Dissolution-reprecipitation vs solid-state diffusion in electrum: examples from metamorphosed Au-bearing, volcanogenic massive sulfide (VMS) deposits

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Abstract

Native Au-Ag alloys (electrum) are the predominant precious metal host in Au-bearing volcanogenic massive sulfide (VMS) deposits. The chemical composition and distribution of electrum records crystal growth and post-crystallization processes. In this study, we present detailed textural and compositional data of electrum from the Ming (Canada) and Boliden (Sweden) Au-bearing VMS deposits.

Electron probe micro-analyzer (EPMA) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analyses of electrum enable characterization of chemical zoning in heterogeneous electrum grains. Electrum from Ming exhibits Ag-rich cores, in gradational contact with an outer Au-rich transition zone also enriched in S, Fe, Cu, Zn, and Pb, which is in sharp contact with Ag-rich rims. The textural observations, coupled with \textit{in situ} LA-ICP-MS data, highlight that the electrum zoning arises from a complex interaction between fluid facilitated solid-state...
diffusion (SSD) within the grain, and coupled dissolution and reprecipitation (CDR) reactions at the grain interface, in response to changing fluid composition and extrinsic parameters, such as temperature, pH, and redox state at Ming. Electrum from Boliden, in contrast, shows a Au-rich core in contact with a gradually increasing Ag-rich rim enriched in Se, Bi, Sb, Te, Sn, S, and Zn, which indicates the formation by fluid facilitated SSD reactions. The different local re-equilibrium caused by SSD from two deposits are attributed to different transport ligands and effects of physicochemical parameters of fluids (e.g., pH and $f_{O_2}$), resulting in different compositional zoning patterns within electrum. The long-lived metamorphic events that affected the occurrence and compositions of electrum at both VMS deposits, probably provided the elevated temperature and deformation to allow pervasive fluids to remobilize trace metals in electrum, which resulted in the complex chemical zoning in electrum. This study provides insights from in situ, textural and chemical analyses to understand the formation of complex chemical zoning in electrum in metamorphosed VMS deposits.

Keywords

Zoned electrum; Dissolution and reprecipitation (CDR); Solid-state diffusion (SSD); Ming; Boliden; Au-bearing VMS.

Introduction

Chemically zoned mineral grains record a time series of reaction conditions experienced by minerals (Spear and Selverstone, 1983). Coupled
dissolution-reprecipitation (CDR) is the most common mineral reaction mechanism in
nature (Putnis, 2009; Ruiz-Agudo et al., 2014; Spruzeniece et al., 2017; Konrad-Schmolke et al., 2018; Huang and Beaudoin, 2019; Li et al., 2019a). Coupled
dissolution-reprecipitation reactions result in readjustment of pre-existing mutual
grain boundaries under hydrothermal conditions, which has been widely recognized in
various geological settings (Tenailleau et al., 2006; Putnis, 2009; Zhao et al., 2009;
Zhao et al., 2013; Liu et al., 2017). In hydrothermal systems, complex mineral
chemical zoning can be interpreted to reflect chemical changes in fluid compositions,
or re-equilibrium related to a number of physicochemical conditions (e.g., Borg et al.,
2014). The mechanism of re-equilibration via CDR during fluid-mineral interaction
involves the partial or complete dissolution of the parent mineral and reprecipitation
of the replacement phase at the interface (Goldsmith and Laves, 1954; Ruiz-Agudo et
al., 2014). Recent studies confirm that the chemical composition of placer gold can be
modified by repeated episodes of dissolution and precipitation reactions in supergene
environments (Reith et al., 2012; Shuster et al., 2017; Melchiorre et al., 2018; Rea et
al., 2019; Dos Santos Alves et al., 2020). This mechanism has previously been
suggested to explain the formation of electrum with complex zoning textures in
hydrothermal systems (Huston et al., 1992; Zhao et al., 2013; Liu et al., 2017; Rosell
et al., 2018; Li et al., 2019b).

Pseudomorphic replacement reactions, characterized by the preservation of the
shape and volume of the replaced minerals, are common in nature during
hydrothermal alteration, metamorphism, diagenesis, and chemical weathering (Putnis,
However, pseudomorphic replacement in zoned minerals is alternatively attributed to solid-state diffusion reactions (SSD) under hydrothermal conditions, which preserve external morphology and aspects of the crystal structure (Eda et al., 2005; Eda et al., 2006; Putnis, 2009; Xia et al., 2009). Solid-state diffusion reactions controlling the growth of precious metal alloys have been previously reported both in nature (e.g., Au-Ag alloy, Czamanske et al., 1973; Au-Ag-Sb alloy, Zachariáš et al., 2017) and synthetic material studies (e.g., Au-Ag alloy, Hodak et al., 2000; Au-Sn alloy, Baheti et al., 2018; Au-Cu alloy, Xiong et al., 2014). The lack of porosity and a gradational contact between the parent and product phases may be the key crystallographic feature for SSD reactions (Putnis and Putnis, 2007; Zhao et al., 2013). However, a sharp contact instead of a diffusion profile between the parent and product phases is a feature for CDR reactions (Putnis, 2009, 2014; Robert, 2014). Although the microstructures of final products by CDR and SSD are different, the fundamental mechanism remains the same as both involve a re-equilibration of cation exchange (Putnis, 2009).

The Au-Ag system forms a complete miscible alloy, according to the Hume-Rothery rules, due to the similar atomic radii, crystal structure, and valence of Au and Ag (Guisbiers et al., 2015). The term *electrum* is used to refer to Au-Ag alloys between 20 wt% and 80 wt% Au, whereas native gold is used for alloys with more than 80 wt% Au (Boyle, 1979). Previous studies have explained Au and Ag solubility during transport and precipitation from fluids based on experimental data (Huston et al., 1992; Gammons and Williams-Jones, 1995; Pal’yanova and Kolonin, 2007).
Shikazono and Shimizu, (1987) used Ag/Au ratios of electrum to discuss variations in Eh, pH, temperature, and sulfur contents in auriferous vein deposits. Hagemann et al. (1998) suggested that Ag-rich electrum is related to reduced fluids which reacted with more oxidized ultramafic rocks at the Archean Transvaal gold deposit (Australia).

Zoned electrum has been reported in epithermal deposits in the United States, Spain, and Japan (Desborough et al., 1971; Rosúa et al., 2002; Yokoyama et al., 2011). Silver-zoned electrum grains have been investigated in volcanogenic massive sulfide (VMS) deposits in Eastern Australia (Huston et al., 1992) and the Baochun skarn gold deposit (China, Lu et al., 2000). Healy and Petruk (1990) reported zoning of Au-Ag-Hg alloys is a consequence of crystallization of increasingly Ag-rich fluids during retrograde metamorphism at the Trout Lake VMS deposit, Flin Flon (Canada).

Gold-bearing VMS deposits are key exploration targets because their gold contents contribute significantly to the ore value (Dubé et al., 2007; Mercier-Langevin et al., 2011). It has been shown that gold can be remobilized from the massive sulfide bodies into veins peripheral to, or within the VMS deposits during deformation and metamorphism (Huston et al., 1992; Tourigny et al., 1993; Sinclair et al., 2000; Larocque et al., 1995). Deformation and metamorphism have been proposed to cause coarsening of gold and upgrading in some VMS deposits (Huston et al., 1992; Årebäck et al., 2005; Wagner et al., 2007; Vikentev, 2016; Mercier-Langevin et al., 2011). However, the effect of metamorphism on electrum compositional zoning still remains unclear.

We selected two Au-bearing VMS deposits, Ming (Canada) and Boliden (Sweden),
because both have common gold mineralization characteristics: (1) occurrence of zoned electrum, (2) an overlap of VMS and epithermal (Ag, As, Sb, Hg) mineralization with interpreted magmatic contributions (e.g., Bi, Te), (3) complex ore mineralogy with abundant sulfides and sulfosalts, (4) association with andesite-dacite-rhyodacite-rhyolite rocks, and (5) metamorphism and deformation overprints resulting in remobilization of gold (Mercier-Langevin et al., 2011; Mercier-Langevin et al., 2013; Brueckner et al., 2014; Brueckner et al., 2016). Here, we present in situ textural and chemical composition results of electrum from the Boliden and Ming deposits, to investigate compositional zoning characteristics in electrum grains and to constrain the mechanisms responsible for chemical zoning in electrum. Our results provide new insights into how SSD and CDR reactions can form compositional zoning in electrum, and into the effects of metamorphism on precious metal mobility in greenschist to amphibolite facies rocks.

Geology of the selected deposits and sample description

Three electrum-bearing representative samples were selected from the Ming (n=1, Canada) and Boliden (n=2, Sweden) deposits. The geology of the two deposits and their geochemistry are well documented in literature (Bergman Weihed et al., 1996; Wagner et al., 2007; Mercier-Langevin et al., 2013; Pilote and Piercey, 2013; Brueckner et al., 2014; Brueckner et al., 2015; Brueckner et al., 2016; Pilote et al., 2016; Pilote et al., 2020), and only a brief summary is presented here.

Ming deposit

The Ming deposit is a Cambro-Ordovician bimodal-mafic VMS deposit (3.65Mt at
2.26 wt% Cu, 1.13 g/t Au, 6.78 g/t Ag, and 0.32 wt% Zn) located in the northern central part of the Baie Verte Peninsula of Newfoundland (Canada, Pilote and Piercey, 2013; Brueckner et al., 2016). The deposit is hosted in the upper part of the Rambler Rhyolite Formation (Figure 1), which is a folded, dome-shaped, sequence of quartz-phyric rhyodacite, quartz-bearing intermediate to felsic tuff and tuff breccia formed during the Cambrian-Ordovician (ca. 487 Ma, Skulski et al., 2010; Pilote et al., 2016). Upper greenschist to lower amphibolite facies metamorphism affected most of Rambler Rhyolite Formation, including four phases of regional deformation (Hibbard, 1983; Castonguay et al., 2009). There are five massive sulfide orebodies hosted within variously hydrothermally altered volcaniclastic rocks, which are the 1807, 1806, Ming North, Ming South and Lower Footwall zones. The ore mineralogy in the 1807 zone consists of (1) pyrite, chalcopyrite, sphalerite, pyrrhotite, arsenopyrite, and galena, (2) uncommon tellurides, selenides, and sulfo-animonides, (3) sulfosalts (tennantite-tetrahedrite), (4) precious metals (electrum, Ag-sulfosalts, and minor silver), and (5) oxides (magnetite, ilmenite, chromite) (Brueckner et al., 2016; Pilote et al., 2016). Precious metal (Au-Ag) emplacement is syngenetic (Brueckner et al., 2014). Gold remobilization and recrystallization during deformation and metamorphism at the Ming deposit is described by Brueckner et al. (2014), Brueckner et al. (2016), and Pilote et al. (2020). Electrum, which occurs along fractures in cataclastic and recrystallized pyrite, and interstitial between recrystallized pyrite ± arsenopyrite, has been interpreted to be the product of Silurian-Devonian metamorphism of pre-existing precious metals at peak temperature up to 500°C.
Sample M1807, collected from the massive sulfide orebody in the 1807 zone of the Ming deposit, is composed of pyrite, chalcopyrite, sphalerite, galena, electrum, and native silver. Electrum is the major precious metal alloy, either adjacent to chalcocite or intergrown with bornite and chalcopyrite (Figure 3). Bornite occurs as anhedral grains associated with chalcopyrite and electrum. Native silver predominantly occurs as veins along fractures and between sulfide minerals.

**Boliden deposit**

The Boliden deposit is a Au-Cu-As VMS deposit (8.3 Mt at 15.9g/t Au, 50 g/t Ag, 1.42 wt% Cu, 0.9 wt% Zn, 0.3 wt% Pb, and 6.8 wt% As) located in the eastern part of the Skellefte district, Sweden (Figure 2), which was formed between ca. 1894 and 1891 Ma (Mercier-Langevin et al., 2013). The deposit is hosted in the uppermost part of the rhyolitic metavolcanic Skellefte Group that consists of Early Proterozoic felsic to mafic volcanic rocks with lesser intrusive and sedimentary rocks (Allen et al., 1996; Mercier-Langevin et al., 2013). The Skellefte belt was affected by regional Svecokarelian metamorphism at greenschist to amphibolite grade at ca.1.83-1.81Ga and the peak metamorphic conditions in the Boliden area were estimated as 430°C and 5-7 kbar (Berglund and Ekström, 1980; Billstrom and Weihed, 1996). The ore lenses were flattened and the sulfide assemblages were highly folded and foliated during tectonic deformation (Wagner and Jonsson, 2001; Mercier-Langevin et al., 2013). The main massive sulfide mineralization in Boliden consists of brecciated pyrite, foliated chalcopyrite, fine-grained arsenopyrite, pyrrhotite, and Cu-Pb-Bi-Sb...
sulfosalts. The pyrite and arsenopyrite are strongly recrystallized and form granular masses or are aligned along foliation (Wagner et al., 2007; Mercier-Langevin et al., 2013).

Two typical Au-rich samples were selected from the main massive orebody in Boliden. Sample BLD210 is from the fine-grained massive arsenopyrite ore, whereas sample BLD-1 comes from a chlorite-altered massive pyrite with strong foliation. Electrum is the predominant Au-Ag alloy and is adjacent to arsenopyrite, pyrite, and intergrown with chalcopyrite, whereas native gold was also found as very small (10-20 μm) grains along the boundaries of electrum (Figure 5m).

Analytical methods

Ten polished thin sections from the Ming deposit and twelve from the Boliden deposit, were cut in order to yield significant numbers of electrum grains for study, which were examined by optical microscopy. Backscattered electron (BSE) imaging was used to identify mineralogical and textural relationships using a JEOL JSM-840A scanning electron microscope (SEM) at Université Laval (Canada). The accelerating voltage was 15 kV and the beam current was 60 μA, at a working distance of 20 mm. Electrum grains were analyzed for their major (Au, Ag) and minor elements (Zn, Cu, Co, Fe, Pb, S, Hg, Pt, Se, As) using a Cameca SX-100 Electron Probe Micro-Analyzer (EPMA) at Université Laval (Canada), equipped with five wavelength-dispersive spectrometers. The analyses used a 25 kV accelerating voltage with 100 nA beam current for minor elements and 20 nA for major elements, both with a 5 μm beam size. Simple oxides (GEO standards block) and pure metals from
the Astimex company were used as standard materials. Analysis time was 40 s and 20 s of background measurement. Detection limits for each element and precisions calculated from three analyses of gold standard (NA-Au-31) are listed in Supplementary data 1. Electrum compositional maps were obtained by wavelength-dispersive spectroscopy (WDS) X-ray for Au and Ag at an accelerating voltage of 15 kV and a beam current of 100 nA, and a counting time of 20 ms/pixel with a resolution of $577 \times 527$ pixels.

The trace element analyses of native electrum were carried out at the University of New Brunswick (Canada). Electrum grains were analyzed using a Resonetics S-155-LR 193 nm Excimer laser ablation system coupled with an Agilent 7700x quadrupole ICP-MS. To investigate trace element distributions in electrum, lines were used to ablate across a single grain to generate profiles. A beam size of 10 - 24 μm was used for compositional analysis. Rastering speed for each line was modified based on the beam size to achieve maximum resolution (5 μm/s for 10 μm beam size, 8 μm/s for 24 μm beam size). Acquisition time was set to 0.002 s for all the elements resulting in a total sweep time of ~0.8 s. Electrum grains were ablated using energy density of 2.3 J/cm$^2$, and the beam operating at 10 Hz frequency. Trace element contents, including Mg, Al, Si, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Pb, Cd, Sn, Sb, Te, Pt, Pb, Bi, Hg, S, Ti, Mo, In, and Tl, were measured by LA-ICP-MS in this study. The external standard NIST610 was used for calibration of Mg, Al, Si, S, Ti, Mo, In, and Tl (Rocholl et al., 1997). The USGS synthetic MASS-1, a pressed powder pellet, was used for calibration of Hg (Wilson et al., 2002). A synthetic gold standard (NA-Au-31)
was used for calibration of Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Pd, Cd, Sn, Sb, Te, Pt, Pb, and Bi, whereas a second gold standard (NA-Au-30) was used for quality control of LA-ICP-MS analyses (Milidragovic et al., 2016). The standards were analyzed every eight spots with the same ablation spot size as the unknown sample analysis. Data were reduced using Iolite3.0 software (Longerich, 1996; Paton et al., 2011). Trace element concentrations were internally normalized to Ag values acquired by EPMA at Université Laval. The average detection limit for each electrum sample and precisions calculated from routine analyses (n=43) of gold standard (NA-Au-31) are reported in Supplementary data 1 and the comparison of routine analyses of trace elements in reference materials (NA-Au-31, NIST610, and MASS-1) by LA-ICP-MS and certificate values is given in Supplementary data 3.

**Electrum textures**

In massive sulfides from Ming 1807 zone, ten electrum grains from ten thin sections have been investigated and they are either adjacent to, or along fractures in pyrite, and are intergrown with silicates quartz, epidote, or biotite, and sulfides chalcocite, bornite, or chalcopyrite (Figure 3a). Seven of the ten electrum grains are zoned, and they occur as irregular inclusions in bornite, associated with cataclastic pyrite and chalcopyrite (Figure 3b), whereas they can also form anhedral grains and veinlets along the boundaries of chalcocite and bornite (Figure 3c). Native silver occurs as veins or thin films surrounding the electrum grain or along the boundaries of chalcocite (Figure 3c). The internal microstructure of electrum, observed in BSE images, show a light grey core and dark grey rim (Figure 4). Incongruent layers
developed towards the electrum margin, between the light grey zone and dark grey rim, and show an abrupt contact (Figures 4 b-f). Several dark grey layers towards the edge of the grain contain more pores than the light grey zone and show various widths in different areas of individual grains (Figures 4 b and c). Within the electrum, the contact between the dark grey core and light grey transition zone, shows a gradational contact (Figures 5a and 6a).

At Boliden, twenty-six electrum grains from twelve thin sections were investigated and they occur predominantly as coarse anhedral grains along boundaries of fine-grained, massive, and crystalline arsenopyrite, and at contacts with aurostibite, which are commonly enclosed in quartz in the massive arsenopyrite ore (Figures 3 d and f). Six of twenty-six electrum grains are zoned and occur as veinlets filling in fractures in brecciated pyrite, chalcopyrite, and arsenopyrite in the chlorite-altered massive pyrite ore (Figure 3g). These electrum grains are oriented parallel to the main foliation (Figure 3h). Under BSE, zoned electrum has a light grey core in gradational contact with a dark grey rim (Figures 4 g-i). Fine-grained native gold is not common but can be observed as disseminated grains adjacent to electrum in association with pyrite and chalcopyrite, which is not zoned (Figure 5n). Native silver veins are not observed in the Boliden ore samples. However, fissures transecting electrum both in massive arsenopyrite and foliated pyrite consisted of Ag-rich electrum (Figures 5 m-o).

**Chemical composition of electrum**

The zoned electrum grains were identified in the petrographic and BSE images. To
quantify the chemical characteristics of these zoned electrum grains, WDS X-ray maps, EPMA profiles and LA-ICP-MS profiles were used. The major and minor element compositions of electrum grains from Ming and Boliden are presented in Table 1. Chemical composition variations in zoned electrum grains are shown in Figures 5-8.

In the 1807 zone of the Ming deposit, zoned electrum grains commonly show a variation in Ag contents from 20 wt% to 40 wt% and Au contents from 62 wt% to 79 wt% (Table 1). The WDS X-ray map shows that dark grey cores are Au-poor, surrounded by a light grey transitional zone with higher Au content, and an outer, dark grey, Ag-rich rim (Figure 5b). Profiles across the zoned grain (lines 1 and 3), show that the dark grey core has a high and constant concentration of Ag (24 wt%) and low concentration of Au (75 wt%, Figures 5e). Silver exhibits a progressively decreasing variation from the dark grey core to the rim, whereas Au shows a gradational increase (Figures 6 b and c). There is an abrupt increase of Ag, and decrease of Au, at the light grey transition from grain to the rim (Figure 6b). According to the WDS X-ray map, the Ag-rich rim can be divided into two layers (the inner rim1 and outer rim 2 in Figures 6 a and b). The contact between rims 1 and 2 is sharp in BSE images with an abrupt increase in Ag in rim 2 (Figure 6b). The dark grey core of electrum grains has Au ranging from 65 wt% to 77 wt%, compared to Au in the light grey transition zone ranging from 71 wt% to 78 wt% (Table 1). Gold in dark rims 1 and 2, ranges from 62 wt% to 69 wt%, which is lower compared to Au in the dark grey core (65 wt% to 77 wt%) and light grey transition zone (71 wt% to 78 wt%). The dark grey core has a
range of Ag from 21 wt% to 35 wt%, whereas the light grey transitional zone is relatively depleted in Ag, ranging from 20 wt% to 30 wt%. The average fineness 

\[
\{1000 \times \frac{\text{Au wt\%}}{\text{Au wt\%} + \text{Ag wt\%}}\}
\]

value in the dark core is 651, which is lower than that in the light grey transitional zone, 761. Rim 1 is dark grey and has an average gold fineness value of 672, compared to rim 2, which has a gold fineness of 609, is slightly darker. Native silver veins filling fractures or along the electrum grain boundaries have up to 99 wt% Ag (Figure 5c).

Copper content in the zoned electrum from Ming ranges from 0.03 wt% to 2.9 wt%, shows an increase in concentration from the light grey zone to the dark grey rims (Figures 6 d-f). The dark grey rim 2 has Cu contents of 0.8 wt%, higher than the dark grey core with 0.3 wt%, and light grey transitional zone with 0.1 wt% (Table 1).

Sulfur in the dark grey core has an average of 0.05 wt%, a similar amount at 0.06 wt% in the light grey transition, and elevated contents in the dark grey rims up to 0.13 wt% (Table 1). Mercury yields an average 0.7 wt% in the dark grey core, 0.6 wt% in the light grey transition zone, and 0.1 wt% in the dark grey rim (Table 1). Mercury is relatively enriched in the dark grey core and the dark grey rims compared with the light grey zone (Figures 6 d-f). Mercury in Ag-rich veins reaches up to 6.2 wt%, which is lower than the Hg measured in electrum with a range of 8 wt% to 21 wt% in samples from the 1806 zone of the Ming deposit (Brueckner et al., 2014).

A LA-ICP-MS profile in a zoned electrum grain from Ming is used to illustrate trace element contents between the dark and light grey zones (Figure 8a and Supplementary data 3). Figure 8b shows that the light grey zone has relatively higher

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Fe, Cu, Zn, Te, Pb, Bi and S than the dark grey zone, whereas Sn and Sb show similar range and average values.

At the Boliden deposit, zoned electrum has a light grey core and a dark grey rim that are coincident with a wide range of Ag concentrations from 6 wt% to 46 wt% and of Au concentrations ranging from 48 wt% to 90 wt% (Table 1). The EPMA spot analyses were arranged along three profiles across the dark and light grey zones in the zoned electrum (Figure 7a). The light grey core has Au concentrations ranging from 55 wt% to 90 wt% Au (average 70 wt%) with Au fineness value ranges from 575 to 936, whereas the dark rim is Au-poor with a range from 48 wt% to 69 wt% Au (average 61 wt%) with Au fineness values range from 511 to 738 (Figures 5k and 7).

In contrast, the Ag concentration in the light grey core ranges from 6 wt% to 40 wt%, whereas Ag is relatively enriched in the dark grey rim, ranging from 25 wt% to 46 wt% (Figure 7). Copper content in the zoned electrum varies from 0.002 wt% to 5 wt% (Figures 7e and f). The light grey core has relatively low Cu, S, and Hg contents with averages of 0.06 wt%, 0.05 wt%, and 1.4 wt%, respectively. The dark grey rim has higher averages of 0.5 wt% Cu, 0.36 wt% S, and 1.9 wt% Hg (Figure 7).

A line of LA-ICP-MS spot analyses across the light core to the dark rim is used to investigate trace element variations for the zoned electrum grain from the Boliden deposit (Figure 8c and Supplementary data 3). Generally, the dark grey zone has higher Fe, Cu, Zn, Se, Sn, Sb, Te, Pb, Bi, and S than the light grey zone (Figure 8d).

Discussion

The zoned electrum from the Ming deposit is characterized by a Ag-rich core, a
gradational contact with a Au-rich transition zone, and an abrupt contact with a Ag-rich rim (Figure 5a). In contrast, the zoned electrum from the Boliden deposit is characterized by a Au-rich core with a gradational contact with a Ag-rich rim (Figure 5i), which was previously reported both in massive and vein orebodies in the deposit (Bergman Weihed et al., 1996). The gradational chemical contact was observed in both VMS deposits; however, the abrupt chemical contact is only observed in electrum from the Ming deposit. Zoned electrum in both VMS deposits exhibits an opposite zoning pattern of Au-Ag composition from the core to the margin, which likely records different crystal growth and post-crystallization processes. The content of Au and Ag in electrum grains are controlled by their solubilities in hydrothermal fluids under different conditions (Pal’yanova and Kolonin, 2007). Therefore, different compositional zoning characteristics in electrum likely indicate different precipitation conditions.

Formation of zoned electrum at Ming

At Ming, the close mineralogical association of the Ag-rich electrum core with arsenopyrite, chalcopyrite, pyrrhotite, and sphalerite suggests that Au was transported by bisulfide complexes at a temperature < 300°C, in reduced fluids, whereas the association of Ag-rich electrum rim with galena and chalcopyrite suggests that Ag was transported by chloride complexes (Seward, 1973; Huston et al., 1992; Williams-Jones et al., 2009; Brueckner et al., 2016). The silver-rich electrum core suggests a low pH solution, because silver chloride complexes are far more soluble than the bisulfide complexes at low pH, indicating Ag is more mobile than Au (Mann,
1984; Wilson, 1984; Gammons and Barnes, 1989). The formation of electrum grains along fractures in recrystallized pyrite or arsenopyrite has been interpreted to be of syngenetic origin between 260°C to 300°C at Ming, whereas the regional Silurian-Devonian deformation indicates a peak metamorphic temperature of 500°C (Brueckner et al., 2016). At elevated temperature, silver likely tends to be dissolved via reaction (1), leading to the increase in Au content to form the Au-rich zone with a gradational contact with the electrum core (Gammons and Williams-Jones, 1995; Migdisov et al., 1999).

\[ \text{Ag}_{\text{alloy}} + 2\text{Cl}^- + \text{H}^+ + 1/4\text{O}_2(g) = \text{AgCl}_2^- + 1/2\text{H}_2\text{O} \] (1)

The incongruent layers near the Ag-rich margin of electrum at Ming likely indicates dissolution from the core to the margin (Figure 4b). The Ag-rich rim of electrum grains at the Ming deposit precipitated on the exterior of Au-rich zone and exhibits an epitaxial relationship with the parent electrum (Figures 4e and f). The presence of sharp interfaces between the Au-rich zone and Ag-rich rims is generated by repeated coupled dissolution and reprecipitation (Figure 4b and f, Bowell, 1992). The coexisting mineral assemblage of bornite + chalcocite also implies a higher temperature event, because bornite + chalcocite precipitates in oxidized conditions during an input of Cu-rich fluid (> 300°C) in VMS deposits (Hannington, 1999; Koski, 2010). The general trend of increasing Ag with Cu composition in the Ag-rich rims likely suggests the later pulse of Cu-rich chloride complex fluid may be rich in Ag and precipitated silver-rich veins in fractures (Figure 9a). Under a decreasing temperature and oxidized condition, the dissolution of Au and reprecipitation of Ag at
the interface are facilitated by reaction (2) and (3) to form the sharp compositional
contact (Figures 4d and f, Gammons and Williams-Jones, 1995).

\[ \text{Au}_{\text{alloy}} + 2\text{Cl}^- + \text{H}^+ + \frac{1}{4} \text{O}_2(g) = \text{AuCl}_2^- + \frac{1}{2} \text{H}_2\text{O} \quad (2) \]

and

\[ \text{Au}_{\text{alloy}} + \text{AgCl}_2^- = \text{AuCl}_2^- + \text{Ag}_{\text{alloy}} \quad (3) \]

In addition, there is an enrichment of S-Fe-Cu-Zn-Pb suite from the Ag-rich core to
the Au-rich transition zone at Ming (Figure 11a), likely because these elements were
mobilized and readily re-incorporated into electrum from fluids during prograde
metamorphism (Lockington et al., 2014). Native silver is not common throughout the
Ming deposit because the syngenetic fluids conditions did not favor Ag solubility
(Brueckner et al., 2016). Native silver rims precipitated in fractures and along the
boundaries of bornite and chalcocite (Figures 3c and 5) are likely remobilized from
sulfides under metamorphic conditions due to its high mobility and ductile behavior.
Hence, the mobilization of silver from proximal sulfides under low- to medium-grade
metamorphic environments favors un upgrading of Ag contents at the rim of electrum.

It is worth noting that porosity, as an integral microstructural feature of CDR, is
essential to sustain fluids to transport and react at the interface between the parent and
product phases (Putnis, 2009). The small pores in the incongruent layers in the
electrum from Ming, allowing fluids to react with parent electrum, are likely the
consequence of CDR at the interface (Figures 4b and c). The generation of grain-scale
fractures in parent electrum also provides possible pathways for pervasive transport of
fluids to react with the electrum interface, which facilitated CDR, resulting in multiple
thin layers of Ag-rich rims (Figure 4b-f). It appears that the compositional zoning in electrum is related to the fractures within the grain, or the grain edge, indicating a post-precipitation re-equilibration (Figures 4 and 5). The existence of nanoscale porosity in electrum will need to be further assessed by transmission electron microscopy.

**Formation of zoned electrum at Boliden**

At Boliden, a gradational contact between the Au-rich core and Ag-rich rim is observed and Ag-rich veins are precipitated in the fractures of electrum (Figures 4h and 5o). The sericite-quartz and sericite-chlorite alteration assemblages and the association of electrum with arsenopyrite ± pyrite ± pyrrhotite indicate a more reduced fluid and gold bisulfide complexes were likely dominant at low temperatures (< 300°C) (Huston et al., 1992; Mercier-Langevin et al., 2013). This reduced fluid contained high H₂S and sufficient HCl to produce the necessary acidity to leach the host rocks to precipitate a large amount of arsenopyrite (Bergman Weihed et al., 1996). At elevated temperature, the solubility of gold in sulfide complexes tends to be sensitive to changes in pH and redox potential (Stefánsson and Seward, 2004). In the presence of electrum, aH₂S has significant effects on gold solubility and fO₂ has moderate impacts on gold solubility. The wall rocks of Boliden massive sulfide ore display a zoned alteration pattern with an inner envelope dominated by white mica ± andalusite and outer chlorite ± sericite zone (Bergman Weihed et al., 1996), indicating an acidic fluid responsible for the advanced argillic alteration that precipitated the Au-rich electrum (Marquis et al., 1990). Gold solubility can be increased through
reaction (4), and the solubility of Ag can be increased by reaction (5) with decreasing pH in oxidizing fluids (Gammons and Williams-Jones, 1995).

\[
\text{Au}^\text{(s)} + 2\text{H}_2\text{S}^\text{(aq)} + \frac{1}{4}\text{O}_2^\text{(g)} = \text{Au(HS)}_2^- + \text{H}^+ + \frac{1}{2}\text{H}_2\text{O} \quad (4)
\]

and

\[
\text{Ag}^\text{(s)} + 2\text{H}_2\text{S}^\text{(aq)} + \frac{1}{4}\text{O}_2^\text{(g)} = \text{Ag(HS)}_2^- + \text{H}^+ + \frac{1}{2}\text{H}_2\text{O} \quad (5)
\]

Under elevated temperature (> 300°C, corresponding to the peak metamorphism) and/or \(a_{\text{H}_2\text{S}}\), the Au-rich electrum is dissolved via reaction (6) to form a gradational diffusion contact at the interface (Huston et al., 1992; Gammons and Williams-Jones, 1995).

\[
\text{Au}_{\text{alloy}} + \text{Ag(HS)}_2^- = \text{Au(HS)}_2^- + \text{Ag}_{\text{alloy}} \quad (6)
\]

The general trend of increasing Cu with Ag composition in the Ag-rich rim, likely suggests a later pulse of Cu-rich fluid (Figure 9b). With increasing pH and decreasing temperature, the Ag-rich electrum rim precipitated, coarsening the electrum grain and decreasing gold fineness during retrograde metamorphism. The gradual variations in Au and Ag observed in BSE images, EPMA and LA-ICP-MS line profiles, suggest the SSD of metals is facilitated by reaction (6), across the gradational contact between the light and dark zones (Figures 4, 7, and 8).

**Diffusion trends in zoned electrum grains**

Opposite diffusion trends are observed in Au-Ag-Cu composition diagrams from each deposit. This suggests that precipitation conditions controlling the zoned electrum compositions in the Ming and Boliden deposits are different (Figure 9). At Ming, the parent electrum core is Ag-rich, and Ag is leached from electrum to form
Au-rich electrum, with irregularly gradual contact generated by SSD reactions facilitated by Au-rich, low pH fluids with increasing temperature (Figures 9a and 10b, Hough et al., 2007; Rosell et al., 2018). These fluids seem to be enriched in Fe, Cu, Zn, Te, Pb, Bi and S, and these elements are redistributed and incorporated into electrum during the modification of Ag-rich electrum (Figures 8b, 10b, and 11a). In contrast, the parent electrum is Au-rich at Boliden, and Ag in electrum is soluble and is easy to be mobilized at low pH, under reduced conditions (Figures 10 d and e, Gibert et al., 1998; Williams-Jones et al., 2009). The gradational contact between the Au-rich core and Ag-rich rim, and absence of multiple layers, suggest a SSD reaction that mobilizes Ag from Au-rich electrum, which is slow at 300°C but faster at temperature > 300°C facilitated by Ag-rich fluids (Figure 10f, Huston et al., 1992; Gammons and Williams-Jones, 1995; Marshall et al., 2000). These Ag-rich fluids can also mobilize Fe, Cu, Zn, Se, Sn, Sb, Te, Pb, Bi, and S, and these elements are incorporated in the Ag-rich electrum (Figures 8d, 10e, and 11b).

Gammons and Williams-Jones (1995) indicated that electrum precipitation from aqueous sulfide-rich solutions is sensitive to pH, where a drop in pH causes a continuous increase in Au content in electrum, when Au is transported by bisulfide complexes \(\{\text{Au(HS)}_2^-\}\) in fluids (Figure 9b). The composition of electrum is highly sensitive to changes in the amount of Au and Ag in solutions and temperature, under oxidized conditions, where Au is transported by a bisulfide complex \(\{\text{Au(HS)}_2^-\}\) and Ag by a chloride complex \(\{\text{AgCl}_2^-\}\) at Ming (Gammons and Williams-Jones, 1995). It is likely that the local re-equilibrium caused by SSD in electrum, due to different
transport ligands and interrelated effects of physicochemical parameters of fluids (e.g., temperature and pH), resulted in opposite diffusion trends compared with electrum in Au-Ag-Cu compositions in Boliden (Figure 9).

**Relationship between zoning in electrum and metamorphism**

Post-depositional deformation and metamorphism have effects on the occurrence of electrum in VMS deposits (Huston et al., 1992). In addition to coarsening the grain size of electrum under metamorphic environments, the composition can also be modified due to SSD reactions, particularly at higher metamorphic grade (Boyle, 1979; Huston et al., 1992). The SSD modification during metamorphism on electrum composition has been previously reported in the Trout Lake VMS deposit (Flin Flon district, Healy and Petruk, 1990). In both the Ming and Boliden deposits, silver-rich electrum tends to occur along fractures in or along grain boundaries between sulfides, and is intergrown with ductile-deformed sulfide minerals, in addition, shows an enrichment of Hg in EPMA profiles (Figures 6 and 7). The Ag-rich electrum rim with elevated Hg is considered to have formed below the peak metamorphic temperature, because pervasive homogenization of Au-Ag-Hg by volume diffusion during the extensive period of prograde metamorphism will erase the growth zoning in electrum grains (Oberthuer and Saager, 1986). The diffusion-induced zoning with trace element remobilization and incorporation at the near surface or mineral interface has been documented during regional metamorphism of ore deposits (Healy and Petruk, 1990; Watson, 1996; Reeder and Rakovan, 1999; Marshall et al., 2000). Thus, we consider that prograde metamorphism can provide the elevated temperature and pressure to
form fractures that allow metamorphic fluids to dissolve the parent electrum, and to mobilize trace metals (e.g., S-Fe-Cu-Zn-Pb at Ming, Se-Bi-Sb-Te-Sn-S-Zn at Boliden), that are incorporated into the electrum rim by SSD reactions during the retrograde metamorphic process (Figure 11).

Implications

This study investigated chemical zoning textures in electrum grains from the Ming and Boliden VMS deposits. Electrum from the Ming deposit is zoned, with a Ag-rich core that gradually shifts to a Au-rich transition zone that is in sharp contact with an outer Ag-rich rim, whereas electrum from the Boliden deposit is zoned with a Au-rich core with a gradational contact with a Ag-rich rim. The compositional variation and textural zoning of the electrum confirm the fluid facilitated solid-state diffusion (SSD) reactions within the electrum, and dissolution and reprecipitation (CDR) reactions at the interface between the Au-rich zone and Ag-rich zone in electrum. Both reactions can occur during the ambient greenschist to amphibolite grade metamorphism. The local re-equilibrium caused by SSD, due to different transport ligands and interrelated impacts of physicochemical parameters of fluids (e.g., pH and $fO_2$), forms different compositional zoning patterns within electrum. The long-lived metamorphism event probably provides the elevated temperature and fracture pathways, to allow pervasive fluid infiltration to remobilize trace metals to be incorporated into electrum. This study provides mineralogical evidence for different precipitation fluid conditions which can result in different textural and chemical zoning patterns in electrum via SSD and CDR under metamorphic conditions.
Acknowledgments

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Figure captions

Figure 1  Simplified geological map of the Ming VMS deposit within the Pacquet Complex, modified after Castonguay et al. (2009), the orebodies are projected on the surface by Brueckner et al. (2016).

Figure 2  Simplified geological map of the major Skellefte VMS deposit region showing the location of the Boliden VMS deposit, modified after Wagner et al. (2007).

Figure 3  Representative ore samples from Ming (a-c) and Boliden (d-f) showing mineral associations and electrum textures. (a) Anhedral electrum occurs along the boundaries of bornite and is associated with chalcocite; sample M1807. (b) Anhedral electrum intergrowths with bornite, chalcocite and cataclastic massive pyrite; sample M1807. (c) Elongated electrum with light white Ag-rich rims along the boundary of bornite and in contact with chalcocite; sample M1807. (d) Anhedral electrum occurs along the boundaries of arsenopyrite in quartz matrix; sample BLD210. (e) Anhedral electrum under reflected light showing a dark-yellow Au-rich core and light-yellow Ag-rich rim, in contact with aurostibite; sample BLD210. (f) Anhedral electrum intergrows with recrystallized arsenopyrite and in contact with aurostibite; sample BLD210. (g) Electrum intergrows with chalcopyrite and is associated with minor arsenopyrite, pyrite, and trace stibnite; sample BLD-1. (h) Anhedral electrum occurs as veinlets filling in the fractures of quartz vein material with foliated pyrite; sample BLD-1. (i) Anhedral electrum intergrows with fractured pyrite and chalcopyrite; sample BLD-1. Abbreviations: Apy = arsenopyrite, Aur = aurostibite, Bn = bornite,
Cc = chalcocite, Ccp = chalcopyrite, El = electrum, Py = pyrite.

**Figure 4** Backscattered electron images showing internal microstructures in zoned electrum from the Ming and Boliden deposits. Electrum in (a) and (d) correspond to the samples in Figures 3a and b, whereas electrum in (g) corresponds to the sample in Figure 3g. (b) Example of the incongruent layers and porous texture at the interface between the Au-rich transition and Ag-rich rim. The light grey layers are Au-rich, whereas the dark grey layers are Ag-rich. The yellow arrows indicate the reaction front with a sharp contact. (c) Variations in thickness of reprecipitated multiple Ag-rich layers. (e) The yellow arrows indicate the gradational contact between the Au-rich electrum core (light grey) and Ag-rich electrum rim (dark grey). (f) The sharp and jagged contacts show the consequence of CDR reactions at the interface. (h) Example of the gradational contact between a Au-rich core (light grey) and Ag-rich rim (dark grey). (i) The yellow arrows show the gradational contact between the core and rim.

**Figure 5** Backscattered electron images and chemical X-ray maps of zoned electrum from the Ming and Boliden deposits. Electrum grains from the Ming deposit are characterized by Au-poor core, Au-rich transition, and Ag-rich rim chemical zoning textures which correspond to the BSE images. There are no significant Cu variations in electrum from (d) and (h). (i) Example of electrum is characterized by a Au-rich core and Au-depleted rim. There are no significant Fe variations in electrum from (l) and (p). (m) The latter Ag-rich veins are filling in the tiny fractures in electrum and fine-grained native gold grains occur along the boundary of electrum.
Figure 6 Chemical variation profiles showing compositional measurement by EPMA of zoned electrum from the Ming deposit. (a) shows the arranged profiles across the zoned electrum. (b) and (c) show the Au and Ag area intensity of X-ray by EPMA (counted by cps) along the measured line 1 and line 3 across the dark grey core, light grey transition and dark grey rim. (d-f) show Au, Ag, Cu, S, and Hg contents by EPMA point analyses across the zoned electrum.

Figure 7 Chemical variation profiles showing the major element (Au and Ag) and minor element (Cu, S, Hg) contents measured by EPMA on a zoned electrum from the Boliden deposit. (e-f) show Au, Ag, Cu, S, and Hg contents determined by EPMA point analyses along measured lines across the light grey core and dark grey rim.

Figure 8 Multielement box and whisker plots for LA-ICP-MS trace element data showing the compositional differences between the light grey and dark grey zones in electrum. (a) The arranged analysis line transects the dark grey core to the light grey zone on the zoned electrum in Figure 6a. The laser ablation spot size for electrum is 24 μm. (c) The arranged analysis line transects the light grey core to the dark grey rim on the zoned electrum in Figure 7a. The laser ablation spot size for electrum is 10 μm. (b) and (d) Box and whisker plots showing the chemical compositions of LA-ICP-MS data of electrum. Boxes outline the 25th to 75th percentiles, and whiskers extend to the 5% to 95% values. Short lines within the box represent the median value, whereas circles filled by white represent the average value. Red spots outside the whiskers indicate the outliers beyond 5% to 95% of the dataset.

Figure 9 Ternary plot showing Au-Ag-Cu compositional variations between the dark
grey and the light grey zones in compositionally zoned electrum. The compositional data of electrum come from area intensity of X-ray by EPMA (counted by cps). (a) Plot of Au-Ag-Cu variations in zoned electrum from the Ming deposit. The defined dark, light, and rim zones correspond to the same area in Figure 6a. (b) Plot of Au-Ag-Cu variations in the zoned electrum from the Boliden deposit. The defined dark and light zones correspond to the same area in Figure 7a.

**Figure 10** Schematic diagram of fluid facilitated solid-state diffusion (SSD) and coupled dissolution-reprecipitation (CDR) reactions resulting in compositional zoning in electrum from the Ming and Boliden deposits. (a-c) Illustration of the zoned electrum formation from the Ming deposit. (a) The parent Ag-rich electrum precipitated with homogeneous compositional textures from reduced fluids. (b) With increasing temperature and/or $a_{S^2}$, the Ag-rich electrum core was dissolved to form a diffusive contact through a Au-rich fluid that likely leached S-Fe-Cu-Zn-Pb during prograde metamorphism. (c) The Ag-rich electrum rim was reprecipitated on the exterior of electrum from an Ag-Cu-rich fluid with increasing $a_{Cu}$ and $fO_2$ during the retrograde metamorphism. The repeated CDR may result in the epitaxial growth of multiple Ag layers towards the margin of electrum. (d-f) illustrate the zoned electrum formation from the Boliden deposit. (d) The parent Au-rich electrum precipitated with homogeneous compositional textures from reduced fluids. (e) With increasing $a_{H_2S}$ and/or temperature, and decreasing pH, the Au-rich electrum core was dissolved to form a gradational contact through fluids which likely leached Se-Bi-Sb-Te-Sn-S-Zn during the prograde metamorphism. (f) The SSD of Ag results in coarsening of...
electrum and forms a Ag-rich rim with decreasing temperature and increasing pH during the retrograde metamorphism.

**Figure 11** Binary plot showing compositional variations between the core and rim in zoned electrum from the Ming and Boliden deposits. The compositional data of electrum come from the LA-ICP-MS analysis. (a) Plot of Au versus S + Fe + Cu + Zn + Pb, showing the increasing contents of S-Fe-Cu-Zn-Pb during the dissolution of Ag resulting in a Au-rich transition zone, in electrum from the Ming deposit. (b) Plot of Au versus Se + Bi + Sb + Te + Sn + S + Zn, showing the increased contents of Se-Bi-Sb-Te-Sn-S-Zn during the diffusion of Ag from Au-rich core from the Boliden deposit.
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### Table 1 EPMA results of electrum grains from the Ming and Boliden deposits

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<th>Internal texture</th>
<th>Number of analyses</th>
<th>Chemical composition (wt%)</th>
<th>Mineral association</th>
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<td></td>
<td>Au</td>
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<tr>
<td><strong>Ming</strong></td>
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<td></td>
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<tr>
<td>Electrum with zoning</td>
<td>Silver rich rim</td>
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<td>b.d.l.</td>
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<td>Rim</td>
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<tr>
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<td>Core</td>
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<tr>
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</table>

*Note: dataset is from Supplementary data 2. B.d.l. indicates values below the detection limits. Apy: arsenopyrite, Aur: aurostibite, Bn: bornite, Cc: chalcocite, Ccp: chalcopyrite, Py: pyrite*
Figure 9

(a) Dark grey core, Light grey transition, Dark grey rim2, Dark grey rim1

In (a), the graph shows the relationship between temperature and the distribution of different mineral phases. The arrows indicate the direction of increasing and decreasing temperature, with the dashed line representing oxidized conditions.

(b) Light grey core, Dark grey rim

In (b), the graph illustrates the change in pH, with arrows showing the direction of falling and rising pH. The distribution of light grey core and dark grey rim phases is indicated by the different colors and dot density.
Figure 11

(a) S+Fe+Cu+Zn+Pb (ppm)

SSD process

(b) Se+Bi+Sb+Te+S+Zn (ppm)

SSD process

Light grey transition

Dark grey core

Light grey core