Helmholtz-Zentrum Dresden-Rossendorf (HZDR)



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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Originally published:

November 2018

Chemical Geology 499(2018), 1-25

DOI: https://doi.org/10.1016/j.chemgeo.2018.07.032

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1	Weathering of Bi-bearing tennantite
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Abstract

17 The complex sulfosalts of the tennantite-tetrahedrite solid-solution series [called fahlore; 18 $(Cu,Ag)_6Cu_4(Fe,Zn,Cu,Hg,Cd)_2(Sb,As,Bi,Te)_4(S,Se)_{13}$] 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, μ XRD 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).

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

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- ilmenite with HCI-bearing fluids. This is clear evidence, that the diffusive process during the first
 contact with alteration fluids to form cementation zone assemblages is a basic physical process and
 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

1. Introduction

60 Minerals of the tennantite-tetrahedrite solid-solution series (in the following referred to as fahlore) 61 have the general formula of (Cu,Ag)₆Cu₄(Fe,Zn,Cu,Hg,Cd)₂(Sb,As,Bi,Te)₄(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). Maximum reported Bi contents for fahlore are up to 22 wt.% from the Wittichen area in the 66 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.

Under oxidizing, near surface conditions, fahlore is not stable anymore. As a consequence, it undergoes dissolution and/or thermodynamically more stable secondary phases form (e.g., Arroyo and Siebe 2007; Roper et al., 2012; Keim and Markl 2015; Borčinová Radková et al., 2017). During this process, heavy metals and toxic elements are commonly released to the environment (e.g., Reich and Vasconcelos 2015). Which secondary phases form and, hence, which components are released to the environment, depends on the composition of the primary mineral and the physiochemical conditions 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 their weathering, studies on the weathering behaviour of fahlores are surprisingly scarce. Nickel et al. 87 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

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pore-water analyses and therefore suggested, that the formation of these phases may not be 94 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 itself. They found, that these elements show different mobility during weathering. Copper and 98 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) specific to the weathering of the specific, investigated deposit (hydrothermal quartz-siderite-sulfide 104 105 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 (µXRD), 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.

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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 shale and carbonate rocks are partly preserved in some areas, but are mostly eroded due to the 124 Schwarzwald uplift during the Paleogene-Neogene Upper Rhine Graben formation (Geyer and 125 126 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,

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

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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, 2000). Available formation ages of the secondary phases from the investigated deposits are ⁴⁰Ar/³⁹Ar 152 153 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 supergene carbonates have been dated by Walter et al. (in press) between 40.0±11 Ma and 0.6±0.19 158 159 Ma, however, it is in most cases not possible to discriminate between hydrothermal and supergene 160 carbonates. Supergene minerals formed in various settings:

- in the oxidation zone of the veins (Markl et al., 2014a, b) during natural and mining processes
 (e.g., concrete in the Clara mine and fire-setting; Kolitsch, 2000; Keim et al., 2017)
- after the mining within the abandoned mines (e.g., pyromorphite, arsenates and sinters in
 mines, (Burmann 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).

Primary minerals of the investigated mines were exploited for Ag, Co (Wittichen area only) and Cu and additionally for azurite as pigment in Neubulach (Werner and Dennert, 2004). Mining occurred mainly in the 13th (Neubulach) and 17th to 19th century (Werner and Dennert, 2004; Markl, 2005), 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.

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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 (±fluorite) veins (Staude et al., 2010) are exposed to 184 weathering. Samples were collected from the mining areas of Neubulach, Königswart, Freudenstadt and Wittichen/Reinerzau (Alte Gabe Gottes mine and Schmiedestollen dump; electronic 185 supplementary material (ESM) Figs. 1 and 2, see Markl, 2015 and 2016 for detailed descriptions of 186 187 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 fahlore. The carbonate synchysite-(Ce) frequently forms small euhedral crystals together with
hematite, both enclosed by quartz in the sample from the Alte Gabe Gottes mine, whereas other
primary carbonates were not observed in other samples.

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3. Analytical Methods

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

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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 µm 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 α - with the Bi M α -lines for the elemental maps, the Bi M β -line was used instead.

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218 3.2. μXRD analysis

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

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226 3.3. Raman

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

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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 column around the optical axis. Each SDD has an active area of 30 mm², adding up to an overall 236 237 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 μ s. The overall measurement time for the elemental STEM-EDX mapping was about 4 243 hours.

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245 3.5. LA-ICP-MS

Elemental concentrations in minerals were determined by ICP-MS analyses with an AGILENT 7700 246 247 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 maximum (100% = 4 mJ at a spot diameter of 150 μ m), at a laser pulse frequency of 10 Hz. In a 249 250 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 Mineraux du CNRS. Lithium-borate glass disks of both were prepared using 0.6 g of powder of these 256 257 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 and data evaluation was developed by Massone et al. (2013) and Baggio et al. (2018). 268

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

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

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281 MLA

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

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290 **3.6. Analytical limitations**

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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 μ m-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 of in the vacuum the microprobe (e.g., bariopharmacosiderite 300 $[Ba_{0.5}Fe^{3+}_4(AsO_4)_3(OH)_4 \cdot 5H_2O]$ 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.

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4. Results

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4.1. Identified phases

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

Secondary sulfides are covellite [CuS], spionkopite [Cu₃₉S₂₈], chalcocite [Cu₂S], acanthite [Ag₂S], and cinnabar [HgS) based on EMPA, TEM-EDX, and Raman. In all cases, a unique identification by μ XRD of these sulfides was not possible due to the small grain size or intergrowth with amorphous phases.

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

Frequently, Sb-Fe, Sb-Bi-Fe, and Bi-Fe oxide phases were found. The Sb-Fe phase was qualitatively analysed by EDX mapping and is interpreted to be tripuhyite $[Fe^{3+}Sb^{5+}O_4]$ or hydroxyferroroméite $[(Fe^{2+}_{1.5}\Box_{0.5})Sb^{5+}_2O_6(OH)]$, 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 Cu_{1.0}Sb_{1.1}Bi_{1.0}As_{0.3}Fe_{0.7}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 the tetragonal phase tripuhyite. In two electron diffraction patterns from different locations in a 328 329 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 tripuhyite-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 tripuhyite/hydroxiferroroméite if used for a specific chemistry. Interestingly, Walenta (1983) described from Neubulach the occurrence of an Sb-Bi-Fe-phase called 341 "bismutostibiconite" $[Fe^{3+}_{0.5}Bi^{3+}_{1.3}Sb^{5+}_{1.7}O_7]$, the IMA status of which as a mineral, however, was 342 343 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.

Frequently, a Cu-As phase was found, which is characterized by either no crystallinity or nm-sized crystal aggregates in an amorphous ground mass. Raman measurements show that As is present as arsenate with some evidence of H₂O (ESM Fig 4). Other identified phases are amorphous and botryoidal Cu-Silicates, amorphous red Fe-Cu-oxides, and amorphous Bi-carbonates.

The well-crystallized arsenates mixite $[BiCu_6(AsO_4)_3(OH)_6 \cdot 3H_2O]$, olivenite $[Cu_2AsO_4(OH)]$, zálesiite 351 352 $[CaCu_6(AsO_4)_2(AsO_3OH))OH)_6 \cdot 3H_2O],$ tangdanite $[Ca_2Cu_9(AsO_4)_4(SO_4)_{0.5}(OH)_9 \cdot 9H_2O],$ dussertite- $[BaFe_3^{3+}(AsO_4)(AsO_3OH)(OH)_6;$ 353 arsenogoreceixite $BaAl_3(AsO_4)(AsO_3OH)(OH)_6],$ and bariopharmacosiderite were identified by Raman, μ XRD and EMPA (Table 4 ; ESM Figs. 3 and 4) as 354 355 were the Cu-carbonate minerals malachite and azurite.

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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

362 4.2.1. Stage 1 weathering

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

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

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

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

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

If chalcopyrite is intergrown with fahlore, nothing changes with respect to fahlore weathering stage
Some of the veinlets stop at the contact to chalcopyrite, some continue into it, in which case, the
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.

Stage 3 weathering textures are specific for a certain sample location and, hence, not part of ageneral weathering process occurring in the same way at each locality.

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

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

In a sample from Königswart, amorphous Cu-silicates cement brecciated clasts of fahlore and weathering assemblage 2 (Fig. 10). The clasts are overgrown by botryoidal aggregates of an amorphous Cu-silicate I, followed by homogeneous amorphous Cu-silicate II which also hosts 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 locality to locality (Table 4). Where malachite and azurite occur in the same sample, azurite typically 444 445 forms in or close to fahlore, whereas malachite is the dominant mineral further away. In one sample, a quartz-hosted azurite vein cuts through hydrothermal gangue minerals and through fahlore-446 447 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

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

The matrix of stage 1 assemblage, the Cu-oxide phase, contains up to 3.1 wt.% As₂O₅, 1.2 wt.% Bi₂O₃,
1.6 wt.% SO₃ and other trace elements below 1 wt.% (Table 1).

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

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}
(normalized to 1 apfu Bi; see section 4.1). It contains traces of SiO₂, Al₂O₃, BaO, P₂O₅, and SO₃ (Table
1). A mixture of all stage 1 phases from Neubulach, analysed by LA-ICP-MS, resulted in up to 10 ppm
V, 150 ppm Mn, 15 ppm Cr, 120 ppm Co, 10 ppm Ni, and 85 ppm Pb (Table 3, Fig. 13). Sample points
where Cu-sulfides and the matrix were dissolved during stage 3, leaving voids and only the RGM
behind, show higher Mn (up to 330 ppm) and Pb (up to 280 ppm) as well as lower Co (up to 6 ppm)
and Ni (up to 2 ppm).

The amorphous red oxide phase in weathering stage 1 of chalcopyrite is dominated by Fe and Cu and was analysed from Wittichen and Königswart (n=10). Normalised to 100 mol%, the Fe content varies between 20.3 mol% and 33.6 mol%, the Cu contents between 7.7 mol% and 14.1 mol%. Other main 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 with up to 7.4 wt.%.

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488 4.3.3. Secondary weathering phases – stage 2

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The amorphous Cu-arsenates of stage 2 have variable amounts of Bi₂O₃ (up to 12.3 wt.%) and other components (Table 4). Some data of the Cu-arsenate phase are close to the stoichiometric composition of olivenite, however, the bulk of the data shows variable Cu/As ratios (Fig. 12c; Table 4). The totals of the EMPA range from 59 to 97 %, reflecting variable water content and a high and variable porosity.

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

The green amorphous to nano-crystalline arsenates of stage 3 (Fig. 9) are too small for identification
by EMPA but were investigated by TEM. They contain 65.5 wt.% CuO, 13.0 wt.% As₂O₃, 10.0 wt.%
SO₃, and 4.7 wt.% Bi₂O₃ (TEM-EDX) besides other trace elements presented in Table 1.

The two silicate-bearing phases from Königswart were analysed by EMPA. The botryoidal Cu-silicate has a higher silica content (22.6 wt.% SiO₂) and a higher total (89.3 %) compared to the homogeneous silicate (11.9 wt.% SiO₂, total: 73.6 %). The botryoidal phase also contains more As₂O₃ (6.4 compared to 5.1 wt.%), FeO (2.4 compared to 0.1 wt.%), and Bi₂O₃ (4.1 compared to 1.8 wt.%). Whether the lower total of the homogenous phase is due to a higher water or carbonate content, or due to porosity, remains unclear.

510

511 4.3.5. Secondary weathering phases – stage 4

The well-crystallized minerals of stage 4 are in most cases large enough for EMPA, however, a distinct identification was not always possible. Azurite was only analysed from Neubulach and contains up to 2.0 wt.% As₂O₅ and 1.1 wt.% FeO. Malachite was analysed from Neubulach, Freudenstadt, Königswart and Wittichen with ZnO up to 2800 ppm in Freudenstadt, Wittichen, and Neubulach, and up to 2.7 wt.% from Königswart. In analyses from Wittichen and Königswart, 3.8 and 0.14 wt.% Bi₂O₃ were detected, respectively. Other trace elements are not specific for a location and are As₂O₃ up to 2.9 wt.%, Sb₂O₅ up to 5300 ppm, and BaO up to 1400 ppm. Mixite group minerals are abundant minerals of stage 4 from Königswart, Wittichen and Neubulach.
Wittichen samples show Ca-bearing mixite, samples from Neubulach and Königswart Bi-bearing
zalesiite (Table 4, see also Göb et al., 2011). All analysed mixite group minerals have SiO₂ up to 3.7
wt.%. Göb et al. (2011) also report rare earth elements from Neubulach with up to 1.07 wt.% Ce₂O₃.
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

527 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.

The mass balance calculation is more robust for main than for trace elements, because of the higher analytical error for the latter. Small secondary phases cause nugget effects (eg., acanthite, cinnabar) and, hence, a large error. Additionally, a small variation in trace elements has a bigger effect on the result (e.g., 1 ppm in fahlore compared to 2 ppm in its weathering product would result in a 100% addition of that element) and is, thus, not comparable to main elements. Therefore, only main elements of fahlore (Cu, Fe, Zn, As, Sb, Bi, S) will be considered in the following calculations (see 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 3552 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 phases considering the porosity. The fraction of each phase and its respective chemical composition 556 557 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 0.02 g Bi in the Cu-oxide phase for each cubic centimetre, resulting in 0.53 g Bi per cubic cm of 562 563 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 tripuhyite/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.

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

If fahlore contains elevated Ag contents, nm- to μm-sized acanthite grains are found between the Cusulfides of stage 1 (or enclosed in the amorphous phase of stage 2). In a sample from Freudenstadt, acanthite was found next to a fahlore zone with 6000 ppm Ag; no acanthite was found in the next fahlore zone which contains 2000 ppm Ag. In a sample containing 4300 ppm to 8500 ppm Hg in fahlore, small cinnabar grains were found in between the Bi-Sb-bearing RGM. Hence, Ag and Hg can 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

Calculation of the stage 2 element mobilization from all investigated samples shows that almost no
As is mobilized during the formation of the amorphous phase (Fig. 14d). The most striking feature of
stage 2 weathering is the survival of the fahlore zonation caused by Bi in the supergene amorphous
arsenate phase (Fig. 6). Bismuth-rich zones show no mobilization of Bi, but Bi-poor zones show an
apparent addition (Fig. 14d). This is, however, most likely an effect of the low concentration of Bi and
hence of the larger error of the method (Freudenstadt sample: 0.1-2.4 wt.% Bi in low Bi-fahlore, 0.23.8 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.

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629

5.2.3. Element mobility during stage 3

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

636

637

5.2.4. Element mobility during stage 4

Stage 4 weathering minerals (e.g., azurite, mixite group minerals, bariopharmacosiderite) are spatially not directly related to fahlore and only in exceptional cases, they replace older weathering products. Hence, a mass balance calculation is not meaningful. The mineral assemblage, however, shows that Ca, Si, Ba, Al, and C must have been added from external sources. The dissolution of host rock (limestone, clastic redbeds, granite) and gangue (barite, quartz, fluorite) delivers elements like C, Si, Ba, Al and Ca. This is particularly striking at Neubulach, where stage 4 minerals are (due to the 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 only Sb-bearing phase is the dusserite-arsenogorceixite solid-solution from Freudenstadt. Possibly, at
other localities, especially Neubulach, where dissolution of stage 2 was observed and no secondary
Sb minerals are known besides the RGM according to Walenta (1992), both elements were released
into the fluid during this weathering stage.

The mineral assemblage shows that during stage 4, Cu, As, Bi, Sb, and Fe are mobile. As discussed above, the source of these elements is probably the dissolution of older weathering assemblages (e.g., stages 1 and 2). A renewed dissolution of fahlore to form stage 4 minerals was not observed, but cannot be ruled out. Also, weathering of other minerals of the primary mineral assemblage (e.g., chalcopyrite, emplectite, arsenides) could deliver elements like Cu, Bi, or As, to form stage 4 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, Dietrich et al., 1969) to name just a few. 666

667

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

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

The formation of secondary phases during weathering and/or alteration in general can be due to incongruent dissolution (scorodite dissolution; Harvey et al., 2006), dissolution and re-precipitation in an aqueous solution (weathering of electrum, Mann, 1984), support by bacteria (sulfide conversion to schwertmannite; Dockrey et al., 2014), or reaction of an aqueous solution with the primary mineral to form a gel-like fluid in which later secondary phases may crystallize by dehydration (hematite from poorly crystalline ferrihydrite; Cudennec and Lecerf, 2006). An incongruent dissolution during fahlore weathering can be excluded based on the observed textures (e.g., fingerlike tubes) and based on the fact, that during incongruent dissolution, the primary phase is successively coated by the secondary phases thus significantly reducing its reactivity (Harvey et al., 2006). No secondary coating of any phase was observed around fahlore. A bacterial influence is also 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).

The fahlore weathering textures of stage 1 look remarkably similar to the patterns found in the low-HCl-concentration experiment by Janssen et al. (2010). Along the centre of the finger-like tubes in Janssens experiments runs an open crack and resembles the quartz and RGM found in the centre of the stage 1 textures. The experiment by Janssen et al. (2010) with the more concentrated HClsolution replaces the mineral completely, but leaves a pattern of alternating high porosity areas with inhomogeneous layers of the product. This is similar to the stage 2 textures, where inhomogeneous arsenate phases alternate with high porosity areas (Fig. 6a). The experiments by Janssen et al. (2010) were driven by different HCl concentrations in the fluid and therefore different acidity. In the case of the fahlore weathering, the driving force for the formation of new phases is the oxidation potential of the weathering fluid (see next section 5.4). It is therefore likely, that the stage 1 weathering assemblage formed by reaction with a fluid of lower oxygen fugacity than stage 2, and hence can explain the similarities to the textures found in the experimental observations.

Similar tube-like weathering or alteration textures have also been observed in the study on ilmenite by Janssen et al. (2010), in basaltic glass on the sea floor (Fig. 2 in Dultz et al., 2014), in galena forming quartz, acanthite, and native Au in the assemblage (Fig. 5 in Kamenov et al., 2013), and in native Bi, wittichenite, emplectite, pyrite, gersdorffite, and nickeline in samples investigated in the course of this study. Hence, this short compilation is a very general, basic process reflected in always 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 that sulfur is most likely partially oxidized to sulfate and transported away besides the precipitation 736 as S^{2-} in the Cu-sulfides. This implies that f_{02} during this stage is somewhere around the sulfide-737 sulfate transition. Antimony and Fe in fahlore (Sb³⁺, Fe²⁺) are oxidized to Sb⁵⁺ in the RGM phases, and 738 to Fe^{3+} in tripuhyite (in hydroxyferroroméite, it is reported to be Fe^{2+} , Mills et al., 2017). Stable Sb⁵⁺ 739 (and Fe³⁺) compounds in similar environments were also reported by Leverett et al. (2012) and 740 741 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).

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

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

The partial loss of Cu in stage 2 and the addition of Cu in stage 1 could point to mobilization of Cu from upper parts of the weathering profile (e.g., oxidation zone) down to the cementation zone, or an evolution of the fluid from a stage 2 fluid towards a stage 1 fluid. For such a fluid evolution, however, there is no textural evidence on the small scale; rather, it appears to be a process on the scale of a deposit. An opposite evolution of a stage 1 towards a stage 2 fluid by fluid-mineral interaction can be ruled out as during stage 1, oxygen is consumed and hence, the f_{o2} in the fluid decreases – stage 2 phases, however, require an increased f_{o2} (see above).

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

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

775

776 6. Summary and conclusions

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

779 The first stage forms irregular finger-like veinlets within fahlore with crystalline Cu-sulfides 1. 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 guartz 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).

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

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

chemical gradients and fluid/mineral ratios are greatest, and secondary minerals form spatiallyindependent from the original fahlore location.

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

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

826

827 Acknowledgments

We are grateful to T. Wenzel, C. Berthold, H. Schulz, T. Kiemle (all from Tübingen), and S. Gilbricht (Freiberg) for analytical help and S. Schafflick (Tübingen) for the great sample preparation. J. Harsch and M. Schlaich are thanked for help during the early study of the project and T. Wenzel (Tübingen) for discussions, comments and an initial review of the draft manuscript. This work is a contribution of the r⁴ project "ResErVar—Ressourcenpotential hydrothermaler Lagerstätten der Varisziden" funded by the German Ministry of Education and Research (BMBF; Project reference number 033R129E).

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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 from1083 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) occurence. (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 in small veinlets, that represent phase and grain boundaries. (e) BSE image showing the location of 1091 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 sample1097 thickness.

1098

1099 Figure 4

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

1104

1105 Figure 5

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

1111

1112 Figure 6

(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

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

- 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

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

a groundmass. (e) EDS map of Ag, Bi, and Cu showing the spatial relation between a 50 nm-sized Ag-

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

porous phase in the green stage 3 assemblage, all intergrown with the Bi-Sb-Fe phase.

1147

1148 Figure 10

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

1152

1153 Figure 11

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

- 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
- 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

- (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 % without1169 volatiles).
- 1170

1171 Figure 13

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

1179

1180 Figure 14

(a) BSE image of a representative stage 1 assemblage from Neubulach. (b) Colour coded picture of (a)
to highlight each phase and its quantity of this weathering stage (CuOx: Cu oxide, CuSulf: Cu-sulfide,
RGM: roméite group mineral). (c) Results of stage 1 mass balance calculation presented in Table 4
from Neubulach and Freudenstadt (FDS) (d) Results of the mass balance calculation for stage 2
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.

37

1187

1188 Figure 15

- (a) Illustration of a typical weathering profile and element speciation through a hydrothermal vein
- 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 guartz. (d) Hand specimen from the Dorothea mine near Freudenstadt showing fahlore 1206 with covellite of weathering stage 1.

1207

1208 Supplementary Fig. 3

(a) μXRD pattern of mixed phases of stage 3 from Königswart of Fig. 10. The Cu-arsenates and Cusilicates cannot be identified and most likely represent the broad elevated background reflecting
amorphous phases, whereas the intergrown barite of stage 4 is accountable for all reflexes. (b) and
(c) μXRD pattern of stage 4 radial green minerals of a sample from Wittichen were identified as
mixite (b) and malachite (c), both intergrown with quartz. (d) μXRD pattern of azurite from
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.
- 1220 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
- 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.

Stage	Number of analyses	Phase	Locality	Sample		Δs	Cu	Fe	Sh	Bi	s				
Juge	Number of unaryses	Thuse	Locality	Sample		A 3	cu	TC .	55	ы	[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	Sb₂O₅	Bi ₂ O ₃	SO₃	SiO2	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

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

					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	AI	Ва	Р		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	

Locality	Sample	Mineral	As	S	Bi	Cu	Pb	Hg	Ag	Zn	Sb	Fe	Ni	Со	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
			As	S	Bi	Cu	Pb	Hg	Ag	Zn	Sb	Fe	Ni	Со	Se	Normalized to
									[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 2. Representative EMP results for sulfides including data in wt.% and calculated apfu for each analyses. b.d. = below detection limit

Sample	Locality	Mineral	stage	Р	v	Cr	Mn	Со	Ni	Zn	Ga	Ge	Se	Мо	Ag	Cd	In	Sn	ті	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

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

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_2O_3	SO₃	Bi ₂ O ₃	CuO	Al_2O_3	PbO	HgO	Ce ₂ O ₃	Ag2O	ZnO	Sb_2O_3	Fe_2O_3	CaO	BaO	SiO2	Theor. H_2O	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.	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 (zalesiite)	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 (zalesiite)	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/	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
	arsenogorceixite																				
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	SO₃	Bi ₂ O ₃	CuO	AI_2O_3	PbO	HgO	Ce_2O_3	Ag2O	ZnO	Sb_2O_3	Fe_2O_3	CaO	BaO	SiO2	Normalized to
									1	mol %l								

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	Α	Pb	Hg	Ce	Ag	Zn	Sb	Fe	Са	Ва	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		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 aptu 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	5 apfu Cu
4	Dussertite/	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
	arsenogorceixite																		
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

	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)
	·	sta	age 1	•			sta	age 2	Ŭ	
average fahlore analyses Average secondary	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
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 5. Mass balance calculation for stage 1 and 2 weathering displayed in Fig. 14. See text for calculation and discussion.

Table 6. Comparison of the different weathering stages

	Stage 1	Stage 2	Stage 3	Stage 4
5	Oxides	No oxides	No oxides	No oxides
	Sulfides (Cu sulfides, acanthite,	Minor sulfate (barite), minor	No sulfide or sulphate	Sulfate (barite)
	cinnabar)	amounts of sulfides (acanthite,		
		cinnabar)		
	No arsenate	arsenate	arsenate	arsenate
	Nano-meter to micro- meter sized	Amorphous, local nano meter-sized	Amorphous and botryoidal textures	Up to cm large crystals
	crystals	crystals		
Hydrous phases present	No hydrous phases	Hydrous phases	No hydrous phases	Hydrous phases
Addition of elements	Si, Cu	Ba, Fe	Si	local Ca, Si, Ba, Al, and/or C
Loss of elements	As, Zn, S, (Fe and Sb if fahlore is Bi-	S, Zn, Sb, Cu	Not investigated	Not investigated
	poor)		5	5
Immobile elements	Bi (Fe and Sb if fahlore contains Bi)	Bi, As	Not investigated	Not investigated
	Replaces fahlore	Replaces fahlore	Replaces older weathering phases	Spatially not related to fahlore,
				partly replaces older weathering
				phases
	Finger-like tubes forming 3D	Weathering assemblage forms	Weathering assemblage forms	Secondary minerals sealing cracks,
	network through fahlore	fronts through fahlore, partly	fronts through older weathering	local replacement of older
	crystallizing from a gel-like	alternating phases, lavers with nm-	phases and/or cements them	weathering phases
	precursor phase	sized porosity	F	
	Hydrous phases present Addition of elements Loss of elements Immobile elements	Stage 1 s Oxides Sulfides (Cu sulfides, acanthite, cinnabar) No arsenate Nano-meter to micro- meter sized crystals Hydrous phases present Addition of elements No hydrous phases Si, Cu Loss of elements As, Zn, S, (Fe and Sb if fahlore is Bi- poor) Immobile elements Bi (Fe and Sb if fahlore contains Bi) Replaces fahlore Finger-like tubes forming 3D network through fahlore crystallizing from a gel-like precursor phase	Stage 1Stage 2sOxidesNo oxidesSulfides (Cu sulfides, acanthite, cinnabar)Minor sulfate (barite), minor amounts of sulfides (acanthite, cinnabar)No arsenatearsenateNano-meter to micro- meter sized crystalsAmorphous, local nano meter-sized crystalsHydrous phases presentNo hydrous phasesAddition of elementsSi, CuLoss of elementsAs, Zn, S, (Fe and Sb if fahlore is Bi- poor)Immobile elementsBi (Fe and Sb if fahlore contains Bi) Replaces fahloreFinger-liketubesFinger-liketubestubesforming 3D rcystallizingWeathering alternating phases, layers with nm- sized porosity	Stage 1Stage 2Stage 3OxidesNo oxidesNo oxidesSulfides (Cu sulfides, acanthite, cinnabar)Minor sulfate (barite), minor amounts of sulfides (acanthite, cinnabar)No sulfide or sulphateNo arsenatearsenatearsenateNano-meter to micro- meter sized crystalsAmorphous, local nano meter-sized crystalsAmorphous and botryoidal texturesHydrous phases presentNo hydrous phasesHydrous phasesNo hydrous phasesAddition of elementsSi, CuBa, FeSiLoss of elementsSi (Fe and Sb if fahlore is Bi- poor)Sz, Zn, Sb, CuNot investigated Replaces fahloreImmobile elementsBi (Fe and Sb if fahlore contains Bi) networkBi, As frontsNot investigated Replaces fahloreNot investigated Replaces fahloreFringer-liketubes forming 3D reystallizingWeathering assemblage forms



Figure2

spionkopitedominated

azurite

fahlore

stage

chalcocitedominated

covellitedominated

100µm









Figure7



















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