1	Revision 2 for manuscript 5931R									
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3	Formation of basic lead phases during fire-setting and other									
4	natural and man-made processes									
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12	Keywords: basic lead phases, fire-setting, stability relation, leadhillite, lanarkite,									
13	hydrocerussite, caledonite.									
14										

Abstract

16 Basic lead phases are relatively rare compounds occurring in various natural and 17 anthropogenically influenced environments, most importantly those related to fire-setting 18 (FS). The medieval FS mining method and subsequent alteration processes lead to a complex 19 set of basic lead phases including caledonite, hydrocerussite, leadhillite, and lanarkite. Although basic lead phases have been known for over 100 years, their mode of formation and 20 stability relations are only insufficiently known. In this study, the formation of this interesting 21 phase assemblage is described in detail including textures, genesis, and conditions of 22 23 formation. Samples include ones collected in a medieval mining district in SW-Germany and 24 ones which underwent short-term (50 days) experiments mimicking FS and subsequent mine dump processes. The mode of occurrence and the stability relation of basic lead phases 25 26 formed during FS is discussed using thermodynamic models which are adapted to also explain 27 their occurrence in other anthropogenic and in natural environments.

Textures indicate a three step development of the FS assemblage starting with formation of 28 29 cerussite during supergene weathering of primary galena prior to FS. This is followed by the 30 decarbonisation of the supergene cerussite during FS leading to the formation of lead oxides. 31 Finally, the newly formed lead oxides were hydrated by rain and soil water in the mine dumps 32 producing basic lead phases. Chemical composition of partially produced melt indicates that FS temperatures of up to 950°C were reached in rare cases, whereas the lack of melt phase 33 and predominance of litharge and lead oxycarbonates in most other samples implies that 34 35 temperatures in most cases do not exceed 540°C.

Calculated stability diagrams reveal that most basic lead phases are stable at moderate to high pH and low P_{CO2} . Thermodynamic models quantitatively explain their formation in the medieval mine dumps by the reaction of the lead oxides with a weathering fluid which increases pH and consumes CO_2 which favors the precipitation of basic lead phases. This also explains the occurrence of basic lead phases in other anthropogenic environments like slag

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dumps, lead contaminated soils or in contact to concrete, where the reaction of a fluid with portlandite produces high pH and low P_{CO2} -environments. One possible explanation for the rare formation of basic lead minerals in natural oxidation zones in the absence of lead oxides is the alteration of primary galena under elevated temperatures, since the stability fields of the basic lead phases hydrocerussite and lanarkite are enlarged under elevated temperatures.

The short-term experiments show that the precipitation of basic lead phases is almost independent of the external fluid from which they precipitate. Hence, their stability is controlled by microenvironments formed at the mineral-water interface. Consequently, no closed systems in terms of CO_2 or external high pH-fluids are needed to stabilize basic lead phases in contact with lead oxides. Analyses of the experimental fluid phase show that the solubility of lead in environments, where lead oxides predominate, is mainly controlled by the basic lead phase hydrocerussite.

The present study can be used to quantify the formation of basic lead phases at lead contaminated sites or in natural environments. The observations on the natural samples and the experiments show that in specific rock types, like the medieval FS ones, basic lead phases control the availability of the toxic element lead better than anglesite or cerussite over a wide pH-range. In addition, the described FS phase assemblage can help mining archeologists to understand the details of the FS method even without mining traces and provide constraints on temperatures reached during this process.

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Introduction

The worldwide used FS process is one of the oldest technologies for mining resistive rocks (Craddock 1992; Willies and Weisgerber 2000). The process includes stacking of wood against the rock surface followed by igniting and burning it (Agricola 1556). By this treatment, the uppermost centimeters of the rock are heated up to partial melting (in rare cases) and cracks develop. In some cases, the hot rock was doused with water after the fire

67 ceased. Depending on the rock type this causes further cracking (Haupt 1884; Craddock 1992). At these sites, a characteristic phase assemblage first described by Wittern (1988, 68 1994) developed. The assemblage involves the oxides minium, massicot, litharge, and tenorite 69 and the basic lead phases hydrocerussite, caledonite, leadhillite, lanarkite, elvite, chenite, and 70 71 others. Mineral names used in this paper are for phases having natural equivalents; all phases 72 used in the text, including their formulae, are summarized alphabetically in Table 1. The 73 assemblage was initially known from various locations in Germany (Markl, 1991) and has 74 now been found in other places in Europe as well (e.g., Kolitsch 1997). According to Kolitsch 75 and Tillmanns (2003) also lead nitrates like $[Pb_2(OH)_3(NO_3)]$ belong to the FS assemblage. 76 The detailed conditions under which the FS assemblage and related melts form have remained 77 unclear.

Basic lead phases also form in other anthropogenically influenced environments like in
smelting slags (e.g., Schnorrer-Köhler et al. 1982; Schnorrer-Köhler 1987, 1988; Ettler et al.
2009b), lead contaminated soils (e.g., Lin et al. 1995; Lin 1996; Essington et al. 2004, Ma et
al. 2007; Li et al. 2015) or if lead ores come in contact with concrete (Kolitsch 2000, Lee
2007). Additionally, basic lead minerals are formed in rare cases during natural supergene
weathering of galena (e.g., Ingwersen, 1990; Stalder et al. 1998; Young et al. 2005;
Anserment 2012; Bowell and Clifford 2014).

Basic lead phases are known to be stable under neutral to alkaline pH-conditions only (Abdul-85 86 Samad et al. 1982a, Ingwersen 1990). Stability relations of leadhillite, hydrocerussite, and 87 caledonite were evaluated by Abdul-Samad et al. (1982a) under low P_{CO2} at 25°C, at variable pH values and sulfur activities. These diagrams show a relatively small intermediate 88 89 leadhillite field appearing between the anglesite and cerussite/hydrocerussite boundary (hydrocerussite being stable below a $logP_{CO2}$ of -3.7). The stability of lanarkite in the Pb-S-O 90 91 system was calculated by Treiman (1999) which indicates that lanarkite is stable over a wide range of P₀₂ and aSO₄ at slightly basic pH. These data are, however, at odds with the 92

observation, how rare this mineral is in natural environments – less than 10 natural
occurrences are known. Little is known about the stability relations of basic lead phases under
increased temperatures and under variable (low) P_{CO2} but Essington et al. (2004) mention the
enlargement of the hydrocerussite stability field towards lower P_{CO2} at slightly higher
temperatures of 35°C.
In this study, the stability relations and modes of formation of caledonite, hydrocerussite,
lanarkite, and leadhillite were evaluated with the help of new stability diagrams and fluid path

100 modeling to explain their occurrence during FS. These models were adapted also to unravel 101 the basic lead phase occurrence at other anthropogenic and natural localities. Furthermore, the 102 first detailed textural and chemical study and experiments on the formation of the FS 103 assemblage are presented.

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Geologic background

106 Samples of this study originate from the former mining area at the Alternannfels south of Badenweiler in the Southern Schwarzwald, SW Germany (see Fig. A1 of Appendix A). The 107 Alternantfels is a prominent, tens of meters high quartz rock formed by hydrothermal waters 108 109 on the Rhinegraben boundary fault which separates the Rhinegraben in the west from the Variscan basement in the east (Geyer and Gwinner, 2011). This rock is mainly composed of 110 111 different generations of quartz, barite, and fluorite as gangue, which are mineralized by galena, chalcopyrite, and minor sphalerite. Supergene weathering produced secondary lead 112 113 and copper minerals like anglesite, cerussite, pyromorphite, mimetite, malachite, and azurite (Metz et al. 1957, Schlomann and Steen 1990). Mining at Badenweiler was proven to have 114 115 started probably in Roman times (Kirchheimer 1976). Mineral samples for this study were taken from an old mine dump right in front of a medieval FS place. Charcoal found in the 116 mine dump was age dated by the CEZ Archaeometry GmbH, Mannheim, Germany, to an age 117 of about 750 \pm 21 A.D. (Markl, unpubl. data). Besides charcoal relics, the smooth rock face 118

119	with few or no tool marks, the shape, ash layers, blackened surfaces, and dumps containing
120	typically red colored rock specimens are distinctive features for such former FS sites.
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122	Methods
123	All phase and water analyses were conducted at the Department of Geosciences, University
124	Tübingen, Germany.
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126	Electron microprobe analysis (EMPA) and scanning electron microscopy (SEM)
127	For quantitative and qualitative determination of the major and minor element compositions
128	of the FS-related melt a JEOL 8900 electron microprobe in wavelength-dispersive mode
129	(WDS) was used. The analyses were conducted using a focused beam with 20 nA current and
130	20 kV acceleration voltage. Matrix corrections were performed according to JEOL $\phi\rho z$
131	method (Armstrong, 1991). The elements for the quantitative program were selected after
132	qualitative analyses in energy dispersive mode (EDS). Fluorine was not included in the
133	program, since WDS-scans on the fluorine K_{α} -line yielded no significant signal. For details of
134	the WDS-configuration used, including standards, counting times of the peak/background,
135	and the average detection limits see Table A1 in the Appendix A. On the SEM, visual images
136	and qualitative EDS spectra were obtained using a Hitachi TM3030 Tabletop Microscope.
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138 Geochemical modeling

To evaluate the stability relations among the basic lead phases, stability diagrams were
calculated using The Geochemist Workbench in the version 10.0 (Bethke and Yeakel 2015).
Fluid evolution paths and saturation indices were calculated using Phreeqc in the version
2.18.3 (Parkhurst and Appelo 1999). All calculations are based on the Thermoddem database
(Blanc et al. 2012).

Solubility constants $(\log K_{sp})$ for leadhillite, caledonite, and linarite were taken from Abdul-144 Samad et al. (1982a). Since Abdul-Samad eta al. (1982a) did not provide adequate 145 information about the thermodynamic data used for the determination of the logK_{sp}, there is a 146 potential source of error combining the solubility constants from Abdul-Samad et al (1982a) 147 148 with the Thermoddem database. Therefore, we decided to re-determine the solubility 149 constants of caledonite, linarite, and leadhillite with Phreeqc, using the solution composition 150 of the solubility experiments from Abdul-Samad et al. (1982a). In order to correct the 151 electrical charge balance of the solutions, we chose NO_3^- as passive anion. The re-determined 152 $\log K_{sp}$ for caledonite (-26.24) differs only slightly (1.35%) from the literature value (-26.60). Also for linarite, the calculated $logK_{sp}$ (-3.64) only differs by 1.1 % from the literature value 153 (-3.60). These small differences have only small effects on the size of the calculated stability 154 fields. 155

For leadhillite, however, Phreeqc failed to converge on the solution composition from Abdul-156 157 Samad et al. (1982a) and it was not possible to re-determine the logK_{sp} in the same manner as for caledonite and linarite. We therefore assume that for leadhillite the discrepancy between 158 the value of Abdul-Samad et al. (1982a) and a re-determined value would be in the same 159 160 range as for caledonite/linarite (maximum deviation of 1.35%). For plotting leadhillite in the stability diagrams, we decided to take the logK_{sp} value from the literature (-26,70, Abdul-161 Samad et al., 1982a) adding a precental error of $\pm 1.35\%$ to it. In order to show these 162 uncertainties, the stability field of leadhillite is bounded by thick grey bars instead of thin 163 164 black lines. The thickness of the grey bars represents the $\pm 1,35\%$ uncertainty. For the 165 calculation of the fluid path and the saturation indices, consistently the solubility constant of -166 26.30 (-26.70 + 1.35%) for leadhillite was taken. The input codes for the calculated fluid 167 paths are presented in Appendix B, the used $\log K_{sp}$ and delta H values are reported in Appendix A, Table A2. 168

170 Microraman spectroscopy

Microraman analyses of phase grains and thin sections were performed using a confocal Reinshaw InVia Reflex Raman spectrometer with a laser wavelength of 532 nm and 20-25 mW power. The used 50x objective results in a numerical aperture of 0.55 with an opening angle of 66.7°. The diameter of the laser spot is $\sim 2 \mu m$. Measurement time was set to 30 s with a three to five-rate accumulation. WiRE 3.0 software was used and the measured Raman shifts were compared with the RRUFFTM database (Downs 2006).

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178 μXRD analysis

179 X-ray microdiffraction was used to characterize fine-grained phase aggregates or mixtures. 180 Measurements were performed on a Bruker D8 Discover GADDS Θ/Θ microdiffractometer 181 with a Co-Anode (wavelength $\lambda = 1.79$ Å) at 30kV, 30 mA, and room temperature. 182 Monocapillary optics of 500 µm with 300 µm pinhole and a two dimensional VÅNTEC500 183 detector was used (see Berthold et al. 2009). The patterns were integrated individually for 184 each sample with a step size of 0.05 °2 Θ . The incident angle was fixed to 15° and 185 measurement time was set to 120 s per frame.

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187 Experimental setup to simulate the FS process

In order to simulate the FS and the subsequent processes on the mine dump, experiments were conducted. Weathered rock samples from Badenweiler and mineral separates were collected, which consisted of quartz, barite, chalcopyrite and partially weathered galena. Supergene weathering products were mainly cerussite and smaller amounts of malachite, anglesite, pyromorphite, and covellite.

193 The mineral separates (galena, chalcopyrite, malachite, and anglesite) were crushed down to a

194 grain size of 0.5-1.5 mm. It was not possible to crush cerussite in the same way because of its

195 fibrous habit. Generally, cerussite grainsize varied between 15 mm and >1 mm.

For simulating the FS process, the Badenweiler sample material was heated for about 120 196 minutes to \sim 700-800°C using a wood stove. The cerussite and malachite mineral separates 197 198 were heated using small ceramic bowls and a Bunsen burner at ~650°C for about 15 minutes in order to get complete transformation to lead (massicot-litharge) and copper (tenorite) 199 200 oxides, respectively. To simulate the processes in the mine dump, we chose to use two different pH setups in order to figure out the impact of this external factor on the formation of 201 202 basic lead phases and their capability to control the availability of lead in aqueous systems. The first setup (A) was prepared with Milli-Q water equilibrated with the atmosphere, 203 resulting in an initial pH of 6.0. The second setup (B) was prepared from river water mixed 204 205 with wood ash, resulting in an initial pH of 9.7. This was done by mixing 1.0 L river water with 1.8 g wood ash. Since rainwater was not available for setup (B), river water was chosen 206 207 because its composition is closer to rainwater than Milli-Q water. Wood ash was chosen for the high pH setup, since charcoal and wood ash were typically thrown on the mine dump after 208 209 FS (Willies and Weisgerber 2000). This habit was certainly important for creating a high-pH 210 environment.

Five different mineral sets for each pH-setup were chosen (see Table 2). All experiments 211 212 dealing with mineral separates (A1-A4, B1-B4) were conducted with 13 g of mineral material and 60 ml of water (W/R \sim 4.5) and were stored in tumblers at room temperature (\sim 20-25°C) 213 214 for 50 days. Also the Badenweiler sample material was stored in 60 ml of water (W/R of A5 =1.4; W/R of B5 = 1.1). To prevent evaporation of the fluid, the tumblers were covered (not 215 216 airtight). The coverage was removed for 15 minutes every day for equilibration with the 217 atmospheric gases. Water samples were analyzed before the experiments and after 50 days at the end of the experiments by using a pipette removing the supernatant solution. The 218 alkalinity of the solution was calculated, since the amount of water was too low for double 219 titration. 220

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222 Water analyses

Duplicate water analyses were performed before and after the experiments. Temperature, pH, 223 224 and specific conductivity of the weathering solutions were determined using a PCE-PHD1 data logger. Major anions (F⁻, Cl⁻, Br⁻, NO₃⁻, PO₄³⁻, SO₄²⁻) and cations (Li⁺, Na⁺, K⁺, Mg²⁺, 225 Ca²⁺, Ba²⁺) were determined by a Dionex ICS-1000 ion chromatography system equipped 226 227 with an IonPac CS 12-A column for cations. All samples were diluted 1:1 with MilliQ-water 228 in order to get adequate amounts of sample water. Disposable syringe filters (RC-20/25 and 229 PVDF-20/25) were used during injection of the samples. Based on routine standard measurements, errors for major anions and cations are generally $\sim 10\%$ and detection limits 230 generally $<15 \mu g/L$. 231

All samples were analyzed by total reflection X-ray fluorescence (TXRF) (see 232 Klockenkämper, 1996; Wobrauschek, 2007) for the following (trace) metals: Mn, Fe, Co, Ni, 233 Cu, Zn, As, Rb, Sr, Ba, and Pb. First, 190 µL of sample solution were mixed and 234 235 homogenized with 10 µL of 5 ppm Ga solution as internal standard. Then, two aliquots (each 10 μ L) were put onto polished quartz disks, dried at 80°C and subsequently analyzed with a 236 S2 PICOFOX benchtop TXRF system from Bruker AXS Microanalysis equipped with a Mo 237 X-ray tube, operating at 50 kV and 600 μ A for 10 min. Effective detection limits for the 238 above named elements are around 1 μ g/L. Based on the repetitive analysis of various multi-239 240 element standard solutions (Merck, Darmstadt, Germany) and reference material NIST1643c 241 (trace elements in water), the relative standard deviation from the target values for most 242 elements is below 10%; only for Ba and Fe, larger deviations of up to about 15% were detected. The pH values, TDS, conductivity, alkalinity and concentration data of the studied 243 244 water samples are given in Table 3, the original data in Table A3 in the Appendix.

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Results

247 Sample description

The FS assemblage. Macroscopically, the FS samples are typically red colored (Fig. 1a) and 248 249 friable to crumbly. Galena is in situ converted to cerussite and anglesite along its cleavage planes and grain boundaries. Based on textural observations, these phases are interpreted to 250 251 have formed before the FS process as normal weathering products. The following phases are 252 texturally later. Fine grained hematite infiltrates the gangue minerals along cracks and grain 253 boundaries and is responsible for their characteristic reddish color. While anglesite seems to be unaffected, cerussite is frequently replaced by lead oxycarbonates like shannonite and lead 254 oxides like litharge, minium or massicot (Fig. 1b, Fig. 2 a, d). Often, the replacement leads to 255 complete or incomplete pseudomorphs, typically lanced by cracks (Fig. 1c). 256

257 The pseudomorphic lead oxides are frequently overgrown and/or replaced by hydrous phases

like leadhillite, lanarkite, hydrocerussite, caledonite, and lead oxide carbonate hydroxide (Fig.

259 2b, c). The phases occur as euhedral crystals (Fig. 1d) and fine-grained aggregates (Fig. 1e).

260 In many cases, replacement is not complete and lead oxides remain as relics (Fig. 1f).

261 The most frequent newly formed phase is fine-grained hydrocerussite forming white crusts with typical luster on the surface of lead oxides and along cracks (Fig. 1e) or euhedral, 262 hexagonal, colorless platy crystals (Fig. 1g). In some samples, hydrocerussite seems to be an 263 early phase, overgrown by later generations of basic lead phases like caledonite and 264 265 leadhillite. The monoclinic leadhillite has two polymorphs, the trigonal susannite and the orthorhombic macphersonite, with susannite as high temperature modification being 266 267 metastable at ambient conditions (Livingstone 1993). Our XRD results, however, lead to no distinct identification of one of these polymorphs. 268

Lanarkite is often associated with lead oxides, hydrocerussite, and caledonite forming white, asbestos-like needles (Fig. 1g). The most striking phase in this assemblage is elyite forming crusts, spherulites or needles of a typical intense purple color (Fig. 1h, 1b). Elyite is a late phase frequently occurring along cracks and at the margin of lead oxide pseudomorphs and is

sometimes accompanied by light blue chenite (Fig. 1j). Caledonite forms light blue crusts and 273 bunches (Fig. 1d), leadhillite occurs as (pseudo)hexagonal colorless to pale yellow platy 274 275 crystals (Fig. 1d; Fig. 2c) and as fine-grained pale-yellow aggregates (Fig. 1e) associated with 276 lead oxides, anglesite, hydrocerussite, elyite, and caledonite. The rare sulfite scotlandite forms 277 either small, acute brownish crystals growing in cerussite cavities or bulbous vellowish to 278 brownish crystal aggregates (Fig. 1i; Fig. 2c). In most samples, it is almost impossible to 279 determine the paragenetic sequence of the hydrous phases, as they are intergrown chaotically 280 on a very small scale.

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282 Former melt. Very rare specimens show slag-like surfaces or vesicular, glassy, colored crusts which can be macroscopically identified as former melt (Fig. 3a). In thin section, they are 283 284 texturally composed of a deterred melt (µXRD patterns show no crystallinity) and a crystal phase. Typically, the former melt is characterized by round pores of different size 285 286 representing former gas-filled bubbles (Fig. 3b). In reflected light, at least four different types of crystals can be distinguished based on reflectance and shape (Type I-IV). The crystals with 287 high reflectance are fibrous (Type I, Fig. 3c), short needles (Type II, Fig. 3d) and blocky 288 289 (Type III, Fig. 3d). The fourth crystal type forms rectangular, blocky crystals with much lower reflectance (Type IV, Fig. 3d). All of these crystals are intergrown with former melt 290 291 commonly showing straight grain boundaries and as concentric zonation textures.

The former melt phase (glass) can be subdivided texturally in four groups as well (Type i-iv). The first group is glass in direct intergrowth with the different crystal types (Type i; Fig. 3c & 3d), the second is homogeneous glass without crystals (Type ii; Fig. 3b), the third is lanced by numerous small bubbles (Type iii; Fig. 3e) and the fourth forms layered, zoned textures (Type iv; Fig 3f). Frequently, the glass encloses or penetrates mineral grains like barite, fluorite, quartz, and/or sphalerite, which show dissolution textures like well-rounded grain boundaries.

Small, spherical metal inclusions with high reflectance are frequently enclosed in the formermelt (e.g., Fig. 3b & 3d).

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301 Compositional variations of former melt and associated crystal phases

Former deterred melt and crystal phases formed during FS were investigated in four samples with a total of about 300 analyses (the whole dataset is reported in the Appendix A, Table A4). EMP totals of most former melt and crystal phases are close to 100 wt% with an average of 98.8 wt%. Only melt type iv has significantly lower totals on the order of 82 wt%. Type IV crystals have lower totals between 94.4 and 98.8 wt% with an average of 96.8 wt% (see Table 4 for representative analyses). Low melt and crystal totals are interpreted to reflect H_2O incorporation, since EDS analyses did not indicate any missing element.

Figure 4a shows that the former melts and crystals show a large compositional variability, being predominantly composed of silicon, lead, zinc, and calcium. Highest Si contents for the former melt are up to 65 mol% and up to 62 mol% for the crystals, and also the mean contents in the former melts are higher than in the crystal phases. Except for Zn, Ca, and P, all other elements have higher mean contents in the former melt than in the crystal phase.

314 In Figure 4b, 4c, and d, the mean molar ZnO and CaO contents of different crystal types and melt types, which are directly intergrown with the crystals, are plotted against X_{SiO2} (X_{SiO2}) 315 316 defined as SiO₂/(SiO₂+PbO)·100) for the different samples (see Table 5 for structural 317 formula). In sample MK 08, the former melt phase shows relatively low CaO and ZnO 318 contents, with a maximum of 7.5 mol% ZnO and 6.1 mol CaO (Fig. 4b) and ranges in X_{SiO2} between 58.1 and 66.3 mol%. Dark blocky crystals of Type IV have quite variable X_{SiO2} 319 320 between 76.3 and 96.6 mol%, moderate ZnO contents up to 19.4 mol% and high CaO contents up 45.8 mol%. Short needles with of Type II have X_{SiO2} between 52.6 and 57.4 321 mol%, and low ZnO contents up to 2.2 mol% and high CaO contents up to 17.8 mol%. 322 Blocky bright crystals of Type III form two distinct groups. The first group is nearly identical 323

in composition to the bright needles of Type I, just having slightly higher CaO contents up to

- 325 25.6 mol%. The second group, however, has much higher ZnO contents up to 33.0 mol%.
- 326 Fibrous crystals of Type I and the former melt of sample MK_06 (Fig. 4c) only show minor
- amounts of CaO and ZnO below 1 mol%. The X_{SiO2} of the former melt (46.2 -62.0 mol%) is
- slightly higher than in the crystals (45.1-50.3 mol%).
- 329 The former melt phase of sample MK 22 again shows higher X_{SiO2} than the fibrous crystals
- of Type I (Fig. 4d). Former melts and crystals show CaO and ZnO contents below 1 mol% but
- intermediate CaO contents up to 5.6 mol%.

The bulk compositions plotted in Figure 4b, 4c and 4d were recalculated based on BSE image analysis using common graphic software and appropriate crystal and former melt compositions. The bulk compositions represent a mixture of the former melt and the crystal composition the position depends on the portion of former melt and crystal phase. Qualitative EDS analyses of the metal inclusions show that they are either composed of Ag or Pb only, or of Pb + Cu, Ag + S, Cu + S or Ag + Cu + S.

338

339 FS experiments

The experimental setup reproduces a wide spectrum of phases and textures of the medieval FS assemblage. During roasting, supergene cerussite of the Badenweiler sample material was replaced by a mixture of the lead oxides massicot and litharge (Fig. 2e), typically lanced by cracks (Fig. 5a). Also the typical red color, partial melting, and the crumbly appearance of the experimental samples matches the medieval ones. In the experimental setups dealing with mineral separates, phase growth was macroscopically visible in setup A1 after only 12h. In all other experimental setups mineral growth was visible within the first 5 days.

SEM shows that during all experiments hydrocerussite overgrows the lead oxides as finegrained sheds (Fig. 5b, 5c), but in larger amounts in experimental setup A compared to setup
B. The µXRD diagrams indicate that the newly grown phases in parts are not well crystalized.

Subordinately, prismatic cerussite crystals can be found in experimental setup A2, A4, A3,
B2, B4 (Fig. 5d; Fig. 2f), which were newly grown on the lead oxide surface beside
hydrocerussite.

Besides hydrocerussite and cerussite, light blue chenite and purple elyite grows as fiberous needles in experimental setup A4 and B5 (Fig. 5e, 5f; cf. Table 2). It was not possible to determine elyite and chenite by μ XRD analyses, but Raman analyses lead to a unique identification.

357 The pH values of the experimental water in setup A are slightly higher than the initial pH of

358 6.0 (6.2-7.1). Experimental setup B leads to lower pH values than the initial pH of 9.5 (7.0-

8.8). Setup A shows higher lead contents than setup B at least by the factor 1.5 (cf. Table 3).

Lowest amount of lead was found in experimental setup A1 and B1, most in A4 and B4.

Generally, lead contents of the experimental waters are relatively low and show an increase

362 with lower pH values.

Phreeqc calculations show that the waters are undersaturated with regard to most basic lead phases (see Table 6). Only caledonite and linarite show supersaturation in most experiments including initial copper phases. Also hydrocerussite shows supersaturation in setup A2, A3, and A5, leadhillite in A3 and A5. Besides the basic lead minerals, cerussite shows supersaturation in setup A2, A3, A5, B2, B3, and B4, and B5 and pyromorphite in setup A3.

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369 Stability relations of basic lead phases

To evaluate the stability relations of anglesite, cerussite, hydrocerussite, leadhillite, lanarkite, minium, and caledonite, stability diagrams with respect to variable pH, P_{CO2} , Cu concentrations, and temperature were calculated using The Geochemist Workbench. For the basic lead phases elyite and chenite, unfortunately, no thermodynamic data are available, hence no quantitative statements of their stability can be given (a qualitative stability diagram of both phases can be found in Appendix A: Fig. A2).

Figure 6a shows the stability relations of the above named phases with respect to variable pH, 376 P_{CO2} as well as fixed lead and sulfur concentrations. Charge balance was maintained by 377 378 adding nitrate as conservative ion. As shown in Figure 6a for 25°C, anglesite is the stable secondary lead phase at acidic to neutral pH values becoming more stable towards higher pH 379 380 values at low P_{CO2} . The cerussite/hydrocerussite stability field is dependent on P_{CO2} , with 381 cerussite being stable at higher P_{CO2}. Leadhillite has a relatively small stability field around 382 neutral pH-values and moderate to low P_{CO2} and is framed by anglesite and cerussite/hydrocerussite. Lanarkite has a relatively small stability field under neutral to basic 383 pH-values and low P_{CO2}. Minium is stable at slightly basic to basic pH values and low P_{CO2}. 384 385 Figure 6b shows the stability relations of anglesite, cerussite, hydrocerussite, leadhillite, lanarkite, and minium at variable temperatures. Due to the lack of enthalpies for leadhillite, no 386 387 statement can be made on the size of the stability field at higher temperatures than 25°C. Increasing temperatures expand the stability field of hydrocerussite to much higher P_{CO2} . In 388 389 addition, the stability field of lanarkite expands to slightly higher P_{CO2} and lower pH.

Figure 6c and d show the stability relations of anglesite, cerussite, hydrocerussite, leadhillite, lanarkite, minium, caledonite, and linarite with respect to variable pH, P_{CO2} , and Cu concentrations at fixed lead and sulfur concentrations and a fixed temperature of 25°C. At high copper concentrations of 1×10^{-5} M (see Fig. 6c), anglesite is stable at low pH values over the whole P_{CO2} -range. Linarite is stable at low P_{CO2} and caledonite at high P_{CO2} over a wide pH range. At low Cu concentrations of 1×10^{-15} M (see Fig. 6d), the stability field of anglesite enlarges to higher pH values and hydrocerussite becomes additionally stable at high pH.

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Discussion

In the following section, the formation mechanisms of the FS assemblage are discussed and quantified using fluid path models. Additionally, the stability diagrams and fluid path models are used to explain the formation of basic lead minerals in other anthropogenic influenced and

402 natural environments. The short-term experiments provide additional insights to the formation 403 mechanisms and show how the basic lead minerals are capable to control the lead 404 concentration in aqueous solutions. Furthermore, a temperature estimation of the FS process 405 was done by using the mineralogy of lead oxides and the chemical composition of the melt 406 phase.

407

408 Formation steps of the fire-setting assemblage

The observed textures of the FS assemblage and the identified phases imply a three step process (Step I-III), sketched and summarized in Figure 7. The steps are the different processes before, during and after FS. This classification is in good agreement with observations made by Wittern (1994).

413

414 Step I: Supergene weathering: First, supergene weathering of primary galena lead to
415 the formation of thermodynamically more stable secondary lead minerals like cerussite
416 (Eq. 1) and anglesite (Eq. 2) (cerussite dominates in the investigated samples from
417 Badenweiler).

418 PbS (galena) +
$$H_2O + CO_2 + 2O_2 = PbCO_3$$
 (cerussite) + $SO_4^{2^2} + 2H^+$ (1)
419 PbS (galena) + $2O_2 = PbSO_4$ (anglesite) (2)

420 Cerussite and anglesite replace galena along its rims and typical cleavage planes. 421 Within cavities, euhedral or subhedral crystals up to cm-size develop. Whether 422 cerussite and/or anglesite are stable depends, for example, on pH, P_{CO2} , and 423 temperature of the supergene weathering fluid (Keim and Markl 2015).

424

425 **Step II: firesetting:** During the FS process, lead oxides and lead oxycarbonates like 426 shannonite form (cf. Fig. 1b, 1c; Fig. 2a, 2d) due to decarbonisation reactions of 427 cerussite induced by the strong heat impact of the fire. The temperature-dependent

stepwise transformation process of cerussite to lead oxides under atmospheric
pressures was described by Yamaguchi et al. (1980). The modified transformation
reaction is presented in equation. 3a-c. The temperature-dependent formation of lead
oxides is discussed below.

432
$$2PbCO_3 \text{ (cerussite)} \rightarrow \sim_{300^{\circ}C} \rightarrow PbCO_3 \cdot PbO + CO_2$$
 (3a)

433
$$3PbCO_3 \cdot 3PbO \rightarrow \sim_{370^{\circ}C} \rightarrow 2PbCO_3 \cdot 4PbO + CO_2$$
 (3b)

434
$$PbCO_3 \cdot 2PbO \rightarrow \sim_{440^{\circ}C} \rightarrow 3PbO + CO_2$$
 (3c)

435 Conversion of malachite to tenorite during FS has been proposed by Graf (1991) and
436 has been observed at some localities such as Neubulach, Schwarzwald, Germany
437 (Markl, 2015).

Anglesite, pyromorphite or any other phosphates and arsenates (also copper arsenates like olivenite in Cu-dominated environments) remain unaffected during FS (cf. Fig 1b), the only exception being pseudomalachite which reacts to a new, naturally unknown copper phosphate (Markl, 2015). This is also observed during mine fires, where cerussite is converted to oxycarbonates and lead oxides, while anglesite in direct intergrowth is not affected (Skinner and McBriab 1958; Pring et al. 1990). Anglesite starts to decompose in air at temperatures above 880°C (Sajadi 2011).

445 As described, the pseudomorphs are lanced by numerous cracks due to a volume 446 reduction during CO₂ loss of cerussite of about 39%, if converted to minium.

In contrast to Wittern (1994), microscopic observations lead to the result that the typical red color of the samples is not caused by litharge but by fine-grained hematite distributed along cracks and fissures. The low firmness is most likely due to the conversion of low-quartz to high-quartz occurring at 573° C and its reconversion (volume change ~5%).

- 453 **Step III: Processes in the dump:** After FS, material containing no or only little ore 454 was thrown on a dump. Here, basic lead phases could form by the reaction of 455 weathering fluids with lead oxides, which is proven by common replacement and 456 overgrowth textures (cf. Fig. 1b, 1d, 1g, 1h).
- In principle, there are two possibilities (or a combination of both) where this waterlead oxide interactions can take place. 1. During dousing of the hot rock with water after the FS process or 2. during processes in the dump where meteoric and/or developing soil fluids react with lead oxides.
- 461

462 Fluid path models; mode of formation of basic lead phases

In the following, geochemical fluid path models are presented to explain the occurrence of basic lead phases during FS, at slag dumps, and in areas with metallic lead pollutants (Model I). Also the occurrence of basic lead phases in contact to concrete is discussed (Model II). In addition, the stability diagrams were used to explore the conditions under which basic lead minerals can form in oxidation zones of ore deposits.

468

Formation during FS, in contact to lead pollutants and slags (Model I). The basic lead phases of the FS assemblage are texturally closely related to lead oxides (see above). Also in other anthropogenically influenced environments like slag dumps and in contaminated soils, metallic lead alters to lead oxides (e.g., Lin et al. 1995; Lin 1996; Essington et al. 2004; Ma et al. 2007; Ettler et al. 2009a, 2009b; Li et al. 2015). Here, the lead oxides are directly related to basic lead phases like hydrocerussite (Lin 1996; Ma et al. 2007). If the lead oxides come into contact with meteoric fluids, protons are consumed and the pH rises (Eq. 4).

476
$$Pb_2^{4+}Pb_2^{2+}O_4 \text{ (minium)} + 6H^+ = 3Pb^{2+} + 3H_2O + 0.5O_2$$
 (4)

477 If lead carbonates or basic lead carbonates like cerussite (Eq. 5), hydrocerussite (Eq. 6) or 478 caledonite (Eq. 7) precipitate additionally, CO_2 is consumed (see also Ma et al. 2007).

479 PbO (litharge) +
$$HCO_3^-$$
 + H^+ = PbCO₃ (cerussite) + H_2O (5)

480 3PbO (litharge) +
$$2HCO_3^- + 2H^+ = Pb_3(CO_3)_2(OH)_2$$
 (hydrocerussite) + H_2O (6)

481 5PbO (litharge) +
$$2Cu^{2+}$$
 + HCO_3^- + $3SO_4^{2-}$ + H_2O + $3H^+$ = $Pb_5Cu_2(CO_3)(SO_4)_3(OH)_6$
482 (caledonite) (7)

With Phreeqc it is possible to track the fluid evolution during these reactions (Model I) and evaluate the phase saturation during the evolution of the fluid chemistry. Note that this model is not designed to simulate processes at a specific locality, but rather to show general trends during the reaction of lead oxides with weathering fluids.

The FS products, slags, and lead pollutants are likely to interact with rainwater. For this 487 reason, a rain water analysis from Négrel and Roy (1998) was chosen and reacted with 488 1.5x10⁻⁴ M minium in 100 steps (path (i) and (ii)). During each reaction step, the phases 489 anglesite, cerussite, hydrocerussite, lanarkite, litharge, minium, massicot, and leadhillite were 490 allowed to precipitate if supersaturated. For the calculations a system closed to CO_2 was 491 assumed, which is reasonable for microenvironments. For path (ii) the water was additionally 492 reacted with 3x10⁻³ M galena in order to enrich the sulfur-poor rainwater with sulfur and 493 494 slightly change the pH to lower values. This is reasonable since the investigated FS samples 495 and many slags frequently contain sulfide relics (e.g., Ettler et al. 2001; 2009b). The resulting fluid paths are shown in Figure 8a, the appropriate saturation indices for phases reaching 496 saturation (Si = 0) during progressive reaction with minium in Figure 8b. Due to the 497 differences in lead/sulfur activity of the fluid path compared to the stability diagrams, the 498 paths do not exactly plot on the borders of the stability fields. 499

In both models, the CO₂ partial pressure decreases from the starting value of $logP_{CO2} = -2.0$ and the pH value rises during progressive reaction with minium. Path (i) shows that in sulfurpoor systems under moderate pH (pH = 6.0), cerussite is the first stable phase. With progressive reaction, P_{CO2} decreases and hydrocerussite becomes stable. In path (ii) (start pH = 5.7) cerussite and anglesite coprecipitate, followed by leadhillite. The path then ends in the

triple point anglesite-leadhillite-lanarkite. Fluid paths (i) and (ii) explain why lead oxides are often overgrown/replaced by basic lead phases. Whether hydrocerussite, leadhillite, anglesite, or lanarkite are stable depends mainly on the availability of sulfur and the pH-value of the fluid. Higher-pH will favor lead carbonates and/or sulfcarbonates to precipitate. Additional Cu in the fluid can result in the precipitation of caledonite and/or linarite depending on the P_{CO2} (see Figure 6c, d).

The formation of basic lead minerals by the reaction with lead oxides is not restricted to artificial environments only. Alteration of primary metallic lead to lead oxides is also observed rarely in nature (e.g., Karup-Møller 1975).

514

Formation in contact to concrete (Model II). Artificially formed basic lead phases can also 515 be found in contact with concrete. A paragenesis including hydrocerussite and elvite is 516 described from the Clara mine, in the central Schwarzwald, SW Germany, where lead-bearing 517 518 fluids come into contact with shotcrete (Kolitsch 2000; Markl 2015). Furthermore, Lee (2007) 519 reports the stabilization of aqueous lead, liberated from lead contaminants during the reaction with cement by the formation of less soluble leadhillite and lead carbonate hydroxide hydrate 520 521 [3PbCO₃·2Pb(OH)₂·H₂O]. Reaction of water with concrete (portlandite) will rise pH values as follows (Eq. 8): 522

523
$$Ca(OH)_2 (portlandite) + 2H^+ = Ca^{2+} + 2H_2O(8)$$

524 Precipitation of calcite consumes CO_2 (Eq. 9):

525
$$Ca(OH)_2$$
 (portlandite) + $CO_2 = CaCO_3$ (calcite) + H_2O (9)

To track the fluid evolution during reaction of a fluid with concrete (Model II), a water analysis from the Clara underground mine from Bucher et al. (2009) was reacted with portlandite in a system closed to CO_2 . The fluid was reacted with galena (in the model, similar to what is observed in the mine) to enrich it in lead. This modified water was then reacted with $9x10^{-4}$ M portlandite in 100 steps. During each reaction step, the phases anglesite,

cerussite, hydrocerussite, lanarkite, leadhillite, massicot, and minium were allowed to
precipitate if supersaturated.

The resulting fluid paths (iii) and (iv) are shown in Figure 8c, the appropriate saturation indices during progressive reaction with portlandite in Figure 8d. Path (iv) is additionally equilibrated with calcite to reach a slightly higher pH value and. In both fluid paths, the pH values rise and P_{CO2} decreases during progressive reaction with portlandite.

537 On fluid path (iii) (starting pH of 7.), first cerussite, anglesite, and leadhillite are stable. As 538 P_{CO2} decreases and pH rises, the assemblage anglesite plus leadhillite becomes stable and with 539 progressive reaction additionally lanarkite. During the protracted reaction with portlandite, 540 anglesite is not stable anymore and the assemblage lanarkite plus leadhillite becomes stable. 541 The path then ends with precipitating minium, leadhillite, and lanarkite.

Fluid (iv) starts with a higher pH value of 8.0. This results in cerussite, hydrocerussite, and 542 leadhilite being the stable phase assemblage at first. With proceeding reaction, leadhillite 543 544 becomes unstable and the fluid will end up precipitating hydrocerussite. Both fluid paths show that basic lead phases can be formed during the reaction of a fluid with portlandite and 545 that changes in pH, for example due to the dissolution of calcite, can result in different phase 546 547 assemblages. Again, the pH-value of the starting fluid is important for the course of the fluid path. Higher pH-values and additional carbon added to the system by the dissolution of calcite 548 549 will favor the precipitation of lead carbonates and sulfcarbonates (for more details about the aqueous speciation of the ions, see the Phreeqc input code in Appendix B). Overall, the 550 reaction with portlandite and the precipitation of basic lead phases drops the P_{CO2} and 551 increases the pH value in a system closed to CO₂. Again, if Cu is available, caledonite/linarite 552 553 can precipitate (see Figure 6c,d).

Wittern (1994) described the formation of Ca(OH)₂ due to heating of calcite at the FS location
Glücksrad mine, Harz mountains, Germany. Such a reaction is unlikely at Badenweiler since

calcite is lacking there. However, at the Glücksrad mine, Ca(OH)₂ could play an important
role during basic lead phase formation.

558

Formation of basic lead minerals in natural environments. In rare cases, basic lead 559 560 minerals form in oxidation zones of hydrothermal ore deposits such as Tsumeb, Namibia 561 (Ingwersen 1990; Bowell and Clifford 2014); Leadhills, Lanarkshire, Scotland (Temple 562 1956); Tiger, Mammoth ore district, Arizona (Bideaux 1980; Abdul-Samad et al. 1982b), Caldbeck Fells, Cumberland, England (Cooper and Stanley 1997); Friedrich-Christian mine, 563 Schwarzwald, Germany (Walenta 1991); Laquorre mine, Pyrenees, France (Asselborn 2012), 564 and Göschenen, Uri, Switzerland (Stalder et al. 1998). The occurrence of basic lead minerals 565 in such systems is not explainable by the reaction with lead oxides. 566 Formation of basic lead minerals in lead-bearing systems closed to CO2 accompanied by the 567

precipitation of cerussite is not possible. During precipitation of cerussite, CO_2 is consumed and the pH decreases (Eq. 10).

570

$$Pb^{2+} + HCO_3 = PbCO_3 (cerussite) + H^+ (10)$$

Since the pH and HCO_3^- are related, the P_{CO2} of a fluid will not decrease during cerussite precipitation in a closed system. Thus, the fluid will end up precipitating anglesite if the pH is sufficiently low. This is in contrast to the reaction with PbO where the pH increases during basic lead phase precipitation. Consequently, the basic lead mineral assemblage in the oxidation zones cannot be explained by e.g., weathering of galena in a "simple" closed system.

As Figure 6b shows, weathering under elevated temperatures does not necessarily require low
CO₂ partial pressures to stabilize hydrocerussite, since the stability field shifts to higher P_{CO2}.
In nature, alteration/weathering of primary galena under elevated temperatures (about 3050°C) is known from Tsumeb and the Tiger ore deposit based on microthermometric studies
on cerussite (Gilg et al. 2003; Boni et al. 2007). Indeed, the analyzed cerussite is not directly

associated to basic lead minerals, but we assume that in parts of the deposit, where basic lead minerals occur (together with cerussite), similar temperatures were reached during their formation. At the Tiger ore deposit, cerussite is first replaced by leadhillite and/or hydrocerussite which are later again replaced by cerussite (Abdul-Samad et al. 1982b). This paragenetic sequence may indicate temperature fluctuations during oxidation of the deposit, for example due to discontinuous influx of meteoric fluids into a warm (geothermal) fluid system shifting the stability of cerussite and hydrocerussite to higher or lower P_{CO2} .

Nobody has investigated the conditions of weathering in the Alpine fissures (e.g., Göschenen, Switzerland) yet, but it appears reasonable to assume oxidation during cooling of primary (i.e., metamorphic) fluids interacting with ore minerals upon exhumation. At Leadhills and the other localities with basic lead minerals, nothing is known about elevated temperatures during supergene processes, but it appears to be the only reasonable explanation for their formation to date.

595 In summary, the rarity of basic lead minerals in oxidation zones is probably caused by the lack of elevated temperatures during supergene processes in most oxidation zones. The 596 occurrence of lanarkite, however, cannot be explained by elevated temperatures alone, since 597 598 its stability field is not very T-dependent (cf. Fig. 6b). This is most probably the reason, why lanarkite is the rarest of the basic lead minerals discussed here. Consequently, additional 599 600 processes have to be invoked to support lanarkite formation in nature. At much higher 601 temperatures, Ettler et al. (2005) report the minor occurrence of lanarkite in particles from 602 lead smelting, which shows that lanarkite is principally stable under high temperature conditions. 603

604

605 **FS experiments**

The FS experiments confirm the three step formation process predicted by the textures of the medieval sample material (cf. Fig. 7). Dousing the hot rock surface with water is not a

necessary process for the formation of basic lead phases since the experimental FS material 608 was cooled down in static air before it was brought in contact to a fluid phase. This, however, 609 610 does not exclude that dousing with water additionally favors formation of basic lead minerals. 611 All experiments were conducted with water in contact to atmospheric CO_2 . Under these 612 conditions hydrocerussite is thermodynamically not stable (Essington et al. 2004). All CO₂-613 pressures of the experimental waters are higher (between $logP_{CO2} = -1.5$ and -3.5) than needed 614 for hydrocerussite precipitation ($\log P_{CO2} = -3.7$). The reason that still hydrocerussite occurs in all experimental setups leads to two different explanations. First: the thermodynamic data of 615 616 hydrocerussite are not correct or second: microenvironments on the lead oxide-water interface exist where the CO₂ partial pressures are low enough to stabilize hydrocerussite 617 thermodynamically. The quality of the thermodynamic data of hydrocerussite has been 618 discussed in Mercy et al. (1998 and references therein) and it appears that this explanation is 619 not the one to choose here. Hence, basic lead phases can form in environments which are in 620 621 contact to atmospheric CO₂. Consequently, in contrast to the process proposed e.g., by 622 Essigton et al. (2004), no closed or CO_2 -depleted system for the external fluid is necessary to form hydrocerussite if lead oxides are available. The formation of hydrocerussite in 623 624 microenvironments producing high pH and low P_{CO2} was also proposed by Li et al. (2015). The same applies to the pH values of the experimental systems. Only 4 of 6 samples show pH 625 626 values of the experimental waters which are high enough to stabilize hydrocerussite (pH >627 7.7), but all experiments contained this phase. Hence, local equilibria play a major role in the 628 formation of basic lead phases.

Ettler and Johan (2014) show in their long-term leaching experiments with slag from Pb ore processing that the lead concentration of the fluid is controlled by the precipitation of newly formed cerussite and anglesite in a system lacking lead oxides. In contrast, Pb activity in soil waters in environments with predominant lead oxides due to weathering of metallic lead e. g. at shooting ranges (e.g., Li et al. 2015) is most probably controlled by hydrocerussite. Li et al.

634 (2015) report that cerussite and hydrocerussite are more capable of forming a protective layer

that prevents further weathering than lead oxides, because of their lower solubility.

Calculated solubilities including the basic lead phases hydrocerussite, leadhillite, caledonite,
lanarkite in addition to cerussite, anglesite, and litharge show that most basic lead phases
except for lanarkite are less soluble than cerussite, anglesite, litharge under neutral to slightly
basic pH conditions (Fig. 9).

640 In all of our experimental setups, lead oxides were in continuous contact with the weathering fluid. The analyzed waters can hence provide constraints which phases control the availability 641 of lead. For this reason the lead concentration determined in the experiments were plotted in 642 the solubility diagrams and are compared to the different mineral solubilities. It is obvious 643 that the lead concentrations are significantly lower than the solubility of litharge. All 644 experimental setups show that lead concentrations are also below cerussite solubility. All 645 analyses of the experimental setups plot near the hydrocerussite solubility. This indicates that 646 647 the solubility of lead oxides like litharge is controlled by the precipitation of hydrocerussite in all of our experiments. The trend that the lead concentration are highest in the setups with the 648 lowest pH-values is not surprising because of the increasing solubility of lead minerals at 649 650 lower pH (Ma et al. 2007 and references therein).

The observation that less hydrocerussite was formed in experimental setup B (hence, at higher pH values than in setup A) was also observed by Ma et al. (2007) and is explained by the lack of protons required for basic lead mineral precipitation.

Finally, the experiments impressively indicate that crystallization of basic lead minerals is possible in short time periods, since first mineral growth was macroscopically visible after only a few hours.

657

658 Temperature range during FS

The temperatures reached during FS are unclear. Lead oxide stability and the melt 659 compositions analyzed in the present study, however, provide constraints on the temperature 660 range obtained. FS experiments of Willies and Weisgerber (2000) on simple bonefires lead to 661 maximum temperatures of 500°C to 700°C during FS, but according to these authors, fires 662 663 with access to flowing air easily reach higher temperatures. 664 The stability of the divalent lead oxides massicot and litharge is temperature-dependent: 665 Massicot is stable at higher temperatures, the transformation litharge-massicot happens between 489°C and 540°C (Gavrichev et al. 2008). Experiments in static air show that 666 minium forms during prolonged oxidation (370°C) of massicot and litharge (Ciomartan et al. 667 1996). However, this transformation depends on the type of experimental atmosphere. 668 Minium and litharge are the predominant lead oxides occurring in the investigated samples. 669 Massicot subordinately occurs as fine-grained aggregates. The predominance of litharge 670 instead of massicot indicates that in most cases, temperatures did not exceed 540°C. Although 671

massicot is metastable at room temperature (e.g., Perry and Wilkinson 2007), transformation
to litharge during cooling seems unlikely. In our experiments massicot is frequently occurring
beside litharge, which is explained by the relatively high temperatures used for
decarbonisation of cerussite (650-800°C).

Depending on thermal conductivity, the temperature gradient during FS is very large with 676 677 high temperatures at the fire/rock interface and much lower temperatures only centimeters away in the rock (Willies and Weisgerber 2000). The occurrence of shannonite instead of pure 678 679 oxide shows that temperatures in many samples were not sufficiently high for a complete decarbonisation of cerussite (see also Pring et al. 1990). Experiments by Yamaguchi et al. 680 (1980) show that shannonite starts to form from cerussite around 300°C. About 440°C are 681 needed to complete the transformation to lead oxides (cf. Eq. 3a-c). In some samples, lead 682 oxides, oxycarbonates, and unaffected cerussite appear side by side (cf. Fig. 1b) which 683

684 implies a strong temperature gradient on a small scale. The experiments show that complete685 transformation of cerussite to lead oxides was possible in only 15 minutes.

In addition to the lead oxides/oxycarbonates which indicate low temperatures below 500°C during the FS process, the deterred melt provides important information on the maximum temperature reached. Melt was formed in a few cases and probably only in direct contact of blaze and rock. Although the FS experiments were conducted at relatively high temperatures of 700-800°C, only a small amount of sample material shows partial melting.

691 To get an estimate of the minimum temperatures reached during partial melting, the bulk 692 compositions of melt directly associated with crystal type II and I were reintegrated based on 693 image analyses and EMPA data (see Fig. 4b, 4c, 4d). The bulk, crystal and the former melt composition of MK 06 (almost pure Pb-Si-O melt) can be plotted into the experimental PbO-694 SiO₂ phase diagram of Smart and Glasser (1974) (see Fig. 10a & 10b). Both reintegrated bulk 695 compositions (A+B) completely melt around 760°C. The crystal compositions of crystal type 696 697 I correspond well to the mineral alamosite (average chemical composition: $Pb_{1,01}Si_{0.95}O_3$; see Table 5). μ-XRD and Raman measurements, however, do not allow a distinct identification as 698 alamosite. Small differences in composition (A) and (B) are easily explained by different 699 700 portions of additional minor elements like iron or barium (cf. Table 4).

The composition of the Zn-rich crystal type II and the former melt of sample MK_08 are more complex as they include zinc as additional major element. They are plotted into the ZnO-PbO-SiO₂ phase diagram of Jak et al. (1997) (see Fig. 10c). The bulk compositions (C) and (D) are almost identical and entirely melt around 950°C. The crystal composition is close to larsenite (average composition: $Pb_{0.85}Zn_{0.80}Si_{1.28}O_4$). Again the discrepancy in composition is most probably explained by additional elements.

707

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Implications

This paper investigates the formation and stability of basic lead phases in different artificial 709 and natural environments with a special focus on their occurrence during medieval FS. Since 710 711 lead of natural and anthropogenic sources is one of the most widespread pollutants, a better 712 understanding of the stability relations and formation conditions of supergene, low-713 temperature lead phases is of interest. The short term experiments show that in environments where lead oxides predominate, the basic lead hydrocerussite is likely to control the 714 715 availability of lead in aqueous systems, especially at neutral to slightly basic pH conditions. This is of interest for the evaluation of the toxic potential of lead-contaminated sites like 716 medieval mine dumps and shows that relatively rare secondary phases may be important in 717 718 some weathering environments and should be taken in account besides the more common ones. Long-term experiments have to confirm if the basic lead minerals have the potential to 719 720 retain lead over long time periods.

The formation conditions of basic lead minerals in natural oxidation zones are not well understood. The stability diagrams presented in this contribution, show that weathering under elevated temperatures (between 35°C and 75°C) could play a crucial role for their formation.

Finally, the results presented provide a base frame for mining archeologists unraveling FS at places where FS mining traces are missing. The results of the melt remnants offer the possibility to constrain temperatures reached during this widespread medieval mining method.

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Acknowledgments

We are grateful to T. Wenzel for his friendly assistance during EMP analyzes and discussion of the results. We thank M. Keuper for assisting during Micro Raman analysis, C. Berthold, N. Wichtner for her help during μ -XRD measurements and S. Schafflick for the professional sample preparation. G. Stoschek and M. Marks for their help during water analyses. This work is a contribution of the r⁴ project "ResErVar—Ressourcenpotential hydrothermaler

- 734 Lagerstätten der Varisziden" funded by the German Ministry of Education and Research
- 735 (BMBF).
- 736

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Figure captions

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Figure 1. (a) Photograph of typical red-colored barite-quartz FS specimens; width of 924 925 photograph (WoP) = 7 cm. (b) Reflected light image with crossed polarizers of galena 926 weathered to cerussite and anglesite. At the rim, cerussite is converted to lead oxycarbonates 927 which are partly replaced by elyite and hydrocerussite WoP = $860 \mu m$. (c) Photograph of lead oxides pseudomorphic after cerussite with typical shrinkage cracks, partly overgrown by 928 929 hydrocerussite; WoP = 1 cm. (d) Photograph of euhedral leadhillite and caledonite crystals growing on hydrocerussite; WoP = 2 mm. (e) Reflected light image with crossed polarizers of 930 litharge and minium infiltrated by elyite, hydrocerussite and leadhillite along cracks; WoP is 931 932 about 430 μ m. (f) Reflected light image with crossed polarizers of lead oxy carbonates, partly replaced by litharge. Elvite and hydrocerussite occur along cracks; WoP = $860 \mu m$. (g) 933 Photograph of euhedral lanarkite and hydrocerussite; WoP = 1 mm. (h) Photograph of 934 euhedral elyite and hydrocerussite growing on lead oxides; WoP = 7 mm. (i) Photograph of 935 brownish, bulbous scotlandite crystals aggregates accompanied by lanarkite needles; WoP = 1 936 mm. (i) Photograph of a euhedral chenite crystal; WoP = 1.5 mm. Abbreviations: ang = 937 anglesite, cer = cerussite, che = chenite, cld = caledonite, elt = elvite, fl = fluorite, gn =938 939 galenite, hcer = hydrocerussite, lan = lanarkite, lith = litharge, min = minium, oxyc = lead oxy carbonates, PbO = not further distinguished lead oxides, qtz = quartz, scd = scotlandite. 940

941

Figure 2. (a)-(c) representative Raman spectra of the phases litharge, minium, caledonite, elyite, scotlandite, and leadhillite. (d)-(f) μ -XRD patterns of mineral aggregates of the medieval firesetting and the experimental setup. Abbreviations: ang = anglesite, cer = cerussite, hcer = hydrocerussite, lith = litharge, mas = massicot.

946

Figure 3. (a) Photograph of spongy, red-brown colored FS related former melt, lanced by
bubbles on grey chert; (WoP) = 3.5 cm. (b) Reflected light image of melt type ii with large
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round bubbles and small, metal inclusions; WoP = 860 μ m. (c) Reflected light image of crystal type I (light gray) associated to melt type i (dark grey); WoP = 860 μ m. (d) Reflected light image of crystal type II, III and IV associated to melt type i; WoP = 860 μ m. (e) Reflected light image with crossed polarizers of melt type iii, lanced by numerous small bubbles; WoP = 430 μ m.(f) Reflected light image of melt type iv, which is layered and surrounds barite crystals; WoP = 860 μ m. Abbreviations: brt = barite, fl = fluorite, hem = hematite and qtz = quartz.

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Figure 4. (a) Element contents in mol% of former melt phase (white bars) including type i and ii and corresponding crystal phase (grey bars). The mean values of all measurements are plotted as black bars. Note: the y-axis for Pb/Ca is linear, for all other elements logarithmic. **(b)-(d)** Mean molar ZnO and CaO contents versus X_{SiO2} of former melt and the different associated crystals types for each sample MK_08, MK_06 and MK_22.

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Figure 5. (a) Photograph of minium + litharge + massicot pseudomorphic after cerussite; 963 WoP = 6 mm. (b) BSE-image of litharge (see upper left) overgrown by hydrocerussite; WoP 964 = 3 mm. (c) magnified excerpt of image (b) showing hydrocerussite sheds grown on litharge; 965 WoP = 250 μ m. Lower part shows EDS spectra of the analyzed area marked as circle (d) BSE 966 967 image of blocky cerussite crystals together with hydrocerussite; $WoP = 300 \ \mu m$. Lower part 968 shows EDS spectra. (e), (f) fibrous chenite and needle-like elyite crystals together with hydrocerussite; $WoP = 350 \ \mu m$ and $150 \ \mu m$. Lower parts shows EDS spectra. Abbreviations: 969 cer = cerussite, che = chenite, elt = elyite, hcer = hydrocerussite, lith = litharge, min = 970 971 minium, mas = massicot, qtz = quartz.

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973 Figure 6. log P_{CO2}-pH diagram showing (a) stability relation for the lead phases
974 hydrocerussite, lanarkite, minium, anglesite, and cerussite. (b) stability fields of the lead

phases for variable temperatures (35°C, 45°C, 65°C, 75°C), marked as dashed lines. (c) 975 976 stability relation for the basic lead phases hydrocerussite, anglesite, caledonite, and linarite including copper contents of $Cu = 1.0 \times 10^{-5}$ M (d) stability relation for the lead phases 977 including variable copper contents of $Cu = 1.0 \times 10^{-15}$ M. Stability diagrams were calculated 978 for P = 1 bar, \log_{PO2} = -0.68bar, T = 25°C, S = 1x10⁻² M, Pb = 1x10⁻² M. 979 980 981 Figure 7. Three steps process of the FS assemblage with: (I) supergene weathering, (II) FS, and (III) mine dump processes. Additionally listed are sketches of each step, mineral names, 982 mineral formula, representative photo (in Figure 1), formation reaction mentioned in the text, 983 and the paragenetic sequence. 984 985 Figure 8. Fluid path models for the reaction with minium (model I) and portlandite (model 986 II). (a) Shows the evolving fluids (i) + (ii) for model I and (iii) + (iv) for model II plotted in a 987

logP_{CO2}-pH diagram (Fig. 6) (b) the evolving saturation indices during progressive reaction
respectively.

990

Figure 9. Diagram showing Molar solubility of hydrocerussite, leadhillite, caledonite cerussite, anglesite, lanarkite, and litharge at pH 2-12. Water analysis of the experimental setup A1-5 and B1-5 are included as labeled symbols. The solubility of leadhillite includes the uncertainties regarding the solubility constants as grey range (see methods section).

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Figure 10. (a), (b) Reintegrated bulk, crystal and former melt compositions for sample
MK_06 plotted in a binary PbO-SiO₂ system of Smart and Glasser (1974). (c) Reintegrated
bulk, crystal and former melt compositions of sample MK_08 plotted in a ternary ZnO-SiO₂PbO system (Jak et al. 1997).

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Tables

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Table 1. Mineral names, abbreviations, and formulas used in the text.

mineral name	formula		mineral name	formular						
alamosite	PbSiO ₃	-	*leadhillite	Pb ₄ (SO ₄)(CO ₃) ₂ (OH) ₂	ldh					
anglesite	PbSO ₄	ang	linarite	PbCu(SO ₄)(OH) ₂	lin					
calcite	CaCO ₃	-	*litharge	PbO (tetragonal)	lith					
*caledonite	Pb ₅ Cu ₂ (CO ₃)(SO ₄) ₃ (OH) ₆	cld	malachite	$Cu_2(CO_3)(OH)_2$	mal					
*cerussite	PbCO ₃	cer	*massicot	PbO (orthorombic)	mas					
chalcopyrite	CuFeS ₂	сср	mimetite	Pb ₅ (AsO ₄) ₃ Cl	-					
*chenite	Pb ₄ Cu(SO ₄) ₂ (OH) ₆	che	*minium	Pb ⁴⁺ Pb ₂ ²⁺ O ₃	min					
*elyite	CuPb ₄ O ₂ SO ₄ (OH) ₄ ·H ₂ O	elt	portlandite	Ca(OH) ₂	-					
galena	PbS	gn	pyromorphite	Pb ₅ (PO ₄) ₃ Cl	-					
*hydrocerussite	Pb ₃ (CO ₃) ₂ (OH) ₂	hcer	*scotlandite	PbSO ₃	scd					
*lanarkite	Pb ₂ OSO ₄	lan	shannonite	Pb ₂ OCO ₃	shan					
larsenite	Zn ₂ SiO ₄	-	*tenorite	CuO	-					
* minerals of the FS	* minerals of the FS assemblage after Wittern (1988, 1994)									

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1006 **Table 2.** Phase assemblages of the experimental setups.

setup	phase assemblage	initial weight [g]	newly formed phases after 50 days
A1/B1	litharge/masssicot	13	hydrocerussite ^{A,B}
A2/B2	litharge/massicot + tenorite	6.5 / 6.5	hydrocerussite ^{A,B} ; cerussite ^{A,B}
A3/B3	litharge/massicot + chalcopyrite + galena	4.5 / 4.5 / 4.5	hydrocerussite ^{A,B} ; cerussite ^A
	11.4 / 1 1 1		hydrocerussite ^{A,B} ; cerussite ^{A,B} ; elyite ^A ;
A4/B4	litharge/massicot + tenorite + anglesite	4.5 / 4.5 / 4.5	chenite ^A
A5/B5	Badenweiler sample material	43 / 55	hydrocerussite ^{A,B} ; elyite ^B ; chenite ^B
A,B shows	in which experiment the newly formed phases of	occur	

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1009 **Table 3.** Analyzed waters of the experiments.

						sam	ples					
			s	etup A					set	ир В		
	A1	A2	A3	A4	A5	A6	B1	B2	B3	B4	B5	B6
рН	7.4	7.7	7.0	6.2	7.0	6.0	8.8	8.6	7.8	7.1	7.9	9.7
EC [ms]	0.05	0.04	0.05	0.1	0.5	0.001	0.8	1.1	1.1	1.4	1.3	1.1
(HCO₃) ⁻ [mg/l]*	29	17	12	4.0	81		273	155	269	389	314	289
analyzes in [µg/l]						IC-o	data					
Li⁺	1	1	2	1	85	n.d.	12	18	17	8	40	16
Na⁺	1470	1110	2730	990	7980	n.d.	58300	58800	54300	26400	54040	42300
K ⁺	960	922	984	793	60700	n.d.	165000	167000	149976	75200	157000	129000
Mg ²⁺	550	628	473	416	3670	n.d.	536	23400	19800	47300	26700	30400
Ca ²⁺	7270	4880	3880	3410	40100	n.d.	3092	24700	23500	103000	52400	53300
Sr ²⁺	850	418	467	487	3130	n.d.	1464	1970	1870	22300	2720	2120
Ba ²⁺	66	87	18	28	83	n.d.	0.0	90	85	28358	97	107
F	458	72	259	198	3060	n.d.	1230	321	490	1250	2370	610
Cl	36.8	19	24	21	2590	n.d.	593.5	7382	4480	3588	19300	54000
Br	5.8	2.8	n.d.	n.d.	12.8	n.d.	n.d.	n.d.	n.d.	5.9	39	36
(NO ₃) ⁻	26.9	n.d.	n.d.	6.3	422	n.d.	9099	9050	34810	30577	22700	26200
(SO ₄) ²⁻	1217	5140	8290	12300	132000	21.9	110000	196808	189000	269110	244000	172100
(PO ₄) ³⁻	n.d.	n.d.	741	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1220
						TXRF	data					
Mn	<15	<15	<15	<15	148	<15	<15	<15	<15	<15	17	<15
Fe	<2	<2	<2	3.3	<2	2	<2	<2	<2	<2	<2	<2
Co	<3	<3	<3	<3	12	<3	<3	<3	<3	<3	4	<3
Ni	<3	<3	<3	<3	8	<3	<3	<3	<3	<3	<3	<3
Cu	<3	24	10	378	146	0.7	9	17	55	26	32	<3
Zn	9.8	33	50	137	356	9	<1	17	14	44	27	7.4
As	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Rb	3	3	2	0.7	110	<2	178	149	129	124	170	113
Pb	123	269	931	3790	1490	<5	65.8	174	292	529	232	<5

1010 **Table 4.** Representative EMP results of the different former melts and the crystal phases.

	samples (crystal phase) [wt%]											
oxides	МК- 06-111	MK- 06-114	MK- 06-109	R- 1.12	R- 1.13	R- 1.24	MK- 08.46	R- 1.39	R- 1.7	R-1.1	R- 1.47	R- 1.18
Na₂O	0.04	0.07	bdl	0.01	0.02	0.02	bdl	0.03	0.03	bdl	0.02	bdl
SO₃	bdl	0.07	bdl	0.08	0.06	0.04	bdl	bdl	bdl	bdl	0.02	bdl
P ₂ O ₅	0.04	0.08	0.06	0.34	0.29	0.32	0.16	0.17	0.43	0.07	0.03	0.09
Al₂O₃	0.57	1.3	0.03	1.2	1.1	1.06	0.03	1.5	0.05	0.06	0.06	0.36
PbO	78.0	77.6	81.0	66.5	67.0	65.4	57.6	68.5	67.4	5.5	3.2	32.5
Ag ₂ O	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
SiO ₂	18.9	2bdl	18.7	21.6	21.8	23.3	20.1	22.4	20.7	50.3	51.0	31.5
K₂O	0.20	0.35	bdl	0.40	0.30	0.61	0.07	0.66	0.04	0.04	0.01	0.17
BaO	0.06	0.12	0.27	1.0	0.88	0.99	0.40	1.1	0.29	0.09	0.05	0.26
CaO	0.06	bdl	0.02	4.9	6.1	5.1	0.58	2.5	10.7	42.9	44.0	16.8
TiO ₂	0.01	0.01	bdl	0.07	0.04	0.05	bdl	0.06	bdl	0.01	0.01	bdl
ZnO	0.01	0.01	0.03	0.82	0.80	1.43	20.9	1.4	0.24	0.32	0.32	16.9
CuO	Bdl	0.11	0.07	0.06	bdl	bdl	bdl	0.15	bdl	0.09	bdl	bdl
FeO	1.9	0.11	0.12	1.60	1.2	1.2	0.20	1.4	0.20	0.27	0.22	0.25
total	99.7	99.8	100.3	98.5	99.5	99.6	100.0	99.8	100.0	99.7	98.8	98.9
crystal type ¹	I	I	I	П	П	П	ш	ш	ш	IV	IV	IV
				sa	mples (m	elt-phase	e) [wt%]					
							, [, -]					
	MK- 06-103	MK- 06-14	MK- 08-40	MK- 06-61	MK- 06-54	MK- 22-20	MK- 06-50	MK- 06.73	MK- 06.79	MK- 08.13	MK- 08.27	MK- 08.28
oxides												
Na₂O	0.05	0.03	bdl	0.09	0.06	bdl	bdl	0.01	0.02	0.03	0.04	0.05
SO₃	0.33	0.25	0.33	2.8	0.18	0.15	bdl	bdl	bdl	0.01	bdl	bdl
P ₂ O ₅	0.07	0.01	0.18	0.14	0.03	bdl	0.36	0.07	0.01	0.10	0.21	0.08
Al ₂ O ₃	2.6	0.37	0.85	2.3	1.9	0.09	1.4	1.7	2.0	1.8	6.6	0.73
PbO	75.4	68.1	62.0	59.2	68.6	69.6	81.8	69.4	70.3	71.8	38.9	79.4
Ag ₂ O	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.02	bdl
SiO ₂	21.8	29.0	29.1	25.1	28.8	29.1	17.4	30.0	28.4	12.5	28.2	5.6
К2О	0.63	0.45	0.78	0.69	0.88	0.01	0.08	0.26	0.55	0.04	0.04	0.02
BaO	0.15	0.13	0.17	8.69	0.48	0.22	0.03	0.02	bdl	0.11	0.06	0.08
CaO	bdl	bdl	1.94	0.03	0.24	0.11	0.03	0.03	bdl	0.03	0.14	0.01
TiO ₂	0.08	0.02	0.04	0.43	0.11	bdl	0.09	0.01	bdl	0.03	0.08	0.04
ZnO	0.05	0.06	3.06	0.04	bdl	0.01	bdl	bdl	0.01	0.33	0.41	0.14
CuO	bdl	0.97	1.03	0.08	0.02	bdl	bdl	bdl	bdl	0.31	0.59	0.11
FeO	0.06	0.04	0.83	0.23	0.10	0.04	0.30	0.14	0.08	0.77	1.63	0.74
total	101.1	99.4	100.3	99.9	101.3	99.3	101.5	101.6	101.4	87.9	76.9	87.00
melt												
type	:	:	:	;;	::	;;	111	111	111	i.	j.,	iv

¹ for definition of crystal and melt types, see sample description in the text; for structural formula see Table 5; bdl = below detection limit (For detection limits see Table A1)

Table 5. Summary of the structural formulas of the different crystal phases.

				1012
crystal		structural formula		1012
type	description	(EMPA)	natural equivalent	1013
I	high reflectance, fibrous	$Pb_{1.01}Si_{0.95}O_3$	alamosite [PbSiO ₃]	1014
П	high reflectance, short needles	$Pb_{0.72}Ca_{0.25}Si_{0.92}O_{3}\\$	Ca-rich alamosite [(Pb,	Ca)SiO ₃]
		Zn rich: $Pb_{0.84} Zn_{0.83} Si_{1.11}O_4$	larsenite [PbZnSiO ₄]	1015
111	high reflectance, blocky	Ca rich: Pb _{0.99} Ca _{0.62} Si _{1.14} O ₄	no natural equivalent	1016
IV	low reflectance, blocky	$Ca_{1.60}Pb_{0.33}Zn_{0.6}Si_{2.14}O_7$	no natural equivalent	1017

Table 6. Saturation indices of the experimental waters calculated with Phreeqc (supersaturation ismarked bold).

		setup A						set	up B			
mineral/phase	formula	A1	A2	A3	A4	A5	B1	B2	B3	B4	B5	B6
					sa	turatio	n indic	es				
anglesite	PbSO ₄	-3.8	-2.9	-1.0	-0.6	-1.0	-4.5	-3.7	-2.6	-1.8	-2.7	-
barite	BaSO ₄	-0.9	-0.1	-0.5	-0.2	1.0	-	1.1	1.0	3.7	1.2	1.1
calcite	CaCO ₃	-1.6	-1.7	-2.7	-4.0	-1.0	0.1	0.7	0.1	0.1	0.3	1.8
caledonite	Pb ₅ Cu ₂ (CO ₃)(SO ₄) ₃ (OH) ₆	-	5.9	10	9.5	11	-0.5	2.9	6.7	5.6	0.6	-
cerussite	PbCO ₃	-0.2	0.2	1.0	-0.1	0.8	-0.3	0.1	0.4	0.4	0.3	-
hydrocerussite	Pb ₃ (CO ₃) ₂ (OH) ₂	-1.4	0.3	2.2	-1.1	0.6	-1.3	-0.4	-0.3	-1.0	-0.6	-
lanarkite	Pb ₂ OSO ₄	-6.7	-4.8	-2.6	-3.6	-3.7	-7.0	-6.1	-5.5	-5.5	-5.7	-
leadhillite	Pb ₄ (SO ₄)(CO ₃) ₂ (OH) ₂	-4.2	-1.7	2.1	-0.8	0.6	-4.9	-3.1	-2.0	-1.9	-2.4	-
linarite	PbCu(OH) ₂ (SO ₄)	-	1.1	2.0	2.4	2.8	-0.8	0.3	1.6	1.2	1.1	
litharge	PbO (tetragonal)	-5.0	-4.0	-3.8	-5.1	-4.8	-5.0	-4.5	-5.0	-5.8	-5.1	-
massicot	PbO (orthorombic)	-5.1	-4.2	-3.9	-5.2	-5.2	-5.2	-4.6	-5.1	-6.9	-5.2	-
minium	Pb ⁴⁺ Pb ₂ ²⁺ O ₃	-28	-25	-24	-30	-28	-23	-24	-27	-31	-27	-
pyromorphite	Pb ₅ (PO ₄) ₃ Cl	-	-	26.7	-	-	-	-	-	-	-	-

Figure 1







* confirmed by µ-XRD and/or RAMAN

medieval Badenweiler sample material

Figure 3

K_06			 type I forme bulk c 	er melt composition
	70	80		90 I

08		
		type II
T		The former melt
		bulk composition
	70	80 90
Xoir	<u>ר</u>	
SIC		• type I
SIC		 type I former melt bulk composition
SIC		 type I former melt bulk composition
SIC		 type I former melt bulk composition
510		 type I former melt bulk composition
<u> </u>		 type I former melt bulk composition
510		 type I former melt bulk composition
510		 type I former melt bulk composition
SIC		 type I former melt bulk composition
22		 type I former melt bulk composition
510		 type I former melt bulk composition
2.3		 type I former melt bulk composition
SIC		 type I former melt bulk composition
Sic		 type I former melt bulk composition
SIC	70	 ● type I □ former melt ◆ bulk composition

Figure 5

confimed by: *XRD **RAMAN

\overline{b}		mineral name	mineral formular	foto	rct ¹	
	primary ore	galena @	PbS	(1b)		
	ring	cerussite (b)	PbCO ₃	(1b)	(1)	
	eathe	anglesite ©	PbSO ₄	(3b)	(2)	
	ne we	covellite (d)	CuS			
	superge	malachite	Cu ₂ (CO ₃)(OH) ₂			
		shannonite (f)	PbO(CO ₃)			
	fire setting	Pb-oxcarb ² (f)	PbCO ₃ *XPbO			
		massicotite	PbO (orthorombic)	(5a)		
		litharge(f)	PbO (tetragonal)	(5a)		
		minium(f)	$Pb^{2+}_{2}Pb^{4+}O_{4}$	(5a)		
		tenorite (9)	CuO			
		Pb-oxcarbhyd ³	Pb ₁₀ (CO ₃) ₆ (OH) ₆ O	(1f)		
		hydrocerussite (h)	$Pb_{3}(CO_{3})_{2}(OH)_{2}$	(1d)	(6)	
	SS	lanarkite (j)	$Pb_2(SO_4)O$	(1g)		
	ocesse	caledonite	$Pb_5Cu_2(SO_4)_3(CO_3)(OH)_6$	(1d)	(7)	
	ap pro	leadhillite/ susannite()	$Pb_4(CO_3)_2(SO_4)(OH)_2$	(1d)		
	hθ	elyite 🕟	Pb ₄ Cu(SO ₄)O ₂ (OH) ₄ *H ₂ O	(1h)		
		chenite	Pb ₄ Cu(SO ₄) ₂ (OH) ₆	(3j)		
		scotlandite	PbSO ₃	(3i)		
e ² lead ox	ide	carbonate hydroxid	e			

Figure 7

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