 0.02        | 0.02          | 0.01          | 0.09          | 0.01             | 0.03             |
| <b>Total</b>                                 | <b>100.04</b>      | <b>1.03</b> | <b>100.46</b> | <b>98.06</b>  | <b>101.32</b> | <b>98.99</b>     | <b>100.81</b>    |
| Ag [at%]                                     | 86.48              | 2.41        | 85.19         | 84.35         | 92.40         | 85.08            | 87.75            |
| As                                           | 0.00               | 0.06        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Co                                           | 0.06               | 0.15        | 0.01          | 0.00          | 0.72          | 0.00             | 0.05             |
| Ni                                           | 0.03               | 0.05        | 0.02          | 0.00          | 0.22          | 0.01             | 0.04             |
| Sb                                           | 13.11              | 2.61        | 14.59         | 6.74          | 14.81         | 11.74            | 14.64            |
| Hg                                           | 0.20               | 0.19        | 0.12          | 0.03          | 0.69          | 0.08             | 0.27             |
| Bi                                           | 0.16               | 0.10        | 0.13          | 0.01          | 0.36          | 0.07             | 0.25             |
| Pb                                           | 0.01               | 0.02        | 0.01          | 0.00          | 0.06          | 0.00             | 0.03             |
| Fe                                           | 0.00               | 0.01        | 0.00          | 0.00          | 0.04          | 0.00             | 0.02             |
| S                                            | 0.07               | 0.07        | 0.07          | 0.00          | 0.30          | 0.03             | 0.11             |
| <b>Total</b>                                 | <b>100.00</b>      | <b>0.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>    | <b>100.00</b>    |
| <b>Mineral formula based on 1 total atom</b> |                    |             |               |               |               |                  |                  |
| Ag [apfu]                                    | 0.86               | 0.02        | 0.85          | 0.84          | 0.92          | 0.85             | 0.87             |
| As                                           | 0.00               | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Co                                           | 0.00               | 0.00        | 0.00          | 0.00          | 0.01          | 0.00             | 0.00             |
| Ni                                           | 0.00               | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Sb                                           | 0.13               | 0.03        | 0.15          | 0.07          | 0.15          | 0.12             | 0.15             |
| Hg                                           | 0.00               | 0.00        | 0.00          | 0.00          | 0.01          | 0.00             | 0.00             |
| Bi                                           | 0.00               | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Pb                                           | 0.00               | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Fe                                           | 0.00               | 0.00        | 0.00          | 0.00          | 0.01          | 0.00             | 0.00             |
| S                                            | 0.00               | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| <b>Total</b>                                 | <b>1.00</b>        | <b>0.00</b> | <b>1.00</b>   | <b>1.00</b>   | <b>1.00</b>   | <b>1.00</b>      | <b>1.00</b>      |

**Table 3.** Summary statistics for analyzed native silver grains based on occurrence relative to metal oxides (non-oxidized vs oxidized) and Sb content (high-Sb vs low-Sb). Abbreviations: 25<sup>th</sup> – 25<sup>th</sup> percentile, 75<sup>th</sup> – 75<sup>th</sup> percentile, apfu – atoms per formula unit, at% - atomic percentage, Av – average, Med – median, Min – minimum, Max – maximum, Stdev – standard deviation, wt% - weight percentage, n – number of analyses.

| Elements                                     | All native silver [n=79] |             |               |               |               |                  |                  | Non-oxidized low-Sb native silver [n=21] |             |               |               |               |                  |                  |
|----------------------------------------------|--------------------------|-------------|---------------|---------------|---------------|------------------|------------------|------------------------------------------|-------------|---------------|---------------|---------------|------------------|------------------|
|                                              | Av                       | Stdev       | Med           | Min           | Max           | 25 <sup>th</sup> | 75 <sup>th</sup> | Av                                       | Stdev       | Med           | Min           | Max           | 25 <sup>th</sup> | 75 <sup>th</sup> |
| Ag [wt%]                                     | 93.89                    | 1.48        | 93.64         | 89.86         | 96.87         | 92.61            | 95.21            | 95.44                                    | 0.85        | 95.56         | 93.15         | 96.87         | 95.08            | 96.07            |
| As                                           | 0.04                     | 0.05        | 0.03          | 0.03          | 0.36          | 0.03             | 0.03             | 0.07                                     | 0.08        | 0.03          | 0.03          | 0.36          | 0.03             | 0.09             |
| Co                                           | 0.07                     | 0.11        | 0.05          | 0.01          | 0.96          | 0.05             | 0.05             | 0.09                                     | 0.09        | 0.05          | 0.02          | 0.36          | 0.05             | 0.09             |
| Ni                                           | 0.08                     | 0.27        | 0.02          | 0.01          | 2.30          | 0.02             | 0.03             | 0.19                                     | 0.50        | 0.03          | 0.02          | 2.30          | 0.02             | 0.08             |
| Sb                                           | 3.50                     | 1.28        | 4.19          | 0.95          | 5.16          | 1.96             | 4.55             | 1.83                                     | 0.33        | 1.88          | 0.95          | 2.36          | 1.75             | 2.03             |
| Hg                                           | 2.01                     | 0.66        | 2.01          | 0.74          | 5.76          | 1.58             | 2.25             | 1.67                                     | 0.22        | 1.60          | 1.40          | 2.06          | 1.51             | 1.94             |
| Bi                                           | 0.14                     | 0.06        | 0.13          | 0.08          | 0.35          | 0.08             | 0.17             | 0.19                                     | 0.07        | 0.18          | 0.08          | 0.35          | 0.14             | 0.23             |
| Pb                                           | 0.06                     | 0.01        | 0.06          | 0.06          | 0.15          | 0.06             | 0.06             | 0.06                                     | 0.02        | 0.06          | 0.06          | 0.12          | 0.06             | 0.06             |
| Fe                                           | 0.02                     | 0.02        | 0.02          | 0.01          | 0.11          | 0.02             | 0.02             | 0.03                                     | 0.02        | 0.02          | 0.02          | 0.10          | 0.02             | 0.04             |
| S                                            | 0.05                     | 0.11        | 0.02          | 0.01          | 0.88          | 0.01             | 0.04             | 0.09                                     | 0.11        | 0.05          | 0.01          | 0.50          | 0.04             | 0.10             |
| <b>Total</b>                                 | <b>99.86</b>             | <b>0.63</b> | <b>99.93</b>  | <b>98.18</b>  | <b>101.69</b> | <b>99.53</b>     | <b>100.20</b>    | <b>99.66</b>                             | <b>0.80</b> | <b>99.74</b>  | <b>98.18</b>  | <b>101.69</b> | <b>99.15</b>     | <b>100.14</b>    |
| Ag [at%]                                     | 95.27                    | 1.31        | 94.91         | 90.74         | 97.54         | 94.44            | 96.77            | 96.48                                    | 1.19        | 96.89         | 92.59         | 97.54         | 96.39            | 97.08            |
| As                                           | 0.03                     | 0.09        | 0.00          | 0.00          | 0.53          | 0.00             | 0.02             | 0.08                                     | 0.13        | 0.01          | 0.00          | 0.53          | 0.00             | 0.13             |
| Co                                           | 0.07                     | 0.21        | 0.01          | 0.00          | 1.70          | 0.00             | 0.04             | 0.11                                     | 0.18        | 0.03          | 0.00          | 0.65          | 0.00             | 0.17             |
| Ni                                           | 0.13                     | 0.49        | 0.02          | 0.00          | 4.10          | 0.00             | 0.05             | 0.34                                     | 0.90        | 0.06          | 0.00          | 4.10          | 0.03             | 0.15             |
| Sb                                           | 3.15                     | 1.16        | 3.75          | 0.84          | 4.65          | 1.76             | 4.11             | 1.64                                     | 0.30        | 1.71          | 0.84          | 2.14          | 1.55             | 1.81             |
| Hg                                           | 1.10                     | 0.36        | 1.10          | 0.40          | 3.19          | 0.86             | 1.24             | 0.91                                     | 0.12        | 0.87          | 0.76          | 1.12          | 0.82             | 1.07             |
| Bi                                           | 0.07                     | 0.04        | 0.07          | 0.00          | 0.18          | 0.04             | 0.09             | 0.10                                     | 0.04        | 0.09          | 0.03          | 0.18          | 0.07             | 0.12             |
| Pb                                           | 0.01                     | 0.02        | 0.00          | 0.00          | 0.08          | 0.00             | 0.02             | 0.01                                     | 0.02        | 0.00          | 0.00          | 0.06          | 0.00             | 0.02             |
| Fe                                           | 0.03                     | 0.05        | 0.01          | 0.00          | 0.21          | 0.00             | 0.03             | 0.04                                     | 0.06        | 0.02          | 0.00          | 0.20          | 0.00             | 0.07             |
| S                                            | 0.17                     | 0.38        | 0.08          | 0.00          | 2.87          | 0.05             | 0.15             | 0.31                                     | 0.37        | 0.18          | 0.03          | 1.67          | 0.13             | 0.34             |
| <b>Total</b>                                 | <b>100.00</b>            | <b>0.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>    | <b>100.00</b>    | <b>100.00</b>                            | <b>0.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>    | <b>100.00</b>    |
| <b>Mineral formula based on 1 total atom</b> |                          |             |               |               |               |                  |                  |                                          |             |               |               |               |                  |                  |
| Ag [apfu]                                    | 0.95                     | 0.01        | 0.95          | 0.91          | 0.97          | 0.94             | 0.97             | 0.96                                     | 0.01        | 0.97          | 0.93          | 0.97          | 0.96             | 0.97             |
| As                                           | 0.00                     | 0.00        | 0.00          | 0.00          | 0.01          | 0.00             | 0.00             | 0.00                                     | 0.00        | 0.00          | 0.00          | 0.01          | 0.00             | 0.00             |
| Co                                           | 0.00                     | 0.00        | 0.00          | 0.00          | 0.02          | 0.00             | 0.00             | 0.00                                     | 0.00        | 0.00          | 0.00          | 0.01          | 0.00             | 0.00             |
| Ni                                           | 0.00                     | 0.00        | 0.00          | 0.00          | 0.04          | 0.00             | 0.00             | 0.00                                     | 0.01        | 0.00          | 0.00          | 0.04          | 0.00             | 0.00             |
| Sb                                           | 0.03                     | 0.01        | 0.04          | 0.01          | 0.05          | 0.02             | 0.04             | 0.02                                     | 0.00        | 0.02          | 0.01          | 0.02          | 0.02             | 0.02             |
| Hg                                           | 0.01                     | 0.00        | 0.01          | 0.00          | 0.03          | 0.01             | 0.01             | 0.01                                     | 0.00        | 0.01          | 0.01          | 0.01          | 0.01             | 0.01             |
| Bi                                           | 0.00                     | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             | 0.00                                     | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Pb                                           | 0.00                     | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             | 0.00                                     | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Fe                                           | 0.00                     | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             | 0.00                                     | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| S                                            | 0.00                     | 0.00        | 0.00          | 0.00          | 0.03          | 0.00             | 0.00             | 0.00                                     | 0.00        | 0.00          | 0.00          | 0.02          | 0.00             | 0.00             |
| <b>Total</b>                                 | <b>1.00</b>              | <b>0.00</b> | <b>1.00</b>   | <b>1.00</b>   | <b>1.00</b>   | <b>1.00</b>      | <b>1.00</b>      | <b>1.00</b>                              | <b>0.00</b> | <b>1.00</b>   | <b>1.00</b>   | <b>1.00</b>   | <b>1.00</b>      | <b>1.00</b>      |

Table 3. *continued*

| Elements                                     | Non-oxidized high-Sb native silver [n=34] |             |               |               |               |                  |                  | Oxidized, massive native silver [n=10] |             |               |               |               |                  |                  |
|----------------------------------------------|-------------------------------------------|-------------|---------------|---------------|---------------|------------------|------------------|----------------------------------------|-------------|---------------|---------------|---------------|------------------|------------------|
|                                              | Av                                        | Stdev       | Med           | Min           | Max           | 25 <sup>th</sup> | 75 <sup>th</sup> | Av                                     | Stdev       | Med           | Min           | Max           | 25 <sup>th</sup> | 75 <sup>th</sup> |
| Ag [wt%]                                     | 93.11                                     | 1.08        | 92.79         | 89.86         | 95.08         | 92.45            | 93.89            | 92.51                                  | 0.51        | 92.38         | 91.78         | 93.54         | 92.15            | 92.89            |
| As                                           | 0.04                                      | 0.05        | 0.03          | 0.03          | 0.24          | 0.03             | 0.03             | 0.03                                   | 0.00        | 0.03          | 0.03          | 0.03          | 0.03             | 0.03             |
| Co                                           | 0.07                                      | 0.16        | 0.05          | 0.01          | 0.96          | 0.05             | 0.05             | 0.05                                   | 0.01        | 0.05          | 0.03          | 0.05          | 0.05             | 0.05             |
| Ni                                           | 0.05                                      | 0.11        | 0.02          | 0.01          | 0.48          | 0.02             | 0.02             | 0.03                                   | 0.03        | 0.02          | 0.02          | 0.11          | 0.02             | 0.03             |
| Sb                                           | 4.23                                      | 0.50        | 4.41          | 3.11          | 4.92          | 3.81             | 4.60             | 4.53                                   | 0.20        | 4.48          | 4.20          | 4.84          | 4.40             | 4.70             |
| Hg                                           | 2.28                                      | 0.87        | 2.25          | 0.74          | 5.76          | 1.95             | 2.69             | 2.19                                   | 0.08        | 2.18          | 2.07          | 2.30          | 2.13             | 2.26             |
| Bi                                           | 0.13                                      | 0.04        | 0.13          | 0.08          | 0.22          | 0.08             | 0.17             | 0.10                                   | 0.02        | 0.08          | 0.08          | 0.15          | 0.08             | 0.09             |
| Pb                                           | 0.06                                      | 0.02        | 0.06          | 0.06          | 0.15          | 0.06             | 0.06             | 0.06                                   | 0.01        | 0.06          | 0.06          | 0.09          | 0.06             | 0.06             |
| Fe                                           | 0.02                                      | 0.02        | 0.02          | 0.01          | 0.11          | 0.02             | 0.02             | 0.02                                   | 0.00        | 0.02          | 0.02          | 0.02          | 0.02             | 0.02             |
| S                                            | 0.05                                      | 0.15        | 0.02          | 0.01          | 0.88          | 0.01             | 0.04             | 0.02                                   | 0.00        | 0.01          | 0.01          | 0.03          | 0.01             | 0.02             |
| <b>Total</b>                                 | <b>100.05</b>                             | <b>0.58</b> | <b>100.06</b> | <b>98.78</b>  | <b>101.29</b> | <b>99.68</b>     | <b>100.33</b>    | <b>99.53</b>                           | <b>0.51</b> | <b>99.45</b>  | <b>98.74</b>  | <b>100.43</b> | <b>99.20</b>     | <b>99.99</b>     |
| Ag [at%]                                     | 94.54                                     | 0.96        | 94.57         | 90.74         | 95.89         | 94.17            | 95.20            | 94.59                                  | 0.20        | 94.54         | 94.32         | 94.87         | 94.45            | 94.80            |
| As                                           | 0.03                                      | 0.08        | 0.00          | 0.00          | 0.35          | 0.00             | 0.02             | 0.01                                   | 0.02        | 0.00          | 0.00          | 0.06          | 0.00             | 0.00             |
| Co                                           | 0.08                                      | 0.29        | 0.02          | 0.00          | 1.70          | 0.01             | 0.04             | 0.01                                   | 0.02        | 0.00          | 0.00          | 0.06          | 0.00             | 0.01             |
| Ni                                           | 0.08                                      | 0.21        | 0.01          | 0.00          | 0.89          | 0.00             | 0.03             | 0.05                                   | 0.07        | 0.03          | 0.00          | 0.21          | 0.02             | 0.06             |
| Sb                                           | 3.80                                      | 0.45        | 3.97          | 2.82          | 4.39          | 3.45             | 4.16             | 4.11                                   | 0.18        | 4.06          | 3.83          | 4.37          | 3.97             | 4.27             |
| Hg                                           | 1.25                                      | 0.48        | 1.24          | 0.40          | 3.19          | 1.05             | 1.47             | 1.20                                   | 0.04        | 1.19          | 1.14          | 1.27          | 1.17             | 1.25             |
| Bi                                           | 0.06                                      | 0.03        | 0.07          | 0.00          | 0.12          | 0.03             | 0.09             | 0.04                                   | 0.02        | 0.05          | 0.02          | 0.08          | 0.02             | 0.06             |
| Pb                                           | 0.01                                      | 0.02        | 0.00          | 0.00          | 0.08          | 0.00             | 0.02             | 0.01                                   | 0.01        | 0.01          | 0.00          | 0.05          | 0.00             | 0.02             |
| Fe                                           | 0.03                                      | 0.05        | 0.01          | 0.00          | 0.21          | 0.00             | 0.03             | 0.00                                   | 0.01        | 0.00          | 0.00          | 0.02          | 0.00             | 0.01             |
| S                                            | 0.17                                      | 0.48        | 0.07          | 0.01          | 2.87          | 0.04             | 0.13             | 0.04                                   | 0.03        | 0.03          | 0.00          | 0.10          | 0.00             | 0.07             |
| <b>Total</b>                                 | <b>100.00</b>                             | <b>0.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>    | <b>100.00</b>    | <b>100.00</b>                          | <b>0.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>    | <b>100.00</b>    |
| <b>Mineral formula based on 1 total atom</b> |                                           |             |               |               |               |                  |                  |                                        |             |               |               |               |                  |                  |
| Ag [apfu]                                    | 0.94                                      | 0.01        | 0.94          | 0.91          | 0.96          | 0.94             | 0.95             | 0.94                                   | 0.00        | 0.94          | 0.94          | 0.95          | 0.94             | 0.94             |
| As                                           | 0.00                                      | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             | 0.00                                   | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Co                                           | 0.00                                      | 0.00        | 0.00          | 0.00          | 0.02          | 0.00             | 0.00             | 0.00                                   | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Ni                                           | 0.00                                      | 0.00        | 0.00          | 0.00          | 0.01          | 0.00             | 0.00             | 0.00                                   | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Sb                                           | 0.04                                      | 0.00        | 0.04          | 0.03          | 0.04          | 0.03             | 0.04             | 0.04                                   | 0.00        | 0.04          | 0.04          | 0.04          | 0.04             | 0.04             |
| Hg                                           | 0.01                                      | 0.00        | 0.01          | 0.00          | 0.03          | 0.01             | 0.01             | 0.01                                   | 0.00        | 0.01          | 0.01          | 0.01          | 0.01             | 0.01             |
| Bi                                           | 0.00                                      | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             | 0.00                                   | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Pb                                           | 0.00                                      | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             | 0.00                                   | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Fe                                           | 0.00                                      | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             | 0.00                                   | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| S                                            | 0.00                                      | 0.00        | 0.00          | 0.00          | 0.03          | 0.00             | 0.00             | 0.00                                   | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| <b>Total</b>                                 | <b>1.00</b>                               | <b>0.00</b> | <b>1.00</b>   | <b>1.00</b>   | <b>1.00</b>   | <b>1.00</b>      | <b>1.00</b>      | <b>1.00</b>                            | <b>0.00</b> | <b>1.00</b>   | <b>1.00</b>   | <b>1.00</b>   | <b>1.00</b>      | <b>1.00</b>      |

Table 3. *continued*

| Elements                                     | Partly oxidized rosette with native silver [n=8] |             |               |               |               |                  |                  | Native silver vein with oxidized rim [n=6] |             |               |               |               |                  |                  |
|----------------------------------------------|--------------------------------------------------|-------------|---------------|---------------|---------------|------------------|------------------|--------------------------------------------|-------------|---------------|---------------|---------------|------------------|------------------|
|                                              | Av                                               | Stdev       | Med           | Min           | Max           | 25 <sup>th</sup> | 75 <sup>th</sup> | Av                                         | Stdev       | Med           | Min           | Max           | 25 <sup>th</sup> | 75 <sup>th</sup> |
| Ag [wt%]                                     | 93.43                                            | 0.45        | 93.58         | 92.79         | 94.07         | 92.92            | 93.68            | 95.76                                      | 0.28        | 95.85         | 95.21         | 96.00         | 95.61            | 95.93            |
| As                                           | 0.03                                             | 0.00        | 0.03          | 0.03          | 0.03          | 0.03             | 0.03             | 0.03                                       | 0.00        | 0.03          | 0.03          | 0.03          | 0.03             | 0.03             |
| Co                                           | 0.05                                             | 0.02        | 0.05          | 0.02          | 0.07          | 0.03             | 0.06             | 0.05                                       | 0.00        | 0.05          | 0.05          | 0.05          | 0.05             | 0.05             |
| Ni                                           | 0.02                                             | 0.00        | 0.02          | 0.02          | 0.03          | 0.02             | 0.02             | 0.02                                       | 0.00        | 0.02          | 0.02          | 0.02          | 0.02             | 0.02             |
| Sb                                           | 4.73                                             | 0.30        | 4.68          | 4.24          | 5.16          | 4.57             | 5.02             | 1.83                                       | 0.06        | 1.84          | 1.74          | 1.90          | 1.78             | 1.87             |
| Hg                                           | 1.50                                             | 0.10        | 1.52          | 1.34          | 1.66          | 1.42             | 1.58             | 2.04                                       | 0.03        | 2.04          | 2.01          | 2.09          | 2.01             | 2.06             |
| Bi                                           | 0.12                                             | 0.04        | 0.11          | 0.08          | 0.17          | 0.08             | 0.15             | 0.11                                       | 0.06        | 0.08          | 0.08          | 0.24          | 0.08             | 0.12             |
| Pb                                           | 0.06                                             | 0.00        | 0.06          | 0.06          | 0.06          | 0.06             | 0.06             | 0.06                                       | 0.00        | 0.06          | 0.06          | 0.06          | 0.06             | 0.06             |
| Fe                                           | 0.02                                             | 0.00        | 0.02          | 0.02          | 0.02          | 0.02             | 0.02             | 0.03                                       | 0.02        | 0.02          | 0.02          | 0.07          | 0.02             | 0.06             |
| S                                            | 0.02                                             | 0.01        | 0.02          | 0.01          | 0.03          | 0.01             | 0.02             | 0.03                                       | 0.01        | 0.03          | 0.01          | 0.04          | 0.02             | 0.03             |
| <b>Total</b>                                 | <b>99.97</b>                                     | <b>0.40</b> | <b>99.88</b>  | <b>99.44</b>  | <b>100.60</b> | <b>99.65</b>     | <b>100.34</b>    | <b>99.95</b>                               | <b>0.29</b> | <b>100.06</b> | <b>99.38</b>  | <b>100.18</b> | <b>99.81</b>     | <b>100.12</b>    |
| Ag [at%]                                     | 94.73                                            | 0.22        | 94.75         | 94.44         | 95.09         | 94.50            | 94.89            | 97.06                                      | 0.10        | 97.08         | 96.92         | 97.18         | 96.95            | 97.14            |
| As                                           | 0.02                                             | 0.02        | 0.01          | 0.00          | 0.04          | 0.00             | 0.03             | 0.00                                       | 0.00        | 0.00          | 0.00          | 0.01          | 0.00             | 0.00             |
| Co                                           | 0.06                                             | 0.05        | 0.05          | 0.01          | 0.13          | 0.01             | 0.11             | 0.01                                       | 0.01        | 0.00          | 0.00          | 0.02          | 0.00             | 0.02             |
| Ni                                           | 0.02                                             | 0.02        | 0.02          | 0.00          | 0.05          | 0.01             | 0.04             | 0.01                                       | 0.01        | 0.00          | 0.00          | 0.02          | 0.00             | 0.02             |
| Sb                                           | 4.24                                             | 0.27        | 4.20          | 3.82          | 4.65          | 4.10             | 4.51             | 1.64                                       | 0.05        | 1.65          | 1.56          | 1.70          | 1.60             | 1.68             |
| Hg                                           | 0.82                                             | 0.05        | 0.83          | 0.73          | 0.90          | 0.77             | 0.86             | 1.11                                       | 0.02        | 1.11          | 1.09          | 1.14          | 1.10             | 1.12             |
| Bi                                           | 0.05                                             | 0.03        | 0.05          | 0.00          | 0.09          | 0.01             | 0.08             | 0.05                                       | 0.04        | 0.04          | 0.02          | 0.13          | 0.03             | 0.07             |
| Pb                                           | 0.01                                             | 0.02        | 0.00          | 0.00          | 0.04          | 0.00             | 0.03             | 0.01                                       | 0.01        | 0.00          | 0.00          | 0.02          | 0.00             | 0.02             |
| Fe                                           | 0.01                                             | 0.01        | 0.01          | 0.00          | 0.02          | 0.00             | 0.02             | 0.06                                       | 0.05        | 0.05          | 0.01          | 0.13          | 0.02             | 0.12             |
| S                                            | 0.06                                             | 0.02        | 0.06          | 0.02          | 0.09          | 0.05             | 0.07             | 0.09                                       | 0.03        | 0.09          | 0.05          | 0.12          | 0.07             | 0.11             |
| <b>Total</b>                                 | <b>100.00</b>                                    | <b>0.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>    | <b>100.00</b>    | <b>100.00</b>                              | <b>0.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>    | <b>100.00</b>    |
| <b>Mineral formula based on 1 total atom</b> |                                                  |             |               |               |               |                  |                  |                                            |             |               |               |               |                  |                  |
| Ag [apfu]                                    | 0.95                                             | 0.00        | 0.95          | 0.94          | 0.95          | 0.94             | 0.95             | 0.97                                       | 0.00        | 0.97          | 0.97          | 0.97          | 0.97             | 0.97             |
| As                                           | 0.00                                             | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             | 0.00                                       | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Co                                           | 0.00                                             | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             | 0.00                                       | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Ni                                           | 0.00                                             | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             | 0.00                                       | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Sb                                           | 0.04                                             | 0.00        | 0.04          | 0.04          | 0.05          | 0.04             | 0.05             | 0.02                                       | 0.00        | 0.02          | 0.02          | 0.02          | 0.02             | 0.02             |
| Hg                                           | 0.01                                             | 0.00        | 0.01          | 0.01          | 0.01          | 0.01             | 0.01             | 0.01                                       | 0.00        | 0.01          | 0.01          | 0.01          | 0.01             | 0.01             |
| Bi                                           | 0.00                                             | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             | 0.00                                       | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Pb                                           | 0.00                                             | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             | 0.00                                       | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Fe                                           | 0.00                                             | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             | 0.00                                       | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| S                                            | 0.00                                             | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             | 0.00                                       | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| <b>Total</b>                                 | <b>1.00</b>                                      | <b>0.00</b> | <b>1.00</b>   | <b>1.00</b>   | <b>1.00</b>   | <b>1.00</b>      | <b>1.00</b>      | <b>1.00</b>                                | <b>0.00</b> | <b>1.00</b>   | <b>1.00</b>   | <b>1.00</b>   | <b>1.00</b>      | <b>1.00</b>      |

**Table 4.** Summary statistics for analyzed antimonide, arsenides and sulph-arsenides. Abbreviations: 25<sup>th</sup> – 25<sup>th</sup> percentile, 75<sup>th</sup> – 75<sup>th</sup> percentile, apfu – atoms per formula unit, at% - atomic percentage, Av – average, Med – median, Min – minimum, Max – maximum, Stdev – standard deviation, n – number of analyses.

| Elements                               | Antimonide           |             |               |               |               |                  |                  |
|----------------------------------------|----------------------|-------------|---------------|---------------|---------------|------------------|------------------|
|                                        | Breithauptite [n=34] |             |               |               |               |                  |                  |
|                                        | Av                   | Stdev       | Med           | Min           | Max           | 25 <sup>th</sup> | 75 <sup>th</sup> |
| Ag [wt%]                               | 0.06                 | 0.02        | 0.05          | 0.03          | 0.12          | 0.05             | 0.08             |
| As                                     | 1.93                 | 0.47        | 1.88          | 1.17          | 3.20          | 1.55             | 2.30             |
| Co                                     | 0.11                 | 0.20        | 0.03          | 0.01          | 1.01          | 0.01             | 0.12             |
| Ni                                     | 32.61                | 0.18        | 32.65         | 32.12         | 32.90         | 32.54            | 32.74            |
| Sb                                     | 65.37                | 0.52        | 65.45         | 64.17         | 66.24         | 64.85            | 65.78            |
| Hg                                     | 0.11                 | 0.01        | 0.11          | 0.07          | 0.16          | 0.11             | 0.11             |
| Bi                                     | 0.13                 | 0.10        | 0.08          | 0.08          | 0.65          | 0.08             | 0.17             |
| Pb                                     | 0.08                 | 0.01        | 0.08          | 0.06          | 0.14          | 0.08             | 0.08             |
| Fe                                     | 0.06                 | 0.02        | 0.06          | 0.01          | 0.18          | 0.06             | 0.06             |
| S                                      | 0.02                 | 0.00        | 0.02          | 0.01          | 0.04          | 0.02             | 0.02             |
| <b>Total</b>                           | <b>100.49</b>        | <b>0.28</b> | <b>100.57</b> | <b>99.64</b>  | <b>101.16</b> | <b>100.32</b>    | <b>100.66</b>    |
| Ag [at%]                               | 0.03                 | 0.03        | 0.02          | 0.00          | 0.10          | 0.00             | 0.06             |
| As                                     | 2.29                 | 0.55        | 2.24          | 1.39          | 3.78          | 1.85             | 2.74             |
| Co                                     | 0.16                 | 0.30        | 0.04          | 0.00          | 1.50          | 0.00             | 0.18             |
| Ni                                     | 49.52                | 0.30        | 49.58         | 48.11         | 49.93         | 49.44            | 49.69            |
| Sb                                     | 47.87                | 0.57        | 47.96         | 46.63         | 48.74         | 47.45            | 48.29            |
| Hg                                     | 0.04                 | 0.02        | 0.03          | 0.01          | 0.07          | 0.03             | 0.04             |
| Bi                                     | 0.05                 | 0.05        | 0.04          | 0.00          | 0.28          | 0.01             | 0.07             |
| Pb                                     | 0.02                 | 0.02        | 0.01          | 0.00          | 0.06          | 0.00             | 0.03             |
| Fe                                     | 0.02                 | 0.05        | 0.00          | 0.00          | 0.28          | 0.00             | 0.01             |
| S                                      | 0.03                 | 0.02        | 0.02          | 0.00          | 0.10          | 0.01             | 0.04             |
| <b>Total</b>                           | <b>100.00</b>        | <b>0.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>    | <b>100.00</b>    |
| Mineral Formula based on 2 total atoms |                      |             |               |               |               |                  |                  |
| Ag [apfu]                              | 0.00                 | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| As                                     | 0.05                 | 0.01        | 0.04          | 0.03          | 0.08          | 0.04             | 0.05             |
| Co                                     | 0.00                 | 0.01        | 0.00          | 0.00          | 0.03          | 0.00             | 0.00             |
| Ni                                     | 0.99                 | 0.01        | 0.99          | 0.96          | 1.00          | 0.99             | 0.99             |
| Sb                                     | 0.96                 | 0.01        | 0.96          | 0.93          | 0.97          | 0.95             | 0.96             |
| Hg                                     | 0.00                 | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Bi                                     | 0.00                 | 0.00        | 0.00          | 0.00          | 0.01          | 0.00             | 0.00             |
| Pb                                     | 0.00                 | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Fe                                     | 0.00                 | 0.00        | 0.00          | 0.00          | 0.01          | 0.00             | 0.00             |
| S                                      | 0.00                 | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| <b>Total</b>                           | <b>2.00</b>          | <b>0.00</b> | <b>2.00</b>   | <b>2.00</b>   | <b>2.00</b>   | <b>2.00</b>      | <b>2.00</b>      |

Table 4. *continued*

| Arsenides                               |                  |       |        |        |        |                  |                  |                                        |       |        |        |        |                  |                  |
|-----------------------------------------|------------------|-------|--------|--------|--------|------------------|------------------|----------------------------------------|-------|--------|--------|--------|------------------|------------------|
| Elements                                | Maucherite [n=6] |       |        |        |        |                  |                  | Nickeline [n=13]                       |       |        |        |        |                  |                  |
|                                         | Av               | Stdev | Med    | Min    | Max    | 25 <sup>th</sup> | 75 <sup>th</sup> | Av                                     | Stdev | Med    | Min    | Max    | 25 <sup>th</sup> | 75 <sup>th</sup> |
| Ag [wt%]                                | 0.06             | 0.07  | 0.03   | 0.03   | 0.19   | 0.03             | 0.11             | 0.14                                   | 0.30  | 0.04   | 0.03   | 1.12   | 0.03             | 0.09             |
| As                                      | 47.37            | 0.50  | 47.46  | 46.70  | 47.86  | 46.86            | 47.84            | 51.54                                  | 1.12  | 51.88  | 49.55  | 52.96  | 50.62            | 52.48            |
| Co                                      | 4.40             | 0.21  | 4.42   | 4.06   | 4.65   | 4.21             | 4.58             | 2.97                                   | 1.07  | 3.20   | 0.72   | 4.35   | 2.81             | 3.59             |
| Ni                                      | 47.56            | 0.37  | 47.70  | 46.88  | 47.89  | 47.28            | 47.79            | 40.43                                  | 0.75  | 40.31  | 39.29  | 42.45  | 40.03            | 40.78            |
| Sb                                      | 0.45             | 0.15  | 0.41   | 0.29   | 0.67   | 0.33             | 0.61             | 4.03                                   | 1.13  | 3.44   | 2.56   | 5.51   | 3.03             | 5.15             |
| Hg                                      | 0.08             | 0.01  | 0.08   | 0.07   | 0.10   | 0.07             | 0.08             | 0.08                                   | 0.02  | 0.07   | 0.07   | 0.13   | 0.07             | 0.07             |
| Bi                                      | 0.12             | 0.05  | 0.08   | 0.08   | 0.19   | 0.08             | 0.18             | 0.09                                   | 0.02  | 0.08   | 0.08   | 0.16   | 0.08             | 0.08             |
| Pb                                      | 0.07             | 0.01  | 0.07   | 0.06   | 0.08   | 0.06             | 0.08             | 0.07                                   | 0.02  | 0.06   | 0.06   | 0.10   | 0.06             | 0.09             |
| Fe                                      | 0.02             | 0.02  | 0.02   | 0.01   | 0.05   | 0.01             | 0.03             | 0.02                                   | 0.02  | 0.01   | 0.01   | 0.06   | 0.01             | 0.03             |
| S                                       | 0.02             | 0.01  | 0.02   | 0.01   | 0.03   | 0.01             | 0.02             | 0.02                                   | 0.01  | 0.01   | 0.01   | 0.04   | 0.01             | 0.02             |
| Total                                   | 100.14           | 0.68  | 100.11 | 99.44  | 100.88 | 99.52            | 100.78           | 99.38                                  | 0.67  | 99.70  | 97.91  | 100.11 | 98.79            | 99.89            |
| Ag [at%]                                | 0.03             | 0.04  | 0.01   | 0.01   | 0.12   | 0.01             | 0.07             | 0.08                                   | 0.20  | 0.03   | 0.00   | 0.73   | 0.00             | 0.06             |
| As                                      | 41.52            | 0.22  | 41.61  | 41.22  | 41.72  | 41.27            | 41.70            | 47.03                                  | 0.70  | 47.30  | 45.82  | 47.98  | 46.40            | 47.56            |
| Co                                      | 4.90             | 0.22  | 4.90   | 4.55   | 5.16   | 4.71             | 5.13             | 3.44                                   | 1.23  | 3.76   | 0.82   | 5.02   | 3.25             | 4.16             |
| Ni                                      | 53.20            | 0.38  | 53.16  | 52.77  | 53.65  | 52.80            | 53.64            | 47.08                                  | 0.89  | 47.06  | 45.57  | 49.11  | 46.57            | 47.42            |
| Sb                                      | 0.24             | 0.08  | 0.22   | 0.16   | 0.36   | 0.18             | 0.33             | 2.27                                   | 0.65  | 1.93   | 1.44   | 3.14   | 1.69             | 2.90             |
| Hg                                      | 0.01             | 0.01  | 0.02   | 0.00   | 0.03   | 0.00             | 0.02             | 0.02                                   | 0.01  | 0.01   | 0.00   | 0.05   | 0.01             | 0.03             |
| Bi                                      | 0.03             | 0.02  | 0.02   | 0.00   | 0.06   | 0.01             | 0.06             | 0.02                                   | 0.02  | 0.02   | 0.00   | 0.05   | 0.01             | 0.04             |
| Pb                                      | 0.01             | 0.01  | 0.01   | 0.00   | 0.02   | 0.00             | 0.01             | 0.01                                   | 0.01  | 0.02   | 0.00   | 0.03   | 0.00             | 0.03             |
| Fe                                      | 0.02             | 0.02  | 0.02   | 0.00   | 0.06   | 0.01             | 0.04             | 0.02                                   | 0.02  | 0.01   | 0.00   | 0.07   | 0.00             | 0.03             |
| S                                       | 0.03             | 0.02  | 0.04   | 0.01   | 0.06   | 0.01             | 0.05             | 0.03                                   | 0.02  | 0.03   | 0.00   | 0.08   | 0.02             | 0.05             |
| Total                                   | 100.00           | 0.00  | 100.00 | 100.00 | 100.00 | 100.00           | 100.00           | 100.00                                 | 0.00  | 100.00 | 100.00 | 100.00 | 100.00           | 100.00           |
| Mineral formula based on 19 total atoms |                  |       |        |        |        |                  |                  | Mineral formula based on 2 total atoms |       |        |        |        |                  |                  |
| Ag [apfu]                               | 0.01             | 0.01  | 0.00   | 0.00   | 0.02   | 0.00             | 0.01             | 0.00                                   | 0.00  | 0.00   | 0.00   | 0.01   | 0.00             | 0.00             |
| As                                      | 7.88             | 0.04  | 7.90   | 7.83   | 7.92   | 7.84             | 7.92             | 0.94                                   | 0.01  | 0.95   | 0.92   | 0.96   | 0.93             | 0.95             |
| Co                                      | 0.93             | 0.04  | 0.93   | 0.86   | 0.98   | 0.90             | 0.97             | 0.07                                   | 0.02  | 0.08   | 0.02   | 0.10   | 0.07             | 0.08             |
| Ni                                      | 10.10            | 0.07  | 10.09  | 10.03  | 10.19  | 10.03            | 10.19            | 0.94                                   | 0.02  | 0.94   | 0.91   | 0.98   | 0.93             | 0.95             |
| Sb                                      | 0.05             | 0.02  | 0.04   | 0.03   | 0.07   | 0.03             | 0.06             | 0.05                                   | 0.01  | 0.04   | 0.03   | 0.06   | 0.03             | 0.06             |
| Hg                                      | 0.00             | 0.00  | 0.00   | 0.00   | 0.01   | 0.00             | 0.01             | 0.00                                   | 0.00  | 0.00   | 0.00   | 0.00   | 0.00             | 0.00             |
| Bi                                      | 0.01             | 0.00  | 0.01   | 0.00   | 0.01   | 0.01             | 0.01             | 0.00                                   | 0.00  | 0.00   | 0.00   | 0.00   | 0.00             | 0.00             |
| Pb                                      | 0.00             | 0.00  | 0.00   | 0.00   | 0.00   | 0.00             | 0.00             | 0.00                                   | 0.00  | 0.00   | 0.00   | 0.00   | 0.00             | 0.00             |
| Fe                                      | 0.00             | 0.00  | 0.00   | 0.00   | 0.01   | 0.00             | 0.01             | 0.00                                   | 0.00  | 0.00   | 0.00   | 0.00   | 0.00             | 0.00             |
| S                                       | 0.01             | 0.00  | 0.01   | 0.01   | 0.01   | 0.01             | 0.01             | 0.00                                   | 0.00  | 0.00   | 0.00   | 0.00   | 0.00             | 0.00             |
| Total                                   | 19.00            | 0.00  | 19.00  | 19.00  | 19.00  | 19.00            | 19.00            | 2.00                                   | 0.00  | 2.00   | 2.00   | 2.00   | 2.00             | 2.00             |

Table 4. *continued*

| Elements                                      | Safflorite [n=25] |             |               |               |               |               |               | Arsenides     |             |               |               |               |               |               |
|-----------------------------------------------|-------------------|-------------|---------------|---------------|---------------|---------------|---------------|---------------|-------------|---------------|---------------|---------------|---------------|---------------|
|                                               | Av                | Stdev       | Med           | Min           | Max           | 25th          | 75th          | Av            | Stdev       | Med           | Min           | Max           | 25th          | 75th          |
| Ag [wt%]                                      | 0.05              | 0.04        | 0.03          | 0.03          | 0.17          | 0.03          | 0.05          | 0.09          | 0.06        | 0.09          | 0.03          | 0.19          | 0.04          | 0.15          |
| As                                            | 69.70             | 0.40        | 69.69         | 68.96         | 70.44         | 69.46         | 69.89         | 70.01         | 1.58        | 70.31         | 67.52         | 71.72         | 68.62         | 71.26         |
| Co                                            | 27.66             | 0.39        | 27.64         | 26.94         | 28.30         | 27.33         | 28.00         | 23.88         | 2.45        | 25.29         | 20.42         | 25.90         | 21.30         | 25.77         |
| Ni                                            | 0.72              | 0.27        | 0.68          | 0.37          | 1.27          | 0.48          | 0.92          | 4.04          | 1.85        | 3.68          | 2.34          | 6.82          | 2.43          | 5.83          |
| Sb                                            | 0.42              | 0.19        | 0.37          | 0.13          | 0.83          | 0.25          | 0.57          | 1.03          | 1.09        | 0.64          | 0.19          | 2.91          | 0.32          | 1.92          |
| Hg                                            | 0.07              | 0.01        | 0.07          | 0.07          | 0.12          | 0.07          | 0.07          | 0.07          | 0.00        | 0.07          | 0.07          | 0.07          | 0.07          | 0.07          |
| Bi                                            | 0.10              | 0.03        | 0.08          | 0.08          | 0.23          | 0.08          | 0.08          | 0.10          | 0.03        | 0.08          | 0.08          | 0.15          | 0.08          | 0.12          |
| Pb                                            | 0.06              | 0.01        | 0.06          | 0.06          | 0.09          | 0.06          | 0.06          | 0.06          | 0.00        | 0.06          | 0.06          | 0.06          | 0.06          | 0.06          |
| Fe                                            | 0.11              | 0.07        | 0.10          | 0.02          | 0.28          | 0.06          | 0.15          | 1.05          | 1.32        | 0.63          | 0.22          | 3.38          | 0.28          | 2.02          |
| S                                             | 0.10              | 0.04        | 0.09          | 0.03          | 0.21          | 0.08          | 0.11          | 0.22          | 0.15        | 0.19          | 0.08          | 0.40          | 0.09          | 0.38          |
| <b>Total</b>                                  | <b>98.98</b>      | <b>0.40</b> | <b>98.88</b>  | <b>98.22</b>  | <b>99.78</b>  | <b>98.66</b>  | <b>99.27</b>  | <b>100.55</b> | <b>0.98</b> | <b>101.05</b> | <b>99.29</b>  | <b>101.44</b> | <b>99.51</b>  | <b>101.35</b> |
| Ag [at%]                                      | 0.02              | 0.03        | 0.01          | 0.00          | 0.11          | 0.00          | 0.04          | 0.06          | 0.05        | 0.06          | 0.00          | 0.13          | 0.02          | 0.09          |
| As                                            | 65.46             | 0.28        | 65.45         | 64.84         | 65.93         | 65.31         | 65.64         | 64.70         | 0.92        | 64.81         | 63.34         | 65.76         | 63.85         | 65.49         |
| Co                                            | 33.02             | 0.42        | 33.04         | 32.26         | 33.62         | 32.67         | 33.39         | 28.08         | 3.12        | 29.43         | 23.80         | 30.89         | 24.80         | 30.69         |
| Ni                                            | 0.86              | 0.33        | 0.81          | 0.45          | 1.52          | 0.58          | 1.10          | 4.75          | 2.13        | 4.30          | 2.81          | 7.97          | 2.91          | 6.82          |
| Sb                                            | 0.24              | 0.11        | 0.21          | 0.08          | 0.48          | 0.15          | 0.33          | 0.59          | 0.63        | 0.36          | 0.11          | 1.68          | 0.18          | 1.10          |
| Hg                                            | 0.02              | 0.01        | 0.02          | 0.00          | 0.04          | 0.01          | 0.03          | 0.01          | 0.01        | 0.00          | 0.00          | 0.03          | 0.00          | 0.02          |
| Bi                                            | 0.02              | 0.02        | 0.02          | 0.00          | 0.08          | 0.00          | 0.03          | 0.03          | 0.01        | 0.02          | 0.01          | 0.05          | 0.02          | 0.04          |
| Pb                                            | 0.01              | 0.01        | 0.01          | 0.00          | 0.04          | 0.00          | 0.02          | 0.02          | 0.01        | 0.02          | 0.01          | 0.02          | 0.01          | 0.02          |
| Fe                                            | 0.14              | 0.08        | 0.13          | 0.03          | 0.35          | 0.07          | 0.19          | 1.29          | 1.62        | 0.78          | 0.28          | 4.16          | 0.35          | 2.49          |
| S                                             | 0.21              | 0.09        | 0.20          | 0.06          | 0.45          | 0.17          | 0.25          | 0.49          | 0.32        | 0.40          | 0.17          | 0.85          | 0.20          | 0.82          |
| <b>Total</b>                                  | <b>100.00</b>     | <b>0.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>0.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> |
| <b>Mineral formula based on 3 total atoms</b> |                   |             |               |               |               |               |               |               |             |               |               |               |               |               |
| Ag [apfu]                                     | 0.00              | 0.00        | 0.00          | 0.00          | 0.00          | 0.00          | 0.00          | 0.00          | 0.00        | 0.00          | 0.00          | 0.00          | 0.00          | 0.00          |
| As                                            | 1.96              | 0.01        | 1.96          | 1.94          | 1.98          | 1.96          | 1.97          | 1.94          | 0.03        | 1.94          | 1.90          | 1.97          | 1.92          | 1.96          |
| Co                                            | 0.99              | 0.01        | 0.99          | 0.97          | 1.01          | 0.98          | 1.00          | 0.84          | 0.09        | 0.88          | 0.71          | 0.93          | 0.74          | 0.92          |
| Ni                                            | 0.03              | 0.01        | 0.02          | 0.01          | 0.05          | 0.02          | 0.03          | 0.14          | 0.06        | 0.13          | 0.08          | 0.24          | 0.09          | 0.20          |
| Sb                                            | 0.01              | 0.00        | 0.01          | 0.00          | 0.01          | 0.00          | 0.01          | 0.02          | 0.02        | 0.01          | 0.00          | 0.05          | 0.01          | 0.03          |
| Hg                                            | 0.00              | 0.00        | 0.00          | 0.00          | 0.00          | 0.00          | 0.00          | 0.00          | 0.00        | 0.00          | 0.00          | 0.00          | 0.00          | 0.00          |
| Bi                                            | 0.00              | 0.00        | 0.00          | 0.00          | 0.00          | 0.00          | 0.00          | 0.00          | 0.00        | 0.00          | 0.00          | 0.00          | 0.00          | 0.00          |
| Pb                                            | 0.00              | 0.00        | 0.00          | 0.00          | 0.00          | 0.00          | 0.00          | 0.00          | 0.00        | 0.00          | 0.00          | 0.00          | 0.00          | 0.00          |
| Fe                                            | 0.00              | 0.00        | 0.00          | 0.00          | 0.01          | 0.00          | 0.01          | 0.04          | 0.05        | 0.02          | 0.01          | 0.12          | 0.01          | 0.07          |
| S                                             | 0.01              | 0.00        | 0.01          | 0.00          | 0.01          | 0.00          | 0.01          | 0.01          | 0.01        | 0.01          | 0.01          | 0.03          | 0.01          | 0.02          |
| <b>Total</b>                                  | <b>3.00</b>       | <b>0.00</b> | <b>3.00</b>   | <b>3.00</b>   | <b>3.00</b>   | <b>3.00</b>   | <b>3.00</b>   | <b>3.00</b>   | <b>0.00</b> | <b>3.00</b>   | <b>3.00</b>   | <b>3.00</b>   | <b>3.00</b>   | <b>3.00</b>   |

Table 4. *continued*

| Elements                                      | Ni-S-rich Safflorite [n=6] |             |               |               |               |                  |                  | Arsenides     |             |               |               |               |                  |                  |
|-----------------------------------------------|----------------------------|-------------|---------------|---------------|---------------|------------------|------------------|---------------|-------------|---------------|---------------|---------------|------------------|------------------|
|                                               | Av                         | Stdev       | Med           | Min           | Max           | 25 <sup>th</sup> | 75 <sup>th</sup> | Av            | Stdev       | Med           | Min           | Max           | 25 <sup>th</sup> | 75 <sup>th</sup> |
| Ag [wt%]                                      | 0.20                       | 0.38        | 0.04          | 0.03          | 0.98          | 0.03             | 0.31             | 0.03          | 0.01        | 0.03          | 0.03          | 0.04          | 0.03             | 0.03             |
| As                                            | 64.51                      | 1.55        | 64.85         | 62.06         | 65.96         | 63.12            | 65.88            | 70.69         | 0.26        | 70.65         | 70.43         | 71.04         | 70.57            | 70.78            |
| Co                                            | 22.54                      | 1.15        | 22.57         | 20.90         | 23.97         | 21.63            | 23.51            | 13.75         | 4.73        | 15.66         | 6.79          | 16.88         | 12.79            | 16.61            |
| Ni                                            | 4.97                       | 2.78        | 4.04          | 2.00          | 9.90          | 3.17             | 7.19             | 3.28          | 2.92        | 3.03          | 0.41          | 6.64          | 1.08             | 5.22             |
| Sb                                            | 3.07                       | 1.36        | 2.74          | 1.21          | 4.97          | 2.15             | 4.46             | 0.09          | 0.07        | 0.08          | 0.02          | 0.19          | 0.05             | 0.12             |
| Hg                                            | 0.07                       | 0.00        | 0.07          | 0.07          | 0.07          | 0.07             | 0.07             | 0.08          | 0.02        | 0.07          | 0.07          | 0.10          | 0.07             | 0.08             |
| Bi                                            | 0.14                       | 0.10        | 0.10          | 0.08          | 0.34          | 0.08             | 0.20             | 0.08          | 0.00        | 0.08          | 0.08          | 0.08          | 0.08             | 0.08             |
| Pb                                            | 0.09                       | 0.04        | 0.07          | 0.06          | 0.15          | 0.06             | 0.14             | 0.06          | 0.01        | 0.06          | 0.06          | 0.08          | 0.06             | 0.06             |
| Fe                                            | 2.39                       | 1.46        | 2.18          | 0.18          | 4.21          | 1.43             | 3.88             | 11.42         | 2.98        | 11.62         | 7.58          | 14.85         | 10.52            | 12.52            |
| S                                             | 2.38                       | 0.33        | 2.35          | 1.92          | 2.93          | 2.17             | 2.61             | 0.30          | 0.21        | 0.28          | 0.08          | 0.59          | 0.20             | 0.38             |
| <b>Total</b>                                  | <b>100.37</b>              | <b>0.51</b> | <b>100.44</b> | <b>99.43</b>  | <b>100.82</b> | <b>100.07</b>    | <b>100.81</b>    | <b>99.79</b>  | <b>0.67</b> | <b>99.97</b>  | <b>98.87</b>  | <b>100.35</b> | <b>99.50</b>     | <b>100.26</b>    |
| Ag [at%]                                      | 0.12                       | 0.24        | 0.02          | 0.00          | 0.61          | 0.00             | 0.19             | 0.01          | 0.01        | 0.01          | 0.00          | 0.03          | 0.00             | 0.02             |
| As                                            | 58.44                      | 1.51        | 58.62         | 55.85         | 60.05         | 57.35            | 59.74            | 65.16         | 0.50        | 65.31         | 64.48         | 65.54         | 64.94            | 65.54            |
| Co                                            | 25.96                      | 1.43        | 26.05         | 23.92         | 27.77         | 24.75            | 27.16            | 16.10         | 5.50        | 18.42         | 7.97          | 19.60         | 15.12            | 19.40            |
| Ni                                            | 5.74                       | 3.18        | 4.69          | 2.31          | 11.37         | 3.68             | 8.26             | 3.86          | 3.44        | 3.57          | 0.48          | 7.82          | 1.28             | 6.14             |
| Sb                                            | 1.71                       | 0.76        | 1.52          | 0.67          | 2.79          | 1.20             | 2.49             | 0.05          | 0.04        | 0.05          | 0.01          | 0.10          | 0.03             | 0.07             |
| Hg                                            | 0.01                       | 0.01        | 0.00          | 0.00          | 0.03          | 0.00             | 0.02             | 0.02          | 0.01        | 0.03          | 0.01          | 0.04          | 0.02             | 0.03             |
| Bi                                            | 0.05                       | 0.03        | 0.04          | 0.02          | 0.11          | 0.03             | 0.06             | 0.02          | 0.01        | 0.02          | 0.00          | 0.03          | 0.01             | 0.02             |
| Pb                                            | 0.03                       | 0.02        | 0.02          | 0.01          | 0.05          | 0.01             | 0.04             | 0.01          | 0.01        | 0.01          | 0.00          | 0.02          | 0.01             | 0.01             |
| Fe                                            | 2.91                       | 1.78        | 2.64          | 0.21          | 5.12          | 1.75             | 4.73             | 14.12         | 3.70        | 14.38         | 9.36          | 18.38         | 12.91            | 15.59            |
| S                                             | 5.04                       | 0.68        | 5.00          | 4.09          | 6.16          | 4.59             | 5.49             | 0.66          | 0.45        | 0.60          | 0.17          | 1.25          | 0.42             | 0.83             |
| <b>Total</b>                                  | <b>100.00</b>              | <b>0.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>    | <b>100.00</b>    | <b>100.00</b> | <b>0.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>    | <b>100.00</b>    |
| <b>Mineral formula based on 3 total atoms</b> |                            |             |               |               |               |                  |                  |               |             |               |               |               |                  |                  |
| Ag [apfu]                                     | 0.00                       | 0.01        | 0.00          | 0.00          | 0.02          | 0.00             | 0.01             | 0.00          | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| As                                            | 1.75                       | 0.04        | 1.76          | 1.68          | 1.80          | 1.72             | 1.79             | 1.95          | 0.02        | 1.96          | 1.93          | 1.97          | 1.95             | 1.97             |
| Co                                            | 0.78                       | 0.04        | 0.78          | 0.72          | 0.83          | 0.74             | 0.81             | 0.48          | 0.16        | 0.55          | 0.24          | 0.59          | 0.45             | 0.58             |
| Ni                                            | 0.17                       | 0.10        | 0.14          | 0.07          | 0.34          | 0.11             | 0.25             | 0.12          | 0.10        | 0.11          | 0.01          | 0.23          | 0.04             | 0.18             |
| Sb                                            | 0.05                       | 0.02        | 0.05          | 0.02          | 0.08          | 0.04             | 0.07             | 0.00          | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Hg                                            | 0.00                       | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             | 0.00          | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Bi                                            | 0.00                       | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             | 0.00          | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Pb                                            | 0.00                       | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             | 0.00          | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Fe                                            | 0.09                       | 0.05        | 0.08          | 0.01          | 0.15          | 0.05             | 0.14             | 0.42          | 0.11        | 0.43          | 0.28          | 0.55          | 0.39             | 0.47             |
| S                                             | 0.15                       | 0.02        | 0.15          | 0.12          | 0.18          | 0.14             | 0.16             | 0.02          | 0.01        | 0.02          | 0.01          | 0.04          | 0.01             | 0.02             |
| <b>Total</b>                                  | <b>3.00</b>                | <b>0.00</b> | <b>3.00</b>   | <b>3.00</b>   | <b>3.00</b>   | <b>3.00</b>      | <b>3.00</b>      | <b>3.00</b>   | <b>0.00</b> | <b>3.00</b>   | <b>3.00</b>   | <b>3.00</b>   | <b>3.00</b>      | <b>3.00</b>      |

Table 4. *continued*

| Elements             | Löllingite<br>[n=1] | Arsenides                                     |             |               |               |               |                  |                  |
|----------------------|---------------------|-----------------------------------------------|-------------|---------------|---------------|---------------|------------------|------------------|
|                      |                     | Skutterudite [n=12]                           |             |               |               |               |                  |                  |
|                      |                     | Av                                            | Stdev       | Med           | Min           | Max           | 25 <sup>th</sup> | 75 <sup>th</sup> |
| Ag [wt%]             | 0.03                | 0.06                                          | 0.04        | 0.03          | 0.03          | 0.16          | 0.03             | 0.07             |
| As                   | 71.15               | 77.99                                         | 0.39        | 78.03         | 77.12         | 78.66         | 77.83            | 78.25            |
| Co                   | 1.90                | 19.91                                         | 0.89        | 20.17         | 18.32         | 20.78         | 18.94            | 20.66            |
| Ni                   | 1.00                | 0.61                                          | 0.41        | 0.64          | 0.01          | 1.27          | 0.19             | 0.90             |
| Sb                   | 0.02                | 0.08                                          | 0.08        | 0.05          | 0.02          | 0.23          | 0.02             | 0.16             |
| Hg                   | 0.07                | 0.08                                          | 0.02        | 0.07          | 0.07          | 0.14          | 0.07             | 0.10             |
| Bi                   | 0.08                | 0.09                                          | 0.02        | 0.08          | 0.08          | 0.15          | 0.08             | 0.08             |
| Pb                   | 0.06                | 0.07                                          | 0.03        | 0.06          | 0.06          | 0.15          | 0.06             | 0.06             |
| Fe                   | 26.06               | 0.70                                          | 0.51        | 0.54          | 0.16          | 1.64          | 0.31             | 1.19             |
| S                    | 0.76                | 0.07                                          | 0.06        | 0.05          | 0.01          | 0.24          | 0.03             | 0.11             |
| <b>Total</b>         | <b>101.13</b>       | <b>99.66</b>                                  | <b>0.57</b> | <b>99.61</b>  | <b>98.66</b>  | <b>100.82</b> | <b>99.27</b>     | <b>99.94</b>     |
| Ag [at%]             | 0.00                | 0.03                                          | 0.03        | 0.02          | 0.00          | 0.11          | 0.01             | 0.05             |
| As                   | 63.79               | 74.06                                         | 0.18        | 74.04         | 73.83         | 74.32         | 73.86            | 74.24            |
| Co                   | 2.17                | 24.03                                         | 1.09        | 24.43         | 22.13         | 25.20         | 22.84            | 24.96            |
| Ni                   | 1.14                | 0.73                                          | 0.49        | 0.77          | 0.01          | 1.53          | 0.23             | 1.09             |
| Sb                   | 0.00                | 0.05                                          | 0.05        | 0.03          | 0.00          | 0.13          | 0.00             | 0.09             |
| Hg                   | 0.00                | 0.02                                          | 0.02        | 0.02          | 0.00          | 0.05          | 0.00             | 0.04             |
| Bi                   | 0.00                | 0.02                                          | 0.02        | 0.01          | 0.00          | 0.05          | 0.00             | 0.03             |
| Pb                   | 0.00                | 0.01                                          | 0.02        | 0.01          | 0.00          | 0.05          | 0.00             | 0.01             |
| Fe                   | 31.34               | 0.90                                          | 0.65        | 0.69          | 0.20          | 2.09          | 0.39             | 1.51             |
| S                    | 1.60                | 0.16                                          | 0.14        | 0.10          | 0.02          | 0.53          | 0.07             | 0.24             |
| <b>Total</b>         | <b>100.00</b>       | <b>100.00</b>                                 | <b>0.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>    | <b>100.00</b>    |
| <b>3 total atoms</b> |                     | <b>Mineral formula based on 4 total atoms</b> |             |               |               |               |                  |                  |
| Ag [apfu]            | 0.00                | 0.00                                          | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| As                   | 1.91                | 2.96                                          | 0.01        | 2.96          | 2.95          | 2.97          | 2.95             | 2.97             |
| Co                   | 0.06                | 0.96                                          | 0.04        | 0.98          | 0.88          | 1.01          | 0.91             | 1.00             |
| Ni                   | 0.03                | 0.03                                          | 0.02        | 0.03          | 0.00          | 0.06          | 0.01             | 0.04             |
| Sb                   | 0.00                | 0.00                                          | 0.00        | 0.00          | 0.00          | 0.01          | 0.00             | 0.00             |
| Hg                   | 0.00                | 0.00                                          | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Bi                   | 0.00                | 0.00                                          | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Pb                   | 0.00                | 0.00                                          | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Fe                   | 0.94                | 0.04                                          | 0.03        | 0.03          | 0.01          | 0.08          | 0.02             | 0.06             |

|              |             |             |             |             |             |             |             |             |
|--------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| S            | 0.05        | 0.01        | 0.01        | 0.00        | 0.00        | 0.02        | 0.00        | 0.01        |
| <b>Total</b> | <b>3.00</b> | <b>4.00</b> | <b>0.00</b> | <b>4.00</b> | <b>4.00</b> | <b>4.00</b> | <b>4.00</b> | <b>4.00</b> |

Table 4. *continued*

| Elements                                      | Sulph-arsenides |             |                  |               |               |                  |                  | Cobaltite-Gersdorffite <i>solid solution</i> [n=8] |             |               |               |               |                  |                  |
|-----------------------------------------------|-----------------|-------------|------------------|---------------|---------------|------------------|------------------|----------------------------------------------------|-------------|---------------|---------------|---------------|------------------|------------------|
|                                               | Av              | Stdev       | Cobaltite [n=20] |               |               | 25 <sup>th</sup> | 75 <sup>th</sup> | Av                                                 | Stdev       | Med           | Min           | Max           | 25 <sup>th</sup> | 75 <sup>th</sup> |
| Ag [wt%]                                      | 0.14            | 0.20        | 0.08             | 0.03          | 0.93          | 0.03             | 0.17             | 0.21                                               | 0.50        | 0.03          | 0.03          | 1.44          | 0.03             | 0.07             |
| As                                            | 44.10           | 0.55        | 44.06            | 42.79         | 45.28         | 43.92            | 44.38            | 45.81                                              | 0.50        | 45.89         | 44.82         | 46.39         | 45.55            | 46.22            |
| Co                                            | 33.23           | 1.28        | 33.20            | 31.43         | 35.81         | 32.09            | 34.22            | 29.18                                              | 2.00        | 29.79         | 25.82         | 31.41         | 27.15            | 30.64            |
| Ni                                            | 2.37            | 1.16        | 2.31             | 0.75          | 4.70          | 1.41             | 3.25             | 4.88                                               | 1.56        | 4.73          | 3.36          | 7.94          | 3.45             | 5.82             |
| Sb                                            | 0.21            | 0.22        | 0.10             | 0.03          | 0.73          | 0.06             | 0.33             | 0.54                                               | 0.80        | 0.28          | 0.06          | 2.45          | 0.11             | 0.59             |
| Hg                                            | 0.08            | 0.01        | 0.08             | 0.07          | 0.12          | 0.07             | 0.08             | 0.09                                               | 0.03        | 0.08          | 0.07          | 0.17          | 0.07             | 0.08             |
| Bi                                            | 0.08            | 0.00        | 0.08             | 0.08          | 0.08          | 0.08             | 0.08             | 0.08                                               | 0.00        | 0.08          | 0.08          | 0.08          | 0.08             | 0.08             |
| Pb                                            | 0.08            | 0.02        | 0.08             | 0.06          | 0.14          | 0.08             | 0.10             | 0.09                                               | 0.02        | 0.08          | 0.06          | 0.12          | 0.08             | 0.11             |
| Fe                                            | 0.25            | 0.32        | 0.16             | 0.01          | 1.22          | 0.06             | 0.31             | 0.92                                               | 0.52        | 1.02          | 0.12          | 1.56          | 0.36             | 1.36             |
| S                                             | 19.01           | 0.41        | 18.96            | 18.09         | 19.73         | 18.77            | 19.40            | 18.13                                              | 0.51        | 18.17         | 17.27         | 18.75         | 17.69            | 18.56            |
| <b>Total</b>                                  | <b>99.56</b>    | <b>0.78</b> | <b>99.63</b>     | <b>98.21</b>  | <b>100.62</b> | <b>99.08</b>     | <b>100.31</b>    | <b>99.93</b>                                       | <b>0.62</b> | <b>99.96</b>  | <b>99.08</b>  | <b>101.02</b> | <b>99.33</b>     | <b>100.23</b>    |
| Ag [at%]                                      | 0.07            | 0.10        | 0.04             | 0.00          | 0.48          | 0.01             | 0.09             | 0.11                                               | 0.27        | 0.02          | 0.00          | 0.77          | 0.00             | 0.04             |
| As                                            | 32.82           | 0.53        | 32.74            | 31.90         | 33.96         | 32.44            | 33.13            | 34.38                                              | 0.45        | 34.40         | 33.68         | 34.94         | 33.98            | 34.84            |
| Co                                            | 31.44           | 1.12        | 31.44            | 29.69         | 33.41         | 30.58            | 32.51            | 27.84                                              | 1.82        | 28.45         | 24.50         | 29.76         | 26.24            | 29.22            |
| Ni                                            | 2.25            | 1.09        | 2.21             | 0.70          | 4.43          | 1.34             | 3.10             | 4.67                                               | 1.50        | 4.54          | 3.20          | 7.56          | 3.29             | 5.65             |
| Sb                                            | 0.10            | 0.10        | 0.05             | 0.01          | 0.34          | 0.03             | 0.15             | 0.25                                               | 0.37        | 0.13          | 0.03          | 1.13          | 0.05             | 0.27             |
| Hg                                            | 0.01            | 0.01        | 0.01             | 0.00          | 0.03          | 0.00             | 0.02             | 0.01                                               | 0.02        | 0.00          | 0.00          | 0.05          | 0.00             | 0.02             |
| Bi                                            | 0.01            | 0.01        | 0.01             | 0.00          | 0.03          | 0.00             | 0.02             | 0.01                                               | 0.01        | 0.01          | 0.00          | 0.03          | 0.00             | 0.01             |
| Pb                                            | 0.02            | 0.01        | 0.02             | 0.00          | 0.04          | 0.01             | 0.03             | 0.02                                               | 0.01        | 0.02          | 0.00          | 0.03          | 0.01             | 0.03             |
| Fe                                            | 0.25            | 0.32        | 0.16             | 0.01          | 1.21          | 0.06             | 0.31             | 0.93                                               | 0.53        | 1.02          | 0.12          | 1.60          | 0.36             | 1.37             |
| S                                             | 33.04           | 0.57        | 32.91            | 31.70         | 34.24         | 32.79            | 33.38            | 31.79                                              | 0.69        | 31.72         | 30.85         | 32.69         | 31.11            | 32.43            |
| <b>Total</b>                                  | <b>100.00</b>   | <b>0.00</b> | <b>100.00</b>    | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>    | <b>100.00</b>    | <b>100.00</b>                                      | <b>0.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>    | <b>100.00</b>    |
| <b>Mineral formula based on 3 total atoms</b> |                 |             |                  |               |               |                  |                  |                                                    |             |               |               |               |                  |                  |
| Ag [apfu]                                     | 0.00            | 0.00        | 0.00             | 0.00          | 0.01          | 0.00             | 0.00             | 0.00                                               | 0.01        | 0.00          | 0.00          | 0.02          | 0.00             | 0.00             |
| As                                            | 0.98            | 0.02        | 0.98             | 0.96          | 1.02          | 0.97             | 0.99             | 1.03                                               | 0.01        | 1.03          | 1.01          | 1.05          | 1.02             | 1.04             |
| Co                                            | 0.94            | 0.03        | 0.94             | 0.89          | 1.00          | 0.92             | 0.97             | 0.83                                               | 0.05        | 0.85          | 0.73          | 0.89          | 0.79             | 0.88             |
| Ni                                            | 0.07            | 0.03        | 0.07             | 0.02          | 0.13          | 0.04             | 0.09             | 0.14                                               | 0.04        | 0.14          | 0.10          | 0.23          | 0.10             | 0.17             |
| Sb                                            | 0.00            | 0.00        | 0.00             | 0.00          | 0.01          | 0.00             | 0.00             | 0.01                                               | 0.01        | 0.00          | 0.00          | 0.03          | 0.00             | 0.01             |
| Hg                                            | 0.00            | 0.00        | 0.00             | 0.00          | 0.00          | 0.00             | 0.00             | 0.00                                               | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Bi                                            | 0.00            | 0.00        | 0.00             | 0.00          | 0.00          | 0.00             | 0.00             | 0.00                                               | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Pb                                            | 0.00            | 0.00        | 0.00             | 0.00          | 0.00          | 0.00             | 0.00             | 0.00                                               | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Fe                                            | 0.01            | 0.01        | 0.00             | 0.00          | 0.04          | 0.00             | 0.01             | 0.03                                               | 0.02        | 0.03          | 0.00          | 0.05          | 0.01             | 0.04             |
| S                                             | 0.99            | 0.02        | 0.99             | 0.95          | 1.03          | 0.98             | 1.00             | 0.95                                               | 0.02        | 0.95          | 0.92          | 0.98          | 0.93             | 0.97             |
| <b>Total</b>                                  | <b>3.00</b>     | <b>0.00</b> | <b>3.00</b>      | <b>3.00</b>   | <b>3.00</b>   | <b>3.00</b>      | <b>3.00</b>      | <b>3.00</b>                                        | <b>0.00</b> | <b>3.00</b>   | <b>3.00</b>   | <b>3.00</b>   | <b>3.00</b>      | <b>3.00</b>      |

**Table 5.** Summary statistics for analyzed carbonates. Abbreviations: 25<sup>th</sup> – 25<sup>th</sup> percentile, 75<sup>th</sup> – 75<sup>th</sup> percentile, apfu – atoms per formula unit, at% - atomic percentage, Av – average, Med – median, Min – minimum, Max – maximum, Stdev – standard deviation, wt% - weight percentage

| Elements                                             | Dolomite [n=9] |             |              |              |              |                  |                  | Ferroan Dolomite [n=28] |             |              |              |               |                  |                  |
|------------------------------------------------------|----------------|-------------|--------------|--------------|--------------|------------------|------------------|-------------------------|-------------|--------------|--------------|---------------|------------------|------------------|
|                                                      | Av             | Stdev       | Med          | Min          | Max          | 25 <sup>th</sup> | 75 <sup>th</sup> | Av                      | Stdev       | Med          | Min          | Max           | 25 <sup>th</sup> | 75 <sup>th</sup> |
| SiO <sub>2</sub> [wt%]                               | 0.04           | 0.04        | 0.01         | 0.01         | 0.14         | 0.01             | 0.06             | 0.01                    | 0.01        | 0.01         | 0.01         | 0.06          | 0.01             | 0.01             |
| FeO                                                  | 2.90           | 1.28        | 2.31         | 1.89         | 5.83         | 2.02             | 3.58             | 11.35                   | 1.91        | 12.31        | 7.53         | 13.38         | 9.64             | 12.75            |
| MnO                                                  | 0.86           | 0.45        | 0.71         | 0.45         | 1.85         | 0.57             | 1.06             | 2.69                    | 0.60        | 2.63         | 1.35         | 4.00          | 2.41             | 3.12             |
| MgO                                                  | 18.89          | 1.79        | 19.67        | 15.44        | 21.08        | 17.58            | 19.82            | 11.83                   | 1.66        | 11.05        | 10.19        | 15.69         | 10.68            | 12.70            |
| CaO                                                  | 29.75          | 1.25        | 29.45        | 28.55        | 32.88        | 29.11            | 29.87            | 29.00                   | 0.46        | 28.94        | 28.30        | 30.50         | 28.65            | 29.24            |
| SO <sub>3</sub>                                      | 0.02           | 0.01        | 0.02         | 0.02         | 0.03         | 0.02             | 0.02             | 0.04                    | 0.09        | 0.02         | 0.02         | 0.47          | 0.02             | 0.02             |
| CO <sub>2</sub>                                      | 47.00          | 0.48        | 47.21        | 46.20        | 47.49        | 46.56            | 47.29            | 44.72                   | 0.51        | 44.51        | 44.20        | 45.93         | 44.37            | 44.95            |
| <b>Total</b>                                         | <b>99.45</b>   | <b>0.25</b> | <b>99.50</b> | <b>98.88</b> | <b>99.80</b> | <b>99.41</b>     | <b>99.54</b>     | <b>99.64</b>            | <b>0.25</b> | <b>99.63</b> | <b>98.87</b> | <b>100.03</b> | <b>99.49</b>     | <b>99.84</b>     |
| Si [wt%]                                             | 0.04           | 0.02        | 0.03         | 0.03         | 0.06         | 0.03             | 0.06             | 0.03                    | 0.00        | 0.03         | 0.03         | 0.03          | 0.03             | 0.03             |
| Fe                                                   | 2.25           | 0.99        | 1.80         | 1.47         | 4.54         | 1.57             | 2.79             | 8.82                    | 1.48        | 9.57         | 5.85         | 10.40         | 7.49             | 9.91             |
| Mn                                                   | 0.67           | 0.35        | 0.55         | 0.35         | 1.43         | 0.44             | 0.82             | 2.08                    | 0.46        | 2.04         | 1.05         | 3.09          | 1.86             | 2.42             |
| Mg                                                   | 11.39          | 1.08        | 11.86        | 9.31         | 12.71        | 10.60            | 11.95            | 7.13                    | 1.00        | 6.67         | 6.15         | 9.46          | 6.44             | 7.66             |
| Ca                                                   | 21.26          | 0.89        | 21.05        | 20.40        | 23.50        | 20.80            | 21.35            | 20.72                   | 0.33        | 20.69        | 20.23        | 21.80         | 20.48            | 20.90            |
| S                                                    | 0.00           | 0.01        | 0.00         | 0.00         | 0.01         | 0.00             | 0.01             | 0.01                    | 0.04        | 0.01         | 0.00         | 0.19          | 0.00             | 0.01             |
| C                                                    | 12.83          | 0.13        | 12.88        | 12.61        | 12.96        | 12.70            | 12.91            | 12.21                   | 0.14        | 12.15        | 12.06        | 12.53         | 12.11            | 12.27            |
| O                                                    | 51.02          | 0.48        | 51.21        | 50.14        | 51.60        | 50.65            | 51.30            | 48.64                   | 0.54        | 48.42        | 48.05        | 49.96         | 48.28            | 48.90            |
| <b>Total</b>                                         | <b>99.44</b>   | <b>0.25</b> | <b>99.48</b> | <b>98.87</b> | <b>99.80</b> | <b>99.39</b>     | <b>99.52</b>     | <b>99.63</b>            | <b>0.25</b> | <b>99.62</b> | <b>98.86</b> | <b>100.02</b> | <b>99.47</b>     | <b>99.81</b>     |
| <b>Mineral formula based on 6 total oxygen atoms</b> |                |             |              |              |              |                  |                  |                         |             |              |              |               |                  |                  |
| Si [apfu]                                            | 0.00           | 0.00        | 0.00         | 0.00         | 0.00         | 0.00             | 0.00             | 0.00                    | 0.00        | 0.00         | 0.00         | 0.00          | 0.00             | 0.00             |
| Fe                                                   | 0.08           | 0.03        | 0.06         | 0.05         | 0.16         | 0.05             | 0.09             | 0.31                    | 0.06        | 0.34         | 0.20         | 0.37          | 0.26             | 0.35             |
| Mn                                                   | 0.02           | 0.01        | 0.02         | 0.01         | 0.05         | 0.02             | 0.03             | 0.07                    | 0.02        | 0.07         | 0.04         | 0.11          | 0.07             | 0.09             |
| Mg                                                   | 0.88           | 0.08        | 0.91         | 0.73         | 0.97         | 0.83             | 0.92             | 0.58                    | 0.07        | 0.54         | 0.51         | 0.75          | 0.53             | 0.62             |
| Ca                                                   | 1.00           | 0.05        | 0.99         | 0.95         | 1.12         | 0.98             | 1.00             | 1.02                    | 0.02        | 1.02         | 0.99         | 1.08          | 1.00             | 1.03             |
| S                                                    | 0.00           | 0.00        | 0.00         | 0.00         | 0.00         | 0.00             | 0.00             | 0.00                    | 0.00        | 0.00         | 0.00         | 0.01          | 0.00             | 0.00             |
| C                                                    | 2.01           | 0.00        | 2.01         | 2.00         | 2.02         | 2.01             | 2.01             | 2.01                    | 0.01        | 2.01         | 2.00         | 2.02          | 2.00             | 2.01             |
| <b>Total</b>                                         | <b>3.99</b>    | <b>0.00</b> | <b>3.99</b>  | <b>3.98</b>  | <b>3.99</b>  | <b>3.99</b>      | <b>3.99</b>      | <b>3.99</b>             | <b>0.01</b> | <b>3.99</b>  | <b>3.97</b>  | <b>4.00</b>   | <b>3.99</b>      | <b>4.00</b>      |

Table 5. *continued*

| Elements                                             | Calcite [n=5] |             |              |              |              |              |              |
|------------------------------------------------------|---------------|-------------|--------------|--------------|--------------|--------------|--------------|
|                                                      | Av            | Stdev       | Med          | Min          | Max          | 25th         | 75th         |
| SiO <sub>2</sub> [wt%]                               | 0.05          | 0.08        | 0.01         | 0.01         | 0.19         | 0.01         | 0.10         |
| FeO                                                  | 0.29          | 0.24        | 0.20         | 0.12         | 0.69         | 0.12         | 0.51         |
| MnO                                                  | 0.56          | 0.12        | 0.54         | 0.40         | 0.70         | 0.46         | 0.67         |
| MgO                                                  | 0.32          | 0.12        | 0.29         | 0.20         | 0.52         | 0.23         | 0.42         |
| CaO                                                  | 53.60         | 0.69        | 53.43        | 52.85        | 54.50        | 52.99        | 54.31        |
| SO <sub>3</sub>                                      | 0.03          | 0.02        | 0.02         | 0.02         | 0.06         | 0.02         | 0.05         |
| CO <sub>2</sub>                                      | 44.19         | 0.09        | 44.20        | 44.07        | 44.30        | 44.10        | 44.28        |
| <b>Total</b>                                         | <b>99.05</b>  | <b>0.32</b> | <b>99.11</b> | <b>98.66</b> | <b>99.45</b> | <b>98.73</b> | <b>99.35</b> |
| Si [wt%]                                             | 0.09          | 0.00        | 0.09         | 0.09         | 0.09         | 0.09         | 0.09         |
| Fe                                                   | 0.23          | 0.19        | 0.16         | 0.09         | 0.54         | 0.09         | 0.40         |
| Mn                                                   | 0.44          | 0.09        | 0.42         | 0.31         | 0.54         | 0.36         | 0.52         |
| Mg                                                   | 0.19          | 0.07        | 0.17         | 0.12         | 0.31         | 0.14         | 0.25         |
| Ca                                                   | 38.31         | 0.49        | 38.18        | 37.78        | 38.95        | 37.87        | 38.82        |
| S                                                    | 0.01          | 0.01        | 0.01         | 0.01         | 0.03         | 0.01         | 0.02         |
| C                                                    | 12.06         | 0.03        | 12.06        | 12.03        | 12.09        | 12.04        | 12.09        |
| O                                                    | 47.79         | 0.09        | 47.81        | 47.66        | 47.89        | 47.69        | 47.87        |
| <b>Total</b>                                         | <b>99.04</b>  | <b>0.33</b> | <b>99.11</b> | <b>98.65</b> | <b>99.44</b> | <b>98.72</b> | <b>99.34</b> |
| <b>Mineral formula based on 3 total oxygen atoms</b> |               |             |              |              |              |              |              |
| Si [apfu]                                            | 0.00          | 0.00        | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         |
| Fe                                                   | 0.00          | 0.00        | 0.00         | 0.00         | 0.01         | 0.00         | 0.01         |
| Mn                                                   | 0.01          | 0.00        | 0.01         | 0.01         | 0.01         | 0.01         | 0.01         |
| Mg                                                   | 0.01          | 0.00        | 0.01         | 0.01         | 0.01         | 0.01         | 0.01         |
| Ca                                                   | 0.96          | 0.01        | 0.96         | 0.95         | 0.97         | 0.95         | 0.97         |
| S                                                    | 0.00          | 0.00        | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         |
| C                                                    | 1.01          | 0.00        | 1.01         | 1.00         | 1.01         | 1.01         | 1.01         |
| <b>Total</b>                                         | <b>1.99</b>   | <b>0.00</b> | <b>1.99</b>  | <b>1.99</b>  | <b>1.99</b>  | <b>1.99</b>  | <b>1.99</b>  |

**Table 6.** Summary statistics for analyzed metal oxide phases. Abbreviations: 25<sup>th</sup> – 25<sup>th</sup> percentile, 75<sup>th</sup> – 75<sup>th</sup> percentile, apfu – atoms per formula unit, at% - atomic percentage, Av – average, Max – maximum, Med – median, Min – minimum, n – number of analyzed grains, Stdev – standard deviation, wt% - weight percentage

| <b>Arsenian Valentinite [n=4]</b>              |               |              |               |               |               |                        |                        |
|------------------------------------------------|---------------|--------------|---------------|---------------|---------------|------------------------|------------------------|
| <b>Elements</b>                                | <b>Av</b>     | <b>Stdev</b> | <b>Med</b>    | <b>Min</b>    | <b>Max</b>    | <b>25<sup>th</sup></b> | <b>75<sup>th</sup></b> |
| Hg [wt%]                                       | 0.04          | 0.04         | 0.04          | 0.00          | 0.07          | 0.00                   | 0.07                   |
| Pb                                             | 0.07          | 0.05         | 0.06          | 0.02          | 0.14          | 0.03                   | 0.12                   |
| Fe                                             | 0.01          | 0.00         | 0.01          | 0.00          | 0.01          | 0.00                   | 0.01                   |
| Co                                             | 0.03          | 0.02         | 0.02          | 0.01          | 0.05          | 0.01                   | 0.04                   |
| Ni                                             | 0.24          | 0.27         | 0.19          | 0.00          | 0.57          | 0.01                   | 0.52                   |
| Mn                                             | 0.00          | 0.00         | 0.00          | 0.00          | 0.00          | 0.00                   | 0.00                   |
| S                                              | 0.01          | 0.00         | 0.01          | 0.01          | 0.02          | 0.01                   | 0.02                   |
| As                                             | 9.46          | 4.41         | 9.97          | 3.72          | 14.20         | 5.01                   | 13.42                  |
| Sb                                             | 75.91         | 4.77         | 75.02         | 71.24         | 82.37         | 71.87                  | 80.84                  |
| O_calculated                                   | 14.12         | 0.50         | 14.14         | 13.63         | 14.56         | 13.66                  | 14.55                  |
| Ag                                             | 0.04          | 0.05         | 0.03          | 0.00          | 0.11          | 0.01                   | 0.09                   |
| Bi                                             | 0.08          | 0.01         | 0.08          | 0.06          | 0.09          | 0.07                   | 0.09                   |
| <b>Total</b>                                   | <b>100.00</b> | <b>0.00</b>  | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>          | <b>100.00</b>          |
| Hg [wt%]                                       | 0.01          | 0.01         | 0.01          | 0.00          | 0.03          | 0.00                   | 0.03                   |
| Pb                                             | 0.04          | 0.04         | 0.03          | 0.01          | 0.09          | 0.01                   | 0.08                   |
| Fe                                             | 0.00          | 0.00         | 0.00          | 0.00          | 0.00          | 0.00                   | 0.00                   |
| Co                                             | 0.04          | 0.02         | 0.03          | 0.02          | 0.07          | 0.02                   | 0.06                   |
| Ni                                             | 0.51          | 0.60         | 0.40          | 0.00          | 1.24          | 0.01                   | 1.12                   |
| Mn                                             | 0.00          | 0.00         | 0.00          | 0.00          | 0.00          | 0.00                   | 0.00                   |
| S                                              | 0.04          | 0.00         | 0.04          | 0.04          | 0.04          | 0.04                   | 0.04                   |
| As                                             | 2.59          | 3.36         | 1.60          | 0.02          | 7.14          | 0.03                   | 6.14                   |
| Sb                                             | 31.00         | 10.99        | 30.97         | 19.43         | 42.62         | 20.60                  | 41.42                  |
| O                                              | 65.80         | 13.20        | 64.71         | 54.13         | 79.63         | 54.32                  | 78.36                  |
| Ag                                             | 0.02          | 0.03         | 0.00          | 0.00          | 0.06          | 0.00                   | 0.05                   |
| Bi                                             | 0.01          | 0.01         | 0.01          | 0.00          | 0.02          | 0.00                   | 0.02                   |
| <b>Total</b>                                   | <b>100.00</b> | <b>0.00</b>  | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>          | <b>100.00</b>          |
| HgO [wt%]                                      | 0.04          | 0.04         | 0.04          | 0.00          | 0.08          | 0.00                   | 0.08                   |
| PbO                                            | 0.08          | 0.06         | 0.07          | 0.02          | 0.16          | 0.03                   | 0.14                   |
| FeO                                            | 0.01          | 0.01         | 0.01          | 0.00          | 0.01          | 0.00                   | 0.01                   |
| CoO                                            | 0.03          | 0.02         | 0.03          | 0.01          | 0.06          | 0.02                   | 0.05                   |
| NiO                                            | 0.30          | 0.35         | 0.24          | 0.00          | 0.73          | 0.01                   | 0.66                   |
| MnO                                            | 0.00          | 0.00         | 0.00          | 0.00          | 0.00          | 0.00                   | 0.00                   |
| SO3                                            | 0.04          | 0.01         | 0.03          | 0.03          | 0.05          | 0.03                   | 0.05                   |
| As2O3                                          | 12.50         | 5.82         | 13.16         | 4.91          | 18.75         | 6.61                   | 17.71                  |
| Sb2O3                                          | 91.06         | 5.72         | 89.99         | 85.46         | 98.81         | 86.22                  | 96.98                  |
| Ag2O                                           | 0.04          | 0.05         | 0.03          | 0.00          | 0.12          | 0.01                   | 0.10                   |
| Bi2O                                           | 0.09          | 0.01         | 0.10          | 0.07          | 0.10          | 0.08                   | 0.10                   |
| <b>Mineral formula based on 3 oxygen atoms</b> |               |              |               |               |               |                        |                        |
| Hg [apfu]                                      | 0.00          | 0.00         | 0.00          | 0.00          | 0.00          | 0.00                   | 0.00                   |
| Pb                                             | 0.00          | 0.00         | 0.00          | 0.00          | 0.00          | 0.00                   | 0.00                   |
| Fe                                             | 0.00          | 0.00         | 0.00          | 0.00          | 0.00          | 0.00                   | 0.00                   |
| Co                                             | 0.00          | 0.00         | 0.00          | 0.00          | 0.00          | 0.00                   | 0.00                   |
| Ni                                             | 0.01          | 0.01         | 0.01          | 0.00          | 0.02          | 0.00                   | 0.02                   |
| Mn                                             | 0.00          | 0.00         | 0.00          | 0.00          | 0.00          | 0.00                   | 0.00                   |
| S                                              | 0.00          | 0.00         | 0.00          | 0.00          | 0.00          | 0.00                   | 0.00                   |
| As                                             | 0.32          | 0.14         | 0.34          | 0.13          | 0.47          | 0.17                   | 0.44                   |
| Sb                                             | 1.60          | 0.15         | 1.58          | 1.44          | 1.79          | 1.47                   | 1.75                   |
| Ag                                             | 0.00          | 0.00         | 0.00          | 0.00          | 0.00          | 0.00                   | 0.00                   |
| Bi                                             | 0.00          | 0.00         | 0.00          | 0.00          | 0.00          | 0.00                   | 0.00                   |

|              |             |             |             |             |             |             |             |
|--------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| <b>Total</b> | <b>2.04</b> | <b>0.00</b> | <b>2.04</b> | <b>2.04</b> | <b>2.04</b> | <b>2.04</b> | <b>2.04</b> |
|--------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|

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Table 6. *continued*

| Elements                                       | Av            | Stdev       | Stibioclaudeite [n=10] |               |               | 25 <sup>th</sup> | 75 <sup>th</sup> |
|------------------------------------------------|---------------|-------------|------------------------|---------------|---------------|------------------|------------------|
|                                                |               |             | Med                    | Min           | Max           |                  |                  |
| Hg [wt%]                                       | 0.04          | 0.03        | 0.02                   | 0.01          | 0.08          | 0.01             | 0.07             |
| Pb                                             | 0.07          | 0.04        | 0.06                   | 0.03          | 0.16          | 0.03             | 0.08             |
| Fe                                             | 0.13          | 0.13        | 0.07                   | 0.02          | 0.37          | 0.04             | 0.26             |
| Co                                             | 0.07          | 0.09        | 0.02                   | 0.00          | 0.22          | 0.01             | 0.17             |
| Ni                                             | 0.08          | 0.08        | 0.03                   | 0.01          | 0.24          | 0.01             | 0.15             |
| Mn                                             | 0.03          | 0.02        | 0.02                   | 0.01          | 0.08          | 0.02             | 0.05             |
| Ca                                             | 0.06          | 0.06        | 0.04                   | 0.00          | 0.20          | 0.02             | 0.08             |
| S                                              | 0.02          | 0.02        | 0.01                   | 0.00          | 0.07          | 0.00             | 0.02             |
| As                                             | 35.09         | 2.19        | 35.91                  | 31.64         | 37.82         | 32.57            | 36.48            |
| Sb                                             | 50.87         | 2.69        | 50.13                  | 46.83         | 56.66         | 49.45            | 52.08            |
| O_calculated                                   | 13.48         | 1.15        | 13.66                  | 11.07         | 15.00         | 12.95            | 14.13            |
| Ag                                             | 0.05          | 0.05        | 0.03                   | 0.01          | 0.15          | 0.01             | 0.09             |
| Bi                                             | 0.15          | 0.06        | 0.13                   | 0.09          | 0.27          | 0.10             | 0.18             |
| <b>Total</b>                                   | <b>100.00</b> | <b>0.00</b> | <b>100.00</b>          | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>    | <b>100.00</b>    |
| Hg [at%]                                       | 0.01          | 0.01        | 0.01                   | 0.00          | 0.03          | 0.00             | 0.02             |
| Pb                                             | 0.02          | 0.01        | 0.02                   | 0.01          | 0.04          | 0.01             | 0.02             |
| Fe                                             | 0.14          | 0.14        | 0.07                   | 0.02          | 0.38          | 0.04             | 0.28             |
| Co                                             | 0.07          | 0.09        | 0.02                   | 0.00          | 0.21          | 0.01             | 0.16             |
| Ni                                             | 0.07          | 0.08        | 0.03                   | 0.01          | 0.23          | 0.01             | 0.14             |
| Mn                                             | 0.04          | 0.03        | 0.03                   | 0.01          | 0.08          | 0.02             | 0.05             |
| Ca                                             | 0.08          | 0.09        | 0.06                   | 0.00          | 0.28          | 0.03             | 0.11             |
| S                                              | 0.03          | 0.03        | 0.02                   | 0.00          | 0.11          | 0.01             | 0.03             |
| As                                             | 26.98         | 1.50        | 27.54                  | 24.19         | 28.49         | 26.10            | 27.90            |
| Sb                                             | 24.14         | 2.18        | 23.59                  | 20.99         | 29.34         | 23.18            | 25.22            |
| O                                              | 48.44         | 2.36        | 48.73                  | 43.63         | 51.46         | 47.22            | 50.11            |
| Ag                                             | 0.03          | 0.03        | 0.01                   | 0.00          | 0.08          | 0.01             | 0.05             |
| Bi                                             | 0.04          | 0.02        | 0.04                   | 0.02          | 0.08          | 0.03             | 0.05             |
| <b>Total</b>                                   | <b>100.00</b> | <b>0.00</b> | <b>100.00</b>          | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>    | <b>100.00</b>    |
| HgO [wt%]                                      | 0.04          | 0.03        | 0.03                   | 0.01          | 0.09          | 0.01             | 0.07             |
| PbO                                            | 0.08          | 0.05        | 0.07                   | 0.03          | 0.18          | 0.04             | 0.09             |
| FeO                                            | 0.17          | 0.17        | 0.09                   | 0.02          | 0.48          | 0.05             | 0.34             |
| CoO                                            | 0.09          | 0.12        | 0.02                   | 0.00          | 0.28          | 0.01             | 0.22             |
| NiO                                            | 0.10          | 0.11        | 0.04                   | 0.01          | 0.31          | 0.01             | 0.19             |
| MnO                                            | 0.04          | 0.03        | 0.03                   | 0.01          | 0.10          | 0.02             | 0.06             |
| CaO                                            | 0.08          | 0.09        | 0.06                   | 0.00          | 0.27          | 0.02             | 0.11             |
| SO <sub>3</sub>                                | 0.04          | 0.05        | 0.02                   | 0.00          | 0.16          | 0.01             | 0.05             |
| As <sub>2</sub> O <sub>3</sub>                 | 46.33         | 2.90        | 47.41                  | 41.77         | 49.93         | 43.00            | 48.16            |
| Sb <sub>2</sub> O <sub>3</sub>                 | 61.03         | 3.23        | 60.14                  | 56.17         | 67.97         | 59.32            | 62.48            |
| Ag <sub>2</sub> O                              | 0.05          | 0.05        | 0.03                   | 0.01          | 0.16          | 0.01             | 0.10             |
| Bi <sub>2</sub> O                              | 0.18          | 0.07        | 0.16                   | 0.10          | 0.32          | 0.12             | 0.21             |
| <b>Mineral formula based on 3 oxygen atoms</b> |               |             |                        |               |               |                  |                  |
| Hg [apfu]                                      | 0.00          | 0.00        | 0.00                   | 0.00          | 0.00          | 0.00             | 0.00             |
| Pb                                             | 0.00          | 0.00        | 0.00                   | 0.00          | 0.00          | 0.00             | 0.00             |
| Fe                                             | 0.01          | 0.01        | 0.00                   | 0.00          | 0.01          | 0.00             | 0.01             |
| Co                                             | 0.00          | 0.00        | 0.00                   | 0.00          | 0.01          | 0.00             | 0.01             |
| Ni                                             | 0.00          | 0.00        | 0.00                   | 0.00          | 0.01          | 0.00             | 0.01             |
| Mn                                             | 0.00          | 0.00        | 0.00                   | 0.00          | 0.00          | 0.00             | 0.00             |
| Mg                                             | 0.09          | 0.00        | 0.09                   | 0.09          | 0.09          | 0.09             | 0.09             |
| Ca                                             | 0.00          | 0.00        | 0.00                   | 0.00          | 0.01          | 0.00             | 0.00             |
| S                                              | 0.00          | 0.00        | 0.00                   | 0.00          | 0.00          | 0.00             | 0.00             |
| As                                             | 1.02          | 0.06        | 1.04                   | 0.92          | 1.09          | 0.96             | 1.05             |
| Sb                                             | 0.91          | 0.05        | 0.89                   | 0.84          | 1.01          | 0.88             | 0.95             |

|              |             |             |             |             |             |             |             |
|--------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Ag           | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        |
| Bi           | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        |
| <b>Total</b> | <b>2.03</b> | <b>0.00</b> | <b>2.03</b> | <b>2.03</b> | <b>2.04</b> | <b>2.03</b> | <b>2.03</b> |

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Table 6. *continued*

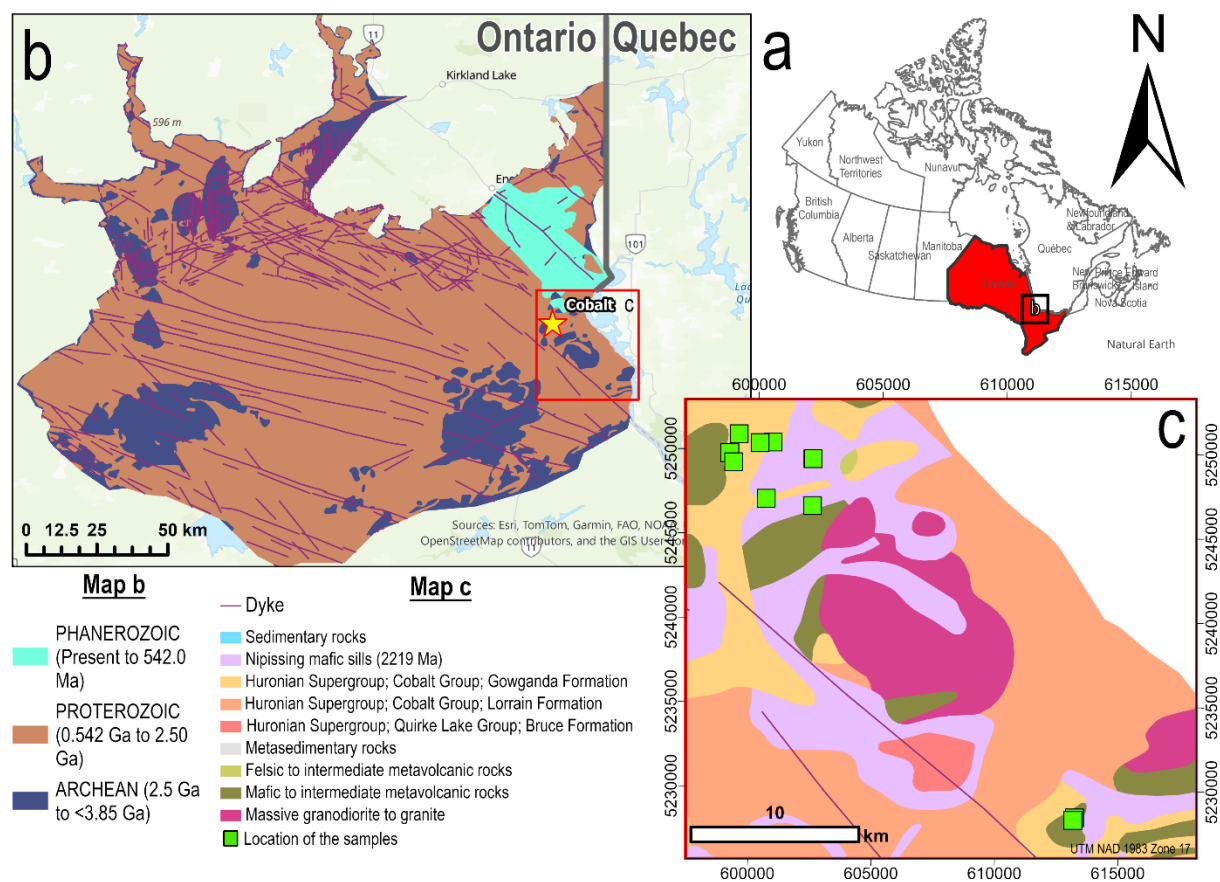
| Arsenian Annabergite [n=11]                    |               |             |               |               |               |                  |                  |
|------------------------------------------------|---------------|-------------|---------------|---------------|---------------|------------------|------------------|
| Elements                                       | Av            | Stdev       | Med           | Min           | Max           | 25 <sup>th</sup> | 75 <sup>th</sup> |
| Si [wt%]                                       | 0.08          | 0.03        | 0.08          | 0.05          | 0.13          | 0.05             | 0.10             |
| Hg                                             | 0.06          | 0.04        | 0.06          | 0.02          | 0.13          | 0.02             | 0.10             |
| Pb                                             | 0.04          | 0.03        | 0.03          | 0.00          | 0.08          | 0.01             | 0.07             |
| Fe                                             | 0.91          | 0.45        | 0.99          | 0.02          | 1.57          | 0.63             | 1.23             |
| Co                                             | 0.65          | 0.58        | 0.47          | 0.15          | 1.94          | 0.22             | 0.79             |
| Ni                                             | 28.78         | 1.31        | 28.84         | 26.43         | 30.35         | 27.74            | 30.00            |
| Mn                                             | 0.48          | 0.27        | 0.42          | 0.16          | 1.07          | 0.32             | 0.68             |
| Mg                                             | 0.24          | 0.20        | 0.19          | 0.02          | 0.64          | 0.07             | 0.42             |
| Ca                                             | 0.66          | 0.66        | 0.47          | 0.14          | 2.51          | 0.31             | 0.76             |
| S                                              | 0.03          | 0.04        | 0.02          | 0.01          | 0.12          | 0.01             | 0.03             |
| As                                             | 24.55         | 2.15        | 24.91         | 20.96         | 28.77         | 22.70            | 25.52            |
| Sb                                             | 4.14          | 2.69        | 2.82          | 1.46          | 8.66          | 1.86             | 6.83             |
| O_calculated                                   | 38.84         | 1.31        | 38.83         | 35.41         | 40.40         | 38.55            | 39.79            |
| Ag                                             | 0.64          | 1.21        | 0.24          | 0.01          | 3.61          | 0.05             | 0.47             |
| Bi                                             | 0.21          | 0.21        | 0.17          | 0.04          | 0.56          | 0.06             | 0.37             |
| <b>Total</b>                                   | <b>100.00</b> | <b>0.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>    | <b>100.00</b>    |
| Si [at%]                                       | 0.09          | 0.03        | 0.08          | 0.05          | 0.14          | 0.05             | 0.11             |
| Hg                                             | 0.01          | 0.01        | 0.01          | 0.00          | 0.02          | 0.00             | 0.01             |
| Pb                                             | 0.01          | 0.00        | 0.00          | 0.00          | 0.01          | 0.00             | 0.01             |
| Fe                                             | 0.49          | 0.24        | 0.52          | 0.01          | 0.83          | 0.33             | 0.66             |
| Co                                             | 0.33          | 0.29        | 0.24          | 0.07          | 0.97          | 0.11             | 0.39             |
| Ni                                             | 14.63         | 0.73        | 14.69         | 13.59         | 16.14         | 13.99            | 15.06            |
| Mn                                             | 0.26          | 0.15        | 0.23          | 0.09          | 0.58          | 0.17             | 0.36             |
| Mg                                             | 0.30          | 0.24        | 0.23          | 0.02          | 0.78          | 0.08             | 0.51             |
| Ca                                             | 0.49          | 0.49        | 0.35          | 0.10          | 1.85          | 0.23             | 0.57             |
| S                                              | 0.03          | 0.03        | 0.02          | 0.01          | 0.11          | 0.01             | 0.03             |
| As                                             | 9.79          | 0.96        | 9.66          | 8.42          | 11.99         | 9.06             | 10.08            |
| Sb                                             | 1.02          | 0.66        | 0.70          | 0.35          | 2.14          | 0.47             | 1.68             |
| O                                              | 72.43         | 1.23        | 72.86         | 69.09         | 73.39         | 71.93            | 73.11            |
| Ag                                             | 0.18          | 0.34        | 0.07          | 0.00          | 1.01          | 0.01             | 0.13             |
| Bi                                             | 0.03          | 0.03        | 0.03          | 0.01          | 0.08          | 0.01             | 0.05             |
| <b>Total</b>                                   | <b>100.00</b> | <b>0.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b>    | <b>100.00</b>    |
| SiO2 [wt%]                                     | 0.17          | 0.06        | 0.17          | 0.10          | 0.27          | 0.11             | 0.22             |
| HgO                                            | 0.07          | 0.05        | 0.06          | 0.02          | 0.14          | 0.02             | 0.11             |
| PbO                                            | 0.04          | 0.04        | 0.03          | 0.00          | 0.09          | 0.01             | 0.09             |
| FeO                                            | 1.17          | 0.58        | 1.28          | 0.03          | 2.02          | 0.81             | 1.58             |
| CoO                                            | 0.82          | 0.74        | 0.60          | 0.19          | 2.47          | 0.28             | 1.01             |
| NiO                                            | 36.62         | 1.66        | 36.70         | 33.63         | 38.63         | 35.30            | 38.17            |
| MnO                                            | 0.62          | 0.35        | 0.54          | 0.21          | 1.39          | 0.41             | 0.88             |
| MgO                                            | 1.90          | 0.20        | 1.84          | 1.67          | 2.29          | 1.72             | 2.08             |
| CaO                                            | 0.92          | 0.92        | 0.66          | 0.19          | 3.52          | 0.44             | 1.07             |
| SO3                                            | 0.08          | 0.09        | 0.04          | 0.02          | 0.30          | 0.04             | 0.08             |
| As2O3                                          | 32.42         | 2.84        | 32.88         | 27.68         | 37.99         | 29.96            | 33.69            |
| Sb2O3                                          | 4.97          | 3.22        | 3.38          | 1.75          | 10.39         | 2.23             | 8.20             |
| Ag2O                                           | 0.68          | 1.30        | 0.26          | 0.02          | 3.87          | 0.05             | 0.51             |
| Bi2O                                           | 0.25          | 0.25        | 0.21          | 0.05          | 0.66          | 0.07             | 0.44             |
| <b>Mineral formula based on 8 oxygen atoms</b> |               |             |               |               |               |                  |                  |
| Si [apfu]                                      | 0.02          | 0.01        | 0.02          | 0.01          | 0.03          | 0.01             | 0.03             |
| Hg                                             | 0.00          | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Pb                                             | 0.00          | 0.00        | 0.00          | 0.00          | 0.00          | 0.00             | 0.00             |
| Fe                                             | 0.11          | 0.05        | 0.12          | 0.00          | 0.20          | 0.08             | 0.16             |
| Co                                             | 0.08          | 0.07        | 0.06          | 0.02          | 0.23          | 0.03             | 0.09             |

|              |             |             |             |             |             |             |             |
|--------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Ni           | 3.40        | 0.15        | 3.46        | 3.15        | 3.60        | 3.31        | 3.56        |
| Mn           | 0.06        | 0.03        | 0.05        | 0.02        | 0.13        | 0.04        | 0.09        |
| Mg           | 0.33        | 0.04        | 0.33        | 0.27        | 0.39        | 0.30        | 0.36        |
| Ca           | 0.11        | 0.11        | 0.08        | 0.02        | 0.42        | 0.05        | 0.14        |
| S            | 0.01        | 0.01        | 0.00        | 0.00        | 0.03        | 0.00        | 0.01        |
| As           | 2.27        | 0.14        | 2.27        | 2.00        | 2.46        | 2.15        | 2.36        |
| Sb           | 0.24        | 0.16        | 0.16        | 0.08        | 0.51        | 0.10        | 0.40        |
| Ag           | 0.04        | 0.08        | 0.02        | 0.00        | 0.24        | 0.00        | 0.03        |
| Bi           | 0.01        | 0.01        | 0.01        | 0.00        | 0.02        | 0.00        | 0.01        |
| <b>Total</b> | <b>6.67</b> | <b>0.04</b> | <b>6.67</b> | <b>6.60</b> | <b>6.72</b> | <b>6.64</b> | <b>6.69</b> |

**Table 7.** Summary statistics for (trace) elements analyzed by LA-ICP-MS in carbonates. All values are in parts per million (ppm). Abbreviations: 25<sup>th</sup> – 25<sup>th</sup> percentile, 75<sup>th</sup> – 75<sup>th</sup> percentile, Av – average, Med – median, Min – minimum, Max – maximum, Stdev – standard deviation

| Elem<br>ents | All analyses [n=29]       |               |               |               |               |               |               | Lattice bound metals [n=12] |              |               |               |               |               |               |
|--------------|---------------------------|---------------|---------------|---------------|---------------|---------------|---------------|-----------------------------|--------------|---------------|---------------|---------------|---------------|---------------|
|              | Av                        | Stdev         | Med           | Min           | Max           | 25th          | 75th          | Av                          | Stdev        | Med           | Min           | Max           | 25th          | 75th          |
| Ca           | 235931                    | 56718         | 217000        | 217000        | 400000        | 217000        | 217000        | 232250                      | 52828        | 217000        | 217000        | 400000        | 217000        | 217000        |
| Mg           | 70170                     | 39747         | 63571         | 417           | 150088        | 56514         | 101388        | 55485                       | 42840        | 57279         | 417           | 150088        | 13959         | 65833         |
| Fe           | 52394                     | 42581         | 29337         | 1026          | 127591        | 17550         | 96533         | 69388                       | 46221        | 94601         | 1026          | 127591        | 9509          | 96716         |
| Al           | 87.99                     | 165           | 28.00         | 0.32          | 646           | 5.46          | 58.41         | 25.76                       | 27.20        | 17.49         | 0.32          | 76.26         | 1.07          | 51.88         |
| Si           | 1592                      | 4187          | 293           | 62            | 18243         | 116           | 705           | 229                         | 185          | 145           | 62            | 700           | 103           | 338           |
| S            | 266                       | 192           | 209           | 111           | 1135          | 170           | 256           | 187                         | 61.51        | 177           | 111           | 351           | 147           | 202           |
| Co           | 377                       | 977           | 17.04         | 0.24          | 3806          | 12.86         | 192           | 9.71                        | 6.22         | 12.86         | 0.24          | 17.77         | 2.55          | 14.46         |
| Ni           | 24482                     | 116635        | 28.94         | 0.33          | 629407        | 2.88          | 938           | 5.16                        | 6.61         | 2.13          | 0.33          | 22.21         | 1.01          | 8.14          |
| As           | 26809                     | 117343        | 412           | 9.82          | 634059        | 78.96         | 2735          | 94.91                       | 97.22        | 69.31         | 9.82          | 318           | 17.17         | 169           |
| Se           | 24.88                     | 9.64          | 22            | 13.35         | 59.66         | 19.94         | 25.80         | 20.58                       | 7.36         | 19.88         | 13.35         | 41.08         | 15.28         | 20.55         |
| Ag           | 4476                      | 13756         | 23.35         | 0.06          | 70950         | 2.52          | 308           | 23.31                       | 43.74        | 2.46          | 0.06          | 142           | 0.82          | 21.85         |
| Sb           | 25563                     | 71506         | 487           | 0.40          | 344229        | 33.44         | 6010          | 36.29                       | 43.10        | 17.90         | 0.40          | 113           | 1.02          | 68.57         |
| Te           | 0.74                      | 0.52          | 0.63          | 0.07          | 3.04          | 0.49          | 0.85          | 0.55                        | 0.29         | 0.58          | 0.07          | 1.17          | 0.36          | 0.71          |
| Bi           | 946                       | 4604          | 4.24          | 0.09          | 24861         | 0.44          | 132           | 2.35                        | 4.62         | 0.20          | 0.09          | 16.30         | 0.10          | 3.11          |
| <b>Sum1</b>  | <b>358495</b>             | <b>49405</b>  | <b>366884</b> | <b>219378</b> | <b>494679</b> | <b>343134</b> | <b>376729</b> | <b>357123</b>               | <b>74022</b> | <b>370388</b> | <b>219378</b> | <b>494679</b> | <b>350838</b> | <b>378605</b> |
| <b>Sum2</b>  | <b>82945</b>              | <b>304516</b> | <b>1631</b>   | <b>153</b>    | <b>16.3e5</b> | <b>372</b>    | <b>13992</b>  | <b>379</b>                  | <b>205</b>   | <b>306</b>    | <b>153</b>    | <b>766</b>    | <b>238</b>    | <b>485</b>    |
| Elem<br>ents | Inclusion of metals [n=5] |               |               |               |               |               |               | Oxidized ore phases [n=12]  |              |               |               |               |               |               |
|              | Av                        | Stdev         | Med           | Min           | Max           | 25th          | 75th          | Av                          | Stdev        | Med           | Min           | Max           | 25th          | 75th          |
| Ca           | 253600                    | 81840         | 217000        | 217000        | 400000        | 217000        | 308500        | 232250                      | 52828        | 217000        | 217000        | 400000        | 217000        | 217000        |
| [ppm]        |                           |               |               |               |               |               |               |                             |              |               |               |               |               |               |
| Mg           | 87375                     | 48578         | 107992        | 660           | 112493        | 52527         | 111915        | 77686                       | 29942        | 89876         | 4208          | 102499        | 60385         | 101001        |
| Fe           | 13396                     | 8168          | 16803         | 1698          | 21023         | 4974          | 20114         | 51650                       | 38048        | 29597         | 1363          | 100926        | 23725         | 97072         |
| Al           | 402                       | 195           | 365           | 178           | 646           | 223           | 600           | 19.28                       | 17.26        | 10.17         | 0.47          | 57.10         | 6.61          | 33.51         |
| Si           | 7249                      | 8474          | 2090          | 632           | 18243         | 677           | 16400         | 597                         | 913          | 311           | 94.38         | 3407          | 142           | 649           |
| S            | 572                       | 321           | 454           | 357           | 1135          | 377           | 827           | 217                         | 31.93        | 223           | 166           | 263           | 188           | 244           |
| Co           | 1959                      | 1691          | 1145          | 317           | 3806          | 543           | 3783          | 84.06                       | 94.54        | 28.50         | 3.62          | 287           | 16.02         | 168           |
| Ni           | 141112                    | 273276        | 20927         | 2589          | 629407        | 8354          | 333962        | 363                         | 618          | 72.05         | 6.37          | 1903          | 29.66         | 437           |
| As           | 152372                    | 269383        | 34645         | 23937         | 634059        | 24857         | 338751        | 1205                        | 1042         | 704           | 287           | 3077          | 446           | 2280          |
| Se           | 38.01                     | 14.41         | 36.26         | 24.17         | 59.66         | 25.26         | 51.64         | 23.72                       | 2.64         | 23.93         | 20.33         | 29.49         | 21.44         | 25.42         |
| Ag           | 25152                     | 26020         | 14287         | 7866          | 70950         | 9915          | 45820         | 315                         | 826          | 33.86         | 2.52          | 2912          | 9.29          | 188           |
| Sb           | 141405                    | 124390        | 123475        | 6745          | 344229        | 50129         | 241647        | 2822                        | 3723         | 1093          | 33            | 10903         | 585           | 4487          |
| Te           | 1.37                      | 0.98          | 1.24          | 0.59          | 3.04          | 0.66          | 2.14          | 0.68                        | 0.18         | 0.70          | 0.39          | 0.94          | 0.54          | 0.87          |
| Bi           | 382                       | 343           | 288           | 109           | 971           | 147           | 664           | 2126                        | 7160         | 5.87          | 0.69          | 24861         | 2.36          | 141           |
| <b>Sum1</b>  | <b>354371</b>             | <b>27302</b>  | <b>341795</b> | <b>336589</b> | <b>402358</b> | <b>338594</b> | <b>376437</b> | <b>361586</b>               | <b>21034</b> | <b>356790</b> | <b>336358</b> | <b>405571</b> | <b>344947</b> | <b>376196</b> |
| <b>Sum2</b>  | <b>462994</b>             | <b>656292</b> | <b>210525</b> | <b>110409</b> | <b>16.3e5</b> | <b>127933</b> | <b>924290</b> | <b>7156</b>                 | <b>7678</b>  | <b>4271</b>   | <b>1104</b>   | <b>26431</b>  | <b>1632</b>   | <b>11928</b>  |

## Figures.



**Figure 1. Simplified geologic map of the Cobalt Embayment. (a)** Inlay of Canada highlighting the location of map b with black rectangle. **(b)** Simplified geologic map of the Huronian Supergroup with Archean basement and Phanerozoic cover. The red rectangle highlights the location of the study area in c, and the star is the town of Cobalt (Jambor et al., 1971). **(c)** Simplified geologic map of the Cobalt Embayment with sample locations in green rectangles. Detailed sample info is shown in Table 1. Coordinates are in UTM NAD 1983 Zone 17. Map modified after Ontario Geological Survey.

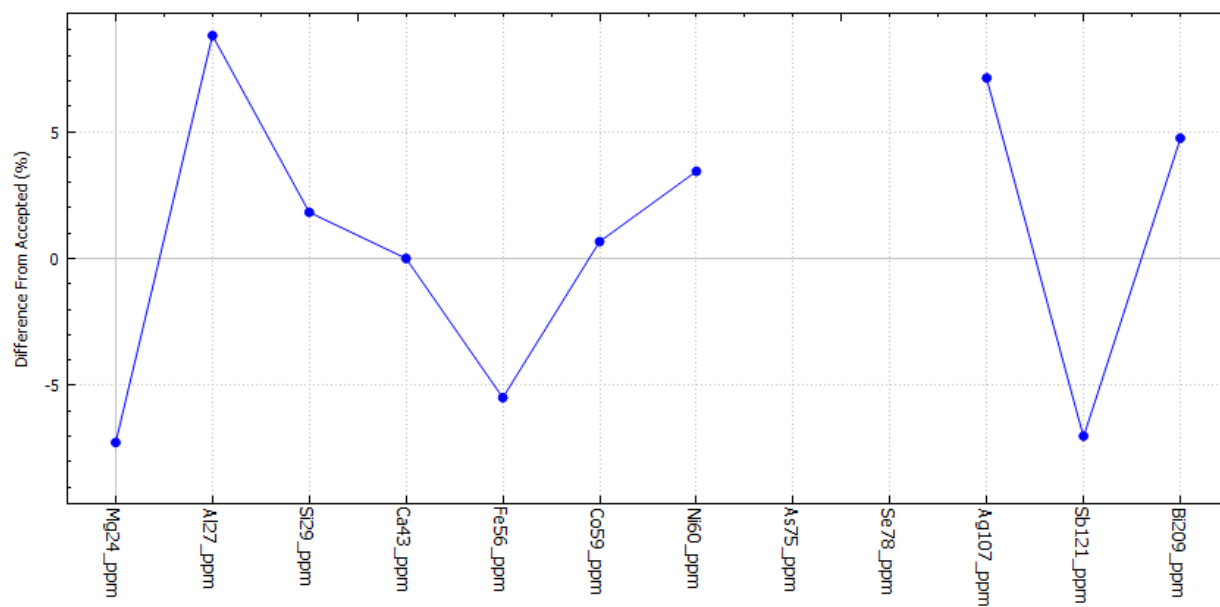
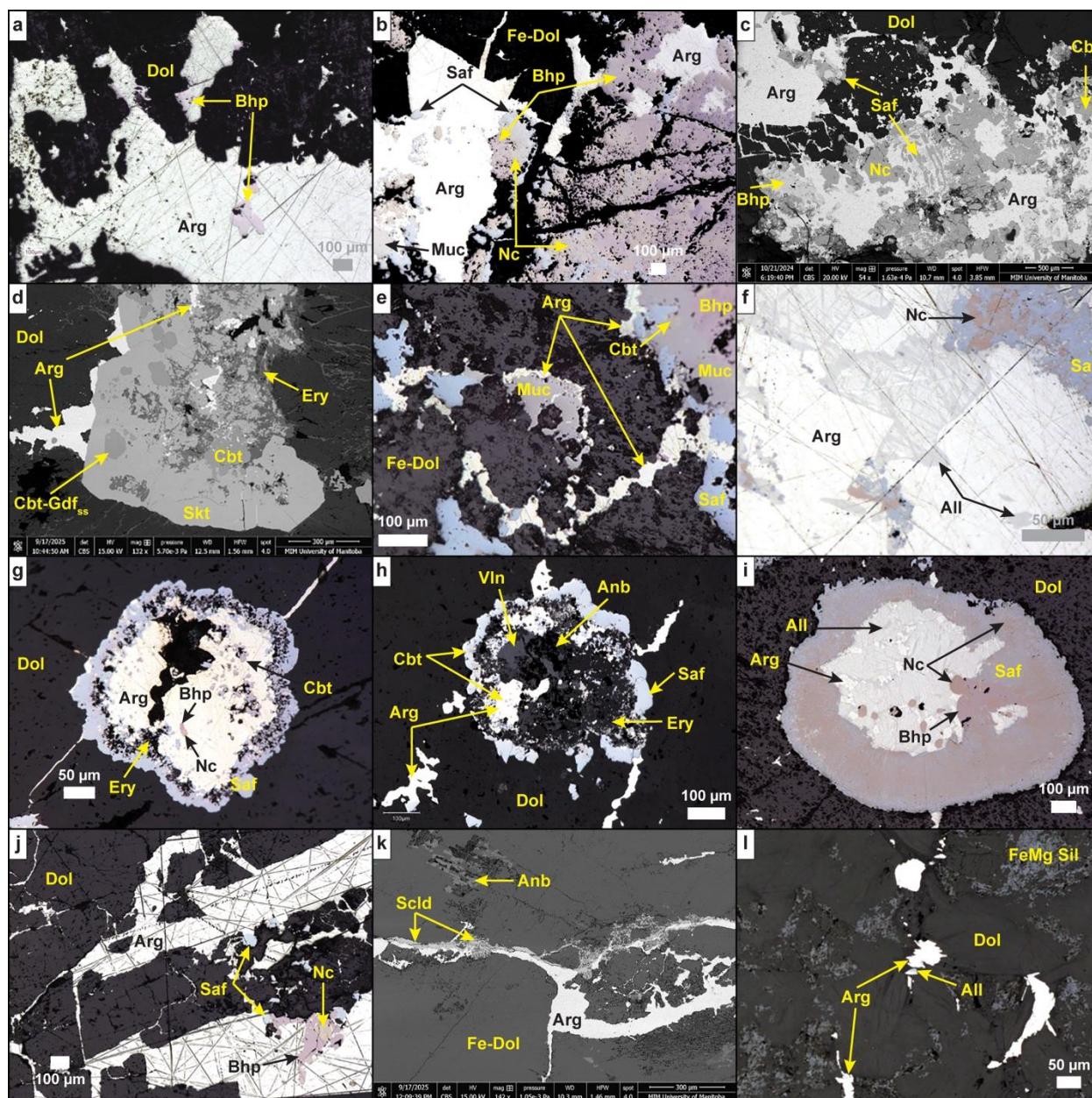
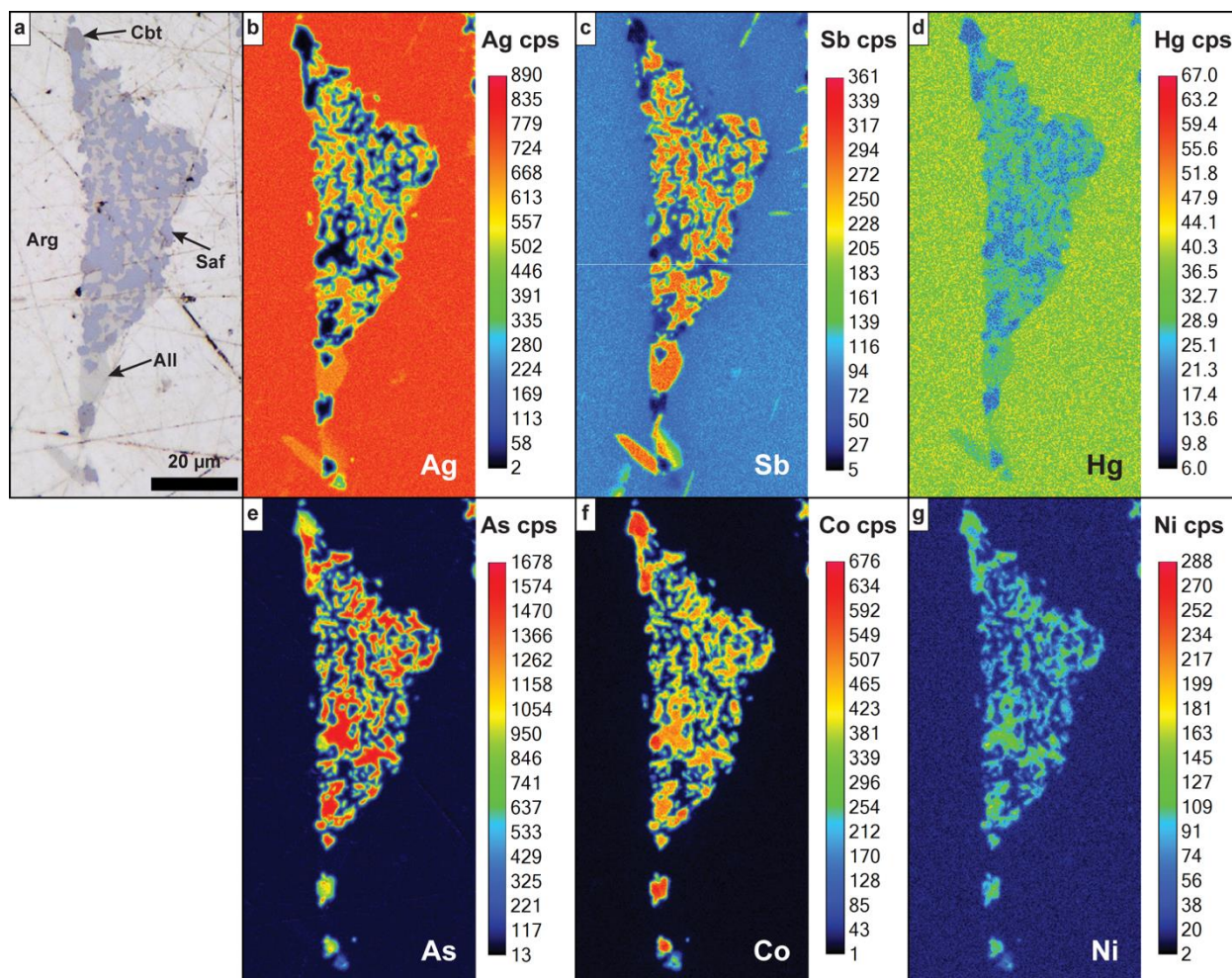


Figure 2. Accuracy displayed for analyzed elements in NIST-610 relative to certified values.

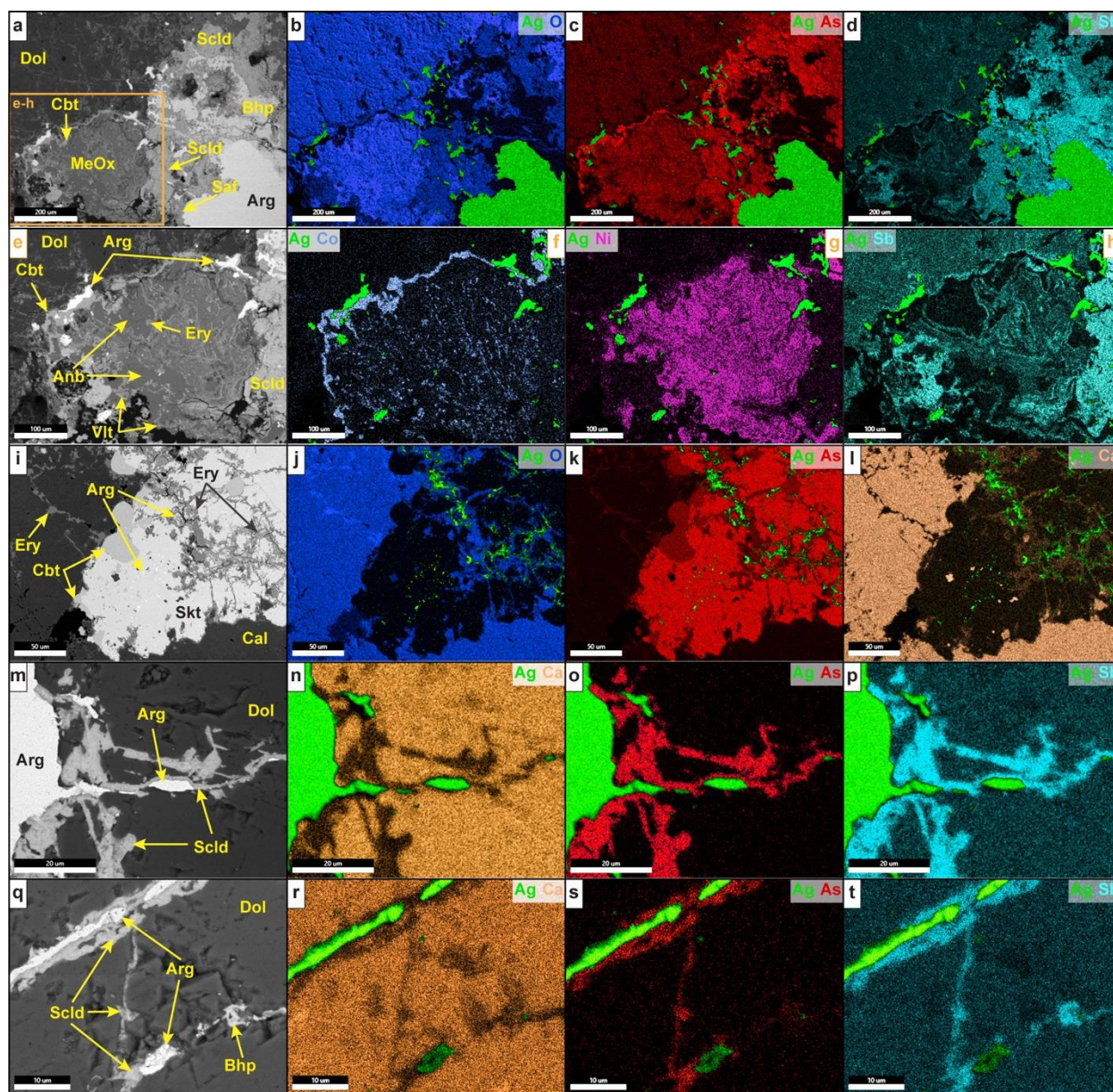


**Figure 3. Ore assemblage and textures of native silver.** (a-f) Massive native silver, (sulph)-arsenides and breithauptite. (a) Massive native silver with breithauptite in dolomite. Smaller grains of silver show anhedral dissemination in carbonate (upper right, reflected light image, M39127, scale bar is 100  $\mu\text{m}$ ). (b) Massive native silver with arsenides (maucherite, nickeline, safflorite) and breithauptite in Fe-dolomite. Arsenides and breithauptite show complex intergrowth. Inclusions in native silver are common (reflected light, M8922, scale bar is 100  $\mu\text{m}$ ). (c) Massive native silver with varying abundance of anhedral (sulph)-arsenides (safflorite, nickeline, cobaltite) and breithauptite in dolomite. Thin native silver veins free of other phases cross-cut dolomite matrix (upper left; back-scattered electron image, M31018, scale bar is 500  $\mu\text{m}$ ). (d) Anhedral, massive skutterudite with inclusions of cobaltite, cobaltite-gersdorffite *solid solution* and irregular native silver. Native silver is either overgrown by skutterudite (left), forms minute, round inclusions, is interstitially in cobaltite (lower centre) or associated with dendritic veinlets of erythrite due to oxidation of skutterudite. (back-scattered electron image, Cob-3b, scale bar is 300  $\mu\text{m}$ ). (e) Massive (sulph)-arsenides and breithauptite occur with native silver which is either on margins of (sulph)-arsenides, forms small, round inclusions, is interstitially in cobaltite, or associated with dendritic veinlets of erythrite. (back-scattered electron image, Cob-3b, scale bar is 300  $\mu\text{m}$ ). (f) Massive native silver with varying abundance of anhedral (sulph)-arsenides (safflorite, nickeline, cobaltite) and breithauptite in dolomite. Thin native silver veins free of other phases cross-cut dolomite matrix (upper left; back-scattered electron image, M31018, scale bar is 500  $\mu\text{m}$ ). (g) Massive native silver with breithauptite in dolomite. Smaller grains of silver show anhedral dissemination in carbonate (upper right, reflected light image, M39127, scale bar is 100  $\mu\text{m}$ ). (h) Massive native silver with arsenides (maucherite, nickeline, safflorite) and breithauptite in Fe-dolomite. Arsenides and breithauptite show complex intergrowth. Inclusions in native silver are common (reflected light, M8922, scale bar is 100  $\mu\text{m}$ ). (i) Massive native silver with varying abundance of anhedral (sulph)-arsenides (safflorite, nickeline, cobaltite) and breithauptite in dolomite. Thin native silver veins free of other phases cross-cut dolomite matrix (upper left; back-scattered electron image, M31018, scale bar is 500  $\mu\text{m}$ ). (j) Anhedral, massive skutterudite with inclusions of cobaltite, cobaltite-gersdorffite *solid solution* and irregular native silver. Native silver is either overgrown by skutterudite (left), forms minute, round inclusions, is interstitially in cobaltite (lower centre) or associated with dendritic veinlets of erythrite due to oxidation of skutterudite. (back-scattered electron image, Cob-3b, scale bar is 300  $\mu\text{m}$ ). (k) Massive (sulph)-arsenides and breithauptite occur with native silver which is either on margins of (sulph)-arsenides, forms small, round inclusions, is interstitially in cobaltite, or associated with dendritic veinlets of erythrite. (back-scattered electron image, Cob-3b, scale bar is 300  $\mu\text{m}$ ). (l) Massive native silver with varying abundance of anhedral (sulph)-arsenides (safflorite, nickeline, cobaltite) and breithauptite in dolomite. Thin native silver veins free of other phases cross-cut dolomite matrix (upper left; back-scattered electron image, M31018, scale bar is 500  $\mu\text{m}$ ).

deformed veinlets or is disseminated in Fe dolomite. (reflected light, M8922, scale bar is 100  $\mu\text{m}$ ). **(f)** Massive native silver with exsolution of allargentum and irregular aggregates of intergrown safflorite, nickeline and allargentum. Exsolution of allargentum is dominantly as thin, geometric exsolution lamellae or, less common, as more irregular, thicker patches often adjacent or in the vicinity of exsolution lamellae. (reflected light, M39035, scale bar is 50  $\mu\text{m}$ ). **(g-i)** Partly oxidized rosettes of native silver. **(g)** Rosette of native silver rimmed by safflorite and with inclusions of cobaltite and breithauptite. Oxidation of safflorite either on the contact to native silver or within it results in the formation of erythrite. Thin native silver veins shoot out from the rosette. (reflected light image, M39035, scale bar is 50  $\mu\text{m}$ ). **(h)** Core of rosette is almost completely oxidized to various metal oxides (valentinite, annabergite, erythrite). Remnant native silver is rimmed by safflorite oxidized to erythrite. Small native silver veinlets shoot off from rosette. Anhedral native silver is disseminated in dolomite. (reflected light, M39011, scale bar is 100  $\mu\text{m}$ ). **(i)** Rosette with core of native silver showing exsolution lamellae of allargentum and inclusions of nickeline. Very fine intergrowth of safflorite with nickeline and local breithauptite overgrew the rosette from the outside. Dolomite is strongly altered and has small irregular, dissemination of native silver. (reflected light, M39035, scale bar is 100  $\mu\text{m}$ ). **(j-k)** Veins of native silver cross-cutting carbonate gangue. **(j)** Network of native silver veins and veinlets, locally rimmed by arsenides and breithauptite. The thinner native silver veinlets cross-cut dolomite along alteration fabrics. (reflected light, M31018, scale bar is 100  $\mu\text{m}$ ). **(k)** Native silver vein that is locally rimmed by oxidized Sb-arsenate (stibioclaudeite, light grey). Fe dolomite is locally altered, even when not cross-cut by native silver veins. (back-scattered electron image, M31018, scale bar is 300  $\mu\text{m}$ ). **(l)** Disseminated native silver in dolomite locally altered to clay phases. Disseminated native silver occur interstitially between carbonate grains and along dolomite margins. (reflected light, Cob-3b, scale bar is 50  $\mu\text{m}$ ). *Mineral abbreviations are after Wanner (2021):* All – allargentum, Anb – annabergite, Arg – native silver, Bhp – breithauptite, Cbt – cobaltite, Cbt-Gdf ss – cobaltite-gersdorffite *solid solution*, Dol – dolomite, Ery – erythrite, Fe-Dol – ferroan dolomite, FeMg Sil- FeMg silicate (clay), Muc – maucherite, Nc – nickeline, Saf – safflorite, Scld – stibioclaudeite, Skt – skutterudite, Vln – valentinite.

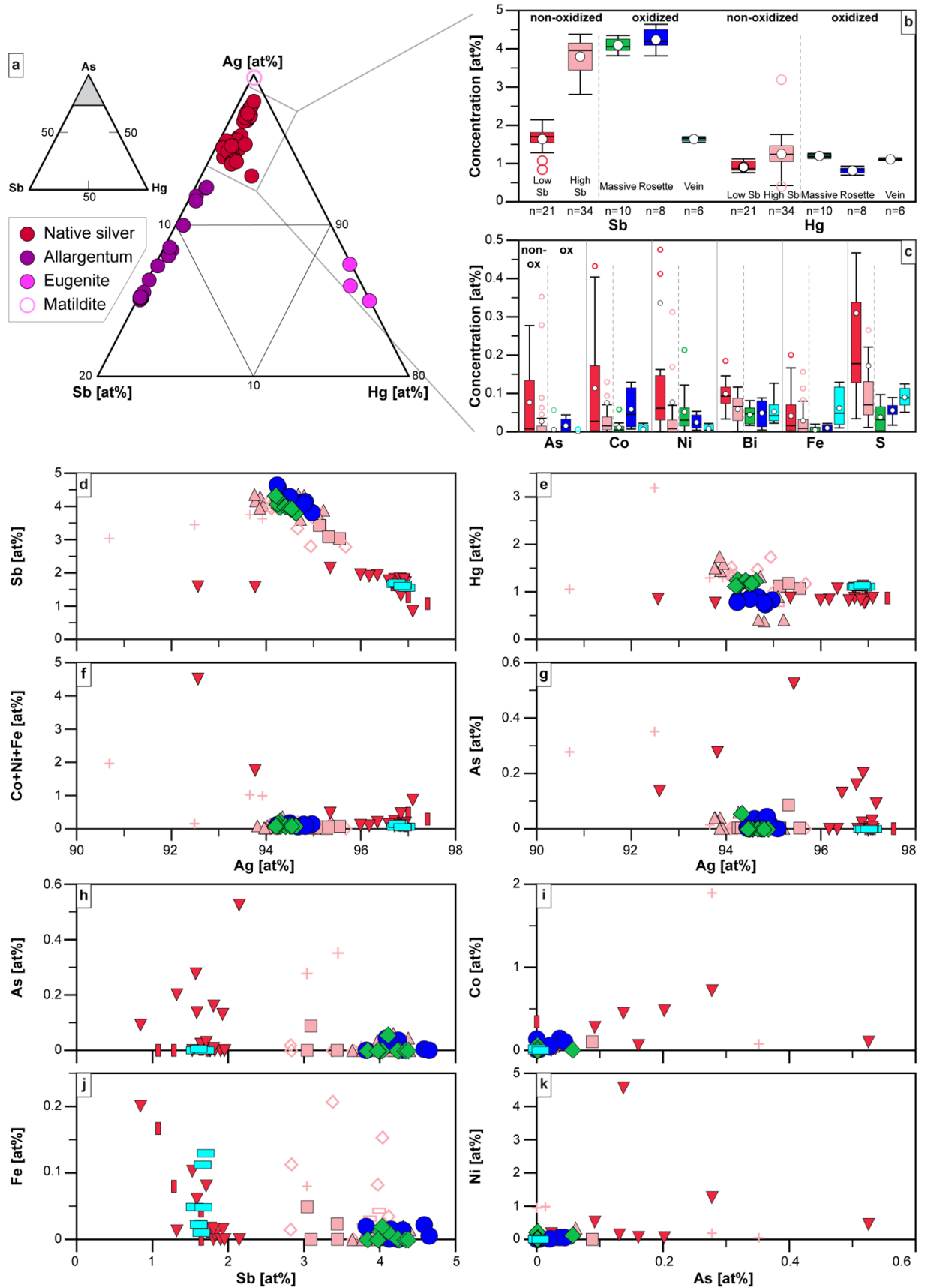


**Figure 4. Compositional map of allargentum intergrown with safflorite and cobaltite in native silver.** Analyses were done on the EPMA. (a) Reflected light image (M39035, scale bar of 20 µm is the same for all images). (b-g) Compositional maps showing counts per second (cps). (b) Ag. (c) Sb. (d) Hg. (e) As. (f) Co. (g) Ni. *Mineral abbreviations are after Wanner (2021): All – allargentum, Arg – native silver, Cbt – cobaltite, Saf – safflorite.*



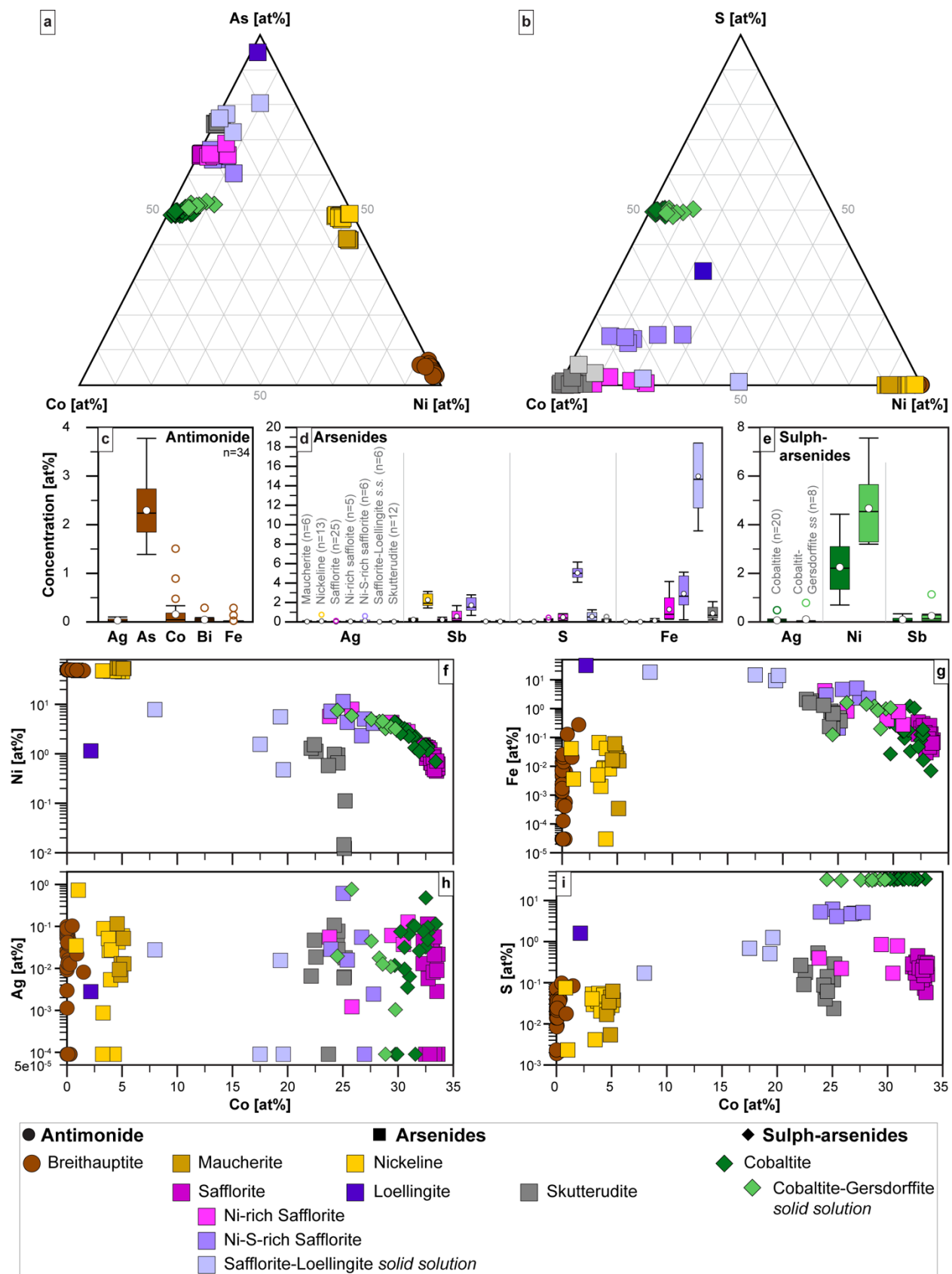
**Figure 5. Assemblages of different native silver textures with metal oxides documented at EDS-SEM. (a-d)** Massive native silver with breithauptite and surrounded by various metal oxides. (M39127, scale bar is 200  $\mu\text{m}$ ). **(a)** Back-scattered image. Orange rectangle highlights close-up of metal oxides shown in (e-h). **(b)** Elemental map of Ag (green) with O (blue). **(c)** Elemental map of Ag (green) with As (red). **(d)** Elemental map of Ag (green) with Sb (turquoise). There is a weak interference of Sb with Ca showing dolomite with weak Sb signal in upper left corner. **(e-h)** Close-up of metal oxide occurrence in dolomite. (M39127, scale bar is 100  $\mu\text{m}$ ). **(e)** Back-scatter electron image shows various metal oxides with small, irregular, disseminated native silver and adjacent to remnant safflorite and breithauptite. Note the banded texture of different metal oxides rimmed by stibioclaudetite. **(f)** Elemental map of Ag (green) with Co (grey-blue). **(g)** Elemental map of Ag (green) with Ni (magenta). **(h)** Elemental map of Ag (green) with Sb (turquoise). There is a weak interference of Sb with Ca showing dolomite with weak Sb signal in upper left corner. **(i-l)** Oxidation of skutterudite. **(i)** Back-scattered electron image of skutterudite with cobaltite inclusions. This is a close-up of Figure 3d. Native silver occurs either as inclusion or within secondary, dendritic veins of erythrite. These veinlets occur both in skutterudite and altered calcite. (Cob-3b, scale bar is 50  $\mu\text{m}$ ). **(j)** Elemental map of Ag

(green) with Co (grey-blue). **(k)** Elemental map of Ag (green) with As (red). **(l)** Elemental map of Ag (green) with Ca (peach). There is a weak interference of Ca with Sb showing erythrite veinlets with weak Sb signal within skutterudite. **(m-p)** Massive native silver with small veinlet and rimmed by stibioclaudeite. (31018, scale bar is 50  $\mu\text{m}$ ). **(m)** Back-scattered electron image of native silver rimmed by AsSb oxide (stibioclaudeite). No other phases are associated with native silver. **(n)** Elemental map of Ag (green) with Ca (peach). **(o)** Elemental map of Ag (green) with As (red). **(p)** Elemental map of Ag (green) with Sb (turquoise). There is a weak interference of Sb with Ca showing dolomite with weak Sb signal in on central to right side. **(q-t)** Thin native silver veinlet cross-cutting altered dolomite and rimmed by stibioclaudeite. (31018, scale bar is 10  $\mu\text{m}$ ). **(q)** Back-scattered electron image of native silver veinlets rimmed by AsSb oxide (stibioclaudeite). Syibioclaudeite veinlets cross-cut dolomite even when not rimming native silver veinlets (centre). Small irregular breithauptite is disseminated in dolomite. **(r)** Elemental map of Ag (green) with Ca (peach). **(s)** Elemental map of Ag (green) with As (red). **(t)** Elemental map of Ag (green) with Sb (turquoise). There is a weak interference of Sb with Ca showing dolomite with weak Sb signal. Mineral abbreviations are after Wanner (2021): Anb – annabergite, Arg – native silver, Bhp – breithauptite, Cbt – cobaltite, Dol – dolomite, Ery – erythrite, Saf – safflorite, Scld – stibioclaudeite, Skt – skutterudite, Vln – valentinite.

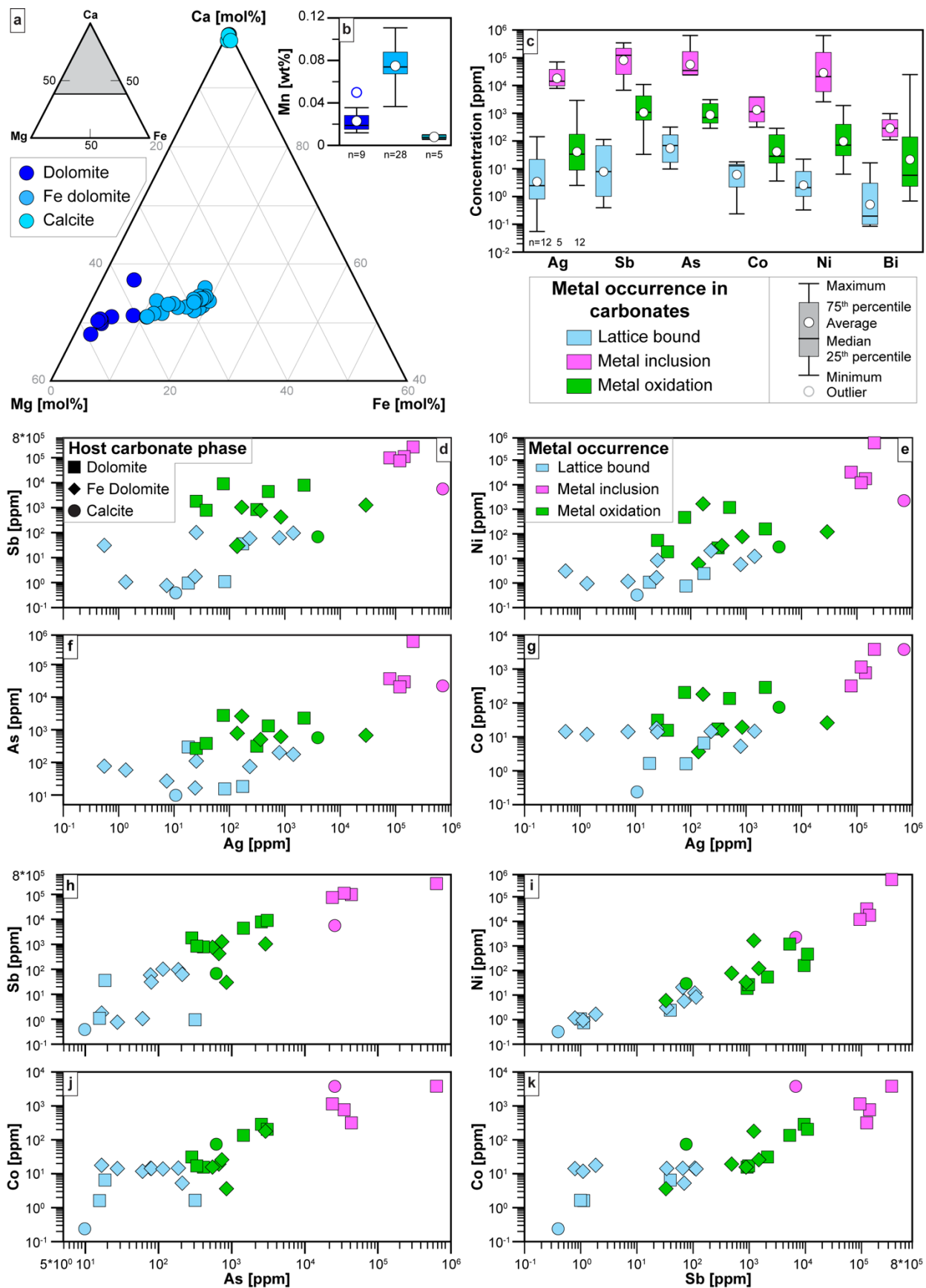


|                       | Silver with non-oxidized assemblage                                                                                                                                               | Silver with oxidized assemblage                                          |
|-----------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------|
| <b>Low Sb silver</b>  | ▼ Massive silver with (sulph-)arsenides and breithauptite<br>■ Silver vein with (sulph-)arsenides and breithauptite                                                               | ■ Silver vein with oxidized rim                                          |
| <b>High Sb silver</b> | ■ Massive silver<br>▲ Massive silver with allargentum<br>◇ Disseminated silver in carbonate<br>□ Silver vein, locally with allargentum<br>+ Inclusions of and interstitial silver | ◆ Massive silver near oxidized area<br>● Silver rosette, partly oxidized |

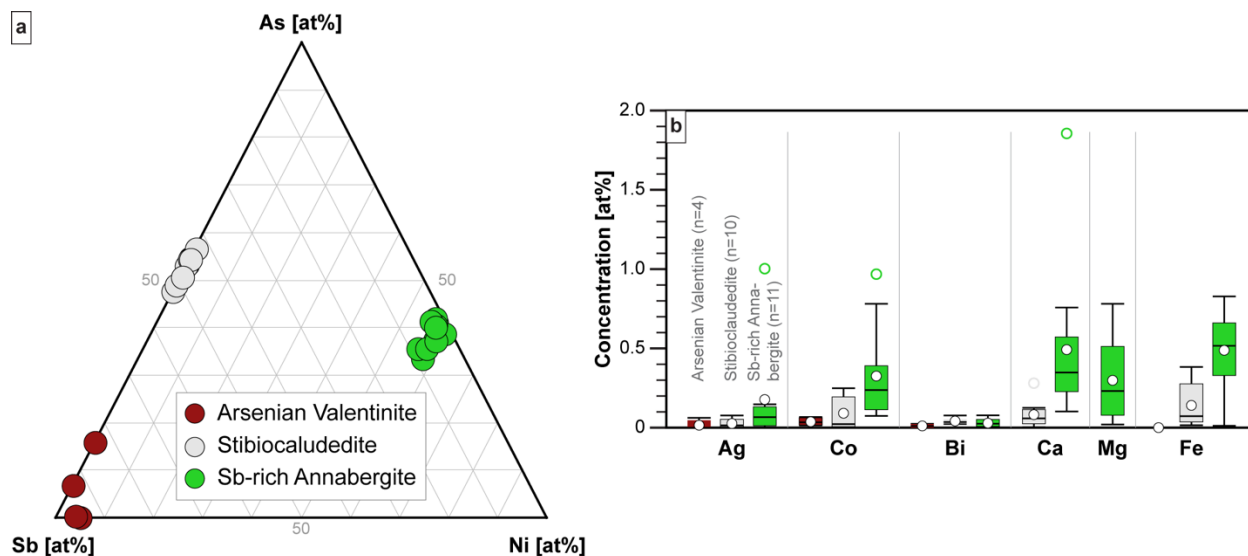
**Figure 6. Major and minor element composition of silver phases analyzed by EPMA.** *previous pages* (a) Ternary plot of Ag-Sb-Hg (in at%) highlighting the compositional variations in native silver, allargentum, and eugenite. Inlay shows range of ternary shown. Composition of native silver with variations regarding textures and association with (non-)oxidized areas is shown in (b-k). (b-c) Box-Whisker plots showing range in minor elements in native silver. Plots are in Tukey mode with a legend shown in Figure 8. (b) Range in Sb and Hg concentration (in at%) in native silver that is associated with no oxidation (i.e., “non-oxidized”) and associated with oxidation (i.e., “oxidized”) of neighbouring phases. (c) Range in As, Co, Fe, Bi and S concentration (in at% in native silver that is associated with no oxidation (non-oxidized) and associated with oxidation (oxidized) of neighbouring phases. Outliers exceeding 0.5 at% are not shown (d-k) Binary plots showing range in silver composition in at% for massive native silver (green), rosettes (blue) and native silver veins (aquamarine) associated with metal oxides. Non-oxidized native silver assemblages reflected by different textures are distinguished into low-Sb (red) and high-Sb (pink) native silver. (d) Ag vs Sb. (e) Ag vs Hg. (f) Ag vs Co+Ni+Fe. (g) Ag vs As. (h) Sb vs As. (i) As vs Co. (j) Sb vs Fe. (k) As vs Ni. *Abbreviations:* at% - atomic percentage., n – number of analyses.



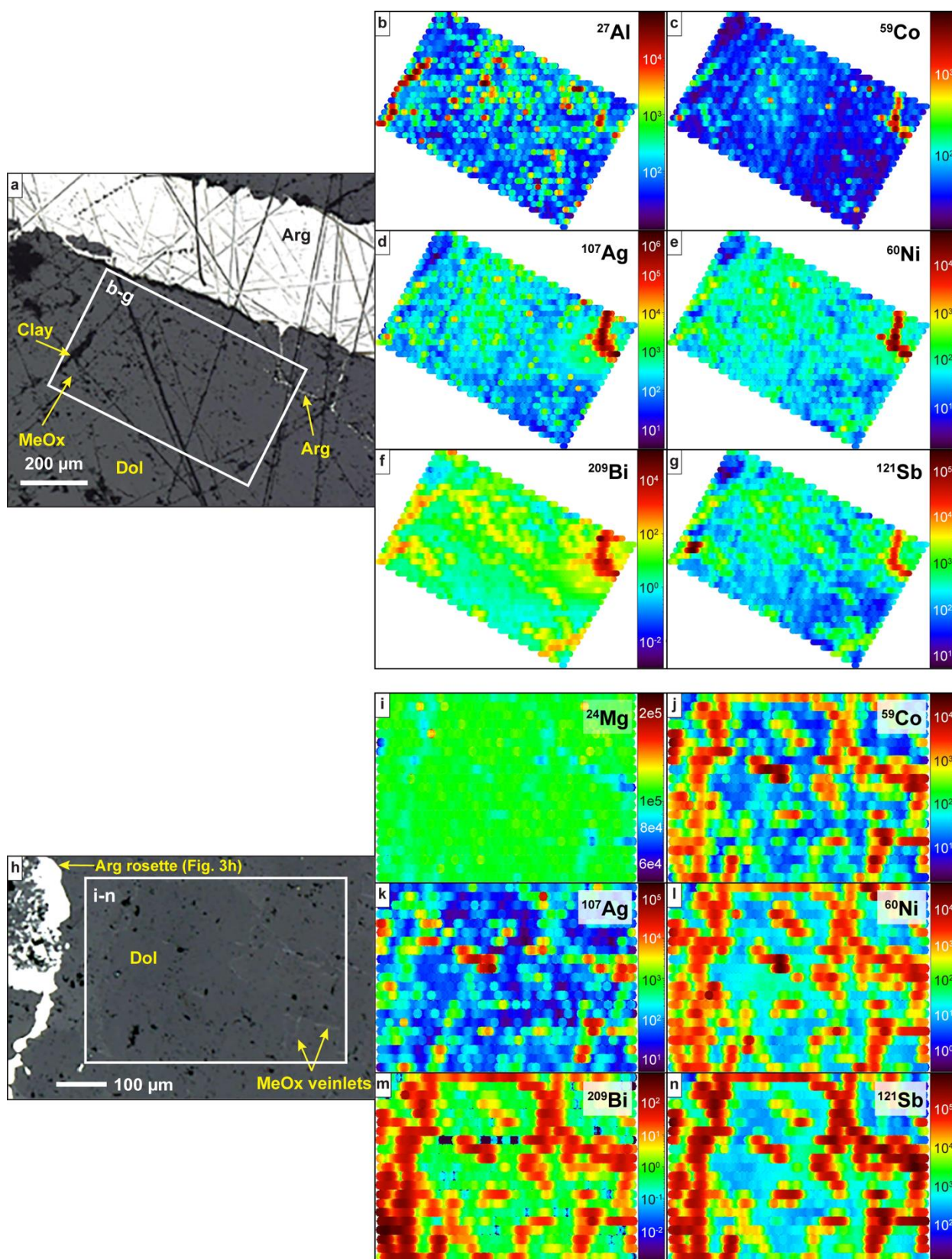
**Figure 7. Major and minor element composition of antimonide, arsenides and sulph-arsenides analyzed by EPMA.** *previous page* **(a-b)** Ternary plot of As-Co-Ni (in at%) highlighting the compositional variations within the various phases. Compositional variations of these phases are shown (b-i). **(c-e)** Box-Whisker plots showing range in minor elements in antimonide, arsenides, and sulph-arsenides. Plots are in Tukey mode with a legend shown in Figure 8. **(b)** Range in Ag, As, Co, Fe, and Bi concentration (in at%) in breithauptite. **(c)** Range in Ag, Sb, S, and Fe in arsenides with at least three analyses. **(d)** Range in Ag, Ni, and Sb in cobaltite and cobaltite-gerssdorffite *solid solution*. **(f-i)** Binary plots showing range in Co and associated elements for arsenides and sulph-arsenides. All units are in at% **(f)** Co vs Ni. **(g)** Co vs Fe. **(h)** Co vs Ag. **(i)** Co vs S. *Abbreviations:* at% – atomic percentage, n – number of analyses.



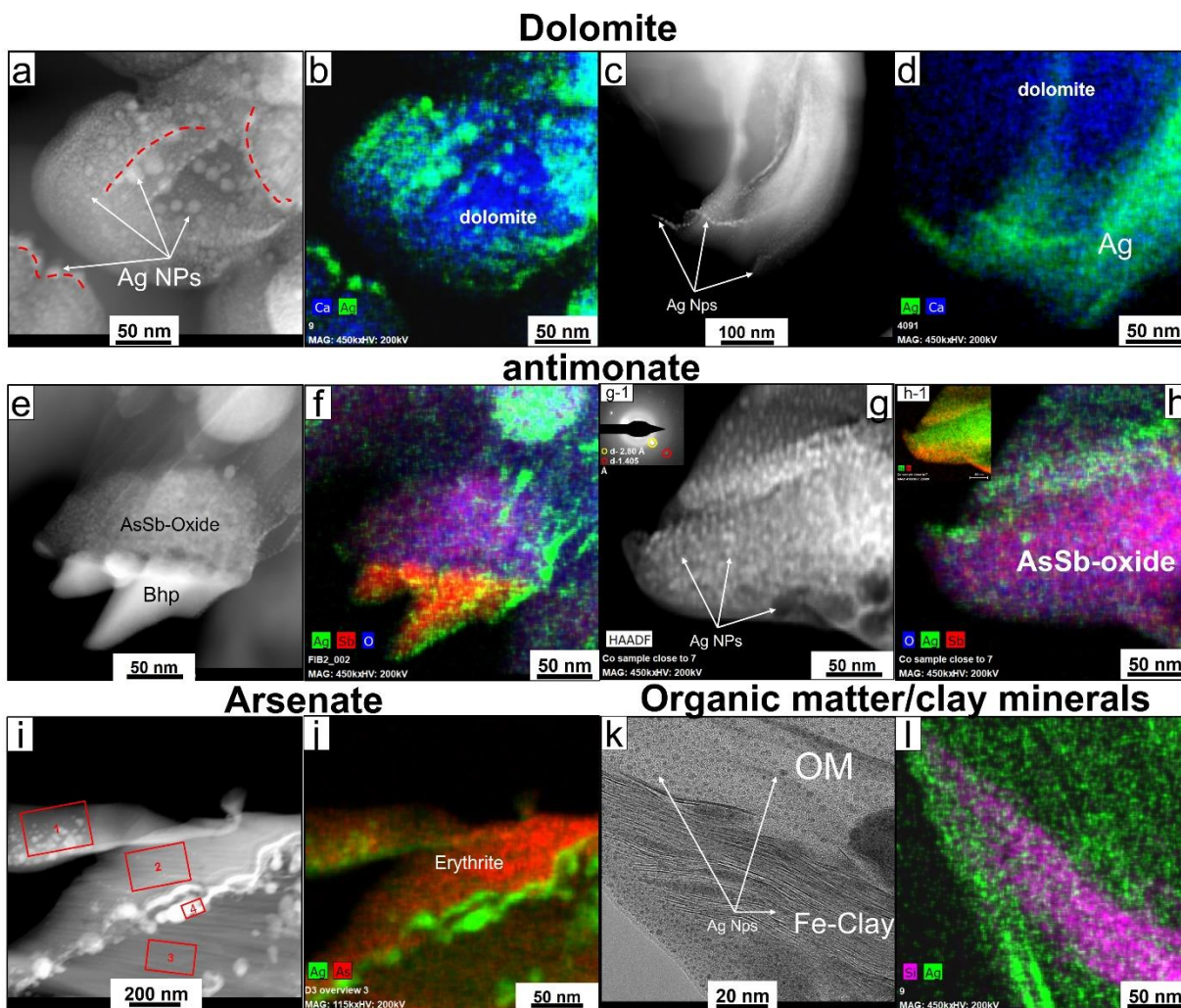
**Figure 8. Major, minor and trace element composition of carbonates analyzed by EPMA and LA-ICP-MS.** *previous page* **(a)** Ternary plot of Ca-Mg-Fe (in mol%) highlighting the compositional variations within the various carbonates. Inlay shows range of ternary. Compositional variations of carbonate phases are shown (b-k). **(b-c)** Box-Whisker plots showing range in minor and trace elements in carbonates with concentration given as wt% and ppm, respectively. **(b)** Range in Mn in carbonates analyzed by EPMA. **(c)** Range in Ag, Sb, As, Co, Ni and Bi analyzed by LA-ICP-MS. Based on how metals occur in carbonates they are distinguished into lattice-bound metals (powder blue), occurring as (micro-)inclusions (magenta) or are associated with oxidation (green). **(d-k)** Binary plots of trace metal content in calcite, dolomite and Fe dolomite for lattice-bound metals, metal inclusions, and metal oxides. **(d)** Ag vs Sb. **(e)** Ag vs Ni. **(f)** Ag vs As. **(g)** Ag vs Co. **(h)** As vs Sb. **(i)** Sb vs Ni. **(j)** As vs Co. **(k)** Sb vs Co. *Abbreviation:* mol% – molecular percentage, n – number of samples, ppm – parts per million, wt% - weight percentage.



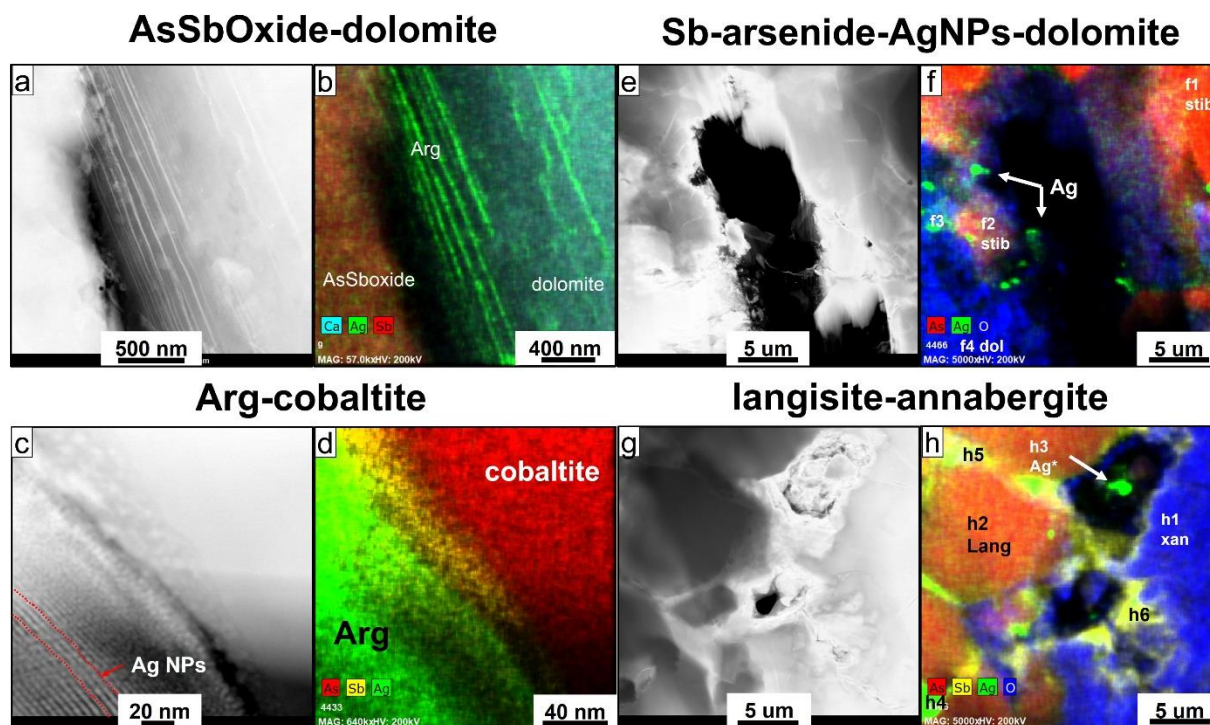
**Figure 9. Major and minor composition of metal oxides analyzed via EPMA. (a)** Ternary plot of As-Sb-Ni (in at%) displaying variations in major composition of arsenian valentinite, stibioclaudeite and Sb-rich annabergite. **(b)** Box-Whisker plot showing range in the three analyzed metal oxide phases. Chalcophile elements Ag, Co and Bi occur in all three phases above detection limit whereas lithophile elements Ca and Mg do not occur in stibioclaudeite (Ca), and arsenian valentinite and stibioclaudeite (Mg). The third element, Fe, prevalent in carbonates is close to detection limit in arsenian valentinite. Plots are in Tukey mode with a legend shown in Figure 8.



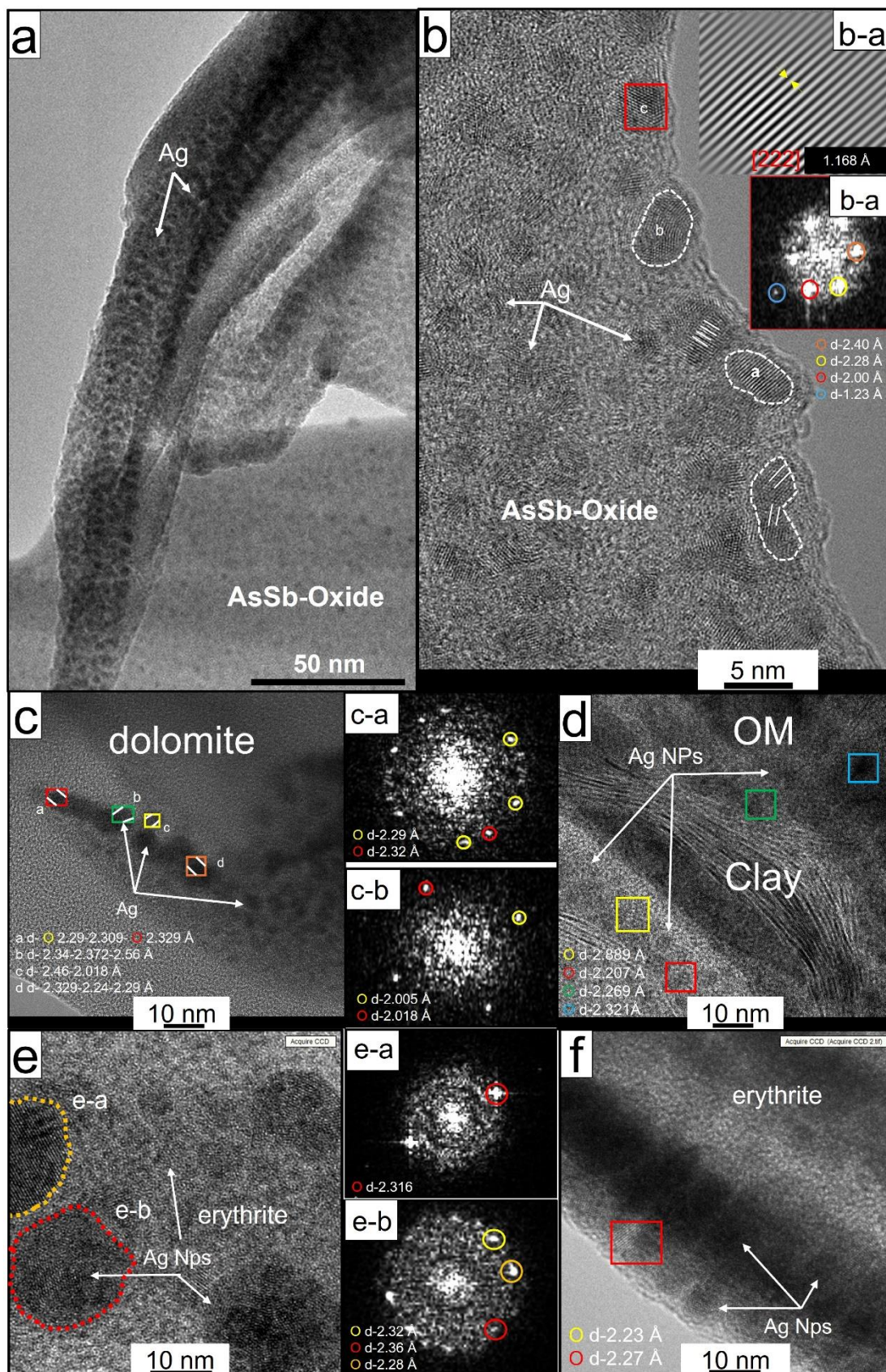
**Figure 10. Compositional maps for carbonates analyzed by LA-ICP-MS.** *previous page* **(a-g)** Dolomite adjacent to native silver vein is locally altered and has small native silver veinlet in upper right. White rectangle shows mapped area. (reflected light, M31018, scale bar is 200  $\mu\text{m}$  and the same for the maps. **(b-g)** Compositional maps with scale bars on right side of each map. Unit is ppm. **(b)**  $^{27}\text{Al}$ . **(c)**  $^{59}\text{Co}$ . **(d)**  $^{107}\text{Ag}$ . **(e)**  $^{60}\text{Ni}$ . **(f)**  $^{209}\text{Bi}$ . **(g)**  $^{121}\text{Sb}$ . **(h-n)** Dolomite near partly oxidized native silver rosette with native silver veinlets (Fig. 3h). Dolomite is strongly altered with thin metal oxide veinlets cross-cutting it. White rectangle shows mapped area (reflected light, M31018, scale bar is 100  $\mu\text{m}$  and the same for (the maps). **(h-n)** Compositional maps with scale bars on right side of each map. Unit is ppm. **(b)**  $^{24}\text{Mg}$ . **(c)**  $^{59}\text{Co}$ . **(d)**  $^{107}\text{Ag}$ . **(e)**  $^{60}\text{Ni}$ . **(f)**  $^{209}\text{Bi}$ . **(g)**  $^{121}\text{Sb}$ . *Mineral abbreviations after Wanner (2021):* Arg – native silver, Dol – dolomite, MeOx – metal oxide.



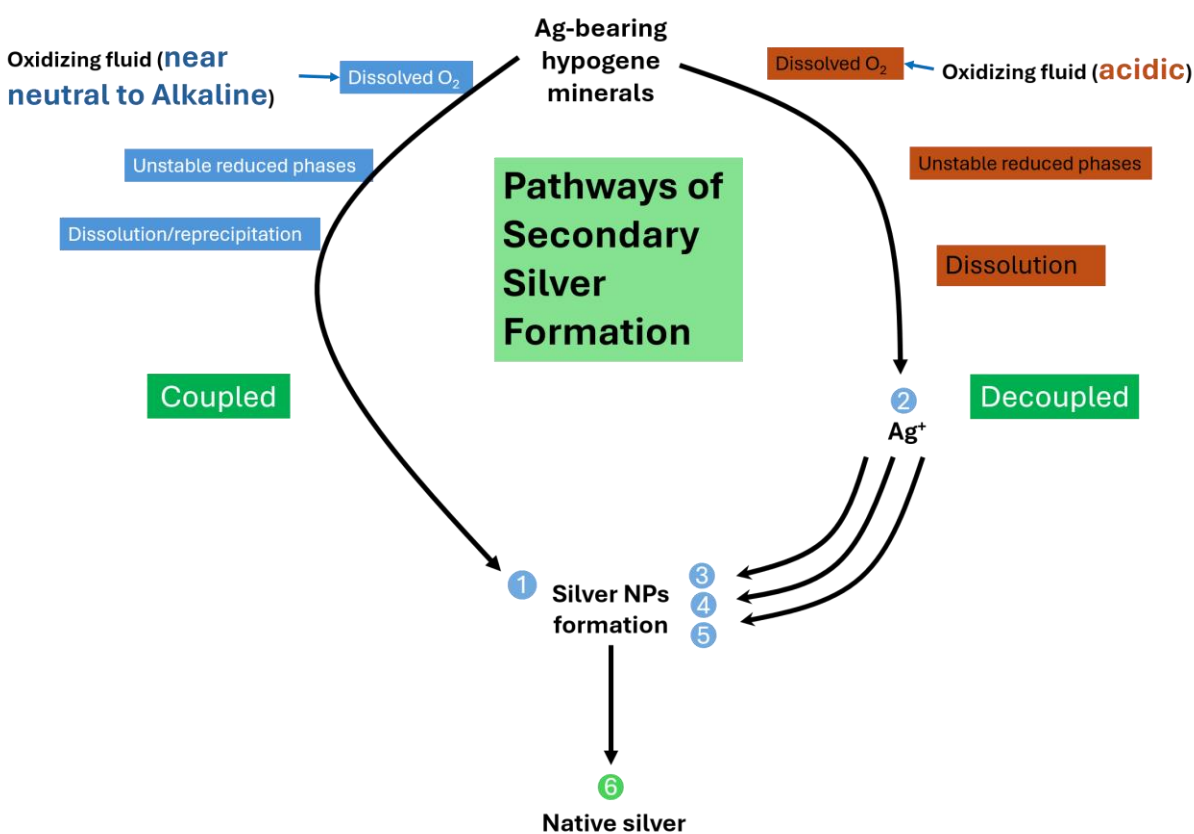
**Figure 11:** Textural and chemical characterization of Ag NPs in diverse mineral matrices using TEM/STEM and EDS mapping from sample C31018a-b. **(a)** STEM image showing Ag NPs in dolomite. **(b)** STEM-EDS elemental map corresponding to **(a)**, showing the distribution of Ag and Ca. **(c)** STEM image showing Ag NPs in dolomite. **(d)** STEM-EDS elemental map corresponding to **(c)**, showing the distribution of Ag and Ca. **(e)** STEM image highlighting Ag NPs within an AsSb-oxide phase. **(f)** STEM-EDS elemental distribution map of Ag, Sb, and O corresponding to **(e)**. **(g)** STEM image showing Ag NPs within an AsSb-oxide phase. **(g1)** Selected area diffraction (SAED) pattern of the matrix shown in **(g)**. **(h)** STEM-EDS elemental distribution map of Ag, Sb, and O corresponding to **(g)**. **(h1)** STEM-EDS elemental distribution map of Sb and Ni. **(i)** STEM image showing Ag NPs within erythrite and four sections marked by red frames. **(j)** STEM-EDS elemental map corresponding to **(i)**, showing the distribution of Ag and As. **(k)** TEM image of the framed area in **(A)** showing Ag NPs associated with Fe-Clay. **(l)** STEM-EDS elemental map corresponding to **(k)**, showing the distribution of Si and Ag.



**Figure 12:** Textural and chemical characterization of silver and Ag NPs at contact interfaces between 2 or more phases. **(a)** STEM image within sample C31018, showing the interface between AsSbOxide-dolomite. **(b)** STEM-EDS of **(A)** showing elemental distributions of Ca, Ag, and Sb. **(c)** STEM image within sample M39127 representing the interface between silver and cobaltite. **(d)** STEM-EDS of **(c)** showing elemental distributions of Ag, As, and Sb. **(e)** Low-magnification STEM image within sample M39127, corresponding to the interface between stibarsen, silver and dolomite. **(f)** Elemental maps of **(e)** showing elemental distributions of As, Sb, and O. **(g)** STEM image within sample M39127, showing the contact between langisite and annabergite. **(h)** STEM-EDS elemental map corresponding to **(g)**, showing the distribution of Ag, As, O, and Sb.



**Figure 13:** Crystallization through particle attachment (CPA) as evidence with TEM images of silver NPs associated with different phases and minerals from sample C31018. **(a)** TEM image showcasing silver NPs forming a wire in AsSb-oxide. **(b)** A high-resolution TEM image of individual and aggregated Ag NPs is shown; the orientation of the lattice fringes in the particle labelled “a” is shown in the inset (b-a). The images were created using fast FFT and inverse FFT algorithms, which filtered out noise in the TEM image. **(c)** Higher magnification TEM image of **(Fig. 11c)** corresponding to individual and aggregated Ag Nps within carbonate (dolomite). The d-spacing corresponding to the distances between the atomic planes at the “a”, “b”, “c”, and “d” locations in (c) is indicated. Insets **(c-a, c-b)** show the FFT patterns for locations “a” and “b”. **(d)** TEM image of silver NPs associated with clay and organic matter (OM). **(e)** Silver Nps in erythrite. **ea-eb-** FFT pattern of “a” and “b” location from E. **(f)** Silver NPs forming a wire in erythrite.



**Figure 14: Model for supergene silver enrichment processes via nanoparticle pathways.** This schematic outlines the key stages: Silver sourced from hypogene minerals; Ag NP formation on various substrates (steps 1–5); and Aggregation into silver (step 6). Each step is further explained in the table below.

**Table 8.** Descriptive summary and explanation of the processes observed in figure 14.

| Pathways | The process                                                                                           | Figures |
|----------|-------------------------------------------------------------------------------------------------------|---------|
| 0        | <ul style="list-style-type: none"> <li>Antimonides and Sulfarsenide with trace Ag contents</li> </ul> | Fig. 7  |
|          | Ag NP formation coupled with dissolution of original Ag-host                                          |         |

|                                                                |                                                                                                                                                                                                                                        |                   |
|----------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------|
| 1                                                              | <ul style="list-style-type: none"> <li>• Direct formation of AgNPs along the dissolving antimonide or sulfarsenide surface</li> </ul>                                                                                                  | Fig. 5, 12        |
| Ag NP formation decoupled from dissolution of original Ag-host |                                                                                                                                                                                                                                        |                   |
| 2                                                              | <ul style="list-style-type: none"> <li>• Oxidizing conditions lead to their dissolution and the release of <math>\text{Ag}^+</math></li> </ul>                                                                                         |                   |
| 3                                                              | <ul style="list-style-type: none"> <li>• Template-directed formation of Ag NPs on <math>\text{Fe}^{2+}</math>- bearing clay mineral surfaces via Eq. 7</li> <li>• Nucleation sites for Ag NPs and prevent their aggregation</li> </ul> | Fig. 11k-l        |
| 4                                                              | <ul style="list-style-type: none"> <li>• Ag NPs formation in organic matter through reduction on reduced functional groups</li> </ul>                                                                                                  | Fig. 11k-l        |
| 5                                                              | <ul style="list-style-type: none"> <li>• Ag NPs formation in highly porous calcite through neutralization of acidic solution</li> </ul>                                                                                                | Fig. 11c-d, 12a-b |
| Crystallization through particle attachment                    |                                                                                                                                                                                                                                        |                   |
| 6                                                              | <ul style="list-style-type: none"> <li>• Ag NPs OA and NOA to silver particles and nanowires</li> </ul>                                                                                                                                | Fig. 13           |

## Chapter 3

### 3.1 Knowledge gaps and open questions

#### 3.1.1 Secondary enrichment models:

By establishing the coupled and decoupled Ag NP formation pathways operating at Cobalt, this study provides a framework for assessing the spatial extent and relative contributions of secondary silver enrichment at the district scale. Ag NP occurrence is linked to the oxidation of hypogene ore phases and the subsequent release of Ag and may represent a mechanism for silver upgrading in the Cobalt embayment, the full-scale extent of which remains to be quantified. Future work should systematically assess the extent of these secondary processes at a regional level, using rock and drill core samples with known depth relationships and spatial context within the Cobalt embayment stratigraphy.

Two questions remain open and merit further investigation. (1) What are the relative contributions of top-down mechanical reworking and bottom-up NP precipitation to the Ag NP populations associated with As-Sb oxide? (2) What is the spatial extent of Ag NP-driven enrichment relative to the primary ore?

Question (1) may be addressed through targeted crystallographic analysis of NP morphologies and grain-boundary characteristics in the samples, as top-down mechanical reworking yields angular NPs with compositions closely matching those of the parent phase, whereas bottom-up precipitation generates euhedral, spherical, crystalline new phases. Further investigation of the spatial relationships between Ag NPs and micro- to macroscale silver, including their relative orientations and proximity, could clarify whether NPs represent daughter products of bulk silver reworking or newly precipitated phases independent of the parent material.

Addressing question (2) requires the systematic characterization of additional Ag occurrences at Cobalt and, where relevant, in other five-element vein deposits. Such investigations would provide insight into element transport pathways, mineral transition sequences, and the conditions governing secondary enrichment, with implications for understanding ore-forming processes in comparable systems worldwide (McLeish et al., 2021; Saunders, 2022). Such investigations are, however, limited by the considerable costs and time demands of nanoscale analysis. Unlike studies conducted at the micrometre scale, nanoscale investigations require multi-scale characterization prior to complex sample preparation, and the size constraints of TEM foils mean that only a small portion of any sample can be examined at high resolution, introducing potential sampling bias that must be acknowledged in the interpretation of results.

Despite these constraints, the nanoscale framework established here for the Cobalt embayment provides a replicable approach for investigating secondary silver enrichment in five-element vein systems, and the open questions identified above define a tractable research agenda for future studies at the district and deposit scale.

### **3.1.2 Five-element vein deposits of Cobalt**

The processes underlying primary native silver deposition remain obscure and highly debated, but Ag solubility is too low to account for traditional transport and deposition models, including those involving saline fluids. Hence a future study should address the process and origin of Ag, Sb, Hg and As to investigate to what extent As-complexes may be involved in Ag transport, what role magmatic fluids/sources play due to the presence of Sb and Hg commonly attributed to a magmatic source (e.g., epithermal deposits) and what role does mineralized (e.g., source of As and other metals, unrelated) Archean interflow sedimentary rocks play.

### 3.2 References

McLeish, D. F., Williams-Jones, A. E., Vasyukova, O. V, Clark, J. R., & Board, W. S. (2021).

Colloidal transport and flocculation are the cause of the hyperenrichment of gold in nature.

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Saunders, J. A. (2022). Colloids and Nanoparticles: Implications for Hydrothermal Precious

Metal Ore Formation. *SEG Discovery*, (130), 15–21. <https://doi.org/10.5382/segnews.2022->

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## **4 Appendix (supplementary data)**

## Appendix A. TEM preparation of the samples

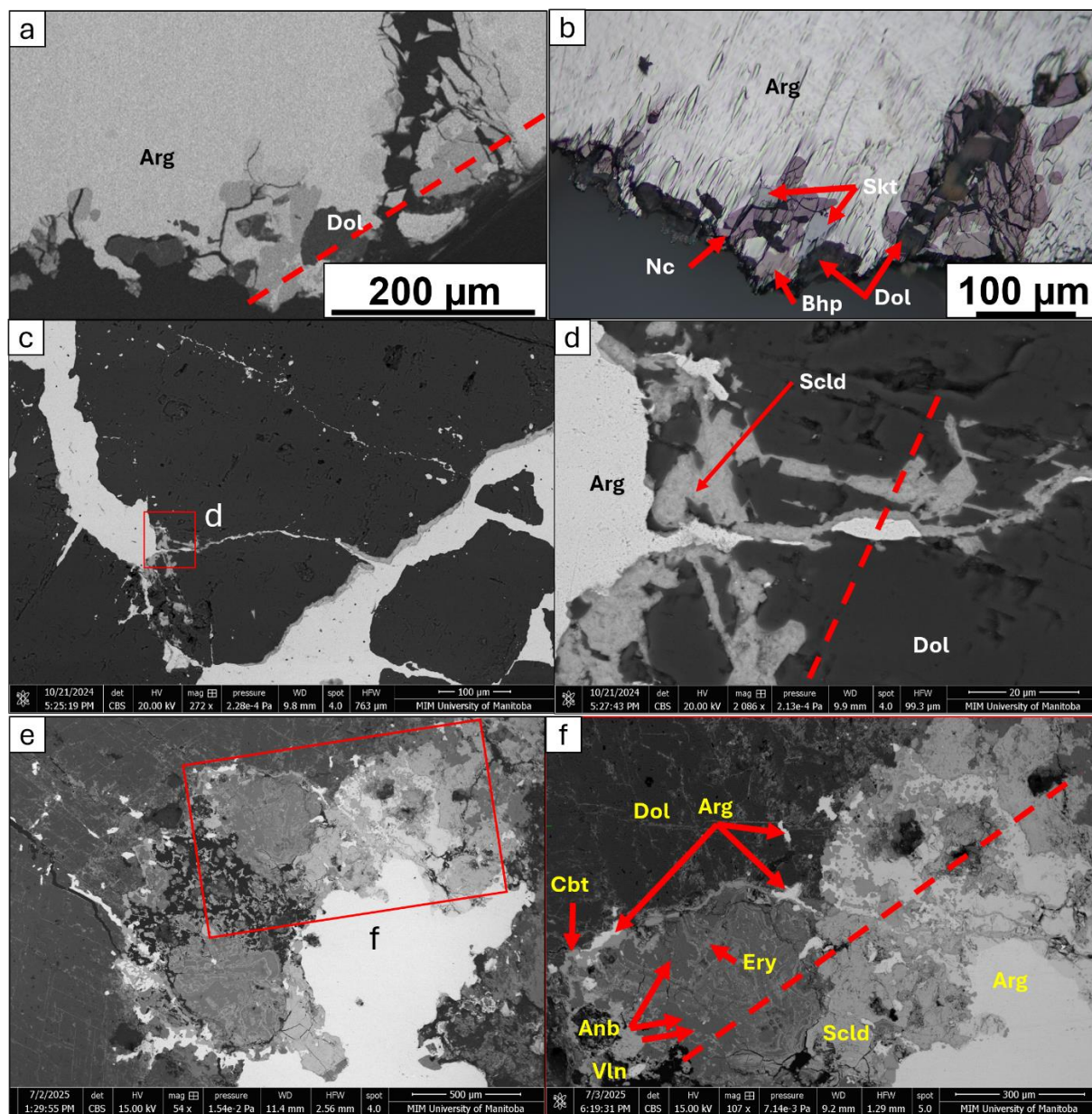


Figure S1: Compilation of the area of interest in the samples for TEM. Sample C31018a: (a) SEM-EDS backscattered electron image (BSE) of the area of interest, (b) Reflected light microscopy image after the ion milling process; the red dashed line represents the preferred area for TEM analysis. Sample C31018b: (c) SEM-EDS backscattered electron image (BSE) of the area of interest, (d) SEM-EDS BSE image of the framed red area in a and c; the red dashed line represents the preferred area for TEM analysis. Sample M39127: (e) SEM-EDS backscattered electron image (BSE) of the area of interest; (f) SEM-EDS BSE image of the framed red area in a and e; the red dashed line represents the preferred area for TEM analysis.

## Appendix B. Supplementary materials related to TEM results

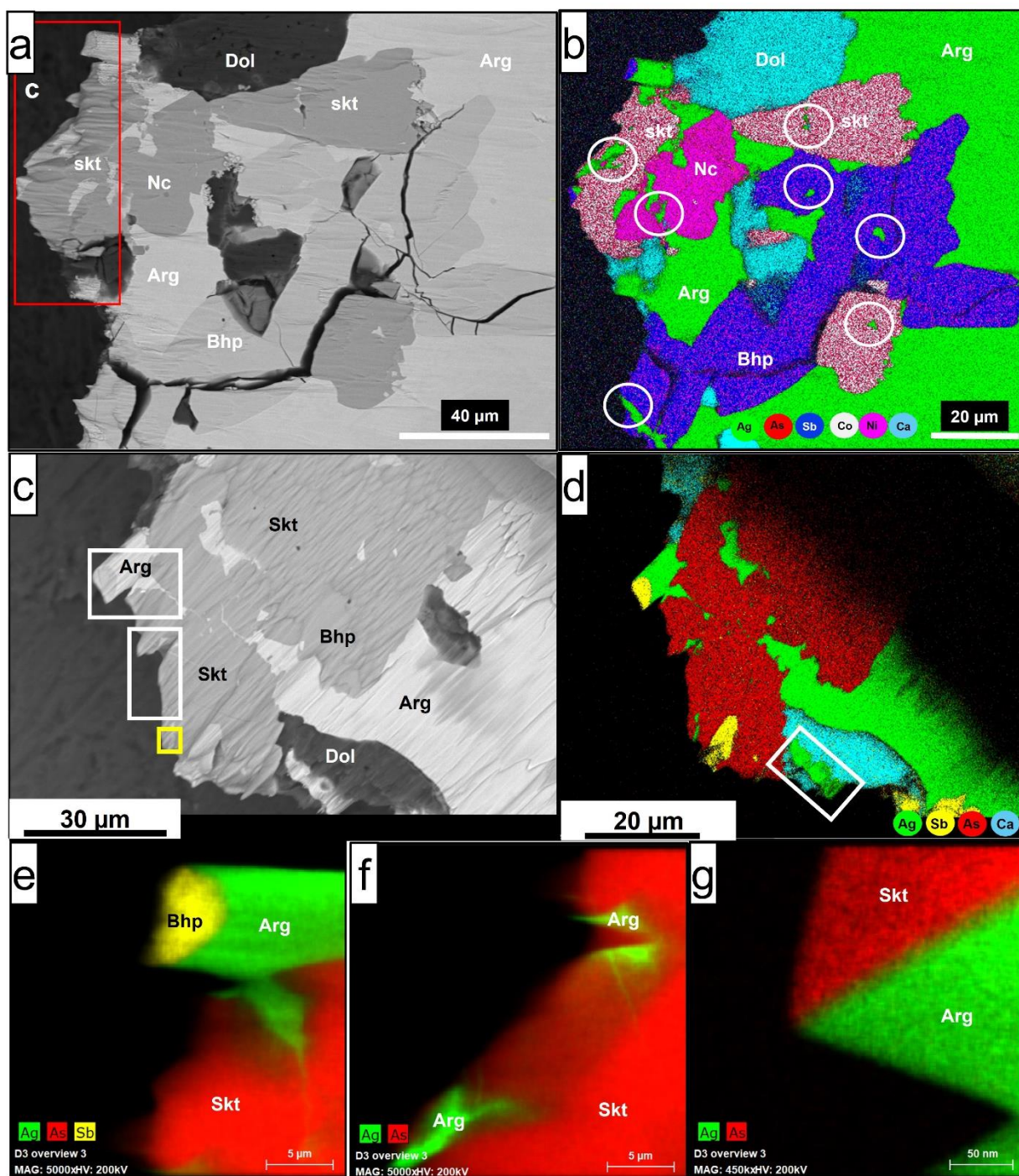


Figure S2. Investigation of Primary silver association at the nanoscale in sample 31018 from the Cobalt embayment: (a) SEM image in backscattering mode; (b) STEM-EDS chemical distribution map of (a); (c) BSE image of the area c from (a). (d) STEM-EDS chemical distribution map of (c). (e)-(g) STEM chemical distribution of the corresponding zone from (c). Mineral abbreviations after Warr (2021): All = allargentum; Bhp = breithauptite; Cbt = cobaltite; Dol = dolomite; Fe-Dol = Fe-dolomite; Muc= maucherite; Nc = nickeline; Saf = safflorite; Skt = skutterudite, Scld= stibioclauderite. The chemical maps display Ag in green, As in red, Sb in yellow, Co in white, Ni in magenta, Ca in light blue; the areas shown in (c) are indicated in (a) and the areas shown in (e)-(g) are labelled in c



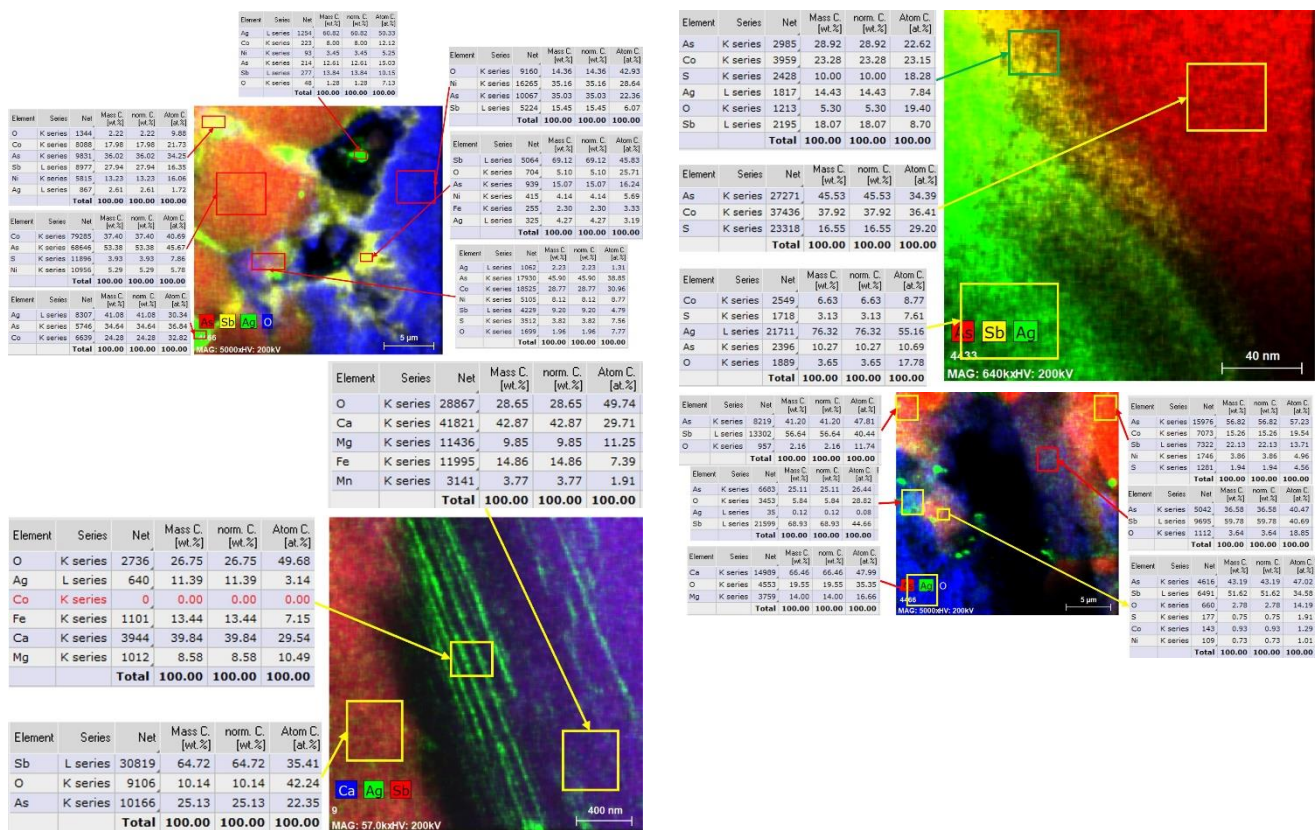


Figure S4. STEM images and their associated EDS quantification provide further information to Fig. 12.

### **Appendix C. Detailed results of EPMA and LA-ICP-MS analysis**

Detailed results of EPMA and LA-ICP-MS analysis can be viewed using the following Excel file link: [Appendix C. data\\_all analyses.xlsx](#), comprising four sheets: C1\_Summary all phases, C2\_all ore phases, C3\_all carbonates, and C4\_Oxides.

### **Appendix D. Detection limits for LA-ICP-MS; results for EPMA and LA-ICP-MS reference materials**

Appendix D1 comprises data reduction scheme settings, QA/QC, raw data, and reference materials for LA-ICP-MS and can be viewed via the following Excel file link: [Appendix D1. LAICPMS\\_Carbonate\\_Spots\\_NIST610\\_Ca.xlsx](#).

Appendices D2 and D3 correspond to the original raw, unfiltered data obtained during the EPMA analysis of the ore and carbonate phases. They comprise information on the instrumentation, detection limits, errors, and standards. It is accessible using the following link: [Appendices D2-3 EPMA.xlsx](#).

## Appendix E. Photos of rock samples and thin sections.



Figure S5. Photos of rock samples, thin sections and pucks of the selected samples from the Cobalt Embayment.