Formation of basic lead phases during fire-setting and other natural and man-made processes

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Basic lead phases are relatively rare compounds occurring in various natural and anthropogenically influenced environments, most importantly those related to fire-setting (FS). The medieval FS mining method and subsequent alteration processes lead to a complex 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 stability relations are only insufficiently known. In this study, the formation of this interesting phase assemblage is described in detail including textures, genesis, and conditions of formation. Samples include ones collected in a medieval mining district in SW-Germany and 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 formed during FS is discussed using thermodynamic models which are adapted to also explain their occurrence in other anthropogenic and in natural environments.

Textures indicate a three step development of the FS assemblage starting with formation of cerussite during supergene weathering of primary galena prior to FS. This is followed by the decarbonisation of the supergene cerussite during FS leading to the formation of lead oxides. Finally, the newly formed lead oxides were hydrated by rain and soil water in the mine dumps 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 and predominance of litharge and lead oxycarbonates in most other samples implies that 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 $P_{CO_2}$. 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.
dumps, lead contaminated soils or in contact to concrete, where the reaction of a fluid with 
portlandite produces high pH and low $P_{CO_2}$-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.

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
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, 1994) developed. The assemblage involves the oxides minium, massicot, litharge, and tenorite and the basic lead phases hydrocerussite, caledonite, leadhillite, lanarkite, elyite, chenite, and others. Mineral names used in this paper are for phases having natural equivalents; all phases used in the text, including their formulae, are summarized alphabetically in Table 1. The assemblage was initially known from various locations in Germany (Markl, 1991) and has now been found in other places in Europe as well (e.g., Kolitsch 1997). According to Kolitsch and Tillmanns (2003) also lead nitrates like \([\text{Pb}_2(\text{OH})_3(\text{NO}_3)]\) belong to the FS assemblage. The detailed conditions under which the FS assemblage and related melts form have remained 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-Samad et al. 1982a, Ingwersen 1990). Stability relations of leadhillite, hydrocerussite, and caledonite were evaluated by Abdul-Samad et al. (1982a) under low \(P_{\text{CO}_2}\) at 25°C, at variable pH values and sulfur activities. These diagrams show a relatively small intermediate leadhillite field appearing between the anglesite and cerussite/hydrocerussite boundary (hydrocerussite being stable below a \(\log P_{\text{CO}_2}\) of –3.7). The stability of lanarkite in the Pb-S-O system was calculated by Treiman (1999) which indicates that lanarkite is stable over a wide range of \(P_{\text{O}_2}\) and \(a\text{SO}_4\) at slightly basic pH. These data are, however, at odds with the
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 modeling to explain their occurrence during FS. These models were adapted also to unravel the basic lead phase occurrence at other anthropogenic and natural localities. Furthermore, the first detailed textural and chemical study and experiments on the formation of the FS assemblage are presented.

**Geologic background**

Samples of this study originate from the former mining area at the Altemannfels south of Badenweiler in the Southern Schwarzwald, SW Germany (see Fig. A1 of Appendix A). The Altemannfels is a prominent, tens of meters high quartz rock formed by hydrothermal waters 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 different generations of quartz, barite, and fluorite as gangue, which are mineralized by galena, chalcopyrite, and minor sphalerite. Supergene weathering produced secondary lead 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 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 mine dump was age dated by the CEZ Archaeometry GmbH, Mannheim, Germany, to an age of about 750 ± 21 A.D. (Markl, unpubl. data). Besides charcoal relics, the smooth rock face
with few or no tool marks, the shape, ash layers, blackened surfaces, and dumps containing typically red colored rock specimens are distinctive features for such former FS sites.

Methods

All phase and water analyses were conducted at the Department of Geosciences, University Tübingen, Germany.

Electron microprobe analysis (EMPA) and scanning electron microscopy (SEM)

For quantitative and qualitative determination of the major and minor element compositions of the FS-related melt a JEOL 8900 electron microprobe in wavelength-dispersive mode (WDS) was used. The analyses were conducted using a focused beam with 20 nA current and 20 kV acceleration voltage. Matrix corrections were performed according to JEOL φρz method (Armstrong, 1991). The elements for the quantitative program were selected after qualitative analyses in energy dispersive mode (EDS). Fluorine was not included in the program, since WDS-scans on the fluorine Kα-line yielded no significant signal. For details of the WDS-configuration used, including standards, counting times of the peak/background, and the average detection limits see Table A1 in the Appendix A. On the SEM, visual images and qualitative EDS spectra were obtained using a Hitachi TM3030 Tabletop Microscope.

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 (logKsp) for leadhillite, caledonite, and linarite were taken from Abdul-Samad et al. (1982a). Since Abdul-Samad et al. (1982a) did not provide adequate information about the thermodynamic data used for the determination of the logKsp, there is a potential source of error combining the solubility constants from Abdul-Samad et al. (1982a) with the Thermoddem database. Therefore, we decided to re-determine the solubility constants of caledonite, linarite, and leadhillite with Phreeqc, using the solution composition of the solubility experiments from Abdul-Samad et al. (1982a). In order to correct the electrical charge balance of the solutions, we chose NO\textsubscript{3}\textsuperscript{-} as passive anion. The re-determined logKsp for caledonite (-26.24) differs only slightly (1.35%) from the literature value (-26.60). Also for linarite, the calculated logKsp (-3.64) only differs by 1.1% from the literature value (-3.60). These small differences have only small effects on the size of the calculated stability fields.

For leadhillite, however, Phreeqc failed to converge on the solution composition from Abdul-Samad et al. (1982a) and it was not possible to re-determine the logKsp in the same manner as for caledonite and linarite. We therefore assume that for leadhillite the discrepancy between the value of Abdul-Samad et al. (1982a) and a re-determined value would be in the same range as for caledonite/linarite (maximum deviation of 1.35%). For plotting leadhillite in the stability diagrams, we decided to take the logKsp value from the literature (-26.70, Abdul-Samad et al., 1982a) adding a precental error of \(\pm\ 1.35\%\) to it. In order to show these uncertainties, the stability field of leadhillite is bounded by thick grey bars instead of thin black lines. The thickness of the grey bars represents the \(\pm\)1.35% uncertainty. For the calculation of the fluid path and the saturation indices, consistently the solubility constant of -26.30 (-26.70 + 1.35%) for leadhillite was taken. The input codes for the calculated fluid paths are presented in Appendix B, the used logKsp and delta H values are reported in Appendix A, Table A2.
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 ~2 µm. 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 RRUFF™ database (Downs 2006).

µXRD analysis

X-ray microdiffraction was used to characterize fine-grained phase aggregates or mixtures. Measurements were performed on a Bruker D8 Discover GADDS Θ/Θ microdiffractometer with a Co-Anode (wavelength λ = 1.79 Å) at 30kV, 30 mA, and room temperature. Monocapillary optics of 500 µm with 300 µm pinhole and a two dimensional VÂNTEC500 detector was used (see Berthold et al. 2009). The patterns were integrated individually for each sample with a step size of 0.05 °2Θ. The incident angle was fixed to 15° and measurement time was set to 120 s per frame.

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.

The mineral separates (galena, chalcopyrite, malachite, and anglesite) were crushed down to a grain size of 0.5-1.5 mm. It was not possible to crush cerussite in the same way because of its fibrous habit. Generally, cerussite grain size varied between 15 mm and >1 mm.
For simulating the FS process, the Badenweiler sample material was heated for about 120 minutes to ~700-800°C using a wood stove. The cerussite and malachite mineral separates 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) 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 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, resulting in an initial pH of 6.0. The second setup (B) was prepared from river water mixed 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 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 FS (Willies and Weisgerber 2000). This habit was certainly important for creating a high-pH environment.

Five different mineral sets for each pH-setup were chosen (see Table 2). All experiments dealing with mineral separates (A1-A4, B1-B4) were conducted with 13 g of mineral material and 60 ml of water (W/R ~4.5) and were stored in tumblers at room temperature (~20-25°C) 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 airtight). The coverage was removed for 15 minutes every day for equilibration with the 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 alkalinity of the solution was calculated, since the amount of water was too low for double titration.
Water analyses

Duplicate water analyses were performed before and after the experiments. Temperature, pH, and specific conductivity of the weathering solutions were determined using a PCE-PHD1 data logger. Major anions (F\(^{-}\), Cl\(^{-}\), Br\(^{-}\), NO\(_3\)\(^{-}\), PO\(_4^{3-}\), SO\(_4^{2-}\)) and cations (Li\(^{+}\), Na\(^{+}\), K\(^{+}\), Mg\(^{2+}\), Ca\(^{2+}\), Ba\(^{2+}\)) were determined by a Dionex ICS-1000 ion chromatography system equipped with an IonPac CS 12-A column for cations. All samples were diluted 1:1 with MilliQ-water in order to get adequate amounts of sample water. Disposable syringe filters (RC-20/25 and 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 generally <15 \(\mu\)g/L.

All samples were analyzed by total reflection X-ray fluorescence (TXRF) (see Klockenkämper, 1996; Wobrauschek, 2007) for the following (trace) metals: Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Ba, and Pb. First, 190 \(\mu\)L of sample solution were mixed and homogenized with 10 \(\mu\)L of 5 ppm Ga solution as internal standard. Then, two aliquots (each 10 \(\mu\)L) were put onto polished quartz disks, dried at 80°C and subsequently analyzed with a S2 PICOFOX benchtop TXRF system from Bruker AXS Microanalysis equipped with a Mo X-ray tube, operating at 50 kV and 600 \(\mu\)A for 10 min. Effective detection limits for the above named elements are around 1 \(\mu\)g/L. Based on the repetitive analysis of various multi-element standard solutions (Merck, Darmstadt, Germany) and reference material NIST1643c (trace elements in water), the relative standard deviation from the target values for most 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 water samples are given in Table 3, the original data in Table A3 in the Appendix.

Results
Sample description

The FS assemblage. Macroscopically, the FS samples are typically red colored (Fig. 1a) and 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 have formed before the FS process as normal weathering products. The following phases are texturally later. Fine grained hematite infiltrates the gangue minerals along cracks and grain 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 oxides like litharge, minium or massicot (Fig. 1b, Fig. 2a, d). Often, the replacement leads to complete or incomplete pseudomorphs, typically lanced by cracks (Fig. 1c).

The pseudomorphic lead oxides are frequently overgrown and/or replaced by hydrous phases like leadhillite, lanarkite, hydrocerussite, caledonite, and lead oxide carbonate hydroxide (Fig. 2b, c). The phases occur as euhedral crystals (Fig. 1d) and fine-grained aggregates (Fig. 1e). In many cases, replacement is not complete and lead oxides remain as relics (Fig. 1f).

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, hexagonal, colorless platy crystals (Fig. 1g). In some samples, hydrocerussite seems to be an early phase, overgrown by later generations of basic lead phases like caledonite and leadhillite. The monoclinic leadhillite has two polymorphs, the trigonal susannite and the orthorhombic macphersonite, with susannite as high temperature modification being metastable at ambient conditions (Livingstone 1993). Our XRD results, however, lead to no distinct identification of one of these polymorphs.

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 bunches (Fig. 1d), leadhillite occurs as (pseudo)hexagonal colorless to pale yellow platy crystals (Fig. 1d; Fig. 2c) and as fine-grained pale-yellow aggregates (Fig. 1e) associated with lead oxides, anglesite, hydrocerussite, elyite, and caledonite. The rare sulfite scotlandite forms either small, acute brownish crystals growing in cerussite cavities or bulbous yellowish to brownish crystal aggregates (Fig. 1i; Fig. 2c). In most samples, it is almost impossible to determine the paragenetic sequence of the hydrous phases, as they are intergrown chaotically on a very small scale.

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 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 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 high reflectance are fibrous (Type I, Fig. 3c), short needles (Type II, Fig. 3d) and blocky (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 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 former melt (e.g., Fig. 3b & 3d).

**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 H2O 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.

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} \((=\frac{SiO_2}{SiO_2+PbO} \cdot 100)\) for the different samples (see Table 5 for structural formula). In sample MK_08, the former melt phase shows relatively low CaO and ZnO 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} 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 mol%, and low ZnO contents up to 2.2 mol% and high CaO contents up to 17.8 mol%.

Blocky bright crystals of Type III form two distinct groups. The first group is nearly identical
in composition to the bright needles of Type I, just having slightly higher CaO contents up to 25.6 mol%. The second group, however, has much higher ZnO contents up to 33.0 mol%.

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 $X_{\text{SiO}_2}$ of the former melt (46.2 - 62.0 mol%) is slightly higher than in the crystals (45.1 - 50.3 mol%).

The former melt phase of sample MK_22 again shows higher $X_{\text{SiO}_2}$ 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.

**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 fine-grained sheds (Fig. 5b, 5c), but in larger amounts in experimental setup A compared to setup B. The $\mu$XRD 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 µXRD analyses, but Raman analyses lead to a unique identification.

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

**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, $P_{CO_2}$, 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, $P_{CO_2}$ as well as fixed lead and sulfur concentrations. Charge balance was maintained by 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 values at low $P_{CO_2}$. The cerussite/hydrocerussite stability field is dependent on $P_{CO_2}$, with cerussite being stable at higher $P_{CO_2}$. Leadhillite has a relatively small stability field around neutral pH-values and moderate to low $P_{CO_2}$ and is framed by anglesite and cerussite/hydrocerussite. Lanarkite has a relatively small stability field under neutral to basic pH-values and low $P_{CO_2}$. Minium is stable at slightly basic to basic pH values and low $P_{CO_2}$.

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 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 $P_{CO_2}$. In addition, the stability field of lanarkite expands to slightly higher $P_{CO_2}$ 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, $P_{CO_2}$, and Cu concentrations at fixed lead and sulfur concentrations and a fixed temperature of 25°C. At high copper concentrations of 1x10^{-5} M (see Fig. 6c), anglesite is stable at low pH values over the whole $P_{CO_2}$-range. Linarite is stable at low $P_{CO_2}$ and caledonite at high $P_{CO_2}$ over a wide pH range. At low Cu concentrations of 1x10^{-15} M (see Fig. 6d), the stability field of anglesite enlarges to higher pH values and hydrocerussite becomes additionally stable at high pH.

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

**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).

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

\[
PbS (\text{galena}) + H_2O + CO_2 + 2O_2 = PbCO_3 (\text{cerussite}) + SO_4^{2-} + 2H^+ \quad (1)
\]

\[
PbS (\text{galena}) + 2O_2 = PbSO_4 (\text{anglesite}) \quad (2)
\]

Cerussite and anglesite replace galena along its rims and typical cleavage planes. Within cavities, euhedral or subhedral crystals up to cm-size develop. Whether cerussite and/or anglesite are stable depends, for example, on pH, P\text{CO}_2, and temperature of the supergene weathering fluid (Keim and Markl 2015).

**Step II: firesetting:** During the FS process, lead oxides and lead oxycarbonates like shannonite form (cf. Fig. 1b, 1c; Fig. 2a, 2d) due to decarbonisation reactions of 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.

\[
\begin{align*}
2\text{PbCO}_3 \text{ (cerussite)} & \rightarrow \sim 300^\circ C \rightarrow \text{PbCO}_3 \cdot \text{PbO} + \text{CO}_2 \\
3\text{PbCO}_3 \cdot 3\text{PbO} & \rightarrow \sim 370^\circ C \rightarrow 2\text{PbCO}_3 \cdot 4\text{PbO} + \text{CO}_2 \\
\text{PbCO}_3 \cdot 2\text{PbO} & \rightarrow \sim 440^\circ C \rightarrow 3\text{PbO} + \text{CO}_2
\end{align*}
\]

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

As described, the pseudomorphs are lanced by numerous cracks due to a volume 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%).

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Step III: Processes in the dump: After FS, material containing no or only little ore was thrown on a dump. Here, basic lead phases could form by the reaction of weathering fluids with lead oxides, which is proven by common replacement and overgrowth textures (cf. Fig. 1b, 1d, 1g, 1h).

In principle, there are two possibilities (or a combination of both) where this water-lead 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.

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.

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).

\[
Pb^4+Pb_{2}^{2+}O_4 \text{ (minium)} + 6H^+ = 3Pb^{2+} + 3H_2O + 0.5O_2 \quad (4)
\]

If lead carbonates or basic lead carbonates like cerussite (Eq. 5), hydrocerussite (Eq. 6) or caledonite (Eq. 7) precipitate additionally, CO₂ is consumed (see also Ma et al. 2007).
\[
PbO \text{ (litharge)} + HCO_3^- + H^+ = PbCO_3 \text{ (cerussite)} + H_2O \quad (5)
\]

\[
3PbO \text{ (litharge)} + 2HCO_3^- + 2H^+ = Pb_3(CO_3)_2(OH)_2 \text{ (hydrocerussite)} + H_2O \quad (6)
\]

\[
5PbO \text{ (litharge)} + 2Cu^{2+} + HCO_3^- + 3SO_4^{2-} + H_2O + 3H^+ = Pb_5Cu_2(CO_3)(SO_4)_3(OH)_6 \text{ (caledonite)} \quad (7)
\]

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 reason, a rain water analysis from Négrél and Roy (1998) was chosen and reacted with \(1.5 \times 10^{-4} \text{ M} \) minium in 100 steps (path (i) and (ii)). During each reaction step, the phases anglesite, cerussite, hydrocerussite, lanarkite, litharge, minium, massicot, and leadhillite were allowed to precipitate if supersaturated. For the calculations a system closed to CO\(_2\) was assumed, which is reasonable for microenvironments. For path (ii) the water was additionally reacted with \(3 \times 10^{-3} \text{ M} \) galena in order to enrich the sulfur-poor rainwater with sulfur and slightly change the pH to lower values. This is reasonable since the investigated FS samples 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 saturation (\(Si = 0\)) during progressive reaction with minium in Figure 8b. Due to the differences in lead/sulfur activity of the fluid path compared to the stability diagrams, the paths do not exactly plot on the borders of the stability fields.

In both models, the CO\(_2\) partial pressure decreases from the starting value of \(\log P_{CO_2} = -2.0\) and the pH value rises during progressive reaction with minium. Path (i) shows that in sulfur-poor systems under moderate pH (pH = 6.0), cerussite is the first stable phase. With progressive reaction, \(P_{CO_2}\) 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).

Formation in contact to concrete (Model II). Artificially formed basic lead phases can also be found in contact with concrete. A paragenesis including hydrocerussite and elyite is described from the Clara mine, in the central Schwarzwald, SW Germany, where lead-bearing fluids come into contact with shotcrete (Kolitsch 2000; Markl 2015). Furthermore, Lee (2007) 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 [3\text{PbCO}_3\cdot2\text{Pb(OH)}_2\cdot\text{H}_2\text{O}]. Reaction of water with concrete (portlandite) will rise pH values as follows (Eq. 8):

$$\text{Ca(OH)}_2 \text{ (portlandite)} + 2\text{H}^+ = \text{Ca}^{2+} + 2\text{H}_2\text{O} \quad (8)$$

Precipitation of calcite consumes CO_2 (Eq. 9):

$$\text{Ca(OH)}_2 \text{ (portlandite)} + \text{CO}_2 = \text{CaCO}_3 \text{ (calcite)} + \text{H}_2\text{O} \quad (9)$$

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 $P_{CO_2}$ decreases during progressive reaction with portlandite.

On fluid path (iii) (starting pH of 7.), first cerussite, anglesite, and leadhillite are stable. As $P_{CO_2}$ decreases and pH rises, the assemblage anglesite plus leadhillite becomes stable and with progressive reaction additionally lanarkite. During the protracted reaction with portlandite, anglesite is not stable anymore and the assemblage lanarkite plus leadhillite becomes stable.

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 leadhillite being the stable phase assemblage at first. With proceeding reaction, leadhillite 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 that changes in pH, for example due to the dissolution of calcite, can result in different phase 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 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 reaction with portlandite and the precipitation of basic lead phases drops the $P_{CO_2}$ and increases the pH value in a system closed to CO$_2$. Again, if Cu is available, caledonite/linarite 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.

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

Formation of basic lead minerals in lead-bearing systems closed to CO$_2$ accompanied by the
precipitation of cerussite is not possible. During precipitation of cerussite, CO$_2$ is consumed
and the pH decreases (Eq. 10).

$$\text{Pb}^{2+} + \text{HCO}_3^- = \text{PbCO}_3 \text{ (cerussite)} + \text{H}^+ \text{ (10)}$$

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
CO$_2$ 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 30-
50°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 $\text{PCO}_2$.

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.

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 occurrence of lanarkite, however, cannot be explained by elevated temperatures alone, since 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 processes have to be invoked to support lanarkite formation in nature. At much higher temperatures, Ettler et al. (2005) report the minor occurrence of lanarkite in particles from lead smelting, which shows that lanarkite is principally stable under high temperature conditions.

**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 was cooled down in static air before it was brought in contact to a fluid phase. This, however, does not exclude that dousing with water additionally favors formation of basic lead minerals. All experiments were conducted with water in contact to atmospheric CO$_2$. Under these conditions hydrocerussite is thermodynamically not stable (Essington et al. 2004). All CO$_2$-pressures of the experimental waters are higher (between logP$_{CO_2}$ = -1.5 and -3.5) than needed for hydrocerussite precipitation (logP$_{CO_2}$ = -3.7). The reason that still hydrocerussite occurs in all experimental setups leads to two different explanations. First: the thermodynamic data of hydrocerussite are not correct or second: microenvironments on the lead oxide-water interface exist where the CO$_2$ partial pressures are low enough to stabilize hydrocerussite thermodynamically. The quality of the thermodynamic data of hydrocerussite has been discussed in Mercy et al. (1998 and references therein) and it appears that this explanation is not the one to choose here. Hence, basic lead phases can form in environments which are in contact to atmospheric CO$_2$. Consequently, in contrast to the process proposed e.g., by 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 microenvironments producing high pH and low P$_{CO_2}$ 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 values of the experimental waters which are high enough to stabilize hydrocerussite (pH > 7.7), but all experiments contained this phase. Hence, local equilibria play a major role in the 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.
(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).

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 of lead. For this reason the lead concentration determined in the experiments were plotted in the solubility diagrams and are compared to the different mineral solubilities. It is obvious that the lead concentrations are significantly lower than the solubility of litharge. All experimental setups show that lead concentrations are also below cerussite solubility. All analyses of the experimental setups plot near the hydrocerussite solubility. This indicates that 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 lowest pH-values is not surprising because of the increasing solubility of lead minerals at 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.

Temperature range during FS
The temperatures reached during FS are unclear. Lead oxide stability and the melt compositions analyzed in the present study, however, provide constraints on the temperature range obtained. FS experiments of Willies and Weisgerber (2000) on simple bonefires lead to maximum temperatures of 500°C to 700°C during FS, but according to these authors, fires with access to flowing air easily reach higher temperatures.

The stability of the divalent lead oxides massicot and litharge is temperature-dependent: 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 minium forms during prolonged oxidation (370°C) of massicot and litharge (Ciomartan et al. 1996). However, this transformation depends on the type of experimental atmosphere.

Minium and litharge are the predominant lead oxides occurring in the investigated samples. Massicot subordinately occurs as fine-grained aggregates. The predominance of litharge instead of massicot indicates that in most cases, temperatures did not exceed 540°C. Although 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 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 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. (1980) show that shannonite starts to form from cerussite around 300°C. About 440°C are needed to complete the transformation to lead oxides (cf. Eq. 3a-c). In some samples, lead oxides, oxycarbonates, and unaffected cerussite appear side by side (cf. Fig. 1b) which
implies a strong temperature gradient on a small scale. The experiments show that complete 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.

To get an estimate of the minimum temperatures reached during partial melting, the bulk compositions of melt directly associated with crystal type II and I were reintegrated based on 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-SiO₂ phase diagram of Smart and Glasser (1974) (see Fig. 10a & 10b). Both reintegrated bulk compositions (A+B) completely melt around 760°C. The crystal compositions of crystal type I correspond well to the mineral alamosite (average chemical composition: Pb₁.₀₁Si₀.₉₅O₃; see Table 5). µ-XRD and Raman measurements, however, do not allow a distinct identification as alamosite. Small differences in composition (A) and (B) are easily explained by different 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: Pb₀.ₘ₅Zn₀.₈₀Si₁.₂₈O₄). Again the discrepancy in composition is most probably explained by additional elements.

Implications
This paper investigates the formation and stability of basic lead phases in different artificial and natural environments with a special focus on their occurrence during medieval FS. Since lead of natural and anthropogenic sources is one of the most widespread pollutants, a better understanding of the stability relations and formation conditions of supergene, low-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 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 medieval mine dumps and shows that relatively rare secondary phases may be important in 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 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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Lagerstätten der Varisziden" funded by the German Ministry of Education and Research (BMBF).
References cited


Figure captions
Figure 1. (a) Photograph of typical red-colored barite-quartz FS specimens; width of photograph (WoP) = 7 cm. (b) Reflected light image with crossed polarizers of galena weathered to cerussite and anglesite. At the rim, cerussite is converted to lead oxycarbonates which are partly replaced by elyite and hydrocerussite WoP = 860 µm. (c) Photograph of lead oxides pseudomorphic after cerussite with typical shrinkage cracks, partly overgrown by 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 litharge and minium infiltrated by elyite, hydrocerussite and leadhillite along cracks; WoP is about 430 µm. (f) Reflected light image with crossed polarizers of lead oxycarbonates, partly replaced by litharge. Elyite and hydrocerussite occur along cracks; WoP = 860 µm. (g) Photograph of euhedral lanarkite and hydrocerussite; WoP = 1 mm. (h) Photograph of euhedral elyite and hydrocerussite growing on lead oxides; WoP = 7 mm. (i) Photograph of brownish, bulbous scotlandite crystals aggregates accompanied by lanarkite needles; WoP = 1 mm. (j) Photograph of a euhedral chenite crystal; WoP = 1.5 mm. Abbreviations: ang = anglesite, cer = cerussite, che = chenite, cld = caledonite, elt = elyite, fl = fluorite, gn = galenite, hcer = hydrocerussite, lan = lanarkite, lith = litharge, min = minium, oxyC = lead oxycarbonates, PbO = not further distinguished lead oxides, qtz = quartz, scd = scotlandite.

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.

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
round bubbles and small, metal inclusions; WoP = 860 µm. (c) Reflected light image of crystal type I (light gray) associated to melt type i (dark grey); WoP = 860 µm. (d) Reflected light image of crystal type II, III and IV associated to melt type i; WoP = 860 µm. (e) Reflected light image with crossed polarizers of melt type iii, lanced by numerous small bubbles; WoP = 430 µm. (f) Reflected light image of melt type iv, which is layered and surrounds barite crystals; WoP = 860 µm. Abbreviations: brt = barite, fl = fluorite, hem = hematite and qtz = quartz.

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.

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

Figure 6. log P_{CO2}-pH diagram showing (a) stability relation for the lead phases 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) stability relation for the basic lead phases hydrocerussite, anglesite, caledonite, and linarite including copper contents of Cu = 1.0x10^{-5} M (d) stability relation for the lead phases including variable copper contents of Cu = 1.0x10^{-15} M. Stability diagrams were calculated for P = 1 bar, log_{PO2} = -0.68bar, T = 25°C, S = 1x10^{-2} M, Pb = 1x10^{-2} M.

**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, mineral formula, representative photo (in Figure 1), formation reaction mentioned in the text, and the paragenetic sequence.

**Figure 8.** Fluid path models for the reaction with minium (model I) and portlandite (model II). (a) Shows the evolving fluids (i) + (ii) for model I and (iii) + (iv) for model II plotted in a log_{PCO2}-pH diagram (Fig. 6) (b) the evolving saturation indices during progressive reaction respectively.

**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).

**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-SiO2-PbO system (Jak et al. 1997).
Table 1. Mineral names, abbreviations, and formulas used in the text.

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<td>alamosite</td>
<td>PbSiO$_3$</td>
<td>*leadhillite</td>
<td>Pb$_4$(SO$_4$)$_2$(CO$_3$)$_2$(OH)$_2$</td>
</tr>
<tr>
<td>anglesite</td>
<td>PbSO$_4$</td>
<td>linarite</td>
<td>PbCu(SO$_4$)(OH)$_2$</td>
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<td>*litharge</td>
<td>PbO (tetragonal)</td>
</tr>
<tr>
<td>*caledonite</td>
<td>Pb$_2$Cu$_2$(CO$_3$)(SO$_4$)$_2$(OH)$_6$</td>
<td>malachite</td>
<td>Cu$_2$(CO$_3$)(OH)$_2$</td>
</tr>
<tr>
<td>*cerussite</td>
<td>PbCO$_3$</td>
<td>*massicot</td>
<td>PbO (orthorombic)</td>
</tr>
<tr>
<td>chalcopyrite</td>
<td>CuFeS$_2$</td>
<td>mimetic</td>
<td>Pb$_5$(AsO$_4$)$_3$Cl</td>
</tr>
<tr>
<td>*chenite</td>
<td>Pb$_4$Cu$_2$(SO$_4$)$_2$(OH)$_6$</td>
<td>*minimum</td>
<td>Pb$_4^+$Pb$_2^+$O$_3$</td>
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<td>*elyite</td>
<td>CuPb$_2$O$_2$SO$_4$(OH)$_2$H$_2$O</td>
<td>portlandite</td>
<td>Ca(OH)$_2$</td>
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<td>galena</td>
<td>PbS</td>
<td>pyromorphite</td>
<td>Pb$_2$(PO$_4$)$_3$Cl</td>
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<td>*scotlandite</td>
<td>Pb$_5$(SO$_4$)$_3$</td>
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<td>*tenorite</td>
<td>CuO</td>
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* minerals of the FS assemblage after Wittern (1988, 1994)

Table 2. Phase assemblages of the experimental setups.

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<th>initial weight [g]</th>
<th>newly formed phases after 50 days</th>
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<tbody>
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<td>A1/B1</td>
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<td>13</td>
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<td>A2/B2</td>
<td>litharge/massicott + tenorite</td>
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<td>hydrocerussite$^{A,B}$; cerussite$^{A,B}$</td>
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<tr>
<td>A3/B3</td>
<td>litharge/massicott + chalcopyrite + galena</td>
<td>4.5 / 4.5 / 4.5</td>
<td>hydrocerussite$^{A,B}$; cerussite$^A$; chenite$^A$; eilRITE$^A$; elyite$^B$;</td>
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<tr>
<td>A4/B4</td>
<td>litharge/massicott + tenorite + anglesite</td>
<td>4.5 / 4.5 / 4.5</td>
<td>hydrocerussite$^{A,B}$; cerussite$^{A,B}$; eilRITE$^A$; chenite$^A$</td>
</tr>
<tr>
<td>A5/B5</td>
<td>Badenweiler sample material</td>
<td>43 / 55</td>
<td>hydrocerussite$^{A,B}$; eilRITE$^B$; chenite$^B$</td>
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$^A,B$ shows in which experiment the newly formed phases occur.
Table 3. Analyzed waters of the experiments.

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<td>0.05</td>
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<td>289</td>
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n.d. = not detected; *calculated by charge balance
Table 4. Representative EMP results of the different former melts and the crystal phases.

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| crystal type¹ | I | I | I | II | II | II | III | III | III | IV | IV | IV |

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</tr>
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<td>Ag₂O</td>
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<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
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<td>bdl</td>
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<td>SiO₂</td>
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<td>K₂O</td>
<td>0.63</td>
<td>0.45</td>
<td>0.78</td>
<td>0.69</td>
<td>0.88</td>
<td>0.01</td>
<td>0.08</td>
<td>0.26</td>
<td>0.55</td>
<td>0.04</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>BaO</td>
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<td>0.13</td>
<td>0.17</td>
<td>8.69</td>
<td>0.48</td>
<td>0.22</td>
<td>0.03</td>
<td>0.02</td>
<td>bdl</td>
<td>0.11</td>
<td>0.06</td>
<td>0.08</td>
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<td>CaO</td>
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<td>bdl</td>
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<td>0.24</td>
<td>0.11</td>
<td>0.03</td>
<td>0.03</td>
<td>bdl</td>
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<td>0.01</td>
<td>0.01</td>
</tr>
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<td>TiO₂</td>
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<td>0.02</td>
<td>0.04</td>
<td>0.43</td>
<td>0.11</td>
<td>bdl</td>
<td>0.09</td>
<td>0.01</td>
<td>bdl</td>
<td>0.03</td>
<td>0.08</td>
<td>0.04</td>
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<tr>
<td>ZnO</td>
<td>0.05</td>
<td>0.06</td>
<td>3.06</td>
<td>0.04</td>
<td>bdl</td>
<td>0.01</td>
<td>bdl</td>
<td>0.01</td>
<td>0.33</td>
<td>0.41</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>CuO</td>
<td>bdl</td>
<td>0.97</td>
<td>1.03</td>
<td>0.08</td>
<td>0.02</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>0.31</td>
<td>0.59</td>
<td>0.11</td>
<td>0.11</td>
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<td>FeO</td>
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<td>0.04</td>
<td>0.83</td>
<td>0.23</td>
<td>0.10</td>
<td>0.04</td>
<td>0.30</td>
<td>0.14</td>
<td>0.08</td>
<td>0.77</td>
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<td>100.3</td>
<td>99.9</td>
<td>101.3</td>
<td>99.3</td>
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<td>101.6</td>
<td>101.4</td>
<td>87.9</td>
<td>76.9</td>
<td>87.00</td>
</tr>
</tbody>
</table>

| melt type¹ | i | i | i | ii | ii | ii | iii | iii | iii | iv | iv | 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.

<table>
<thead>
<tr>
<th>Crystal Type</th>
<th>Description</th>
<th>Structural Formula (EMPA)</th>
<th>Natural Equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>High reflectance, fibrous</td>
<td>Pb₁₄Si₀.₉₅O₃</td>
<td>Alamosite [PbSiO₃]</td>
</tr>
<tr>
<td>II</td>
<td>High reflectance, short needles</td>
<td>Pb₀.₇₂Ca₀.₃₅Si₀.₉₂O₃</td>
<td>Ca-rich alamosite [(Pb,Ca)SiO₃]</td>
</tr>
<tr>
<td>III</td>
<td>High reflectance, blocky</td>
<td>Zn rich: Pb₀.₈₄Zn₀.₁₆Si₁.₁₄O₄</td>
<td>Larsenite [PbZnSiO₄]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ca rich: Pb₀.₉₉Ca₀.₆₂Si₁.₁₄O₄</td>
<td>No natural equivalent</td>
</tr>
<tr>
<td>IV</td>
<td>Low reflectance, blocky</td>
<td>Ca₁₀₆Pb₀.₃₂Zn₀.₆Si₁₂.₁₄O₇</td>
<td>No natural equivalent</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Mineral/Phase</th>
<th>Formula</th>
<th>Setup A</th>
<th>Setup B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anglesite</td>
<td>PbSO₄</td>
<td>-3.8</td>
<td>-2.9</td>
</tr>
<tr>
<td>Barite</td>
<td>BaSO₄</td>
<td>-0.9</td>
<td>-0.1</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>-1.6</td>
<td>-1.7</td>
</tr>
<tr>
<td>Caledonite</td>
<td>Pb₅Cu₂(CO₃)(SO₄)₃(OH)₆</td>
<td>-1.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Cerussite</td>
<td>PbCO₃</td>
<td>-0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Hydrocerussite</td>
<td>Pb₅(CO₃)₃(OH)₁₂</td>
<td>-1.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Lanarkite</td>
<td>Pb₂SO₄₆</td>
<td>-6.7</td>
<td>-4.8</td>
</tr>
<tr>
<td>Leadhillite</td>
<td>Pb₄(SO₄)(CO₃)₂(OH)₂</td>
<td>-4.2</td>
<td>-1.7</td>
</tr>
<tr>
<td>Linarite</td>
<td>PbCu(OH)₂(SO₄)</td>
<td>-1.1</td>
<td>2.0</td>
</tr>
<tr>
<td>Litharge</td>
<td>PbO (tetragonal)</td>
<td>-5.0</td>
<td>-4.0</td>
</tr>
<tr>
<td>Massicot</td>
<td>PbO (orthorhombic)</td>
<td>-5.1</td>
<td>-4.2</td>
</tr>
<tr>
<td>Minium</td>
<td>Pb₄⁺Pb₂⁺O₃</td>
<td>-28</td>
<td>-25</td>
</tr>
<tr>
<td>Pyromorphite</td>
<td>Pb₅(PO₄)₃Cl</td>
<td>-30</td>
<td>-28</td>
</tr>
</tbody>
</table>

Saturation indices calculated with Phreeqc (supersaturation is marked bold).
Figure 2

medieval Badenweiler sample material

(a) Litharge
(b) Caledonite
(c) Elyite
(d) Leadhillite

Experimental setup
Figure 3

(a) Chert
(b) Bubbles and metal inclusions
(c) Metal inclusions
(d) Metal inclusions
(e) III
(f) BRT and IV
Figure 5

(a) before experiment
(b) after experiment
(c) hcer*
(d) cer*
(e) che**
(f) elt**

cps/eV

confirmed by: *XRD **RAMAN
<table>
<thead>
<tr>
<th>Mineral Name</th>
<th>Mineral Formular</th>
<th>RCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>galena @</td>
<td>PbS</td>
<td>(1b)</td>
</tr>
<tr>
<td>cerussite @</td>
<td>PbCO₃</td>
<td>(1b)</td>
</tr>
<tr>
<td>anglesite @</td>
<td>PbSO₄</td>
<td>(3b)</td>
</tr>
<tr>
<td>covellite @</td>
<td>CuS</td>
<td>(2)</td>
</tr>
<tr>
<td>malachite @</td>
<td>Cu₂(CO₃)(OH)₂</td>
<td>(2)</td>
</tr>
<tr>
<td>shannonite @</td>
<td>PbO(CO₃)</td>
<td>(5a)</td>
</tr>
<tr>
<td>Pb-oxcarb² @</td>
<td>PbCO₃*XPbO</td>
<td>(5a)</td>
</tr>
<tr>
<td>massicotite @</td>
<td>PbO (orthorombic)</td>
<td>(5a)</td>
</tr>
<tr>
<td>litharge @</td>
<td>PbO (tetragonal)</td>
<td>(5a)</td>
</tr>
<tr>
<td>minium @</td>
<td>Pb²⁺₂⁺Pb⁴⁺O₄</td>
<td>(5a)</td>
</tr>
<tr>
<td>tenorite @</td>
<td>CuO</td>
<td>(5a)</td>
</tr>
<tr>
<td>Pb-oxcarbhyd³</td>
<td>Pb₁₀(CO₃)₆(OH)₆O</td>
<td>(1f)</td>
</tr>
<tr>
<td>hydrocerussite @</td>
<td>Pb₃(CO₃)₂(OH)₂</td>
<td>(1d)</td>
</tr>
<tr>
<td>lanarkite @</td>
<td>Pb₂(SO₄)O</td>
<td>(1g)</td>
</tr>
<tr>
<td>caledonite</td>
<td>Pb₉Cu₂(SO₄)₃(CO₃)(OH)₆</td>
<td>(1d)</td>
</tr>
<tr>
<td>leadhillite/</td>
<td>Pb₄(CO₃)₂(SO₄)(OH)₂</td>
<td>(1d)</td>
</tr>
<tr>
<td>susannite @</td>
<td>Pb₄Cu(SO₄)O₂(OH)₄*H₂O</td>
<td>(1h)</td>
</tr>
<tr>
<td>elyite @</td>
<td>Pb₄Cu(SO₄)₂(OH)₆</td>
<td>(3j)</td>
</tr>
<tr>
<td>chenite</td>
<td>Pb₄Cu(SO₄)₂(OH)₆</td>
<td>(3i)</td>
</tr>
<tr>
<td>scotlandite</td>
<td>PbSO₃</td>
<td>(3i)</td>
</tr>
</tbody>
</table>

¹RCT = reaction  ²Lead-ox-y-carbonate  ³Lead oxide carbonate hydroxide