

1 **Formation, remobilisation and alteration processes at inactive hydrothermal vents: insights from elemental**
2 **analysis of Cu-(Fe-)S sulfides from TAG, Mid-Atlantic Ridge**

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10 **Abstract**

11 Chalcopyrite is the main Cu mineral in mafic hosted marine hydrothermal systems. Its trace element budget and that of
12 its alteration products may hold valuable information on formation, remobilisation and alteration processes of the
13 hydrothermal system. In this study we analysed chalcopyrite from five inactive seafloor massive sulfide (SMS) sites from
14 the TAG hydrothermal field on the Mid-Atlantic Ridge by electron probe microanalysis (EPMA) and laser ablation
15 inductively coupled plasma mass spectrometry (LA-ICP-MS) for 24 elements. Twelve of them are discussed in detail. In
16 general, trace element concentrations range between sub-parts per million (ppm) to several hundreds of ppm. The
17 elements Se and Co are incorporated into the lattice at high temperatures of >300 °C, whereas As, Ge, Ga substitute into
18 the structure at intermediate to low temperatures. Other elements, e.g. Zn, are either accommodated into the mineral lattice
19 or form inclusions, whereas V and Mn, which originate from seawater, get adsorbed onto the mineral surface. Idaite,
20 chalcocite, and covellite exhibit similar trace element patterns to those of the precursor chalcopyrite. However, the
21 secondary copper minerals show enrichment of Ag and Mo. Factors controlling the incorporation are predominantly
22 related to changes in physicochemical conditions with the host rock composition playing only a minor role.

23

24 **Key words:** TAG hydrothermal field, seafloor massive sulfides, trace elements, LA-ICP-MS

25

26 **Introduction**

27 SMS deposits formed through hydrothermal venting in today's oceans are considered the modern analogue of ancient
28 volcanogenic massive sulfide deposits (VMS). Based on their tectonic setting SMS can be rich in metals such as copper,
29 zinc and gold (Hannington et al. 2005, Monecke et al. 2016). Currently, there are more than 600 SMS sites known
30 (Beaulieu et al. 2015) containing an estimated global resource of 600 million tonnes of sulfide with a median grade of 9
31 wt.% Zn, 3 wt.% Cu, 100 g/t Ag and 2 g/t Au (Hannington et al. 2011, Monecke et al. 2016). With the increasing interest

32 of our society to move towards a sustainable low carbon footprint future with renewable energies and efficient
33 technologies (Mudd et al. 2017), and to decouple metal production from carbon emission (Wang and Feng 2019), the
34 mining industry is looking for alternative metal sources to meet these goals. Although it will be unlikely that SMS are
35 targeted because of their base and precious metal grades (Singer 2014), they might be of interest with regard to their trace
36 metal budget. Previous work on this topic is scarce with Monecke et al. (2016) presenting the most comprehensive study
37 so far. However, they considered only bulk geochemical data, which does not decipher the host mineral for a specific
38 trace element though this is essential information for metal extraction processes (Rankin 2017).

39 LA-ICP-MS provides high sensitivity, multi element analyses at a spatial resolution of a few micrometres; this utility
40 permits the in depth investigation of trace elements in specific minerals. Pyrite and sphalerite are the predominant minerals
41 investigated from SMS sites with regard to their trace element budget (Melekestseva et al. 2014, Wohlgemuth-
42 Ueberwasser et al. 2015, Keith et al. 2016, Melekestseva et al. 2017, Grant et al. 2018, Maslennikov et al. 2020, Meng et
43 al. 2020). In situ LA-ICP-MS on pyrite and sphalerite has shown that the combination of trace element concentrations of
44 different mineral generations can be used to decipher processes related to precipitation, metal remobilisation and source
45 of the metals (Wohlgemuth-Ueberwasser et al. 2015, Keith et al. 2016, Melekestseva et al. 2017, Grant et al. 2018,
46 Melekestseva et al. 2020). Studies on chalcopyrite, a common phase in mafic and ultramafic hosted SMS sites, are,
47 however limited. Where chalcopyrite was analysed the data only consider a few of elements (Butler and Nesbitt 1999,
48 Wohlgemuth-Ueberwasser et al. 2015, Dekov et al. 2018, Yuan et al. 2018) with limited studies reporting Ga, Ge, Se and
49 In (Wang et al. 2017, Grant et al. 2018). Whilst chalcopyrite is a common copper mineral and is one of the main sources
50 for copper in the mining industry, it was thought that it was a poor host for trace elements (George et al. 2016). However,
51 George et al. (2018) showed this not to be the case.

52 In this study, in situ LA-ICP-MS trace element composition of chalcopyrite and its secondary alteration phases from five
53 hydrothermally inactive SMS sites from the TAG hydrothermal field are presented and discussed. All SMS sites are
54 hosted in basalt and should exhibit very similar trace element patterns, if the host rock had a significant influence on the
55 trace metal composition (Wohlgemuth-Ueberwasser et al. 2015). However, the trace element composition should vary if
56 the host rock only had a minor role with Keith et al. (2016) proposing that changes of pH, temperature, redox potential
57 and salinity being the key factors influencing the trace element composition of hydrothermal precipitates. Our results
58 show that all Cu-(Fe-)S sulfides can host a wide range of trace elements, ranging in the concentrations from sub-ppm to
59 several hundred ppm, with the majority being incorporated into the mineral lattice.

60

61 **Geological Setting**

62 The basalt hosted TAG hydrothermal field at 26°09'N is one of the largest and best studied hydrothermal systems on
63 earth (Rona et al. 1986, 1993, Hannington et al. 1998, Tivey et al. 2003, Humphris et al. 2015). Numerous active and
64 relict mound shaped hydrothermal sites are located in an area of 5 km² on the eastern side of the axial valley of the Mid-
65 Atlantic Ridge with mounds varying in size, stage of development and age. The active TAG mound, located in the
66 southwest of the area (Fig. 1), is currently in a high temperature venting stage, i.e. metal rich black smoker fluids at ~365
67 °C are being discharged through multiple chimneys on the so called “upper platform”. At the “lower platform” a ~50 °C
68 diffuse flow has been detected (Humphris et al. 2015). The main lithology on the “upper platform” is an anhydrite rich
69 massive sulfide that is partially brecciated and predominantly composed of chalcopyrite and pyrite (Hannington et al.
70 1991). On the “lower platform” a silica rich massive sulfide predominates and contains sphalerite, marcasite and pyrite.
71 During Ocean Drilling Programme Leg 158, in the mid 1990s, the active TAG mound was drilled to a depth of 125 metre
72 below seafloor (mbsf). Lithologies encountered were massive pyrite breccia, anhydrite rich pyrite breccia, silica rich
73 pyrite breccia and altered wall rock and basalt in the deepest parts of the mound (Humphris et al. 2015, Grant et al. 2018).
74 Only the upper five meters of the mound seem to be enriched in minerals of economic interest, with the remaining mound
75 being composed of barren pyrite (Hannington et al. 1998).

76 North northeast of the active TAG mound several hydrothermal extinct mounds occur: Southern, Rona, Double, Shinkai,
77 New Mound 2 and New Mound 3 (Fig. 1). Surface samples from Shinkai mound, New Mound 2 and 3 comprise chimney
78 fragments whereas pyrite rich sulfide breccia and massive sulfides were recovered from the surface and subsurface of
79 Southern and Rona mound (Lehrmann et al. 2018, Murton et al. 2019).

80 Another hydrothermally inactive SMS area of around 1 km², the MIR zone, is located 2 km to the north northeast of the
81 active TAG mound (Fig. 1). In comparison to the other mounds, large distinctive surface features (e.g., upright chimneys)
82 are absent in the MIR zone, although White et al. (1998) documented a small mound of 100 m diameter and 10 m height.
83 The main surface rock types comprise chimney fragments and blocks of massive sulfides (Stepanova et al. 1996), though
84 drilling in 2016 revealed the occurrence of a pyrite rich sulfide breccia at depth (Lehrmann et al. 2018, Murton et al.
85 2019).

86 Radiometric ²³⁰Th/²³⁴U dating of sulfides indicates that the MIR zone is the oldest sulfide zone within the TAG
87 hydrothermal field, with activity starting ~100,000 years ago, which ceased around 600 years ago (Lalou et al. 1995). At
88 the active TAG mound hydrothermal activity first started 50,000 years ago. Sulfides from the Shinkai mound yield ages
89 of 23,000 - 2,000 years. Although thoroughly studied, no true resource estimates exist for the active TAG mound or the
90 inactive mounds. However, based on the thickness of the sulfide zone derived from composite sections of the active
91 mound Hannington et al. (1998) propose 2.7 million metric tons (Mt) of massive sulfides at 2% copper in the mound and
92 additionally 1.5 Mt of sulfide breccia at 1% copper in the underlying stockwork zone.

93

94 **Methodology**

95 Sampling and petrological analyses

96 Surface and subsurface samples were collected during expedition JC138 on *RRS James Cook* using a robotic underwater
97 vehicle (RUV HyBIS, National Oceanography Centre Southampton) and a robotic lander type seafloor drilling rig (RD2,
98 British Geological Survey). In total, 29 surface samples and 9.5 m drill core were obtained from five hydrothermally
99 inactive sites from the TAG hydrothermal field and after macroscopic description, 10 copper rich samples were selected
100 for this study. Polished thick sections (200 μm) were prepared from the selected samples. These were visually
101 characterised using optical and scanning electron microscopy (SEM) in backscattered electron mode and the mineral
102 abundance was estimated optically.

103

104 EPMA and SEM element mapping

105 Quantitative analyses of major elements in the Cu rich sulfides, i.e. chalcopyrite, idaite, chalcocite, and covellite were
106 carried out using a Cameca SX100 electron microprobe at the University of Edinburgh. In addition, a Zeiss Sigma HD
107 Field Emission Gun Analytical SEM at Cardiff University was used to obtain high resolution X-ray element maps.
108 Operating conditions for EPMA were an accelerating voltage of 20 kV and a beam current of 10nA and for SEM analyses
109 an Oxford Instruments 150 mm² energy dispersive X-ray spectrometer was used with an accelerating potential of 15 kV.
110 Calibration of EPMA and SEM was performed on natural mineral standards (CuFeS₂: Cu, S; FeS₂: Fe) monitoring the
111 following spectral lines: Cu K α , Fe K α , S K α . Wherever possible, spots were placed on areas free of visible inclusions or
112 exsolutions of other minerals. Each spot location analysed was marked on a photomicrograph or backscatter electron
113 image for later trace element analyses by LA-ICP-MS to ensure the analyses were made on the same grain.

114

115 LA-ICP-MS analyses

116 Trace elements were analysed by LA-ICP-MS using a New Wave UP 193 FX laser ablation system coupled to a Thermo
117 Scientific X Series 2 quadrupole ICP-MS at the School of Ocean and Earth Science, University of Southampton. The
118 laser used a mixed He (1 l/min) and N₂ (0.01 l/min) carrier gas, a beam diameter of 25 μm , a 5 Hz pulse rate with an
119 energy density of 5-6 J/cm². The total analysis time for each spot was 45 s, including 20 s for gas blank analysis. In total
120 300 spots were analysed for chalcopyrite, 17 for idaite, 11 for chalcocite and 8 for covellite. 24 elements were monitored
121 for quantitative analyses (⁵¹V, ⁵⁵Mn, ⁵⁷Fe, ⁵⁹Co, ⁶⁰Ni, ⁶⁵Cu, ⁶⁶Zn, ⁶⁹Ga, ⁷²Ge, ⁷⁵As, ⁸²Se, ⁹⁵Mo, ¹⁰⁷Ag, ¹¹¹Cd, ¹¹⁵In, ¹¹⁸Sn,
122 ¹²¹Sb, ¹²⁵Te, ¹³⁷Ba, ¹⁹⁷Au, ²⁰⁵Tl, ²⁰⁸Pb, ²⁰⁹Bi, ²³⁸U) in addition to ⁷⁷ArCl and ⁸³Kr for interference correction on ⁸²Se.
123 Calibration was achieved using NIST SRM 610 and NIST SRM 612 (Jochum et al. 2005) with Fe as an internal standard.

124 Accuracy was monitored by the repeated analysis of MASS-1 (Wilson et al. 2002) and is reported as percent relative
125 differences (%RD). For the majority of elements, excellent accuracy was yielded, i.e. %RD of $\pm 0-3$ (Jenner 1996). ^{60}Ni ,
126 ^{75}As , ^{115}In , ^{197}Au and ^{205}Tl show very good accuracy (between 3 and 7%) and only ^{82}Se and ^{111}Cd have poor accuracy of
127 $>10\%$. After measurement, the trace element concentrations were calculated with the PlasmaLab 2.6.1.335 software
128 (Thermo Scientific) using Fe as internal standard as determined by EPMA. Mean minimum detection limits were
129 calculated following the protocol of Longerich et al. (1996) and can be found in the Electronic Supplementary Materials
130 (ESM), Table S1.

131

132 **Results**

133 Petrography

134 Three main seafloor massive sulfide sample types were identified in the surface and subsurface samples recovered (Table
135 1). They comprise chimney fragments (Fig. 2a), massive sulfides (Fig. 2b), and sulfide breccia (Fig. 2c). Chimney
136 fragments are characterised by intact fluid conduits and the predominance of Cu rich sulfide minerals such as chalcopyrite
137 and isocubanite. While the chalcopyrite displays various habits, ranging from tetrahedral to coarse grained anhedral (Fig.
138 2d-e), the isocubanite forms exsolution lamella (Fig. 2e). Other copper minerals that occur in the chimney fragments are
139 idaite, which lines the inner fluid conduit, and covellite that formed along grain boundaries and micro-fractures (Fig. 2d,
140 i). Massive sulfides and sulfide breccia predominately comprise pyrite which is either intercalated with chalcopyrite (Fig.
141 2f) or surrounds fossil remnants of tubular organism that got replaced by chalcopyrite (Fig. 2g). Along micro-fractures,
142 chalcocite can be observed (Fig. 2h).

143

144 EPMA major element composition

145 The EPMA was performed to both confirm the identity of the secondary copper minerals and to provide iron
146 concentrations to use as an internal standard for processing the LA-ICP-MS data. EPMA data show chalcopyrite from all
147 sites to be stoichiometric CuFeS_2 with Cu and Fe concentrations varying from 32.78 to 35.40 wt.% and 29.72 to 31.81
148 wt.%, respectively (ESM, Table S2). A light orange to copper red coloured mineral that only occurs in chimney fragments
149 from New Mound 2 was determined to be idaite (Fig. 3). In addition, the EPMA data show that the idaite (in this study)
150 correlates well with the composition of idaite-II of Vaughan and Craig (1978) giving a stoichiometry of Cu_3FeS_4 . Two
151 blue coloured copper minerals with Cu concentrations of 77.70 to 78.27 wt.% and 65.31 to 67.62 wt.% are chalcocite
152 (Cu_2S) and covellite (CuS). However, both minerals contain trace amounts of Fe (ESM, Table S2).

153

154 LA-ICP-MS trace element distribution

155 Though 24 elements were analysed by LA-ICP-MS in this study, only twelve of them will be discussed in detail (V, Mn,
156 Co, Zn, Ga, Ge, As, Se, Mo, Ag, In, Sn, ESM Table S3 and S4). The other elements (Cd, Sb, Te, Au, Tl, Bi, U) yielded
157 either values below the calculated, mean minimum detection limit or had concentrations of less than 1ppm. Significant
158 Ba concentrations in some chalcopyrite grains reflect contamination by inclusions of barite and will not be considered
159 any further. The elemental composition of chalcopyrite was studied considering different scales; within a single grain,
160 across one sample, surface versus subsurface of one site, and between different sites.

161

162 Single grain scale

163 In comparison to other sulfides, such as pyrite and sphalerite, chalcopyrite crystals do not show optical zoning. A transect
164 across a single chalcopyrite grain from a high temperature chimney fragment of New Mound 3 (Fig. 4) confirms this.
165 Concentrations of Co, Zn, Ag and Mn across the grain are uniform yielding mean values of 160 ± 10 ppm, 70 ± 5 ppm,
166 31 ± 3 ppm and 44 ± 1 ppm, respectively. However, Se and Ge have heterogeneous compositions, with the highest values,
167 755 ppm Se and 2 ppm Ge, occurring in the centre of the grain; the overall range of those element concentrations stays
168 within one order of magnitude. Concentrations of In show the opposite behaviour to those of Se and Ge, i.e., they decrease
169 from the rim to the core. Though the concentrations of V are very low, ranging from 0.2 to 0.6 ppm, they show a depletion
170 from one side of the chalcopyrite grain to the other. Mo and As concentrations are either very close to the detection limit
171 or below.

172

173 Sample scale

174 Different generations of chalcopyrite occur within a chimney fragment from New Mound 2 (Fig. 5). Chalcopyrite 1 (Ccp1)
175 is coarse grained and is associated with amorphous silica (blue). A second generation of chalcopyrite (Ccp2) forms a
176 massive band and represents the outer layer of the fluid conduit wall. This chalcopyrite is associated with idaite. Separated
177 by a thin band of marcasite the third generation of chalcopyrite (Ccp3) lines the inner walls of the conduit. Parts of this
178 conduit are filled with goethite and very rare grains of sphalerite (not shown) occur.

179 Comparison of the trace element concentrations of three chalcopyrite generations of sample 55-1A (Ccp1, Ccp2, Ccp3)
180 with chalcopyrite of the chimney fragment sample 55-6A are shown in Fig. 6. This chimney sample shows the highest
181 concentrations of Se and Co (Fig. 6a-b). Average concentrations of 685 ± 158 ppm for Se and 178 ± 32 ppm for Co which
182 are several orders of magnitude higher than the concentrations of Ccp1, Ccp2 and Ccp3 of the other chimney fragment
183 55-1A (ESM, Table S3). In addition, concentrations of Ag, In and Sn of chimney 55-6A are consistently higher than those
184 measured in Ccp3 of chimney fragment 55-1A, but show very similar concentration in Ccp1 and Ccp2 (Fig. 6c-e).
185 Concentrations of As, Ge, and Ga are consistently higher in Ccp3 of chimney 55-1A than in Ccp1 and Ccp2 of the same

186 chimney (Fig. 6f, h-i). The highest concentrations of Zn can be found in sample 55-6A and Ccp3 of sample 55-1A (Fig.
187 6j). However, Zn concentrations of more than 500 ppm are considered to come from the accident ablation of micro or
188 nano inclusions of sphalerite. Concentration of V in Ccp1 and Ccp2 of sample 55-1A and in 55-6A is ≤ 5 ppm, whereas
189 Ccp3 of sample 55-1A yields concentrations between 9 and 52 ppm (Fig. 6l).

190

191 Intra SMS mound variations and differences between mounds

192 As shown in the previous section, some chalcopyrite generations have 10s to 100s ppm of Se, Co and Ag incorporated,
193 whereas other chalcopyrite are enriched in As, Ga, Ge and Mo. Chalcopyrite occurring in surface and subsurface samples
194 of Southern mound (21-3B and 50-14) and from the deeper sample collected at MIR zone (73-29) shows elevated
195 concentrations of Se (Fig. 7a). Co is only enriched in chalcopyrite from both Southern mound samples, yielding average
196 values of 22 ± 2 ppm and 3 ± 1 ppm, but it does not show elevated concentrations in Rona mound and MIR zone (Fig.
197 7b). However, the measured concentrations are still two to three orders of magnitude lower than in chalcopyrite of
198 chimney fragment 55-6A. All chalcopyrites from Rona mound and the shallower subsurface sample of the MIR zone (73-
199 18) show similar concentrations of As, Mo, Ga and Ge to those determined in chimney fragment 55-1A-Ccp3 (Fig. 7f-i).
200 By contrast, the Se rich chalcopyrite from Southern mound and the chimney fragment 55-6A exhibit the lowest
201 concentrations of these elements with As being absent in 55-6A. The chimney fragments yield the highest concentrations
202 of Ag (Fig. 7c). The shallower samples from Southern mound and Mir zone have higher concentrations of Ag than their
203 deeper counterparts. All chalcopyrite from Rona mound show similar concentrations suggesting that concentrations are
204 very similar to uniform within one hydrothermal site, though they differ between different sulfide mounds. This can also
205 be observed for the elements In and Sn (Fig. 7d-e).

206 Finally, Zn concentrations in chalcopyrite from Southern mound and MIR zone appear to be uniform within the sulfide
207 mounds and are one to two orders of magnitude lower than those determined in the chimney fragments 55-6A and 55-
208 1A-Ccp3 (Fig. 7j). By contrast, samples from the Rona mound display a wider range, with the deeper samples 65-13 and
209 65-23 showing higher Zn concentrations possibly due to the presence of micro and nano inclusions of sphalerite.

210

211 Secondary copper minerals

212 Copper minerals other than chalcopyrite occur only in the surface samples (Table 1). In this study, three different
213 secondary copper minerals were analysed. These are idaite from New Mound 2 (55-1A), chalcocite from Rona mound
214 (45-7C) and covellite from Southern mound (21-3B) and New Mound 3 (55-6A). Due to the size of the minerals, only 36
215 spot analyses were performed. Covellite is characterised by high concentrations (100s to 1000s ppm) of Se and Co (Fig.
216 8a-b), low concentrations (<10 ppm) of Mo, Ge and Ga and the absence of As (Fig. 8f-i). Chalcocite and idaite have trace

217 elements incorporated that are found in chalcopyrite of Rona mound and chimney fragment 55-1A. While Co
218 concentrations are low (<1 ppm) and Se low (<10 ppm) to absent, As, Ge, Mo, and Ga are present in concentrations of
219 several 10s to 100s ppm (ESM, Table S4). Concentrations of Sn, Zn and Mn are relatively uniform in each mineral phase
220 and do not differ between the different copper minerals (Fig. 8e,j,l). For In, with the exception of covellite from Southern
221 mound, which shows average concentrations of 3 ± 1 ppm (Fig. 8d), the other copper minerals have average
222 concentrations between 8 and 11 ppm. The highest concentrations of Ag are found in covellite from New Mound 3 (55-
223 6A) and idaite from New Mound 2 (55-1A). Their average concentrations of 243 ± 23 ppm and 262 ± 62 ppm are one
224 order of magnitude higher than in covellite from Southern mound (Fig. 8c) and two orders of magnitude higher than in
225 chalcocite from Rona mound. Concentrations of V are lowest in covellite from Southern mound and New Mound 3 (Fig.
226 8k). Idaite exhibits slightly higher concentrations of V, whereas the highest concentrations are found in chalcocite from
227 Rona mound, with an average concentration of 15 ± 7 ppm.

228

229 **Discussion**

230 Copper mineral assemblages and relative precipitation temperatures

231 Five Cu-(Fe)-sulfides were identified, which are hosted in three main sample types: (1) chimney fragments, (2) massive
232 sulfides and (3) sulfide breccia. While chalcopyrite can be found in all three sample types, the occurrence of isocubanite
233 and idaite is restricted to chimney fragments of New Mound 2 and 3. While chalcocite occurs only along micro-fractures,
234 cutting through earlier chalcopyrite hosted in a sulfide breccia at Rona mound, covellite either lines the rims of
235 chalcopyrite or idaite of chimney fragment samples or can be found filling micro-fractures in a massive sulfide sample of
236 Southern mound.

237 Based on petrographic and textural observation and a comparison with published data from active and inactive SMS and
238 ancient VMS systems, it is possible to assign relative formation and alteration temperatures to the different Cu-(Fe)-
239 sulfides found in this study. Precipitation of chalcopyrite in SMS systems occurs at temperatures between >350 °C to 280
240 °C (Large 1992) with black smoker hydrothermal fluids at the active TAG hydrothermal vent yielding 370 °C (Tivey et
241 al. 1995). Isocubanite, according to Large (1992), is also a high temperature Cu-(Fe)-sulfide, and formed through
242 exsolution from chalcopyrite, with a temperature stability field ranging from 252 °C to 400 °C (Nenasheva and
243 Kravchenko 2015). Idaite is quite rare in SMS systems, though its occurrence has been reported at the TAG mound and
244 in VMS deposits of Cyprus (Constantinou 1975, Mozgova et al. 2000). The formation of the mineral is still not fully
245 constrained. It has been proposed that idaite is a supergene alteration product of bornite (Frenzel 1959, Vaughan and
246 Craig 1978), however, Constantinou (1975) proposed that the mineral formed through oxidative leaching of chalcopyrite
247 by an acidic ferric rich solution that formed during the alteration of pyrite to goethite at low temperatures. Idaite from

248 New Mound 2 and 3 is associated with chalcopyrite, Fe poor sphalerite (Lehrmann et al. 2018) and goethite, i.e. a similar
249 mineral assemblage to that of VMS deposits from Cyprus, and hence a low temperature formation is assumed for Ccp3
250 of chimney fragment 55-1A. The temperature window in which idaite is stable ranges from <256 °C to 50 °C (Wang
251 1984). Because of their distinctive association with isocubanite and idaite, chalcopyrite from chimney fragment 55-6a is
252 of high temperature origin, whereas Ccp3 of 55-1A formed at low hydrothermal temperatures.

253 Chalcocite shows a monocline crystal system at temperatures of <103 °C but inverts into the hexagonal system at 103°C
254 and remains in this crystal system to temperatures of ~435 °C (Fleet 2006). It is not known which crystal system the
255 chalcocite of this study exhibits; however, based on its occurrence, it is clearly an alteration phase thus low formation
256 temperatures are considered most likely. Covellite can be stable at temperatures of up to 507 °C (Fleet 2006). In this
257 study, however, covellite is clearly a secondary alteration phase as it is lining the rims and fractures of earlier idaite and
258 chalcopyrite. Hence, its formation temperature is likely to be in the range of those from idaite.

259

260 Trace element budget of chalcopyrite

261 Despite chalcopyrite being the predominant source for copper, one would assume that the valence state of Cu and Fe,
262 which occupies the cation sites of the mineral structure, is known; however, there is ongoing debate as to the valence state
263 of these elements. While Todd et al. (2003) propose Cu and Fe to be divalent ($\text{Cu}^{2+}\text{Fe}^{2+}\text{S}_2^{2-}$), Pearce et al. (2006) suggest
264 Cu to be monovalent and Fe to be trivalent ($\text{Cu}^+\text{Fe}^{3+}\text{S}_2^{2-}$). However, Li et al. (2013) suggested that due to covalent bonding
265 of atoms in the structure of chalcopyrite, an intermediate valence state is valid, i.e. both valence states for Cu and Fe are
266 present. Because of this uncertainty, mechanisms for trace element incorporation are more complex and highly dependent
267 on the presence or absence of co-crystallising sulfides (George et al. 2016) and fluid temperature (Seyfried and Ding
268 1995, Schmidt et al. 2007). In general, trace elements can be hosted in a mineral in three different ways: (1) structurally
269 bound in the mineral lattice, (2) as micro and nano inclusions, or (3) adsorbed to the surface of the mineral. Wohlgemuth-
270 Ueberwasser et al. (2015) noted that LA-ICP-MS is unable to distinguish between lattice bound elements and uniformly
271 distributed nano inclusions within a mineral due to the size of the spot. This is also valid within this study where we used
272 an ablation spot size of 25 µm.

273 Chalcopyrite associated with isocubanite is thought to be of high temperature origin and is characterised by high
274 concentrations of Se and Co (Fig. 9a). While Se substitutes for S (Huston et al. 1995), Co gets incorporated into the
275 position of Fe (George et al. 2018). The temperature window for Se and Co incorporation into the structure of chalcopyrite
276 is >300 °C, or even ~350 °C (Auclair et al. 1987, Huston et al. 1995). According to Metz and Trefry (2000), there is a
277 sharp drop in Co concentrations in the vent fluid at <350 °C, with Liu et al. (2011) suggesting that Co and Cu
278 concentrations are very low at temperatures of <250 °C. This would explain why the mineral assemblage in black smoker

279 precipitates is dominated by chalcopyrite.; However, in precipitates from white smokers, sphalerite is predominant, with
280 chalcopyrite being only an accessory phase. As high fluid temperatures are needed to transport Se, it is considered to be
281 immobile during recrystallisation events as long the temperatures do not exceed 300 °C. Overall, this suggests that not
282 only chalcopyrite of New Mound 3 (55-6A) formed at high temperatures, but also chalcopyrite from both Southern mound
283 samples and the deeper sub-seafloor sample from MIR zone (73-29).

284 The highest concentrations of Ag occur in the chimney fragment 55-6A (Fig. 9a) and are several orders of magnitude
285 higher than in any other analysed chalcopyrite. In general, Ag substitutes for Cu (Huston et al. 1995, George et al. 2018).
286 In the previous section (Fig. 7c) the hypothesis was that Ag concentrations are linked to high formation temperature. This
287 would explain the Ag rich chalcopyrite of chimney fragment 55-6A, but it does not explain why concentrations of Ag in
288 the other chalcopyrite samples from Southern mound and MIR zone record low concentrations. This suggests a different
289 explanation. One hypothesis is that Ag concentrations are linked to the occurrence of isocubanite which was only
290 identified in sample 55-6A. Another hypothesis is that the occurrence of Ag is linked to the sample type, i.e., even the
291 chalcopyrite hosted in the chimney fragment of 55-1A has higher Ag than any other Cu-(Fe)- sulfide found in the massive
292 sulfide and sulfide breccia samples. Other chimney samples analysed by Butler and Nesbitt (1999), Maslennikov et al.
293 (2009), Wohlgemuth-Ueberwasser et al. (2015), and Melekestseva et al. (2017) confirm the presence of Ag in
294 chalcopyrite. Alternatively, an explanation could be the paragenetic stage of the samples; the chimney fragments being
295 the youngest, i.e., less altered, whereas the samples from the other sulfide mounds have undergone low and high
296 temperature alteration which changed the trace metal budget.

297 The trace elements In, Sn, As, Ga, Ge, Mo, and Zn are thought to be able to incorporate into the lattice of chalcopyrite by
298 either direct or coupled substitution, predominately partitioning into the Fe site and to a minor degree the Cu site (Huston
299 et al. 1995, Maslennikov et al. 2009, George et al. 2016, 2018, Grant et al. 2018). While the window of incorporation into
300 the lattice of chalcopyrite for Sn, In and Mo is considered to be in the medium to high temperature range (Maslennikov
301 et al. 2009, Monecke et al. 2016), As, Ga, Ge and Zn occur in chalcopyrite that formed at low to medium temperatures
302 (Metz and Trefry 2000, Maslennikov et al. 2009, Monecke et al. 2016). All samples from Southern mound, the deeper
303 MIR zone and the chimney fragment that were considered to be of high temperature origin exhibit Mo concentrations that
304 are either below the mean detection limit (Fig. 9c) or are one to two orders of magnitude lower than concentrations found
305 in Ccp3 from the inner chimney orifice (55-1A), Rona mound samples and the shallower sample of MIR zone (73-18). A
306 similar pattern can be observed for Ga, As and Ge which are also enriched in the Rona mound and chalcopyrite from New
307 Mound 2 (Fig. 9b,d). The high Ga and Sn concentrations only found in chalcopyrite of Rona mound are not only related
308 to the lower fluid temperature but also to the occurrence of sphalerite in the shallower part of the subsurface (Lehrmann

309 et al. 2018). George et al. 2018 suggest that Ga and Sn can be remobilised from pre-existing sphalerite and incorporated
310 into the chalcopyrite.

311 Zn is not only hosted in the lattice of chalcopyrite but it can also occur as inclusions. Kojima and Sugaki (1985) propose
312 that up to 1800 ppm can be incorporated into the chalcopyrite at 300 °C, however maximum Zn concentrations related to
313 incorporation into the chalcopyrite lattice are 235 ppm (Fig. 9e). Everything above this value is thought to be related to
314 Zn bearing mineral inclusions.

315 Vanadium is neither known to be incorporated into the lattice of the chalcopyrite nor to form inclusions, but rather gets
316 absorbed onto the mineral surface (Butler and Nesbitt 1999) with V originating from cold seawater. Once the V is fixed
317 to the surface, it is very difficult to remobilise (Butler and Nesbitt 1999). Concentrations of V are quite constant within
318 different chalcopyrite samples. Two exceptions are from the surface of Rona mound and Ccp3 of 55-1A (Fig. 9f). The
319 reason why those two samples yield V concentrations of more than one order of magnitude higher to those in the other
320 samples can be explained by the rock type they are hosted in. Chalcopyrite of 45-7C occurs within a sulfide breccia where
321 it is heavily pervaded by micro-fractures that act as pathways for seawater ingress. The other V rich chalcopyrite is found
322 in the inner conduit of a chimney, which is naturally more permeable than massive sulfide blocks. Goethite that
323 precipitated within the inner conduit confirms that the chimney sample 55-1A underwent seafloor weathering, and hence
324 extensive exposure to seawater. In this way, V can be used as a useful tracer of seawater interaction within SMS deposits
325 (Butler and Nesbitt 1999 and references therein). Manganese is highly soluble in reduced fluids at high temperature, thus
326 does not precipitate (Maslennikov et al. 2009). However, at low temperatures and in oxygenated conditions, it precipitates
327 directly from a hydrothermal fluid or adsorbed from seawater onto a mineral surface (Grant et al. 2018). Chalcopyrite
328 hosted in samples taken from the surface of sulfide mounds exhibit concentrations that are one order of magnitude higher
329 than those from the subsurface (Fig. 9f), suggesting the absorption of seawater derived Mn. Several analyses of
330 chalcopyrite hosted in subsurface samples exhibit very high Mn concentrations of several 100s ppm. However, these
331 chalcopyrite are Se and/or Co rich chalcopyrite, i.e., formed at high temperatures, hence cannot be related to surface
332 adsorption. Thus, they are assumed to be related to Mn rich mineral inclusions. While some high Mn concentrations
333 correlate with high Zn, for others, no correlation exists with any of the discussed elements.

334 Secondary copper alteration minerals

335 The predominant oxidation stage in the copper minerals idaite (Cu_3FeS_4), chalcocite (Cu_2S) and covellite (CuS) is
336 monovalent for Cu and trivalent for Fe (Fleet 2006). The identical valence states of Cu and Fe in the secondary copper
337 minerals to those in chalcopyrite mean that similar element distributions are expected in the alteration phases. Those
338 elements that are only mobile at high temperatures, e.g. Se will also be retained in low temperature alteration phases. In
339 comparison to chalcopyrite of the inner (Ccp3) and outer (Ccp2) conduit of sample 55-1A, idaite exhibits trace element

340 concentrations that fall between those of the other two chalcopyrite generations (Fig. 10a). The exceptions are Mo and
341 Ag that are enriched in idaite by one to two orders of magnitude to those in Ccp2 and Ccp3. In addition, Co and Mn
342 concentrations are almost identical in the chalcopyrite and idaite and V shows higher concentration in Ccp3 than Ccp2
343 and the idaite.

344 Chalcocite does not differ significantly with regard to its trace element pattern in comparison to earlier paragenetic
345 chalcopyrite (Fig. 10b). As with idaite only Ag and Mo are enriched. Covellite from Southern mound and New Mound 3
346 are also enriched in Mo and Ag in comparison to associated chalcopyrite (Fig. 10c-d). Other elements enriched in covellite
347 from Southern mound are V and Se. While higher concentrations of V can be explained by exposure to seawater that
348 entered the mineral structure through micro-fractures, the high Se concentration exhibited in the covellite is inherited
349 from the precursor chalcopyrite as a low temperature fluid cannot mobilise nor precipitate Se (Genna and Gaboury 2015).
350 Overall, Ag and Mo appear to be the elements getting incorporated into the lattice of secondary copper minerals during
351 alteration, with Ag substituting for monovalent Cu. The elevated concentration of Ag in chalcocite suggests that the
352 mineral has a monovalent crystal structure and thus formed at temperatures of <103 °C as hexagonal chalcocite, which
353 formed at higher temperature is Ag poor (Cook et al. 2011). Although the end members covellite and chalcocite do not
354 host any Fe according to Vaughan and Craig (1978), here, up to percent level concentrations of Fe play an important role
355 allowing the substitution of trivalent Fe by trivalent Mo which has almost the same ionic radius.

356

357 Source of trace elements

358 In general, it is proposed that chemical composition and mineralogy of SMS deposits vary in different tectonic settings,
359 which have a specific geology and composition of hydrothermal fluids (Hannington et al. 2005). Key parameters
360 influencing the composition of the hydrothermal fluid are source rock composition and input of magmatic volatiles
361 (Hannington et al. 2005). Mafic to ultramafic systems are known to be Cu and Co rich, whereas felsic systems are
362 enriched in Zn, As, Sb, and Pb (Hannington et al. 2005, Monecke et al. 2016). The TAG mound is a basalt hosted system
363 and basalt is expected to underlie the other sulfide mounds investigated here, hence a similar trace element pattern should
364 be observed in the various chalcopyrite grains. To decipher the origin of the trace elements in chalcopyrite requires trace
365 element data for source rock, seawater and hydrothermal vent fluids. However, available vent fluid data from the TAG
366 mound or elsewhere do not include data for concentrations of V, Ga, Ge, Se, As, and Sn (Douville et al. 2002). Primitive
367 mantle normalised mean trace element patterns of the high and low temperature chimney fragments from 55-6A (New
368 Mound 3) and 55-1A-Ccp3 (New Mound 2) are quite distinctive (Fig. 11a). While Se, Ag, In, and Sn are enriched in the
369 high temperature chimney fragment with respect to primitive mantle, elements that originate from seawater such as V and
370 Mn are depleted. In the low temperature chimney fragment, V concentrations are two orders of magnitude higher than in

371 chalcopyrite from the high temperature chimney, suggesting that this chimney fragment has had longer exposure to
372 seawater. Other elements that are enriched are the intermediate to low temperature elements As, Ge, Ga, and Mo. Seawater
373 Mo concentrations are 10.1 parts per billion (Douville et al. 2002) and therefore 21 times higher than in the hydrothermal
374 fluid at TAG. The presence of Mo suggests that ascending hydrothermal fluid mixed with seawater. Normalised mean
375 trace element patterns of chalcopyrite from Southern mound surface and subsurface are very similar (Fig. 11b) with the
376 exception of slightly higher concentrations of V and Mn which suggest a longer exposure to seawater. In addition, both
377 samples have different concentrations of Mo and Ag, with the surface sample exhibiting lower concentrations of Mo and
378 higher concentrations of Ag than those of the subsurface. The lower concentrations of Mo could either indicate that the
379 element was not precipitated and lost by emission through the vent, was precipitated in an associated mineral phase, was
380 depleted in the vent fluid or was removed from the mineral structure during a later hydrothermal stage. The trace element
381 patterns of chalcopyrite from Rona mound are consistent (Fig. 11c). The surface sample exhibits the highest
382 concentrations of V and Mn and correlates well with extended exposure to seawater (as well as having the lowest
383 concentration of Sn). Sn is presumed to originate from recrystallisation of earlier precipitated sphalerite, hence the higher
384 Sn concentrations observed in all subsurface chalcopyrite. Interestingly, the shallowest subsurface sample from Rona
385 mound (65-9) shows the lowest concentration of V and Mo, whereas concentrations found in deeper parts of the mound
386 are higher. This suggests that below the sample location of 65-9, the mound is cut by a fracture that allows ingress of
387 seawater to the deeper part without affecting the composition of the shallower chalcopyrite. The existence of such
388 fractures was confirmed visually during expedition JC138 (Murton et al. 2019). Chalcopyrite from the shallower
389 subsurface sample of MIR zone shows higher concentrations of seawater derived V and Mo and lower concentrations of
390 Se and Sn (Fig. 11d). The absence of a sphalerite rich zone at the MIR zone suggests the Sn is unlikely to have originated
391 from earlier precipitated sphalerite and is assumed to have precipitated directly from the vent fluid.

392

393 **Conclusions**

- 394 • In the absence of co-precipitating sulfides, hydrothermal chalcopyrite can incorporate a diverse trace element
395 suite up to several hundreds of ppm that represent different formation, remobilisation and alteration stages.
- 396 • Trace element concentrations of chalcopyrite do not only vary between different chalcopyrite generations within
397 one sample, but also show variations from surface to subsurface within a single sulfide mound. In addition,
398 chalcopyrite from different mounds show distinguishable concentrations of certain trace elements.
- 399 • The incorporation of trace elements is dependent on a change in the physicochemical conditions. Contrary to
400 previous expectations, the host rock composition plays only a minor role with regard to the trace element budget.

- 401 • Typical high temperature indicators are high concentrations of Se, Co and to a certain degree Ag, As, Ga, and
402 Ge are found in chalcopyrite that formed at low temperatures with Ga and Sn originating from earlier precipitated
403 sphalerite at some sites. Exposure to seawater can be identified by elevated concentrations of Mo, Mn and V.
- 404 • Secondary copper minerals display very similar trace element patterns to the primary chalcopyrite, with high
405 temperature element signatures often being retained. Elevated concentrations of Ag and Mo suggest that these
406 elements substitute, due to similar ionic radii into the site of the monovalent Cu and trivalent Fe. Due to micro-
407 fractures and hence increased permeability, V and Mn concentrations can be higher in the secondary phase
408 because of alteration.
- 409 • The absence of certain trace elements suggests that an element either was depleted in the vent fluid, escaped
410 through a vapour phase or got leached from the mineral and reprecipitated elsewhere in the sulfide mound.

411

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423

424 **Declarations**

425 **Conflicts of interest/Competing interests**

426 The authors have no conflicts of interest to declare that are relevant to the content of this article.

427 **Availability of data and material**

428 The complete analytical data set is included in the electronic supplementary material.

429 **Code availability**

430 Not applicable

431

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596 **Table captions**

597 **Table 1** Sample list for analysed Cu-(Fe)-sulfides and their estimated mineral abundance

598 Abbreviations: -- absent, o trace (≤1%), x minor (1-5%), + common (5-25%), ++ abundant (25-50%), +++ dominant (≥50%); Ccp (chalcopyrite), Cct (chalcocite), Cv (covellite), Id
 599 (idaite), Iso (isocubanite), Mrc (marcasite), Py (pyrite), Sp (sphalerite), Others include holes, silicates, barite, jarosite, atacamite and iron-oxyhydroxides

600

601

602

603 **Figure captions**

604 **Fig. 1** Bathymetric map of the TAG hydrothermal field and its active and inactive hydrothermal sites (data source
 605 GeoMapApp: KN142-05 (TAG94), DSL120 2m grid White). The inset shows the location on the Mid-Atlantic
 606

607 **Fig. 2** Images and reflected light photomicrographs of representative surface and sub-surface sulfide samples from
 608 inactive seafloor massive sulfides sites from the TAG hydrothermal field; a: chimney fragment predominately composed
 609 of chalcopyrite and marcasite with a visible fluid conduit (55-1A), b: massive sulfide composed of pyrite with intercalated
 610 chalcopyrite and partial brecciation at the sample rim (21-3B), c: sulfide breccia composed of pyrite crossed by a band of
 611 chalcopyrite (73-29), d: cross section of a chimney fluid conduit composed of two generations of chalcopyrite and
 612 subhedral idaite showing alteration to covellite; rare sphalerite and goethite occur in the orifice (55-1A), e: chalcopyrite

613 with exsolution lamella of isocubanite (55-6A), f: two generations of pyrite with intercalated chalcopyrite (73-29), g:
614 chalcopyrite in a matrix of pyrite with fossil remnants of tubular organism, which is highlighted by a red box (73-29), h:
615 chalcopyrite altered to chalcocite along micro-fractures (45-7C), i: covellite surrounding chalcopyrite (55-6A). Mineral
616 abbreviations: Ccp: chalcopyrite, Cct: chalcocite, Cv: covellite, Id: idaite, Iso: isocubanite, Mrc: marcasite, Py: pyrite,
617 Sp: sphalerite, Gth: goethite

618

619 **Fig. 3** Selection of minerals reported in the Cu-Fe-S system after Vaughan and Craig (1978) in atomic percent (at.-%)
620 and the composition of the copper sulfides investigated in this study. Abbreviations: bn (bornite), cc (chalcocite), cp
621 (chalcopyrite), cv (covellite), di (digenite), dj (djurleite), id-I (idaite, Cu_5FeS_6), id-II (idaite, Cu_3FeS_4)

622

623 **Fig. 4** LA-ICP-MS transect across a chalcopyrite grain of a chimney fragment from New Mound 3 (55-6A). a:
624 photomicrograph of transect and spots of laser ablation ICP-MS analyses; b: transect of logarithmic scaled concentrations
625 of selected elements

626

627 **Fig. 5** Scanning electron microscope elemental EDS map of a fluid conduit section from a chimney fragment (55-1A)
628 illustrating the major element distribution on the scale of several mm. Three chalcopyrite (Ccp) generations occur. Ccp1
629 is coarse grained, Ccp2 is massive and forms the outer layer of the orifice. Ccp3 lines the inner wall of the orifice. Other
630 minerals present are idaite (Id), goethite (Gth) and marcasite (Mrc)

631

632 **Fig. 6** Semi logarithmic scale histograms illustrating the variation in concentrations of selected elements in chalcopyrite
633 from different chimney fragments of two sulfide mounds

634

635 **Fig. 7** Box and whisker plots of selected trace element concentrations in chalcopyrite ($n = 279$) of different inactive sulfide
636 mounds from the TAG hydrothermal field. Boxes show the upper and lower quartiles; the line between the boxes
637 represents the median with the line bars indicating the variability outside the quartiles and the stars indicate minimum (*)
638 and maximum (*) outliers. Chimney fragments: 55-6A (New Mound 3, $n = 33$) and 55-1A-Ccp3 (New Mound 2, $n = 7$)
639 are plotted as representative samples for a high and low temperature composition; Southern mound: 21-3B ($n = 21$), 50-14
640 (6.68 mbsf, $n = 39$); Rona mound: 45-7C ($n = 25$), 65-9 (10.53 mbsf, $n = 33$), 65-13 (11.40 mbsf, $n = 32$), 65-23 (12.37 mbsf,
641 $n = 28$); MIR Zone: 73-18 (4.35 mbsf, $n = 32$), 73-29 (7.04 mbsf, $n = 29$)

642

643 **Fig. 8** Box and whisker plots of selected trace element concentrations (n = 36) in copper minerals others than chalcopyrite
644 of different inactive sulfide mounds from the TAG hydrothermal field. Boxes show the upper and lower quartiles; the line
645 between the boxes represents the median with the line bars indicating the variability outside the quartiles and the stars
646 indicate minimum (*) and maximum (*) outliers. Covellite: 21-3B_cv (n=6), 55-6A_cv (n= 2); chalcocite: 45-7C_cct
647 (n=11); idaite: 55-1A_id (n= 17)

648

649 **Fig. 9** Log-log plots of LA-ICP-MS trace metal concentrations in chalcopyrite showing relationships and correlations
650 between selected elements

651

652 **Fig. 10** Concentrations of selected trace elements in chalcopyrite and their associated secondary alteration copper mineral
653 from New Mound 2, 55-1A, (a), Rona mound (b), Southern mound (c) and New Mound 3, 55-6A (d)

654

655 **Fig. 11** Primitive mantle normalised metal pattern for chalcopyrite from different hydrothermally inactive sulfide mounds
656 from the TAG hydrothermal field. All mean trace metals concentrations were normalised to primitive mantle values from
657 Palme and O'Neill (2014)

Table

Sample ID	Characteristics	Location	Latitude	Longitude	Depth	Sampling	Ccp	Iso	Id	Cct	Cv	Py	Mrc	Sp	Others
JC138-021-3B	Massive sulfide	Southern Mound	26°09.35'N	44°49.02'W	3550	HyBIS	+	--	--	--	x	+++	--	o	+
JC138-050-14	Massive sulfide	Southern Mound	26°09.34'N	44°48.97'W	3541	RD2	+	--	--	--	--	+++	--	o	+
JC138-045-7C	sulfide breccia	Rona Mound	26°09.36'N	44°48.82'W	3535	HyBIS	++	--	--	+	o	++	x	o	x
JC138-065-9	Massive sulfide	Rona Mound	26°09.37'N	44°48.80'W	3541	RD2	x	--	--	--	--	+++	--	o	+
JC138-065-13	Massive sulfide	Rona Mound	26°09.37'N	44°48.80'W	3541	RD2	+	--	--	--	--	+++	--	o	x
JC138-065-23	Massive sulfide	Rona Mound	26°09.37'N	44°48.80'W	3542	RD2	+	--	--	--	--	+++	--	o	x
JC138-055-1A	Chimney	New Mound 2	26°09.51'N	44°49.17'W	3589	HyBIS	+++	--	+	--	+	++	+	x	+
JC138-055-6A	Chimney	New Mound 3	26°09.56'N	44°49.19'W	3598	HyBIS	++	x	--	--	x	+	++	x	++
JC138-073-18	Sulfide breccia	MIR Zone	26°08.61'N	44°48.41'W	3440	RD2	++	--	--	--	--	++	--	--	x
JC138-073-29	Sulfide breccia	MIR Zone	26°08.61'N	44°48.41'W	3443	RD2	++	--	--	--	--	+++	--	o	x

Abbreviations: -- absent, o traces ($\leq 1\%$), x minor (1-5%), + common (5-25%), ++ abundant (25-50%), +++ dominant ($\geq 50\%$)

Ccp (chalcopyrite), Iso (iscocubanite), Id (idaite), Cct (chalcocite), Cv (covellite), Py (pyrite), Mrc (marcasite), Sp (sphalerite),

Others include holes, silicates, barite, jarosite, atacamite, iron-oxhydroxides

Figure 1

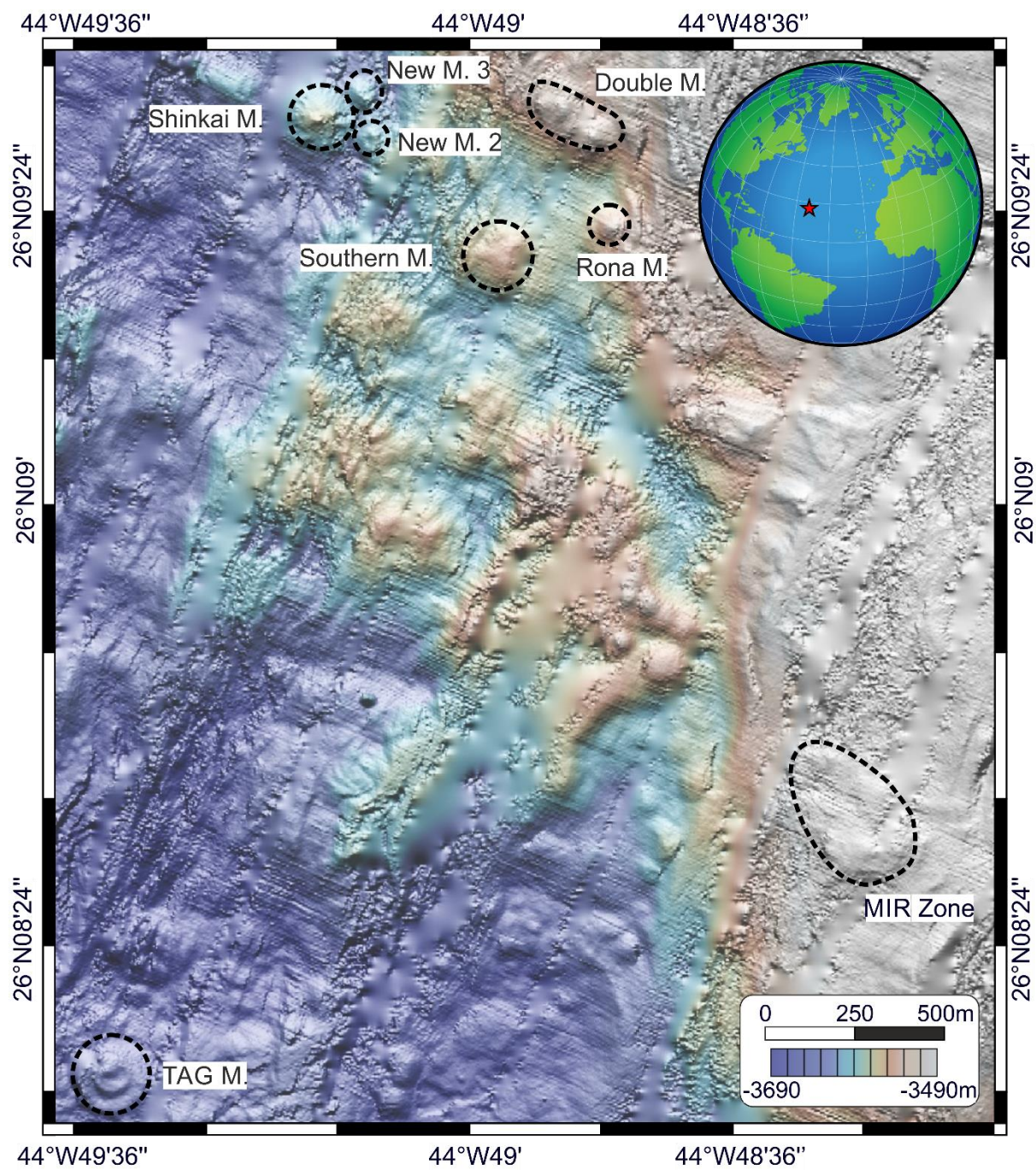


Figure 2

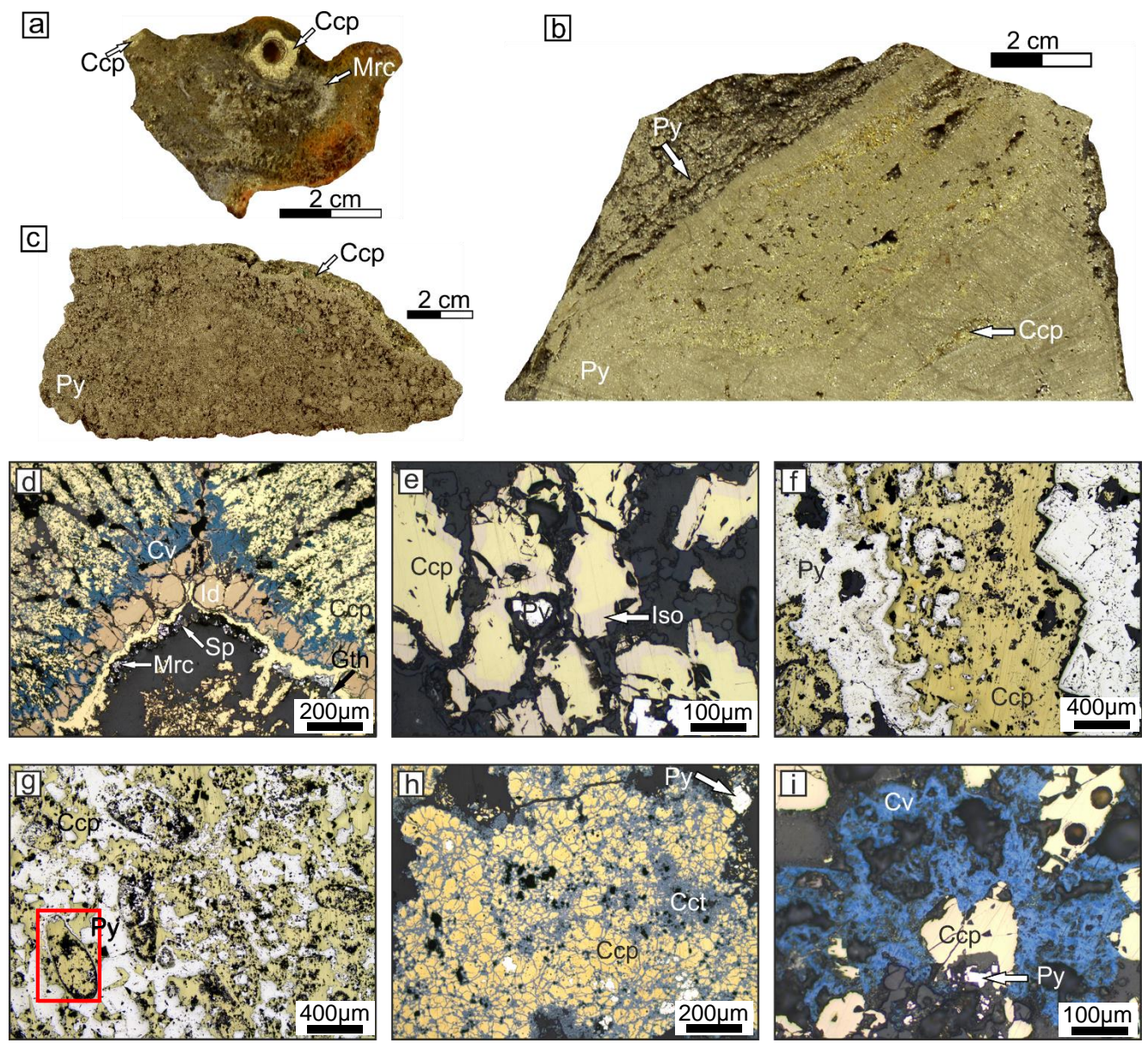


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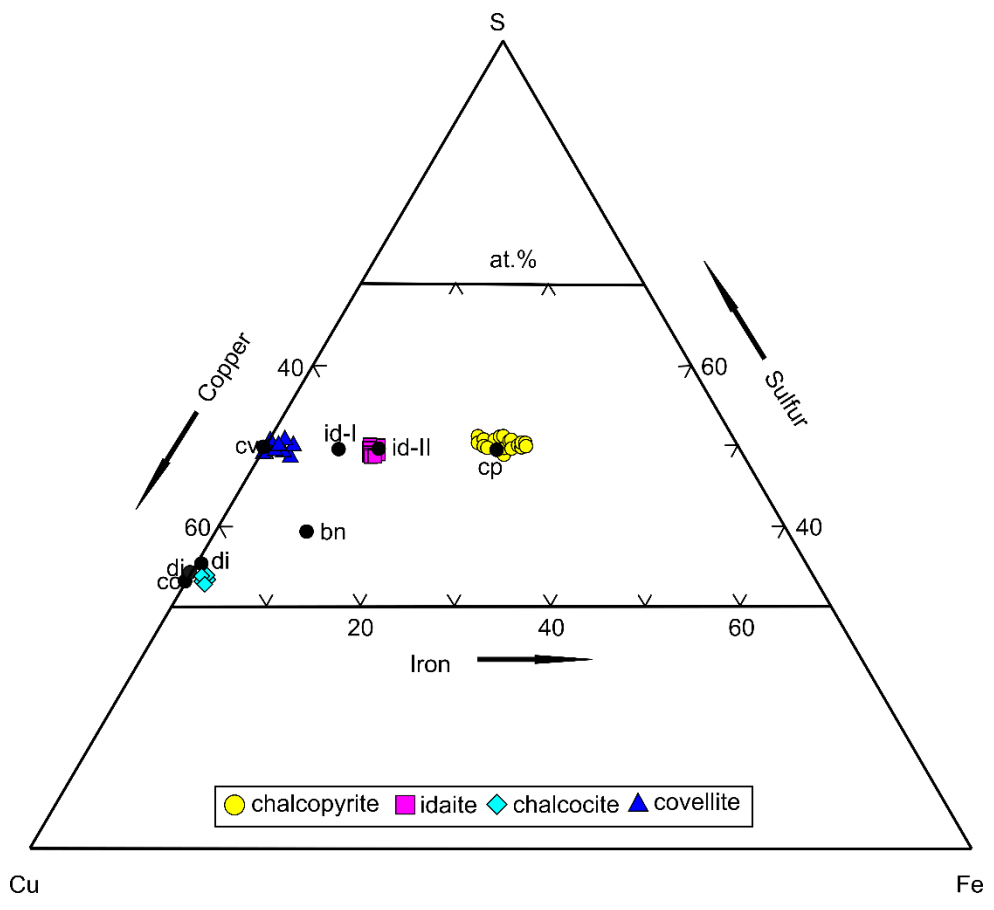


Figure 4

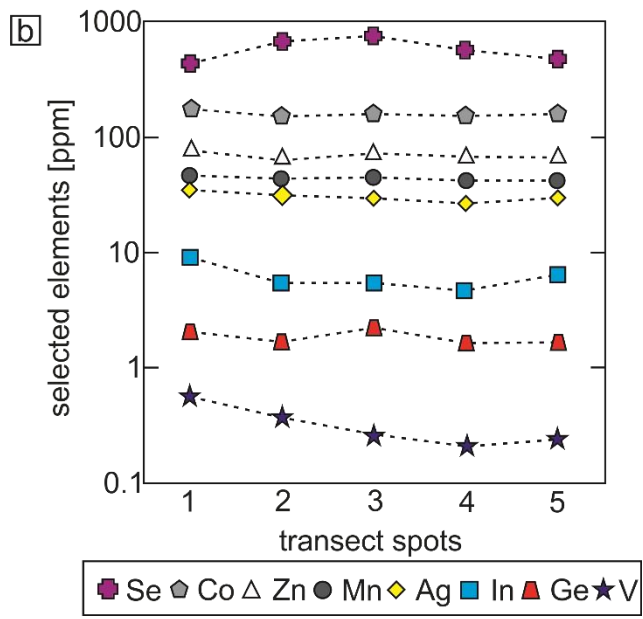
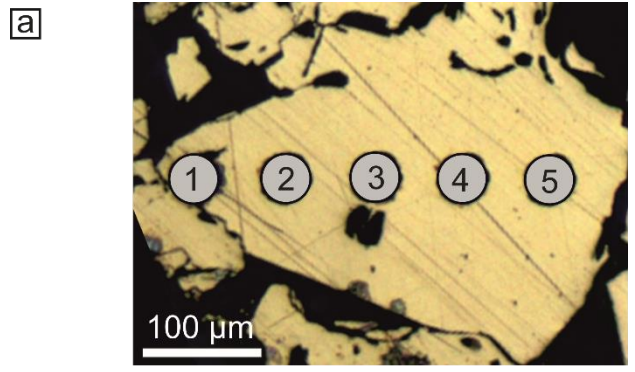


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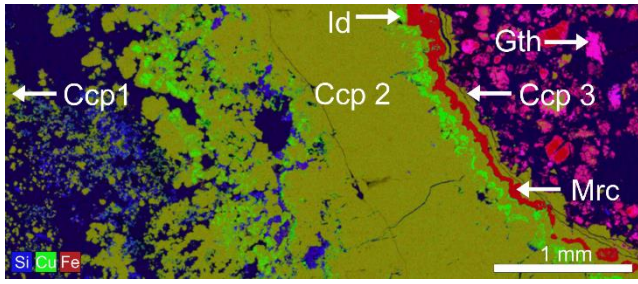


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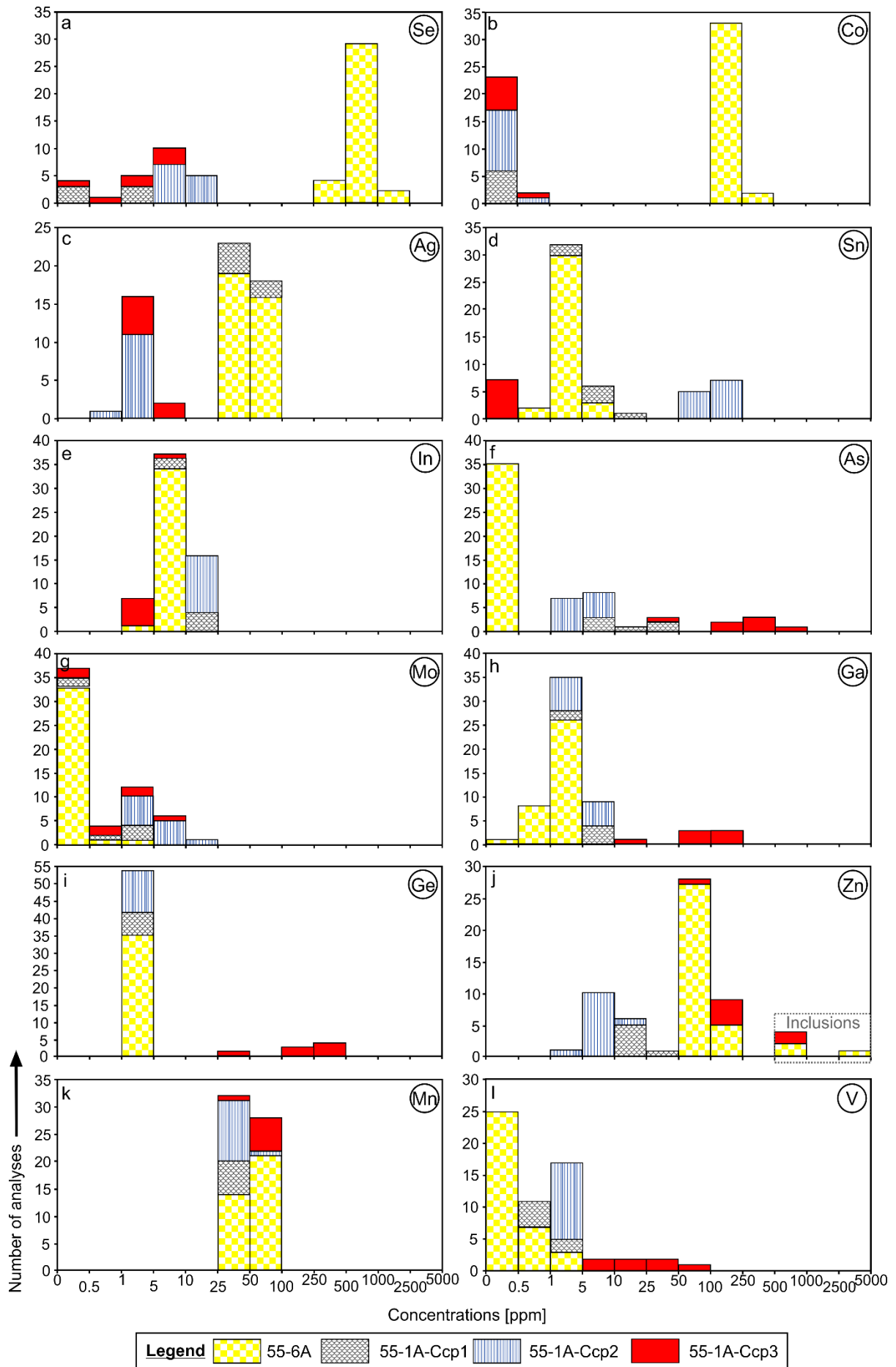


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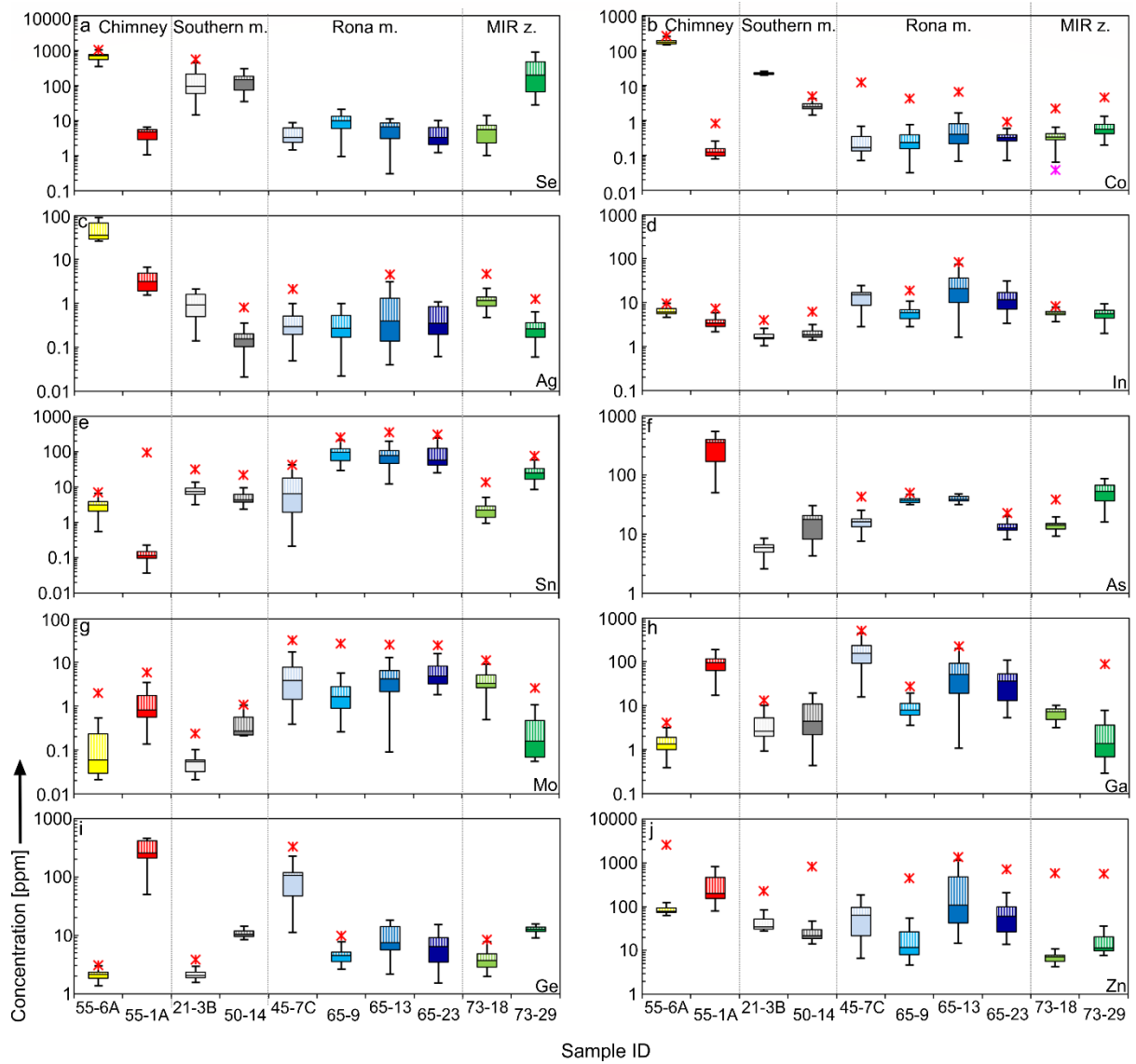


Figure 8

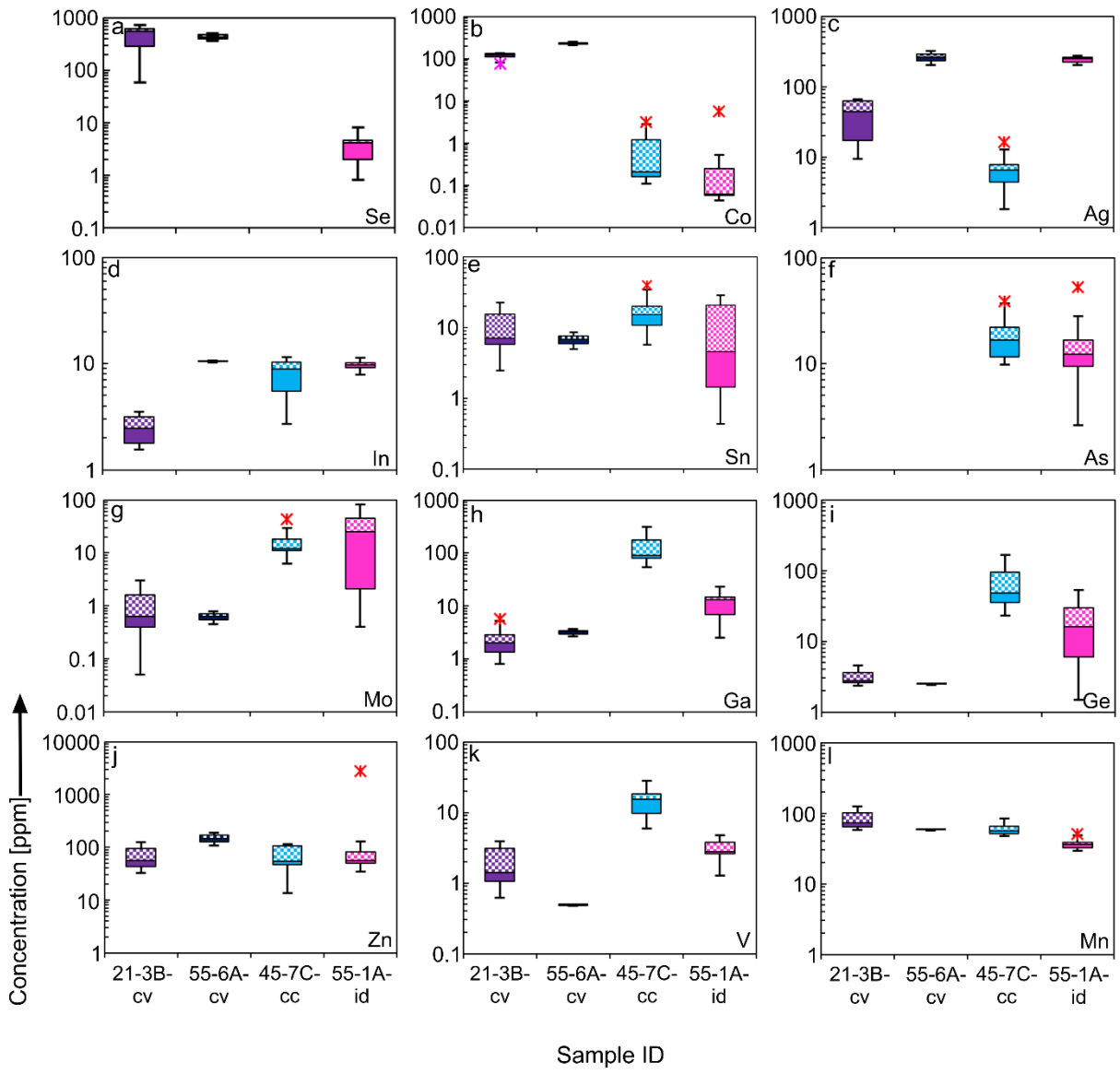


Figure 9

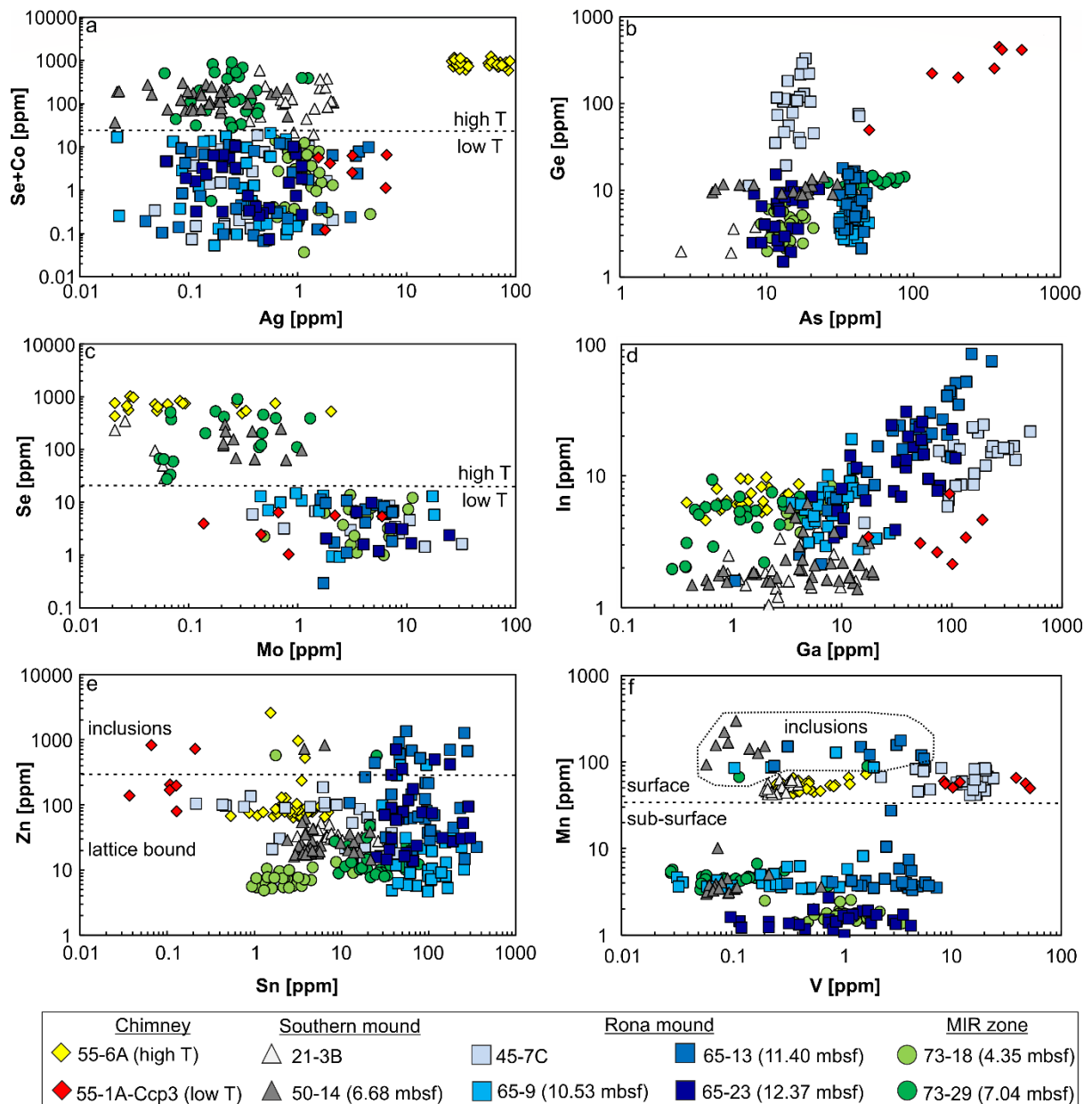


Figure 10

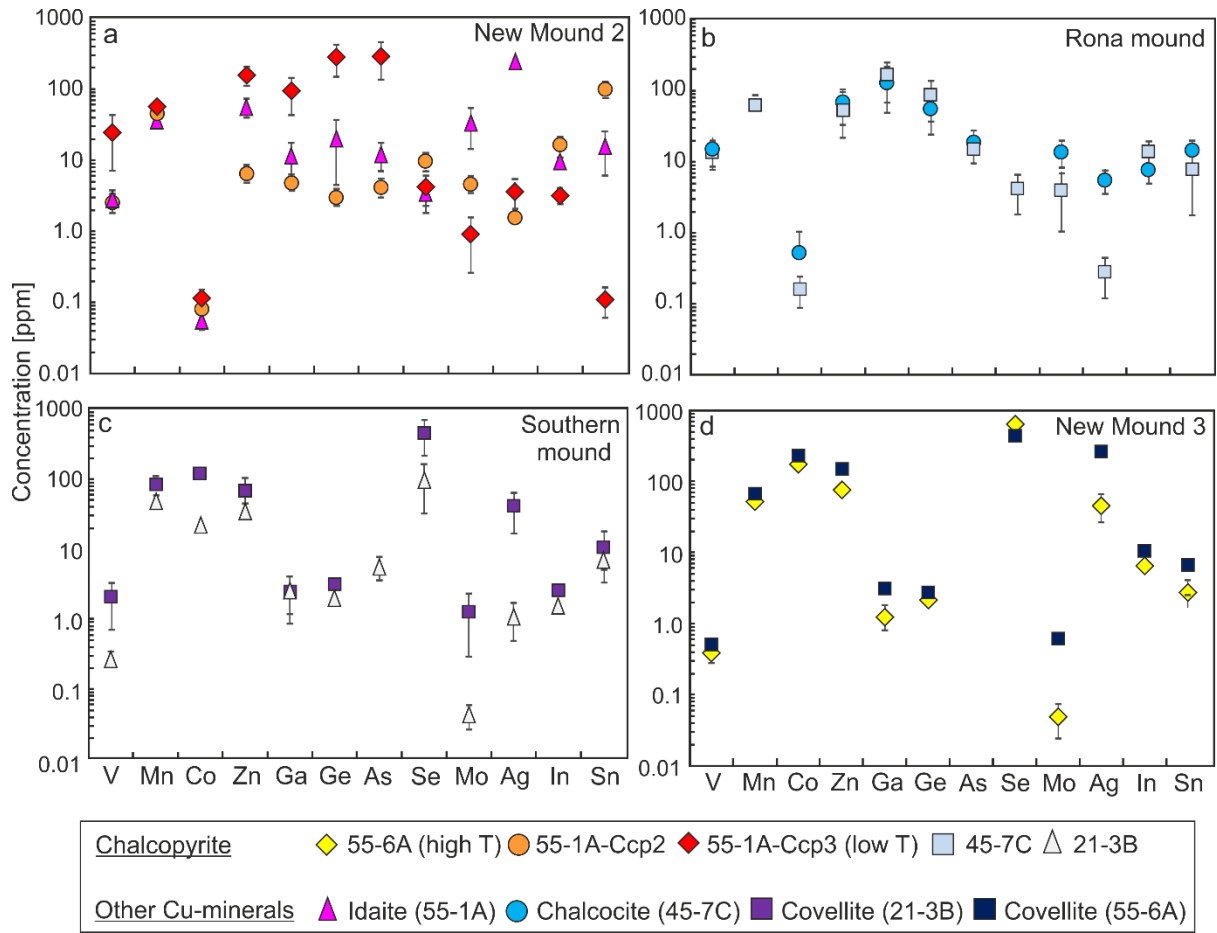
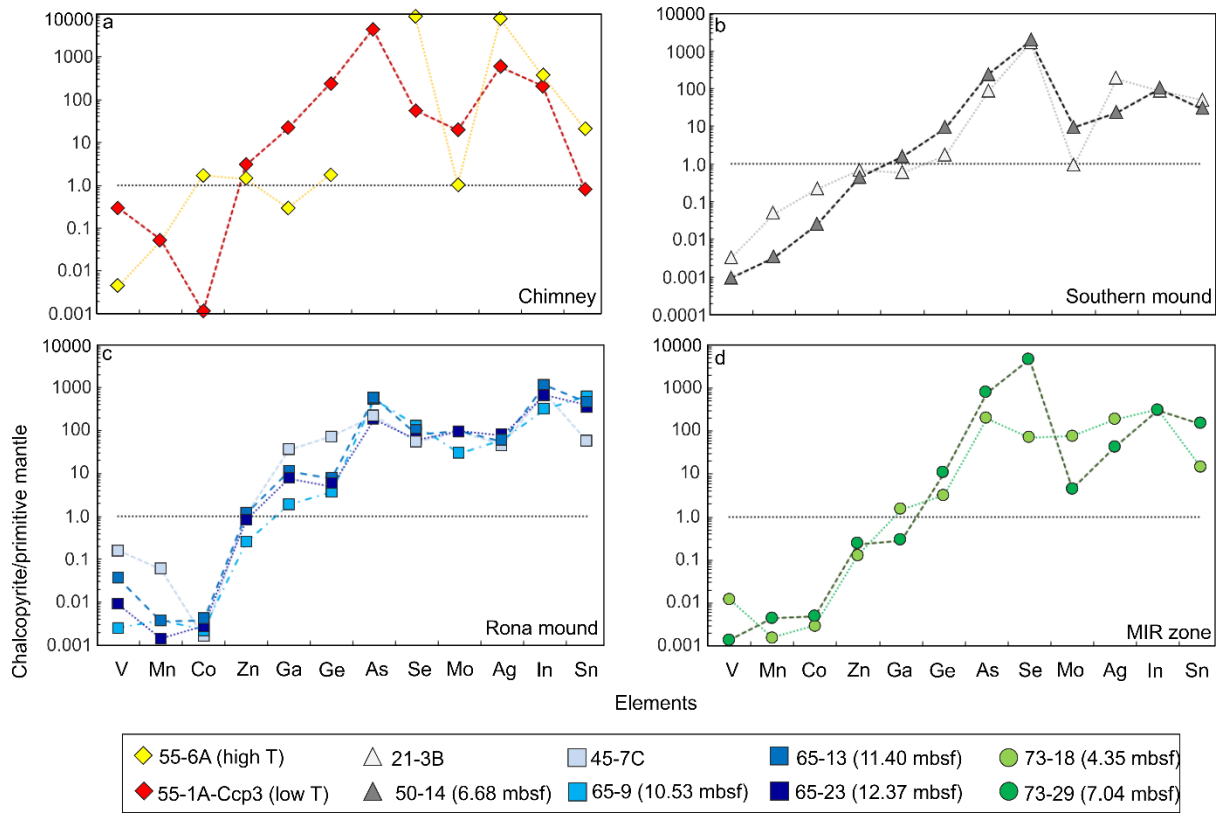


Figure 11





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