

The mineralogy of weathering products of Bi-bearing tennantite – clues for the process and the mobilisation of heavy metals and toxic elements

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Weathering of Bi-bearing tennantite

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17 The complex sulfosalts of the tennantite-tetrahedrite solid-solution series [called fahlore;
18 $(\text{Cu,Ag})_6\text{Cu}_4(\text{Fe,Zn,Cu,Hg,Cd})_2(\text{Sb,As,Bi,Te})_4(\text{S,Se})_{13}$] are widespread in many geological environments
19 and since they incorporate heavy metal and toxic elements, a better understanding of their
20 weathering process and the element mobility is important to evaluate environmental risks. In this
21 study, the weathering of Bi-rich members of this mineral group were investigated using microscopy,
22 EMPA, SEM, TEM, LA-ICP-MS, Raman, μXRD and MLA.

23 Observations reveal a succession of four distinct stages of weathering: During stage 1, irregular tubes
24 within the fahlore show an assemblage of nm- to μm -sized roméite group minerals, tripuhyite,
25 crystalline Cu-oxides, and crystalline Cu-sulfides, all of which crystallized from a gel-like phase. The
26 textural appearance and the occurrence of these secondary sulfides indicates a low redox-potential
27 during this stage and a low fluid/rock ratio, typical of cementation zones. Mass balance calculations
28 show that during this stage all Zn and the majority of As and S are released to the weathering fluids,
29 whereas Cu and Si are added externally. Bismuth is immobile in this stage and Sb and Fe are
30 immobile, if Bi is sufficiently available from fahlore, but both are partly released into the fluid, if the
31 fahlore did not contain sufficient Bi. During stage 2, amorphous and nano-crystalline arsenates
32 replace fahlore as weathering fronts. Such assemblages indicate a higher redox-potential than in
33 stage 1, typical for oxidation zones. Mass balance calculations reveal that Zn, Sb, and S and partially
34 Cu are lost, whereas Fe and Ba are added during this stage. Arsenic and Bi are immobile. Stage 3
35 occurs only locally, dissolving former weathering stages and/or precipitating amorphous Cu-
36 arsenates and Cu-silicates, respectively, and reflects processes in micro-compartments, not
37 characteristic for the general weathering process. Stage 4 is characterized by the formation of
38 crystalline Bi-, Cu-, Ba-, Ca- or Al-bearing arsenates and Cu-carbonates mostly along cracks, spatially
39 independent of the precursor fahlore. Copper and As originate from older weathering assemblages,
40 whereas many other elements are derived externally (Ca, Ba, Al). This stage reflects the increasing
41 importance of the local host rock and gangue mineralogy, as it is typical in near surface environments
42 of oxidation zones or on mine dumps, where elements are highly mobile and a high fluid/rock ratio
43 prevails (gossan mineralization).

44 The temporal evolution of fahlore weathering textures reflects the transition from fresh ore to
45 cementation zone, oxidation zone and finally gossan textures and assemblages in one hand
46 specimen. Thus, one fahlore grain can record the uplift and erosion and the increasing fluid/rock
47 interaction of a weathered ore deposit with time. Tube-like textures similar to the ones observed in
48 the stage 1 have been reported from other weathering environments and from a variety of element,
49 oxide, arsenide, and sulfide phases. They also were produced during experimental reaction of

50 ilmenite with HCl-bearing fluids. This is clear evidence, that the diffusive process during the first
51 contact with alteration fluids to form cementation zone assemblages is a basic physical process and
52 that it is not only valid for fahlore.

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55

56 **Keywords**

57 Tennantite-tetrahedrite, fahlore, weathering, bismuth, element mobility, cementation zone, oxidation
58 zone, Schwarzwald

60 Minerals of the tennantite-tetrahedrite solid-solution series (in the following referred to as fahlore)
61 have the general formula of $(\text{Cu,Ag})_6\text{Cu}_4(\text{Fe,Zn,Cu,Hg,Cd})_2(\text{Sb,As,Bi,Te})_4(\text{S,Se})_{13}$ (Johnson et al., 1986;
62 Breskova and Tarkian 1994; Makovicky, 2006 and references therein; Moëlo et al., 2008). Between
63 the common As- and Sb-endmembers, a complete solid-solution is known (Johnson et al., 1986).
64 Bismuth-rich varieties of fahlore, however, are rare in nature (Johnson et al., 1986) and up to date,
65 no endmember has been found in nature or has been synthesized (Gołębiowska et al., 2012).
66 Maximum reported Bi contents for fahlore are up to 22 wt.% from the Wittichen area in the
67 Schwarzwald ore district, Germany (Staude et al., 2010; George et al., 2017).

68 Fahlore was and is economically important, as it is one of the most widespread silver-bearing ore
69 minerals (Wu and Petersen 1977). It is the most common sulfosalt (Wu and Petersen 1977) occurring
70 in a wide variety of geological settings, mostly in hydrothermal veins, but also in regional
71 metamorphic, skarn, SEDEX, VMS, MVT, black shale and orogenic gold deposits, as well as in
72 porphyry and active black smoker systems (e.g., Leach et al., 1988; Vavelidis and Melfos 2004; Staude
73 et al., 2010; Mueller and Muhling, 2013; Kozub, 2014; Plotinskaya et al., 2015; Repstock et al., 2015;
74 Wohlgemuth-Ueberwasser et al., 2015; George et al., 2017). Therefore, fahlore found its way to
75 relatively small mine dumps from the Bronze Age (e.g., Ixer, 2001) to today's giant mine and tailings
76 dumps of these various types of deposits.

77 Under oxidizing, near surface conditions, fahlore is not stable anymore. As a consequence, it
78 undergoes dissolution and/or thermodynamically more stable secondary phases form (e.g., Arroyo
79 and Siebe 2007; Roper et al., 2012; Keim and Markl 2015; Borčinová Radková et al., 2017). During this
80 process, heavy metals and toxic elements are commonly released to the environment (e.g., Reich and
81 Vasconcelos 2015). Which secondary phases form and, hence, which components are released to the
82 environment, depends on the composition of the primary mineral and the physiochemical conditions
83 of the weathering fluids (e.g., Keim and Markl 2015; Lara et al., 2016; Keim et al., 2017).

84 The wide range of toxic elements like Sb, As, Cu, Hg, and Cd (Prasad, 2013) incorporated in fahlore
85 makes a further understanding of fahlore weathering crucial to identify their behaviour in near-
86 surface environments. Given their widespread occurrence, and the environmental risks linked to
87 their weathering, studies on the weathering behaviour of fahlores are surprisingly scarce. Nickel et al.
88 (2007) investigated the secondary mineral assemblage of tennantite from Bali Lo (Australia) which
89 weathered in the presence of a Pb-rich fluid to form euhedral Cu- and Pb-bearing arsenates in voids
90 (boxwork) of the dissolved fahlore. Weathering of tennantite and sphalerite from tailings material of
91 a tungsten mine (Mt. Pleasant, Canada) was investigated by Petrunic et al. (2009). They found that a
92 nano-crystalline or amorphous Fe-Zn-As-oxidic phase formed together with Cu-sulfides. They also
93 concluded that the chemistry of nano-scale phases is inconsistent with saturation indices based on

94 pore-water analyses and therefore suggested, that the formation of these phases may not be
95 thermodynamically controlled. Only recently, the weathering chemistry and mineralogy of Sb-
96 dominated fahlore was investigated by Borčinová Radková et al. (2017) focusing on the mobility of
97 the potentially toxic elements As, Sb and Cu during the weathering process, but not on the process
98 itself. They found, that these elements show different mobility during weathering. Copper and
99 arsenic are generally retained by mostly X-ray amorphous phases, while antimony is only partially
100 bound by triphuyite and roméite. Zinc and S are generally lost during weathering of fahlore. Arsenic-
101 dominated fahlore forms an X-ray amorphous weathering phase with Cu, As and Fe (Borčinová
102 Radková et al., 2017). The investigation by Borčinová Radková et al. (2017) deals with a certain
103 geological environment (e.g., fahlore composition, chemistry, pH, and fO_2 of weathering fluid)
104 specific to the weathering of the specific, investigated deposit (hydrothermal quartz-siderite-sulfide
105 vein-type deposits at Špania Dolina-Piesky and L'ubietová-Svätodušná, Central Slovakia). In order to
106 understand the common processes active during fahlore weathering in general, and the differences
107 of the processes related to various geochemical environments, it is important to broaden the
108 observation base.

109 In this contribution, we present the first study of Bi-bearing (up to 15.9 wt.% Bi) and As-dominated
110 fahlore (with variable As/Sb ratios) exposed to long-term weathering from different geological
111 environments in the Schwarzwald (SW Germany) using scanning electron (SEM) and light microscopy,
112 electron-microprobe (EMP), Raman, micro X-ray diffraction (μ XRD), laser-ablation inductively-
113 coupled plasma mass spectrometry (LA-ICP-MS), mineral liberation analyses (MLA), and transmission
114 electron microscopy (TEM) in order to evaluate the general weathering processes and the mobility of
115 elements.

116

117 **2. Geological background**

118 The northern Schwarzwald hydrothermal veins are partly hosted by Variscan basement rocks
119 (granites and metasedimentary gneisses), but mostly by Permian to Lower Triassic clastic redbed
120 sediments (Geyer and Gwinner, 2011; Villinger and Zedler, 2006; Rupf and Nitsch, 2008) which were
121 unconformably deposited on the basement. The multi-element veins at Wittichen are situated in the
122 granitic basement directly underneath the unconformity, whereas the other investigated deposits
123 (Neubulach, Freudenstadt, Königswart) are hosted by the Lower Triassic sediments. Middle Triassic
124 shale and carbonate rocks are partly preserved in some areas, but are mostly eroded due to the
125 Schwarzwald uplift during the Paleogene-Neogene Upper Rhine Graben formation (Geyer and
126 Gwinner, 2011). The veins do not cut these Middle Triassic rocks, but in the vicinity of the veins of
127 Neubulach, <5 m of Middle Triassic limestone is still preserved on ridges next to the veins (Metz,

128 1977; Göb et al., 2015). More information on the investigated veins and their geology can be found in
129 Metz (1977); Werner and Dennert (2004); Werner (2012); Staude et al. (2010, 2011, 2012a, b); Markl
130 et al. (2014a); Markl (2015, 2016); and Göb et al. (2015).

131 The primary hydrothermal veins were formed during post-Variscan extensional tectonics (Franzke
132 and Werner, 1994; Pfaff et al., 2009; Staude et al., 2009) by mixing of an ascending metal- and Na-Ca-
133 rich brine with a stagnating Na-dominated brine near the basement-cover unconformity (Bons et al.,
134 2014; Burisch et al., 2016). About 100 of the Schwarzwald hydrothermal mineralizations were age-
135 dated and reveal an intermittent activity since 310 Ma with peaks during Permian pull-apart basin
136 formation, the Jurassic opening of the North Atlantic and the Paleogene-Neogene formation of the
137 Upper Rhine Graben (Walter et al. in press; Pfaff et al., 2009 and references therein). The types of
138 mineralization and their metal content vary with age and also with their spatial distribution within
139 the Schwarzwald (Metz et al., 1957; Bliedtner and Martin, 1986; Staude et al., 2009; Walter et al.,
140 2016). The area of investigation is dominated by quartz veins with variable amounts of barite and
141 minor amounts of fluorite. Sulfide minerals are Bi-bearing As-dominated fahlore, chalcopyrite, pyrite,
142 and locally large amounts of emplectite, wittichenite, native Bi, and various Cu-sulfides (Staude et al.,
143 2010, 2012a). Formation temperatures for these veins as recorded by fluid inclusions range from
144 50°C to 150°C reflecting the varying proportions of fluids involved in mixing (Staude et al., 2012a;
145 Walter et al., 2018).

146

147 **2.1. Weathering of hydrothermal veins in the Schwarzwald**

148 The secondary mineralization and its elemental redistribution processes in the Schwarzwald were
149 investigated by Göb et al. (2011, 2013a); Burmann et al. (2013); Markl et al. (2014a, b); Haßler et al.
150 (2014); Göb et al. (2015); Keim and Markl (2015); and Keim et al. (2016). They occurred since the
151 uplift of the Schwarzwald in the Neogene and Quaternary (after 15 Ma, Hautmann and Lippolt,
152 2000). Available formation ages of the secondary phases from the investigated deposits are $^{40}\text{Ar}/^{39}\text{Ar}$
153 ages on secondary hollandite from Wittichen (1.0 ± 0.1 Ma; Hautmann and Lippolt, 2000) and a U-Pb
154 isochron age on secondary calcite from Wittichen (5.2 ± 0.3 Ma; Staude et al., 2012b). Other ages
155 from Schwarzwald supergene weathering minerals are 1.7 ± 0.4 Ma (Pfaff et al., 2009) and 0.3 ± 0.04
156 (Hofmann and Eikenberg, 1991) for supergene uranium phosphates, and eight ages between
157 10.1 ± 0.3 and 0.84 ± 0.03 Ma on botryoidal goethite (Lippolt et al., 1998). 64 hydrothermal and
158 supergene carbonates have been dated by Walter et al. (in press) between 40.0 ± 11 Ma and 0.6 ± 0.19
159 Ma, however, it is in most cases not possible to discriminate between hydrothermal and supergene
160 carbonates. Supergene minerals formed in various settings:

- 161 - in the oxidation zone of the veins (Markl et al., 2014a, b) during natural and mining processes
- 162 (e.g., concrete in the Clara mine and fire-setting; Kolitsch, 2000; Keim et al., 2017)
- 163 - after the mining within the abandoned mines (e.g., pyromorphite, arsenates and sinters in
- 164 mines, (Burmam et al., 2013; Markl et al., 2014a, b; Göb et al., 2015) or
- 165 - on waste dumps (Markl et al., 2014a; Keim et al., 2017).

166 Primary minerals of the investigated mines were exploited for Ag, Co (Wittichen area only) and Cu
167 and additionally for azurite as pigment in Neubulach (Werner and Dennert, 2004). Mining occurred
168 mainly in the 13th (Neubulach) and 17th to 19th century (Werner and Dennert, 2004; Markl, 2005),
169 exposing large parts of the dumps to weathering for several centuries.

170 The geochemistry of water responsible for weathering of primary mineralization and precipitation of
171 secondary minerals were investigated by Zhu et al. (2003); Bucher et al. (2009); Göb et al. (2013b,
172 2015); and Markl et al. (2014a) using recent mine waters, partly directly taken in the vicinity of newly
173 formed arsenates and sinters inside the Wittichen mines. The investigated water was influenced by
174 seasonal changes (amount of rain, melting of snow; Göb et al., 2015), organic material (organic
175 phosphate to form pyromorphite, Burmann et al. (2013), farming (fertilizers; Göb et al., 2015 and
176 references therein), or other human activity (salt on roads in winter; Göb et al., 2015). In Neubulach,
177 Göb et al. (2015) showed that water dripping from sinters is more influenced by fluid-rock interaction
178 than water flowing on the mine floor, and that the sinter-forming water dissolved azurite and
179 precipitated malachite.

180

181 **2.3. Sample description**

182 Samples were collected from the northern part of the Schwarzwald ore district (SW Germany) where
183 fahlore-bearing hydrothermal quartz-barite (\pm fluorite) veins (Staude et al., 2010) are exposed to
184 weathering. Samples were collected from the mining areas of Neubulach, Königswart, Freudenstadt
185 and Wittichen/Reinerzau (Alte Gabe Gottes mine and Schmiedestollen dump; electronic
186 supplementary material (ESM) Figs. 1 and 2, see Markl, 2015 and 2016 for detailed descriptions of
187 these localities). The sample suite covers Bi-bearing fahlore as the main sulfide mineral (Neubulach
188 and Freudenstadt veins, Alte Gabe Gottes mine, Reinerzau), Bi-bearing fahlore together with large
189 quantities of emplectite (Königswart veins), and Bi-bearing fahlore together with large amounts of
190 emplectite, native Bi, wittichenite, other Cu-dominated minerals, Co-Ni arsenides, and frequently
191 hematite in the gangue (Schmiedestollen dump, Wittichen). Generally, fahlore in the investigated
192 deposits is often overgrown by euhedral quartz and barite and only rarely shows euhedral surfaces.
193 Chalcopyrite and pyrite are present in most samples in small quantities and they are overgrown by

194 fahlore. The carbonate synchysite-(Ce) frequently forms small euhedral crystals together with
195 hematite, both enclosed by quartz in the sample from the Alte Gabe Gottes mine, whereas other
196 primary carbonates were not observed in other samples.

197

198

3. Analytical Methods

199 EMPA, SEM, Raman spectroscopy, and μ XRD were performed at the University of Tübingen,
200 Germany, LA-ICP-MS at the University of Stuttgart, Germany, TEM at the Bayerisches Geoinstitut
201 Bayreuth, Germany, and MLA at the Geometallurgy Laboratory of the Helmholtz Institute Freiberg,
202 Germany.

203

204 3.1. EMPA, SEM

205 For qualitative and quantitative determination of the major and minor element compositions of the
206 fahlores and weathering products, a JEOL 8900 electron microprobe was used. Analyses were carried
207 out in wavelength-dispersive (WD) mode using an acceleration voltage of 25 kV (sulfides) or 20 kV
208 (secondary phases) and a probe current of 20 nA. For the sulfides, a focused beam and for the
209 weathering products a 2-5 μ m probe diameter was used. The peak overlap of As and Sb was
210 corrected by a factor of 0.0128, of S and Co by 0.0003, of Pb and Bi by 0.0209, and of Ce and Ba by
211 0.0630. The elements for the quantitative program were selected after qualitative analyses using
212 energy dispersive X-ray spectroscopy (EDS) mode. Details of the used WD-configuration, including
213 standards, counting times of the peak/background, analyzed fluorescence lines and the average
214 detection limits are presented in Table 1 and 2 in the ESM. Visual images and qualitative EDS spectra
215 were obtained using a TM3030+ Tabletop microscope from Hitachi. To avoid the peak overlap of the
216 S $K\alpha$ - with the Bi $M\alpha$ -lines for the elemental maps, the Bi $M\beta$ -line was used instead.

217

218 3.2. μ XRD analysis

219 μ XRD was used to characterize the weathering products of fahlore using a Bruker D8 Discover GADDS
220 Θ/Θ micro-diffractometer. A Co anode (wavelength $\lambda = 1.79 \text{ \AA}$) at 30 kV, 30 mA, and room
221 temperature was used. A mono-capillary with a 50 μ m pinhole was used together with a VÅNTEC500
222 detector (Berthold et al., 2009). The patterns were integrated individually for each sample using a
223 step size of 0.05 $^{\circ}2\Theta$. The incident angle of the beam was fixed to 15 $^{\circ}$ and measurement time was set
224 to 120 s per frame. Representative XRD patterns are shown in the ESM Fig. 3.

225

226 **3.3. Raman**

227 Raman analyses were performed to identify the fahlore weathering phases. A confocal Renishaw
228 InVia Reflex Raman spectrometer with a laser wavelength of 532 nm and WiRE 3.0 software was
229 used. The spectra were compared to reference spectra of the RRUFFTM database (Downs, 2006).
230 Representative Raman spectra are shown in the ESM Fig. 4.

231

232 **3.4. TEM**

233 TEM was performed using a FEI TitanG2 80-200 at 200 kV acceleration combining diffraction
234 methods with spectroscopy and imaging. Chemical composition was determined by EDS using the
235 ChemiSTEM technology with four SDDs (XFlash 5030 detector) symmetrically mounted in the TEM
236 column around the optical axis. Each SDD has an active area of 30 mm², adding up to an overall
237 detector area of 120 mm² covering a solid angle of 0.9 sr. The element distribution maps were
238 acquired in scanning transmission electron microscopy mode (STEM). At each pixel of the map a full
239 energy dispersive X-ray spectrum was acquired. In order to obtain a high image resolution, the
240 smallest condenser lens (C2) aperture of 50 µm was used while having a count rate of about 2000
241 counts per second by operation at relatively high electron currents of about 0.2 nA. The dwell time
242 was set to 3 µs. The overall measurement time for the elemental STEM-EDX mapping was about 4
243 hours.

244

245 **3.5. LA-ICP-MS**

246 Elemental concentrations in minerals were determined by ICP-MS analyses with an AGILENT 7700
247 spectrometer after laser ablation with a CETAC LSX-213 laser system. In a first series of
248 measurements, the diameter of the ablated spots was 50 µm. The laser energy was set to 40% of the
249 maximum (100% = 4 mJ at a spot diameter of 150 µm), at a laser pulse frequency of 10 Hz. In a
250 second series, a spot diameter of 25 µm and a laser energy of 60% was used. A mixed helium and
251 argon gas flow with 500 ml/min and 800 ml/min, respectively, served as carrier of the ablated
252 material. Reference materials were DLH8 from P&H Developments Ltd., a NIST (National Institute of
253 Standards and Technology, USA) 612 glass and sphalerite standard MULZnS-1 (Onuk et al., 2017). The
254 validity of the calibration with the DLH and the NIST glass and reproducibility were checked with the
255 reference materials Diorite (DRN) and Zinnwaldite (ZW-C) from Service d'Analyses des Roches et des
256 Mineraux du CNRS. Lithium-borate glass disks of both were prepared using 0.6 g of powder of these
257 reference materials and 3.6 g of lithium borate.

258 The data acquisition was performed using the Agilent Mass Hunter software (version B.01.01). Each
259 analysis comprised the acquisition of the individual background ion intensities (gas-blank) for 20 s
260 followed by the acquisition of the ion intensities on laser irradiation of the sample spot for 40 s. In
261 the off-line data evaluation, the analytical signal of each ion was corrected by the subtraction of the
262 corresponding averaged background intensity. Within a selected appropriate interval of the ablation
263 time profile, after each mass cycle the corrected individual ion intensities were integrated and
264 divided by the integrated corrected intensity of the selected isotope of the reference element. From
265 these values, relative elemental concentrations were calculated from the abundance of the
266 corresponding isotope assuming a natural isotopic distribution and an individual calibration factor
267 which was determined under the same experimental conditions. The software used for calibration
268 and data evaluation was developed by Massone et al. (2013) and Baggio et al. (2018).

269 The following isotopes were monitored: ³¹P, ⁵¹V, ⁵²Cr, ⁵⁵Mn, ⁵⁹Co, ⁶⁰Ni, ⁶⁶Zn, ⁷¹Ga, ⁷²Ge, ⁹⁵Mo,
270 ¹⁰⁷Ag, ¹¹¹Cd, ¹¹⁵In, ¹¹⁸Sn, ²⁰⁵Tl, ²⁰⁸Pb, ²⁰⁹Bi. This selection excludes isobaric interferences with
271 isotopes of other elements. In the case where two isotopes were analyzed, very similar
272 corresponding individual elemental concentrations were obtained, which shows the absence of
273 significant matrix effects. For this reason, the given values are the average of the corresponding
274 individual elemental concentrations. While running the analyses, signals of laser ablation were stable
275 for all samples.

276 All elemental concentrations were calculated relative to the elemental concentrations of Bi
277 (atelestite) and Cu (all other phases) as internal standard elements. The absolute elemental
278 concentrations of both were previously measured with the EMP. The same spot target was applied
279 for both EMP and LA-ICP-MS ablation.

280

281 **MLA**

282 The MLA system used comprises of an FEI Quanta 650F scanning electron microscope equipped with
283 two Bruker Quantax X-Flash 5030 energy-dispersive X-ray spectrometers and the MLA software suite,
284 version 3.1.4, for automated data acquisition. More detailed information about the functionality of
285 the MLA system can be found in Fandrich et al. (2007), details about the data processing are shown
286 in Bachmann et al. (2017). Consistent operating conditions were applied for all samples using the
287 GXMAP measurement mode at 15 kV acceleration voltages, 6 nA probe current, 0.25 $\mu\text{m}/\text{pixel}$, 15 ms
288 acquisition time and a step size of 8 pixel.

289

290 **3.6. Analytical limitations**

291 A successful analysis of the supergene weathering phases by EMPA is limited by the high porosity,
292 the instability of the phases under the electron beam, and the unknown water and carbonate
293 content especially in the amorphous phases, resulting in low totals for most of the EMP analyses. The
294 small grain size of a few μm down to a few nm limits the quantitative determination of the minerals
295 by EMP, since mixed mineral analyses including the surrounding phases are produced. Therefore,
296 only phases large enough to be confidently analysed were investigated by EMP. The qualitative EDX
297 analyses of the μm -nm sized minerals using TEM must be also handled with care, because an overlap
298 of different mineral phases cannot be completely excluded. Moreover, some phases seem to
299 dehydrate in the vacuum of the microprobe (e.g., bariopharmacosiderite
300 $[\text{Ba}_{0.5}\text{Fe}^{3+}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot 5\text{H}_2\text{O}]$ and some amorphous Cu-arsenates) resulting in shrinking cracks and an
301 unknown loss of volatiles (ESM Fig. 5). Raman and LA-ICP-MS measurements are both limited by the
302 small grain size, the occasionally low thermal stability, and porosity of the analysed phases. The μXRD
303 measurements in the thin sections are limited by the intergrowth of many phases (sometimes with
304 preferred orientation) within a single measurement spot, which induces overlaps of mineral reflexes.
305 Moreover, the nm-sized crystals in the amorphous phases did not show distinctive reflexes, which is
306 probably due to their small grain size.

307

308

4. Results

309

4.1. Identified phases

310 Besides optical identification of the large-grained primary sulfide minerals fahlore, chalcopyrite,
311 emplectite, wittichenite, bornite, and Co-Ni-arsenides, the secondary weathering products were
312 identified optically and by EMPA, SEM, TEM, μXRD , and Raman as explained above.

313 Secondary sulfides are covellite $[\text{CuS}]$, spionkopite $[\text{Cu}_{39}\text{S}_{28}]$, chalcocite $[\text{Cu}_2\text{S}]$, acanthite $[\text{Ag}_2\text{S}]$, and
314 cinnabar $[\text{HgS}]$ based on EMPA, TEM-EDX, and Raman. In all cases, a unique identification by μXRD of
315 these sulfides was not possible due to the small grain size or intergrowth with amorphous phases.

316 A fine-grained Cu-oxide phase was found with an average chemical formula of $\text{Cu}_{0.9}\text{O}$ (normalised to
317 1 atom per formula unit (apfu) oxygen; analyzed by TEM-EDX). A unique identification as tenorite
318 $[\text{CuO}]$ by electron diffraction was not successful, and hence, the phase will be named Cu-oxide phase
319 in the following.

320 Frequently, Sb-Fe, Sb-Bi-Fe, and Bi-Fe oxide phases were found. The Sb-Fe phase was qualitatively
321 analysed by EDX mapping and is interpreted to be tripuhyite $[\text{Fe}^{3+}\text{Sb}^{5+}\text{O}_4]$ or hydroxyferroroméite
322 $[(\text{Fe}^{2+}_{1.5}\square_{0.5})\text{Sb}^{5+}_2\text{O}_6(\text{OH})]$, but based on these analyses, it was not possible to distinguish between

323 them. In similar weathering environments, the occurrence of these phases has also been reported
324 (Borčinová Radková et al., 2017; Mills et al., 2017). The Sb-Bi-Fe phase was studied by TEM. EDX
325 mapping gives an average chemical formula of $\text{Cu}_{1.0}\text{Sb}_{1.1}\text{Bi}_{1.0}\text{As}_{0.3}\text{Fe}_{0.7}\text{O}_{7.8}$ (normalized to 1 apfu Bi; see
326 Table 1). There is no known mineral with that composition, however, it is similar to members of the
327 cubic roméite group. The elongated crystal morphology, however, seems to fit better to members of
328 the tetragonal phase triphuyite. In two electron diffraction patterns from different locations in a
329 sample from Neubulach, d-spacings were measured and are listed in ESM Table 3. Unfortunately, the
330 relative positions of the diffraction spots of the diffraction patterns do neither prove a cubic nor a
331 tetragonal symmetry, even in connection with the measured angles in ESM Fig 6. The measured d-
332 spacing, however, shows a good agreement with the d-spacings of roméite, as evident from ESM
333 Table 3. Those d-spacings which are not in agreement with roméite have a reasonable fit with d-
334 spacings of triphuyite, especially considering their nano-crystalline nature. Small crystallite sizes can
335 result in delta d/d errors as large as 5% following the arguments of Biskupek and Kaiser (2004). A
336 mixture of both phases (roméite group mineral and a triphuyite-like phase) is thus a reasonable
337 assumption. While it seems likely that both phases can incorporate elevated amounts of Bi, the exact
338 influence of Bi on the lattice parameters is unknown. In the following, the mixture of the triphuyite-
339 like phase and roméite will be named roméite group mineral (RGM) if used generally or Bi-Fe-bearing
340 RGM, Bi-Sb-bearing RGM, or triphuyite/hydroxiferroméite if used for a specific chemistry.
341 Interestingly, Walenta (1983) described from Neubulach the occurrence of an Sb-Bi-Fe-phase called
342 “bismutostibiconite” $[\text{Fe}^{3+}_{0.5}\text{Bi}^{3+}_{1.3}\text{Sb}^{5+}_{1.7}\text{O}_7]$, the IMA status of which as a mineral, however, was
343 discredited (Atencio et al., 2010; Christy and Atencio, 2013). It is likely, that the mineral analysed by
344 Walenta (1983) is the RGM found during this study. The Bi-Fe-bearing RGM was identified by EDX
345 mapping and could represent another yet unknown member of the RGM, but was not further
346 investigated.

347 Frequently, a Cu-As phase was found, which is characterized by either no crystallinity or nm-sized
348 crystal aggregates in an amorphous ground mass. Raman measurements show that As is present as
349 arsenate with some evidence of H_2O (ESM Fig 4). Other identified phases are amorphous and
350 botryoidal Cu-Silicates, amorphous red Fe-Cu-oxides, and amorphous Bi-carbonates.

351 The well-crystallized arsenates mixite $[\text{BiCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}]$, olivenite $[\text{Cu}_2\text{AsO}_4(\text{OH})]$, zálesiite
352 $[\text{CaCu}_6(\text{AsO}_4)_2(\text{AsO}_3\text{OH})(\text{OH})_6 \cdot 3\text{H}_2\text{O}]$, tangdanite $[\text{Ca}_2\text{Cu}_9(\text{AsO}_4)_4(\text{SO}_4)_{0.5}(\text{OH})_9 \cdot 9\text{H}_2\text{O}]$, dussertite-
353 arsenogoreceixite $[\text{BaFe}_3^{3+}(\text{AsO}_4)(\text{AsO}_3\text{OH})(\text{OH})_6]$; $\text{BaAl}_3(\text{AsO}_4)(\text{AsO}_3\text{OH})(\text{OH})_6$, and
354 bariopharmacosiderite were identified by Raman, μXRD and EMPA (Table 4 ; ESM Figs. 3 and 4) as
355 were the Cu-carbonate minerals malachite and azurite.

356

357

4.2. Weathering stages of fahlore

358 Based on textural evidence, the weathering of fahlore can be subdivided into four weathering stages
359 (Stage 1-4), which are distinguished by textural appearance and phase assemblages. Each weathering
360 stage is developed in variable amounts in the samples and sometimes, one or the other is lacking.

361

4.2.1. Stage 1 weathering

363 This stage occurs in most of the investigated fahlore samples and is characterized by the replacement
364 of fahlore by Cu-sulfides, the Cu-oxide phase, and the RGM-tripuhyite-like phase intergrowth (Figs. 1-
365 4). The Cu-sulfides covellite, spionkopite, and chalcocite commonly occur within the same sample
366 (Fig. 2). Additional Cu-sulfides may be present. Within the Cu-oxide phase, rare nm-sized acanthite or
367 cinnabar grains were observed.

368 In most cases, fahlore is replaced by the secondary assemblage in an irregular network of 30-100 μm
369 thick veinlets and only rarely as a front from outside. These veinlets appear as finger-like tubes
370 without a preferred orientation. They terminate in spherical shape, mostly without evidence of a
371 previous crack in the fahlore (Fig. 1). In general, the finger-like tubes are made up by three different
372 zones, consisting all of RGM and Cu-sulfides in a Cu-oxide groundmass. From the fahlore contact to
373 the centre of the tubes, these zones are:

- 374 • Zone (1) shows layers, which are defined by alternating porosity and small grained (nm-sized)
375 crystal phases.
- 376 • Zone (2) has no porosity, no layering and shows larger grains (several hundred nm to about 5
377 μm), crystals are arranged perpendicular to the tube.
- 378 • Zone (3) in the centre of the tube, forming a central pipe, has crystals arranged parallel to the
379 tube, and sometimes hosts subhedral quartz surrounded by the RGM.

380 The grain size of zones (2) and (3) can show variations between samples, but the overall arrangement
381 of the zones are similar at investigated localities.

382 Depending on the host fahlore chemistry, three different types of RGM phases form (assemblage 1.1:
383 Bi-Sb RGM; assemblage 1.2: Sb-Fe RGM (hydroxyferroroméite); and assemblage 1.3: Bi-Fe RGM). If
384 the fahlore is zoned, assemblage 1.1 to 1.3 can occur within a single fahlore grain (and can change
385 within a single tube; see Figs. 1 and 4), but if the fahlore is homogeneous, only one of the
386 assemblages occurs.

387 If chalcopyrite is intergrown with fahlore, nothing changes with respect to fahlore weathering stage
388 1. Some of the veinlets stop at the contact to chalcopyrite, some continue into it, in which case, the
389 veinlets consist of a red homogeneous amorphous Fe-Cu-oxide phase.

390 Weathered native Bi (which occurs as associated mineral in the fahlore-bearing samples) shows
391 similar finger-like tubes, which are, however, composed of an amorphous Bi-carbonate (Fig. 5).
392 Intergrown aggregates of wittichenite and emplectite in the vicinity of fahlore from Neubulach
393 exhibit the same finger-like textures as observed in fahlore (Fig. 5c). The contact of the tube to
394 wittichenite or emplectite is porous and contains nm-sized Cu-sulfides. Towards the centre of the
395 tube, the groundmass consists of a Bi-carbonate which includes μm -sized Cu-sulfides. The central
396 pipe is composed of aggregates of the Bi-Sb-bearing RGM. Other minerals, in which the finger-like
397 tubes were observed, comprise pyrite, gersdorffite, and nickeline, but it was not the topic of the
398 present research to investigate these further.

399

400 **4.2.2. Stage 2 weathering**

401 This stage is dominated by an amorphous arsenate phase replacing fahlore (Figs. 6-8). In some cases,
402 the stage 1 assemblage is unaffected by younger weathering, but it has also been observed that the
403 Cu-oxides are partially replaced by Cu arsenates, independent of the sample locality. No textural or
404 chemical differences between localities and their different fahlore compositions are observed. Partly,
405 the weathering occurs in poorly developed finger-like textures, but the most common form are
406 arsenate fronts replacing fahlore. The Cu-arsenate phase is texturally highly inhomogeneous:
407 elongate and often curved areas with low porosity alternate with high porosity areas. This porosity is
408 visible on a μm - and nm-scale. Some amorphous layers also show an increased amount of 2-10 nm
409 large crystals of a Cu-oxide phase of unknown composition, whereas other amorphous layers are free
410 of nano-crystals. Often, μm -sized euhedral barite crystals are intergrown or occasionally form
411 alternating layers with the amorphous arsenate (Fig. 9a). Occasionally, small grains of acanthite or
412 cinnabar were observed enclosed by the amorphous Cu-arsenates (Fig. 8). In one sample from
413 Freudenstadt, also bariopharmacosiderite overgrown by barite and the amorphous Cu-arsenate was
414 identified. In this sample, also illite is intergrown with the arsenate. Where chalcopyrite is intergrown
415 with fahlore, an amorphous green arsenate replaces chalcopyrite. Native Bi is frequently surrounded
416 by bismite, partly displaying a zonation (Fig. 5b).

417

418 **4.2.3. Stage 3 weathering**

419 This stage includes weathering steps postdating stage 2, but predating stage 4 weathering textures.
420 Stage 3 weathering textures are specific for a certain sample location and, hence, not part of a
421 general weathering process occurring in the same way at each locality.

422 In Neubulach, weathering stage 3 is characterized by a partial dissolution of stage 1 phases, affecting
423 the Cu-sulfides and Cu-oxide phase, but not the RGM (Fig. 9). The dissolved areas are partly replaced

424 by an amorphous Cu-arsenate-sulfate phase which hosts abundant nm-sized Cu-bearing crystals of
425 unknown composition. This replacement is only observed directly on the unaltered stage 1
426 assemblages (within 100-200 μm), whereas other affected areas leave behind the RGM only, which
427 appears yellow-brown in transmitted light (Fig. 9).

428 In a sample from Königswart, amorphous Cu-silicates cement brecciated clasts of fahlore and
429 weathering assemblage 2 (Fig. 10). The clasts are overgrown by botryoidal aggregates of an
430 amorphous Cu-silicate I, followed by homogeneous amorphous Cu-silicate II which also hosts
431 euhedral quartz crystals.

432

433 **4.2.4. Stage 4 weathering**

434 Weathering stages 1 and 2 replace fahlore in situ. In contrast, assemblages formed during stage 4
435 rarely replace minerals, but (partially) fill cracks or new fracture networks cutting through the
436 primary hydrothermal minerals, the host rock, and older weathering assemblages of stages 1-3 (Fig.
437 11). The most frequent phases are azurite, malachite, and mixite. In one sample, azurite replaced Cu-
438 arsenates of stage 2 (Fig. 11d). In this sample, azurite also infiltrates the stage 1 assemblage,
439 excluding the RGM, but it is unclear whether it replaces it directly or fills the voids of weathering
440 stage 3. No amorphous phases are present in this stage. Minerals identified are olivenite, dussertite-
441 arsenogorceixite, tangdanite, zalesiite, mixite, bariopharmacosiderite, azurite, atelestite, and
442 malachite which are partly accompanied by barite and quartz (the latter also formed during the same
443 weathering process, not representing hydrothermal phases). The mineral assemblage varies from
444 locality to locality (Table 4). Where malachite and azurite occur in the same sample, azurite typically
445 forms in or close to fahlore, whereas malachite is the dominant mineral further away. In one sample,
446 a quartz-hosted azurite vein cuts through hydrothermal gangue minerals and through fahlore-
447 hosted, older weathering assemblages; at the contact with the latter, it changes to an unknown Ca-
448 Cu-arsenate (Fig. 11c).

449

450 **4.3. Mineral chemistry**

451 **4.3.1. Primary hydrothermal minerals**

452 Detailed EMP analyses of fahlore from all localities can be found in Table 2. Samples of this study are
453 all As-dominated showing molar X_{As} ($\text{As}/(\text{As}+\text{Sb})$) between 0.6 and 1.0. The Bi content at each locality
454 is variable, generally ranging between 1 and 12 wt.% (Fig. 12a). Maximum Bi-contents are 15.9 wt.%
455 (Neubulach). Molar X_{Zn} ($\text{Zn}/(\text{Zn}+\text{Fe})$) of the fahlores ranges widely between 0.0 and 0.9. The lowest Zn
456 contents are found in Freudenstadt (median of 1.8 wt.%), followed by Königswart (median of 3.3

457 wt.%), Neubulach (median of 4.2 wt.%), and Wittichen (median of 5.8 wt.%) where also the highest
458 variation is found (from detection limit to 7.9 wt.%). Silver contents reach up to 1.2 wt.%, Hg
459 contents up to 0.9 wt.%, Co and Se contents up to 0.4 wt.%, respectively. Other trace elements
460 identified by LA-ICP-MS are shown in Table 3. Most fahlore shows a growth and occasionally a sector
461 zonation, but the observed weathering textures do not follow a certain chemical zone.

462

463 **4.3.2. Secondary weathering phases – stage 1**

464 Most of stage 1 weathering phases are too small for quantitative analyses by EMPA, however,
465 chemical maps by SEM and TEM, and trace element analyses by LA-ICP-MS provide additional useful
466 information on their composition and elemental distribution and allow to quantify phase
467 compositions, although the attached error is admittedly large.

468 The matrix of stage 1 assemblage, the Cu-oxide phase, contains up to 3.1 wt.% As_2O_5 , 1.2 wt.% Bi_2O_3 ,
469 1.6 wt.% SO_3 and other trace elements below 1 wt.% (Table 1).

470 Covellite, only analysed from Neubulach (TEM-EDX), is almost stoichiometric ($Cu_{0.99}S$; normalised to 2
471 apfu, average of 4 analyses) with Bi up to 5000 ppm as the main trace element (Table 2). Spionkopite
472 was only analysed from Freudenstadt with Ag up to 1.2 wt.%, As up to 1.0 wt.%, and Bi up to 5400
473 ppm besides other trace elements (Table 2). The optically identified chalcocite shows an average
474 chemical formula of $Cu_{2.5}S$ (normalized to 1 apfu S; TEM-EDX) and therefore too high Cu/S ratios.

475 Only the Bi-Sb RGM was analysed by TEM-EDX resulting in the formula $Cu_{1.0}Sb_{1.1}Bi_{1.0}As_{0.3}Fe_{0.7}O_{7.8}$
476 (normalized to 1 apfu Bi; see section 4.1). It contains traces of SiO_2 , Al_2O_3 , BaO, P_2O_5 , and SO_3 (Table
477 1). A mixture of all stage 1 phases from Neubulach, analysed by LA-ICP-MS, resulted in up to 10 ppm
478 V, 150 ppm Mn, 15 ppm Cr, 120 ppm Co, 10 ppm Ni, and 85 ppm Pb (Table 3, Fig. 13). Sample points
479 where Cu-sulfides and the matrix were dissolved during stage 3, leaving voids and only the RGM
480 behind, show higher Mn (up to 330 ppm) and Pb (up to 280 ppm) as well as lower Co (up to 6 ppm)
481 and Ni (up to 2 ppm).

482 The amorphous red oxide phase in weathering stage 1 of chalcopyrite is dominated by Fe and Cu and
483 was analysed from Wittichen and Königswart (n=10). Normalised to 100 mol%, the Fe content varies
484 between 20.3 mol% and 33.6 mol%, the Cu contents between 7.7 mol% and 14.1 mol%. Other main
485 components are variable and include As_2O_5 with up to 4.2 wt.%, SO_3 with up to 3.3 wt.%, and SiO_2
486 with up to 7.4 wt.%.

487

488 **4.3.3. Secondary weathering phases – stage 2**

489 The amorphous Cu-arsenates of stage 2 have variable amounts of Bi_2O_3 (up to 12.3 wt.%) and other
490 components (Table 4). Some data of the Cu-arsenate phase are close to the stoichiometric
491 composition of olivenite, however, the bulk of the data shows variable Cu/As ratios (Fig. 12c; Table
492 4). The totals of the EMPA range from 59 to 97 %, reflecting variable water content and a high and
493 variable porosity.

494 Semi-quantitative TEM/EDX analyses were performed on the Bi-poor and Bi-rich zones of the
495 amorphous Cu-arsenates (Fig. 7a, Table 1). The concentration of Bi_2O_3 is 3.7 and 9.1 wt.%,
496 respectively, which is similar to the EMPA analyses (Table 4). The Bi-poor zone has lower As_2O_5 (17.0
497 wt.%) and CuO (28.5 wt.%) compared to the Bi-rich (27.5 wt.% As_2O_5 and 42.7 wt.% CuO) and higher
498 SO_3 (28.6 wt.% compared to 3.5 wt.%). The Bi-poor zone also has higher Fe_2O_3 and SiO_2 (Table 4).

499

500 **4.3.4. Secondary weathering phases – stage 3**

501 The green amorphous to nano-crystalline arsenates of stage 3 (Fig. 9) are too small for identification
502 by EMPA but were investigated by TEM. They contain 65.5 wt.% CuO, 13.0 wt.% As_2O_3 , 10.0 wt.%
503 SO_3 , and 4.7 wt.% Bi_2O_3 (TEM-EDX) besides other trace elements presented in Table 1.

504 The two silicate-bearing phases from Königswart were analysed by EMPA. The botryoidal Cu-silicate
505 has a higher silica content (22.6 wt.% SiO_2) and a higher total (89.3 %) compared to the
506 homogeneous silicate (11.9 wt.% SiO_2 , total: 73.6 %). The botryoidal phase also contains more As_2O_3
507 (6.4 compared to 5.1 wt.%), FeO (2.4 compared to 0.1 wt.%), and Bi_2O_3 (4.1 compared to 1.8 wt.%).
508 Whether the lower total of the homogenous phase is due to a higher water or carbonate content, or
509 due to porosity, remains unclear.

510

511 **4.3.5. Secondary weathering phases – stage 4**

512 The well-crystallized minerals of stage 4 are in most cases large enough for EMPA, however, a distinct
513 identification was not always possible. Azurite was only analysed from Neubulach and contains up to
514 2.0 wt.% As_2O_5 and 1.1 wt.% FeO. Malachite was analysed from Neubulach, Freudenstadt,
515 Königswart and Wittichen with ZnO up to 2800 ppm in Freudenstadt, Wittichen, and Neubulach, and
516 up to 2.7 wt.% from Königswart. In analyses from Wittichen and Königswart, 3.8 and 0.14 wt.% Bi_2O_3
517 were detected, respectively. Other trace elements are not specific for a location and are As_2O_3 up to
518 2.9 wt.%, Sb_2O_5 up to 5300 ppm, and BaO up to 1400 ppm.

519 Mixite group minerals are abundant minerals of stage 4 from Königswart, Wittichen and Neubulach.
520 Wittichen samples show Ca-bearing mixite, samples from Neubulach and Königswart Bi-bearing
521 zalesiite (Table 4, see also Göb et al., 2011). All analysed mixite group minerals have SiO₂ up to 3.7
522 wt.%. Göb et al. (2011) also report rare earth elements from Neubulach with up to 1.07 wt.% Ce₂O₃.
523 All barite analyses of stage 4 contain Al₂O₃ (up to 9800 ppm), CaO (up to 5300 ppm), and FeO (up to
524 3200 ppm).

525

526

5. Discussion

5.1. Mass Balance Calculations

528 To judge the environmental impact of fahlore weathering, one needs to calculate the amount of each
529 element fixed in the weathering assemblage versus what is released into the fluid. First, one should
530 consider some uncertainties. A certain volume of fahlore needs to be compared to the same volume
531 of its weathering product(s). The volume of the weathering product(s) can be equal, larger or smaller
532 depending on the density of the new phases and whether components were added or lost. Textural
533 criteria are here especially important. In the observed textures of stage 1 are no cracks along or in
534 front of the finger-like tubes and the colloidal phases with irregularly arranged porosity gaps suggest
535 that they formed with only a small volume reduction. The observed weathering stage 2 preserves the
536 habit and Bi-zonation of the original fahlore and includes irregular areas with high porosity;
537 therefore, a volume reduction can be assumed as well. Stage 4 weathering produces fractures
538 throughout the fahlore and beyond into the host rock. These fractures are partially filled with
539 secondary minerals. Therefore, stage 4 weathering textures cannot be used for a quantification of
540 element mobility. Qualitatively, it is obvious that Cu and As are mobile in these stage 4 fluids and
541 leave the immediate vicinity of the weathered fahlore.

542 The mass balance calculation is more robust for main than for trace elements, because of the higher
543 analytical error for the latter. Small secondary phases cause nugget effects (eg., acanthite, cinnabar)
544 and, hence, a large error. Additionally, a small variation in trace elements has a bigger effect on the
545 result (e.g., 1 ppm in fahlore compared to 2 ppm in its weathering product would result in a 100%
546 addition of that element) and is, thus, not comparable to main elements. Therefore, only main
547 elements of fahlore (Cu, Fe, Zn, As, Sb, Bi, S) will be considered in the following calculations (see
548 chapter 5.2, Table 5).

549 For weathering stage 1, the mass balance calculations were performed by graphical volume
550 estimation using BSE images. The observed phases and the amount of porosity of stage 1 weathering
551 were colour coded, and their 2-dimensional surface area was considered equal to their 3-

552 dimensional volume. For the amorphous phases of stage 2, the EMPA analyses were compared
553 directly. The volumes of the phases of both stages were then recalculated using their known or
554 estimated densities (Cu-sulfide: 4.6 g/cm, Cu oxide: 4.0 g/cm, RGM: 7.4 g/cm, Bi-rich Cu arsenate: 4.4
555 g/cm, Bi-poor Cu arsenate: 4.2 g/cm) to their weighted fraction of the total volume of secondary
556 phases considering the porosity. The fraction of each phase and its respective chemical composition
557 determines the total amount of each element present in the total weathering volume. An example of
558 the mass balance calculation is shown in Fig. 14. The colour-coded picture in Fig. 14b shows an RGM
559 content of 12 % by volume which is recalculated using the mentioned densities of the phases to 20
560 wt.%. The RGM was analysed to contain 38.6 wt.% Bi, the Cu-sulfide 1.1 wt.% Bi and the Cu-oxide
561 phase 1.6 wt.% Bi. These numbers calculate to 0.50 g Bi in the RGM, 0.01 g Bi in the Cu-sulfide, and
562 0.02 g Bi in the Cu-oxide phase for each cubic centimetre, resulting in 0.53 g Bi per cubic cm of
563 weathering product. Using the density of fahlore and the analysed Bi content of 12.4 wt.% for the
564 fahlore of Fig. 14, each cubic cm of fahlore has 0.58 g Bi, resulting in 0.05 g loss of Bi (10 %) to the
565 weathering product. Due to the large error of the method it is considered to be immobile. Small
566 changes in the volume estimation of the RGM (which hosts most of the Bi) changes the result
567 significantly (1% change in RGM volume results in 5% elemental mobility). To minimise this
568 uncertainty, multiple colour-coded pictures were analysed to calculate the elemental mobility in Fig.
569 14 and the average mineral content was used in the calculations.

570

571 **5.2. Mineralogy and element mobility during the weathering stages**

572 **5.2.1. Element mobility during stage 1**

573 The investigated fahlores show an intensive primary hydrothermal zonation mostly due to their
574 variable (Sb+As)/Bi ratios. The sharp chemical zoning has a direct influence on the supergene phase
575 assemblages formed during stages 1: If fahlore compositions during stage 1 weathering are
576 compared to the composition of stage 1 veinlets, differences in RGM mineralogy emerge. If bismuth
577 exceeds 0.12 apfu, the weathering textures contain the Bi-Sb-bearing RGM (assemblage 1.1; Fig.
578 12b). This only holds true, if also Sb is present in the fahlore. In zones, where the Bi-content is lower,
579 tripuhite/hydroxyferroroméite develop instead (assemblage 1.2). When fahlore contains less than
580 0.56 apfu Sb at high Bi contents (>10%), the Bi-Fe-bearing RGM forms (assemblage 1.3; Fig. 12b). As
581 As-dominated zones are very thin in the samples studied (Fig. 12a) their weathering is overprinted by
582 the neighbouring high-Bi fahlore and no statement can be made regarding their specific weathering
583 behaviour.

584 Calculation of stage 1 element mobility shows that about one third of the Cu of the secondary
585 assemblage must have been added from an external source (Fig. 14c). Zinc was completely, As and S
586 partially (80-90% and 60-80%, respectively) lost. Different behaviour in element mobility is observed
587 for Fe and Sb, depending on initial fahlore composition. Both elements behave almost immobile if
588 fahlore is Bi-rich. In Bi-poor fahlore, however, more than half of the Fe and Sb of the fahlore is
589 released into the fluid, indicating that Bi stabilizes the RGM phase. Bi behaves basically immobile in
590 all investigated stage 1 assemblages.

591 If fahlore contains elevated Ag contents, nm- to μm -sized acanthite grains are found between the Cu-
592 sulfides of stage 1 (or enclosed in the amorphous phase of stage 2). In a sample from Freudenstadt,
593 acanthite was found next to a fahlore zone with 6000 ppm Ag; no acanthite was found in the next
594 fahlore zone which contains 2000 ppm Ag. In a sample containing 4300 ppm to 8500 ppm Hg in
595 fahlore, small cinnabar grains were found in between the Bi-Sb-bearing RGM. Hence, Ag and Hg can
596 be regarded to behave mostly immobile during stage 1 weathering.

597 Although trace element mobility during weathering cannot be quantified (see section 5.1), some
598 qualitative estimation can be made. From Fig. 13a, it is obvious that at least 90% of the fahlore's Co is
599 lost during stage 1 and 2 weathering. The Co content retained during stage 1 is mostly found in the
600 Cu-sulfide or Cu-oxide phases, whereas the RGM contains an order of magnitude less Co. Manganese
601 and vanadium are about 1 to 2 orders of magnitude higher in the weathering assemblage 1
602 compared to fahlore (Fig. 13b), proving that they were added from an external source by the
603 weathering fluid, whereas stage 2 assemblage has concentrations similar to fahlore – hence, Mn and
604 V are immobile during this stage. In stage 1, Mn, V, Cr, and Pb (Fig. 13b, Table 3) are mostly retained
605 in the RGM, but unfortunately, no conclusion about Cr and Pb mobility can be drawn from the data.

606 During weathering stage 1, Si was added to form quartz. It precipitated first, as it occurs always in the
607 centre of the veinlets and the Bi-Sb-bearing RGM overgrows it.

608

609 **5.2.2. Element mobility during stage 2**

610 Calculation of the stage 2 element mobilization from all investigated samples shows that almost no
611 As is mobilized during the formation of the amorphous phase (Fig. 14d). The most striking feature of
612 stage 2 weathering is the survival of the fahlore zonation caused by Bi in the supergene amorphous
613 arsenate phase (Fig. 6). Bismuth-rich zones show no mobilization of Bi, but Bi-poor zones show an
614 apparent addition (Fig. 14d). This is, however, most likely an effect of the low concentration of Bi and
615 hence of the larger error of the method (Freudenstadt sample: 0.1-2.4 wt.% Bi in low Bi-fahlore, 0.2-
616 3.8 wt.% Bi in amorphous phase). Taking the zonation shown in Fig. 6 into account, it is unlikely that

617 significant amounts of Bi were mobilized and hence, it can be assumed that Bi is immobile also in the
618 low-Bi zones. Elements that are partly mobilized in all investigated samples are Cu (approximately a
619 third) and Sb (approximately half), whereas Zn and S are almost completely mobilized. The only S
620 remaining in stage 2 are sulfides of Ag and Hg and some sulfate to form barite. Elements added are
621 Fe (up to 110% more than previously incorporated in fahlore) and Ba to form barite. Cu-bearing
622 amorphous arsenates have also been described next to fahlore from the Clara mine (Schwarzwald,
623 Germany, Walenta 1992), Špania Dolina-Piesky and L'ubietová-Svätodušná (Slovakia, Borčinová
624 Radková et al., 2017), Mount Cervandone (Swiss-Italian border, Guastoni et al., 2006), Cínovec (Czech
625 Republic, Pauliš et al., 2008), and Mt. Pleasant (Canada, Petrunic et al., 2009) showing that it typically
626 forms during fahlore weathering, even in a wide variety of geological settings and in variable host
627 rocks.

628

629 **5.2.3. Element mobility during stage 3**

630 Stage 3 is a local weathering stage which mostly affects the older weathering assemblage and not the
631 original fahlore. Therefore, no mass balance calculation was done. The assemblage itself shows that
632 Si was externally derived to form Cu-silicates in the Königswart samples (Table 4). In Neubulach it
633 shows that the Cu-oxide phase and the Cu-sulfides are dissolved and, hence, Cu and S are mobile.
634 The formation of the amorphous Cu-arsenate-sulfate also records the mobility of As during this
635 stage.

636

637 **5.2.4. Element mobility during stage 4**

638 Stage 4 weathering minerals (e.g., azurite, mixite group minerals, bariopharmacosiderite) are
639 spatially not directly related to fahlore and only in exceptional cases, they replace older weathering
640 products. Hence, a mass balance calculation is not meaningful. The mineral assemblage, however,
641 shows that Ca, Si, Ba, Al, and C must have been added from external sources. The dissolution of host
642 rock (limestone, clastic redbeds, granite) and gangue (barite, quartz, fluorite) delivers elements like
643 C, Si, Ba, Al and Ca. This is particularly striking at Neubulach, where stage 4 minerals are (due to the
644 limestone relics on top of the deposit) Ca- or carbonate-dominated.

645 Copper to form azurite could be partially derived from older weathering products of stage 1 and 2, as
646 stage 4 minerals were observed to replace them (Fig. 11d). This would indicate that during this stage
647 also As, Bi, Sb, and Fe are released from earlier weathering assemblages, which could represent the
648 formation of the commonly occurring stage 4 mixite group minerals or bariopharmacosiderite. The

649 only Sb-bearing phase is the dusserite-arsenogorceixite solid-solution from Freudenstadt. Possibly, at
650 other localities, especially Neubulach, where dissolution of stage 2 was observed and no secondary
651 Sb minerals are known besides the RGM according to Walenta (1992), both elements were released
652 into the fluid during this weathering stage.

653 The mineral assemblage shows that during stage 4, Cu, As, Bi, Sb, and Fe are mobile. As discussed
654 above, the source of these elements is probably the dissolution of older weathering assemblages
655 (e.g., stages 1 and 2). A renewed dissolution of fahlore to form stage 4 minerals was not observed,
656 but cannot be ruled out. Also, weathering of other minerals of the primary mineral assemblage (e.g.,
657 chalcopyrite, emplectite, arsenides) could deliver elements like Cu, Bi, or As, to form stage 4
658 minerals.

659 Stage 4 minerals cover much larger areas than the previous weathering stages. Therefore, they
660 record the widespread mobilization of elements (e.g., Cu and As) which originated from fahlore. This
661 mobilization is therefore visually the most obvious weathering stage (e.g., ESM Fig. 2a). Other
662 deposits with large amounts of fahlore comprise a similarly large variety of Cu-bearing arsenates as
663 observed at the localities investigated (see Markl, 2015, for mineral lists of these deposits). Other
664 typical and well-known occurrences of such rich supergene arsenate assemblages include the Clara
665 mine (Schwarzwald, Germany; Markl 2015), Tsumeb (Namibia; Bowell 2014), or Bou Skour (Morocco,
666 Dietrich et al., 1969) to name just a few.

667

668 **5.3. The process of fahlore weathering**

669 Weathering of fahlore produces characteristic replacement textures observed independent of
670 deposit type, initial fahlore chemistry, or weathering assemblage (Nickel et al., 2007; Petrunic et al.,
671 2009; Borčinová Radkova et al., 2017; Mills et al., 2017). As described above, two types can be
672 distinguished: (1) A network of finger-/tube-like conduits infiltrating the fahlore without a visible
673 fracture and (2) a replacement front proceeding through the fahlore. Type (1) is the only type found
674 in stage 1 weathering, whereas both types are found in stage (2) where, however, the replacement
675 front is dominant. This difference implies that different processes take place during both stages.

676 The formation of secondary phases during weathering and/or alteration in general can be due to
677 incongruent dissolution (scorodite dissolution; Harvey et al., 2006), dissolution and re-precipitation in
678 an aqueous solution (weathering of electrum, Mann, 1984), support by bacteria (sulfide conversion
679 to schwertmannite; Dockrey et al., 2014), or reaction of an aqueous solution with the primary
680 mineral to form a gel-like fluid in which later secondary phases may crystallize by dehydration
681 (hematite from poorly crystalline ferrihydrite; Cudennec and Lecerf, 2006). An incongruent

682 dissolution during fahlore weathering can be excluded based on the observed textures (e.g., finger-
683 like tubes) and based on the fact, that during incongruent dissolution, the primary phase is
684 successively coated by the secondary phases thus significantly reducing its reactivity (Harvey et al.,
685 2006). No secondary coating of any phase was observed around fahlore. A bacterial influence is also
686 unlikely to explain the observed textures and complex intergrowth of secondary phases.

687 The observed textures of weathering stages 1 and 2 (Figs. 1 to 8) show colloform layered aggregates.
688 Stage 2 phases are X-ray amorphous but partly include nm-sized crystals. Raman analyses identified
689 arsenate but also water within the amorphous phases of stage 2. The textures combined with the
690 analytical results indicate that the weathering product of fahlore forms a gel-like phase, which is in
691 this case a hydrous amorphous phase which could contain nm-sized crystals or from which nm-sized
692 crystals formed due to dehydration during a later stage. The stage 1 assemblage was shown to be
693 completely crystalline, although the textures support also a crystallization from a gel. In this case, the
694 crystallization starts from the centre of the tube and from its margin, forming nm-sized crystals of Cu-
695 sulfides and the Bi-Sb-Fe phase gradually increasing in size towards the inner mantle of the tube. As
696 there are no hydrous phases observed, it can be assumed that the crystallization was initiated by
697 dehydration of the gel.

698 Fracture patterns in mineral replacement reactions were investigated by Malthe-Sørenssen et al.
699 (2006) by theoretical modelling. They found that a volume reduction between reactant and product
700 during chemical processes enhances fluid penetration along contraction fractures into the reactant
701 due to a better diffusion of chemicals. Janssen et al. (2010) used ilmenite to produce alteration
702 products by the reaction with HCl-solutions of different concentrations. They concluded that a highly
703 concentrated solution alters the mineral more quickly, forming a replacement front from the outer
704 surface of the mineral. A solution of low HCl-concentration, on the other hand, forms a network of
705 finger-like veinlets and over a longer reaction time creates its own fractures due to the reaction,
706 according to the process described by Malthe-Sørenssen et al. (2006).

707 The fahlore weathering textures of stage 1 look remarkably similar to the patterns found in the low-
708 HCl-concentration experiment by Janssen et al. (2010). Along the centre of the finger-like tubes in
709 Janssens experiments runs an open crack and resembles the quartz and RGM found in the centre of
710 the stage 1 textures. The experiment by Janssen et al. (2010) with the more concentrated HCl-
711 solution replaces the mineral completely, but leaves a pattern of alternating high porosity areas with
712 inhomogeneous layers of the product. This is similar to the stage 2 textures, where inhomogeneous
713 arsenate phases alternate with high porosity areas (Fig. 6a).

714 The experiments by Janssen et al. (2010) were driven by different HCl concentrations in the fluid and
715 therefore different acidity. In the case of the fahlore weathering, the driving force for the formation
716 of new phases is the oxidation potential of the weathering fluid (see next section 5.4). It is therefore
717 likely, that the stage 1 weathering assemblage formed by reaction with a fluid of lower oxygen
718 fugacity than stage 2, and hence can explain the similarities to the textures found in the experimental
719 observations.

720 Similar tube-like weathering or alteration textures have also been observed in the study on ilmenite
721 by Janssen et al. (2010), in basaltic glass on the sea floor (Fig. 2 in Dultz et al., 2014), in galena
722 forming quartz, acanthite, and native Au in the assemblage (Fig. 5 in Kamenov et al., 2013), and in
723 native Bi, wittichenite, emplectite, pyrite, gersdorffite, and nickeline in samples investigated in the
724 course of this study. Hence, this short compilation is a very general, basic process reflected in always
725 similar textures in a large variety of native elements, oxide, sulfide and arsenide minerals.

726

727 **5.4. Redox processes on the deposit-scale**

728 During fahlore weathering, Cu, As, Fe, Sb and S are increasingly oxidized from stage 1 to stage 4
729 reflecting a stepwise change of the oxidation potential of the weathering fluids interacting with the
730 ore deposit. In the primary deposit, fahlore and the other sulfides are in equilibrium with the
731 surrounding minerals and fluids and no oxidation processes take place. Hence, the elemental budget
732 remains constant. During weathering of stage 1, the surrounding environment of the ore body
733 changes to moderate oxygen fugacity producing the stable assemblage of oxides and sulfides. A
734 moderate oxidation potential is also supported by the finger-like appearance of the weathering
735 phases as discussed above (chapter 5.3). The loss of 60-80 % of sulfur during the first stage reveals
736 that sulfur is most likely partially oxidized to sulfate and transported away besides the precipitation
737 as S^{2-} in the Cu-sulfides. This implies that f_{O_2} during this stage is somewhere around the sulfide-
738 sulfate transition. Antimony and Fe in fahlore (Sb^{3+} , Fe^{2+}) are oxidized to Sb^{5+} in the RGM phases, and
739 to Fe^{3+} in tripuhyite (in hydroxyferroroméite, it is reported to be Fe^{2+} , Mills et al., 2017). Stable Sb^{5+}
740 (and Fe^{3+}) compounds in similar environments were also reported by Leverett et al. (2012) and
741 Borčinová Radková et al. (2017). In contrast to As and Sb, Bi stays in its most stable 3+ oxidation state
742 (Whitmire, 2013). The fact that no arsenates are formed during stage 1 implies that As probably stays
743 in its 3+ oxidation state and is therefore mobile and rapidly lost during this initial weathering stage as
744 shown by the mass balance calculations in chapter 4.2. This observable difference in oxidation
745 behaviour of Sb and As follows the general oxidation potentials of both metals (Norman, 1998).

746 The change from a reducing to a more oxidized environment occurs when ore deposits are exposed
747 to near surface environments, for example by erosional processes. Also an increasing amount of
748 meteoric fluids, e.g., due to climatic variations, can result in deeper infiltration of oxidized fluids (Park
749 and MacDiarmid 1975). The change from reduced to more oxidized conditions during weathering
750 stage 1 is likely to reflect the transition of the primary ore body to the cementation zone and
751 therefore a general change also in the vein-hosting fluid aquifers.

752 Weathering stage 2 records a more aggressive fluid which is far from equilibrium with the fahlore.
753 The occurrence of arsenates and the absence of Cu-sulfides reflects higher oxygen fugacities than
754 during stage 1. Such assemblages are typical of oxidation zones of hydrothermal ore deposits
755 (Magalhaes et al., 1988). The oxidation potential during this stage, however, is not high enough to
756 alter stage 1 (e.g., the sulfides), since both assemblages coexist.

757 The partial loss of Cu in stage 2 and the addition of Cu in stage 1 could point to mobilization of Cu
758 from upper parts of the weathering profile (e.g., oxidation zone) down to the cementation zone, or
759 an evolution of the fluid from a stage 2 fluid towards a stage 1 fluid. For such a fluid evolution,
760 however, there is no textural evidence on the small scale; rather, it appears to be a process on the
761 scale of a deposit. An opposite evolution of a stage 1 towards a stage 2 fluid by fluid-mineral
762 interaction can be ruled out as during stage 1, oxygen is consumed and hence, the f_{O_2} in the fluid
763 decreases – stage 2 phases, however, require an increased f_{O_2} (see above).

764 In contrast to the earlier in-situ stages, stage 1 and 2 phases are dissolved during stages 3 and 4, the
765 solution is transported away and newly formed minerals occur in cracks, fill empty voids or brecciate
766 former weathering stages. Besides the textural change of the weathering products, also a chemical
767 change of the weathering phases can be observed: during stage 3 and 4, mostly carbonates and Cu-,
768 Ca-, Ba-, and/or Al-Arsenates are formed. This shows the change from an in-situ controlled (more or
769 less closed?) system to an open system, and the strong mobility of elements could reflect the gossan
770 in the classical weathering profile of ore deposits.

771 Hence, the temporal evolution of fahlore weathering textures reflects the transition from fresh ore
772 to cementation zone, oxidation zone and finally gossan textures and assemblages in one hand
773 specimen. One fahlore grain can, thus, record the uplift and erosion of an ore deposit and the
774 increasing fluid/rock interaction of a weathered ore deposit with time.

775

776 **6. Summary and conclusions**

777 The weathering of Bi-bearing tennantite-tetrahedrite solid-solution can be classified in four
778 subsequent stages based on texture, mineralogy, and composition:

779 1. The first stage forms irregular finger-like veinlets within fahlore with crystalline Cu-sulfides
780 and minerals of the roméite group (RGM) in a crystalline Cu-oxide groundmass. The chemistry of the
781 RGM is dependent on the fahlore chemistry. During this stage, most of Zn and some of As and S of
782 the fahlore is mobile and lost to the fluid. External Si is added to form quartz during this stage. In Bi-
783 rich fahlore Fe, Bi and Sb are immobile and captured in the RGM, whereas Bi-poor fahlore releases
784 parts of its Fe and Sb to the environment upon weathering. Sulfur is partly immobile and fixed in Cu-
785 sulfides. The secondary sulfides and the addition of Cu suggest that these textures reflect the
786 cementation zone of a classical weathering profile, in which only some elements are already oxidized
787 (e.g., Sb, Fe).

788 2. This stage forms reaction fronts through the fahlore composed of amorphous to nano-
789 crystalline porous Cu-arsenates. Arsenic is immobile during this stage, whereas most of the S, Zn, and
790 Sb is transported away by the fluid. Iron, together with Ba, is added to the assemblage. Bismuth is
791 also immobile during this stage and is incorporated in the arsenate phase; the Bi-zonation of the
792 primary fahlore is retained. This stage is typical of the oxidation zone due to the complete oxidation
793 of the remaining elements (i.e., Cu, S, As).

794 3. This stage is locally restricted and not part of the general process, but represents micro
795 compartments. In the Neubulach samples, stage 3 partly dissolves previous weathering assemblages
796 and crystallized a minor Cu-arsenate-sulfate assemblage. In Königswart samples, older weathering
797 assemblages were brecciated and cemented by amorphous Cu-silicates. The assemblages show that
798 Si, Cu, and As are mobile during this stage.

799 4. This stage is spatially independent from fahlore and secondary minerals form on fractures
800 and partly fill the voids of stage 3. Their mineralogy is dependent on the hydrothermal assemblage
801 and the local host rocks. Calcium- or carbonate-bearing minerals, for example, are most abundant in
802 vicinity to limestones (Neubulach). This stage represents a typical gossan mineralization with a
803 widespread mobilization of metals as it is also observed at the Clara mine (Schwarzwald, Germany;
804 Markl, 2015), from Tsumeb (Namibia; [Bowell, 2014](#)), and Bou Skour (Morocco, [Dietrich et al., 1969](#)).

805 The physical process of weathering reflects the chemical gradient between fahlore and meteoric
806 fluid. During stage 1 in the cementation zone, the chemical gradient (i.e. redox potential) and the
807 fluid/mineral ratio is low. This causes the formation of finger-like tubes, filled by a gel-like phase
808 which then dehydrates and crystallizes. These textures are very similar to textures found by
809 experimental alteration of ilmenite by low-concentrated acid. In the oxidation zone, the chemical
810 gradient between fluid and fahlore and the fluid/mineral ratio is higher; reaction fronts overprint the
811 fahlore in this stage 2 and record a process that is probably orders of magnitude faster than
812 formation of stage 1. These textures are also very similar to textures found by experimental
813 alteration of ilmenite, but in this case by high-concentrated acid. In the final stages 3 and 4, the

814 chemical gradients and fluid/mineral ratios are greatest, and secondary minerals form spatially
815 independent from the original fahlore location.

816 Bismuth is retained in the weathering products during stages 1 and 2. Bi-rich secondary minerals like
817 mixite, bismutite or atelestite formed during stage 4 only at localities, where native Bi or Bi-Cu
818 sulfides (wittichenite, emplectite) are abundant. These phases, in contrast to fahlore, obviously
819 release Bi to weathering fluids.

820 The observed textures of stage 1 are reported from other weathering environments and from a
821 variety of native elements, oxide, arsenide and sulfide phases. This indicates that in weathering
822 environments with a low redox- or chemical potential in general, diffusive weathering processes are
823 very common. This is clear evidence for the fact, that the diffusive process during the first contact
824 with oxidizing fluids to form cementation zone assemblages is a very basic process and not only valid
825 for fahlore.

826

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834 **References**

- 835 Arroyo Y. R. R. and Siebe C. (2007) Weathering of sulphide minerals and trace element speciation in
836 tailings of various ages in the Guanajuato mining district, Mexico. *Catena* **71**(3), 497-506.
- 837 Atencio D. Andrade M. B. Christy A. G. Gieré R. and Kartashov P. M. (2010) The pyrochlore
838 supergroup of minerals: nomenclature. *Can. Mineral.* **48**(3), 673-698.
- 839 Bachmann K. Frenzel M. Krause J. and Gutzmer J. (2017) Advanced identification and quantification
840 of In-bearing minerals by scanning electron microscope-based image analysis. *Microsc. Microanal.*
841 **23**, 527-537.
- 842 Baggio S. B. Hartmann L. A. Lazarov M. Massone H. J. Opitz J. Theye T. and Viefhaus T. (2018) Origin
843 of native copper in the Paraná volcanic province, Brazil, integrating Cu stable isotopes in a multi-
844 analytical approach. *Miner. Deposita* **53**, 417-434.
- 845 Berthold C. Bjeoumikhov A. and Brügemann L. (2009) Fast XRD² Microdiffraction with Focusing X-Ray
846 Microlenses. *Part. Part. Syst. Char.* **26**, 107-111.
- 847 Biskupek J. and Kaiser U. (2004) Practical considerations on the determination of the accuracy of the
848 lattice parameters measurements from digital recorded diffractograms. *J. Electron Microsc.* **53**(6),
849 601-610.
- 850 Bliedtner M. and Martin M. (1986) *Erz- und Minerallagerstätten des Mittleren Schwarzwaldes*. LGRB,
851 Freiburg. pp. 786.
- 852 Bons P. D. Fusswinkel T. Gomez-Rivas E. Markl G. Wagner T. and Walter B. (2014) Fluid mixing from
853 below in unconformity-related hydrothermal ore deposits. *Geology* **42**, 1035-1038.
- 854 Borčinová Radková A. Jamieson H. Lalinská-Voleková B. Majzlan J. Števkó M. and Chovan M. (2017)
855 Mineralogical controls on antimony and arsenic mobility during tetrahedrite-tennantite weathering
856 at historic mine sites Špania Dolina-Piesky and Ľubietová-Svätodušná, Slovakia. *Am. Mineral.* **102**(5),
857 1091-1100.
- 858 Bowell R. J. (2014) Hydrogeochemistry of the Tsumeb deposit: Implications for arsenate mineral
859 stability. *Rev. Mineral. Geochem.* **79**, 589-627.
- 860 Breskovska V. and Tarkian M. (1994) Compositional variation in Bi-bearing fahlores. *Neues JB. Miner.*
861 *Monat.* **5**, 230-240.
- 862 Bucher K. Zhu Y. and Stober I. (2009) Groundwater in fractured crystalline rocks, the Clara mine,
863 Black Forest (Germany). *Int. J. Earth Sci.* **98**(7), 1727-1739.
- 864 Burisch M. Walter B. F. Wälle M. and Markl G. (2016) Tracing fluid migration pathways in the root
865 zone below unconformity-related hydrothermal veins: Insights from trace element systematics of
866 individual fluid inclusions. *Chem. Geol.* **429**, 44-50.
- 867 Burmann F. Keim M. F. Oelmann Y. Teiber H. Marks M. A. W. and Markl G. (2013) The source of
868 phosphate in the oxidation zone of ore deposits: Evidence from oxygen isotope composition of
869 pyromorphite. *Geochim. Cosmochim. Acta* **123**, 427-439.
- 870 Christy A. G. and Atencio D. (2013) Clarification of status of species in the pyrochlore supergroup.
871 *Mineral. Mag.* **77**(1), 13-20.

872 Cudennec Y. and Lecerf A. (2006) The transformation of ferrihydrite into goethite or hematite,
873 revisited. *J. Solid State Chem.* **179**(3), 716-722.

874 Dietrich J. E. Orliac M. and Permingeat F. (1969) L'agardite, une nouvelle espèce minérale, et le
875 problème du chlorotile. *B. Soc. Fr. Mineral Cr.* **92**, 420-434.

876 Dockrey J. W. Lindsay M. B. J. Mayer K. U. Beckie R. D. Norlund K. L. I. Warren L. A. and Southam G.
877 (2014) Acidic microenvironments in waste rock characterized by neutral drainage: Bacteria-mineral
878 interactions at sulfide surfaces. *Minerals* **4**, 170-190.

879 Downs R. T. (2006) The RUFF Project: an integrated study of the chemistry, crystallography, Raman
880 and infrared spectroscopy of minerals. *Program and Abstracts of the 19th General Meeting of the*
881 *International Mineralogical Association*, Kobe, Japan, O03-13.

882 Dultz S. Boy J. Dupont C. Halisch M. Behrens H. Welsch A. M. Erdmann M. Cramm S. Hensch G. and
883 Deubner J. (2014) Alteration of a submarine basaltic glass under environmental conditions
884 conducive for microorganisms: Growth pattern of the microbial community and mechanism of
885 palagonite formation. *Geomicrobiol. J.* **31**, 813-834.

886 Fandrich R. Gu Y. Burrows D. and Moeller K. (2007) Modern SEM-based mineral liberation analysis.
887 *Int. J. Miner. Process.* **84**, 310-320.

888 Franzke H. J. and Werner W. (1994) Wie beeinflusste die Tektonik des Kristallins und des
889 Rheingrabens die hydrothermalen Gangstrukturen des Schwarzwaldes? *Abh. Geol. Landesamt Bad.-*
890 *Württ.* **14**, 99-118.

891 George L. L. Cook N. J. and Ciobanu C. L. (2017) Minor and trace elements in natural tetrahedrite-
892 tennantite: Effects on element partitioning among base metal sulphides. *Minerals* **7**(2) 1-25.

893 Geyer O. F. and Gwinner M. P. (2011) *Geologie von Baden-Württemberg*. Schweizerbart'sche
894 Verlagsbuchhandlung, Stuttgart. pp. 627.

895 Göb S. Wenzel T. Bau M. Jacob D. E. Loges A. and Markl G. (2011) The redistribution of rare-earth
896 elements in secondary minerals of hydrothermal veins, Schwarzwald, Southwestern Germany. *Can.*
897 *Mineral.* **49**, 1305-1333.

898 Göb S. Gühring J. E. Bau M. and Markl G. (2013a) Remobilization of U and REE and the formation of
899 secondary minerals in oxidized U deposits. *Am. Mineral.* **98**, 530-548.

900 Göb S. Loges A. Nolde N. Bau M. Jacob D. E. and Markl G. (2013b) Major and trace element
901 compositions (including REE) of mineral, thermal, mine and surface waters in SW Germany and
902 implications for water-rock interaction. *Appl. Geochem.* **33**, 127-152.

903 Göb S. Bau M. and Markl G. (2015) Chemical composition of waters in a former Cu-As mine: water-
904 rock interaction, REE systematics and stability of secondary copper minerals. *Neues JB. Miner. Abh.*
905 **192**(1) 11-32.

906 Gołębiowska B. Pieczka A. and Parafiniuk J. (2012) Substitution of Bi for Sb and As in minerals of the
907 tetrahedrite series from Rędziny, Lower Silesia, southwestern Poland. *Can. Mineral.* **50**(2), 267-279.

908 Guastoni A. Pezzotta F. and Vignola P. (2006) Characterization and genetic inferences of arsenates,
909 sulfates and vanadates of Fe, Cu, Pb, Zn from Mount Cervandone (Western Alps, Italy). *Period.*
910 *Mineral.* **75**, 414-150.

- 911 Harvey M. C. Schreiber M. E. Rimstidt J. D. and Griffith M. M. (2006) Scorodite dissolution kinetics:
912 Implication for arsenic release. *Environ. Sci. Technol.* **40**, 6709-6714.
- 913 Haßler K. Taubald H. and Markl G. (2014) Carbon and oxygen isotope composition of Pb-, Cu- and Bi-
914 carbonates of the Schwarzwald mining district: Carbon sources, first data on bismutite and the
915 discovery of an oxidation zone formed by ascending thermal water. *Geochim. Cosmochim. Acta* **133**,
916 1-16.
- 917 Hautmann S. and Lippolt H. J. (2000) $^{40}\text{Ar}/^{39}\text{Ar}$ dating of central European K-Mn oxides – a
918 chronological framework of supergene alteration processes during the Neogene. *Chem. Geol.* **170**,
919 37-80.
- 920 Hofmann B. and Eikenberg J. (1991) The Krunkelbach uranium deposit, Schwarzwald, Germany:
921 correlation of radiometric ages (U-Pb, U-Xe-Kr, K-Ar, ^{230}Th - ^{234}U) with mineralogical stages and fluid
922 inclusions. *Econ. Geol.* **86**, 1031-1049.
- 923 Ixer R. A. (2001) An assessment of copper mineralization from the Great Orme mine, Llandudno,
924 North Wales, as ore in the Bronze Age. *P. Yorks. Geol. Soc.* **53**, 213-219.
- 925 Janssen A. Putnis A. Geisler T. and Putnis C. V. (2010) The experimental replacement of ilmenite by
926 rutile in HCl solutions. *Mineral. Mag.* **74**, 633-644.
- 927 Johnson N. E. Craig J. R. and Rimstidt J. D. (1986) Compositional trends in tetrahedrite. *Can. Mineral.*
928 **24**(2), 385-397.
- 929 Kamenov G. D. Melchiorre E. B. Ricker F. N. and DeWitt E. (2013) Insights from Pb isotopes for native
930 gold formation during hypogene and supergene processes at Rich Hill, Arizona. *Econ. Geol.* **108**,
931 1577-1589.
- 932 Keim M. F. and Markl G. (2015) Weathering of galena: Mineralogical processes, hydrogeochemical
933 fluid path modelling, and estimation of the growth rate of pyromorphite. *Am. Mineral.* **100**, 1584-
934 1594.
- 935 Keim M. F. Vaudrin R. and Markl G. (2016) Redistribution of silver during supergene oxidation of
936 argentiferous galena: A case study from the Schwarzwald, SW Germany. *Neues JB. Miner Abh.* **193**(3),
937 295-309.
- 938 Keim M. F. Gassmann B. and Markl G. (2017) Formation of basic lead phases during fire-setting and
939 other natural and man-made processes. *Am. Mineral.* **102**(7), 1482-1500.
- 940 Kolitsch U. (2000) Eine durch Betoneinwirkung entstandene Paragenese von Blei-Verbindungen aus
941 der Grube Clara im mittleren Schwarzwald. *Erzgräber* **14**, 48-53.
- 942 Kozub G. A. (2014) Distribution of Ag in Cu-sulfides in Kupferschiefer deposits, SW Poland.
943 *Geophysical Research Abstracts* **16**, EGU2014-8944.
- 944 Lara R. H. Velázquez L. J. Vazquez-Arenas J. Mallet M. Dossot M. Labastida I. Sosa-Rodríguez F. S.
945 Espinosa-Cristóbal L. F. Escobedo-Bretado M. A. and Cruz, R. (2016) Arsenopyrite weathering under
946 conditions of simulated calcareous soil. *Environ.Sci. Pollut. R.* **23**(4), 3681-3706.
- 947 Leach D. L. Landis and G. P. and Hofstra A. H. (1988) Metamorphic origin of the Coeur d'Alene base-
948 and precious-metal veins in the Belt basin, Idaho and Montana. *Geology* **16**, 122-125.
- 949 Leverett P. Reynolds J. K. Roper A. J. and Williams P. A. (2012) Tripuhyite and schafarzikite: two of the
950 ultimate sinks for antimony in the natural environment. *Mineral. Mag.* **76**(4), 891-902.

- 951 Lippolt H. J. Brander T. and Mankopf N. R. (1998) An attempt to determine formation ages of
952 goethites and limonites by (U+Th)-⁴He dating. *Neues JB. Miner. Monat.* **11**, 505-528.
- 953 Magalhaes M. C. F. Pedrosa de Jesus J. D. and Williams P. A. (1988) The chemistry of formation of
954 some secondary arsenate minerals of Cu(II), Zn(II) and Pb(II). *Mineral. Mag.* **52**, 679–690.
- 955 Makovicky E. (2006) Crystal structures of sulfides and other chalcogenides. *Rev. Mineral. Geochem.*
956 **61**, 7-125.
- 957 Malthe-Sørensen A. Jamtveit B. and Meakin P. (2006) Fracture patterns generated by diffusion
958 controlled volume changing reactions. *Phys. Rev. Lett.* **96**, 245501.
- 959 Mann A. W. (1984) Mobility of gold and silver in lateritic weathering profiles: Some observations
960 from Western Australia. *Econ. Geol.* **79**, 38-49.
- 961 Markl G. (2005) *Bergbau und Mineralienhandel im fürstenbergischen Kinzigtal*. Markstein Verlag,
962 Filderstadt. pp. 448.
- 963 Markl G. Marks M. A. W. Derrey I. and Gühring J. E. (2014a) Weathering of cobalt arsenides: Natural
964 assemblages and calculated stability relations among secondary Ca-Mg-Co arsenates and carbonates.
965 *Am. Mineral.* **99**, 44-56
- 966 Markl G. Marks M. A. W. Holzäpfel J. and Wenzel T. (2014b) Major, minor, and trace element
967 composition of pyromorphite-group minerals as recorder of supergene weathering processes from
968 the Schwarzwald mining district, SW Germany. *Am. Mineral.* **99**, 1133-1146.
- 969 Markl G. (2015) *Schwarzwald: Lagerstätten und Mineralien aus vier Jahrhunderten. Band 1,*
970 *Nordschwarzwald und Grube Clara*. Bode Verlag, Salzhemmendorf. pp. 672.
- 971 Markl G. (2016) *Schwarzwald, Lagerstätten und Mineralien aus vier Jahrhunderten. Band 2: Mittlerer*
972 *Schwarzwald Teil 1*. Bode Verlag, Salzhemmendorf. pp. 648.
- 973 Massone H. J. Opitz J. Theye T. and Nasir S. (2013) Evolution of a very deeply subducted
974 metasediment from As Sifah, northeastern coast of Oman. *Lithos* **156**, 171-185.
- 975 Metz R. Richter M. and Schürenberg H. (1957) Die Blei-Zink-Erzgänge des Schwarzwaldes. *Geol. Jb.*
976 *Beihefte* **29**, 1-277.
- 977 Metz R. (1977) *Mineralogisch-landeskundliche Wanderungen im Nordschwarzwald, besonders in*
978 *desses alten Bergbaurevieren*. Moritz Schaufenburg Verlag, Lahr. pp. 277.
- 979 Mills S. J. Christy A. G. Rumsey M. S. Spratt J. Bittarello E. Favreau G. Ciriotti M. and Berbain C. (2017)
980 Hydroxyferroroméite, a new secondary weathering mineral from Oms, France. *Eur. J. Mineral.* **29**,
981 307-314.
- 982 Moëlo Y. Makovicky E. Mozgova N. N. Jambor J. L. Cook N. Pring A. and Balic-Žunic T. (2008) Sulfosalt
983 systematics: a review. Report of the sulfosalt sub-committee of the IMA Commission on Ore
984 Mineralogy. *Eur. J. Mineral.* **20**(1), 7-46.
- 985 Mueller A. G. and Muhling J. R. (2013) Silver-rich telluride mineralization at Mount Charlotte and Au-
986 Ag zonation in the giant Golden Mile deposit, Kalgoorlie, Western Australia. *Miner. Deposita* **48**, 295-
987 311.

- 988 Nickel E. H. Williams P. A. Downes P. J. Buchert D. E. and Vaughan D. (2007) Secondary minerals in a
989 tennantite boxwork from the Bali Lo prospect, Ashburton Downs, Western Australia. *Aust. J. Miner.*
990 **13**, 31-39.
- 991 Norman N. C. (1998) *Chemistry of Arsenic, Antimony and Bismuth*. Blackie Academic and
992 Professional, London. 487 pp.
- 993 Onuk P. Melcher F. Mertz-Kraus R. Gäbler H. E. and Goldmann S. (2017) Development of a
994 Matrix-Matched Sphalerite Reference Material (MUL-ZnS-1) for Calibration of In Situ Trace Element
995 Measurements by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry. *Geostand.*
996 *Geoanal. Res.* **41**(2), 263-272.
- 997 Park C. F. and MacDiarmid R. A. (1975) *Ore Deposits*. W.H. Freeman and Company, San Francisco. pp.
998 985.
- 999 Pauliš P. Novák F. Kotatko L. Jonáscaron F. Dvořák Z. and Ševců J. (2008) Nové vyskyty nerostů na Sn-
1000 W ložisku Cínovec. *Bull. Mineralogicko-Petrologického Oddelení Národního Muzea v Praze* **16**, 113-
1001 117.
- 1002 Petrunic B. M. Al T. A. Weaver L. and Hall D. (2009) Identification and characterization of secondary
1003 minerals formed in tungsten mine tailings using transmission electron microscopy. *Appl. Geochem.*
1004 **24**, 2222-2233.
- 1005 Pfaff K. Romer R. L. and Markl G. (2009) U-Pb ages of ferberite, chalcedony, agate, 'U-mica' and
1006 pitchblende: constraints on the mineralization history of the Schwarzwald ore district. *Eur. J. Mineral.*
1007 **21**, 817-836.
- 1008 Plotinskaya O. Y. Grabezhev A. I. and Seltmann R. (2015) Fahlores compositional zoning in a
1009 porphyry-epithermal system: Biksizak occurrence, South Urals, Russia as an example. *Geol. Ore*
1010 *Deposit.* **57**, 42-63.
- 1011 Prasad A. S. (2013) *Essential and toxic element: trace elements in human health and disease*. Elsevier.
1012 534 pp.
- 1013 Reich M. and Vasconcelos P. M. (2015) Geological and economic significance of supergene metal
1014 deposits. *Elements* **11**(5), 305-310.
- 1015 Repstock A. Voudouris P. and Kolitsch U. (2015) New occurrences of watanabeite, colusite,
1016 "arsenosulvanite" and "Cu-excess" tetrahedrite-tennantite at the Pefka high-sulfidation epithermal
1017 deposit, northeastern Greece. – *Neues JB. Miner. Abh.* **192**, 135-149.
- 1018 Roper A. J. Williams P. A. and Filella M. (2012) Secondary antimony minerals: phases that control the
1019 dispersion of antimony in the supergene zone. *Geochemistry* **72**, 9-14.
- 1020 Rupf I. and Nitsch E. (2008) Das Geologische Landesmodell von Baden-Württemberg:
1021 Datengrundlagen, technische Umsetzung und erste geologische Ergebnisse. *LGRB Information* **21**, 1-
1022 82.
- 1023 Staude S. Bons P. D. and Markl G. (2009) Hydrothermal vein formation by extension-driven
1024 dewatering of the middle crust: An example from SW Germany. *Earth Planet. Sc. Lett.* **286**, 387-395.
- 1025 Staude S. Mordhorst T. Neumann R. Prebeck W. and Markl G. (2010) Compositional variation of the
1026 tennantite-tetrahedrite solid-solution series in the Schwarzwald ore district (SW Germany): The role
1027 of mineralization processes and fluid source. *Mineral. Mag.* **74**(2), 309-339.

- 1028 Staude S. Göb S. Pfaff K. Ströbele F. Premo W. R. and Markl G. (2011) Deciphering fluid sources of
1029 hydrothermal systems: A combined Sr- and S-isotope study on barite (Schwarzwald, SW Germany).
1030 *Chem. Geol.* **286**, 1-20.
- 1031 Staude S. Werner W. Mordhorst T. Wemmer K. Jacob D. E. and Markl G. (2012a) Multi-stage Ag-Bi-
1032 Co-Ni-U and Cu-Bi vein mineralization at Wittichen, Schwarzwald, SW Germany: geological setting,
1033 ore mineralogy, and fluid evolution. *Miner. Deposita* **47**, 251-276.
- 1034 Staude S. Mordhorst T. Nau S. Pfaff K. Brüggmann G. Jacob D. E. and Markl G. (2012b) Hydrothermal
1035 carbonates of the Schwarzwald ore district, Southwestern Germany: Carbon source and conditions of
1036 formation using $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and fluid inclusions. *Can. Mineral.* **50**, 1404-1434.
- 1037 Vavelidis M. and Melfos V. (2004) Bi-Ag-bearing tetrahedrite-tennantite in the Kapsalina copper
1038 mineralisation, Thasos Island, Northern Greece. *Neues JB. Miner. Abh.* **180**(2), 149-169.
- 1039 Villinger E. and Zedler H. (2006) *Geologische Karte des Schwarzwaldes 1:150 000*. LGRB, Freiburg.
- 1040 Walenta K. (1983) Bismutostibiconite, ein neues Mineral der Stibiconitgruppe aus dem Schwarzwald.
1041 *Chem. Erde* **42**, 77-81.
- 1042 Walenta K. (1992) *Die Mineralien des Schwarzwaldes*. Weise Verlag, München. pp. 336.
- 1043 Walter B. F. Burisch M. and Markl G. (2016) The long-term chemical evolution of continental
1044 basement brines – a field study from the Schwarzwald, SW Germany. *Geofluids* **16**, 604-623.
- 1045 Walter B. F. Burisch M. Fusswinkel T. Marks M. A. W. Steele-MacInnis M. Wälle M. Apukhtina O. B.
1046 and Markl G. (2018) Multi-reservoir fluid mixing processes in rift-related hydrothermal veins,
1047 Schwarzwald, SW-Germany. *J. Geochem. Explor.* **186**, 158-186.
- 1048 Walter B. F. Gerdes A. Kleinhanns I. C. Dunkl I. von Eynatten H. Kreissl S. and Markl G. (in press) The
1049 connection between hydrothermal fluids, mineralization, tectonics and magmatism in a continental
1050 rift setting: fluorite Sm-Nd and hematite and carbonates U-Pb geochronology from the Rhinegraben
1051 in SW Germany. *Geochim. Cosmochim. Acta*.
- 1052 Werner W. and Dennert V. (2004) *Lagerstätten und Bergbau im Schwarzwald*. Landesamt für
1053 Geologie, Rohstoffe und Bergbau Baden-Württemberg, Freiburg. pp. 334.
- 1054 Werner W. (2012) Schätze unter dem Boden: Was wissen wir über die tiefliegenden Rohstoffe in
1055 Baden-Württemberg? *Ber. Naturf. Ges. Freiburg i. Br.* **102**, 37-92.
- 1056 Whitmire K. H. (2013) *Bismuth: Inorganic Chemistry*. Encyclopedia of Inorganic and Bioinorganic
1057 Chemistry. John Wiley & Sons 1–32. DOI: 10.1002/9781119951438.eibc0018.pub2
- 1058 Wohlgemuth-Ueberwasser C. C. Viljoen F. Petersen S. and Vorster C. (2015) Distribution and
1059 solubility limits of trace elements in hydrothermal black smoker sulfides: An in-situ LA-ICP-MS study.
1060 *Geochim. Cosmochim. Acta* **159**, 16-41.
- 1061 Wu I. and Petersen U. (1977) Geochemistry of tetrahedrite and mineral zoning at Casapalca, Peru.
1062 *Econ. Geol.* **72**(6), 993-1016.
- 1063 Zhu Y. Merkel B. J. Stober I. and Bucher K. (2003) The hydrogeochemistry of arsenic in the Clara mine,
1064 Germany. *Mine Water Environ.* **22**(3), 110-117.

1065 **Figure captions**

1066 **Figure 1**

1067 BSE and chemical maps of a stage 1 weathering in zoned fahlore from Neubulach. (a) BSE image
1068 showing fahlore with zonation of its Bi content and finger-like tubes where weathering assemblages
1069 are situated. Note the bright weathering products coincides where fahlore is bright. (b). Close-up of
1070 (a) showing the Bi contents of the fahlore zonation and the complex weathering assemblages of
1071 stage 1. A younger vein contains stage 4 weathering phases. (c) Map of Cu of (b). In areas where the
1072 Bi content of the fahlore is low the weathering assemblage 1 contains more covellite (bright red). (d)
1073 Map of As of (b) showing the lack of As in weathering stage 1 (dark) and arsenate minerals of stage 4
1074 (bright blue line through stage 1). (e) Map of Bi of (b) showing the Bi-zonation in fahlore and the
1075 enrichment of Bi in stage 1 assemblage only where Bi is elevated in fahlore. (f) Map of Sb of (b)
1076 showing a Sb-enrichment in stage 1 assemblage. Where Bi-rich fahlore hosts the weathering
1077 assemblage Sb is found in the Bi-Sb-Fe phase, whereas where hosted by Sb-rich fahlore the Sb-Fe
1078 phase is formed. Note, all EDS elemental maps are false-colour images and colour intensity
1079 represents the distribution of each element.

1080

1081 **Figure 2**

1082 Reflected light photomicrograph in oil, showing different Cu-sulfides of weathering stage 1 from
1083 Neubulach.

1084

1085 **Figure 3**

1086 TEM images of stage 1 weathering from Neubulach. (a) High-angle annular dark field (HAADF) STEM
1087 image of fahlore in contact to weathering assemblage. Note the zonation within the weathering
1088 assemblage, partly due to Cu-sulfide (CuSulf) occurrence. (b) STEM HAADF close up of (a) showing the
1089 distribution of Cu-sulfide and the RGM in a Cu-oxide (CuOx) groundmass. (c) STEM EDS map of Bi of
1090 (b) showing the distribution of the RGM. (d) STEM EDS map of As of (b). Note the concentration of As
1091 in small veinlets, that represent phase and grain boundaries. (e) BSE image showing the location of
1092 the two textures shown in (b-d) and (f, g), respectively. (f) STEM HAADF image showing the spatial
1093 relation between Cu-sulfides and RGM, both elongate, in a Cu-oxide groundmass. (g) STEM EDS map
1094 of Cu and Bi of (f). The circular inset shows the position of the SAD aperture used to obtain the
1095 diffraction pattern in the ESM Fig. 6. Note, all STEM EDS elemental maps are false-colour images and

1096 colour intensity represents the distribution of each element but is also dependent on sample
1097 thickness.

1098

1099 **Figure 4**

1100 Processed mineral liberation analysis (MLA) image of fahlore with Bi-poor zones (dark grey) and Bi-
1101 rich zones (grey) cut by weathering stage 1. The weathering assemblage is colour coded to show the
1102 dominant mineral in each pixel (pixel size: 0.25 by 0.25 μm). As the analytical beam excitement
1103 volume is much larger than the pixel size only areas of the dominant mineral can be shown.

1104

1105 **Figure 5**

1106 (a) BSE image showing finger-like weathering assemblage inside and a replacement front outside
1107 native Bi from Wittichen. Both phases are bismite. (b) Transmitted light photo of native Bi from
1108 Wittichen which is replaced by a front of bismite which then later is cut by a mixite vein. Note the
1109 zonation of bismite. (c) Finger-like weathering assemblage in wittichenite and emplectite from
1110 Wittichen.

1111

1112 **Figure 6**

1113 (a) BSE image of weathering stage 2 from Freudenstadt, which is cut by younger stage 4 minerals.
1114 The Bi-concentration of fahlore and the weathering product, analysed by EMPA, are shown. (b) Map
1115 of S of (a) showing distribution of fahlore. (c) Map of Bi of (a) showing the Bi zonation of fahlore and
1116 in the stage 2 weathering assemblage. (d) BSE image of neighbouring fahlore and chalcopyrite
1117 showing stage 1 and 2 weathering from Neubulach. (e) Map of Sb and As showing the distribution of
1118 weathering stage 1 of fahlore by Sb, which is only minor in chalcopyrite. Stage 2 weathering,
1119 represented by As, is mostly found in chalcopyrite.

1120

1121 **Figure 7**

1122 Detail study of regions shown in Fig. 6a. (a) BSE magnified from Fig 6a highlighting the areas
1123 investigated by TEM in (b-f) from weathering stage 2. (b) Bright field image of the dark zone in (a)
1124 showing colloidal appearance of the phases present. (c) Selected area diffraction pattern of the
1125 central region in (b). The diffusive halo and the absence of discrete diffraction spots is characteristic

1126 for amorphous material. (d) STEM HAADF image of the bright zone in (a) showing nm-sized phases in
1127 a groundmass. (e) EDS map of Ag, Bi, and Cu showing the spatial relation between a 50 nm-sized Ag-
1128 sulfide crystal and the less than 10 nm-sized Cu-oxides in a Cu-arsenate groundmass. Bismuth is
1129 homogeneously distributed and appears to be amorphous. (f) Selected area diffraction pattern of the
1130 central region in (d) indicating the nano-crystalline structure of some phases. Furthermore, a diffuse
1131 halo indicates the presence of amorphous material.

1132

1133 **Figure 8**

1134 (a) BSE image of fahlore weathered by stage 2 which includes μm -sized Ag-sulfide aggregates. Note
1135 the difference in Bi-concentration of the fahlore is reflected in the secondary arsenate. (b) BSE image
1136 overlain by map of As and Hg showing the distribution of stage 1 weathering, represented by the Bi-
1137 Sb-Fe phase and HgS and of stage 2 weathering, represented by As and barite.

1138

1139 **Figure 9**

1140 (a) and (b) Combined reflected and transmitted light photo of weathering stages 1 to 3 from
1141 Neubulach. Stage 1 is characterized by a high Cu-sulfide content which is missing in stages 2 and 3.
1142 Stage 2 is composed of alternating layers of a Cu-arsenate and barite (highlighted in inlet of (a) in BSE
1143 mode; white: barite; grey: Cu-arsenate). Stage 3 is subdivided into a green phase on the contact to
1144 stage 1 and a yellow phase. (c) BSE image of (b) showing the transition from the stage 1 to stage 3
1145 weathering. (d) Close-up of (c) showing Cu-sulfides (CuS) in stage 1 weathering assemblage and a
1146 porous phase in the green stage 3 assemblage, all intergrown with the Bi-Sb-Fe phase.

1147

1148 **Figure 10**

1149 (a) BSE image of stages 2 to 4 weathering from Königswart. (b) Map of Ba, Si, and Bi of (a). Clasts with
1150 weathering assemblage 2 are overgrown by a Si-bearing phase and subhedral quartz which is in turn
1151 cut by barite of stage 4.

1152

1153 **Figure 11**

1154 (a) BSE image of stage 4 weathering which cuts through stage 1 from Neubulach (see Fig. 1). (b) Map
1155 of Cu and Ba of (a) showing the cyclic intergrowth of bariopharmacosiderite and azurite. (c) Azurite

1156 vein of stage 4 cutting through quartz and where it intersects older weathering stages forms an
1157 unknown Ca-Cu-bearing arsenate (transmitted light photograph). (d) Azurite of stage 4 replaces parts
1158 of stage 1 assemblage and completely stage 2. Whether the partly dissolution of stage 1 is part of
1159 stage 3 (compare Fig. 9) or whether it is a direct replacement in stage 4 is unclear. In both stages the
1160 Bi-Sb-Fe phase is preserved.

1161

1162 **Figure 12**

1163 (a) Variation of As-Sb-Bi of the investigated fahlore. Most samples show As-Bi exchange, whereas the
1164 Sb-content characteristic for each vein system. The Sb-rich and Bi-free fahlore from Wittichen
1165 occurred as small older inclusions in the As-Bi-bearing fahlore and did not show effects of
1166 weathering. (b) Same dataset of (a) but only showing analyses where fahlore is cut by stage 1
1167 weathering assemblage and colour coded by the oxide phase neighbouring this fahlore. (c)
1168 Concentration of As and Cu of the amorphous stage 2 phase (calculated to 100 atom % without
1169 volatiles).

1170

1171 **Figure 13**

1172 (a) Co versus Zn and (b) V versus Mn concentrations from LA-ICP-MS analyses of fahlore and
1173 weathering products of stages 1-4. Minerals of stage 4 are labelled, whereas other analyses
1174 represent mixed or amorphous phases. Fahlore has higher Zn and Co but lower Mn and V
1175 concentrations compared to their weathering products. Stage 3 of Neubulach is represented by
1176 dissolution of Cu-sulfides and Cu-oxides leaving the roméite group mineral (RGM) behind. Comparing
1177 this phase with the overall stage 1 assemblage the RGM has lower Co, but higher Mn, and V
1178 concentrations.

1179

1180 **Figure 14**

1181 (a) BSE image of a representative stage 1 assemblage from Neubulach. (b) Colour coded picture of (a)
1182 to highlight each phase and its quantity of this weathering stage (CuOx: Cu oxide, CuSulf: Cu-sulfide,
1183 RGM: roméite group mineral). (c) Results of stage 1 mass balance calculation presented in Table 4
1184 from Neubulach and Freudenstadt (FDS) (d) Results of the mass balance calculation for stage 2
1185 represented in Table 4 for a sample from Neubulach (stage 2 of Fig. 9a) and from Freudenstadt (FDS)
1186 shown in Figs. 6 and 7. See text for discussion.

1187

1188 **Figure 15**

1189 (a) Illustration of a typical weathering profile and element speciation through a hydrothermal vein
1190 including the assumed position of the different weathering stages 1-4 illustrated in (b). Elements
1191 which are originated from fahlore and are oxidized during weathering are bold.

1192

1193 **Supplementary Fig. 1**

1194 Simplified geologic map and main tectonics of the sampled localities located in the Northern and
1195 Central Schwarzwald (modified after Villinger and Zedler, 2006).

1196

1197 **Supplementary Fig. 2**

1198 Underground and hand specimen photos showing typical primary and weathering assemblages of the
1199 fahlore-rich mineralization. (a) Barite-fahlore vein cutting the Lower Triassic sandstone in the
1200 Neubulach visitor mine. Fahlore is still preserved and surrounded by several secondary minerals. (b)
1201 Hand specimen from Neubulach showing fahlore fractured by weathering stage 1 and surrounded by
1202 arsenates of weathering stage 2 (green). This is cut by younger azurite (blue with imprints of quartz
1203 crystals) of weathering stage 3. (c) Hand specimen from the Königswart mine showing abundant
1204 emplectite surround fahlore. The orange and green weathering assemblage is mostly found on
1205 fractures in quartz. (d) Hand specimen from the Dorothea mine near Freudenstadt showing fahlore
1206 with covellite of weathering stage 1.

1207

1208 **Supplementary Fig. 3**

1209 (a) μ XRD pattern of mixed phases of stage 3 from Königswart of Fig. 10. The Cu-arsenates and Cu-
1210 silicates cannot be identified and most likely represent the broad elevated background reflecting
1211 amorphous phases, whereas the intergrown barite of stage 4 is accountable for all reflexes. (b) and
1212 (c) μ XRD pattern of stage 4 radial green minerals of a sample from Wittichen were identified as
1213 mixite (b) and malachite (c), both intergrown with quartz. (d) μ XRD pattern of azurite from
1214 Neubulach.

1215

1216 **Supplementary Fig. 4**

1217 Raman spectra of the Bi-poor and Bi-rich assemblage of stage 1 (Neubulach), the amorphous stage 2
1218 phase of Fig. 6a (Freudenstadt), azurite (Neubulach), and mixite from Wittichen. Stage 2 phase and
1219 mixite show a water content with the broad peak at 3400-3500 cm^{-1} and the arsenate peak at 850
1220 cm^{-1} .

1221

1222 **Supplementary Fig. 5**

1223 (a) BSE image of stage 1 and 4 weathering assemblage (see also Fig. 1) before and after (inlet) the
1224 vacuum of the electron microprobe overnight. Cracks formed predominantly in
1225 bariopharmacosiderite. (b) BSE image of stage 2 and 4 weathering assemblage before the vacuum of
1226 the electron microprobe (see also Fig. 6). (c) SEI image of (b) after the vacuum of the electron
1227 microprobe overnight. Cracks formed mostly in the amorphous arsenate but also in tangdanite of
1228 stage 4.

1229

1230 **Supplementary Fig. 6**

1231 Selected area diffraction patterns of (a) Fig. 3f of the Sb-Bi-bearing RGM, and (b) of Fig. 3g. of a
1232 mixture of Sb-Bi-bearing RGM with Cu-sulfides and the Cu-oxide phase.

Table 1. Representative TEM EDX results including the average compositions in wt.% and calculated apfu

Stage	Number of analyses	Phase	Locality	Sample		As	Cu	Fe	Sb	Bi	S												
												[wt.%]											
1	5	Cu-sulfide	Neubulach	JHa3	Average	0.5	80.4	0.7	0.6	1.1	16.8												
					±	0.5	1.2	0.4	0.6	2.4	3.2												
												As ₂ O ₅	CuO	Fe ₂ O ₃	Sb ₂ O ₅	Bi ₂ O ₃	SO ₃	SiO ₂	Al ₂ O ₃	BaO	P ₂ O ₅		
												[wt.%]											
1	3	Cu-oxide phase	Neubulach	JHa3	Average	2.8	92.0	0.8	0.9	1.0	1.5	0.3	0.4	0.1	0.2								
					±	0.4	0.5	0.1	0.3	0.2	0.3	0.1	0.1	0.2	0.1								
1	5	Bi-Sb RGM	Neubulach	JHa3	Average	5.7	12.7	9.0	29.5	38.6	1.6	1.2	0.8	0.4	0.5								
					±	0.9	1.0	0.6	0.8	1.4	2.6	0.3	0.1	0.2	0.2								
3	6	Amorphous Cu-arsenate	Neubulach	JHa3	Average	13.0	65.5	2.9	2.3	4.7	10.0	0.6	0.6	0.1	0.4								
					±	2.2	9.7	1.1	0.8	1.6	7.0	0.7	0.3	0.2	0.3								
4	5	Amorphous Cu-arsenate, Bi-rich	Freudenstadt	MK65	Average	27.5	42.7	14.4	1.6	9.1	3.5	0.5	0.4	0.1	0.2								
					±	3.7	5.3	0.3	0.4	0.8	1.1	0.1	0.1	0.1	0.1								
4	4	Amorphous Cu-arsenate, Bi-poor	Freudenstadt	MK65	Average	17.0	28.5	8.8	2.0	3.7	28.6	6.8	2.0	1.5	1.1								
					±	5.5	4.6	0.6	1.6	2.9	14.2	0.4	0.3	0.1	0.3								
												As	Cu	Fe	Sb	Bi	S						
												[apfu]											
1		Cu-sulfide	Neubulach	JHa3	Average	<0.1	2.5	<0.1	<0.1	<0.1	1.0												
					±	0.01	0.51	0.02	0.01	0.03	na												
												As	Cu	Fe	Sb	Bi	S	Si	Al	Ba	P	Normalized to	
												[apfu]											
1		Cu-oxide phase	Neubulach	JHa3	Average	<0.1	0.9	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.0	1 apfu O						
					±		0.004	0.001	0.002	0.001	0.002	0.001	0.001	0.001	0.001								
1		Bi-Sb-bearing RGM	Neubulach	JHa3	Average	0.3	1.0	0.7	1.1	1.0	0.1	0.1	0.1	0.0	0.0	7.9	1 apfu Bi						
					±	0.06	0.09	0.04	0.03		0.21	0.03	0.02	0.01	0.02	0.78							
3		Amorphous Cu-arsenate	Neubulach	JHa3	Average	4.0	29.4	1.3	0.5	0.7	4.4	0.4	0.4	0.0	0.2	58.7	100 at.%						
					±	0.7	5.3	0.4	0.2	0.2	2.9	0.4	0.2	0.1	0.2	2.5							
4		Amorphous Cu-arsenate, Bi-rich	Freudenstadt	MK65	Average	8.8	19.7	6.6	0.4	1.4	1.6	0.3	0.3	<0.1	0.1	60.8	100 at.%						
					±	1.1	2.6	0.1	0.1	0.1	0.5	0.1	0.1	<0.1	0.1	1.1							
4		Amorphous Cu-arsenate, Bi-poor	Freudenstadt	MK65	Average	4.3	10.3	3.1	0.4	0.5	9.9	3.2	1.1	0.3	0.4	66.5	100 at.%						
					±	2.0	3.0	0.6	0.4	0.4	4.2	0.2	0.1	0.04	0.1	2.2							

Table 2. Representative EMP results for sulfides including data in wt.% and calculated apfu for each analyses. b.d. = below detection limit

Locality	Sample	Mineral	As	S	Bi	Cu	Pb	Hg	Ag	Zn	Sb	Fe	Ni	Co	Se	Total
[wt.%]																
Neubulach	JHa3.4	Fahlore	16.3	27.3	0.14	42.1	b.d.	0.09	0.21	3.48	9.29	3.30	b.d.	0.04	0.06	99.6
Neubulach	JHa3.12	Fahlore	11.5	26.2	7.60	40.6	b.d.	0.07	0.25	3.73	6.75	2.71	b.d.	0.07	0.08	99.6
Freudenstadt	MK65.1	Fahlore	14.9	26.9	6.85	40.8	b.d.	b.d.	0.47	1.81	3.21	5.07	b.d.	0.36	0.05	100.5
Freudenstadt	MK65.3	Fahlore	16.1	27.9	0.14	41.8	b.d.	0.17	0.55	0.85	5.35	5.26	b.d.	0.43	0.02	99.5
Königswart	JHa4.25	Fahlore	11.7	25.8	12.8	40.2	b.d.	0.32	0.50	2.95	3.16	2.73	b.d.	0.11	0.06	100.5
Königswart	JHa4.19	Fahlore	13.8	27.4	0.11	41.7	b.d.	0.29	0.28	4.05	8.56	3.01	b.d.	0.06	0.07	99.4
Wittichen	JHa6.4	Fahlore	11.7	25.3	15.5	39.8	b.d.	0.48	0.29	5.16	0.65	1.15	b.d.	0.02	0.35	100.5
Wittichen	MK70.6	Fahlore	19.8	28.3	b.d.	43.2	b.d.	0.02	0.06	0.81	0.49	6.67	b.d.	b.d.	0.16	99.5
Wittichen	MK69.9	Chalcopyrite	0.07	34.5	0.05	33.3	b.d.	b.d.	0.14	b.d.	b.d.	31.0	b.d.	0.05	b.d.	99.1
Neubulach	MK63.1	Emplectite	b.d.	19.4	61.4	19.9	b.d.	b.d.	b.d.	0.03	0.26	b.d.	b.d.	b.d.	b.d.	100.9
Wittichen	MK66.16	Wittichenite	b.d.	19.2	41.5	38.8	b.d.	b.d.	0.13	b.d.	0.09	b.d.	b.d.	b.d.	b.d.	99.8
Freudenstadt	JHa12.12	Spionkopite	1.03	25.1	0.54	69.2	b.d.	0.08	1.13	b.d.	0.08	0.23	b.d.	0.02	0.04	97.7
Neubulach	MK66.21	Covellite	0.13	33.0	0.36	64.9	b.d.	b.d.	0.12	b.d.	0.08	0.04	b.d.	b.d.	b.d.	98.6
[apfu]																
Neubulach	JHa3.4	Fahlore	2.8	13.1	<0.1	10.2		<0.1	<0.1	0.8	1.2	0.9		<0.1	<0.1	29 apfu
Neubulach	JHa3.12	Fahlore	2.5	13.1	0.6	10.2		<0.1	<0.1	0.9	0.9	0.8		<0.1	<0.1	29 apfu
Freudenstadt	MK65.1	Fahlore	3.5	13.0	<0.1	10.0		<0.1	<0.1	0.4	0.5	1.5		0.1	<0.1	29 apfu
Freudenstadt	MK65.3	Fahlore	2.8	13.0	0.6	10.1		<0.1	<0.1	0.4	0.6	1.3		0.1	<0.1	29 apfu
Königswart	JHa4.25	Fahlore	2.5	13.1	1.0	10.3		<0.1	0.1	0.7	0.4	0.8		<0.1	<0.1	29 apfu
Königswart	JHa4.19	Fahlore	2.8	13.1	<0.1	10.1		<0.1	<0.1	1.0	1.1	0.8		<0.1	<0.1	29 apfu
Wittichen	JHa6.4	Fahlore	2.6	13.0	1.2	10.3		<0.1	<0.1	1.3	0.1	0.3		<0.1	0.1	29 apfu
Wittichen	MK70.6	Fahlore	3.9	13.0		10.0		<0.1	<0.1	0.2	0.1	1.8			<0.1	29 apfu
Wittichen	MK69.9	Chalcopyrite	<0.1	2.0	<0.1	1.0			<0.1			1.0		<0.1		4 apfu
Neubulach	MK63.1	Emplectite		2.0	1.0	1.0				<0.1	<0.1					4 apfu
Neubulach	MK66.16	Wittichenite		3.0	1.0	3.0			<0.1		<0.1					7 apfu
Freudenstadt	JHa12.12	Spionkopite	0.05	27.8	0.1	38.0		<0.1	0.4		0.1	0.1		<0.1	<0.1	67 apfu
Neubulach	MK66.21	Covellite	<0.1	1.0	<0.1	1.0			<0.1		<0.1	<0.1				2 apfu

Table 3. Representative LA-ICP-MS elemental concentrations in ppm. n.d. = not detected

Sample	Locality	Mineral	stage	P	V	Cr	Mn	Co	Ni	Zn	Ga	Ge	Se	Mo	Ag	Cd	In	Sn	Tl	Pb
JHA-3A	Neubulach	fahlore	0	10	0.3	1.3	1.9	461	1.4	40964	n.d.	0.4	n.d.	0.2	1289	306	4	0.3	0.04	3
JHA-3B	Neubulach	fahlore	0	19	0.1	0.1	n.d.	624	1.2	35566	0.01	0.1	11	0.2	1300	140	13	2	0.02	2
JHA-3C	Neubulach	Stage 1	1	239	6	2	51	32	2	5626	1	2	6	4	1864	435	17	0.4	0.01	73
JHA-3D	Neubulach	Stage 1	1	124	3	1	11	9	3	2657	0.3	2	9	1	2575	52	9	0.2	0.02	34
JHA-3E	Neubulach	azurite	4	51	n.d.	0.03	0.2	5	5	273	n.d.	0.03	n.d.	0.05	0.4	n.d.	0.002	0.1	0.03	0.2
JHA-3F	Neubulach	Bi-Sb RGM	3	687	14	10	330	6	2	4077	0.3	8	7	8	2645	1181	37	0.1	0.05	275
JHA-3G	Neubulach	Bi-Sb RGM	3	332	8	9	195	5	1	2678	0.2	4	4	4	1627	662	23	1	0.004	152
JHA-3I	Neubulach	Stage 1	1	152	3	0.5	130	17	1	3458	n.d.	1	5	1	3750	122	14	0.2	n.d.	9
JHA-3J	Neubulach	Bi-Sb RGM	3	382	10	6	194	4	1	2666	0.2	4	12	4	2195	720	29	0.3	0.02	61
JHA-3K	Neubulach	Bi-Sb RGM	3	314	7	3	134	5	1	2559	0.2	2	4	5	1962	494	23	1	n.d.	52
JHA-3L	Neubulach	Bi-Sb RGM	3	337	7	3	182	4	1	2705	0.2	4	4	4	2303	685	22	0.4	n.d.	67
JHA-7A	Königswart	fahlore	0	29	0.1	2.1	0.2	1212	3	46233	0.3	0.4	30	0.2	4333	167	7	n.d.	0.1	4
JHA-7B	Königswart	Amorphous Cu-arsenates	2	892	0.2	0.2	1	71	1	4774	n.d.	0.4	13	1	2321	48	7	0.3	0.03	7
JHA-7C	Königswart	Amorphous Cu-silicate II	3	776	4	8	3	14	1	2658	0.2	4	n.d.	2	2	26	0.03	0.2	0.1	104
JHA-7D	Königswart	chalcopyrite	0	82	0.1	0.01	0.2	n.d.	0.4	8	n.d.	2	n.d.	0.1	517	n.d.	1	1	n.d.	0.4
JHA-7E	Königswart	Cu-Fe-oxide	1	391	n.d.	0.1	1	8	22	2984	n.d.	4	7	6	64	27	2	4	n.d.	11
JHA-7F	Königswart	mixite	4	379	8	0.01	3	25	26	4952	0.3	0.2	38	34	1	244	1	0.1	0.01	2850
MK-65-B	Freudenstadt	fahlore		72	n.d.	0.5	0.5	3109	1	28511	0.4	0.1	7	42	2220	141	30	n.d.	0.1	58
MK-65-C	Freudenstadt	fahlore	0	158	0.2	0.2	0.8	1345	1	18982	0.1	1	n.d.	19	8324	104	43	0.3	0.03	26
MK-65-D	Freudenstadt	Amorphous Cu-arsenates	2	341	0.2	1	2	215	0.4	3245	0.3	0.2	n.d.	6	7855	40	85	1	0.01	38
MK-65-E	Freudenstadt	Amorphous Cu-arsenates	2	335	0.1	0.3	1	245	n.d.	3367	0.3	0.3	3	7	9326	45	95	2	0.02	33
MK-65-F	Freudenstadt	tangdanite	4	141	0.4	2	1	138	n.d.	3708	1	n.d.	14	19	24	27	0.04	0.2	0.003	1
MK-68-A	Wittichen	mixite	4	217	8	0.4	262	99	1057	72	0.2	n.d.	9	7	0.1	38	n.d.	0.2	0.04	127
MK-68-B	Wittichen	atelestite	4	569	465	0.1	6	10	17	159	0.03	0.4	2	143	5	4	0.1	0.1	1	399
MS-4A	Neubulach	azurite	4	502	1	1	2	4	0.2	714	0.1	0.01	n.d.	0.03	10	4	5	0.3	n.d.	4

MS-4B	Neubulach	Amorphous Cu-arsenates	2	275	2	0.1	14	60	1	10535	0.1	1	n.d.	1	56	149	23	0.1	0.1	31
MS-4C	Neubulach	fahlore	0	30	0.1		1.9	1192	2.4	59422	n.d.	0.3	18	0.8	936	349	11	n.d.	0.3	28
MS-4D	Neubulach	fahlore	0	462	1.5	2.0	47.3	777	1.4	41861	1	0.5	n.d.	0.4	1184	215	17	1	0.2	9
MS-4E	Neubulach	Stage 1	1	1144	2	5	50	45	1	3797	0.01	0.4	n.d.	0.2	1520	40	13	0.2	0.03	6
MS-4F	Neubulach	Stage 1	1	819	11	15	88	117	7	6944	2	6	60	9	1359	2260	38	n.d.	0.1	85

Table 4. Representative EMP results for minerals of stage 1-4 including wt.% and calculated mol% and atoms per formula unit (apfu) for each analysis. b.d. = below detection limit

Stage	Phase	Locality	Sample	As ₂ O ₃	SO ₃	Bi ₂ O ₃	CuO	Al ₂ O ₃	PbO	HgO	Ce ₂ O ₃	Ag ₂ O	ZnO	Sb ₂ O ₃	Fe ₂ O ₃	CaO	BaO	SiO ₂	Theor. H ₂ O	Theor. CO ₂	Total
											[wt.%]										
2	Amorphous Cu-arsenates	Neubulach	JHa3.s18	21.0	0.69	12.3	39.6	b.d.	b.d.	b.d.	0.04	0.20	1.15	3.77	4.56	1.41	0.95	0.19			85.78
2	Amorphous Cu-arsenates	Freudenstadt	MK65.s34	26.4	0.95	1.41	41.8	0.06	b.d.	b.d.	b.d.	0.36	0.14	1.95	11.8	0.14	0.12	0.07			85.17
2	Amorphous Cu-arsenates	Freudenstadt	MK65.s32	23.2	0.69	9.64	39.2	b.d.	b.d.	b.d.	b.d.	0.07	0.16	3.77	9.32	0.08	0.09	0.14			86.44
2	Amorphous Cu-arsenates	Freudenstadt	JHa12.s15	38.1	b.d.	1.15	50.1	0.15	b.d.	b.d.	b.d.	b.d.	0.68	1.41	1.33	0.15	0.13	0.03			93.18
2	Amorphous Cu-arsenates	Königswart	JHa4.s17	21.5	1.29	12.5	31.2	0.08	b.d.	0.09	b.d.	b.d.	0.68	2.85	10.9	1.26	2.76	1.10			86.22
3	Amorphous Cu-silicate I	Königswart	JHa7.s13	6.35	0.98	4.14	49.0	0.06	b.d.	0.30	b.d.	b.d.	0.39	0.36	1.61	2.35	0.60	0.62	22.6		89.33
3	Amorphous Cu-silicate II	Königswart	JHa7.s14	5.05	b.d.	1.84	52.9	0.05	b.d.	b.d.	b.d.	b.d.	0.21	1.27	0.08	0.19	0.11	11.9			73.57
4	Azurite	Neubulach	JHa3.s3	b.d.	b.d.	b.d.	63.4	0.04	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.06	0.10	b.d.	5.2	25.5	63.54
4	Malachite	Neubulach	MK66.s3	1.74	b.d.	b.d.	63.8	0.10	b.d.	b.d.	b.d.	0.04	0.28	0.03	0.03	0.08	0.10	0.03	8.2	19.9	66.25
4	Malachite	Freudenstadt	MK65.s3	0.80	b.d.	b.d.	64.7	b.d.	b.d.	0.12	b.d.	b.d.	0.25	0.40	b.d.	b.d.	0.14	0.05	8.2	19.9	66.45
4	Malachite	Königswart	JHa4.s9	1.37	b.d.	b.d.	61.8	b.d.	b.d.	b.d.	b.d.	b.d.	2.67	0.20	b.d.	b.d.	0.12	0.09	8.2	19.9	66.28
4	Malachite	Wittichen	MK70.s8	2.54	0.38	3.79	60.38	0.03	b.d.	b.d.	b.d.	b.d.	0.22	0.09	0.21	0.08	0.13	0.22	8.2	19.9	68.06
4	Mixite-group (mixite)	Wittichen	MK68.s2	30.3	b.d.	15.5	40.9	0.04	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.13	1.55	0.09	0.08	9.3		88.55
4	Mixite-group (zalesite)	Neubulach	JHa3.s1	31.5	b.d.	7.04	43.6	0.16	b.d.	b.d.	b.d.	b.d.	0.05	b.d.	0.02	5.06	0.10	0.09	11.7		87.58
4	Mixite-group (zalesite)	Königswart	Jha7.s28	30.7	b.d.	6.56	42.0	0.08	0.19	b.d.	b.d.	b.d.	0.24	b.d.	0.24	4.61	0.11	0.07	11.7		84.82
4	Barite	Königswart	JHa7.s20	b.d.	34.2	b.d.	0.10	0.89	b.d.	b.d.	0.08	b.d.	b.d.	b.d.	0.03	0.02	63.4	b.d.			98.71
4	Atelestite	Wittichen	MK68.s4	17.5	b.d.	70.8	0.25	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.05	b.d.	0.48	0.16	0.35	2.0		89.66
4	Olivenite	Freudenstadt	MK65.s28	38.3	0.46	b.d.	53.2	0.06	b.d.	b.d.	b.d.	0.03	0.31	1.71	0.05	0.02	0.14	b.d.	3.2		94.31
4	Cornubite/Cornwallite	Freudenstadt	MK65.s5	27.4	0.79	b.d.	52.8	0.08	b.d.	b.d.	b.d.	b.d.	0.60	2.78	0.32	0.17	0.13	0.53	7.9		85.58
4	Dussertite/ arsenogorceixite	Freudenstadt	MK65.s13	28.84	0.17	1.08	1.49	7.46	b.d.	0.09	b.d.	0.03	0.38	13.99	15.23	0.31	18.79	b.d.	6.7-9.9		87.85
4	Tangdanite	Freudenstadt	MK65.s1	30.0	2.36	b.d.	46.8	0.05	b.d.	b.d.	b.d.	b.d.	0.19	0.19	0.04	7.80	0.18	0.15	15.5		87.76
4	Clinoclase	Königswart	JHa4.s8	25.5	b.d.	0.24	55.0	b.d.	b.d.	b.d.	b.d.	b.d.	1.86	0.69	b.d.	0.09	0.12	0.15	7.1		83.63

Phase	Locality	Sample	As ₂ O ₃	SO ₃	Bi ₂ O ₃	CuO	Al ₂ O ₃	PbO	HgO	Ce ₂ O ₃	Ag ₂ O	ZnO	Sb ₂ O ₃	Fe ₂ O ₃	CaO	BaO	SiO ₂	Normalized to			
											[mol %]										

2	Amorphous Cu-arsenates	Neubulach	JHa3.s18	12.2	1.2	3.5	66.5	0		<0.1	0.1	1.9	1.6	8.5	3.4	0.8	0.4	mol %
2	Amorphous Cu-arsenates	Freudenstadt	MK65.s34	13.8	1.4	0.4	63.0	<0.1			0.2	0.2	0.7	19.7	0.3	0.1	0.1	mol %*
2	Amorphous Cu-arsenates	Freudenstadt	MK65.s32	13.1	1.1	2.7	63.9			<0.1	0.7	1.5	16.8	0.2	0.1	0.3		mol %*
2	Amorphous Cu-arsenates	Freudenstadt	JHa12.s15	19.9		0.3	75.4	0.2			0	1.0	0.5	2.2	0.3	0.1	<0.1	mol %*
2	Amorphous Cu-arsenates	Königswart	JHa4.s17	12.3	2.1	3.6	51.8	0.1	0.1		0	1.1	1.2	20.0	3.0	2.4	2.4	mol %*
3	Amorphous Cu-silicate I	Königswart	JHa7.s13	2.5	1.1	0.8	55.9	0.1	0.1		0.1	0.40	0.45	3.0	1.0	0.4	34.2	mol %*
3	Amorphous Cu-silicate II	Königswart	JHa7.s14	2.4		0.4	73.8	0.1				0.3	0.4	0.1	0.4	0.1	21.9	mol %*
				As	S	Bi	Cu	A	Pb	Hg	Ce	Ag	Zn	Sb	Fe	Ca	Ba	Si
											[apfu]							
4	Azurite	Neubulach	JHa3.s3				3.0	<0.1							<0.1	<0.1		3 apfu Cu
4	Azurite	Freudenstadt	MK65.s14	0.1	0.3		3.0	<0.1			<0.1		<0.1	<0.1	<0.1	<0.1		3 apfu Cu
4	Malachite	Neubulach	MK66.s3	<0.1			2.0	<0.1			<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	2 apfu Cu
4	Malachite	Freudenstadt	MK65.s3	<0.1			2.0		>0.1		>0.1	>0.1				>0.1	>0.1	2 apfu Cu
4	Malachite	Königswart	JHa4.s9	<0.1			2.0					0.1	<0.1			<0.1	<0.1	2 apfu Cu
4	Malachite	Wittichen	MK70.s8	0.1	<0.1	<0.1	2.0	<0.1				<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	2 apfu Cu
4	Mixite-group (mixite)	Wittichen	MK68.s2	3.0		0.8	5.9	<0.1						<0.1	0.3	<0.1	<0.1	10 apfu cations
4	Mixite-group (zalesiite)	Neubulach	JHa3.s1	2.9		0.3	5.8	<0.1				<0.1		<0.1	1.0	<0.1	<0.1	10 apfu cations
4	Mixite-group (zalesiite)	Königswart	Jha7.s28	2.9		0.3	5.8	<0.1	<0.1			<0.1		<0.1	0.9	<0.1	<0.1	10 apfu cations
4	Barite	Königswart	JHa7.s20		1.0		<0.1	<0.1		<0.1				<0.1	<0.1	1.0		1 apfu Ba
4	Atelestite	Wittichen	MK68.s4	1.0		2.0	<0.1						<0.1		<0.1	<0.1	<0.1	2 apfu Bi
4	Olivenite	Freudenstadt	MK65.s28	1.0	<0.1		2.0	<0.1			<0.1	<0.1	<0.1	<0.1	<0.1	<0.1		2 apfu Cu
4	Cornubite/Cornwallite	Freudenstadt	MK65.s5	1.8	<0.1		5.0	<0.1			<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	5 apfu Cu
4	Dussertite/ arsenogorceixite	Freudenstadt	MK65.s13	2.0	<0.1	<0.1	0.1	1.2	<0.1		<0.1	<0.1	0.7	1.7	<0.1	1.0		2 apfu As
4	Tangdanite	Freudenstadt	MK65.s1	3.8	0.4		8.5	<0.1				<0.1	<0.1	<0.1	2	<0.1	<0.1	2 apfu Ca
4	Clinoclase	Königswart	JHa4.s8	1.0		<0.1	3.0					0.1	<0.1		<0.1	<0.1	<0.1	3 apfu Cu

Table 5. Mass balance calculation for stage 1 and 2 weathering displayed in Fig. 14. See text for calculation and discussion.

	Neubulach, JHa3, Bi-rich	Neubulach, JHa3, Bi-poor	Neubulach, MK63, Bi-rich	Freudenstadt, JHa12, medium Bi	Neubulach all fahlore	Neubulach high Bi fahlore	FDS dark zone (Fig. 5a, b-c)	FDS bright zone (Fig. 5a, d-f)	Königswart	Wittichen (Alte Gabe Gottes)
	stage 1					stage 2				
average fahlore analyses	n=6 fahlore	n=9 fahlore	n=8 fahlore	n=8 fahlore	n=18 fahlore	n=9 fahlore	n=10 fahlore	n=10 fahlore	n=19 fahlore	n=11 fahlore
Average secondary assemblage	n=12 graphics	n=7 graphics	n=7 graphics	n=3 graphics	n=3 sek	n=3 sek	n=4 sek	n=3 sek	n=8 sek	n=4 sek
Cu [%]	43	28	43	43	-28	-27	-29	-29	-49	-25
Fe [%]	-19	-55	-2	-61	21	29	55	48	112	50
Zn [%]	-100	-94	-100	-100	-83	-82	-92	-93	-84	-75
As [%]	-83	-85	-83	-86	5	17	-5	11	-5	10
Sb [%]	-10	-56	-5	-14	-69	-62	-68	-36	-39	-65
Bi [%]	-12	-2	-22	0	101	11	76	-7	-3	-24
S [%]	-67	-80	-76	-83	-98	-98	-99	-99	-97	-99

Table 6. Comparison of the different weathering stages

	Stage 1	Stage 2	Stage 3	Stage 4
Mineralogy of weathering products	Oxides Sulfides (Cu sulfides, acanthite, cinnabar)	No oxides Minor sulfate (barite), minor amounts of sulfides (acanthite, cinnabar)	No oxides No sulfide or sulphate	No oxides Sulfate (barite)
Crystallinity of secondary phases	No arsenate Nano-meter to micro- meter sized crystals	arsenate Amorphous, local nano meter-sized crystals	arsenate Amorphous and botryoidal textures	arsenate Up to cm large crystals
Chemistry of secondary phases	Hydrous phases present Addition of elements Loss of elements	No hydrous phases Si, Cu As, Zn, S, (Fe and Sb if fahlore is Bi-poor)	No hydrous phases Si Not investigated	Hydrous phases local Ca, Si, Ba, Al, and/or C Not investigated
Location of weathering products	Immobile elements Bi (Fe and Sb if fahlore contains Bi) Replaces fahlore	Bi, As Replaces fahlore	Not investigated Replaces older weathering phases	Not investigated Spatially not related to fahlore, partly replaces older weathering phases
Weathering texture	Finger-like tubes forming 3D network through fahlore crystallizing from a gel-like precursor phase	Weathering assemblage forms fronts through fahlore, partly alternating phases, layers with nm-sized porosity	Weathering assemblage forms fronts through older weathering phases and/or cements them	Secondary minerals sealing cracks, local replacement of older weathering phases

Figure 1

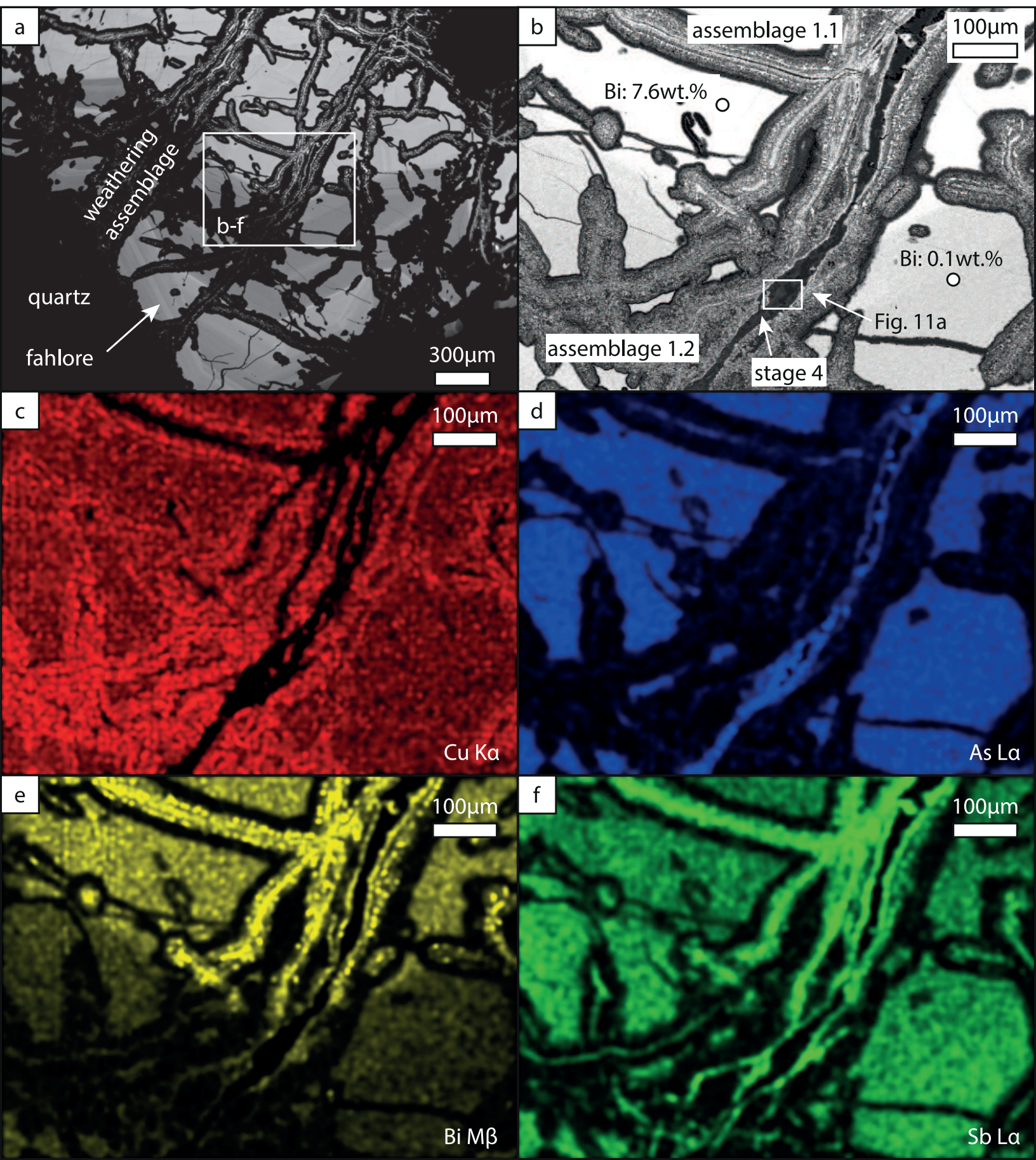


Figure2

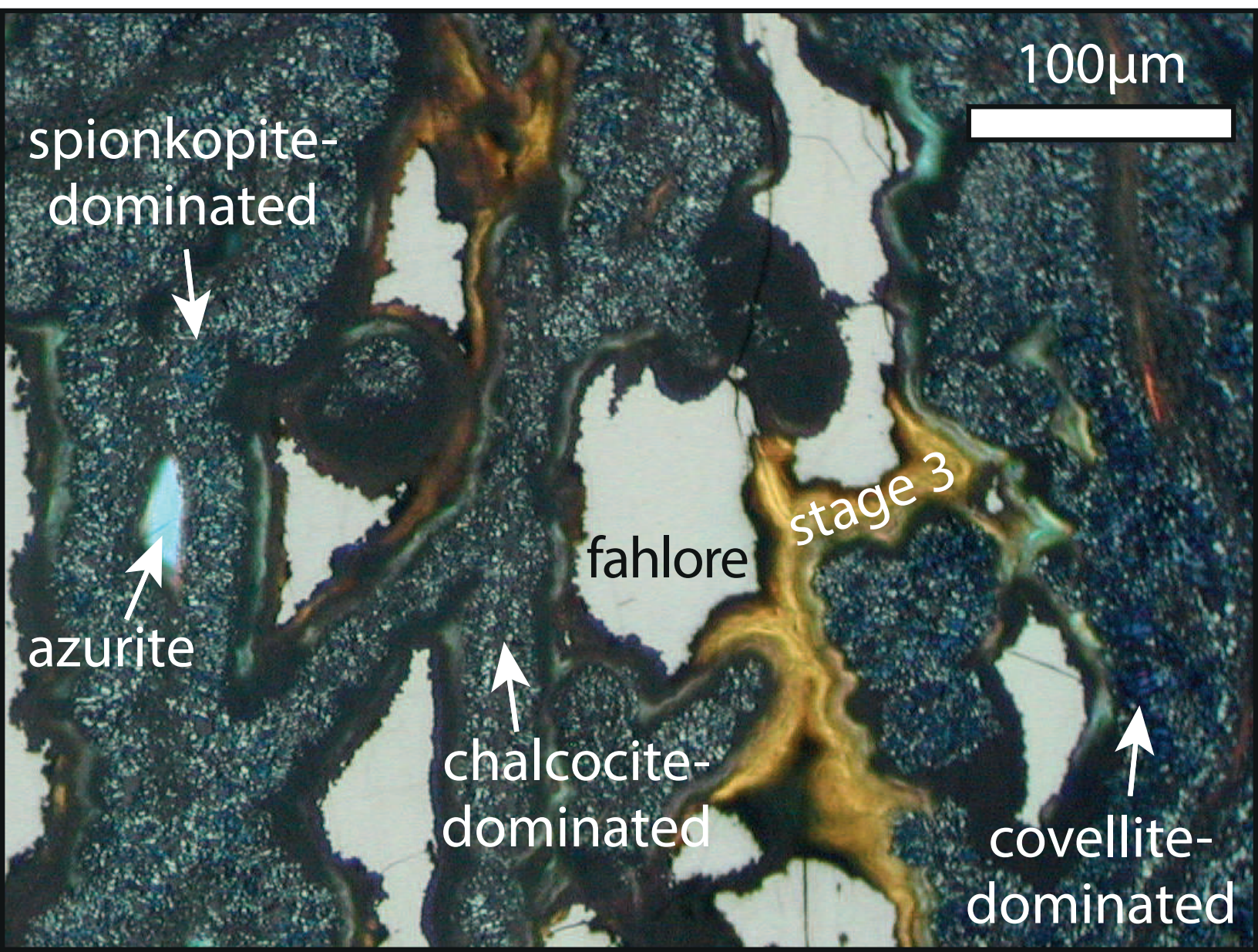


Figure3

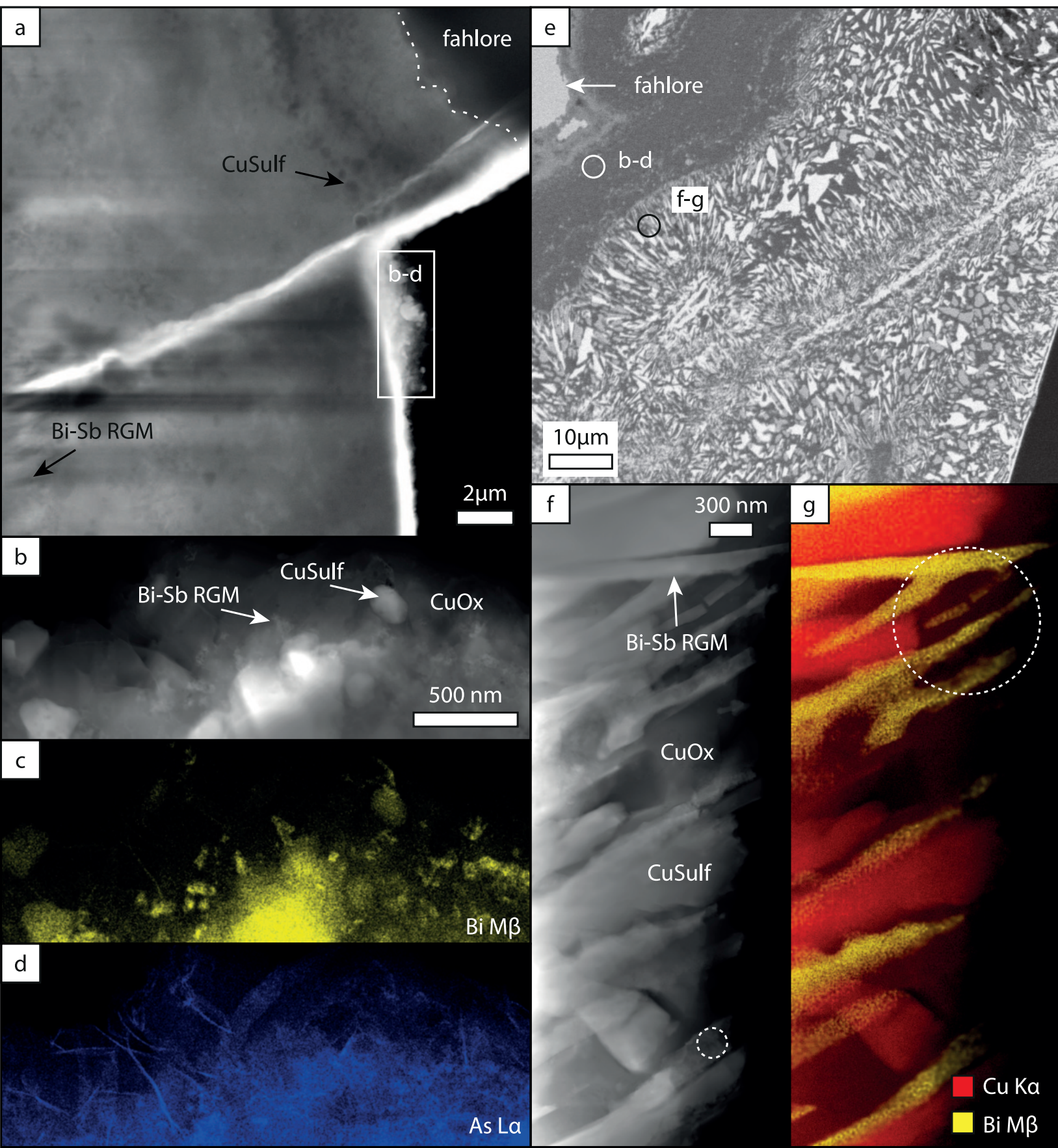
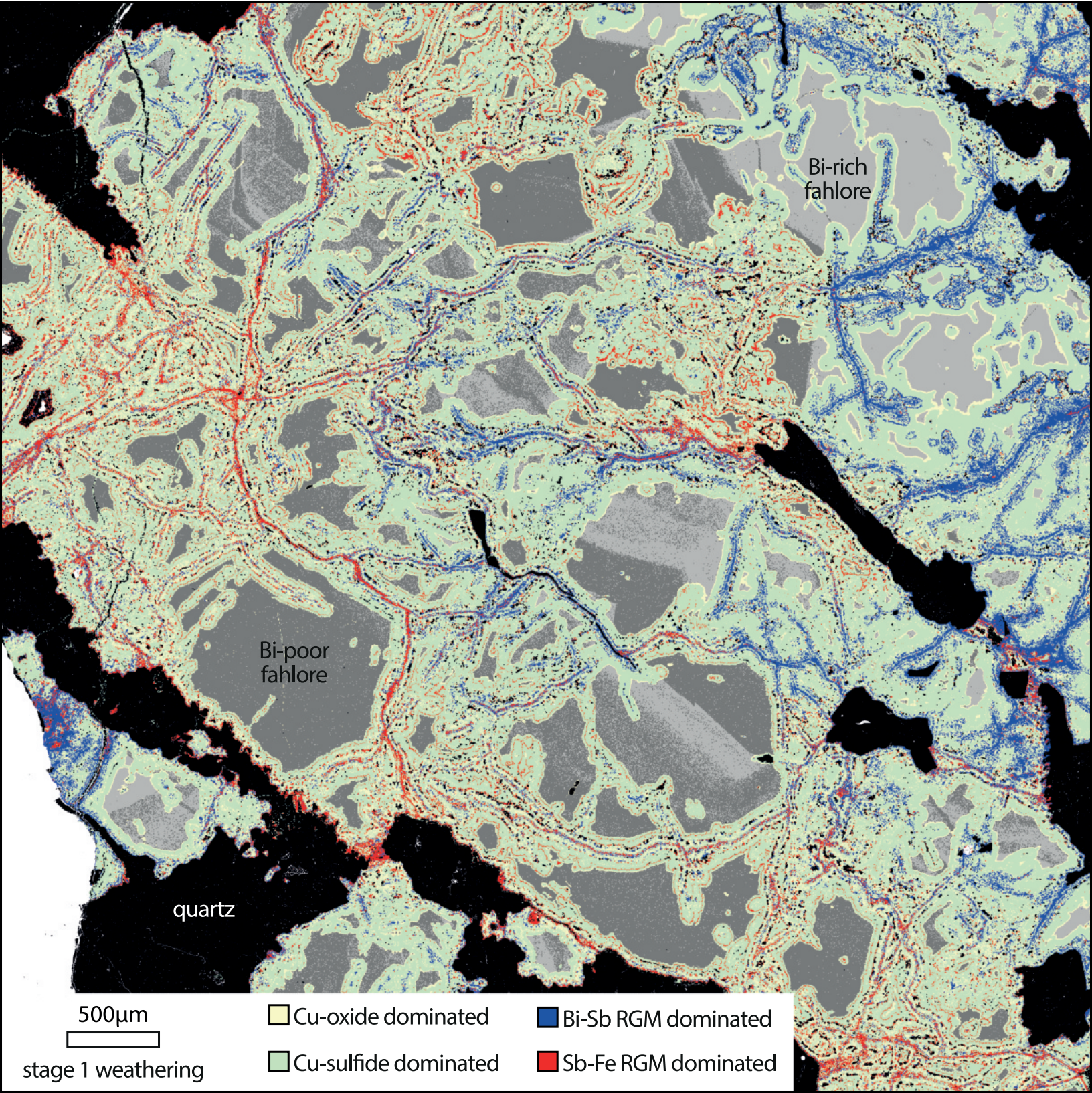
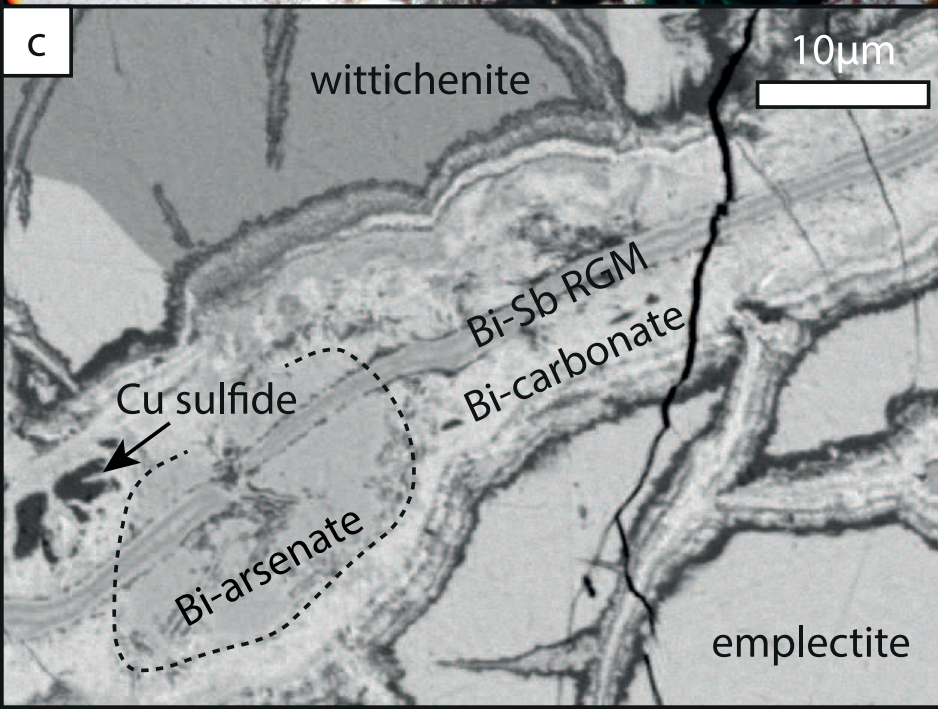
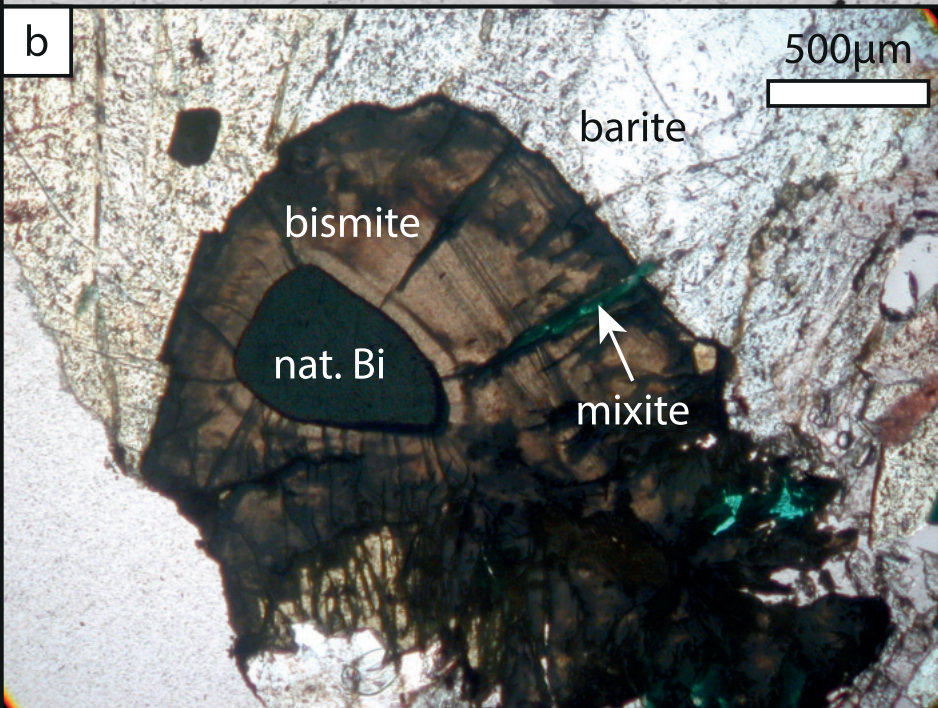
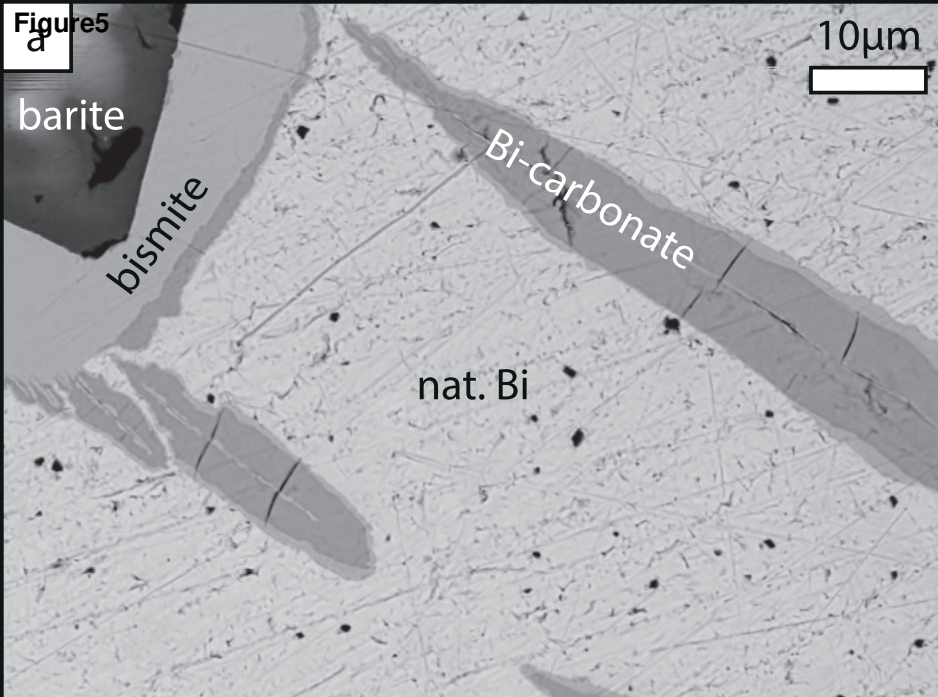


Figure4





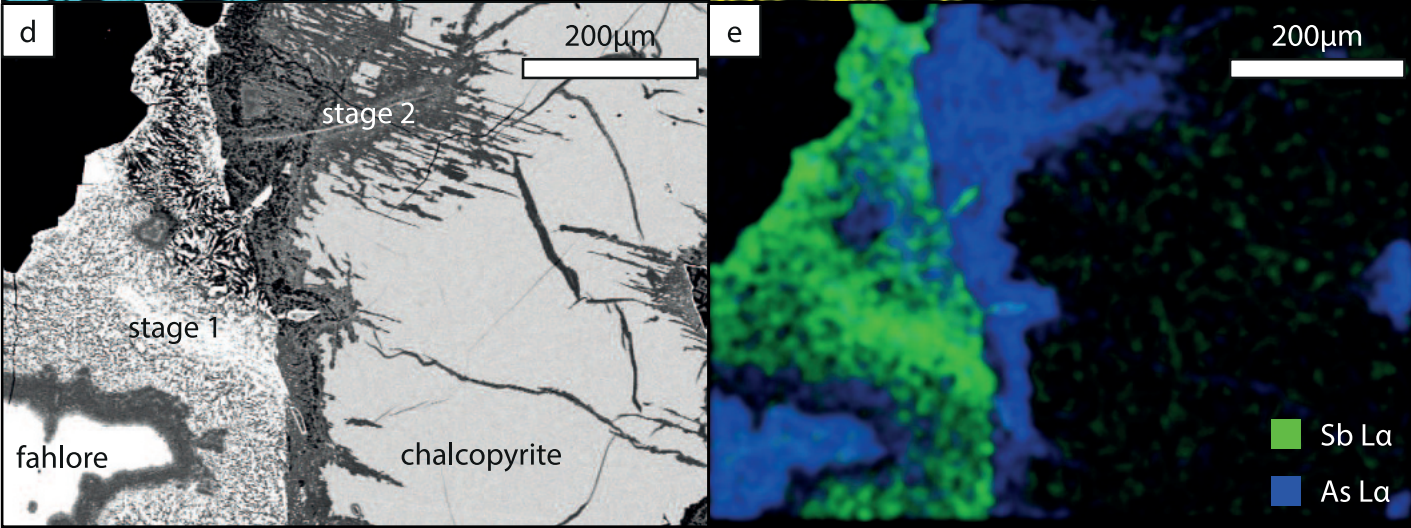
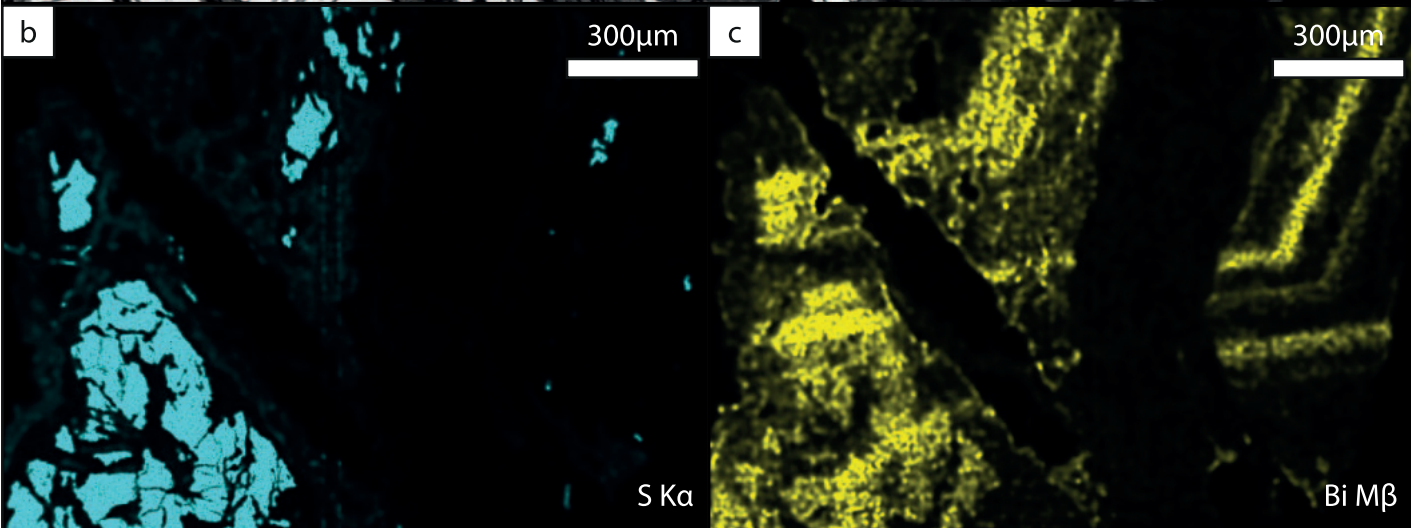
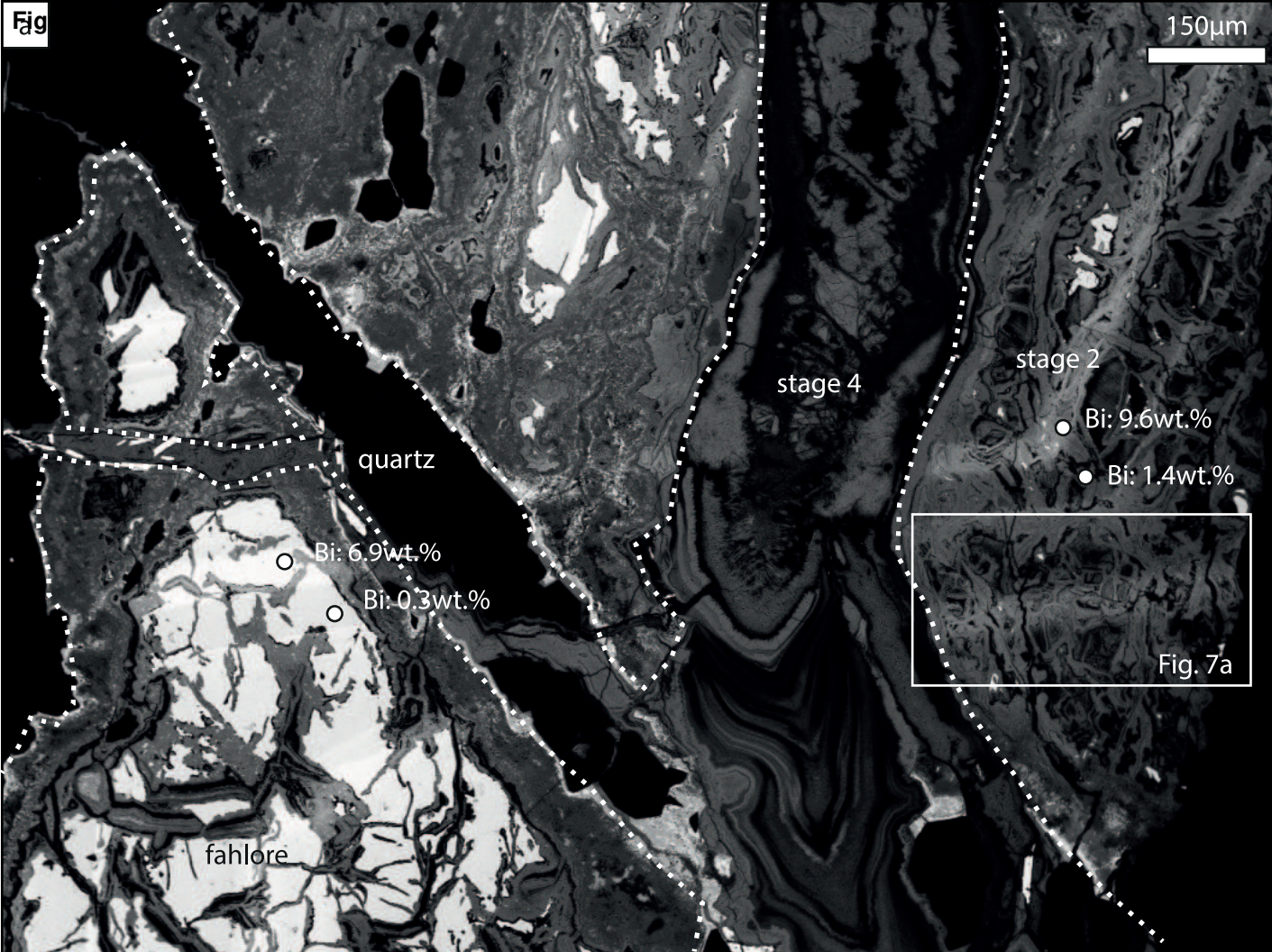


Figure 7

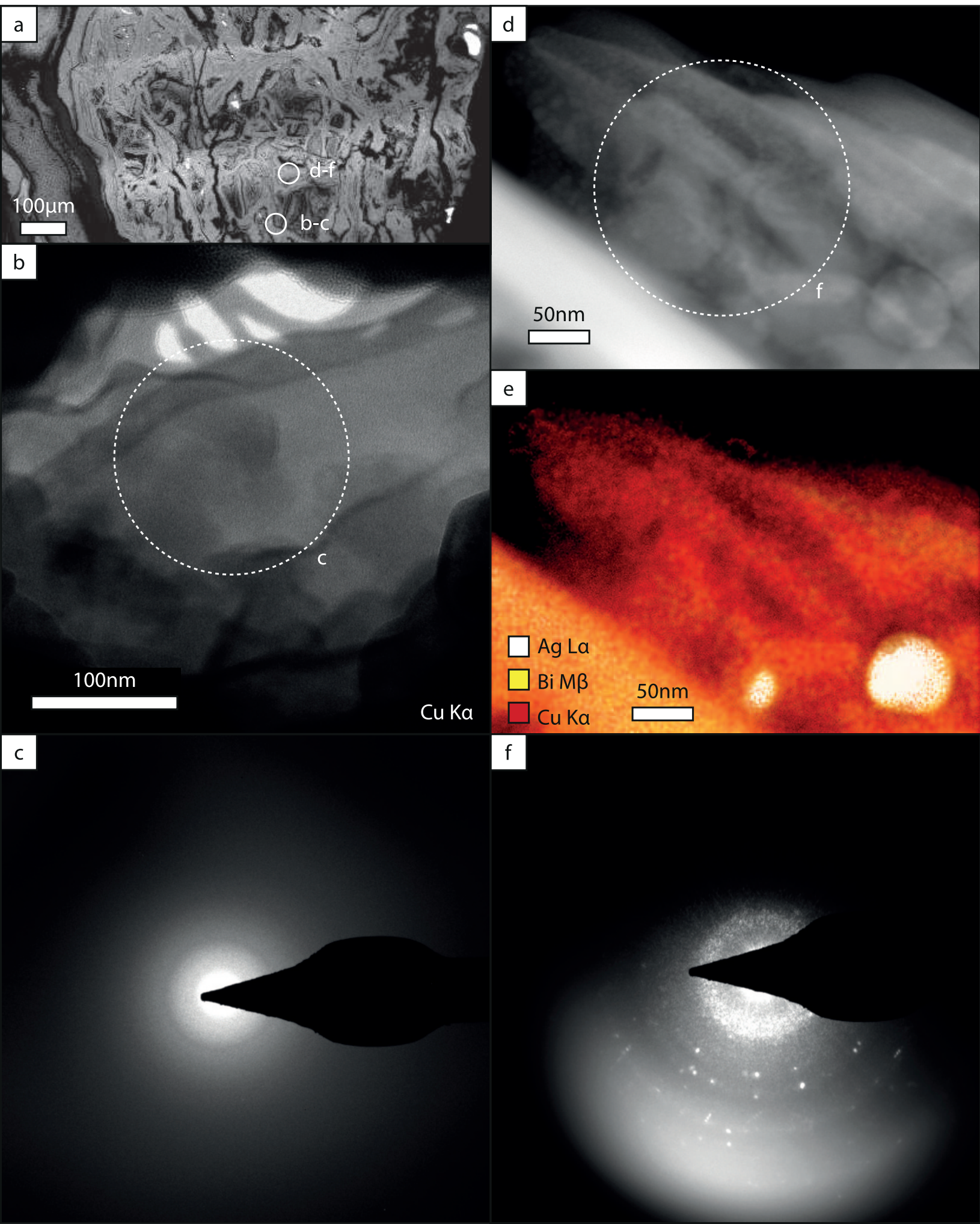


Figure 8

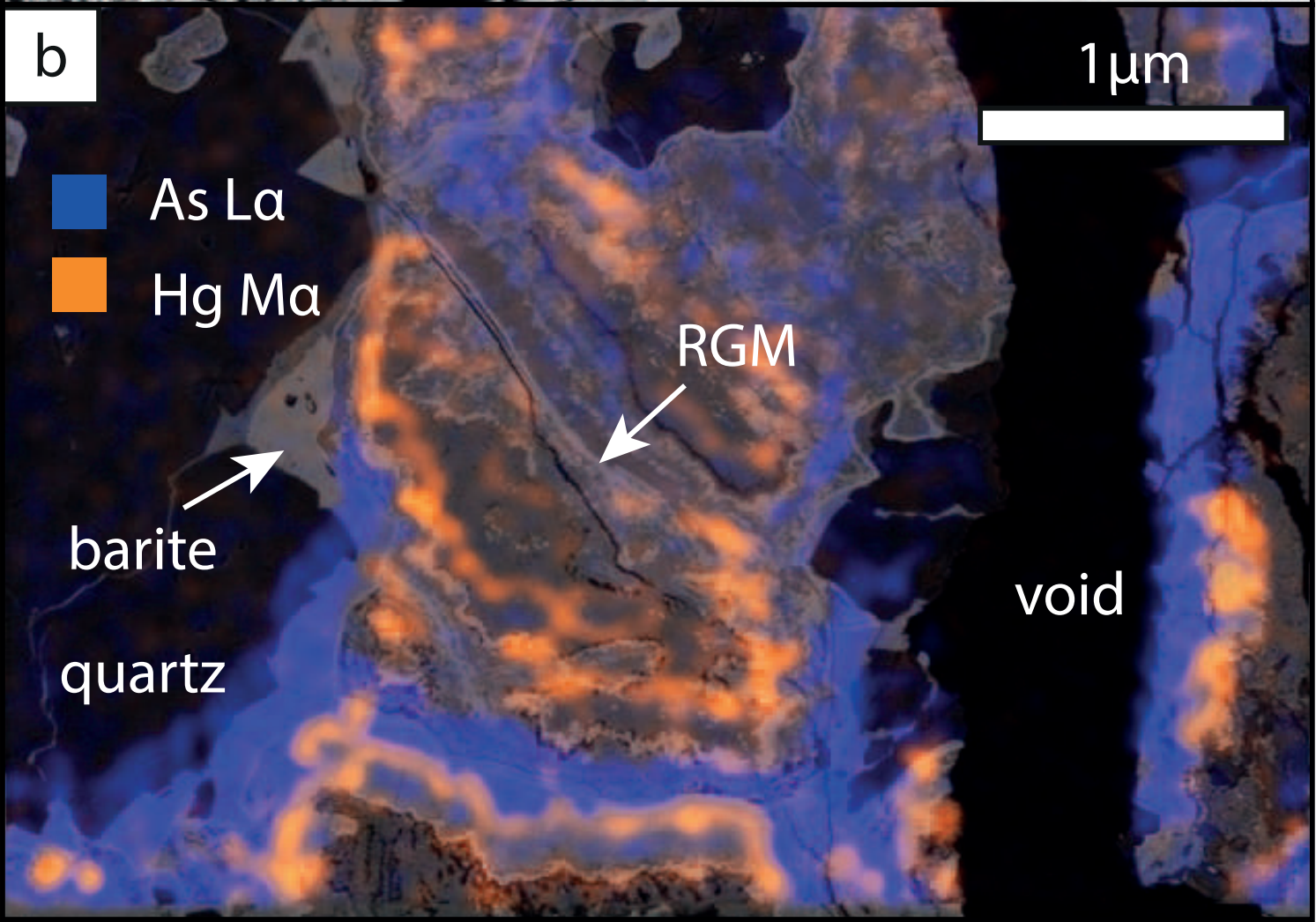
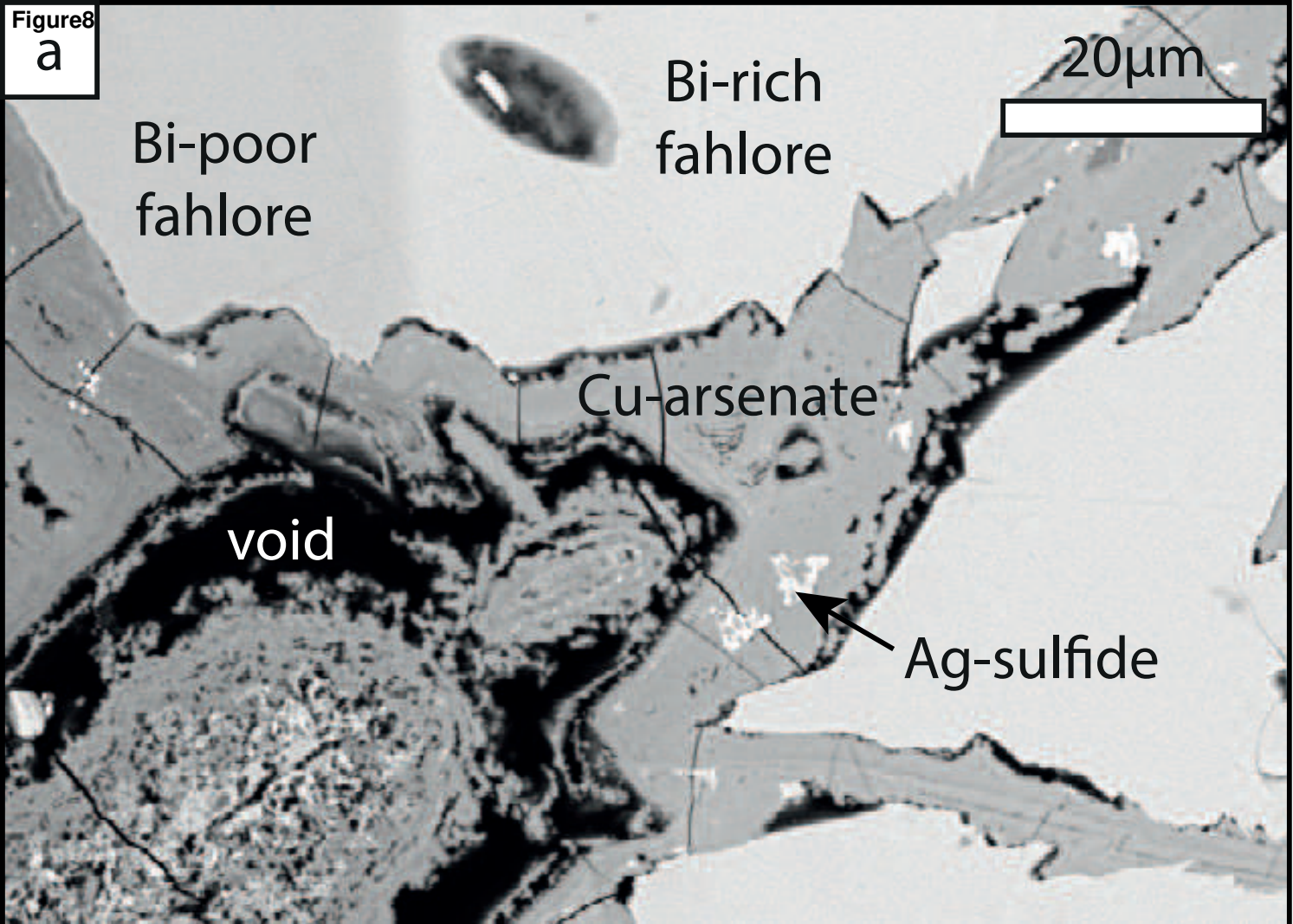
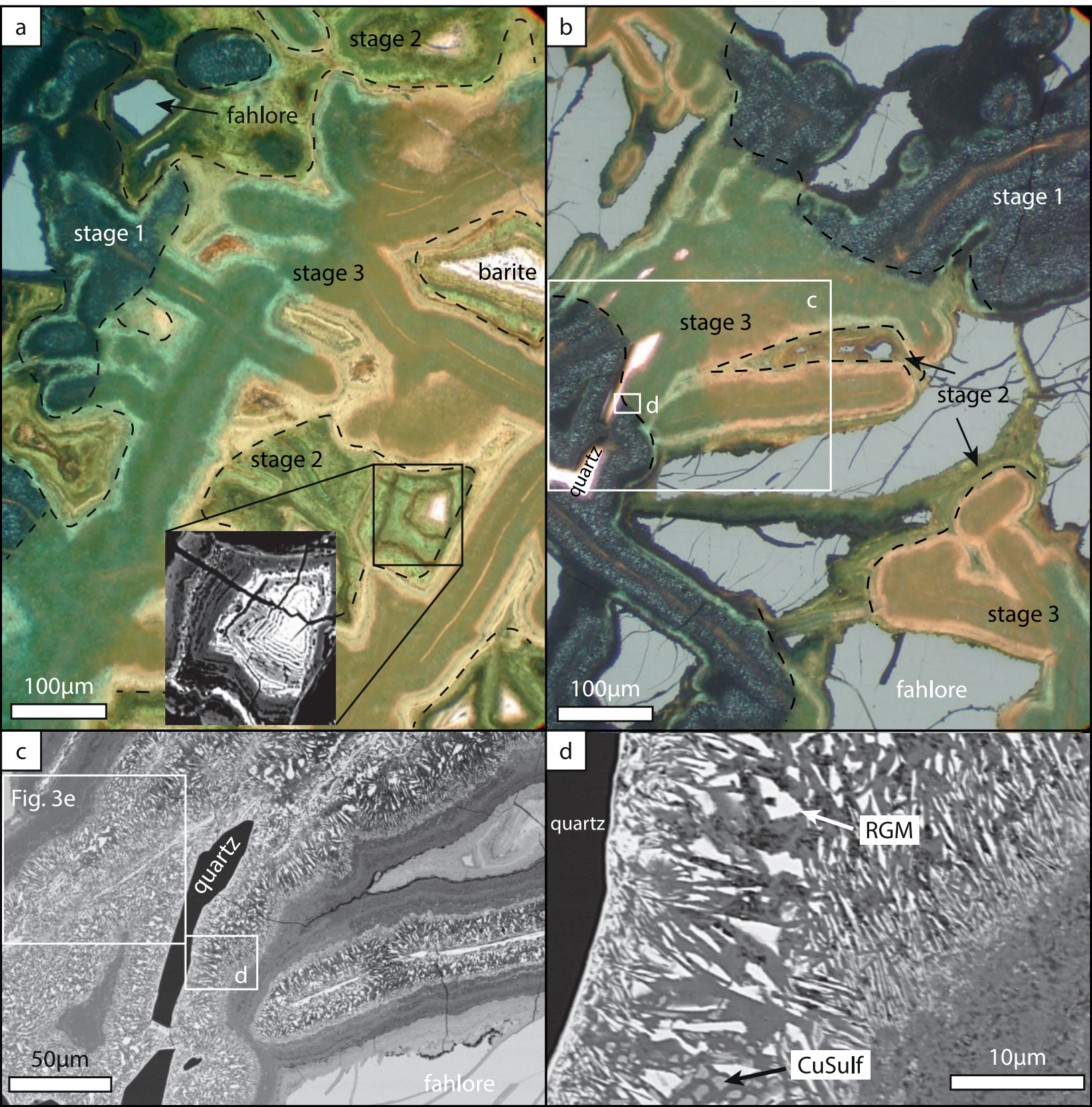


Figure9



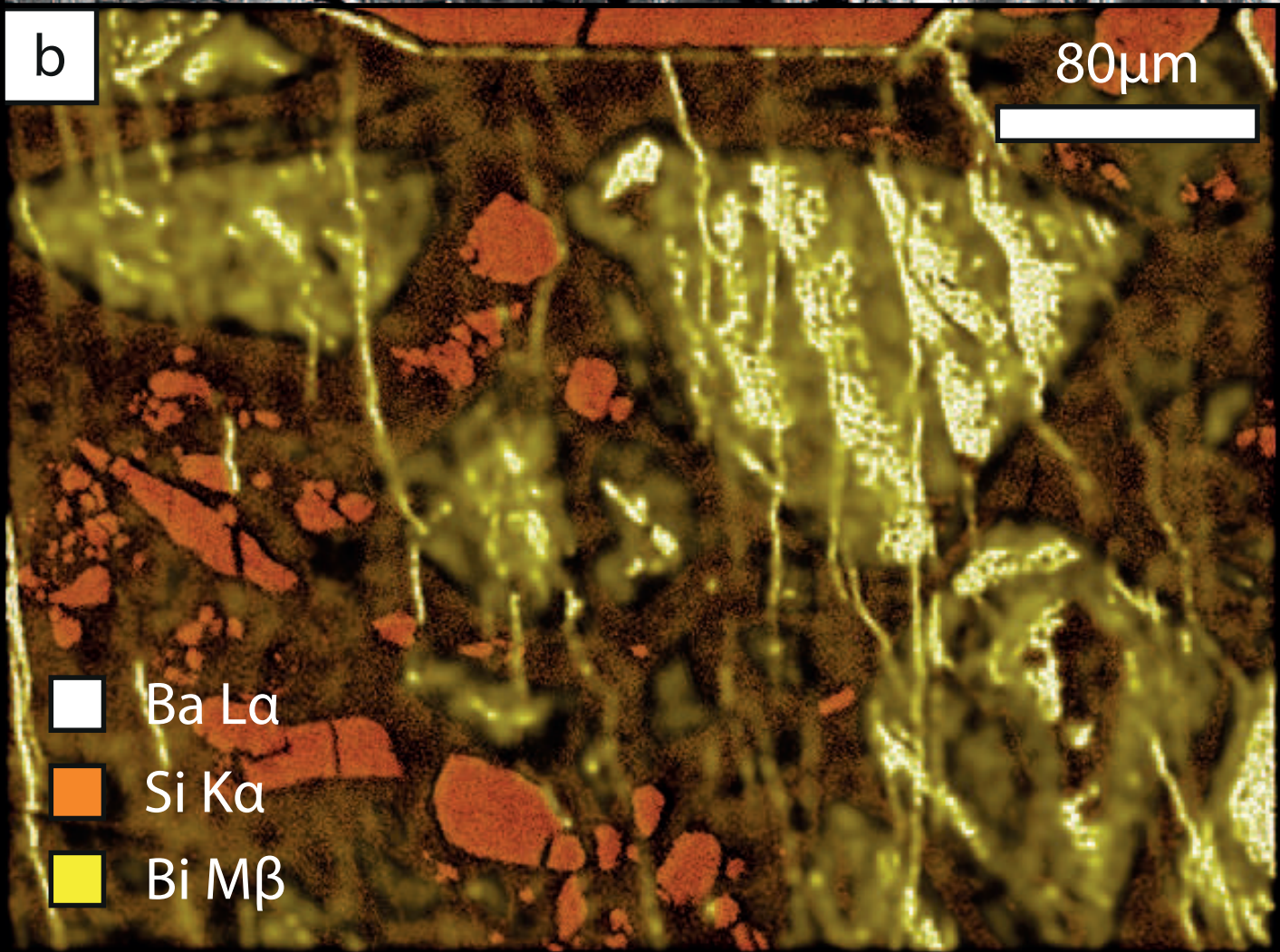
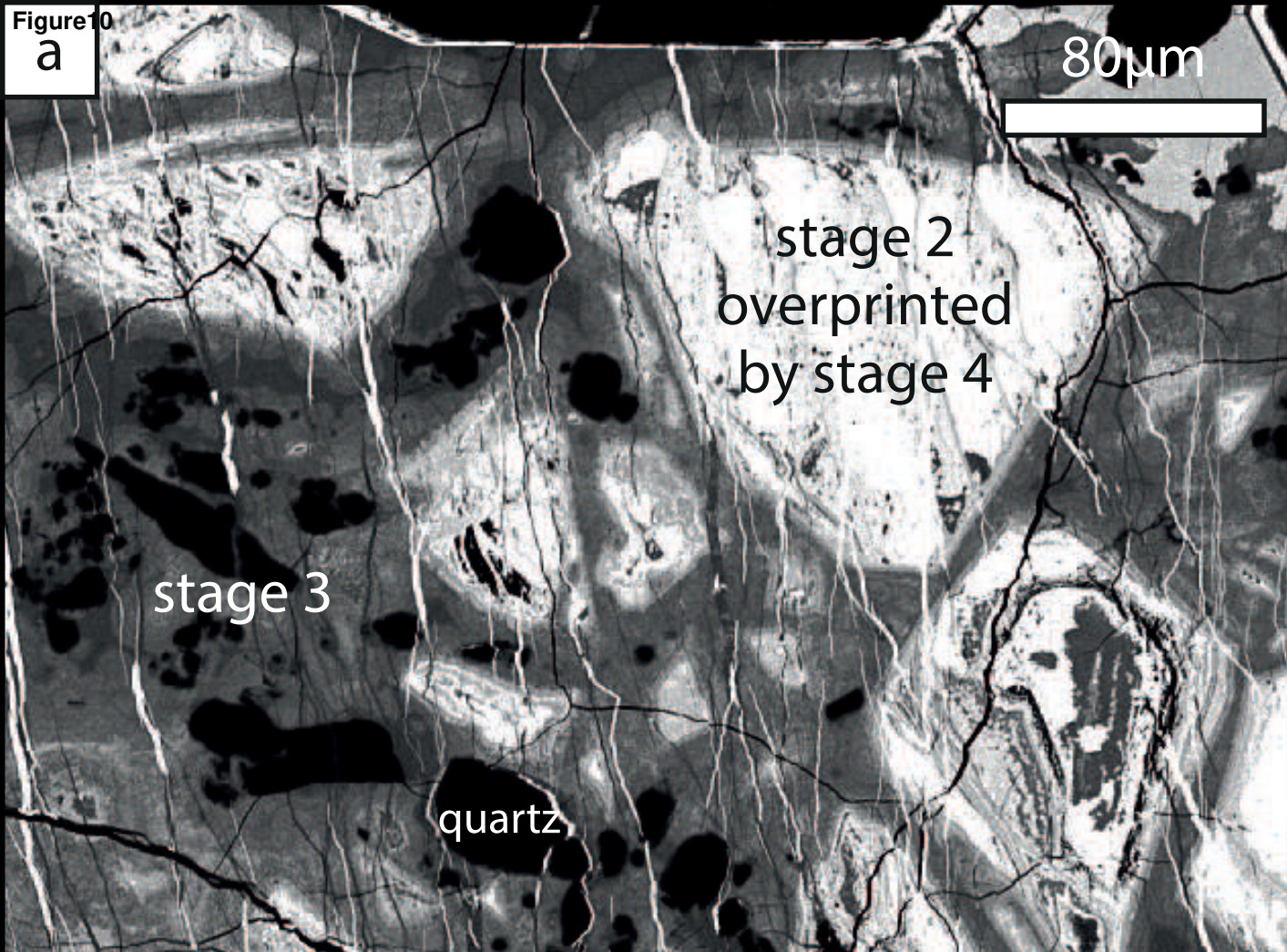
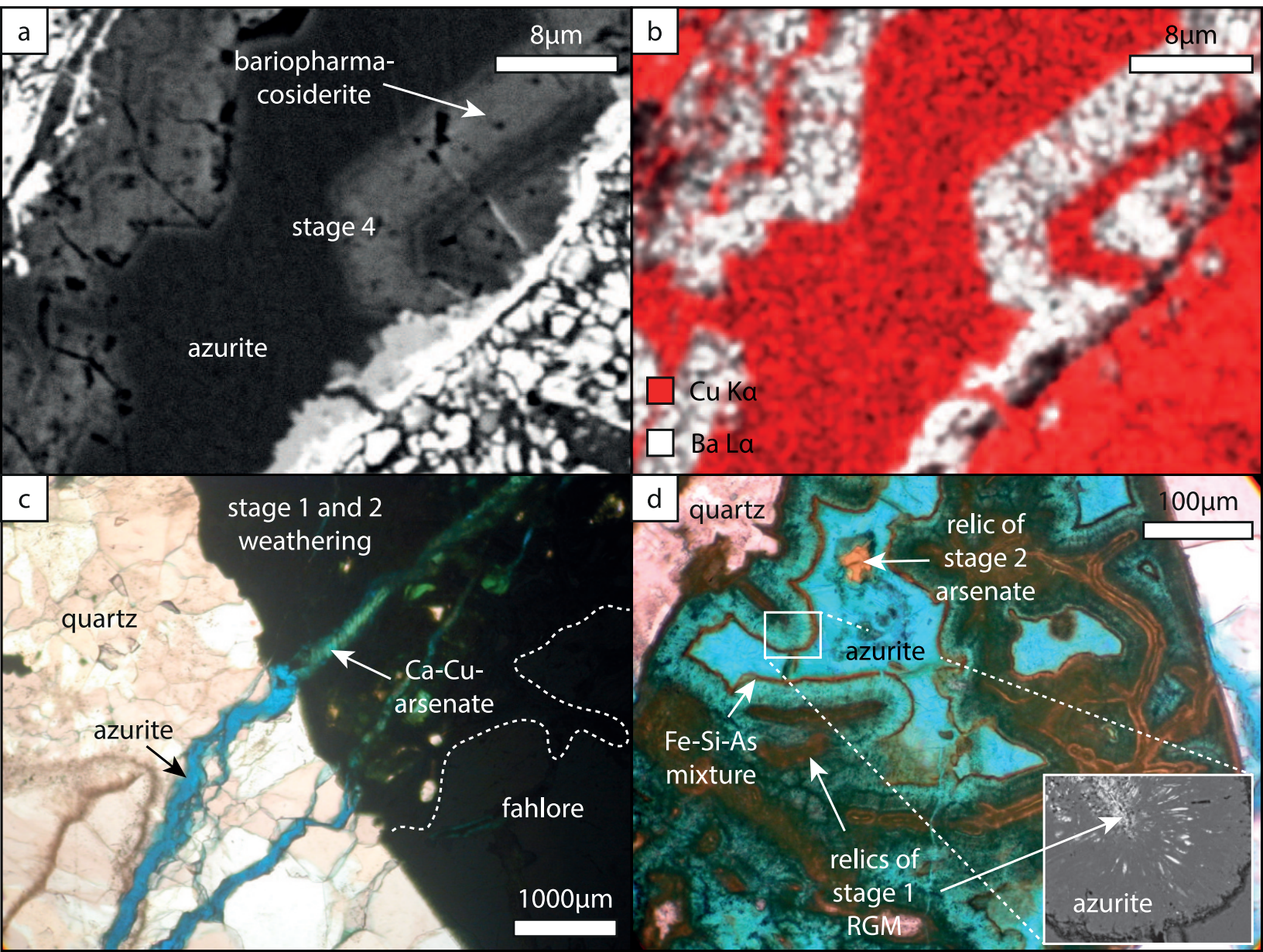
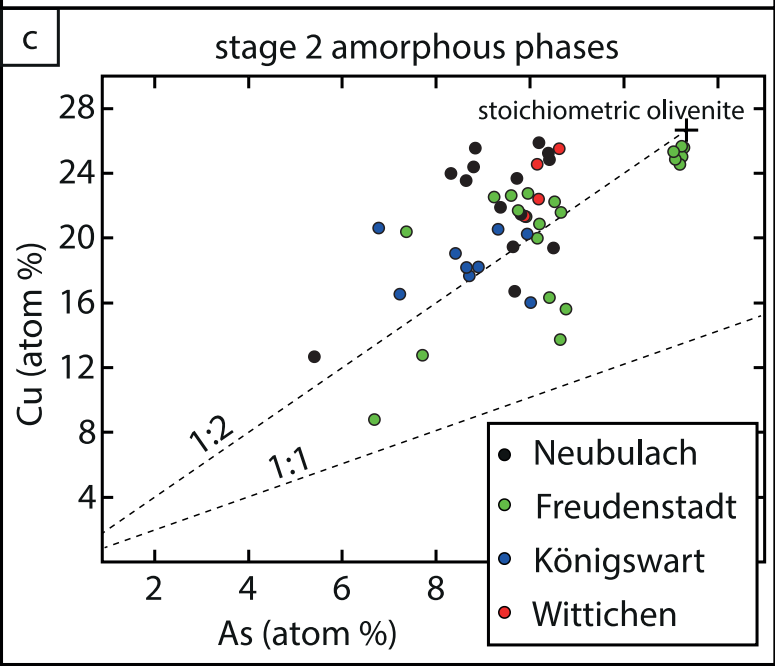
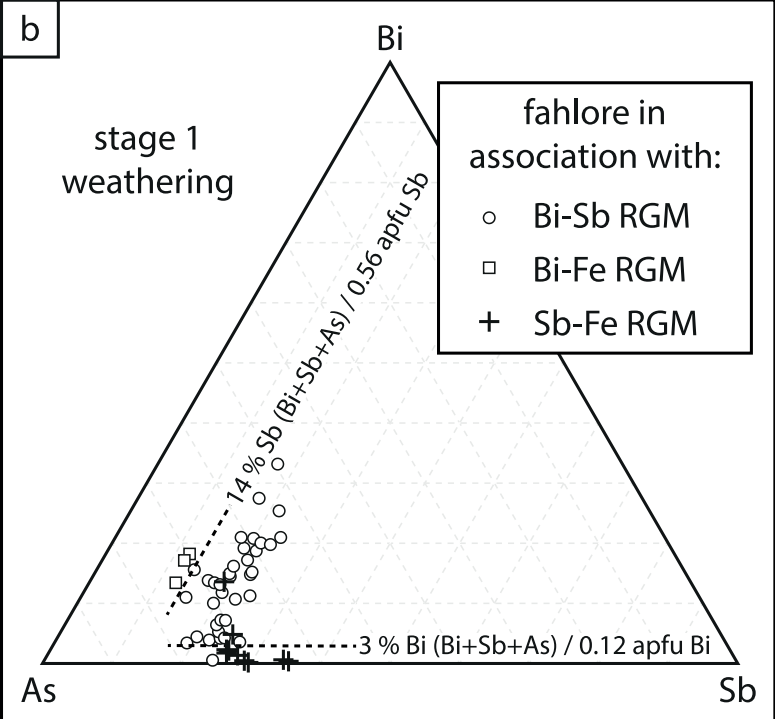
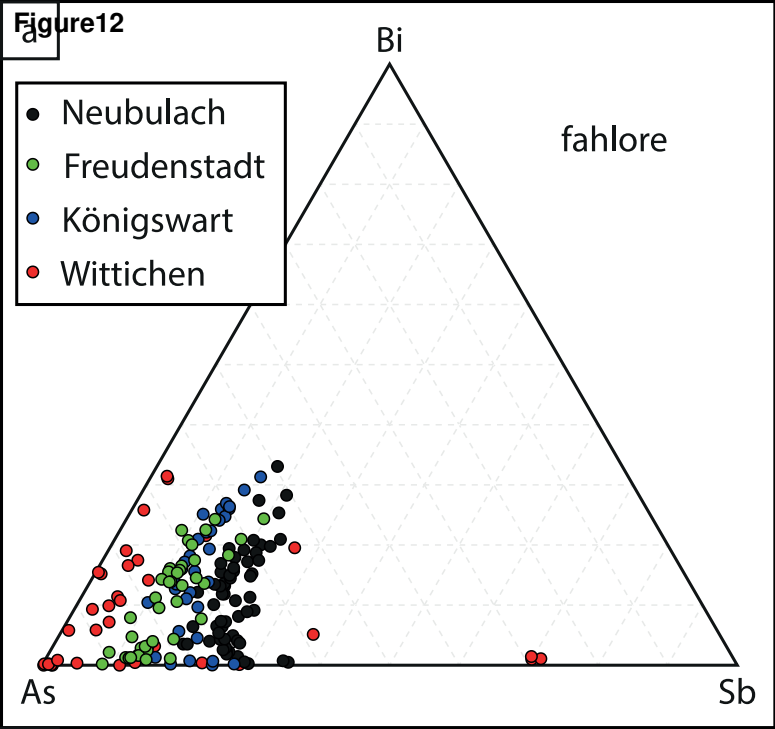


Figure 11





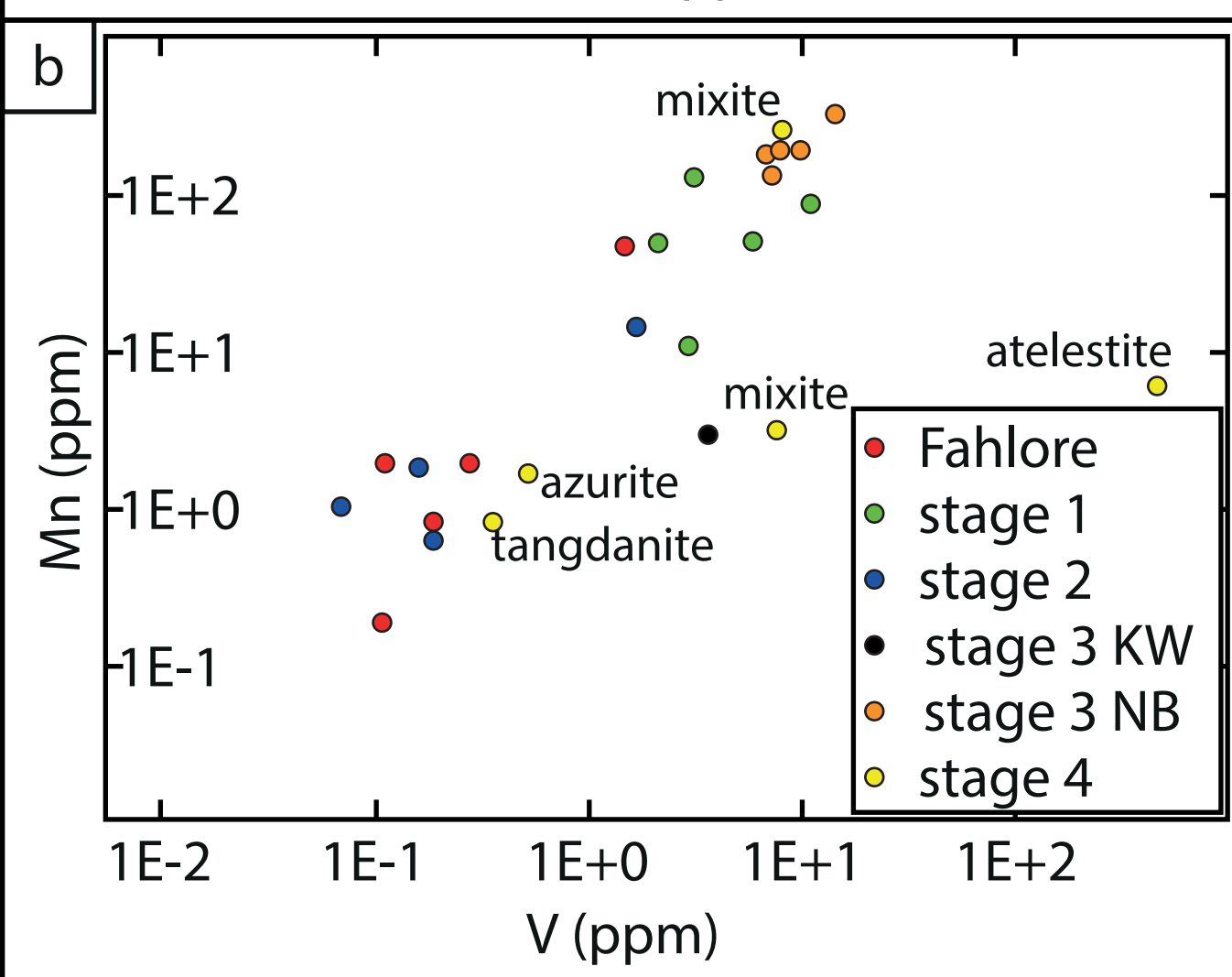
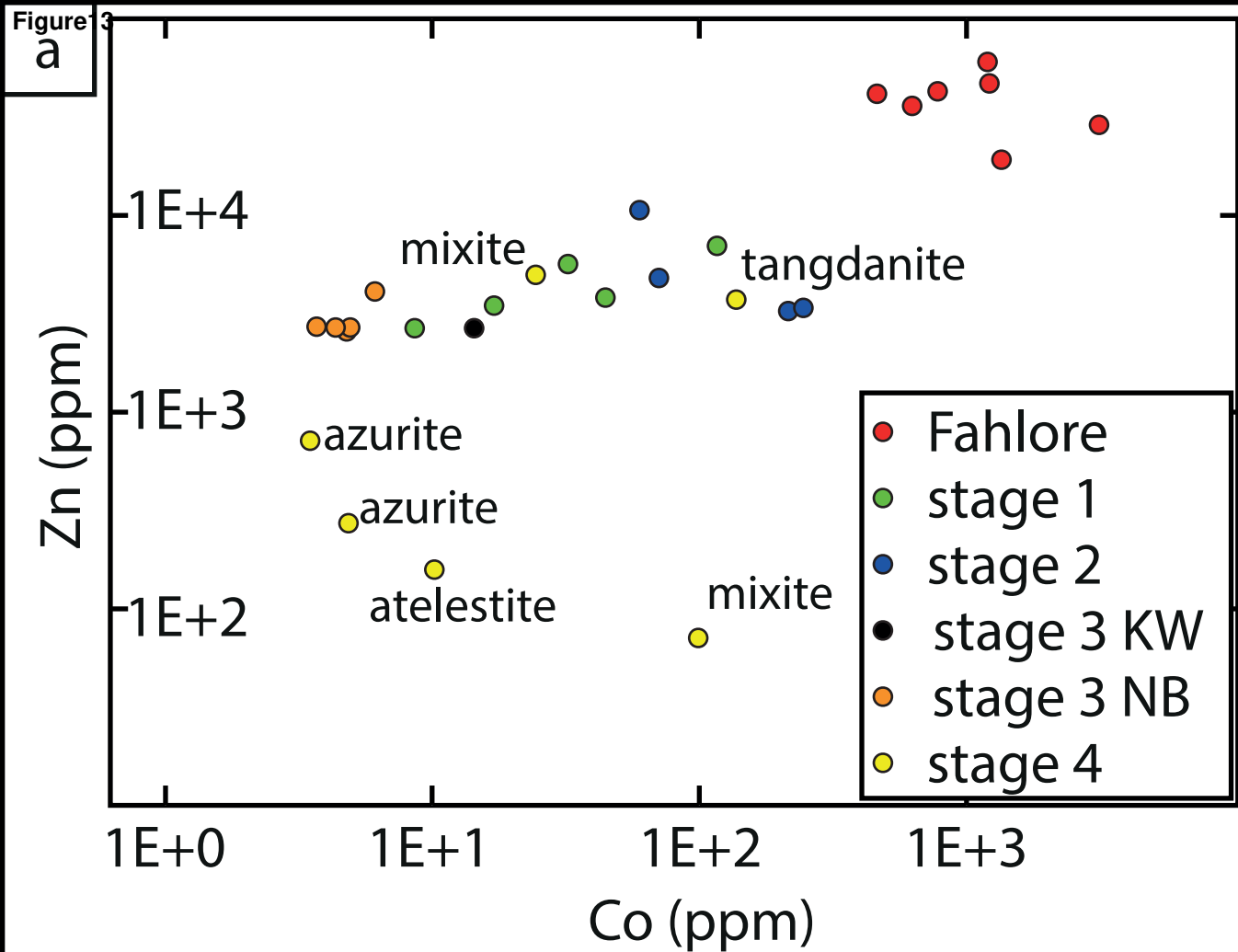


Figure14

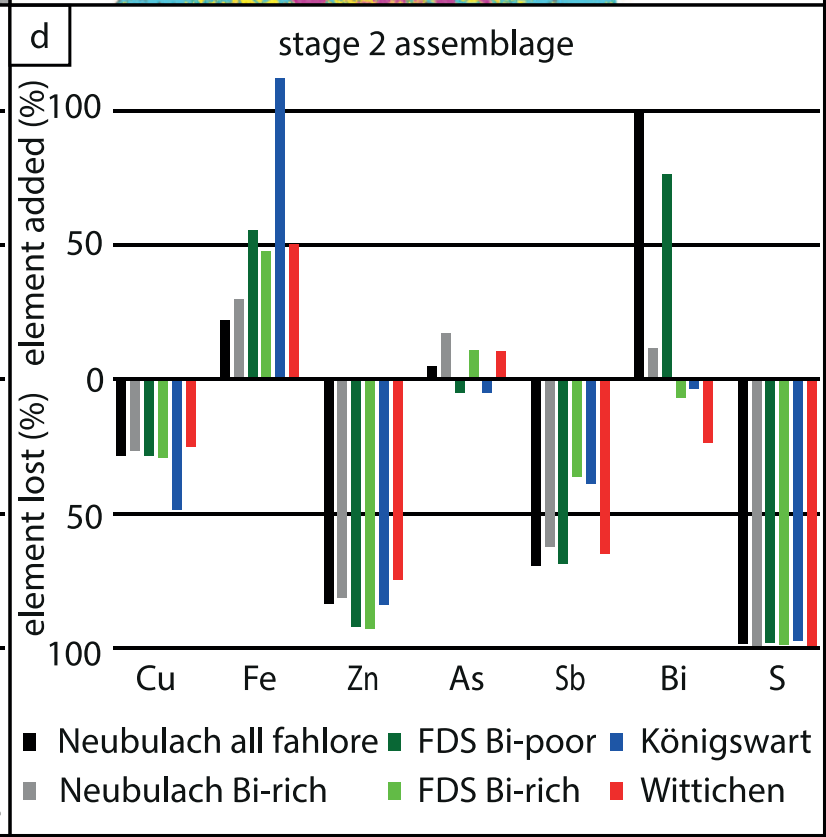
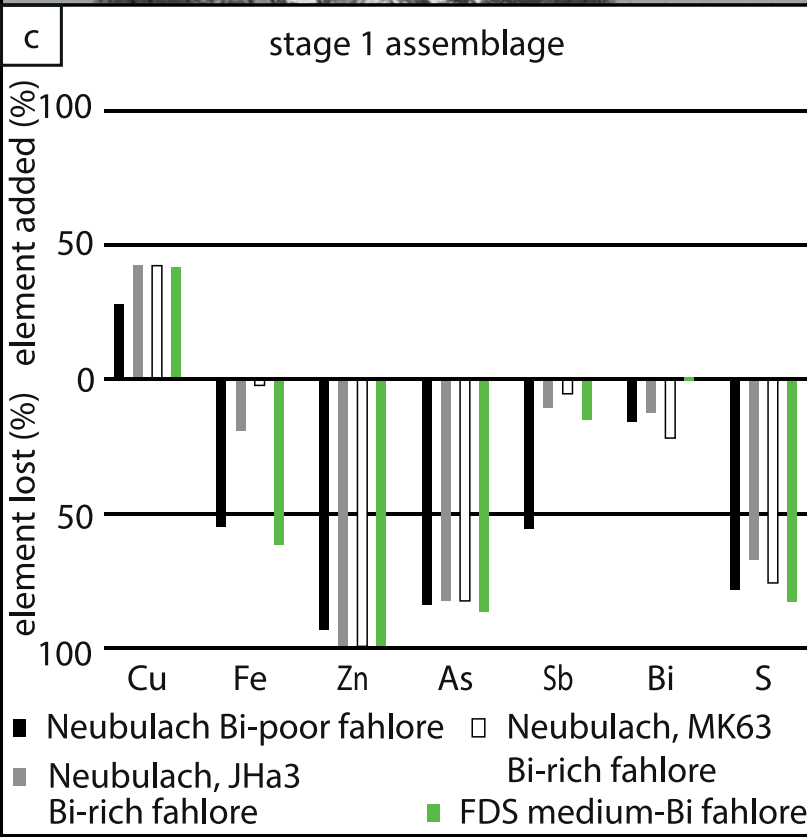
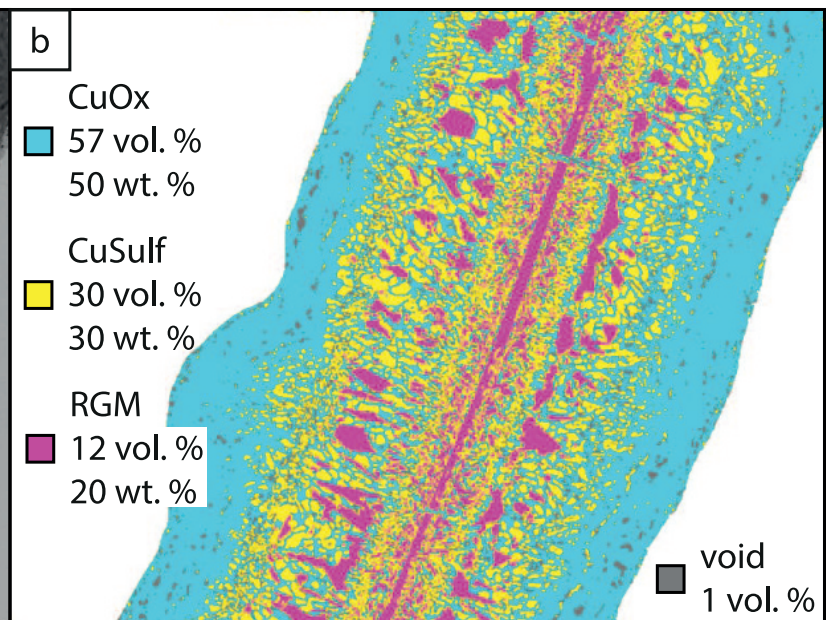
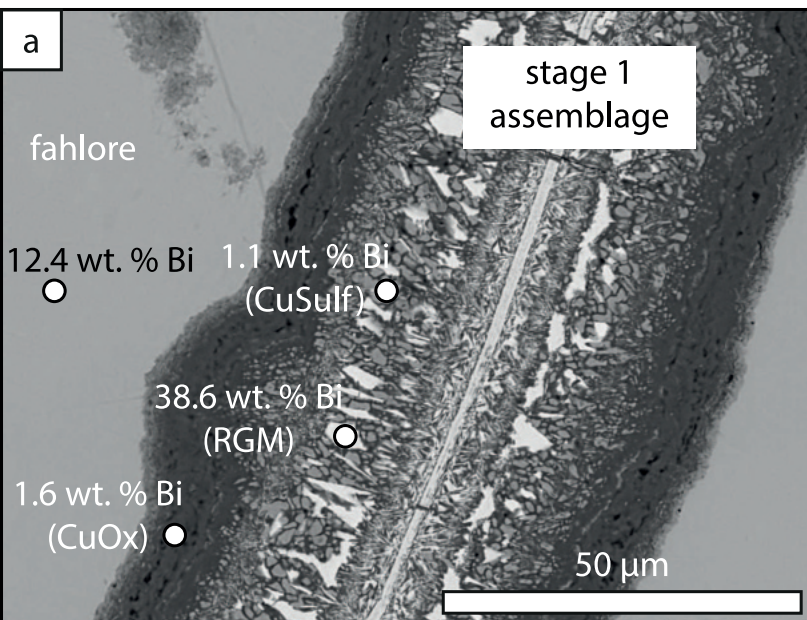
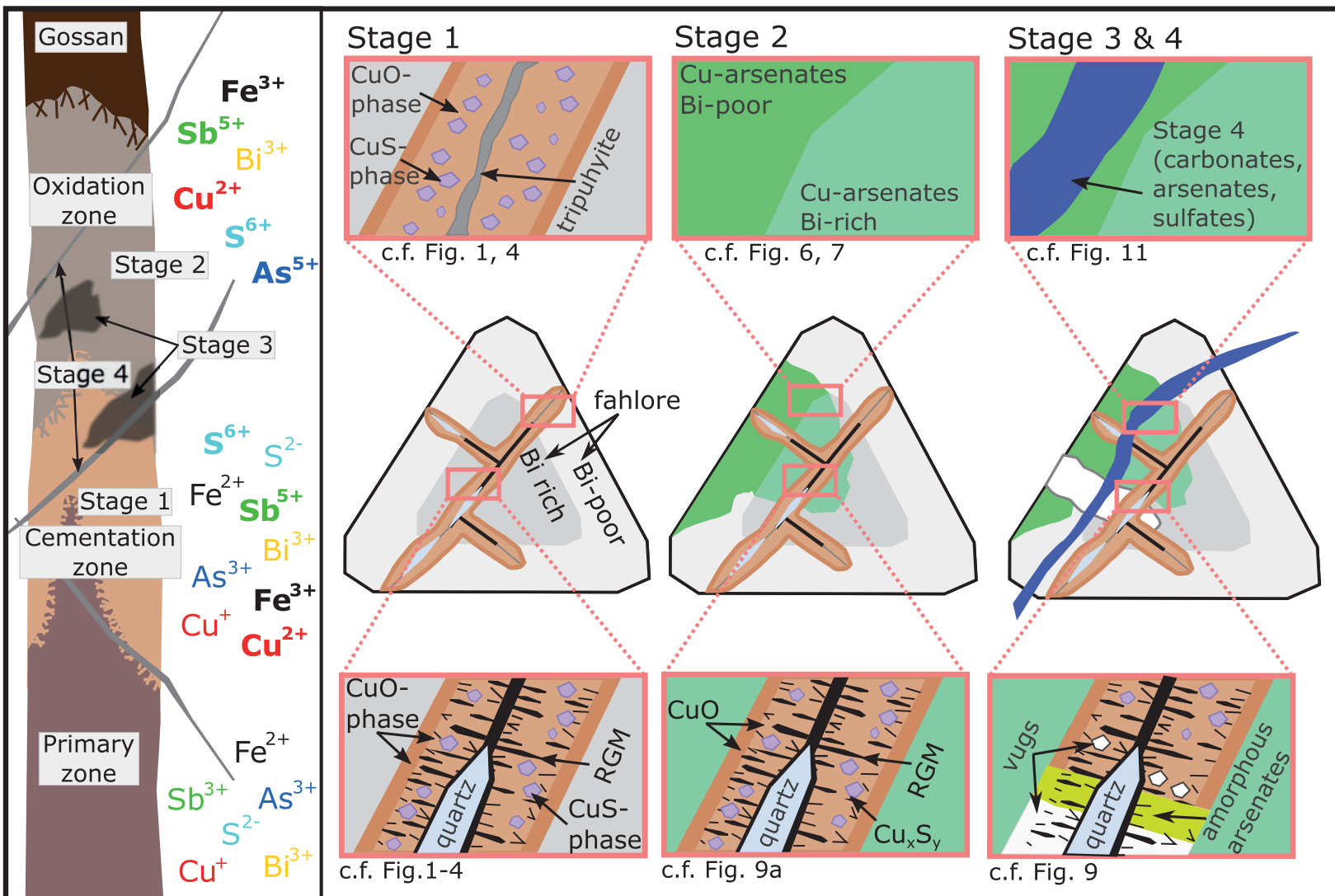


Figure15



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