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3 **Mineralogical and geochemical facets of the massive deposition of**
4 **stibnite-metastibnite at a seafloor hydrothermal field (Wakamiko**
5 **Crater, Kagoshima Bay, Ryukyu Volcanic Arc)**

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34

35 **ABSTRACT**

36 Stibnite precipitates in the form of massive boulders at two active hydrothermal mounds in
37 the submarine Wakamiko Crater (Ryukyu Volcanic Arc) as opposed to commonly observed
38 accessory stibnite in the seafloor hydrothermal deposits. The stibnite dimorph, metastibnite,
39 found here for the first time on the seafloor, appears to always form whenever stibnite is
40 precipitated under submarine hydrothermal conditions. Our study shows that hydrothermal
41 conditions of low temperatures (<50 °C) and low values of *pH* (<6) are favorable for the
42 precipitation of stibnite on the seafloor. The stibnite probably does not precipitate at the measured
43 vent fluid temperatures (i.e., 177.6 – 187.0 °C) along the chimney conduits, but rather at
44 temperatures <50 °C and at slightly reduced to slightly oxic conditions (*Eh* = -0.5 to +0.5 V)
45 within the chimney walls and hydrothermal mounds. Metastibnite deposition appears to be the
46 result of rapid quenching of hot hydrothermal fluid when mixed with cold seawater and rapid
47 precipitation at the interface between stibnite and vent fluid. The low concentrations (usually
48 below detection limits) of the trace elements (Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, P, Pb, Sr, V, Zn)
49 in the stibnite deposits from Wakamiko Crater are likely a result of decreased metal-transporting
50 capacity of the precipitating vent fluid due to its low chlorinity. Low-chlorinity venting implies
51 sub-seafloor boiling and phase separation of the hydrothermal fluid. Sluggish hydrothermal
52 fluid/seawater mixing within the walls of the chimneys and mounds favors the reduction of
53 sulfate dissolved in the hydrothermal fluids and results in a heavy S isotope composition of the
54 sulfate in the vent fluids. Sulfate reduction and disproportionation of magmatic SO₂, both leading
55 to heavy S isotope composition of sulfate in the vent fluids, seem to be common processes in
56 volcanic arc/back-arc submarine hydrothermal settings.

57 **Keywords:** Hydrothermal, metastibnite, stibnite, sulfate reduction, Wakamiko Crater

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INTRODUCTION

61 Stibnite (Sb_2S_3) is a rare and accessory mineral in the seafloor hydrothermal deposits. It has
62 been found in hydrothermal deposits located along submarine volcanic arc (Nedachi et al. 1991;
63 Dekov and Savelli 2004; Yamanaka et al. 2013), back-arc (Halbach et al. 1993; Nakashima et al.
64 1995; Okamoto et al. 2002; Ooki et al. 2012; Dekov et al. 2022) and fore-arc (Petersen et al.
65 2002) tectonic settings. Stibnite appears to be scarce in hydrothermal deposits at mid-ocean ridge
66 (MOR) setting (Firstova et al. 2016). It was also observed to precipitate in artificially induced,
67 seafloor hydrothermal chimneys in a back-arc rift (Iheya-North vent field, Okinawa Trough;
68 Nozaki et al. 2016). Therefore, occurrence of this apparently rare sulfide as boulders in
69 hydrothermal mounds in a submarine volcanic crater (Wakamiko Crater, Kagoshima Bay,
70 Ryukyu Volcanic Arc; Yamanaka et al. 2013) attracts particular scientific interest. This
71 occurrence implies uncommon conditions for hydrothermal precipitation (volatile element
72 concentrations, T , P , pH , Eh), which have persisted over a prolonged time interval.

73 Data on metastibnite (Sb_2S_3), an X-ray semi-amorphous dimorph of stibnite, is rare in the
74 literature (Becker 1888; Hunt 1888; Brookins 1970; Mozgova et al. 1977; Olivier-Fourcade et al.
75 1983). Similarly, we are not aware of any occurrence of metastibnite on the seafloor.

76 Given the limited knowledge on the stibnite and metastibnite precipitation at seafloor
77 hydrothermal conditions, we studied the stibnite-bearing deposits and venting hydrothermal
78 fluids of Wakamiko Crater (Ryukyu Volcanic Arc, Japan). To evaluate whether metastibnite
79 always forms whenever stibnite precipitates under seafloor hydrothermal conditions, we
80 investigated metastibnite occurrence in six stibnite-bearing samples recovered from two other
81 seafloor hydrothermal fields, namely, Daisan-Kume Knoll (Ryukyu Arc) and Daiyon-Yonaguni
82 Knoll (Okinawa Trough).

83

84

GEOLOGICAL SETTING

85 Wakamiko Crater is located in the eastern part of the Kagoshima Bay, Kyushu Island, and
86 represents the northeastern-most extension of the Ryukyu Arc (Fig. 1 a) (Yamanaka et al. 2013).

87 Kagoshima Bay encompasses the submerged Aira and Ata calderas, and the active Wakamiko
88 and Sakurajima volcanoes (not shown in Fig. 1 **b**). The Wakamiko Crater (Fig. 1 **b**) is interpreted
89 to have formed during the Ito eruption ~25000 yr B.P. (Aramaki 1984). The seafloor of the crater
90 (~200 m depth) is covered by ~80 m thick sediment (Hayasaka 1987). Fumarolic activity (Ôki
91 and Hayasaka 1978) and anomalies of relatively high concentrations of volatile elements such as
92 Sb, As, and Hg in the sediments in and around the crater, indicate the existence of active magma
93 chamber beneath the crater (Sakamoto 1985). Three sites discharging focused and relatively hot
94 fluids, and three other sites emanating diffuse (shimmering) hydrothermal fluids, have been
95 reported for the Wakamiko Crater (Yamanaka et al. 2013). The Hairy Cone ($T_{\max} = 198.6$ °C;
96 Figs 1 **b**, 2 **a**) and White Cone ($T_{\max} = 187$ °C; Figs 1 **b**, 2 **b**) chimney-mound sites are composed
97 of a few-meters-thick-mounds of blackish, boulder-sized rubble of sulfides crowned by ~2 m tall
98 whitish chimneys, whereas the Daifukuyama site ($T_{\max} = 111$ °C) is a mound (Yamanaka et al.
99 2013).

100 Daisan-Kume Knoll is a felsic submarine volcano located to the west of Kumejima Island,
101 Ryukyu Arc (Fig. 1 **a**). This volcanic edifice has two calderas: one to the north and another to the
102 south (Minami and Ohara 2017). Surveys conducted by a remotely operated vehicle (ROV) in the
103 southern caldera (Harigane 2015) found evidence for hydrothermal activity (i.e., a chimney field,
104 sulfide deposits, altered rocks, and venting of shimmering fluids), which showed that Daisan-
105 Kume Knoll is indeed a hydrothermally active volcano.

106 Daiyon-Yonaguni Knoll is a seamount located in the southernmost part of the Okinawa
107 Trough (Matsumoto et al. 2001) (Fig. 1 **a**). An active hydrothermal field of the same name is
108 located in an elongated depression covered by thick, muddy sediment adjacent to this seamount
109 (Gena et al. 2005). Four major hydrothermal chimney-mound complexes were observed to
110 discharge both black and clear, relatively hot fluids (Konno et al. 2006; Suzuki et al. 2008;
111 Fujiwara et al. 2015). Diffuse, low-temperature venting was observed in the southern part of the
112 hydrothermal field (Suzuki et al. 2008).

113

114

SAMPLES AND METHODS OF INVESTIGATION

115 Samples

116 In our attempt to characterize the mineralogy and geochemistry of massive stibnite precipitated under seafloor
117 hydrothermal conditions, we studied three stibnite-containing samples collected during the August 2008 R/V

118 *Natsushima* cruise NT08-17 from two hydrothermal mounds in the Wakamiko Crater (Table 1; Fig. 3). The samples
119 recovered from the Hairy Cone and White Cone hydrothermal sites were black to grayish-black, fragile chunks of
120 mound structures (Fig. 3 **a**, **b**, **c**). Sub-samples (small chunks, ~3 g) from each sample were ground to fine powders
121 in an agate mortar for mineralogical and geochemical analyses. Polished thin sections were prepared from each
122 sample for optical microscopy and electron microprobe studies.

123 In addition, six samples of seafloor hydrothermal deposits (finely powdered) recovered from the Daiyon-
124 Yonaguni Knoll, Okinawa Trough (5) and Daisan-Kume Knoll, Ryukyu Arc (1) (Table 1), that contained stibnite
125 (Dekov et al. 2022; and Harigane 2015, respectively) were investigated for the presence of metastibnite only.

126 Two vent fluid samples recovered during the May 2007 R/V *Natsushima* cruise NT07-09 were collected from
127 the White Cone vent using multi-cylinder polycarbonate sample bottles with a rotary switching valve system with an
128 all-titanium sample inlet and attached temperature probe (Table 2). The vent fluid samples were filtered (0.45 μm
129 membrane filters), acidified immediately after recovery, and stored in high density polyethylene (HDPE) bottles for
130 further onshore analyses.

131

132 **Methods of investigation**

133 Details of the methods of investigation of the (1) mineralogy, chemistry and S isotope composition of the
134 hydrothermal deposits, (2) chemistry and S isotope composition of the hydrothermal fluids, and (3) modeling of
135 stability phase diagrams can be found in the Supplementary online material.

136

137 **RESULTS**

138 **Mineralogy of the hydrothermal deposits**

139 XRD investigations (Tables 3, 4; Fig. 4 **a**) show that stibnite is the main mineral in all the
140 Wakamiko Crater samples, consistent with initial macroscopic observations of hand specimens.
141 The calculated unit-cell parameters of this stibnite are reported in Table 5. Stibnite is also present
142 in the Daisan-Kume Knoll (Harigane 2015) and Daiyon-Yonaguni Knoll (Dekov et al. 2022)
143 hydrothermal deposits.

144 Stibnite in the Wakamiko Crater hydrothermal deposits appears as two forms: long (>100
145 μm), both thick (~20 μm) and thin (~2 μm) prismatic crystals (Figs 5 **a**, **b**; 6 **b**, **c**), and rosettes of
146 needle-like crystals (Figs 5 **c-h**; 6 **a**). In reflected cross-polarized light, stibnite crystal
147 terminations (Fig. 5 **d**), crystal peripheries (Fig. 5 **f**), or entire crystals (Fig. 5 **h**) show red internal
148 reflections. As stibnite never shows such red internal reflections, there are two possible
149 explanations of these optical features. The first is oxidation of stibnite (at crystal terminations, at
150 crystal peripheries, or the entire crystal) to kermesite ($\text{Sb}_2\text{S}_2\text{O}$), which typically shows red

151 internal reflections in reflected cross-polarized light. However, there is no evidence from XRD of
152 kermesite in the samples (Table 3). The second possibility is the presence of metastibnite, which
153 also shows red internal reflections in reflected cross-polarized light. Metastibnite has the same
154 mineral chemistry as stibnite (Sb_2S_3), but is X-ray semi-amorphous, usually showing two weak
155 peaks between 56.2 and 56.5 $^{\circ}2\theta$ (Cu K_{α} radiation), a region where there are not any stibnite
156 peak. XRD analysis of random samples in the range 55.5 - 57.0 $^{\circ}2\theta$ using small steps and slow
157 speed (see Supplementary online material, Mineralogy of hydrothermal deposits) produced XRD
158 patterns with an asymmetric peak between 55.9 and 56.5 $^{\circ}2\theta$, i.e., slightly displaced towards
159 lower angles than those of metastibnite (Fig. 4 **b**). This strongly suggests that in addition to
160 stibnite, the Wakamiko Crater samples also contain metastibnite. Similar XRD patterns were
161 obtained for the samples from the stibnite-containing hydrothermal deposits from Daisan-Kume
162 Knoll and Daiyon-Yonaguni Knoll (Fig. 4 **c**, **d**). This suggests that all the studied stibnite-
163 containing samples contain metastibnite as well. The shape of this metastibnite peak (i.e.,
164 asymmetry, intensity) and its displacement relative to the standard metastibnite peak (Lafuente et
165 al. 2015) are different for different samples (Fig. 4 **b-d**).

166 Sulfur, Sb, and As are homogeneously distributed within both morphological types of
167 Wakamiko Crater stibnite, i.e., prismatic (Fig. 7) and rosettes of needle-like crystals (Fig. 8).

168 The chemistry of the Wakamiko Crater stibnite is very close to stoichiometry with rare,
169 minor As and Sn contents (Table 6).

170 Furthermore, a weak, broad (hump-like) peak centered at ~ 7.5 $^{\circ}2\theta$ appears in the XRD
171 patterns of all the Wakamiko Crater stibnite samples (Fig. 4 **a**). The presence of disordered talc in
172 the Wakamiko Crater hydrothermal deposits was reported in a previous study (Yamanaka et al.
173 2013). However, the main peak (001) of the disordered talc is at ~ 9 $^{\circ}2\theta$. The location of the
174 observed hump-like peak (Fig. 4 **a**) at lower angles than that of the 001 peak of the disordered
175 talc might imply the presence of mixed-layer talc-smectites. However, as we have not performed
176 detailed investigations for clay minerals, we can only assume that talc-smectite is present in
177 traces in the samples.

178

179 **Geochemistry of the Wakamiko Crater hydrothermal deposits**

180 The almost pure stibnite samples from the Wakamiko Crater have high Sb, Mg, Al, Fe and
181 Na contents and low (mostly below the detection limits) Ca, Cd, Co, Cr, Cu, K, Li, Mn, Mo, Ni,
182 P, Pb, Sr, V, Zn contents (Table 7).

183

184 **Geochemistry of the Wakamiko Crater hydrothermal fluids**

185 The concentrations of Fe, Sb, Mn, Zn, Mo, Ni and V were relatively high, whereas the
186 concentrations of U, Pb, Co, Cd, Y, and Cu were relatively low in the Wakamiko Crater venting
187 fluids (Table 8). REE concentrations were particularly low, being mostly below the detection
188 limits (Table 8). Cerium anomalies (Ce/Ce*), calculated relative to Nd (because the Pr
189 concentrations were below the detection limit), were slightly positive in both vent fluid samples
190 (Table 8; Fig. 9). The Eu anomaly, calculated relative to Nd (as Sm concentrations were below
191 the detection limit) in one vent fluid sample only, was strongly positive (Table 8; Fig. 9). The
192 REE distribution pattern of the analyzed seawater standard (CASS-6) followed that of the North
193 Pacific Deep Water (Alibo and Nozaki 1999) and shows both negative Ce and Eu anomalies
194 (Table 8; Fig. 9).

195

196 **S isotope composition of the Wakamiko Crater hydrothermal deposits and fluids**

197 Sulfur isotope composition (sulfide S) of the studied Wakamiko Crater hydrothermal
198 deposits ranges from 2.8 to 3.6 ‰ (Table 7). Vent fluids from the White Cone vent (Table 2)
199 have S isotope composition (sulfate S) heavier than that of average modern seawater ($\delta^{34}\text{S}_{\text{sulfate}} =$
200 20.97 ± 0.10 ‰; Paris et al. 2013) (Table 8).

201

202 **Modeling of stability phase diagrams**

203 Using the chemistry data for the studied vent fluid samples (Table 8), we have produced a
204 number of stability phase diagrams with the GWB. In principle, at the seafloor hydrothermal sites
205 the hydrothermal fluids are discharged in two modes: (1) focused, flow through the chimney
206 orifice, and (2) diffused, percolation through the porous chimney walls and mound structures, and
207 slow cooling (conductive and through mixing with seawater) of the fluid. We modeled stability
208 phase diagrams at the measured venting temperatures (Table 8) with the assumption of focused
209 fluid discharge and stibnite precipitation along the chimney conduit in contact with the venting

210 fluid. As the studied stibnite comes from the hydrothermal mound boulders, we also modeled
211 stability phase diagrams related to diffuse discharge through the hydrothermal mound. We
212 supposed fluid temperatures lower than that of the venting fluid (Table 8) and decreasing (150
213 °C, 100 °C, 50 °C and 25 °C) away from a hypothetical conduit of discharge. For simplicity of
214 the modeling and interpretations, we assumed fluid cooling due only to mixing with seawater, but
215 used the chemistry of the fluids venting through the chimney orifice (Table 8). Unfortunately, the
216 “thermo_minteq” database does not contain data for metastibnite and we were not able to model
217 the stability fields of this mineral.

218 In the modeling, we considered all the possible aqueous Sb species (ions) that were
219 available in the “thermo_minteq” database. Because dissolved H₂S (H₂S_(aq)) is the main reduced
220 species in the hydrothermal fluids that, upon reaction with metal and metalloid ions forms metal
221 and metalloid sulfides (e.g., Sb₂S₃), we considered the activity of H₂S_(aq) as one of the main
222 variables in the modeling. The attempt to model log₁₀**a**[H₂S_(aq)]-log₁₀**a**[SbCl₄⁺] diagram produced
223 an empty plot. The diagram log₁₀**a**[H₂S_(aq)]-log₁₀**a**[(NH₄)Sb₂S₄⁻] showed just (NH₄)Sb₂S₄⁻ ion
224 throughout the entire temperature range. Diagrams using the Sb₂S₄²⁻ ion (log₁₀**a**[H₂S_(aq)]-
225 log₁₀**a**[Sb₂S₄²⁻], Eh-log₁₀**a**[Sb₂S₄²⁻]) were identical to those for Sb(OH)_{3(aq)}. The diagrams for
226 both vent fluid samples (687R1 and 687R3) were very similar and therefore, we have shown and
227 discussed the stability phase diagrams log₁₀**a**[H₂S_(aq)]-log₁₀**a**[HSb₂S₄⁻], log₁₀**a**[H₂S_(aq)]-
228 log₁₀**a**[Sb(OH)_{3(aq)}] and log₁₀**a**[H₂S_(aq)]-Eh for sample 687R1 only (Fig. 10).

229

230

DISCUSSION

231 Precipitation of stibnite and metastibnite under seafloor hydrothermal conditions

232 The solubility of stibnite and ion speciation of Sb at hydrothermal conditions are largely
233 controlled by temperature and *pH* (Wilson et al. 2007; Brown 2011). The solubility of stibnite
234 decreases by a few orders of magnitude with a drop in temperature of only a few tens of degrees
235 C (within temperature range 200 – 25 °C) and also with a drop in *pH* of 2-3 units (from slightly
236 alkaline to slightly acid) (Brown 2011). Therefore, low-temperature and low *pH* hydrothermal
237 conditions are conducive to stibnite precipitation and will lead to a quantitative removal of Sb
238 from the hydrothermal solution (Wilson et al. 2007; Brown 2011). In such conditions, stibnite

239 was observed to precipitate as long needle-like crystals (Brown 2011). However, when Sb_2S_3
240 precipitates rapidly rather metastibnite forms (Brown 2011).

241 Previous observations (e.g., Wilson et al. 2007; Brown 2011) of stibnite precipitation under
242 hydrothermal conditions suggest that at the relatively low-temperature (177.6-187.0 °C) and pH
243 (5.86-5.99) conditions of the White Cone vent (Wakamiko Crater) (Table 2), massive stibnite
244 could precipitate. The crystal habit of the Wakamiko Crater stibnite, i.e., long prismatic crystals
245 and rosettes of needle-like crystals (Figs 5, 6, 8), is also consistent with previous observations for
246 the crystal habit of hydrothermally precipitated stibnite (Brown 2011). Similar rosettes of blade-
247 like barite crystals precipitated at other seafloor hydrothermal sites were interpreted to be
248 indicative of quenching and rapid precipitation from mixing hydrothermal fluid and seawater (de
249 Ronde et al. 2003, 2005, 2011; Berkenbosch et al. 2012).

250 The stability phase diagram modeling shows that at the measured venting temperatures
251 (177.6 °C and 187.0 °C; Table 8), the stibnite is stable at $\log_{10}a[\text{H}_2\text{S}_{(\text{aq})}] > -4.5$, $\log_{10}a[\text{HSb}_2\text{S}_4^-]$
252 > -4.5 and $\log_{10}a[\text{Sb}(\text{OH})_3(\text{aq})] > -4.2$ (Fig. 10 **a, e**). With decreasing temperature, the stability
253 field of stibnite enlarges (Fig. 10 **b, c, d, f, g, h**). However, the $\log_{10}a[\text{H}_2\text{S}_{(\text{aq})}]-Eh$ diagrams show
254 that stibnite starts precipitating below 50 °C (Fig. 10 **k**) and its stability field enlarges with
255 decreasing temperature (Fig. 10 **l**). We can conclude, therefore, that stibnite most probably does
256 not precipitate at the measured venting temperatures in the chimney conduits, but rather at
257 temperatures below 50 °C and at slightly reduced to slightly oxic ($Eh = -0.5 - +0.5$ V) conditions
258 (Fig. 10) within the chimney walls and mounds.

259 The occurrence of metastibnite at crystal terminations and margins of Wakamiko Crater
260 stibnite (Figs 5 **c-h**), when combined with previous observations of metastibnite precipitation
261 (Brown 2011), suggest that: (1) metastibnite is not an alteration product after stibnite, (2) it is
262 rather a product of rapid quenching of the hot hydrothermal fluid upon mixing with cold seawater
263 with rapid precipitation at the interface between stibnite and the vent fluid. We suggest that due
264 to rapid precipitation, the Sb_2S_3 cannot form an ordered crystal structure (i.e., stibnite), but rather
265 occurs in a semi-amorphous state (i.e., metastibnite). The occurrence of metastibnite together
266 with stibnite also in the other two stibnite-containing seafloor hydrothermal sites (Daisan-Kume
267 Knoll and Daiyon-Yonaguni Knoll) implies that if stibnite precipitates under seafloor
268 hydrothermal conditions, then metastibnite will always form alongside it. The slight displacement

269 of the metastibnite peaks towards lower angles in the XRD patterns (Fig. 4 **b-d**) may be due to
270 isomorphic replacement of As for Sb in the metastibnite structure.

271 Unit-cell parameters of stibnite from Wakamiko Crater (Table 5) are close to those of pure
272 stibnite (Kyono and Kimata 2004). The small deviations could be due to minor replacement of As
273 and Sn for Sb (Table 6).

274

275 **Geochemistry of the Wakamiko Crater hydrothermal deposits: A result of boiling and** 276 **phase separation of the hydrothermal fluid**

277 A fundamental feature of the seawater chemistry is that the major ions are present in
278 relatively constant ratios. These constant ratios are not necessarily maintained in the seafloor
279 (seawater-based) hydrothermal fluids because of the gains and losses of elements during sub-
280 seafloor seawater-rock interactions. Chlorine is a conservative element during these interactions.
281 Thus, the element/Cl ratios in the hydrothermal fluids are indicators for gains or losses of
282 elements relative to the starting fluid (seawater). Na/Cl of the Wakamiko Crater end-member
283 hydrothermal fluid (0.83) is slightly lower than that of the ambient seawater (0.86) [Table 1 in
284 Yamanaka et al. (2013)]. This means that the seawater has lost a small fraction of its Na during
285 seawater reaction with the basement rocks, presumably due to albitization (German and Von
286 Damm, 2003): Na for Ca replacement reaction in plagioclase. However, the negligible loss of Na
287 from seawater due to its interaction with the crustal rocks and the maintenance of Na/Cl ratio of
288 the fluid (seawater → end-member hydrothermal fluid) is less important than the net decrease in
289 the concentrations of both Na and Cl in the end-member hydrothermal fluid ([Na] = 232 mM,
290 [Cl] = 279 mM) in respect to the seawater ([Na] = 464 mM, [Cl] = 541 mM) (Yamanaka et al.,
291 2013). The observed decrease in fluid chlorinity (salinity) by about 50 % seems to be most likely
292 a result of sub-seafloor boiling of the fluid and its phase separation in high- and low-chlorinity
293 fluids (Von Damm, 1990). Obviously, the studied vent fluids (Table 8) represent the low-
294 chlorinity fractions of the phase-separated fluids. As chloride is the dominant anion in the
295 seafloor hydrothermal fluids (Von Damm, 1990), its concentration plays a major role in their
296 metal-carrying capacities. Decreased fluid chlorinity (due to a probable sub-seafloor boiling and
297 phase separation) seems to result in the low trace metal concentrations in the studied vent fluids
298 (Cu and majority of REE; Table 8). Particularly, the low REE content (Table 8) supports the

299 assumption that the sampled Wakamiko Crater vent fluids are the low-chlorinity fractions of
300 phase-separated hydrothermal fluids: (1) REE are non-volatile elements and will separate in the
301 high-chlorinity phase; (2) REE are mainly complexed by Cl^- ions in the hot acidic seafloor
302 hydrothermal fluids (Douville et al., 1999) and will concentrate in the high-chlorinity phase. All
303 this reasonably explains the low concentrations of all the studied trace elements in the Wakamiko
304 Crater stibnite deposits (Table 7). Other possible reasons for this apparent depletion may be the
305 high water/rock ratio, low temperature in the reaction zone, type of source rock, sub-surface
306 precipitation, etc., but given we have insufficient data, any further discussion of this observation
307 would be a mere speculation.

308 The positive Eu anomaly at the chondrite-normalized REE distribution patterns of the
309 Wakamiko Crater vent fluids (Fig. 9) is typical for the high-temperature seafloor hydrothermal
310 fluids and its origin is discussed elsewhere (Michard et al., 1983; Michard and Albarède, 1986;
311 Michard, 1989; Klinkhammer et al., 1994; Bau and Dulski, 1999; Douville et al., 1999).

312 Relatively high Fe concentrations (with respect to the other trace metals; Table 7) in the
313 stibnite samples may be explained by the presence of Fe-sulfides (not detected by XRD) in
314 contents below the detection limits of the XRD (~4 wt.%). High Mg and Al concentrations in all
315 the samples (Table 7) likely confirm the assumptions from the XRD studies that talc-smectite is
316 present in the samples (see Mineralogy of the hydrothermal deposits).

317

318 **Heavy S isotope composition of the Wakamiko Crater vent fluid sulfate: A common feature** 319 **of the volcanic arc/back-arc systems?**

320 The S isotope composition ($\delta^{34}\text{S}$) of seafloor hydrothermal deposits at arc/back-arc settings
321 shows substantial variability (Fig. 11). The wide variation in $\delta^{34}\text{S}$ is a result of S isotope
322 fractionation due to four processes contributing to the S budget of the seafloor hydrothermal
323 system: (1) basement rock sulfide supplied through the interaction of hydrothermal fluid with
324 basement rocks (Shanks and Seyfried 1987; Shanks 2001; Ono et al. 2007), (2) thermochemical
325 reduction of sulfate supplied by seawater (Shanks and Seyfried 1987; Shanks 2001; Ono et al.
326 2007), (3) disproportionation of SO_2 supplied by magmatic vapors (Kusakabe et al. 2000; de
327 Ronde et al. 2005, 2011, 2015; McDermott et al. 2015; Peters et al. 2021), and (4) bacterial

328 sulfate reduction in sediment-covered hydrothermal systems (Aoyama et al. 2014; LaFlamme et
329 al. 2018).

330 Sulfide sulfur in the Wakamiko Crater hydrothermal deposits has an isotope composition
331 ($\delta^{34}\text{S}$) within the range of that of the hydrothermal deposits of mid-ocean ridges and back-arc
332 basins, and at the heavy end of the S isotope range of the hydrothermal deposits at volcanic arcs
333 (Fig. 11). It falls between the S isotope composition of the terrestrial mantle sulfide and seawater
334 sulfate, but being closer to the former (Table 7; Fig. 11). However, although the S isotope
335 composition of Wakamiko Crater stibnite-bearing deposits is similar to that of the hydrothermal
336 deposits at mid-ocean ridges, it is unlikely that the terrestrial mantle sulfide (represented in mid-
337 ocean ridge basalts) can be responsible for the S isotope composition of a hydrothermal deposit
338 rooted in volcanic arc basement. Sulfur isotope composition of the studied deposits falls within
339 the range of S isotope composition of the island arc volcanic rocks (IAVR) and is close to
340 $\delta^{34}\text{S}_{\text{IAVR}}$ mean value (Fig. 11). This suggests that the S bound in the sulfides of the Wakamiko
341 Crater hydrothermal deposits has derived from the volcanic arc basement rocks. The S isotope
342 composition of the studied sulfide (Sb_2S_3) supports the origin of sulfide S in the overall Ryukyu
343 Arc hydrothermal deposits being generally dominated by basement rock S (Fig. 11). There are no
344 clear isotopic indications either for disproportionation of magmatic SO_2 or for microbial sulfate
345 reduction within the Wakamiko Crater sediments, as any of these processes would have driven
346 the $\delta^{34}\text{S}$ of produced sulfide to negative values.

347 The heavier S isotope composition of sulfate in the White Cone (Wakamiko Crater) vent
348 fluids ($\delta^{34}\text{S}_{\text{sulfate}} = 21.6 - 22.0 \text{ ‰}$) than that of seawater ($\delta^{34}\text{S}_{\text{sulfate}} = 20.97 \pm 0.10 \text{ ‰}$; Paris et al.
349 2013) is similar to the heavy S isotope composition of sulfate in the CLAM (Okinawa Trough;
350 Gamo et al. 1991), Brothers Upper Cone and Macauley (Kermadec Arc; Peters et al. 2021),
351 Niuatahi South-Central, Niuatahi Northern Cone and Niua North (Tonga Arc; Peters et al. 2021)
352 and Daiyon-Yonaguni Knoll (Okinawa Trough; Dekov et al. 2022) hydrothermal fluids ($\delta^{34}\text{S}_{\text{sulfate}}$
353 $> 21.0 \text{ ‰}$) and deserves some consideration.

354 Disproportionation of magmatic SO_2 is invoked to explain the heavy S isotope composition
355 of sulfate ($\delta^{34}\text{S}_{\text{sulfate}} > 20.97 \pm 0.10 \text{ ‰}$) in the acid-sulfate fluids ($[\text{SO}_4]_{\text{vent fluid}} > [\text{SO}_4]_{\text{seawater}}$) of
356 the Tonga-Kermadec Volcanic Arc hydrothermal vents (Peters et al. 2021). However, this
357 mechanism does not seem to be responsible for the heavy S isotope composition of sulfate in

358 non-acid-sulfate hydrothermal fluids ($[\text{SO}_4]_{\text{vent fluid}} < [\text{SO}_4]_{\text{seawater}}$) like those of the Okinawa
359 Trough and Ryukyu Volcanic Arc vent fields: CLAM (Gamo et al. 1991), Daiyon-Yonaguni
360 Knoll (Suzuki et al. 2008) and Wakamiko Crater (Yamanaka et al. 2013).

361 We know that sulfate reduction in a closed system causes an increase in $\delta^{34}\text{S}$ value of the
362 residual sulfate (i.e., removal of the isotopically light sulfide during sulfate reduction) with
363 decreasing sulfate concentration (Ohmoto and Rye 1979; Shanks et al. 1981). Thus, the S isotope
364 composition of the sulfate from the White Cone vent fluids can be interpreted as a result of
365 sulfate reduction. Sulfate reduction or sulfide oxidation depends on the rate of mixing between
366 the hydrothermal fluid and seawater (Peter and Shanks 1992). Slow mixing of the hydrothermal
367 fluid and seawater in the chimney walls or within a mound favors sulfate reduction. This sulfate
368 reduction results in S isotope fractionation approaching equilibrium values and ^{34}S -enriched
369 sulfate resulting from a reservoir effect, as ^{32}S is removed to the sulfide reservoir (Peter and
370 Shanks 1992). Overall, it seems that slow mixing of hydrothermal fluid with seawater within the
371 chimney walls and mounds that favors reduction of the sulfate dissolved in the fluids and results
372 in a heavy S isotope composition of the vent fluid sulfate may be a common process in arc/back-
373 arc settings (Fig. 11). Along with the disproportionation of magmatic SO_2 , it contributes to a
374 more heavy S isotope composition of the seawater sulfate and the magnitude of this heavy S
375 source needs to be further evaluated.

376 In the studied case, the S isotope composition of the Wakamiko Crater vent fluids supports
377 the conclusion of the stability phase diagrams modeling that the stibnite has precipitated within
378 the chimney walls and mounds (i.e., as a result of diffused discharge).

379

380

IMPLICATIONS

381 Stibnite and metastibnite are the world's main resource for Sb. Our knowledge on their
382 occurrence and mode of formation on the vast seafloor is limited. The study on stibnite and
383 metastibnite presented here seems to be the first modest step in gaining insight into the conditions
384 and mode of formation of these minerals at the seafloor. The results of this investigation suggest
385 that future exploration for stibnite-metastibnite deposits on both the seafloor and continents
386 should focus on volcanic arc and back-arc settings (both modern and ancient), where these two
387 minerals may have massively precipitated under low temperature ($<50\text{ }^\circ\text{C}$), low pH , and at

388 slightly reduced to slightly oxic ($Eh = -0.5 - +0.5$ V) hydrothermal conditions. The hydrothermal
389 mounds with their porous structure seem to be suited for stibnite and metastibnite precipitation.
390 Precipitation of stibnite in seafloor hydrothermal conditions should always be accompanied by
391 the precipitation of metastibnite, which we consider is a result of rapid quenching of the hot
392 hydrothermal fluid upon mixing with cold seawater, with rapid mineral precipitation at the
393 stibnite-vent fluid interface. As the studied stibnite and metastibnite proved to have low
394 concentrations of all the analyzed trace elements, the future surveys for stibnite-metastibnite
395 deposits do not need to consider these deposits as possible resource for valuable bi-products.

396 Sulfur isotope study of the hydrothermal fluids precipitating stibnite-metastibnite implies
397 that sulfate reduction within the porous hydrothermal mounds may be a common process at
398 volcanic arc/back-arc hydrothermal settings. This geochemical detail needs to be considered in
399 future interpretations of the mineralogy and geochemistry of massive hydrothermal deposits
400 formed on the seafloor.

401

402

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672
673

674 Figure captions

675

676 **FIGURE 1.** Locations of: **(a)** the Wakamiko Crater (Kagoshima Bay, southern Kyushu Island,
677 Ryukyu Arc), Daisan-Kume Knoll (Ryukyu Arc) and Daiyon-Yonaguni Knoll (Okinawa
678 Trough), and **(b)** the White Cone and Hairy Cone hydrothermal sites within the Wakamiko
679 Crater.

680

681 **FIGURE 2.** Photographs (taken by the ROV *Hyper-Dolphin*) of the Wakamiko Crater sample
682 sites: **(a)** Hairy Cone chimney and mound from which samples H#893 GE1 and H#893 GE2 were
683 collected; **(b)** White Cone chimney and mound from which sample H#886 GE3 was collected.

684

685 **FIGURE 3.** General views of the studied samples: **(a)** sample H#893 GE1 (Hairy Cone vent); **(b)**
686 sample H#893 GE2 (Hairy Cone vent); **(c)** sample H#886 GE3 (White Cone vent).

687

688 **FIGURE 4.** **(a)** XRD pattern of sample H#893 GE1 (Wakamiko Crater) showing the presence of
689 stibnite (all major XRD peaks) and possibly talc-smectite (T-S). The segment between 55.5 and
690 57.0 °2θ (highlighted by the red rectangular box) was further X-ray scanned with small steps
691 (0.02 °2θ) and slow speed (12 s/step) to reveal the presence of the major XRD peaks of
692 metastibnite. The XRD pattern received is shown at **(b)** along with those of samples H#893 GE2
693 and H#886 GE3, metastibnite (Lafuente et al. 2015) and stibnite (Kyono and Kimata 2004)
694 recorded along the same 55.5 - 57.0 °2θ segment. For comparison, the stibnite-containing
695 samples from the Daisan-Kume Knoll and Daiyon-Yonaguni Knoll sites were analyzed with the
696 same XRD conditions and the XRD patterns are given in **(c)** and **(d)**, respectively. Note: to fit the
697 vertical scales of the XRD patterns, the peak intensities (in cps) for metastibnite and stibnite were
698 multiplied by 5 and shifted up by 400 in **(b)** and **(c)**, multiplied by 5 and shifted up by 200 in **(d)**,
699 whereas the peak Intensities (in cps) for sample 2K1267 L1 were divided by 10 in **(d)**.

700

701 **FIGURE 5.** Photomicrographs of stibnite (Sbn) and metastibnite (MsbN) from the studied seafloor
702 hydrothermal deposits (thin polished sections, optical microscope): prismatic stibnite crystals **(a)**:
703 reflected plain-polarized light) and **(b)**: reflected cross-polarized light) (sample H#893 GE2); all
704 stibnites that were confirmed by XRD have highly unusual pinkish to dark purple anisotropy

705 colours (normally, stibnite has a brown to blue grey anisotropy); rosettes of acicular crystals (**c**:
706 reflected plain-polarized light) with red internal reflections (**d**: reflected cross-polarized light)
707 (sample H#886 GE3) possibly represent a transitional stage between stibnite and metastibnite at
708 the crystal terminations; in contrast to metastibnite with its red internal reflections, “normal”
709 stibnite would be completely opaque; examples of larger, coarse-grained rosettes of what is
710 shown above (**e** and **g**: reflected plain-polarized light) but with a more pronounced transparency
711 throughout individual crystals (**f** and **h**: red internal reflections, reflected cross-polarized light)
712 (sample H#893 GE1). At this point, the reason for the atypical optical behaviour of a stibnite with
713 characteristics from metastibnite remains speculation (intergrown subdomains of both minerals?);
714 at the JADE seafloor hydrothermal deposit, typical stibnite exists in conjunction with fibrous
715 material similar to the rosettes displayed here (compare Halbach et al. 1993).

716

717 **FIGURE 6.** SEM photomicrographs (SEI) of stibnite from the studied seafloor hydrothermal
718 deposits: (**a**) general view of a rosette of long prismatic stibnite crystals (sample H#893 GE2); (**b**)
719 close up of a prismatic stibnite crystal (sample H#893 GE1); (**c**) thin, long stibnite crystals
720 (sample H#893 GE2).

721

722 **FIGURE 7.** X-ray maps and BSE image of prismatic stibnite (Sbn) in the studied seafloor
723 hydrothermal deposits (sample H#893 GE2): (**a**) X-ray scan in S $K\alpha$; (**b**) X-ray scan in Sb $L\alpha$; (**c**)
724 X-ray scan in As $L\alpha$; (**d**) BSE image. Color scales (right-hand side), elemental concentrations.

725

726 **FIGURE 8.** X-ray maps and BSE image of a rosette of needle-like stibnite (Sbn) in the studied
727 seafloor hydrothermal deposits (sample H#893 GE1): (**a**) X-ray scan in S $K\alpha$; (**b**) X-ray scan in
728 Sb $L\alpha$; (**c**) X-ray scan in As $L\alpha$; (**d**) BSE image. Color scales (right-hand side), elemental
729 concentrations.

730

731 **FIGURE 9.** CI chondrite-normalized (McDonough and Sun 1995) REE distribution patterns of the
732 studied vent fluids from the Wakamiko Crater hydrothermal field (Ryukyu Arc). NPDW = North
733 Pacific Deep Water (Alibo and Nozaki 1999).

734

735 **FIGURE 10.** Stability phase diagrams for the chemical species (dissolved and solid) in the 687R1
736 vent fluid from the White Cone vent (Wakamiko Crater, Ryukyu Arc): (a), (b), (c) and (d) -
737 $\log_{10}a$ - $\log_{10}a$ diagrams calculated for $H_2S_{(aq)}$ and $HSb_2S_4^-$; (e), (f), (g) and (h) - $\log_{10}a$ - $\log_{10}a$
738 diagrams calculated for $H_2S_{(aq)}$ and $Sb(OH)_3(aq)$; (i), (j), (k) and (l) - $\log_{10}a$ - Eh diagrams
739 calculated for $H_2S_{(aq)}$. Diagrams were calculated at the venting temperature (177.6 °C; a, e, i) and
740 decreasing temperatures.

741

742 **FIGURE 11.** Sulfur-isotope composition (range) of selected hydrothermal deposits from mid-
743 ocean ridges [unsedimented (mafic- and ultramafic-hosted) and sedimented], volcanic arcs and
744 back-arc basins compared to those of studied stibnite-containing deposits and vent fluids (sulfate
745 S) from the Wakamiko Crater. References: terrestrial mantle (Labidi et al. 2012), island arc
746 volcanic rocks [Japanese Island Arc (Ueda and Sakai 1984), Mariana Island Arc (Woodhead et
747 al. 1987; Alt et al., 1993), Indonesia Island Arc (de Hoog et al. 2001); dark grey strip = range of
748 mean values], seawater (Paris et al. 2013), Galapagos Rift (Skirrow and Coleman 1982; Knott et
749 al. 1995), 21°N EPR (Hekinian et al. 1980; Arnold and Sheppard 1981; Styrts et al. 1981;
750 Kerridge et al. 1983; Zierenberg et al. 1984; Woodruff and Shanks 1988; Stuart et al. 1994), 11-
751 13°N EPR (Bluth and Ohmoto 1988; Stuart et al. 1995; Fouquet et al. 1996; Ono et al. 2007), 9-
752 10°N EPR (Ono et al. 2007), 18-21°S EPR (Marchig et al. 1990; Ono et al. 2007), Lucky Strike
753 (Rouxel et al. 2004; Ono et al. 2007), Broken Spur (Duckworth et al. 1995; Butler et al. 1998),
754 TAG (Stuart et al. 1994; Gemmell and Sharpe 1998; Herzig et al. 1998; Shanks 2001), Snakepit
755 (Kase et al. 1990; Stuart et al. 1994), Southern MAR (Peters et al. 2010), Rainbow (Rouxel et al.
756 2004), Logatchev (Rouxel et al. 2004; Peters et al. 2010), Semenov (Melekestseva 2010), Red
757 Sea (Shanks 2001), Juan de Fuca (Shanks et al. 1984; Shanks and Seyfried 1987; Hannington and
758 Scott 1988; Stuart et al. 1994), Escanaba Trough (Shanks 2001), Guaymas Basin (Shanks 2001),
759 Okinawa Trough (Lüders et al. 2001; Ueno et al. 2003; Nishio and Chiba 2012; Kawasumi et al.
760 2016; Yang et al. 2020; Dekov et al. 2022), Manus Basin (Kim et al. 2004), Kermadec Arc (de
761 Ronde et al. 2005; 2011), Mariana Trough (Kusakabe et al. 1990), Lau Basin (Kim et al. 2011),
762 Izu-Bonin Arc (Alt et al. 1998), Aeolian Arc (Peters et al. 2011; Petersen et al. 2014), Ryukyu
763 Arc (Yamanaka unpublished data for Daisan-Kume Knoll, Hatoma Knoll and Tarama Knoll),
764 Kermadec Arc vent fluids (sulfate S) (Peters et al. 2021), Tonga Arc vent fluids (sulfate S)

765 (Peters et al. 2021), Daiyon-Yonaguni Knoll vent fluids (sulfate S) (Dekov et al. 2022), CLAM
766 vent fluids (sulfate S) (Gamo et al. 1991).
767

TABLE 1. Hydrothermal deposit samples

Sample ID	Cruise ID	Sample type	Location	Hydrothermal field	Latitude (N)	Longitude (E)	Depth (m)	Sampling device
H#893 GE1	NT08-17_leg2	stibnite agglomerate, sulfide mound	Ryukyu Arc	Wakamiko Crater, Hairy Cone vent	31°39'59"	130°46'15"	199	ROV <i>Hyper-Dolphin</i>
H#893 GE2	NT08-17_leg2	stibnite agglomerate, sulfide mound	Ryukyu Arc	Wakamiko Crater, Hairy Cone vent	31°39'59"	130°46'15"	199	ROV <i>Hyper-Dolphin</i>
H#886 GE3	NT08-17_leg1	stibnite agglomerate, sulfide mound	Ryukyu Arc	Wakamiko Crater, White Cone vent	31°40'04"	130°45'41"	191	ROV <i>Hyper-Dolphin</i>
2K1271 L1 flange, center upper	NT01-05 Leg2	active chimney flange	Okinawa Trough	Daiyon-Yonaguni Knoll	24°50'59"	122°41'57"	1364	submersible <i>Shinkai 2000</i>
2K1271 L1 flange, outer bottom, Stb	NT01-05 Leg2	active chimney flange	Okinawa Trough	Daiyon-Yonaguni Knoll	24°50'59"	122°41'57"	1364	submersible <i>Shinkai 2000</i>
2K1271 L1 flange, outer top	NT01-05 Leg2	active chimney flange	Okinawa Trough	Daiyon-Yonaguni Knoll	24°50'59"	122°41'57"	1364	submersible <i>Shinkai 2000</i>
2K1271 L1 lower outer	NT01-05 Leg2	active chimney	Okinawa Trough	Daiyon-Yonaguni Knoll	24°50'59"	122°41'57"	1364	submersible <i>Shinkai 2000</i>
2K1267 L1	NT01-05 Leg2	active chimney	Okinawa Trough	Daiyon-Yonaguni Knoll	24°50'56"	122°42'01"	1366	submersible <i>Shinkai 2000</i>
HPD#1761-R09	NT14-22	chimney	Ryukyu Arc	Daisan-Kume Knoll	26°17'20"	126°28'23"	1105	ROV <i>Hyper-Dolphin</i>

TABLE 2. Vent fluid samples (Wakamiko Crater, Ryukyu Arc)

Sample ID	Cruise ID	Location	Vent name	Type of venting fluid	Latitude (N)	Longitude (E)	Depth (m)	Temperature (°C)	pH	Sampling device
687R1	NT07-09	Ryukyu Arc	White Cone	focused discharge	31°40'04"	130°45'40"	194	177.6	5.99	multi-cylinder polycarbonate sample bottles with a rotary switching valve system with an all-titanium sample inlet
687R3	NT07-09	Ryukyu Arc	White Cone	focused discharge	31°40'04"	130°45'40"	194	187.0	5.86	multi-cylinder polycarbonate sample bottles with a rotary switching valve system with an all-titanium sample inlet

TABLE 3. XRD data for studied samples (Wakamiko Crater, Ryukyu Arc)

H#893 GE1		H#893 GE2		H#886 GE3		Minerals
<i>d</i> (Å)	<i>I</i> (%)	<i>d</i> (Å)	<i>I</i> (%)	<i>d</i> (Å)	<i>I</i> (%)	
7.9058	5	7.9921	5	7.9674	7	Sbn ^a
5.6263	49	5.6648	49	5.6554	83	Sbn
5.0270	57	5.0587	55	5.0526	76	Sbn
3.9696	21	3.9890	19	3.9857	23	Sbn
3.6235	6	3.6359	8	3.6310	6	Sbn
3.5629	100	3.5775	100	3.5754	100	Sbn
				3.5551	33	Sbn
3.4476	5	3.4581	6	3.4588	6	Sbn
3.1692	4	3.1787	4	3.1788	4	Sbn
3.1211	31	3.1316	30	3.1314	37	Sbn
3.0434	29	3.0538	30	3.0522	28	Sbn
2.7580	29	2.7669	32	2.7666	30	Sbn
2.6742	12	2.6826	12	2.6822	12	Sbn
2.6016	7	2.6101	7	2.6083	6	Sbn
2.5202	52	2.5279	49	2.5259	65	Sbn
2.4226	7	2.4279	6	2.4262	7	Sbn
2.2737	10	2.2763	11	2.2782	10	Sbn
2.2509	9	2.2538	8	2.2562	10	Sbn
2.2272	15	2.2299	13	2.2321	16	Sbn
2.0954	31	2.0999	30	2.0997	36	Sbn
1.9895	5	1.9937	5	1.9933	6	Sbn
1.9388	32	1.9426	28	1.9422	31	Sbn
1.9273	8	1.9311	8	1.9307	8	Sbn
1.9171	9	1.9208	11	1.9204	11	Sbn
1.8829	7	1.8871	7	1.8861	13	Sbn
1.8570	4	1.8614	3	1.8601	5	Sbn
1.8429	4	1.8477	3	1.8458	4	Sbn
1.7872	3	1.7894	2	1.7883	3	Sbn
1.7259	14	1.7295	12	1.7282	13	Sbn
1.6901	29	1.6928	31	1.6926	26	Sbn
1.5600	4	1.5627	2	1.5629	3	Sbn
1.5424	7	1.5444	5	1.5439	7	Sbn
1.5269	9	1.5294	8	1.5284	6	Sbn
1.4826	6	1.4846	3	1.4843	7	Sbn
1.4428	7	1.4450	5	1.4442	8	Sbn
1.4139	3	1.4160	2	1.4160	3	Sbn
1.4008	7	1.4033	5	1.4033	7	Sbn
1.3108	7	1.3120	6	1.3113	6	Sbn
1.2908	3	1.2921	3	1.2920	4	Sbn

^a Sbn = stibnite (Warr 2021): data from Kyono and Kimata (2004).

TABLE 4. Mineralogy (XRD) of the samples (Wakamiko Crater, Ryukyu Arc)

Sample ID	Mineralogy
H#893 GE1	stibnite, metastibnite, talc-smectite (?)
H#893 GE2	stibnite, metastibnite, talc-smectite (?)
H#886 GE3	stibnite, metastibnite, talc-smectite (?)

TABLE 5. Orthorhombic unit-cell parameters of stibnite (Wakamiko Crater, Ryukyu Arc)

Sample ID	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
H#893 GE1	11.2115(5)	11.2940(4)	3.8317(3)
H#893 GE2	11.2393(5)	11.3174(4)	3.8385(3)
H#886 GE3	11.2349(5)	11.3161(4)	3.8336(2)

TABLE 6. Mineral chemistry (EMP data) and empirical formulae of stibnite (Wakamiko Crater, Ryukyu Arc)

Sample ID	# ^a	(wt.%)								(at.%)								Total	Empirical formulae	
		S	Sn	Sb	Pb	Zn	Fe	Cu	As	S	Sn	Sb	Pb	Zn	Fe	Cu	As			
H#893 GE1	7	27.50	0.43	69.96	0.06	0.12	0.11	0.14	0.39	98.71	59.39	0.25	39.80	0.01	0.06	0.07	0.04	0.36	100.00	(Sb _{1.99} As _{0.02} Sn _{0.01})S _{2.97}
H#893 GE2	14	27.81	0.47	70.29	0.07	0.12	0.05	0.08	0.20	99.09	59.66	0.27	39.72	0.02	0.07	0.03	0.04	0.18	100.00	(Sb _{1.99} As _{0.01} Sn _{0.01})S _{2.98}
H#886 GE3	7	28.00	0.43	70.05	0.07	0.09	0.07	0.10	0.14	98.95	59.99	0.25	39.53	0.02	0.03	0.02	0.02	0.13	100.00	(Sb _{1.98} As _{0.01} Sn _{0.01})S _{3.00}
detection limits (ppm)		78	160	165	144	161	95	131	156											

^a Number of EMP analyses.

TABLE 7. Chemical (ICP-OES) and S isotope compositions of the hydrothermal deposits (Wakamiko Crater, Ryukyu Arc)

Sample ID	Al (ppm)	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	Sr	V	Zn	Sb	($\delta^{34}\text{S}_{\text{sulfide}}$) ^a (‰)
H#893 GE1	8069	b.d.l. ^b	b.d.l.	b.d.l.	b.d.l.	b.d.l.	2385	1359	75.5	46561	b.d.l.	b.d.l.	5297	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	541274	3.6
H#893 GE2	10834	b.d.l.	148	b.d.l.	b.d.l.	b.d.l.	6928	b.d.l.	b.d.l.	13541	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	51.3	40.1	b.d.l.	610371	3.2
H#886 GE3	2939	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	2696	b.d.l.	b.d.l.	5912	b.d.l.	b.d.l.	1110	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	97.1	559576	2.8
<i>Standards</i>																					
Nod-P-1 (measured)	27100	21977	b.d.l.	2299	b.d.l.	11887	59452	9763	141	20923	304094	616	17081	13752	2180	711	644	637	1721		
Nod-P-1 (reference) ^c	25400	22160	22.6	2240	13.3	11500	58050	9960	140	19900	291300	760	16300	13400	2010	560	680	570	1600		
Nod-A-1 (measured)	22512	112062	b.d.l.	3184	b.d.l.	1087	111631	4724	72.6	30234	188632	364	8199	6449	5476	1054	1524	691	627		
Nod-A-1 (reference) ^c	20480	110100	7.5	3110	20.9	1110	109100	4981	76.1	28700	185000	390	7420	6360	5920	846	1630	660	590		
Detection limits (ppm)	1699	1123	48.4	68.2	62.9	76.6	1236	1279	66.0	480	262	213	1006	93.0	1100	407	50.2	38.6	49.8	954	

^a Averages of two duplicate measurements.^b b.d.l. = below detection limits.^c Axelsson et al. (2002).

TABLE 8. Chemical (ICP-MS) and S isotope compositions of the vent fluids (Wakamiko Crater, Ryukyu Arc)

Sample ID	Vent name	T_{\max}^a (°C)	pH^a	Alkalinity ^a (meq/L)	Si ^a (mmol/kg)	H ₂ S ^a	Cl ^a	SO ₄ ²⁻ ^a	Mg ^a	Ca ^a	Na ^a	K ^a	Fe (nmol/kg)	Mn	Zn	Pb	Cu	Ni	Mo	Sb	V	Co
687R1	White Cone	177.6	5.99	8.50	5.20	0.14	340	6.3	10.5	4.9	278	16.5	1839	69.0	45.4	0.13	b.d.l. ^b	34.0	34.8	84.6	18.0	0.32
687R3	White Cone	187.0	5.86	9.50	5.26	0.17	321	5.9	10	4.8	275	16.4	427	75.7	17.6	0.16	b.d.l.	8.22	30.6	220	10.9	0.39
<i>Standard</i>																						
CASS-6 (measured)		-	-	-	n.m. ^c	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	52.6	19.5	22.4	0.13	10.6	7.21	110	n.m.	9.08	1.32
CASS-6 (reference)		-	-	-	-	-	-	-	-	-	-	-	27.4	39.7	19.0	0.05	8.18	6.99	93.4	-	9.62	1.12

^a Data from Yamanaka et al. (2013).^b b.d.l. = below detection limits.^c n.m. = not measured.

Sample ID	Vent name	Cd (nmol/kg)	U	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE (ppb)	(Ce/Ce*) ^d	(Eu/Eu*) ^e	(δ ³⁴ S _{sulfate}) ^f (‰)
687R1	White Cone	0.08	2.68	0.03	0.021	0.078	b.d.l.	0.014	b.d.l.	0.080	b.d.l.	0.03	2.88	-	22.0							
687R3	White Cone	0.07	1.34	0.03	0.031	0.058	b.d.l.	0.019	b.d.l.	0.124	0.007	b.d.l.	0.04	1.45	113	21.6						
<i>Standard</i>																						
CASS-6 (measured)		0.41	10.3	0.23	0.086	0.050	0.012	0.060	0.013	0.002	0.015	b.d.l.	0.011	0.002	0.008	b.d.l.	0.009	0.002	0.04	0.34	0.51	-
CASS-6 (reference)		0.19	12.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

^d Ce/Ce* = 2Ce_{CN} / (La_{CN} + Nd_{CN}); CN = chondrite-normalized (McDonough and Sun 1995).^e Eu/Eu* = 2Eu_{CN} / (Nd_{CN} + Gd_{CN}).^f Averages of two duplicate measurements.

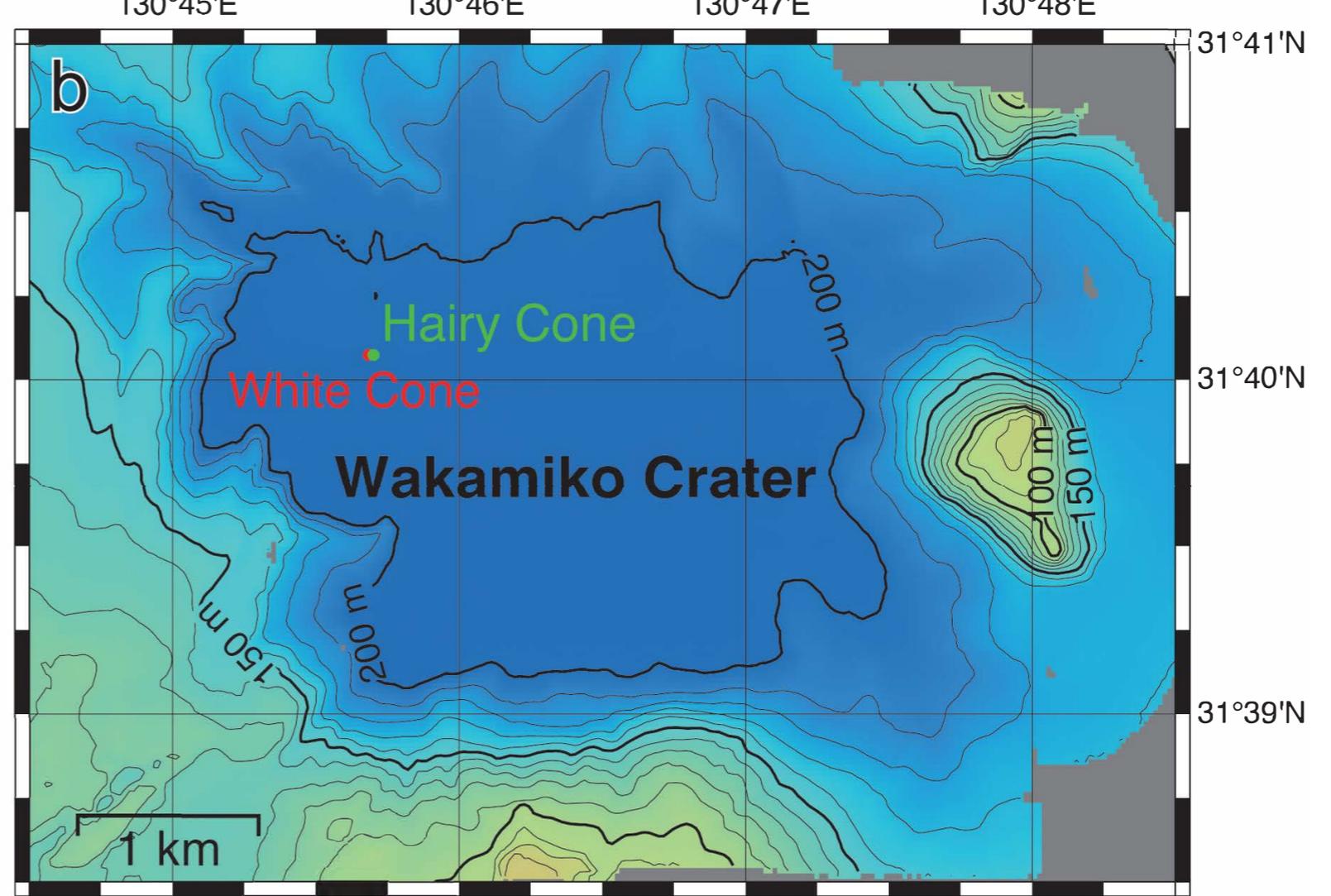
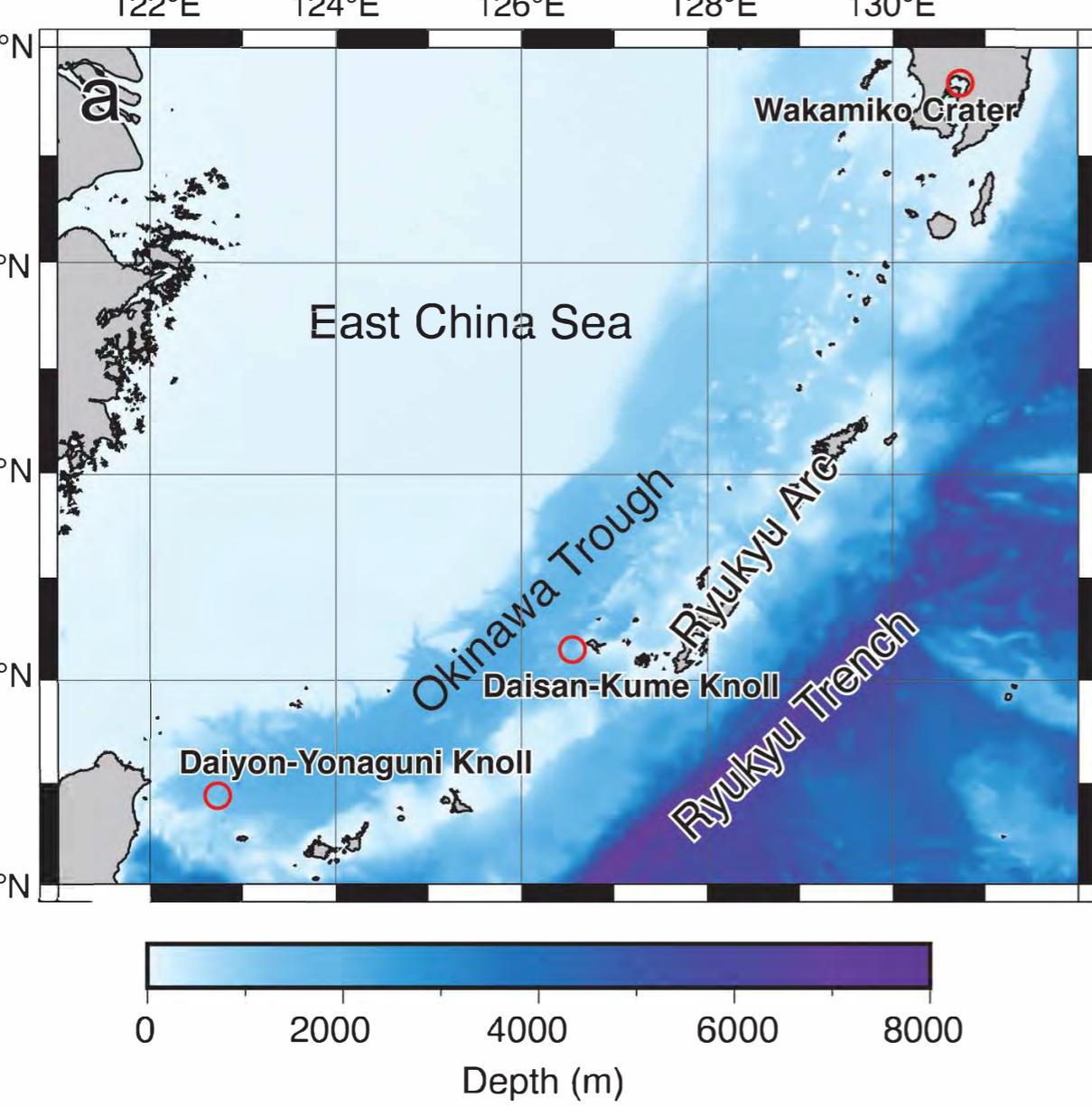


Figure 1

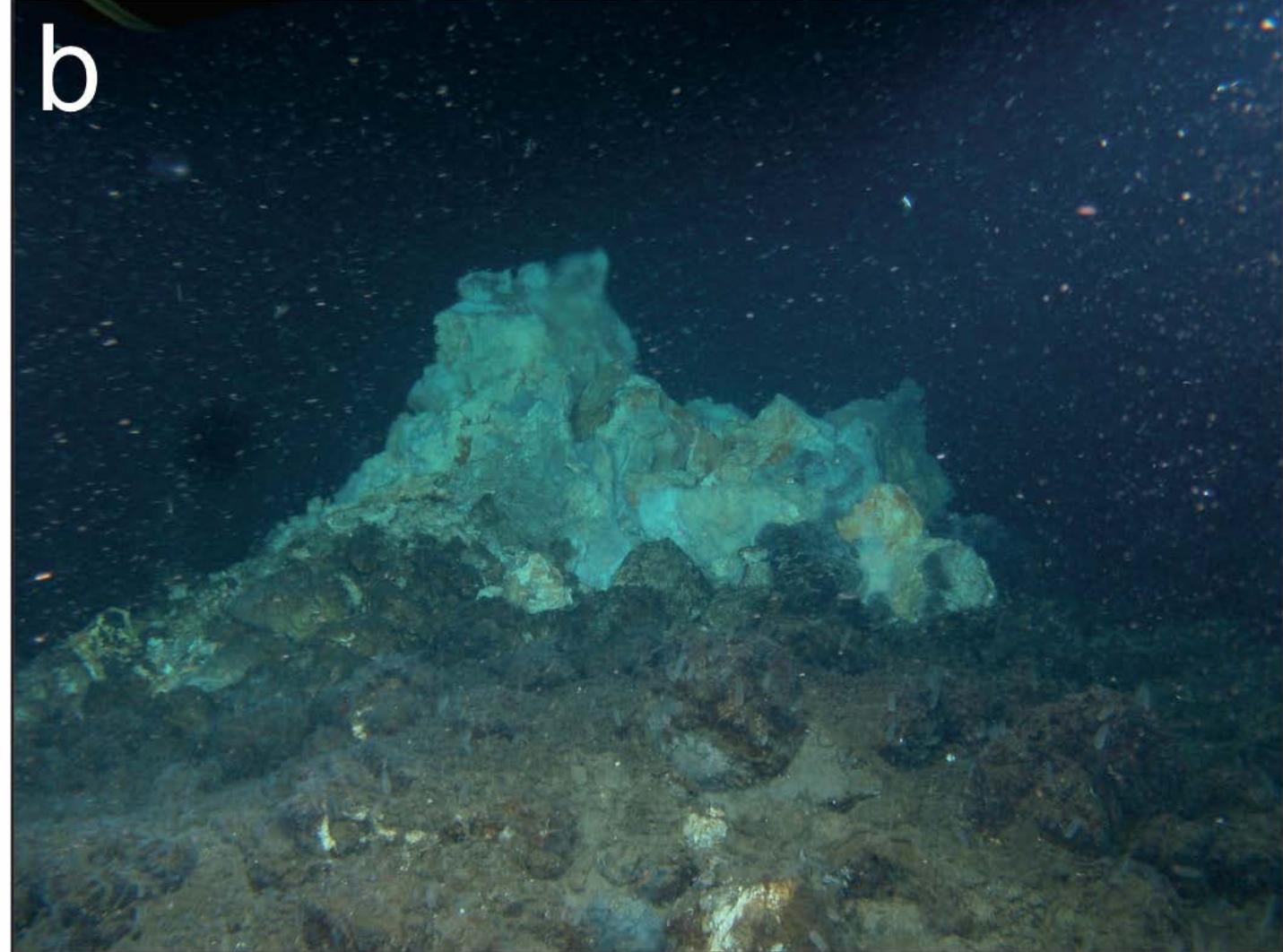
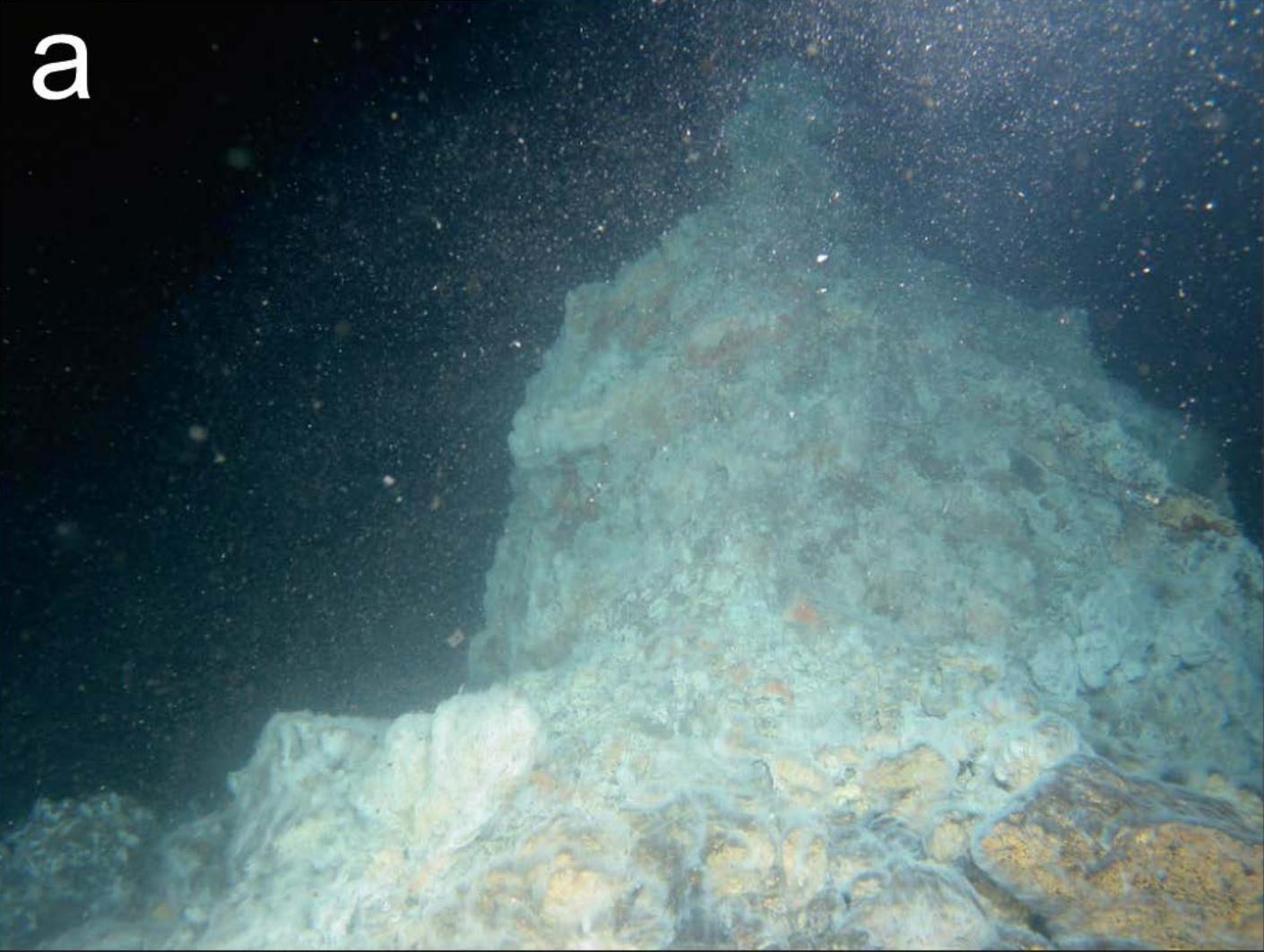


Figure 2

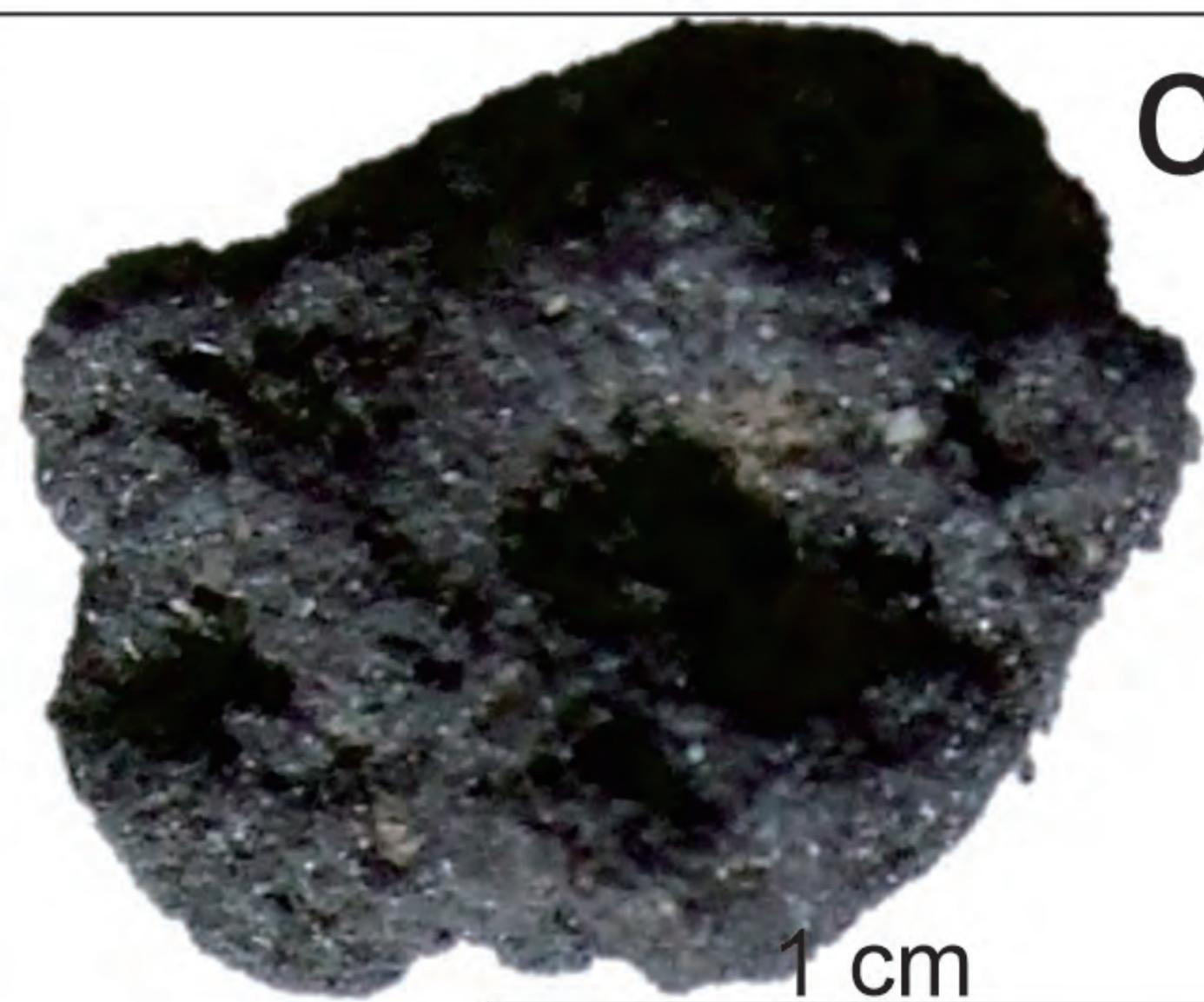


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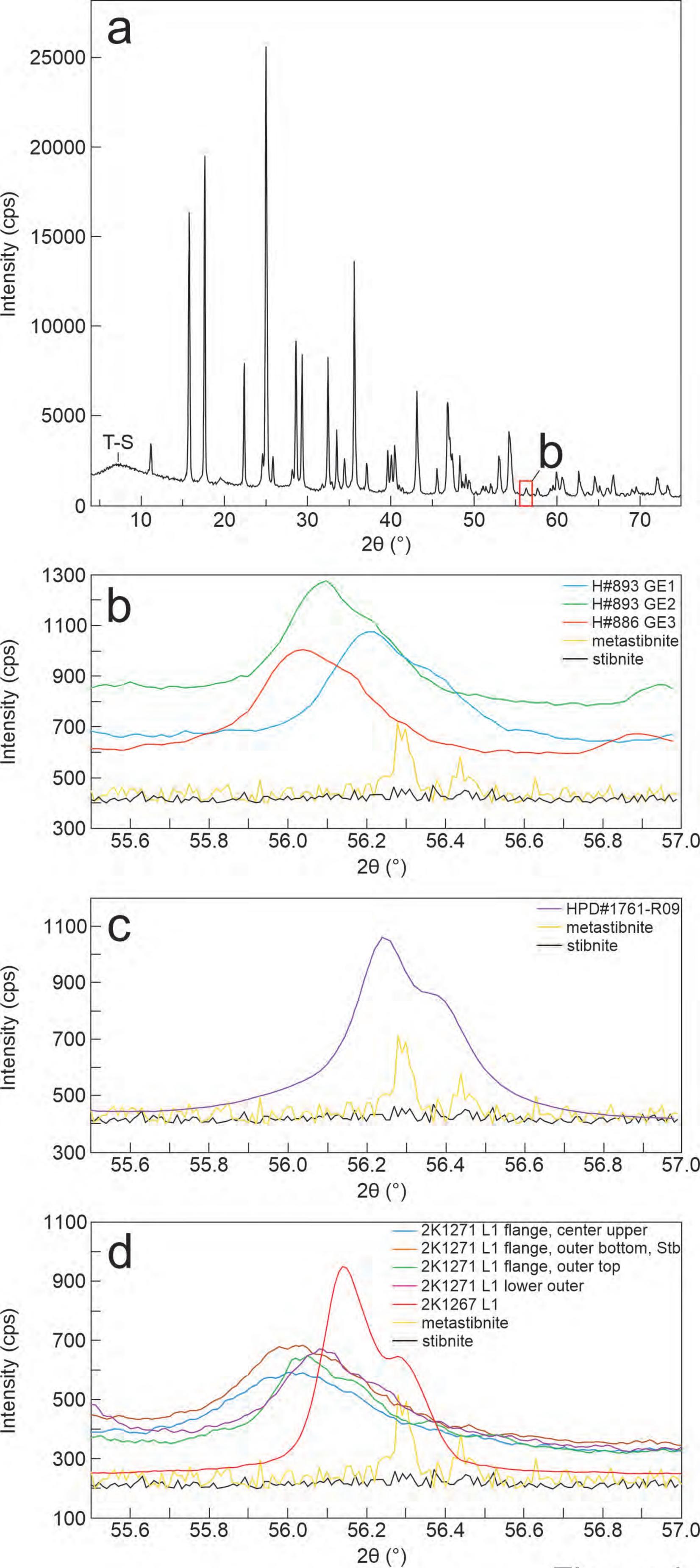


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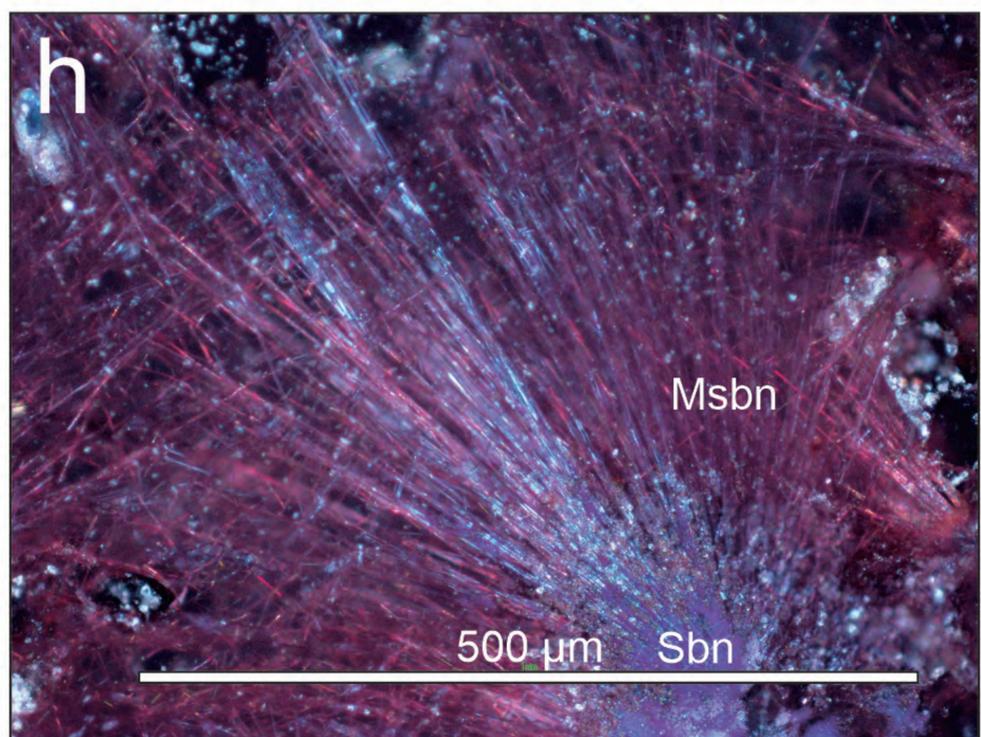
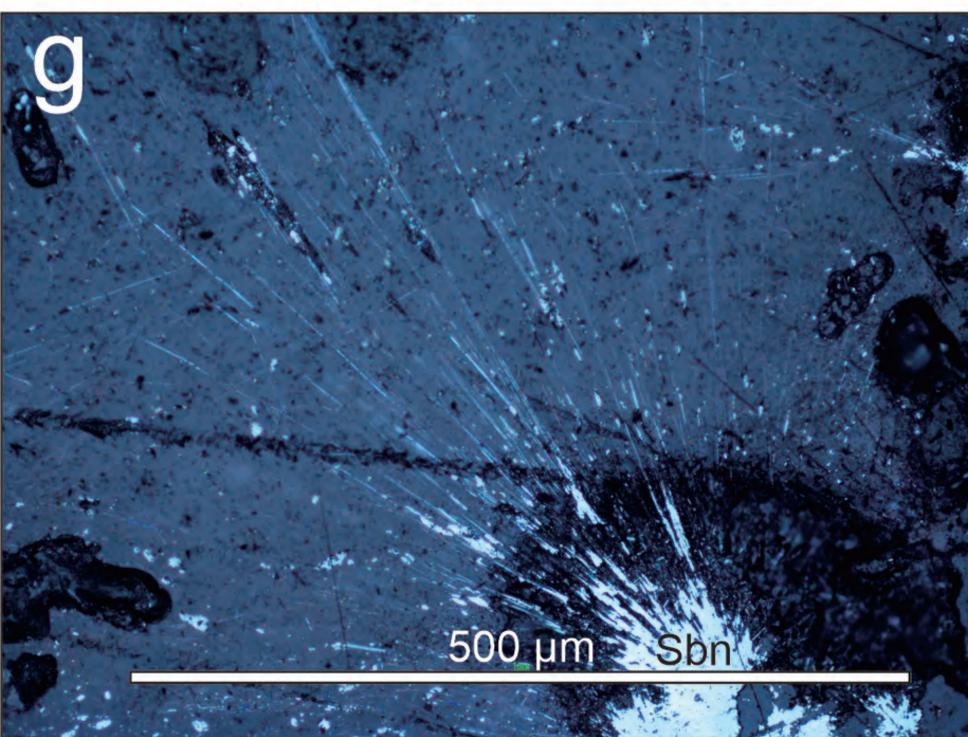
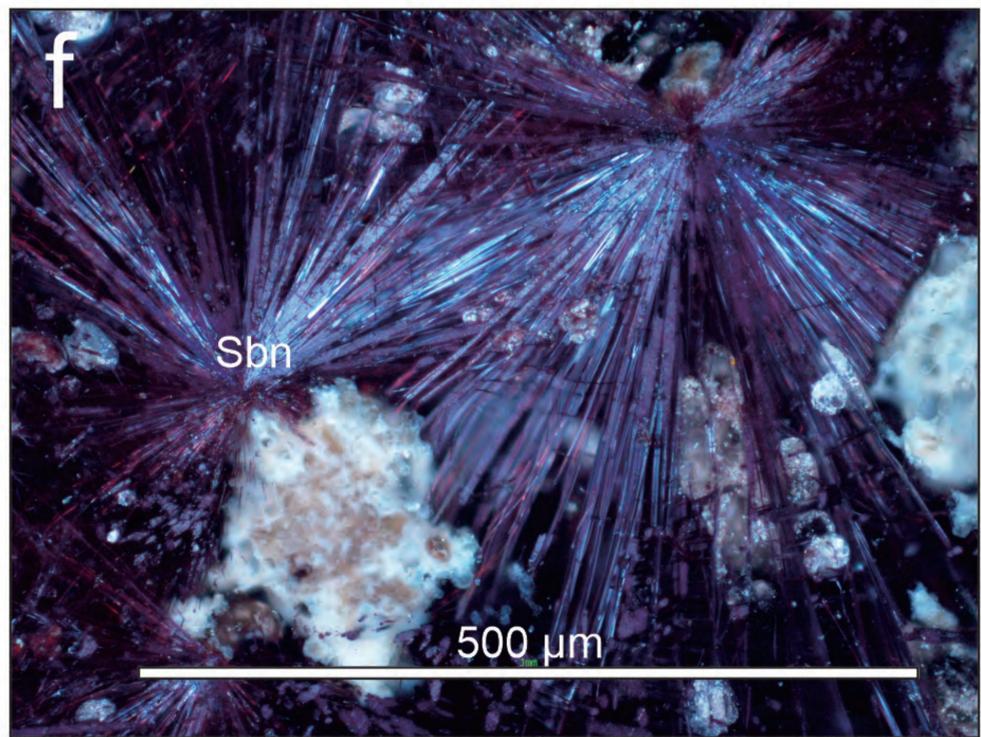
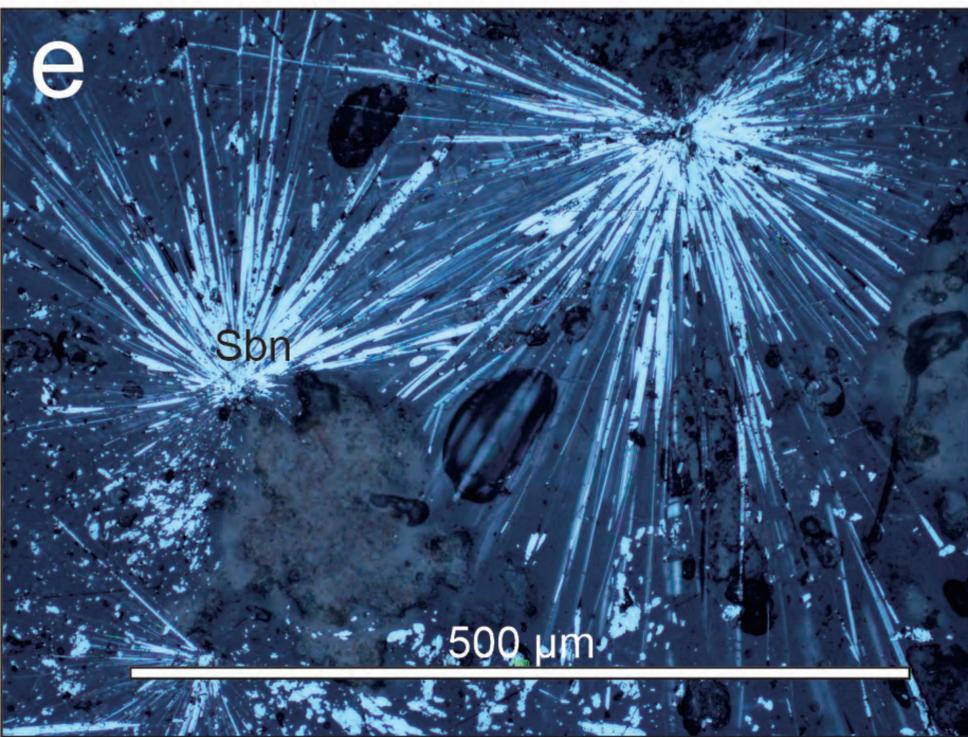
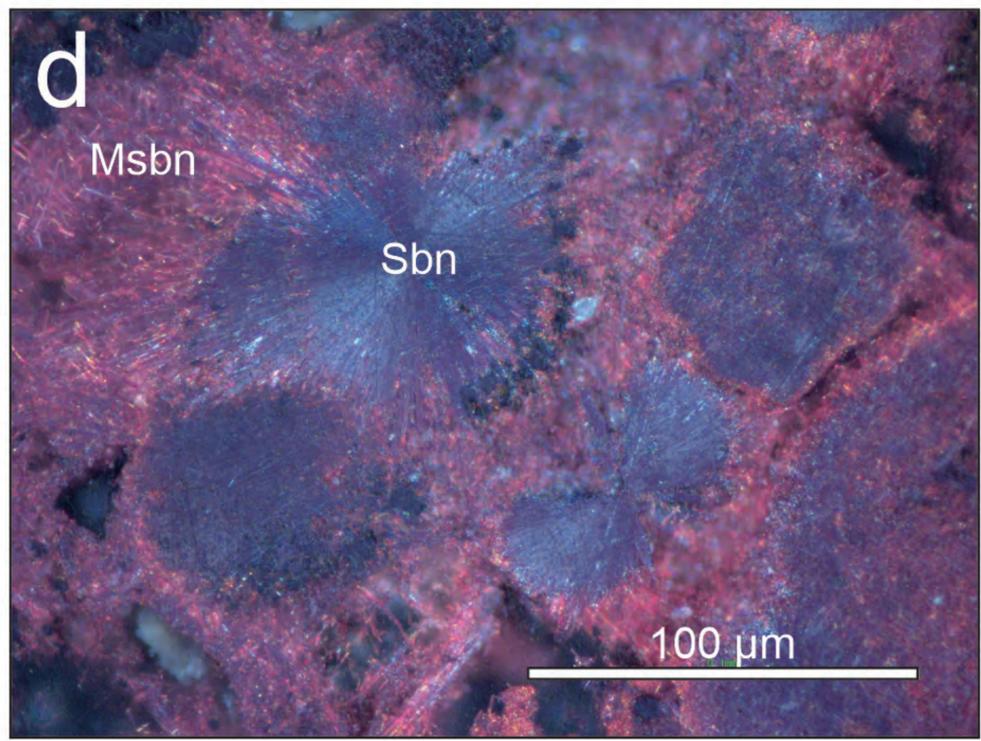
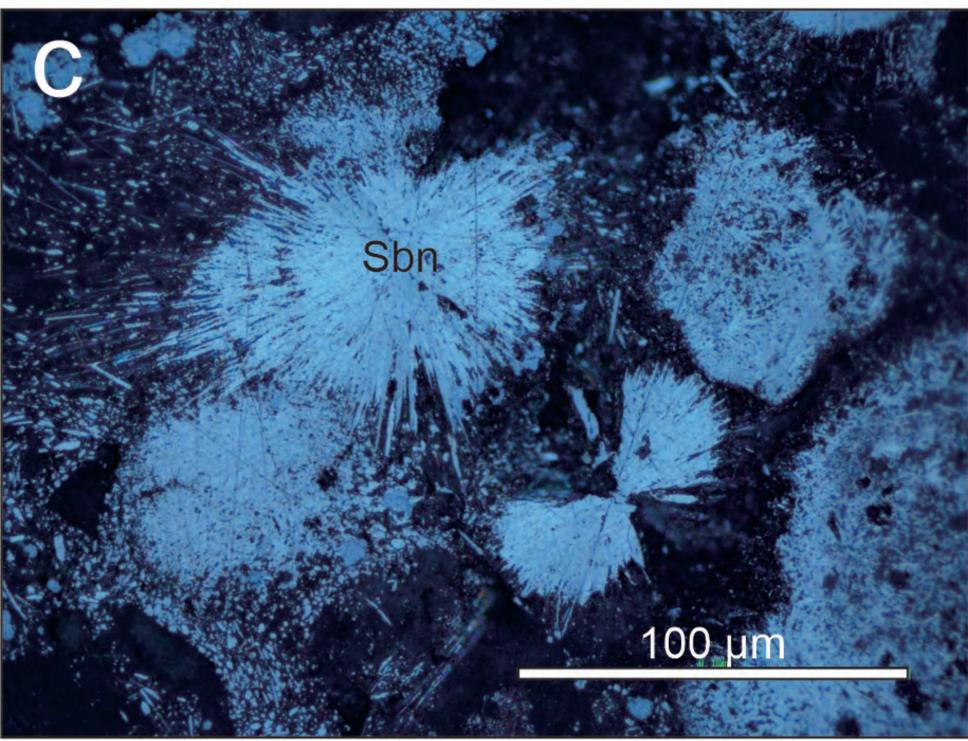
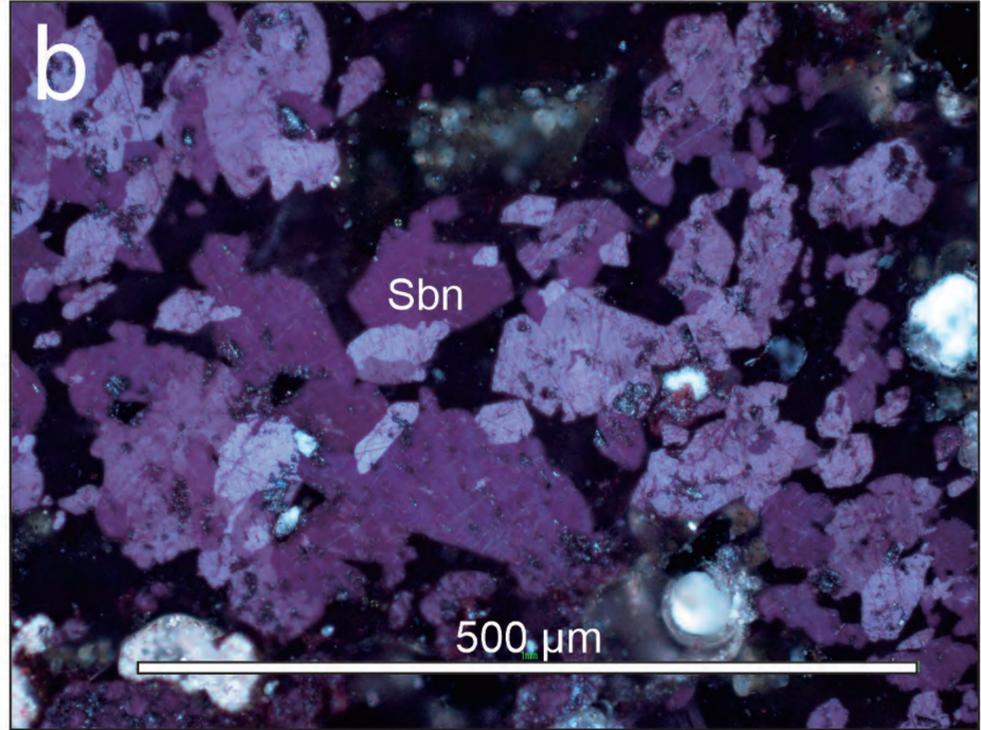
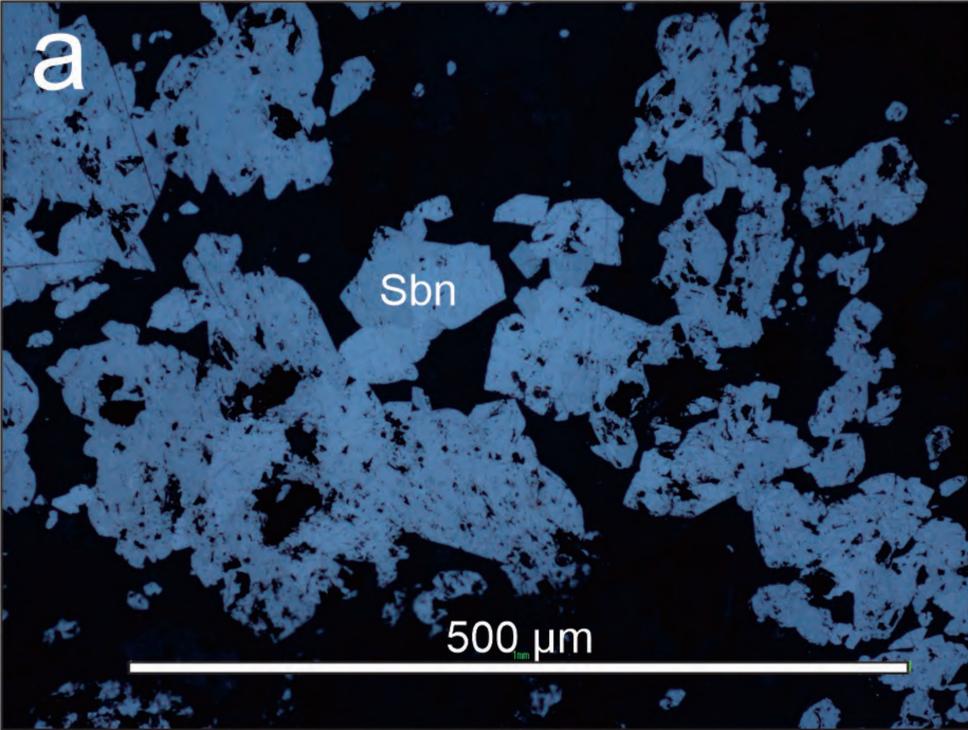


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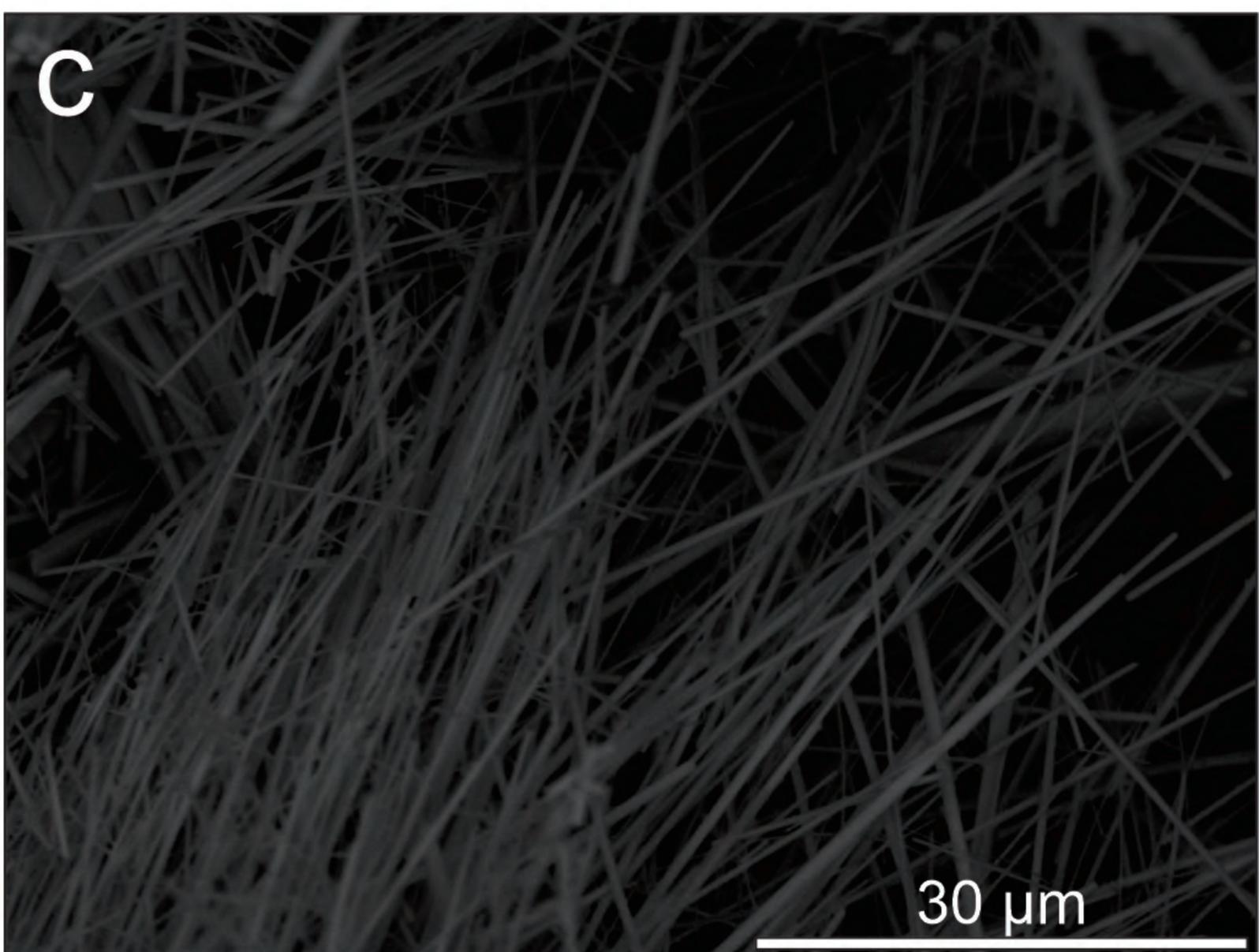
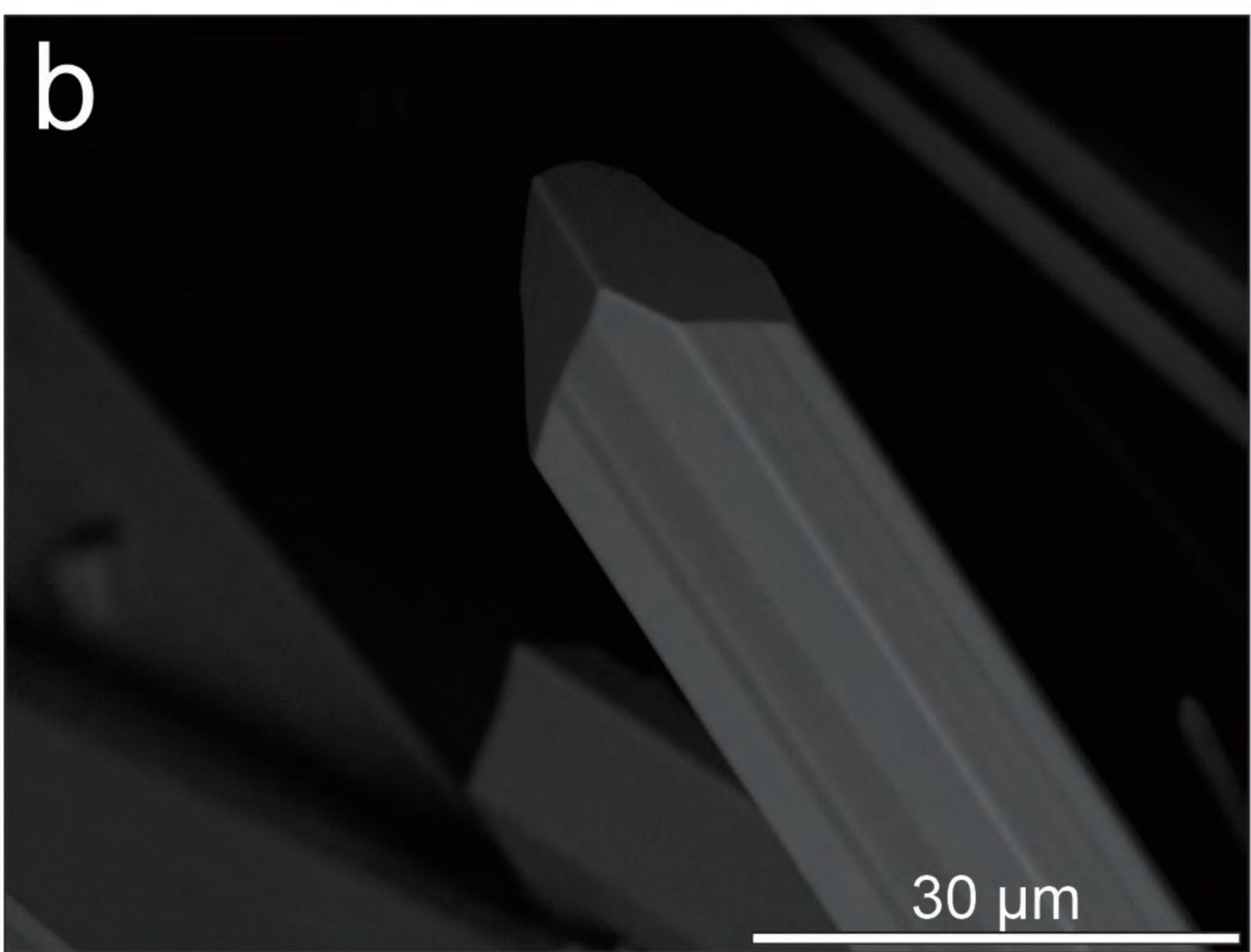
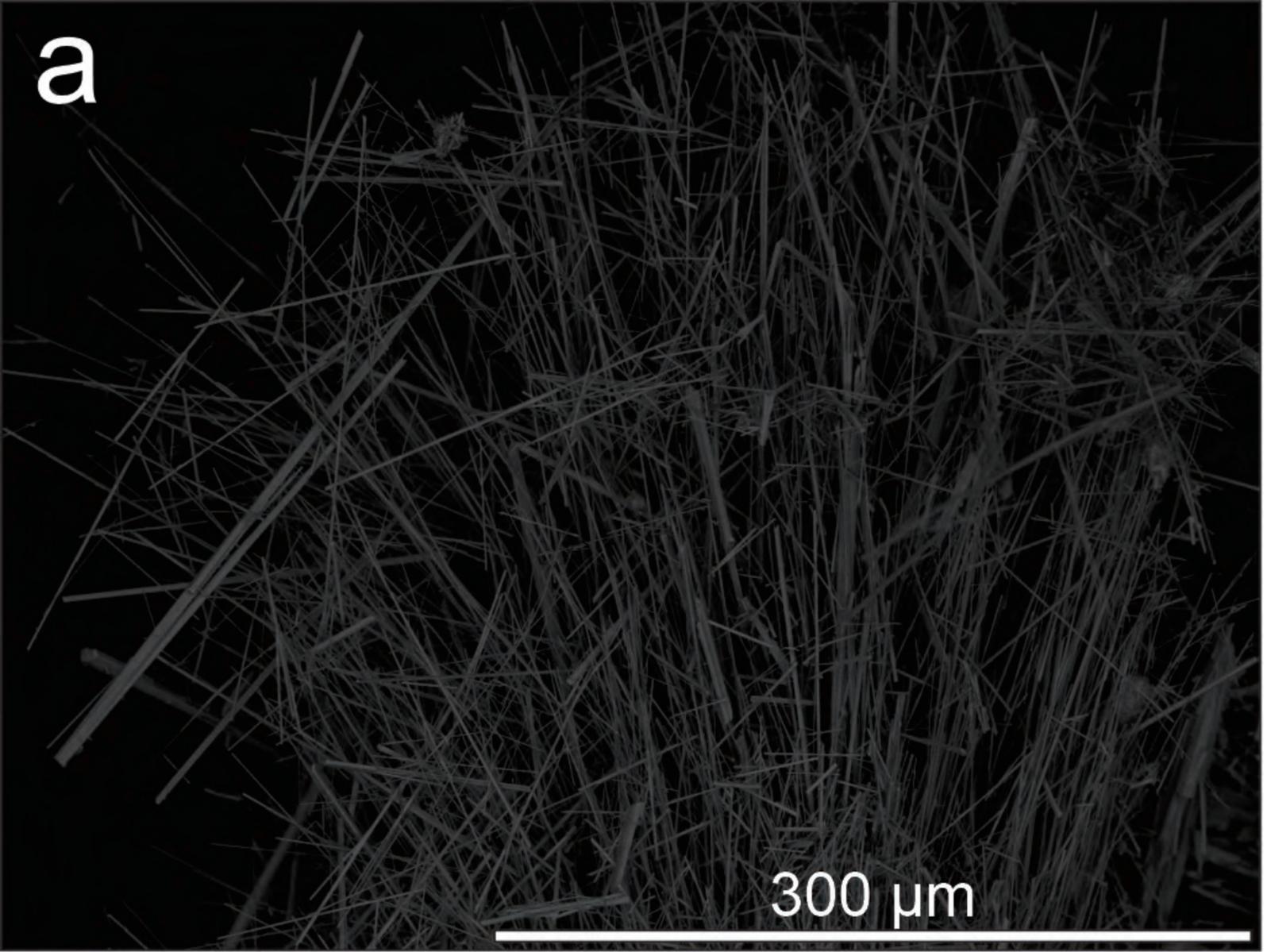


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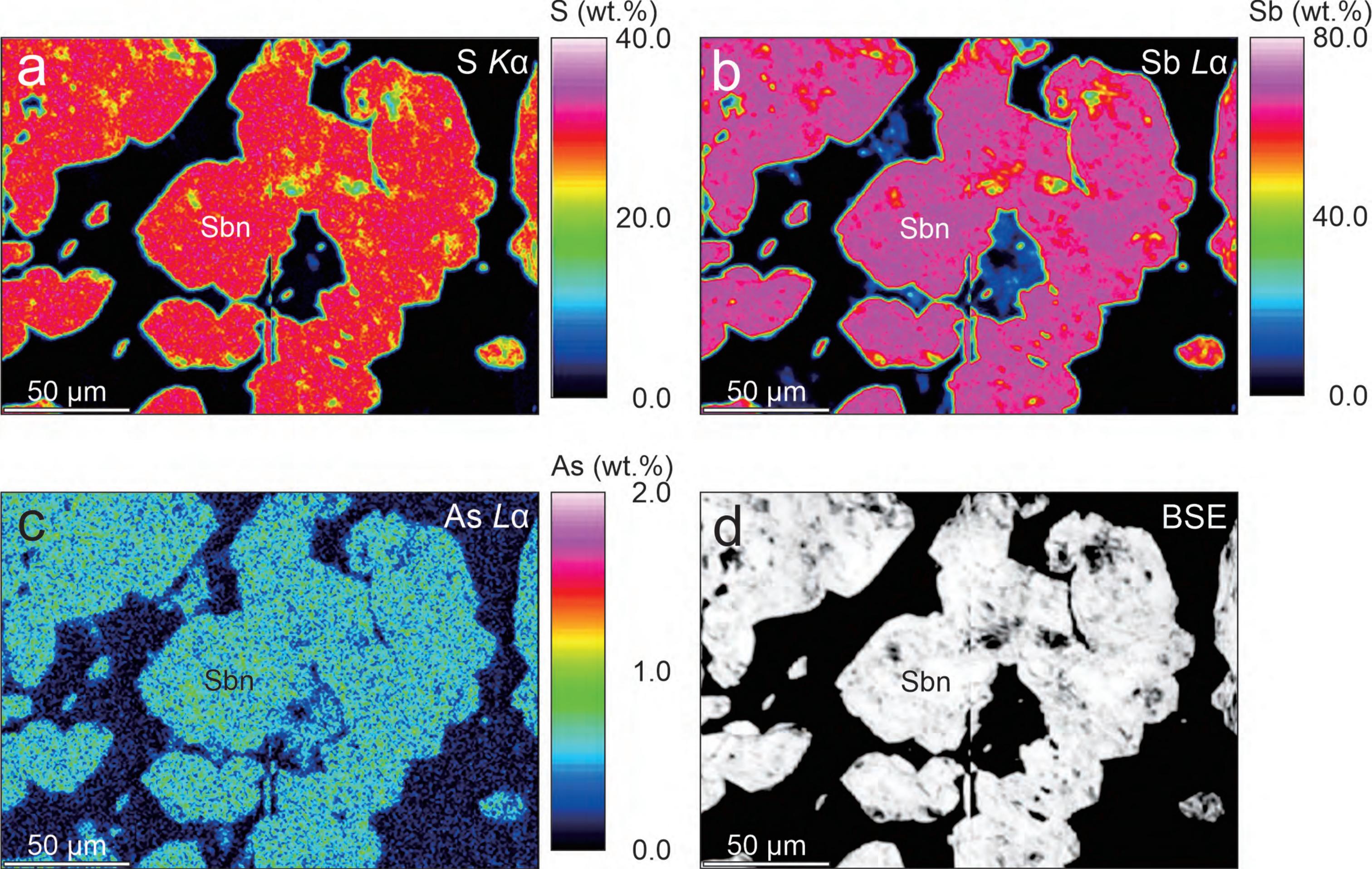


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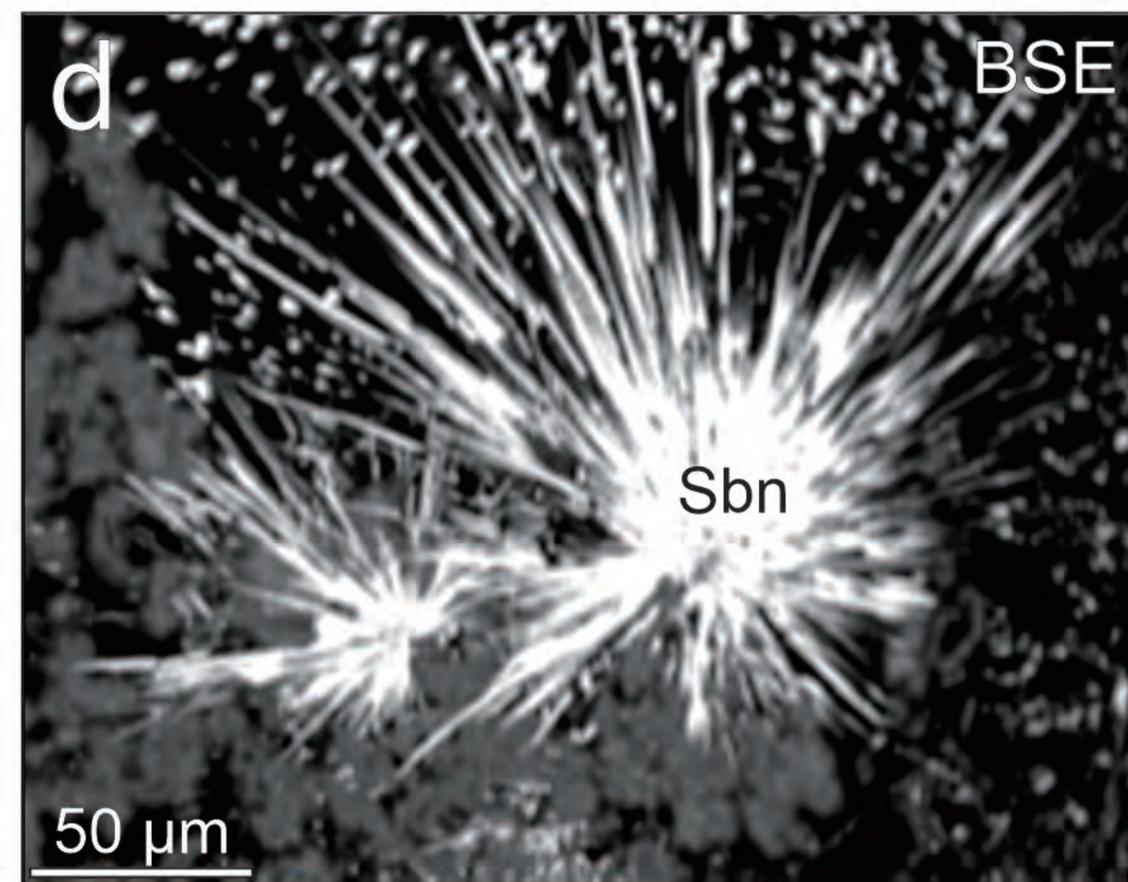
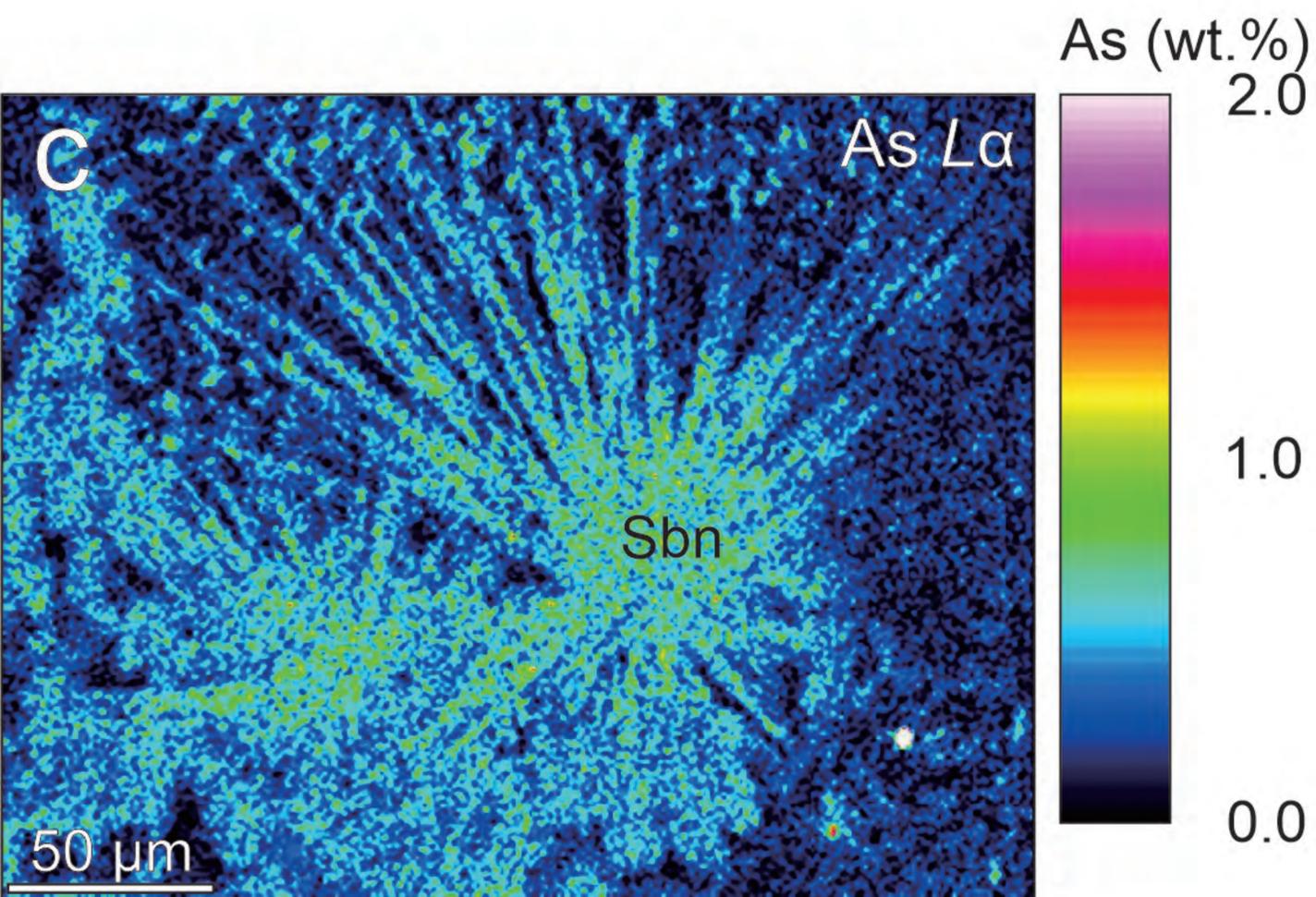
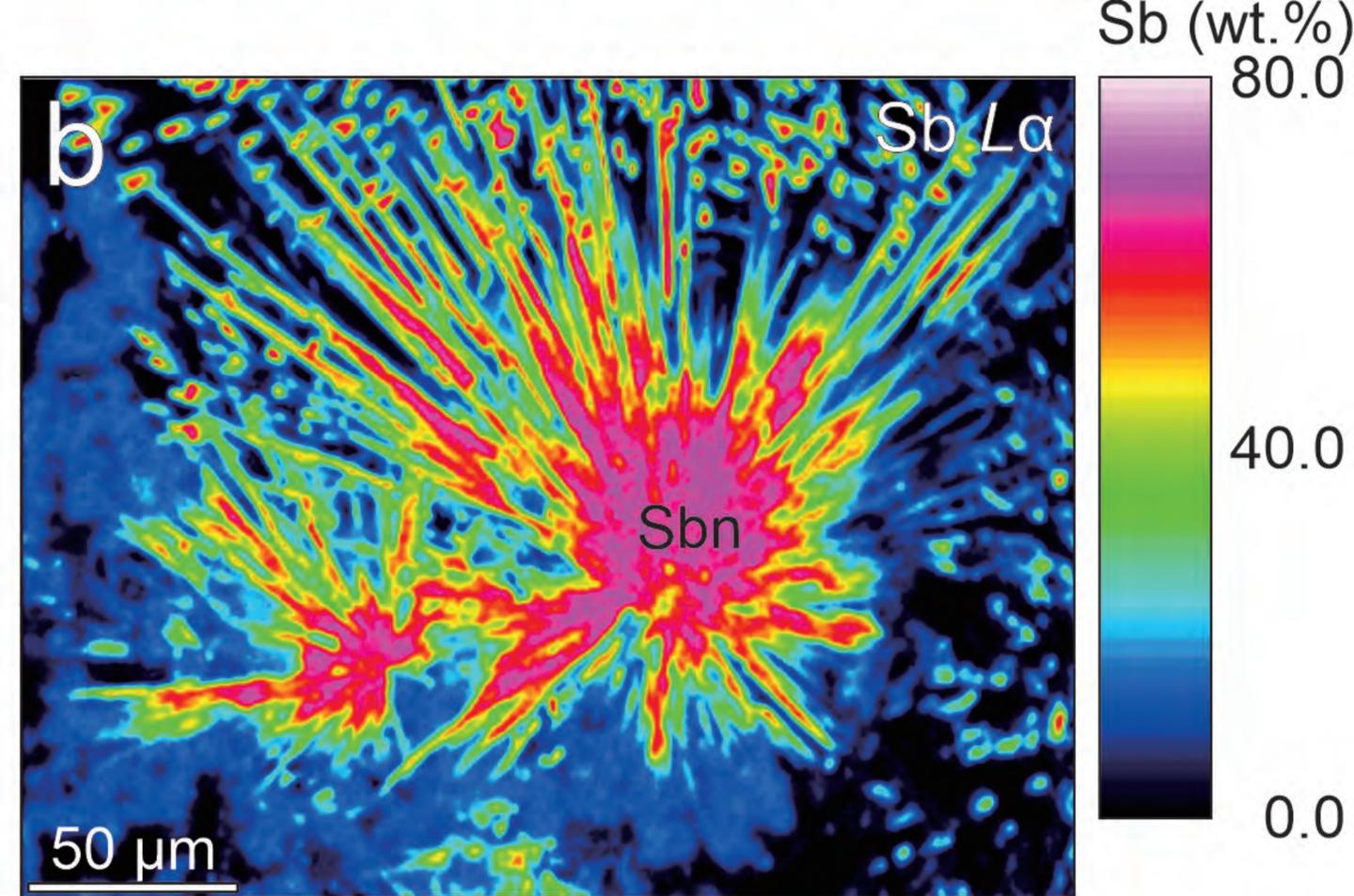
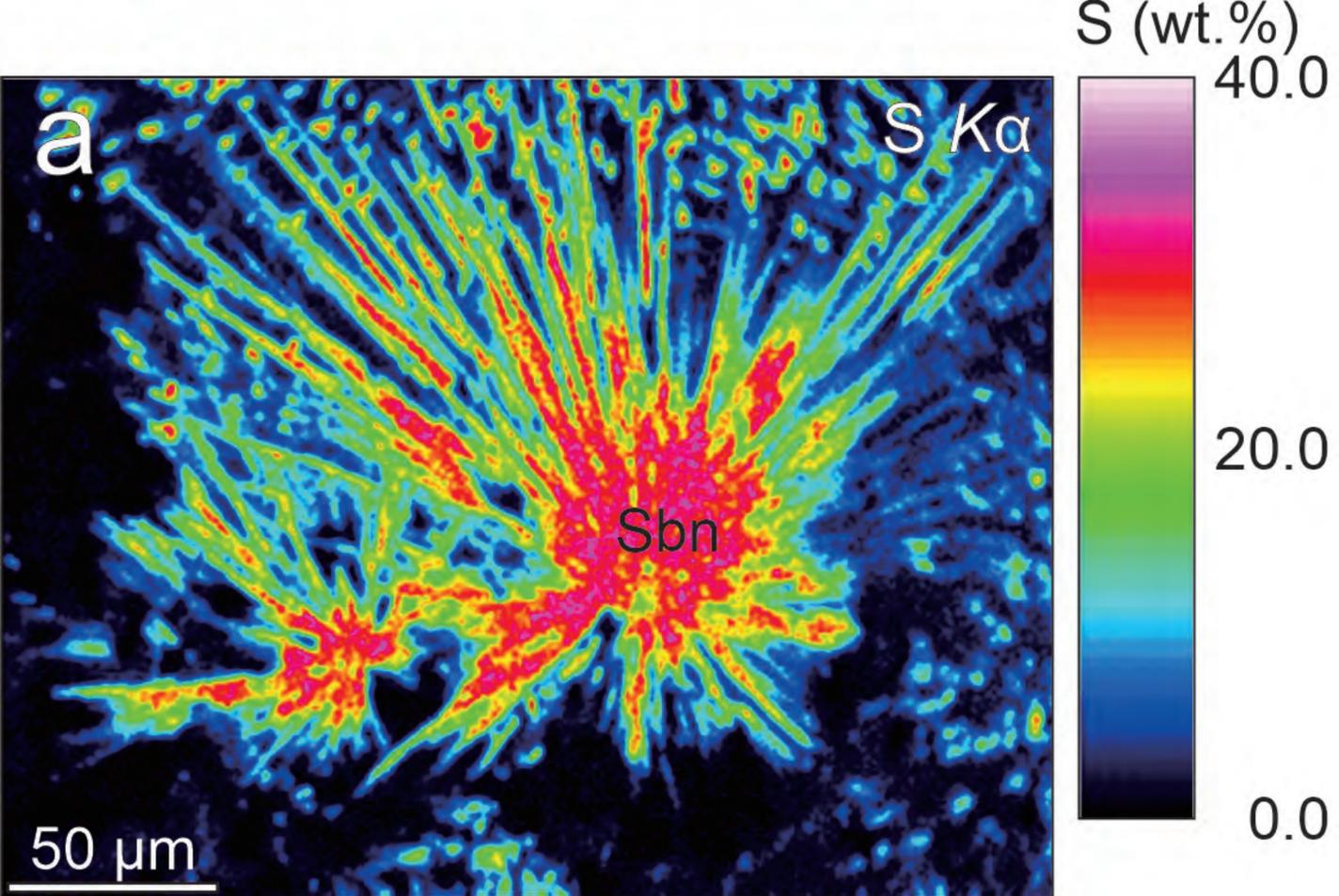


Figure 8

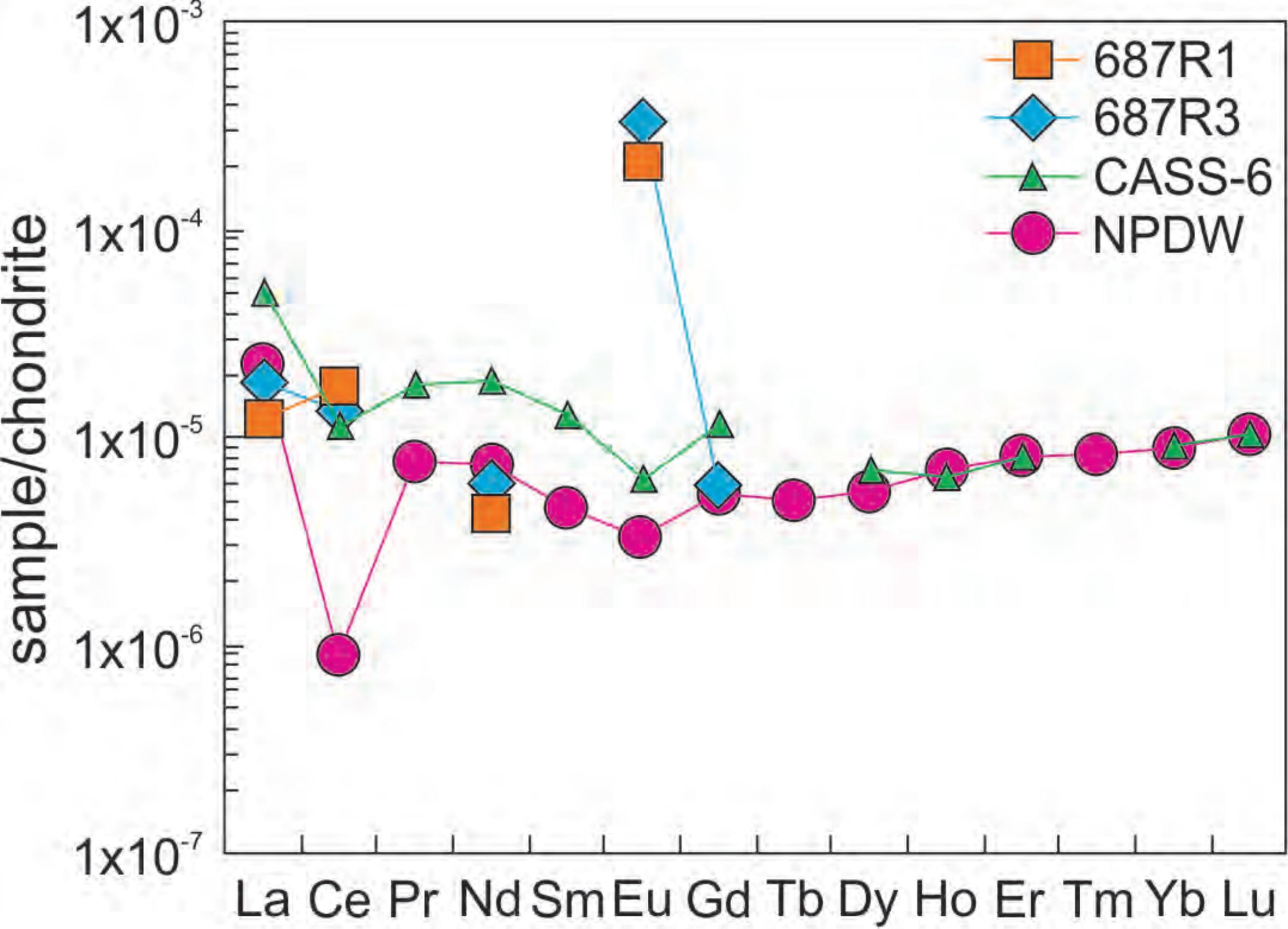


Figure 9

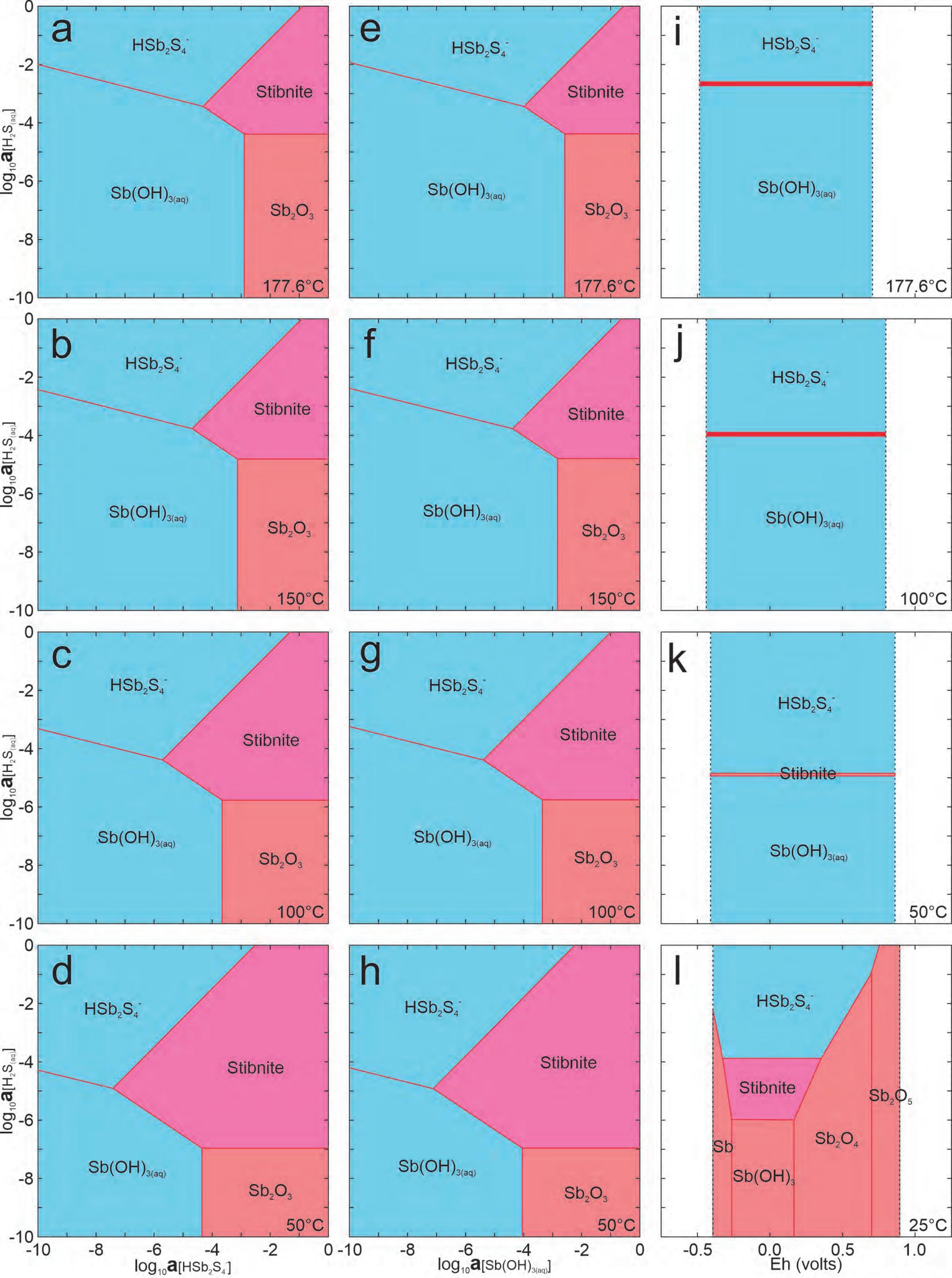


Figure 10

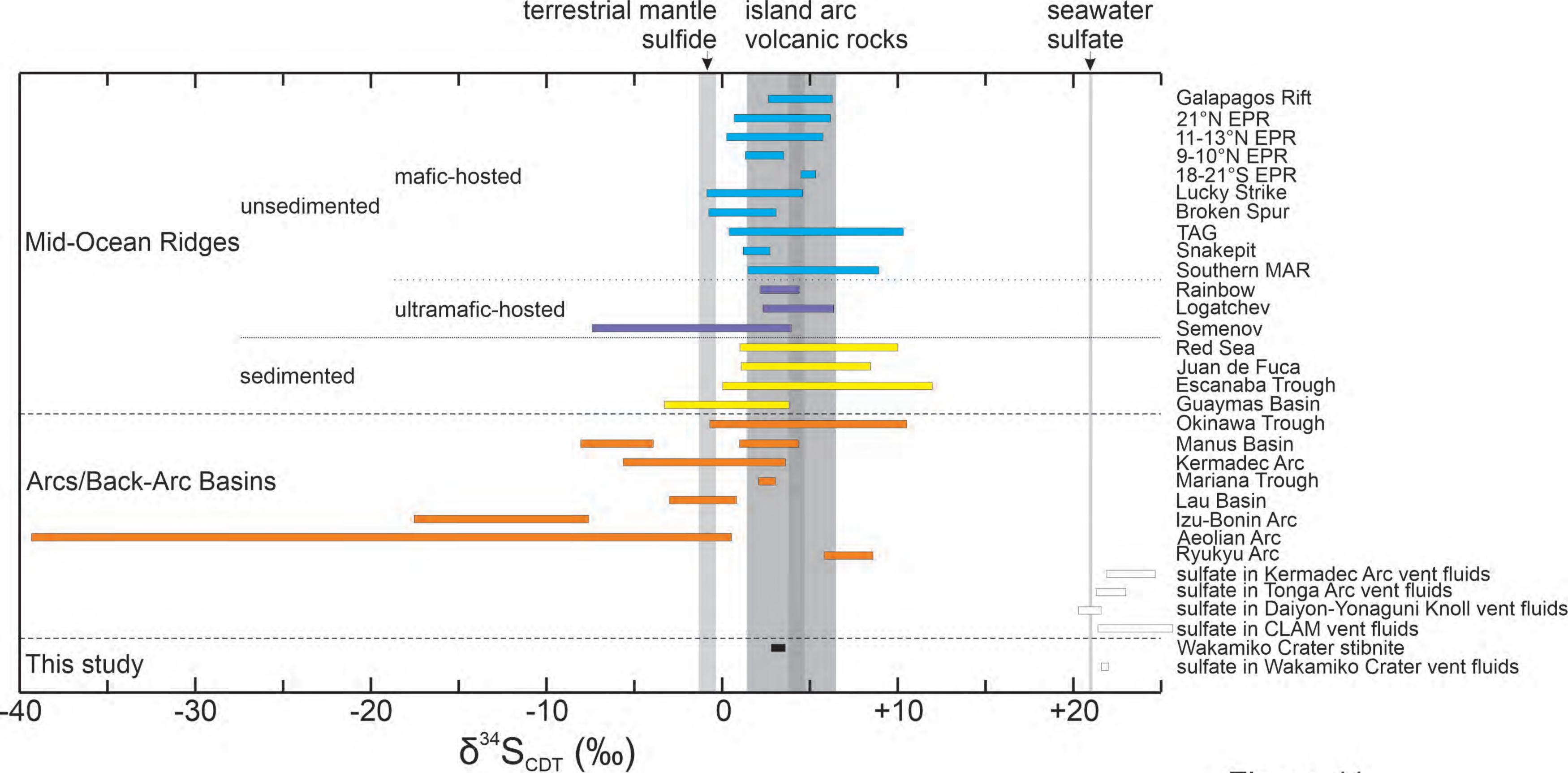


Figure 11