1   **Revision 3**

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3   **Dissolution-reprecipitation *vs* solid-state diffusion in electrum: examples from**

4   **metamorphosed Au-bearing, volcanogenic massive sulfide (VMS) deposits**

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10   **Abstract**

11   Native Au-Ag alloys (electrum) are the predominant precious metal host in

12   Au-bearing volcanogenic massive sulfide (VMS) deposits. The chemical composition

13   and distribution of electrum records crystal growth and post-crystallization processes.

14   In this study, we present detailed textural and compositional data of electrum from the

15   Ming (Canada) and Boliden (Sweden) Au-bearing VMS deposits.

16   Electron probe micro-analyzer (EPMA) and laser ablation-inductively coupled

17   plasma-mass spectrometry (LA-ICP-MS) analyses of electrum enable characterization

18   of chemical zoning in heterogeneous electrum grains. Electrum from Ming exhibits

19   Ag-rich cores, in gradational contact with an outer Au-rich transition zone also

20   enriched in S, Fe, Cu, Zn, and Pb, which is in sharp contact with Ag-rich rims. The

21   textural observations, coupled with *in situ* LA-ICP-MS data, highlight that the

22   electrum zoning arises from a complex interaction between fluid facilitated solid-state

23   diffusion (SSD) within the grain, and coupled dissolution and reprecipitation (CDR)

24   reactions at the grain interface, in response to changing fluid composition and

25   extrinsic parameters, such as temperature, pH, and redox state at Ming. Electrum from

26   Boliden, in contrast, shows a Au-rich core in contact with a gradually increasing

27   Ag-rich rim enriched in Se, Bi, Sb, Te, Sn, S, and Zn, which indicates the formation

28   by fluid facilitated SSD reactions. The different local re-equilibrium caused by SSD

29   from two deposits are attributed to different transport ligands and effects of

30   physicochemical parameters of fluids (e.g., pH and fO_2), resulting in different

31   compositional zoning patterns within electrum. The long-lived metamorphic events

32   that affected the occurrence and compositions of electrum at both VMS deposits,

33   probably provided the elevated temperature and deformation to allow pervasive fluids

34   to remobilize trace metals in electrum, which resulted in the complex chemical zoning

35   in electrum. This study provides insights from *in situ*, textural and chemical analyses

36   to understand the formation of complex chemical zoning in electrum in

37   metamorphosed VMS deposits.

38   **Keywords**

39   Zoned electrum; Dissolution and reprecipitation (CDR); Solid-state diffusion (SSD);

40   Ming; Boliden; Au-bearing VMS.

41   **Introduction**

42   Chemically zoned mineral grains record a time series of reaction conditions

43   experienced   by   minerals   (Spear   and   Selverstone,   1983).   Coupled

44   dissolution-reprecipitation (CDR) is the most common mineral reaction mechanism in

45   nature (Putnis, 2009; Ruiz-Agudo et al., 2014; Spruzeniece et al., 2017;

46   Konrad-Schmolke et al., 2018; Huang and Beaudoin, 2019; Li et al., 2019a). Coupled

47   dissolution-reprecipitation reactions result in readjustment of pre-existing mutual

48   grain boundaries under hydrothermal conditions, which has been widely recognized in

49   various geological settings (Tenailleau et al., 2006; Putnis, 2009; Zhao et al., 2009;

50   Zhao et al., 2013; Liu et al., 2017). In hydrothermal systems, complex mineral

51   chemical zoning can be interpreted to reflect chemical changes in fluid compositions,

52   or re-equilibrium related to a number of physicochemical conditions (e.g., Borg et al.,

53   2014). The mechanism of re-equilibration via CDR during fluid-mineral interaction

54   involves the partial or complete dissolution of the parent mineral and reprecipitation

55   of the replacement phase at the interface (Goldsmith and Laves, 1954; Ruiz-Agudo et

56   al., 2014). Recent studies confirm that the chemical composition of placer gold can be

57   modified by repeated episodes of dissolution and precipitation reactions in supergene

58   environments (Reith et al., 2012; Shuster et al., 2017; Melchiorre et al., 2018; Rea et

59   al., 2019; Dos Santos Alves et al., 2020). This mechanism has previously been

60   suggested to explain the formation of electrum with complex zoning textures in

61   hydrothermal systems (Huston et al., 1992; Zhao et al., 2013; Liu et al., 2017; Rosell

62   et al., 2018; Li et al., 2019b).

63   Pseudomorphic replacement reactions, characterized by the preservation of the

64   shape and volume of the replaced minerals, are common in nature during

65   hydrothermal alteration, metamorphism, diagenesis, and chemical weathering (Putnis,

66   2002). However, pseudomorphic replacement in zoned minerals is alternatively

67   attributed to solid-state diffusion reactions (SSD) under hydrothermal conditions,

68   which preserve external morphology and aspects of the crystal structure (Eda et al.,

69   2005; Eda et al., 2006; Putnis, 2009; Xia et al., 2009). Solid-state diffusion reactions

70   controlling the growth of precious metal alloys have been previously reported both in

71   nature (e.g., Au-Ag alloy, Czamanske et al., 1973; Au-Ag-Sb alloy, Zachariáš et al.,

72   2017) and synthetic material studies (e.g., Au-Ag alloy, Hodak et al., 2000; Au-Sn

73   alloy, Baheti et al., 2018; Au-Cu alloy, Xiong et al., 2014). The lack of porosity and a

74   gradational contact between the parent and product phases may be the key

75   crystallographic feature for SSD reactions (Putnis and Putnis, 2007; Zhao et al., 2013).

76   However, a sharp contact instead of a diffusion profile between the parent and product

77   phases is a feature for CDR reactions (Putnis, 2009, 2014; Robert, 2014). Although

78   the microstructures of final products by CDR and SSD are different, the fundamental

79   mechanism remains the same as both involve a re-equilibration of cation exchange

80   (Putnis, 2009).

81   The Au-Ag system forms a complete miscible alloy, according to the

82   Hume-Rothery rules, due to the similar atomic radii, crystal structure, and valence of

83   Au and Ag (Guisbiers et al., 2015). The term *electrum* is used to refer to Au-Ag alloys

84   between 20 wt% and 80 wt% Au, whereas native gold is used for alloys with more

85   than 80 wt% Au (Boyle, 1979). Previous studies have explained Au and Ag solubility

86   during transport and precipitation from fluids based on experimental data (Huston et

87   al., 1992; Gammons and Williams-Jones, 1995; Pal'yanova and Kolonin, 2007).

88   Shikazono and Shimizu, (1987) used Ag/Au ratios of electrum to discuss variations in

89   Eh, pH, temperature, and sulfur contents in auriferous vein deposits. Hagemann et al.

90   (1998) suggested that Ag-rich electrum is related to reduced fluids which reacted with

91   more oxidized ultramafic rocks at the Archean Transvaal gold deposit (Australia).

92   Zoned electrum has been reported in epithermal deposits in the United States, Spain,

93   and Japan (Desborough et al., 1971; Rosúa et al., 2002; Yokoyama et al., 2011).

94   Silver-zoned electrum grains have been investigated in volcanogenic massive sulfide

95   (VMS) deposits in Eastern Australia (Huston et al., 1992) and the Baochun skarn gold

96   deposit (China, Lu et al., 2000). Healy and Petruk (1990) reported zoning of

97   Au-Ag-Hg alloys is a consequence of crystallization of increasingly Ag-rich fluids

98   during retrograde metamorphism at the Trout Lake VMS deposit, Flin Flon (Canada).

99   Gold-bearing VMS deposits are key exploration targets because their gold contents

100   contribute significantly to the ore value (Dubé et al., 2007; Mercier-Langevin et al.,

101   2011). It has been shown that gold can be remobilized from the massive sulfide bodies

102   into veins peripheral to, or within the VMS deposits during deformation and

103   metamorphism (Huston et al., 1992; Tourigny et al., 1993; Sinclair et al., 2000;

104   Larocque et al., 1995). Deformation and metamorphism have been proposed to cause

105   coarsening of gold and upgrading in some VMS deposits (Huston et al., 1992;

106   Årebäck et al., 2005; Wagner et al., 2007; Vikentev, 2016; Mercier-Langevin et al.,

107   2011). However, the effect of metamorphism on electrum compositional zoning still

108   remains unclear.

109   We selected two Au-bearing VMS deposits, Ming (Canada) and Boliden (Sweden),

110   because both have common gold mineralization characteristics: (1) occurrence of

111   zoned electrum, (2) an overlap of VMS and epithermal (Ag, As, Sb, Hg)

112   mineralization with interpreted magmatic contributions (e.g., Bi, Te), (3) complex ore

113   mineralogy with abundant sulfides and sulfosalts, (4) association with

114   andesite-dacite-rhyodacite-rhyolite rocks, and (5) metamorphism and deformation

115   overprints resulting in remobilization of gold (Mercier-Langevin et al., 2011;

116   Mercier-Langevin et al., 2013; Brueckner et al., 2014; Brueckner et al., 2016). Here,

117   we present in situ textural and chemical composition results of electrum from the

118   Boliden and Ming deposits, to investigate compositional zoning characteristics in

119   electrum grains and to constrain the mechanisms responsible for chemical zoning in

120   electrum. Our results provide new insights into how SSD and CDR reactions can form

121   compositional zoning in electrum, and into the effects of metamorphism on precious

122   metal mobility in greenschist to amphibolite facies rocks.

123   **Geology of the selected deposits and sample description**

124   Three electrum-bearing representative samples were selected from the Ming (n=1,

125   Canada) and Boliden (n=2, Sweden) deposits. The geology of the two deposits and

126   their geochemistry are well documented in literature (Bergman Weihed et al., 1996;

127   Wagner et al., 2007; Mercier-Langevin et al., 2013; Pilote and Piercey, 2013;

128   Brueckner et al., 2014; Brueckner et al., 2015; Brueckner et al., 2016; Pilote et al.,

129   2016; Pilote et al., 2020), and only a brief summary is presented here.

130   ***Ming deposit***

131   The Ming deposit is a Cambro-Ordovician bimodal-mafic VMS deposit (3.65Mt at

132 2.26 wt% Cu, 1.13 g/t Au, 6.78 g/t Ag, and 0.32 wt% Zn) located in the northern

133 central part of the Baie Verte Peninsula of Newfoundland (Canada, Pilote and Piercey,

134 2013; Brueckner et al., 2016). The deposit is hosted in the upper part of the Rambler

135 Rhyolite Formation (Figure 1), which is a folded, dome-shaped, sequence of

136 quartz-phyric rhyodacite, quartz-bearing intermediate to felsic tuff and tuff breccia

137 formed during the Cambrian-Ordovician (ca. 487 Ma, Skulski et al., 2010; Pilote et al.,

138 2016). Upper greenschist to lower amphibolite facies metamorphism affected most of

139 Rambler Rhyolite Formation, including four phases of regional deformation (Hibbard,

140 1983; Castonguay et al., 2009). There are five massive sulfide orebodies hosted

141 within variously hydrothermally altered volcaniclastic rocks, which are the 1807,

142 1806, Ming North, Ming South and Lower Footwall zones. The ore mineralogy in the

143 1807 zone consists of (1) pyrite, chalcopyrite, sphalerite, pyrrhotite, arsenopyrite, and

144 galena, (2) uncommon tellurides, selenides, and sulfo-animonides, (3) sulfosalts

145 (tennantite-tetrahedrite), (4) precious metals (electrum, Ag-sulfosalts, and minor

146 silver), and (5) oxides (magnetite, ilmentite, chromite) (Brueckner et al., 2016; Pilote

147 et al., 2016). Precious metal (Au-Ag) emplacement is syngenetic (Brueckner et al.,

148 2014). Gold remobilization and recrystallization during deformation and

149 metamorphism at the Ming deposit is described by Brueckner et al. (2014), Brueckner

150 et al. (2016), and Pilote et al. (2020). Electrum, which occurs along fractures in

151 cataclastic and recrystallized pyrite, and interstitial between recrystallized pyrite ±

152 arsenopyrite, has been interpreted to be the product of Silurian-Devonian

153 metamorphism of pre-existing precious metals at peak temperature up to 500°C

154   (Brueckner et al., 2016).

155   Sample M1807, collected from the massive sulfide orebody in the 1807 zone of the

156   Ming deposit, is composed of pyrite, chalcopyrite, sphalerite, galena, electrum, and

157   native silver. Electrum is the major precious metal alloy, either adjacent to chalcocite

158   or intergrown with bornite and chalcopyrite (Figure 3). Bornite occurs as anhedral

159   grains associated with chalcopyrite and electrum. Native silver predominantly occurs

160   as veins along fractures and between sulfide minerals.

161   ***Boliden deposit***

162   The Boliden deposit is a Au-Cu-As VMS deposit (8.3 Mt at 15.9g/t Au, 50 g/t Ag,

163   1.42 wt% Cu, 0.9 wt% Zn, 0.3 wt%Pb, and 6.8 wt% As) located in the eastern part of

164   the Skellefte district, Sweden (Figure 2), which was formed between ca. 1894 and

165   1891 Ma (Mercier-Langevin et al., 2013). The deposit is hosted in the uppermost part

166   of the rhyolitic metavolcanic Skellefte Group that consists of Early Proterozoic felsic

167   to mafic volcanic rocks with lesser intrusive and sedimentary rocks (Allen et al., 1996;

168   Mercier-Langevin et al., 2013). The Skellefte belt was affected by regional

169   Svecokarelian metamorphism at greenschist to amphibolite grade at ca.1.83-1.81Ga

170   and the peak metamorphic conditions in the Boliden area were estimated as 430°C

171   and 5-7 kbar (Berglund and Ekström, 1980; Billstrom and Weihed, 1996). The ore

172   lenses were flattened and the sulfide assemblages were highly folded and foliated

173   during tectonic deformation (Wagner and Jonsson, 2001; Mercier-Langevin et al.,

174   2013). The main massive sulfide mineralization in Boliden consists of brecciated

175   pyrite, foliated chalcopyrite, fine-grained arsenopyrite, pyrrhotite, and Cu-Pb-Bi-Sb

176   sulfosalts. The pyrite and arsenopyrite are strongly recrystallized and form granular

177   masses or are aligned along foliation (Wagner et al., 2007; Mercier-Langevin et al.,

178   2013).

179   Two typical Au-rich samples were selected from the main massive orebody in

180   Boliden. Sample BLD210 is from the fine-grained massive arsenopyrite ore, whereas

181   sample BLD-1 comes from a chlorite-altered massive pyrite with strong foliation.

182   Electrum is the predominant Au-Ag alloy and is adjacent to arsenopyrite, pyrite, and

183   intergrown with chalcopyrite, whereas native gold was also found as very small

184   (10-20 μm) grains along the boundaries of electrum (Figure 5m).

185   **Analytical methods**

186   Ten polished thin sections from the Ming deposit and twelve from the Boliden

187   deposit, were cut in order to yield significant numbers of electrum grains for study,

188   which were examined by optical microscopy. Backscattered electron (BSE) imaging

189   was used to identify mineralogical and textural relationships using a JEOL JSM-840A

190   scanning electron microscope (SEM) at Université Laval (Canada). The accelerating

191   voltage was 15 kV and the beam current was 60 μA, at a working distance of 20 mm.

192   Electrum grains were analyzed for their major (Au, Ag) and minor elements (Zn, Cu,

193   Co, Fe, Pb, S, Hg, Pt, Se, As) using a CAMECA SX-100 Electron Probe

194   Micro-Analyzer (EPMA) at Université Laval (Canada), equipped with five

195   wavelength-dispersive spectrometers. The analyses used a 25 kV accelerating voltage

196   with 100 nA beam current for minor elements and 20 nA for major elements, both

197   with a 5 μm beam size. Simple oxides (GEO standards block) and pure metals from

198   the Astimex company were used as standard materials. Analysis time was 40 s and 20

199   s of background measurement. Detection limits for each element and precisions

200   calculated from three analyses of gold standard (NA-Au-31) are listed in

201   Supplementary data 1. Electrum compositional maps were obtained by

202   wavelength-dispersive spectroscopy (WDS) X-ray for Au and Ag at an accelerating

203   voltage of 15 kV and a beam current of 100 nA, and a counting time of 20 ms/pixel

204   with a resolution of 577 × 527 pixels.

205   The trace element analyses of native electrum were carried out at the University of

206   New Brunswick (Canada). Electrum grains were analyzed using a Resonetics

207   S-155-LR 193 nm Excimer laser ablation system coupled with an Agilent 7700x

208   quadrupole ICP-MS. To investigate trace element distributions in electrum, lines were

209   used to ablate across a single grain to generate profiles. A beam size of 10 - 24 μm

210   was used for compositional analysis. Rastering speed for each line was modified

211   based on the beam size to achieve maximum resolution (5 μm/s for 10 μm beam size,

212   8 μm/s for 24 μm beam size). Acquisition time was set to 0.002 s for all the elements

213   resulting in a total sweep time of ~0.8 s. Electrum grains were ablated using energy

214   density of 2.3 J/cm^2, and the beam operating at 10 Hz frequency. Trace element

215   contents, including Mg, Al, Si, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Pd, Cd, Sn, Sb, Te,

216   Pt, Pb, Bi, Hg, S, Ti, Mo, In, and Tl, were measured by LA-ICP-MS in this study. The

217   external standard NIST610 was used for calibration of Mg, Al, Si, S, Ti, Mo, In, and

218   Tl (Rocholl et al., 1997). The USGS synthetic MASS-1, a pressed powder pellet, was

219   used for calibration of Hg (Wilson et al., 2002). A synthetic gold standard (NA-Au-31)

220   was used for calibration of Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Pd, Cd, Sn, Sb, Te, Pt,

221   Pb, and Bi, whereas a second gold standard (NA-Au-30) was used for quality control

222   of LA-ICP-MS analyses (Milidragovic et al., 2016). The standards were analyzed

223   every eight spots with the same ablation spot size as the unknown sample analysis.

224   Data were reduced using Iolite3.0 software (Longerich, 1996; Paton et al., 2011).

225   Trace element concentrations were internally normalized to Ag values acquired by

226   EPMA at Université Laval. The average detection limit for each electrum sample and

227   precisions calculated from routine analyses (n=43) of gold standard (NA-Au-31) are

228   reported in Supplementary data 1 and the comparison of routine analyses of trace

229   elements in reference materials (NA-Au-31, NIST610, and MASS-1) by LA-ICP-MS

230   and certificate values is given in Supplementary data 3.

231   **Electrum textures**

232   In massive sulfides from Ming 1807 zone, ten electrum grains from ten thin

233   sections have been investigated and they are either adjacent to, or along fractures in

234   pyrite, and are intergrown with silicates quartz, epidote, or biotite, and sulfides

235   chalcocite, bornite, or chalcopyrite (Figure 3a). Seven of the ten electrum grains are

236   zoned, and they occur as irregular inclusions in bornite, associated with cataclastic

237   pyrite and chalcopyrite (Figure 3b), whereas they can also form anhedral grains and

238   veinlets along the boundaries of chalcocite and bornite (Figure 3c). Native silver

239   occurs as veins or thin films surrounding the electrum grain or along the boundaries of

240   chalcocite (Figure 3c). The internal microstructure of electrum, observed in BSE

241   images, show a light grey core and dark grey rim (Figure 4). Incongruent layers

242 developed towards the electrum margin, between the light grey zone and dark grey

243 rim, and show an abrupt contact (Figures 4 b-f). Several dark grey layers towards the

244 edge of the grain contain more pores than the light grey zone and show various widths

245 in different areas of individual grains (Figures 4 b and c). Within the electrum, the

246 contact between the dark grey core and light grey transition zone, shows a gradational

247 contact (Figures 5a and 6a).

248   At Boliden, twenty-six electrum grains from twelve thin sections were investigated

249 and they occur predominantly as coarse anhedral grains along boundaries of

250 fine-grained, massive, and crystalline arsenopyrite, and at contacts with aurostibite,

251 which are commonly enclosed in quartz in the massive arsenopyrite ore (Figures 3 d

252 and f). Six of twenty-six electrum grains are zoned and occur as veinlets filling in

253 factures in brecciated pyrite, chalcopyrite, and arsenopyrite in the chlorite-altered

254 massive pyrite ore (Figure 3g). These electrum grains are oriented parallel to the main

255 foliation (Figure 3h). Under BSE, zoned electrum has a light grey core in gradational

256 contact with a dark grey rim (Figures 4 g-i). Fine-grained native gold is not common

257 but can be observed as disseminated grains adjacent to electrum in association with

258 pyrite and chalcopyrite, which is not zoned (Figure 5n). Native silver veins are not

259 observed in the Boliden ore samples. However, fissures transecting electrum both in

260 massive arsenopyrite and foliated pyrite consisted of Ag-rich electrum (Figures 5

261 m-o).

262 **Chemical composition of electrum**

263   The zoned electrum grains were identified in the petrographic and BSE images. To

264   quantify the chemical characteristics of these zoned electrum grains, WDS X-ray

265   maps, EPMA profiles and LA-ICP-MS profiles were used. The major and minor

266   element compositions of electrum grains from Ming and Boliden are presented in

267   Table 1. Chemical composition variations in zoned electrum grains are shown in

268   Figures 5-8.

269   In the 1807 zone of the Ming deposit, zoned electrum grains commonly show a

270   variation in Ag contents from 20 wt% to 40 wt% and Au contents from 62 wt% to 79

271   wt% (Table 1). The WDS X-ray map shows that dark grey cores are Au-poor,

272   surrounded by a light grey transitional zone with higher Au content, and an outer, dark

273   grey, Ag-rich rim (Figure 5b). Profiles across the zoned grain (lines 1 and 3), show

274   that the dark grey core has a high and constant concentration of Ag (24 wt%) and low

275   concentration of Au (75 wt%, Figures 5e). Silver exhibits a progressively decreasing

276   variation from the dark grey core to the rim, whereas Au shows a gradational increase

277   (Figures 6 b and c). There is an abrupt increase of Ag, and decrease of Au, at the light

278   grey transition from grain to the rim (Figure 6b). According to the WDS X-ray map,

279   the Ag-rich rim can be divided into two layers (the inner rim1 and outer rim 2 in

280   Figures 6 a and b). The contact between rims 1 and 2 is sharp in BSE images with an

281   abrupt increase in Ag in rim 2 (Figure 6b). The dark grey core of electrum grains has

282   Au ranging from 65 wt% to 77 wt%, compared to Au in the light grey transition zone

283   ranging from 71 wt% to 78 wt% (Table 1). Gold in dark rims 1 and 2, ranges from 62

284   wt% to 69 wt%, which is lower compared to Au in the dark grey core (65 wt% to 77

285   wt%) and light grey transition zone (71 wt% to 78 wt%). The dark grey core has a

286   range of Ag from 21 wt% to 35 wt%, whereas the light grey transitional zone is

287   relatively depleted in Ag, ranging from 20 wt% to 30 wt%. The average fineness

288    $\{1000 \times Au_{wt\%} / (Au_{wt\%} + Ag_{wt\%})\}$ value in the dark core is 651, which is lower than

289   that in the light grey transitional zone, 761. Rim 1 is dark grey and has an average

290   gold fineness value of 672, compared to rim 2, which has a gold fineness of 609, is

291   slightly darker. Native silver veins filling fractures or along the electrum grain

292   boundaries have up to 99 wt% Ag (Figure 5c).

293   Copper content in the zoned electrum from Ming ranges from 0.03 wt% to 2.9 wt%,

294   shows an increase in concentration from the light grey zone to the dark grey rims

295   (Figures 6 d-f). The dark grey rim 2 has Cu contents of 0.8 wt%, higher than the dark

296   grey core with 0.3 wt%, and light grey transitional zone with 0.1 wt% (Table 1).

297   Sulfur in the dark grey core has an average of 0.05 wt%, a similar amount at 0.06 wt%

298   in the light grey transition, and elevated contents in the dark grey rims up to 0.13 wt%

299   (Table 1). Mercury yields an average 0.7 wt% in the dark grey core, 0.6 wt% in the

300   light grey transition zone, and 0.1 wt% in the dark grey rim (Table 1). Mercury is

301   relatively enriched in the dark grey core and the dark grey rims compared with the

302   light grey zone (Figures 6 d-f). Mercury in Ag-rich veins reaches up to 6.2 wt%,

303   which is lower than the Hg measured in electrum with a range of 8 wt% to 21 wt% in

304   samples from the 1806 zone of the Ming deposit (Brueckner et al., 2014).

305   A LA-ICP-MS profile in a zoned electrum grain from Ming is used to illustrate

306   trace element contents between the dark and light grey zones (Figure 8a and

307   Supplementary data 3). Figure 8b shows that the light grey zone has relatively higher

308   Fe, Cu, Zn, Te, Pb, Bi and S than the dark grey zone, whereas Sn and Sb show similar

309   range and average values.

310   At the Boliden deposit, zoned electrum has a light grey core and a dark grey rim

311   that are coincident with a wide range of Ag concentrations from 6 wt% to 46 wt% and

312   of Au concentrations ranging from 48 wt% to 90 wt% (Table 1). The EPMA spot

313   analyses were arranged along three profiles across the dark and light grey zones in the

314   zoned electrum (Figure 7a). The light grey core has Au concentrations ranging from

315   55 wt% to 90 wt% Au (average 70 wt%) with Au fineness value ranges from 575 to

316   936, whereas the dark rim is Au-poor with a range from 48 wt% to 69 wt% Au

317   (average 61 wt%) with Au fineness values range from 511 to 738 (Figures 5k and 7).

318   In contrast, the Ag concentration in the light grey core ranges from 6 wt% to 40 wt%,

319   whereas Ag is relatively enriched in the dark grey rim, ranging from 25 wt% to 46 wt%

320   (Figure 7). Copper content in the zoned electrum varies from 0.002 wt% to 5 wt%

321   (Figures 7e and f). The light grey core has relatively low Cu, S, and Hg contents with

322   averages of 0.06 wt%, 0.05 wt%, and 1.4 wt%, respectively. The dark grey rim has

323   higher averages of 0.5 wt% Cu, 0.36 wt% S, and 1.9 wt% Hg (Figure 7).

324   A line of LA-ICP-MS spot analyses across the light core to the dark rim is used to

325   investigate trace element variations for the zoned electrum grain from the Boliden

326   deposit (Figure 8c and Supplementary data 3). Generally, the dark grey zone has

327   higher Fe, Cu, Zn, Se, Sn, Sb, Te, Pb, Bi, and S than the light grey zone (Figure 8d).

328   **Discussion**

329   The zoned electrum from the Ming deposit is characterized by a Ag-rich core, a

330   gradational contact with a Au-rich transition zone, and an abrupt contact with a

331   Ag-rich rim (Figure 5a). In contrast, the zoned electrum from the Boliden deposit is

332   characterized by a Au-rich core with a gradational contact with a Ag-rich rim (Figure

333   5i), which was previously reported both in massive and vein orebodies in the deposit

334   (Bergman Weihed et al., 1996). The gradational chemical contact was observed in

335   both VMS deposits; however, the abrupt chemical contact is only observed in

336   electrum from the Ming deposit. Zoned electrum in both VMS deposits exhibits an

337   opposite zoning pattern of Au-Ag composition from the core to the margin, which

338   likely records different crystal growth and post-crystallization processes. The content

339   of Au and Ag in electrum grains are controlled by their solubilities in hydrothermal

340   fluids under different conditions (Pal'yanova and Kolonin, 2007). Therefore, different

341   compositional zoning characteristics in electrum likely indicate different precipitation

342   conditions.

Formation of zoned electrum at Ming

344   At Ming, the close mineralogical association of the Ag-rich electrum core with

345   arsenopyrite, chalcopyrite, pyrrhotite, and sphalerite suggests that Au was transported

346   by bisulfide complexes at a temperature < 300℃, in reduced fluids, whereas the

347   association of Ag-rich electrum rim with galena and chalcopyrite suggests that Ag was

348   transported by chloride complexes (Seward, 1973; Huston et al., 1992;

349   Williams-Jones et al., 2009; Brueckner et al., 2016). The silver-rich electrum core

350   suggests a low pH solution, because silver chloride complexes are far more soluble

351   than the bisulfide complexes at low pH, indicating Ag is more mobile than Au (Mann,

352   1984; Wilson, 1984; Gammons and Barnes, 1989). The formation of electrum grains

353   along fractures in recrystallized pyrite or arsenopyrite has been interpreted to be of

354   syngenetic origin between 260°C to 300°C at Ming, whereas the regional

355   Silurian-Devonian deformation indicates a peak metamorphic temperature of 500°C

356   (Brueckner et al., 2016). At elevated temperature, silver likely tends to be dissolved

357   via reaction (1), leading to the increase in Au content to form the Au-rich zone with a

358   gradational contact with the electrum core (Gammons and Williams-Jones, 1995;

359   Migdisov et al., 1999).

360    $Ag_{alloy}+2Cl^-+H^++1/4O_{2(g)}=AgCl_2^-+1/2H_2O$ (1)
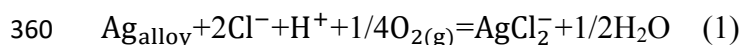
361   The incongruent layers near the Ag-rich margin of electrum at Ming likely

362   indicates dissolution from the core to the margin (Figure 4b). The Ag-rich rim of

363   electrum grains at the Ming deposit precipitated on the exterior of Au-rich zone and

364   exhibits an epitaxial relationship with the parent electrum (Figures 4e and f). The

365   presence of sharp interfaces between the Au-rich zone and Ag-rich rims is generated

366   by repeated coupled dissolution and reprecipitation (Figure 4b and f, Bowell, 1992).

367   The coexisting mineral assemblage of bornite + chalcocite also implies a higher

368   temperature event, because bornite + chalcocite precipitates in oxidized conditions

369   during an input of Cu-rich fluid (> 300°C) in VMS deposits (Hannington, 1999; Koski,

370   2010). The general trend of increasing Ag with Cu composition in the Ag-rich rims

371   likely suggests the later pulse of Cu-rich chloride complex fluid may be rich in Ag

372   and precipitated silver-rich veins in fractures (Figure 9a). Under a decreasing

373   temperature and oxidized condition, the dissolution of Au and reprecipitation of Ag at

374 the interface are facilitated by reaction (2) and (3) to form the sharp compositional

375 contact (Figures 4d and f, Gammons and Williams-Jones, 1995).

376 $Au_{alloy}+2Cl^-+H^++1/4O_{2(g)}=AuCl_2^-+1/2H_2O$ (2)

377 and

378 $Au_{alloy}+AgCl_2^-=AuCl_2^-+Ag_{alloy}$ (3)
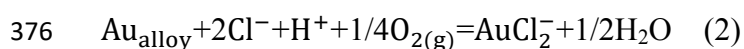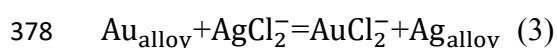
379 In addition, there is an enrichment of S-Fe-Cu-Zn-Pb suite from the Ag-rich core to

380 the Au-rich transition zone at Ming (Figure 11a), likely because these elements were

381 mobilized and readily re-incorporated into electrum from fluids during prograde

382 metamorphism (Lockington et al., 2014). Native silver is not common throughout the

383 Ming deposit because the syngenetic fluids conditions did not favor Ag solubility

384 (Brueckner et al., 2016). Native silver rims precipitated in fractures and along the

385 boundaries of bornite and chalcocite (Figures 3c and 5) are likely remobilized from

386 sulfides under metamorphic conditions due to its high mobility and ductile behavior.

387 Hence, the mobilization of silver from proximal sulfides under low- to medium-grade

388 metamorphic environments favors un upgrading of Ag contents at the rim of electrum.

389 It is worth noting that porosity, as an integral microstructural feature of CDR, is

390 essential to sustain fluids to transport and react at the interface between the parent and

391 product phases (Putnis, 2009). The small pores in the incongruent layers in the

392 electrum from Ming, allowing fluids to react with parent electrum, are likely the

393 consequence of CDR at the interface (Figures 4b and c). The generation of grain-scale

394 fractures in parent electrum also provides possible pathways for pervasive transport of

395 fluids to react with the electrum interface, which facilitated CDR, resulting in multiple

396   thin layers of Ag-rich rims (Figure 4b-f). It appears that the compositional zoning in

397   electrum is related to the factures within the grain, or the grain edge, indicating a

398   post-precipitation re-equilibration (Figures 4 and 5). The existence of nanoscale

399   porosity in electrum will need to be further assessed by transmission electron

400   microscopy.

Formation of zoned electrum at Boliden

402   At Boliden, a gradational contact between the Au-rich core and Ag-rich rim is

403   observed and Ag-rich veins are precipitated in the fractures of electrum (Figures 4h

404   and 5o). The sericite-quartz and sericite-chlorite alteration assemblages and the

405   association of electrum with arsenopyrite ± pyrite ± pyrrhotite indicate a more

406   reduced fluid and gold bisulfide complexes were likely dominant at low temperatures

407   (< 300°C) (Huston et al., 1992; Mercier-Langevin et al., 2013). This reduced fluid

408   contained high H_2S and sufficient HCl to produce the necessary acidity to leach the

409   host rocks to precipitate a large amount of arsenopyrite (Bergman Weihed et al., 1996).

410   At elevated temperature, the solubility of gold in sulfide complexes tends to be

411   sensitive to changes in pH and redox potential (Stefánsson and Seward, 2004). In the

412   presence of electrum, a_{H_2S} has significant effects on gold solubility and fO_2 has

413   moderate impacts on gold solubility. The wall rocks of Boliden massive sulfide ore

414   display a zoned alteration pattern with an inner envelope dominated by white mica ±

415   andalusite and outer chlorite ± sericite zone (Bergman Weihed et al., 1996), indicating

416   an acidic fluid responsible for the advanced argillic alteration that precipitated the

417   Au-rich electrum (Marquis et al., 1990). Gold solubility can be increased through

418   reaction (4), and the solubility of Ag can be increased by reaction (5) with decreasing

419   pH in oxidizing fluids (Gammons and Williams-Jones, 1995).

420    $Au_{(s)}+2H_2S_{(aq)}+1/4O_{2(g)}=Au(HS)_2^-+H^++1/2H_2O$ (4)

421   and

422    $Ag_{(s)}+2H_2S_{(aq)}+1/4O_{2(g)}=Ag(HS)_2^-+H^++1/2H_2O$ (5)
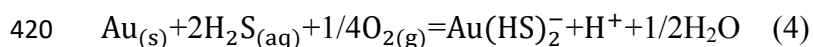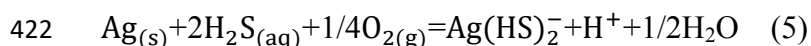
423   Under elevated temperature (> 300°C, corresponding to the peak metamorphism)

424   and/or a_{H_2S}, the Au-rich electrum is dissolved via reaction (6) to form a gradational

425   diffusion contact at the interface (Huston et al., 1992; Gammons and Williams-Jones,

426   1995).

427    $Au_{alloy}+Ag(HS)_2^-=Au(HS)_2^-+Ag_{alloy}$ (6)
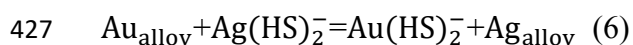
428   The general trend of increasing Cu with Ag composition in the Ag-rich rim, likely

429   suggests a later pulse of Cu-rich fluid (Figure 9b). With increasing pH and decreasing

430   temperature, the Ag-rich electrum rim precipitated, coarsening the electrum grain and

431   decreasing gold fineness during retrograde metamorphism. The gradual variations in

432   Au and Ag observed in BSE images, EPMA and LA-ICP-MS line profiles, suggest the

433   SSD of metals is facilitated by reaction (6), across the gradational contact between the

434   light and dark zones (Figures 4, 7, and 8).

435   *Diffusion trends in zoned electrum grains*

436   Opposite diffusion trends are observed in Au-Ag-Cu composition diagrams from

437   each deposit. This suggests that precipitation conditions controlling the zoned

438   electrum compositions in the Ming and Boliden deposits are different (Figure 9). At

439   Ming, the parent electrum core is Ag-rich, and Ag is leached from electrum to form

440   Au-rich electrum, with irregularly gradual contact generated by SSD reactions

441   facilitated by Au-rich, low pH fluids with increasing temperature (Figures 9a and 10b,

442   Hough et al., 2007; Rosell et al., 2018). These fluids seem to be enriched in Fe, Cu,

443   Zn, Te, Pb, Bi and S, and these elements are redistributed and incorporated into

444   electrum during the modification of Ag-rich electrum (Figures 8b, 10b, and 11a). In

445   contrast, the parent electrum is Au-rich at Boliden, and Ag in electrum is soluble and

446   is easy to be mobilized at low pH, under reduced conditions (Figures 10 d and e,

447   Gibert et al., 1998; Williams-Jones et al., 2009). The gradational contact between the

448   Au-rich core and Ag-rich rim, and absence of multiple layers, suggest a SSD reaction

449   that mobilizes Ag from Au-rich electrum, which is slow at 300°C but faster at

450   temperature > 300°C facilitated by Ag-rich fluids (Figure 10f, Huston et al., 1992;

451   Gammons and Williams-Jones, 1995; Marshall et al., 2000). These Ag-rich fluids can

452   also mobilize Fe, Cu, Zn, Se, Sn, Sb, Te, Pb, Bi, and S, and these elements are

453   incorporated in the Ag-rich electrum (Figures 8d, 10e, and 11b).

454   Gammons and Williams-Jones (1995) indicated that electrum precipitation from

455   aqueous sulfide-rich solutions is sensitive to pH, where a drop in pH causes a

456   continuous increase in Au content in electrum, when Au is transported by bisulfide

457   complexes $\{Au(HS)_2^-\}$ in fluids (Figure 9b). The composition of electrum is highly

458   sensitive to changes in the amount of Au and Ag in solutions and temperature, under

459   oxidized conditions, where Au is transported by a bisulfide complex $\{Au(HS)_2^-\}$ and

460   Ag by a chloride complex $\{AgCl_2^-\}$ at Ming (Gammons and Williams-Jones, 1995). It

461   is likely that the local re-equilibrium caused by SSD in electrum, due to different

462   transport ligands and interrelated effects of physicochemical parameters of fluids (e.g.,

463   temperature and pH), resulted in opposite diffusion trends compared with electrum in

464   Au-Ag-Cu compositions in Boliden (Figure 9).

465   ***Relationship between zoning in electrum and metamorphism***

466   Post-depositional deformation and metamorphism have effects on the occurrence of

467   electrum in VMS deposits (Huston et al., 1992). In addition to coarsening the grain

468   size of electrum under metamorphic environments, the composition can also be

469   modified due to SSD reactions, particularly at higher metamorphic grade (Boyle,

470   1979; Huston et al., 1992). The SSD modification during metamorphism on electrum

471   composition has been previously reported in the Trout Lake VMS deposit (Flin Flon

472   district, Healy and Petruk, 1990). In both the Ming and Boliden deposits, silver-rich

473   electrum tends to occur along fractures in or along grain boundaries between sulfides,

474   and is intergrown with ductile-deformed sulfide minerals, in addition, shows an

475   enrichment of Hg in EPMA profiles (Figures 6 and 7). The Ag-rich electrum rim with

476   elevated Hg is considered to have formed below the peak metamorphic temperature,

477   because pervasive homogenization of Au-Ag-Hg by volume diffusion during the

478   extensive period of prograde metamorphism will erase the growth zoning in electrum

479   grains (Oberthuer and Saager, 1986). The diffusion-induced zoning with trace element

480   remobilization and incorporation at the near surface or mineral interface has been

481   documented during regional metamorphism of ore deposits (Healy and Petruk, 1990;

482   Watson, 1996; Reeder and Rakovan, 1999; Marshall et al., 2000). Thus, we consider

483   that prograde metamorphism can provide the elevated temperature and pressure to

484 form fractures that allow metamorphic fluids to dissolve the parent electrum, and to

485 mobilize trace metals (e.g., S-Fe-Cu-Zn-Pb at Ming, Se-Bi-Sb-Te-Sn-S-Zn at

486 Boliden), that are incorporated into the electrum rim by SSD reactions during the

487 retrograde metamorphic process (Figure 11).

488 **Implications**

489 This study investigated chemical zoning textures in electrum grains from the Ming

490 and Boliden VMS deposits. Electrum from the Ming deposit is zoned, with a Ag-rich

491 core that gradually shifts to a Au-rich transition zone that is in sharp contact with an

492 outer Ag-rich rim, whereas electrum from the Boliden deposit is zoned with a Au-rich

493 core with a gradational contact with a Ag-rich rim. The compositional variation and

494 textural zoning of the electrum confirm the fluid facilitated solid-state diffusion (SSD)

495 reactions within the electrum, and dissolution and reprecipitation (CDR) reactions at

496 the interface between the Au-rich zone and Ag-rich zone in electrum. Both reactions

497 can occur during the ambient greenschist to amphibolite grade metamorphism. The

498 local re-equilibrium caused by SSD, due to different transport ligands and interrelated

499 impacts of physicochemical parameters of fluids (e.g., pH and fO_2), forms different

500 compositional zoning patterns within electrum. The long-lived metamorphism event

501 probably provides the elevated temperature and fracture pathways, to allow pervasive

502 fluid infiltration to remobilize trace metals to be incorporated into electrum. This

503 study provides mineralogical evidence for different precipitation fluid conditions

504 which can result in different textural and chemical zoning patterns in electrum via

505 SSD and CDR under metamorphic conditions.

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,

538   Cc = chalcocite, Ccp = chalcopyrite, El = electrum, Py = pyrite.

539   **Figure 4** Backscattered electron images showing internal microstructures in zoned

540   electrum from the Ming and Boliden deposits. Electrum in (a) and (d) correspond to

541   the samples in Figures 3a and b, whereas electrum in (g) corresponds to the sample in

542   Figure 3g. (b) Example of the incongruent layers and porous texture at the interface

543   between the Au-rich transition and Ag-rich rim. The light grey layers are Au-rich,

544   whereas the dark grey layers are Ag-rich. The yellow arrows indicate the reaction

545   front with a sharp contact. (c) Variations in thickness of reprecipitated multiple

546   Ag-rich layers. (e) The yellow arrows indicate the gradational contact between the

547   Au-rich electrum core (light grey) and Ag-rich electrum rim (dark grey). (f) The sharp

548   and jagged contacts show the consequence of CDR reactions at the interface. (h)

549   Example of the gradational contact between a Au-rich core (light grey) and Ag-rich

550   rim (dark grey). (i) The yellow arrows show the gradational contact between the core

551   and rim.

552   **Figure 5** Backscattered electron images and chemical X-ray maps of zoned electrum

553   from the Ming and Boliden deposits. Electrum grains from the Ming deposit are

554   characterized by Au-poor core, Au-rich transition, and Ag-rich rim chemical zoning

555   textures which correspond to the BSE images. There are no significant Cu variations

556   in electrum from (d) and (h). (i) Example of electrum is characterized by a Au-rich

557   core and Au-depleted rim. There are no significant Fe variations in electrum from (l)

558   and (p). (m) The latter Ag-rich veins are filling in the tiny fractures in electrum and

559   fine-grained native gold grains occur along the boundary of electrum.

560   **Figure 6** Chemical variation profiles showing compositional measurement by EPMA

561   of zoned electrum from the Ming deposit. (a) shows the arranged profiles across the

562   zoned electrum. (b) and (c) show the Au and Ag area intensity of X-ray by EPMA

563   (counted by cps) along the measured line 1 and line 3 across the dark grey core, light

564   grey transition and dark grey rim. (d-f) show Au, Ag, Cu, S, and Hg contents by

565   EPMA point analyses across the zoned electrum.

566   **Figure 7** Chemical variation profiles showing the major element (Au and Ag) and

567   minor element (Cu, S, Hg) contents measured by EPMA on a zoned electrum from the

568   Boliden deposit. (e-f) show Au, Ag, Cu, S, and Hg contents determined by EPMA

569   point analyses along measured lines across the light grey core and dark grey rim.

570   **Figure 8** Multielement box and whisker plots for LA-ICP-MS trace element data

571   showing the compositional differences between the light grey and dark grey zones in

572   electrum. (a) The arranged analysis line transects the dark grey core to the light grey

573   zone on the zoned electrum in Figure 6a. The laser ablation spot size for electrum is

574   24 μm. (c) The arranged analysis line transects the light grey core to the dark grey rim

575   on the zoned electrum in Figure 7a. The laser ablation spot size for electrum is 10 μm.

576   (b) and (d) Box and whisker plots showing the chemical compositions of LA-ICP-MS

577   data of electrum. Boxes outline the 25th to 75th percentiles, and whiskers extend to the

578   5% to 95% values. Short lines within the box represent the median value, whereas

579   circles filled by white represent the average value. Red spots outside the whiskers

580   indicate the outliers beyond 5% to 95% of the dataset.

581   **Figure 9** Ternary plot showing Au-Ag-Cu compositional variations between the dark

582   grey and the light grey zones in compositionally zoned electrum. The compositional

583   data of electrum come from area intensity of X-ray by EPMA (counted by cps). (a)

584   Plot of Au-Ag-Cu variations in zoned electrum from the Ming deposit. The defined

585   dark, light, and rim zones correspond to the same area in Figure 6a. (b) Plot of

586   Au-Ag-Cu variations in the zoned electrum from the Boliden deposit. The defined

587   dark and light zones correspond to the same area in Figure 7a.

588   **Figure 10** Schematic diagram of fluid facilitated solid-state diffusion (SSD) and

589   coupled dissolution-reprecipitation (CDR) reactions resulting in compositional zoning

590   in electrum from the Ming and Boliden deposits. (a-c) Illustration of the zoned

591   electrum formation from the Ming deposit. (a) The parent Ag-rich electrum

592   precipitated with homogeneous compositional textures from reduced fluids. (b) With

593   increasing temperature and/or a_{S_2}, the Ag-rich electrum core was dissolved to form a

594   diffusive contact through a Au-rich fluid that likely leached S-Fe-Cu-Zn-Pb during

595   prograde metamorphism. (c) The Ag-rich electrum rim was reprecipitated on the

596   exterior of electrum from an Ag-Cu-rich fluid with increasing a_{Cu} and fO$_2$ during the

597   retrograde metamorphism. The repeated CDR may result in the epitaxial growth of

598   multiple Ag layers towards the margin of electrum. (d-f) illustrate the zoned electrum

599   formation from the Boliden deposit. (d) The parent Au-rich electrum precipitated with

600   homogeneous compositional textures from reduced fluids. (e) With increasing a_{H_2S}

601   and/or temperature, and decreasing pH, the Au-rich electrum core was dissolved to

602   form a gradational contact through fluids which likely leached Se-Bi-Sb-Te-Sn-S-Zn

603   during the prograde metamorphism. (f) The SSD of Ag results in coarsening of

604   electrum and forms a Ag-rich rim with decreasing temperature and increasing pH

605   during the retrograde metamorphism.

606   **Figure 11** Binary plot showing compositional variations between the core and rim in

607   zoned electrum from the Ming and Boliden deposits. The compositional data of

608   electrum come from the LA-ICP-MS analysis. (a) Plot of Au versus S + Fe + Cu + Zn

609   + Pb, showing the increasing contents of S-Fe-Cu-Zn-Pb during the dissolution of Ag

610   resulting in a Au-rich transition zone, in electrum from the Ming deposit. (b) Plot of

611   Au versus Se + Bi + Sb + Te + Sn + S + Zn, showing the increased contents of

612   Se-Bi-Sb-Te-Sn-S-Zn during the diffusion of Ag from Au-rich core from the Boliden

613   deposit.

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References

Allen, R.L., Weihed, P., Svenson, S.-A. (1996) Setting of Zn-Cu-Au-Ag massive sulfide deposits in the evolution and facies architecture of a 1.9 Ga marine volcanic arc, Skellefte District, Sweden. Economic Geology 91: 1022-1053.

Årebäck, H., Barrett, T.J., Abrahamsson, S., Fagerström, P. (2005) The Palaeoproterozoic Kristineberg VMS deposit, Skellefte district, northern Sweden, part I: geology. Mineralium Deposita 40: 351-367.

Baheti, V.A., Kashyap, S., Kumar, P., Chattopadhyay, K., Paul, A. (2018) Solid–state diffusion–controlled growth of the phases in the Au–Sn system. Philosophical Magazine 98: 20-36.

Berglund, S., Ekström, T. (1980) Arsenopyrite and sphalerite as TP indicators in sulfide ores from northern Sweden. Mineralium Deposita 15: 175-187.

Bergman Weihed, J., Bergstrom, U., Billstrom, K., Weihed, P. (1996) Geology, tectonic setting, and origin of the Paleoproterozoic Boliden Au-Cu-As deposit, Skellefte district, northern Sweden. Economic Geology 91: 1073-1097.

Billstrom, K., Weihed, P. (1996) Age and provenance of host rocks and ores in the Paleoproterozoic Skellefte District, northern Sweden. Economic Geology 91: 1054-1072.

Borg, S., Liu, W., Pearce, M., Cleverley, J., MacRae, C. (2014) Complex mineral zoning patterns caused by ultra-local equilibrium at reaction interfaces. Geology 42: 415-418.

Bowell, R. (1992) Supergene gold mineralogy at Ashanti, Ghana: implications for the supergene behaviour of gold. Mineralogical Magazine 56: 545-560.

Boyle, R.W. (1979) The geochmistry of gold and its deposits. Geol. Surv. Can. Bull. 280.

Brueckner, S.M., Piercey, S.J., Layne, G.D., Piercey, G., Sylvester, P.J. (2015) Variations of sulphur isotope signatures in sulphides from the metamorphosed Ming Cu (− Au) volcanogenic massive sulphide deposit, Newfoundland Appalachians, Canada. Mineralium Deposita 50: 619-640.

644 Brueckner, S.M., Piercey, S.J., Pilote, J.-L., Layne, G.D., Sylvester, P.J. (2016)
645   Mineralogy and mineral chemistry of the metamorphosed and precious
646   metal-bearing Ming deposit, Canada. Ore Geology Reviews 72: 914-939.

647 Brueckner, S.M., Piercey, S.J., Sylvester, P.J., Maloney, S., Pilgrim, L. (2014)
648   Evidence for syngenetic precious metal enrichment in an Appalachian
649   volcanogenic massive sulfide system: The 1806 zone, Ming mine, Newfoundland,
650   Canada. Economic Geology 109: 1611-1642.

651 Castonguay, S., Skulski, T., van Staal, C., Currie, M. (2009) New insights on the
652   structural geology of the Pacquet Harbour group and Point Rousse complex, Baie
653   Verte peninsula, Newfoundland. Newfoundland and Labrador Department of
654   Natural Resources, Geological Survey, Report 1: 147-158.

655 Czamanske, G.K., Desborough, G.A., Goff, F.E. (1973) Annealing history limits for
656   inhomogeneous, native gold grains as determined from Au-Ag diffusion rates.
657   Economic Geology 68: 1275-1288.

658 Desborough, G., Heidel, R., Raymond, W., Tripp, J. (1971) Primary distribution of
659   silver and copper in native gold from six deposits in the Western United States.
660   Mineralium Deposita 6: 321-334.

661 Dos Santos Alves, K., Sánchez, S.B., Barreiro, J.G., Palomares, R.M., Prieto, J.M.C.
662   (2020) Morphological and compositional analysis of alluvial gold: The Fresnedoso
663   gold placer (Spain). Ore Geology Reviews: 103489.

664 Dubé, B., Gosselin, P., Mercier-Langevin, P., Hannington, M., Galley, A. (2007)
665   Gold-rich volcanogenic massive sulphide deposits. Geological Association of
666   Canada, Mineral Deposits Division: 75-94.

667 Eda, K., Chin, K., Sotani, N., Whittingham, M.S. (2005) Hydrothermal synthesis of
668   potassium molybdenum oxide bronzes: structure-inheriting solid-state route to blue
669   bronze and dissolution/deposition route to red bronze. Journal of Solid State
670   Chemistry 178: 158-165.

671 Eda, K., Uno, Y., Nagai, N., Sotani, N., Chen, C., Whittingham, M.S. (2006)
672   Structure-inheriting solid-state reactions under hydrothermal conditions. Journal of
673   Solid State Chemistry 179: 1453-1458.

674 Gammons, C.H., Barnes, H. (1989) The solubility of Ag2S in near-neutral aqueous

675   sulfide solutions at 25 to 300 C. Geochimica et Cosmochimica Acta 53: 279-290.

676 Gammons, C.H., Williams-Jones, A. (1995) Hydrothermal geochemistry of electrum;

677   thermodynamic constraints. Economic Geology 90: 420-432.

678 Gibert, F., Pascal, M.-L., Pichavant, M. (1998) Gold solubility and speciation in

679   hydrothermal solutions: Experimental study of the stability of hydrosulphide

680   complex of gold (AuHS) at 350 to 450 C and 500 bars. Geochimica et

681   Cosmochimica Acta 62: 2931-2947.

682 Goldsmith, J.R., Laves, F. (1954) The microcline-sanidine stability relations.

683   Geochimica et Cosmochimica Acta 5: 1-19.

684 Guisbiers, G.g., Mendoza-Cruz, R.n., Bazán-Díaz, L., Velázquez-Salazar, J.J.s.,

685   Mendoza-Perez, R., Robledo-Torres, J.A., Rodriguez-Lopez, J.-L.,

686   Montejano-Carrizales, J.M., Whetten, R.L., José-Yacamán, M. (2015) Electrum,

687   the gold–silver alloy, from the bulk scale to the nanoscale: synthesis, properties,

688   and segregation rules. ACS nano 10: 188-198.

689 Hagemann, S.G., Brown, P.E., Ridley, J., Stern, P., Fournelle, J. (1998) Ore petrology,

690   chemistry, and timing of electrum in the Archean hypozonal Transvaal lode gold

691   deposit, Western Australia. Economic Geology 93: 271-291.

692 Hannington, M., W. Bleeker, I. Kjarsgaard (1999) Sulfide mineralogy, geochemistry,

693   and ore genesis of the Kidd Creek deposit: Part II. The bornite zone. Econ. Geol.

694   Mono. 10: 225-266.

695 Healy, R.E., Petruk, W. (1990) Petrology of Au-Ag-Hg alloy and" invisible" gold in

696   the Trout Lake massive sulfide deposit, Flin Flon, Manitoba. The Canadian

697   Mineralogist 28: 189-206.

698 Hibbard, J. (1983) Geology of the Baie Verte Peninsula, Newfoundland. Mineral

699   Development Division, Department of Mines and Energy, Government

700   of Newfoundland and Labrador, 2.

701 Hodak, J.H., Henglein, A., Giersig, M., Hartland, G.V. (2000) Laser-induced

702   inter-diffusion in AuAg core− shell nanoparticles. The Journal of Physical

703   Chemistry B 104: 11708-11718.

704   Hough, R., Butt, C., Reddy, S., Verrall, M. (2007) Gold nuggets: Supergene or
705   hypogene? Australian Journal of Earth Sciences 54: 959-964.

706   Huang, X., Beaudoin, G. (2019) Textures and Chemical Compositions of Magnetite
707   from Iron Oxide Copper-Gold (IOCG) and Kiruna-Type Iron Oxide-Apatite (IOA)
708   Deposits and Their Implications for Ore Genesis and Magnetite Classification
709   Schemes. Economic Geology 114: 953-979.

710   Huston, D.L., Bottrill, R.S., Creelman, R.A., Zaw, K., Ramsden, T.R., Rand, S.W.,
711   Gemmell, J.B., Jablonski, W., Sie, S., Large, R.R. (1992) Geologic and
712   geochemical controls on the mineralogy and grain size of gold-bearing phases,
713   eastern Australian volcanic-hosted massive sulfide deposits. Economic Geology 87:
714   542-563.

715   Konrad-Schmolke, M., Halama, R., Wirth, R., Thomen, A., Klitscher, N., Morales, L.,
716   Schreiber, A., Wilke, F.D.H. (2018) Mineral dissolution and reprecipitation
717   mediated by an amorphous phase. Nature Communications 9: 1637.

718   Koski, R. (2010) Supergene ore and gangue characteristics in volcanogenic massive
719   sulfide occurrence model. US Geological Survey Scientific Investigation Report.

720   Larocque, A.C., Hodgson, C.J., Cabri, L.J., Jackman, J.A. (1995) Ion-microprobe
721   analysis of pyrite, chalcopyrite and pyrrhotite from the Mobrun VMS deposit in
722   northwestern Quebec; evidence for metamorphic remobilization of gold. The
723   Canadian Mineralogist 33: 373-388.

724   Li, K., Pring, A., Etschmann, B., Xia, F., Brugger, J. (2019a) Coupling between
725   mineral replacement reactions and co-precipitation of trace elements: an example
726   from the giant Olympic Dam deposit. Ore Geology Reviews: 103267.

727   Li, W., Cook, N.J., Ciobanu, C.L., Xie, G., Wade, B.P., Gilbert, S.E. (2019b) Trace
728   element distributions in (Cu)-Pb-Sb sulfosalts from the Gutaishan Au-Sb deposit,
729   South China: Implications for formation of high fineness native gold. American
730   Mineralogist: Journal of Earth and Planetary Materials 104: 425-437.

731   Liu, J., Zhai, D., Dai, H., de Fourestier, J., Yu, C., Gu, X., Wang, Y., Yu, H., Wang, J.,
732   Liu, Z. (2017) Nanoscale Characterization of Au2Te Grains From the Sandaowanzi
733   Gold Deposit, Northeast China. The Canadian Mineralogist 55: 181-194.

734 Lockington, J.A., Cook, N.J., Ciobanu, C.L. (2014) Trace and minor elements in
735   sphalerite from metamorphosed sulphide deposits. Mineralogy and Petrology 108:
736   873-890.

737 Longerich, H. (1996) Laser ablation inductively coupled plasma mass spectrometric
738   transient signal data acquisition and analyte concentration calculation. J. Anal. At.
739   Spectrom. 9: 899-904.

740 Lu, J., Wang, R., Hu, H., Gao, J. (2000) A new mechanism of formation of the
741   silver-rim structure on primary gold grains. Chinese Journal of Geochemistry 19:
742   134.

743 Mann, A. (1984) Mobility of gold and silver in lateritic weathering profiles; some
744   observations from Western Australia. Economic Geology 79: 38-49.

745 Marquis, P., Brown, A., Hubert, C., Rigg, D. (1990) Progressive alteration associated
746   with auriferous massive sulfide bodies at the Dumagami mine, Abitibi greenstone
747   belt, Quebec. Economic Geology 85: 746-764.

748 Marshall, B., Vokes, F., Larocque, A. (2000) Regional metamorphic remobilization:
749   upgrading and formation of ore deposits. Reviews in Economic Geology 11: 19-38.

750 Melchiorre, E., Orwin, P., Reith, F., Rea, M., Yahn, J., Allison, R. (2018) Biological
751   and geochemical development of placer gold deposits at Rich Hill, Arizona, USA.
752   Minerals 8: 56.

753 Mercier-Langevin, P., Hannington, M.D., Dubé, B., Bécu, V. (2011) The gold content
754   of volcanogenic massive sulfide deposits. Mineralium Deposita 46: 509-539.

755 Mercier-Langevin, P., McNicoll, V., Allen, R.L., Blight, J.H., Dubé, B. (2013) The
756   Boliden gold-rich volcanogenic massive sulfide deposit, Skellefte district, Sweden:
757   new U–Pb age constraints and implications at deposit and district scale.
758   Mineralium Deposita 48: 485-504.

759 Migdisov, A.A., Williams-Jones, A., Suleimenov, O. (1999) Solubility of chlorargyrite
760   (AgCl) in water vapor at elevated temperatures and pressures. Geochimica et
761   Cosmochimica Acta 63: 3817-3827.

762 Milidragovic, D., Beaudoin, G., Jackson, S. (2016) In-situ trace element
763   characterization of three gold reference materials using EPMA and LA-ICP-MS.

764   Geological Survey of Canada. Open File 8096, 1.zip file, doi, 10.4095/299097.

765   Oberthuer, T., Saager, R. (1986) Silver and mercury in gold particles from the

766   Proterozoic Witwatersrand placer deposits of South Africa; metallogenic and

767   geochemical implications. Economic Geology 81: 20-31.

768   Pal'yanova, G., Kolonin, G. (2007) Geochemical mobility of Au and Ag during

769   hydrothermal transfer and precipitation: Thermodynamic simulation. Geochemistry

770   International 45: 744-757.

771   Paton, C., Hellstrom, J., Paul, B., Woodhead, J., Hergt, J. (2011) Iolite: Freeware for

772   the visualisation and processing of mass spectrometric data. Journal of Analytical

773   Atomic Spectrometry 26: 2508-2518.

774   Pilote, J.-L., Piercey, S.J. (2013) Volcanostratigraphy of the 1807 zone of the Ming

775   Cu-Au volcanogenic massive-sulphide deposit, Baie Verte peninsula, northern

776   Newfoundland. Current Research 2013-20, 13 p.

777   Pilote, J.-L., Piercey, S.J., Brueckner, S.M., Grant, D. (2016) Resolving the Relative

778   Timing of Au Enrichment in Volcanogenic Massive Sulfide Deposits Using

779   Scanning Electron Microscopy-Mineral Liberation Analyzer: Empirical Evidence

780   from the Ming Deposit, Newfoundland, Canada. Economic Geology 111:

781   1495-1508.

782   Pilote, J.-L., Piercey, S.J., Mercier-Langevin, P. (2020) Evolution of the subseafloor

783   hydrothermal system associated with the Ming VMS deposit, Newfoundland

784   Appalachians, and its controls on base and precious metal distribution. Mineralium

785   Deposita 55: 913-936.

786   Putnis, A. (2002) Mineral replacement reactions: from macroscopic observations to

787   microscopic mechanisms. Mineralogical Magazine 66: 689-708.

788   Putnis, A. (2009) Mineral replacement reactions. Reviews in Mineralogy and

789   Geochemistry 70: 87-124.

790   Putnis, A. (2014) Why mineral interfaces matter. Science 343: 1441-1442.

791   Putnis, A., Putnis, C.V. (2007) The mechanism of reequilibration of solids in the

792   presence of a fluid phase. Journal of Solid State Chemistry 180: 1783-1786.

793   Rea, M.A.D., Wulser, P.-A., Brugger, J., Etschmann, B., Bissett, A., Shuster, J., Reith,

794   F. (2019) Effect of physical and biogeochemical factors on placer gold

795   transformation in mountainous landscapes of Switzerland. Gondwana Research 66:

796   77-92.

797   Reeder, R.J., Rakovan, J. (1999) Surface structural controls on trace element

798   incorporation during crystal growth, Growth, dissolution and pattern formation in

799   geosystems. Springer, pp. 143-162.

800   Reith, F., Stewart, L., Wakelin, S.A. (2012) Supergene gold transformation:

801   Secondary and nano-particulate gold from southern New Zealand. Chemical

802   Geology 320: 32-45.

803   Robert, J.C. (2014) Mineral Dissolution and Precipitation Kinetics:: Macroscopic,

804   Microscopic and Nanoscopic Techniques. Macla: revista de la Sociedad Española

805   de Mineralogía: 20-28.

806   Rocholl, A.B., Simon, K., Jochum, K.P., Bruhn, F., Gehann, R., Kramar, U., Luecke,

807   W., Molzahn, M., Pernicka, E., Seufert, M. (1997) Chemical Characterisation of

808   NIST Silicate Glass Certified Reference Material SRM 610 by ICP-MS, TIMS,

809   LIMS, SSMS, INAA, AAS and PIXE. Geostandards Newsletter 21: 101-114.

810   Rosell, J.R., Serra, J.P., Aiglsperger, T., Plana-Ruiz, S., Trifonov, T., Proenza, J.A.

811   (2018) Au crystal growth on natural occurring Au—Ag aggregate elucidated by

812   means of precession electron diffraction (PED). Journal of Crystal Growth 483:

813   228-235.

814   Rosúa, F.J.C., Ruano, S.M., Hach-Alí, P.F. (2002) The three generations of gold in the

815   Palai–Islica epithermal deposit, southeastern Spain. The Canadian Mineralogist 40:

816   1465-1481.

817   Ruiz-Agudo, E., Putnis, C., Putnis, A. (2014) Coupled dissolution and precipitation at

818   mineral–fluid interfaces. Chemical Geology 383: 132-146.

819   Seward, T.M. (1973) Thio complexes of gold and the transport of gold in

820   hydrothermal ore solutions. Geochimica et Cosmochimica Acta 37: 379-399.

821   Shikazono, N., Shimizu, M. (1987) The Ag/Au ratio of native gold and electrum and

822   the geochemical environment of gold vein deposits in Japan. Mineralium Deposita

823   22: 309-314.

824 Shuster, J., Reith, F., Cornelis, G., Parsons, J.E., Parsons, J.M., Southam, G. (2017)
825   Secondary gold structures: Relics of past biogeochemical transformations and
826   implications for colloidal gold dispersion in subtropical environments. Chemical
827   Geology 450: 154-164.

828 Sinclair, B., Berry, R., Gemmell, J. (2000) Mineralogy and textures of the Battle Zone
829   massive sulfide lenses, Myra Falls district, British Columbia, Canada, Volcanic
830   Environments and Massive Sulfide Deposits, pp. 197-200.

831 Skulski, T., Castonguay, S., McNicoll, V., van Staal, C., Kidd, W., Rogers, N., Morris,
832   W., Ugalde, H., Slavinski, H., Spicer, W. (2010) Tectonostratigraphy of the Baie
833   Verte oceanic tract and its ophiolite cover sequence on the Baie Verte Peninsula.
834   Newfoundland and Labrador Department of Natural Resources, Geological Survey,
835   Report 1: 315-337.

836 Spear, F.S., Selverstone, J. (1983) Quantitative PT paths from zoned minerals: theory
837   and tectonic applications. Contributions to Mineralogy and Petrology 83: 348-357.

838 Spruzeniece, L., Piazolo, S., Maynard-Casely, H.E. (2017) Deformation-resembling
839   microstructure created by fluid-mediated dissolution–precipitation reactions.
840   Nature Communications 8: 14032.

841 Stefánsson, A., Seward, T. (2004) Gold (I) complexing in aqueous sulphide solutions
842   to 500 C at 500 bar. Geochimica et Cosmochimica Acta 68: 4121-4143.

843 Tenailleau, C., Pring, A., Etschmann, B., Brugger, J., Grguric, B., Putnis, A. (2006)
844   Transformation of pentlandite to violarite under mild hydrothermal conditions.
845   American Mineralogist 91: 706-709.

846 Tourigny, G., Doucet, D., Bourget, A. (1993) Geology of the Bousquet 2 Mine; an
847   example of a deformed, gold-bearing, polymetallic sulfide deposit. Economic
848   Geology 88: 1578-1597.

849 Vikentev, I. (2016) Selenium, tellurium and precious metal mineralogy in Uchalinsk
850   copper-zinc-pyritic district, the Urals, IOP Conference Series: Materials Science
851   and Engineering. IOP Publishing, p. 012027.

852 Wagner, T., Jonsson, E. (2001) Mineralogy of sulfosalt-rich vein-type ores, Boliden
853   massive sulfide deposit, Skellefte district, northern Sweden. The Canadian

854   Mineralogist 39: 855-872.

855   Wagner, T., Klemd, R., Wenzel, T., Mattsson, B. (2007) Gold upgrading in

856   metamorphosed massive sulfide ore deposits: Direct evidence from laser-ablation–

857   inductively coupled plasma–mass spectrometry analysis of invisible gold. Geology

858   35: 775-778.

859   Watson, E.B. (1996) Surface enrichment and trace-element uptake during crystal

860   growth. Geochimica et Cosmochimica Acta 60: 5013-5020.

861   Williams-Jones, A.E., Bowell, R.J., Migdisov, A.A. (2009) Gold in solution. Elements

862   5: 281-287.

863   Wilson, A.F. (1984) Origin of quartz-free gold nuggets and supergene gold found in

864   laterites and soils—a review and some new observations. Journal of the Geological

865   Society of Australia 31: 303-316.

866   Wilson, S., Ridley, W., Koenig, A. (2002) Development of sulfide calibration

867   standards for the laser ablation inductively-coupled plasma mass spectrometry

868   technique. Journal of Analytical Atomic Spectrometry 17: 406-409.

869   Xia, F., Brugger, J., Chen, G., Ngothai, Y., O'Neill, B., Putnis, A., Pring, A. (2009)

870   Mechanism and kinetics of pseudomorphic mineral replacement reactions: A case

871   study of the replacement of pentlandite by violarite. Geochimica et Cosmochimica

872   Acta 73: 1945-1969.

873   Xiong, G., Clark, J.N., Nicklin, C., Rawle, J., Robinson, I.K. (2014) Atomic diffusion

874   within individual gold nanocrystal. Scientific reports 4: 6765.

875   Yokoyama, K., Takeuchi, S., Nakai, I., Tsutsumi, Y., Sano, T., Shigeoka, M.,

876   Miyawaki, M., Matsubara, M. (2011) Chemical Compositions of Electrum Grains

877   in Ore and Placer Deposits in the Japanese Islands. National Museum of Nature

878   and Science.

879   Zachariáš, J., Němec, M., O'Driscoll, B. (2017) Gold to aurostibite transformation and

880   formation of Au-Ag-Sb phases: the Krásná Hora deposit, Czech Republic.

881   Mineralogical Magazine 81: 987-999.

882   Zhao, J., Brugger, J., Grundler, P.V., Xia, F., Chen, G., Pring, A. (2009) Mechanism

883   and kinetics of a mineral transformation under hydrothermal conditions: Calaverite

884   to metallic gold. American Mineralogist 94: 1541-1555.

885   Zhao, J., Brugger, J., Xia, F., Ngothai, Y., Chen, G., Pring, A. (2013)

886   Dissolution-reprecipitation vs. solid-state diffusion: Mechanism of mineral

887   transformations in sylvanite,(AuAg) 2Te4, under hydrothermal conditions.

888   American Mineralogist 98: 19-32.

889

Table 1 EPMA results of electrum grains from the Ming and Boliden deposits

| | | Internal texture | Number of analyses | Chemical composition (wt%) | | | | | Mineral association |
				Au	Ag	Cu	Hg	S	
Ming	Electrum with zoning	Silver rich rim	3	b.d.l-0.99	84.70-99.29	0.17-2.11	0.01-6.24	0.05-0.13	Ccp, Bn, Cc, Py
		Rim	4	62.13-69.01	33.06-39.85	0.21-1.43	0.07-0.22	0.02-0.04	
		Transition	26	71.62-78.76	20.74-30.09	0.03-0.45	b.d.l.-0.16	0.01-0.36	
		Core	13	65.35-77.42	21.71-35.00	0.03-1.59	b.d.l.-6.77	0.02-0.13	
	Electrum without zoning		8	69.15-90.56	10.54-30.73	0.25-2.85	b.d.l.-0.18	0.04-0.26	
Boliden	Electrum with zoning	Rim	17	47.89-69.43	24.54-46.08	b.d.l.-5.07	b.d.l.-2.77	0.02-4.46	Apy, Ccp, Py, Aur, (Cu)-Pb-Sb sulfosalts
		Transition	5	54.90-65.37	32.17-40.43	0.06-0.30	1.39-2.08	0.06-0.07	
		Core	21	62.01-89.97	6.04-34.67	b.d.l.-0.21	b.d.l.-1.68	0.01-0.10	
	Electrum witout zoning		25	45.74-92.23	6.37-50.79	b.d.l.-0.05	b.d.l.-3.03	0.02-0.15	

*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

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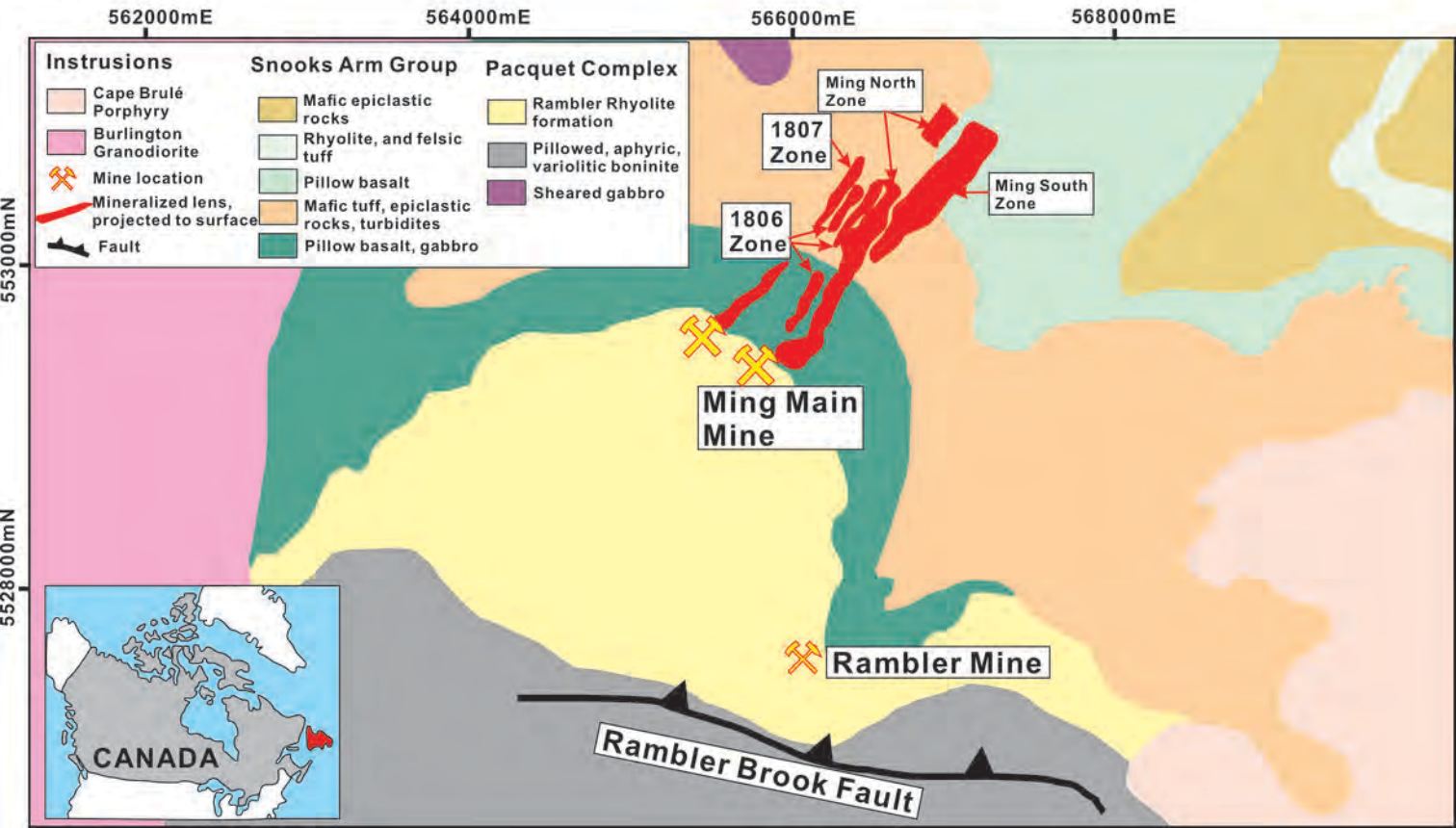
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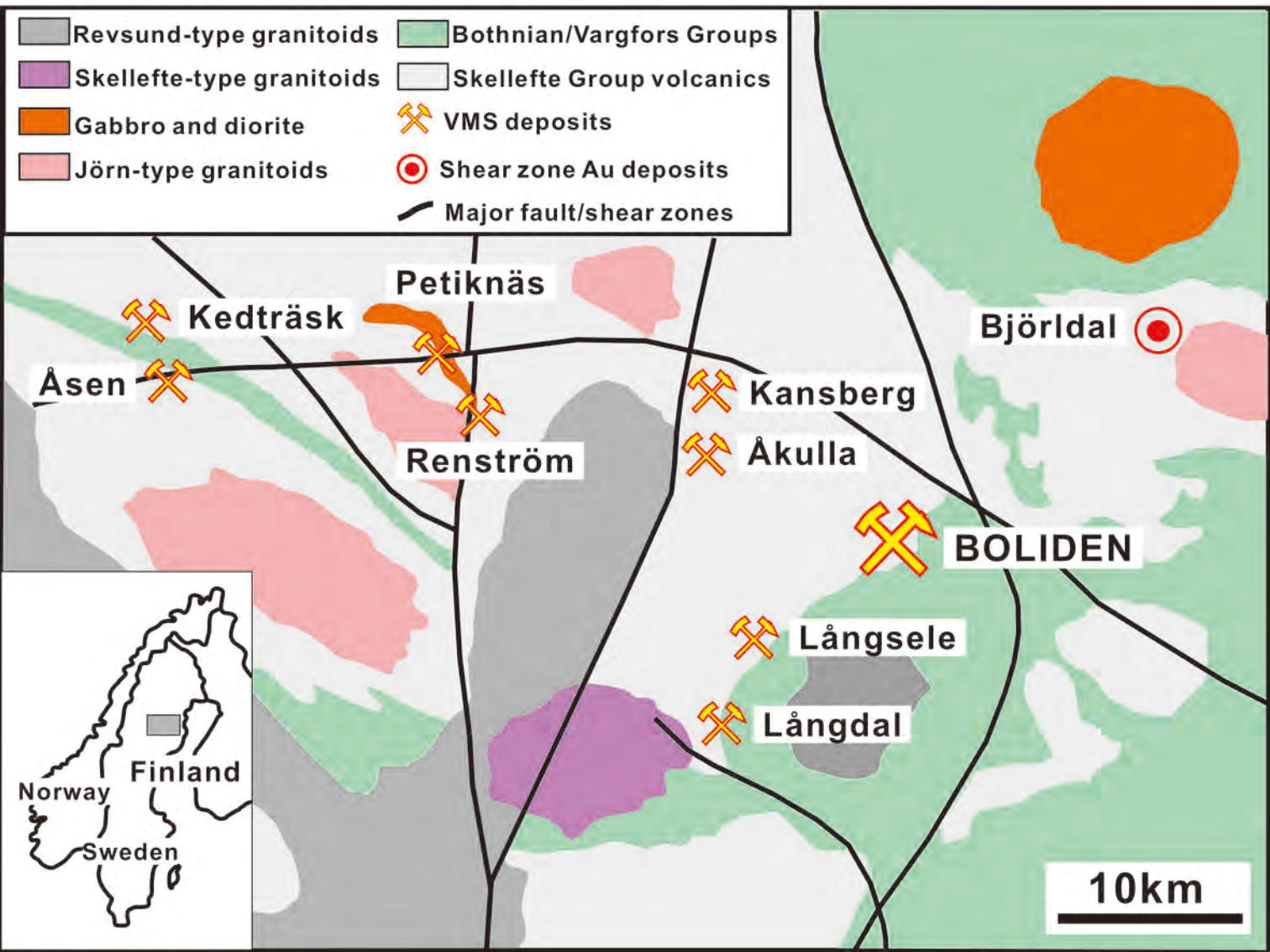
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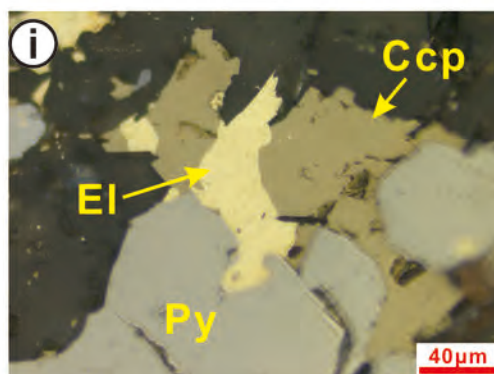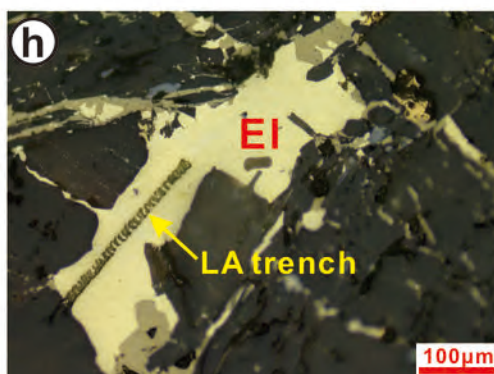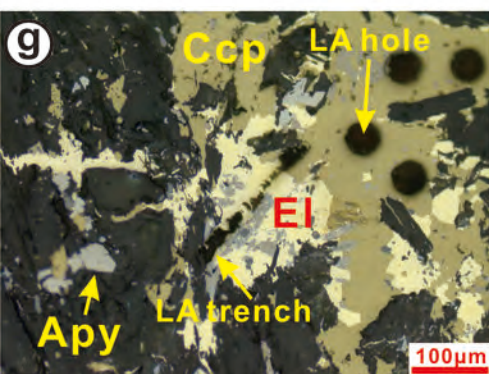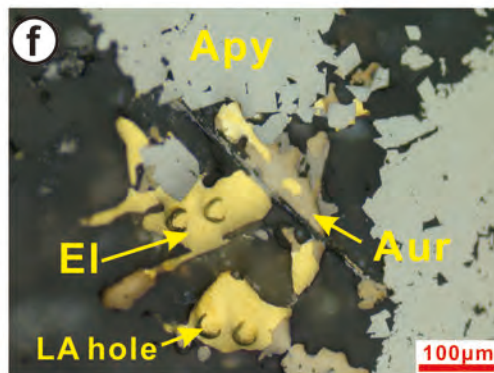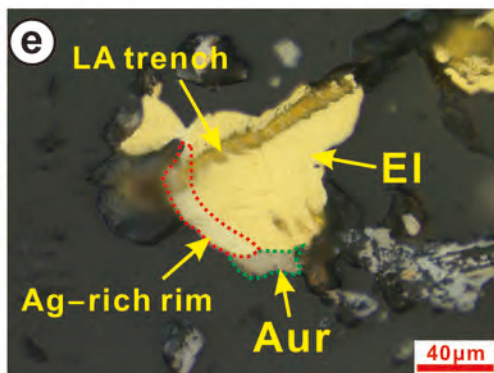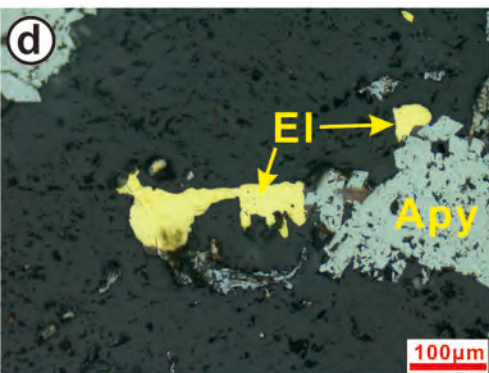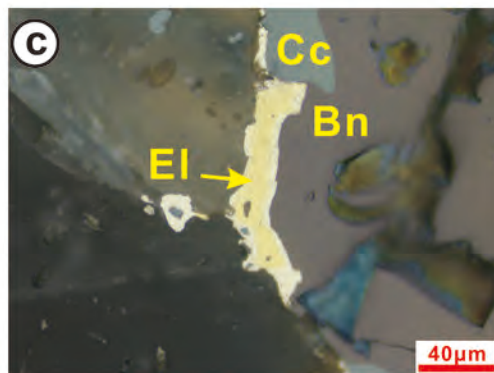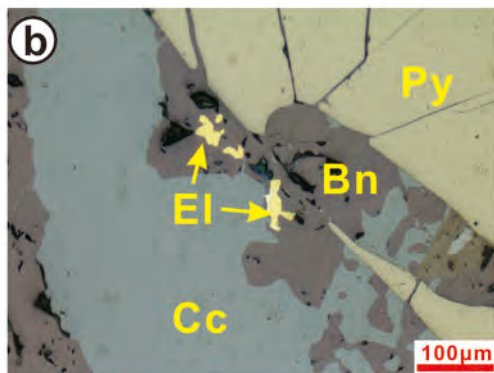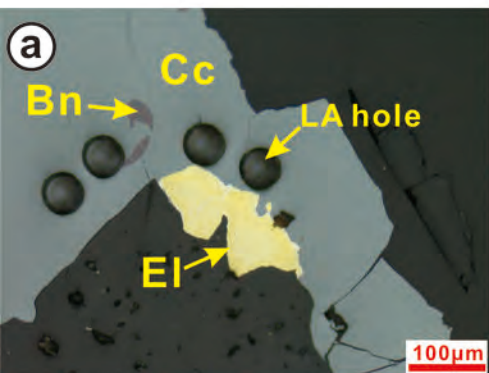
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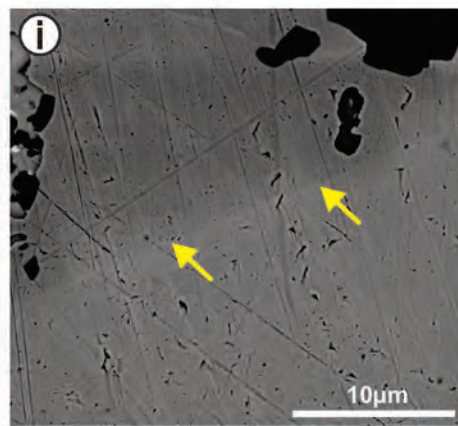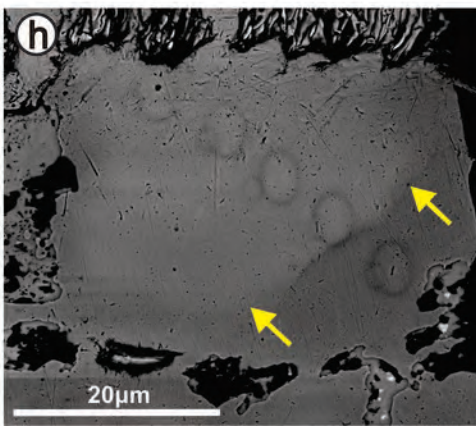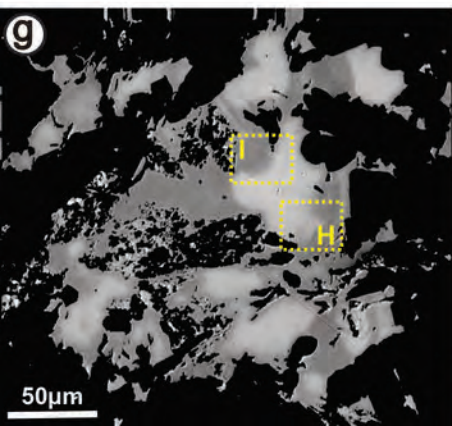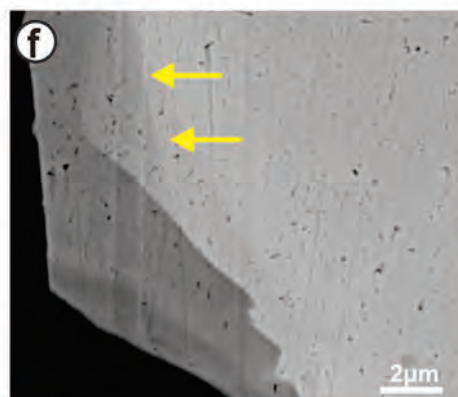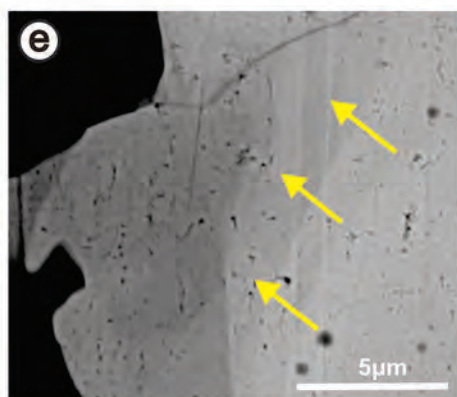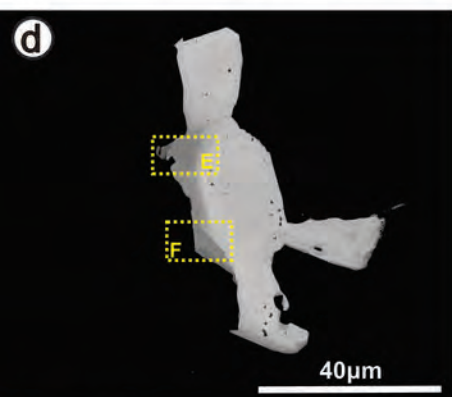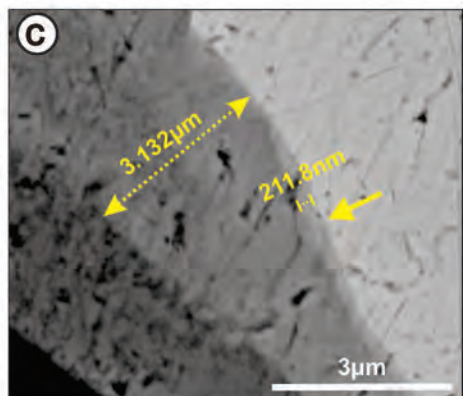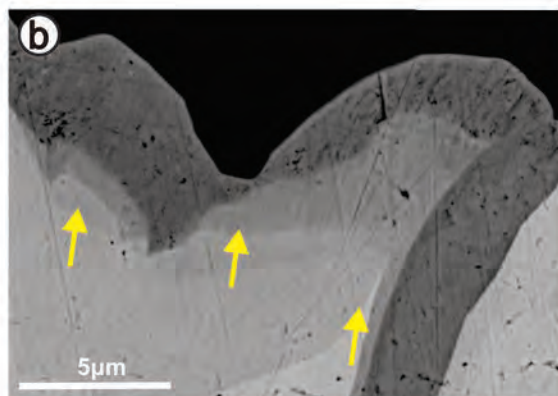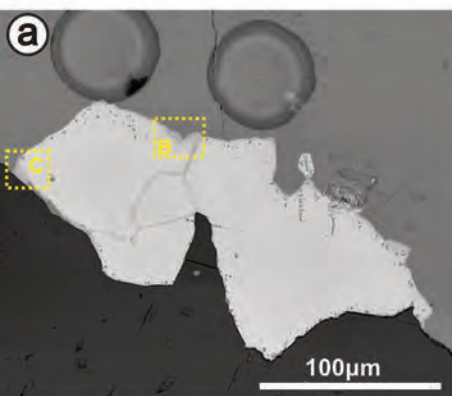
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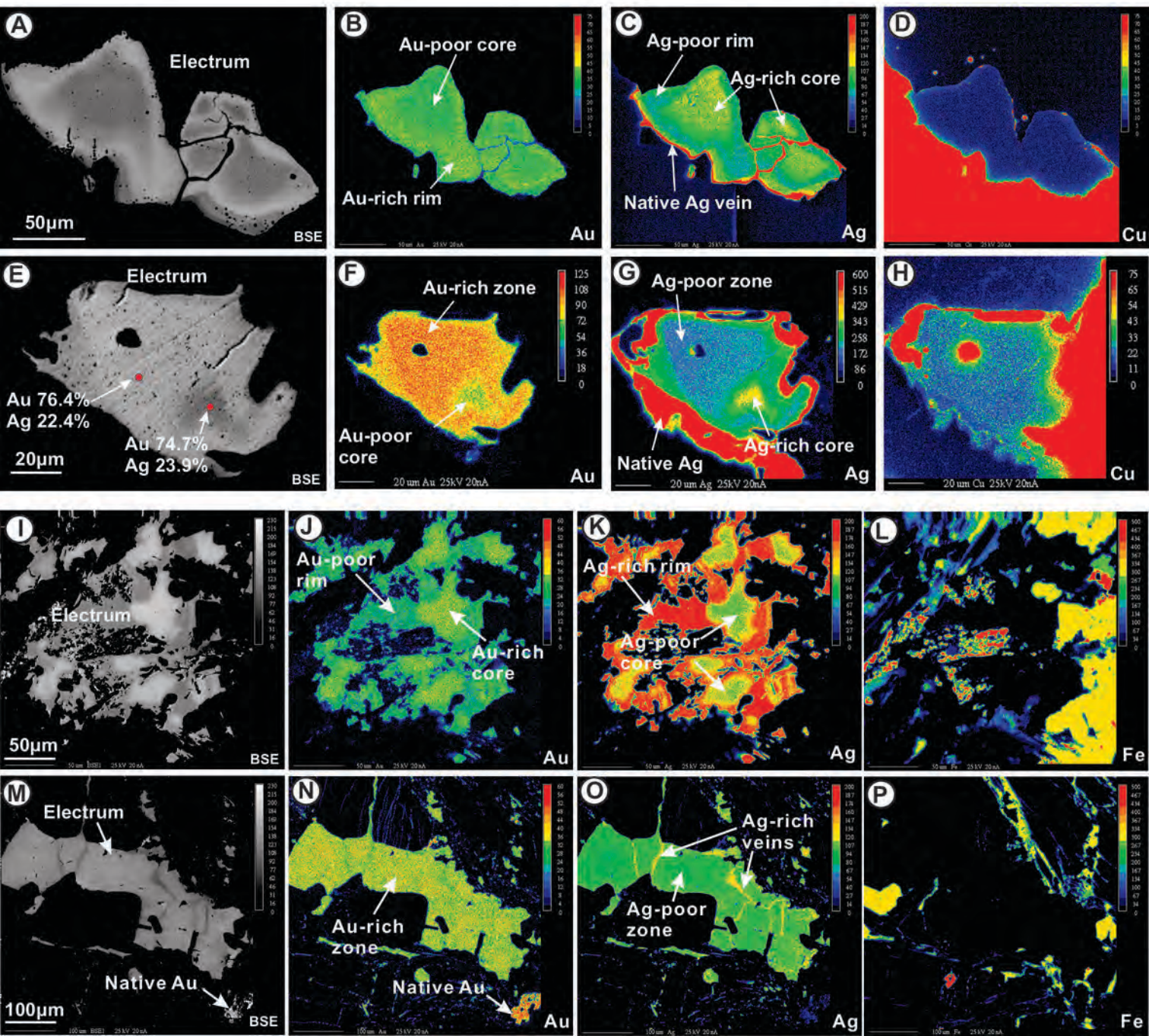
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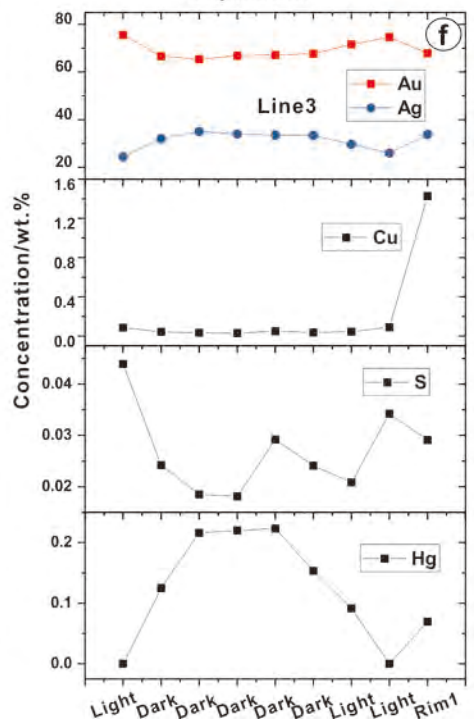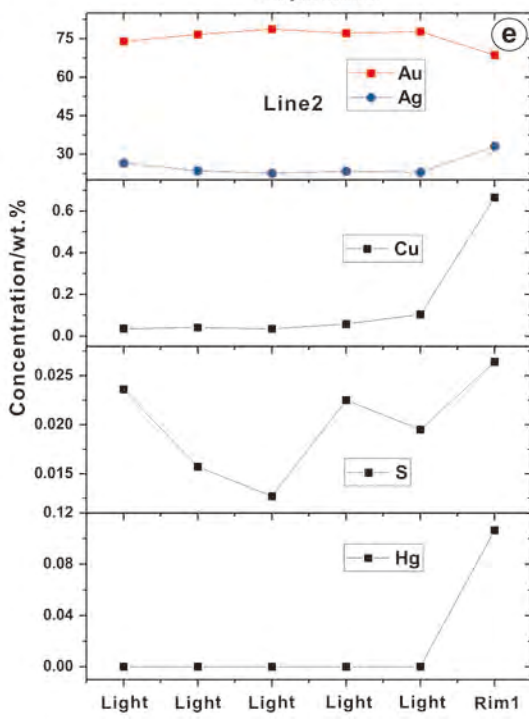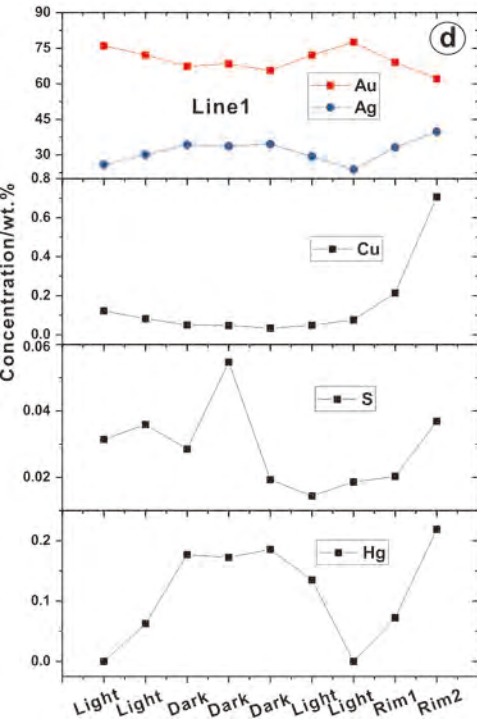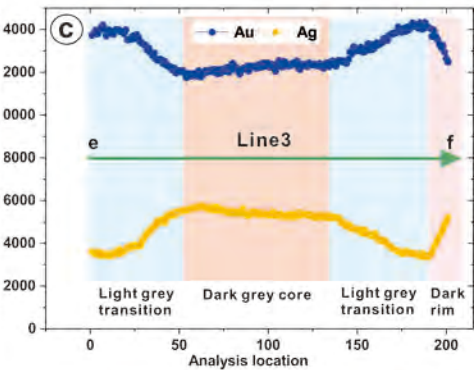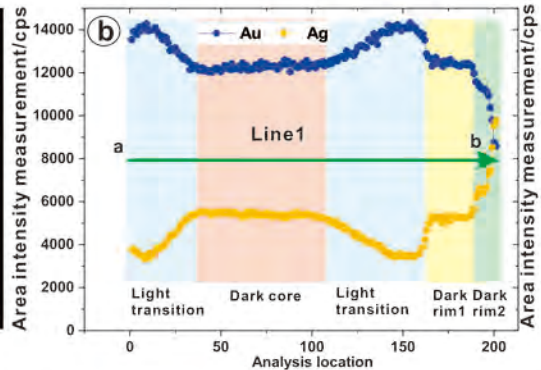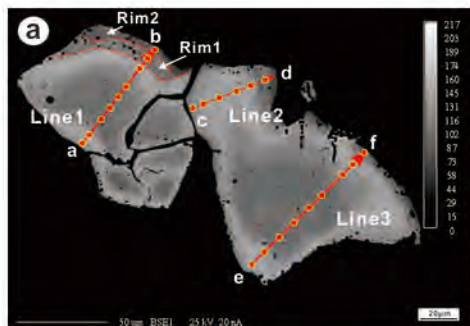
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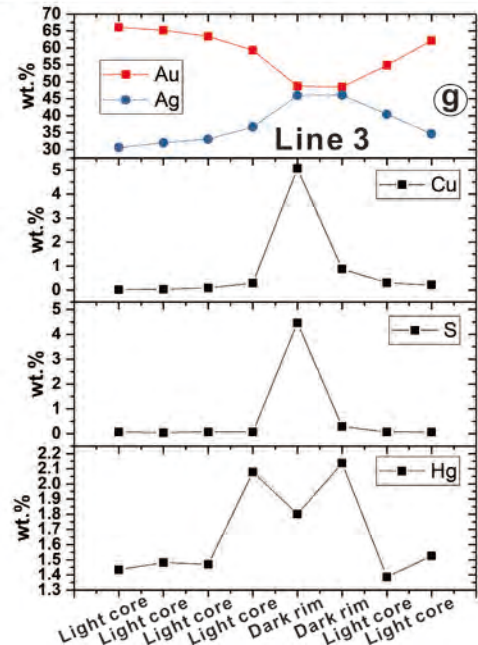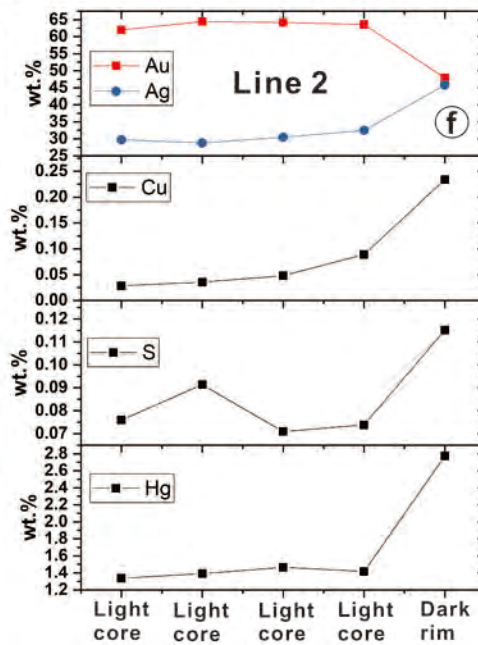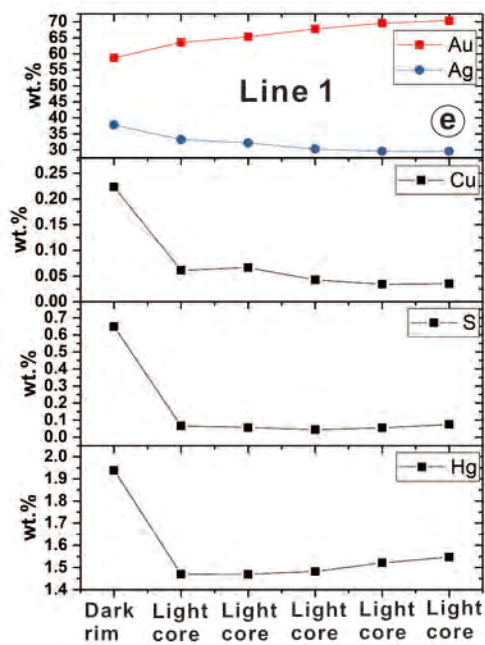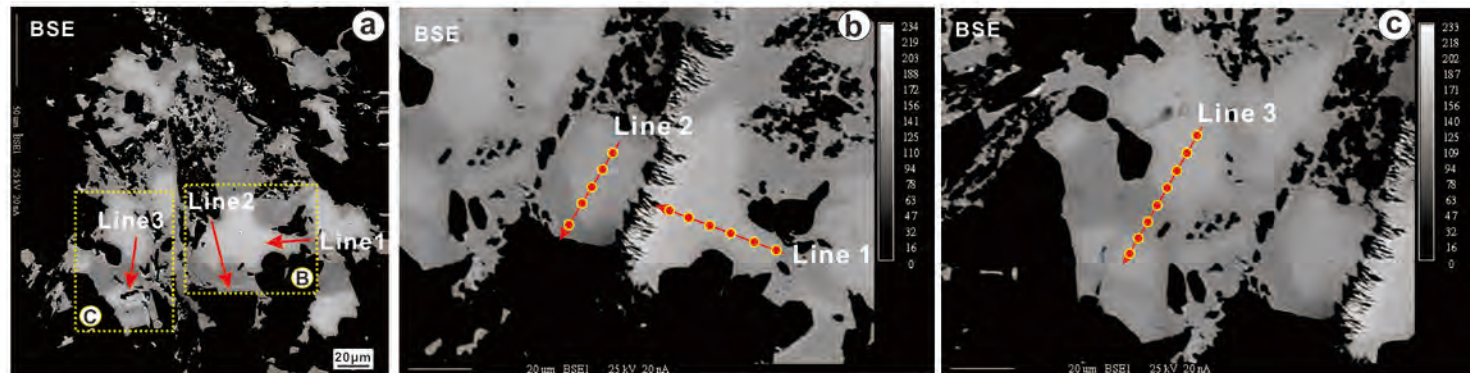
Figure 8

Figure 9

Figure 10

SSD

CDR

(a) Host sulfides

Ag-rich electrum from Ming

Increasing T and/or a_{S_2}

(b) Fe
S
Cu   Zn   Pb

Ag-rich electrum core

Decreasing T

Increasing a_{Cu} and f_{O_2}

(c) Zoned electrum

Ag-rich rim

Ag-rich electrum rim

SSD

(d) Host sulfides

Au-rich electrum from Boliden

Increasing T and/or a_{H_2S}

Decreasing pH

(e) Se   Sn
Bi
Sb
Te   Zn   S

Au-rich electrum core

Decreasing T

Increasing pH

(f) Zoned electrum

Ag-rich electrum rim

Figure 11