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Original paper

Remarks on the origin of cerussite in the Upper Silesian Zn-Pb deposits, Poland

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Abstract. Cerussite, the most important oxidized lead mineral in the Upper Silesian Zn-Pb deposits, occurs in two readily distinct types: fine-grained cerussite replacing galena in-situ and macrocrystalline cerussite filling open fractures and cavities. Microscopic observations and thermodynamic considerations lead to the conclusion that galena can be oxidized to lead carbonate directly, not necessarily through an intermediate sulphate phase. Locally present iron sulphides undergoing oxidation acidify solutions and provide ferric ions which are important oxidizing agents. In such microenvironments, anglesite can preferentially form.

Cerussite and galena commonly coexist together with non-oxidized zinc sulphides. It is difficult to explain such assemblages if galvanic couplings made of these two sulphides are not considered. These couplings are only formed when these two sulphides are in direct contact. In such an assemblage, galena undergoes oxidation, mostly to cerussite, and sphalerite is passivated. When there is no direct contact between sulphides, the galvanic couplings do not exist. Galena surfaces become covered by oxidation products which inhibit further oxidation. As such a cover does not form on sphalerite, it can be easily oxidized.

Key-words: Zn-Pb deposits, Upper Silesia, cerussite, oxidation, galvanic coupling

1. Introduction

Non-sulphide and oxidized Zn-Pb ores are currently being studied intensively because of their importance in the world mining. This is mainly due to recent developments in the technological methods for the treatment of these ores (Hitzman et al. 2003). The studies include

a broad range of investigations from descriptions of the geology of ore deposits (e.g. Boni et al. 2003; Borg et al. 2003; Coppola et al. 2009) to investigations of the mechanisms of sulphide oxidation (e.g. Sangameshwar, Barnes 1983; da Silva et al. 2003; Reichert, Borg 2008). The latter are important because a better understanding of oxidation processes in Zn-Pb sulphide deposits is necessary in the search for new ores and for exploration around already known ore bodies. It is also a significant problem in flotation processes and acid mine drainage.

The oxidation zone of the Silesian-Cracovian Zn-Pb deposits was the subject of extensive mineralogical and geochemical studies in the early 1960s, mainly by Źabiński (1960, 1964). In these works, Źabiński described all of the minerals from the oxidation zones of most of the ore bodies that were either found by him or were known from the accessible literature, and gave explanations for several chemical relationships in the zone. Lead carbonate – cerussite (PbCO_3) – was found to be the most important product of galena oxidation and lead sulphates to be relatively rare. The reason for this is that the Upper Silesian ores are located in carbonates, most typically in the “Ore Bearing Dolomite” (OBD). Plumbojarosite ($\text{PbFe}_6(\text{SO}_4)_4(\text{OH})_{12}$) and anglesite (PbSO_4) were found to occur in microenvironments where the pH is significantly acid – typically in the neighbourhood of iron sulphides undergoing oxidation. In 1960, Źabiński suggested that lead sulphates constituted the initial steps in galena oxidation: sulphide \rightarrow sulphate \rightarrow carbonate; this opinion has been accepted by some of his successors (e.g. Cabała 1996). In the present paper, the authors re-evaluate this hypothesis and propose that an intermediate sulphate step is neither necessary nor of significant importance.

Cabała (1996, 2001) described different microscopic cerussite appearances and found it difficult to explain the anomaly that cerussite and galena often coexist together with non-oxidized iron and zinc sulphides. Assuming that cerussite is formed through the oxidation of galena, which is confirmed by microscopic observations (Cabała 1996; the present paper), this relationship is surprising. The surface of galena is quickly covered with its oxidation products inhibiting further oxidation (galena armouring), whereas such a cover does not form on sphalerite and iron sulphides (Źabiński 1960; Hitzman et al. 2003; Reichert, Borg 2008). Thus, the iron and zinc sulphides should be substantially more oxidized. However, in the investigated ores, Cabała (1996, 2001) and the present authors record quite the opposite. In this paper, the authors propose an explanation based on the galvanic coupling process for these features.

2. Materials and methods of investigation

Several samples (e.g. Fig. 1 and 2) were taken from nests of the sulphide part of the ore in the Pomorzany Mine in the Upper Silesian Zn-Pb deposits. Only slightly-oxidized samples were investigated because, in highly-oxidized samples, the genetic relationship between galena and lead oxide minerals is usually obscured.

Samples were initially examined under a polarizing microscope, using reflected and transmitted light. The chemical composition of particular minerals identified optically was examined by a field-emission SEM (HITACHI S-4700) equipped with a BSE (YAG) detector and EDS analyser (NORAN Vantage). A FTIR spectrometer (BIO-RAD FTS 135) was used to confirm the presence of cerussite and anglesite. Samples corresponding to prepared thin sections were drilled with a micro-drill and 0.8 mg of powders recovered were mixed with 200 mg of KBr in preparing pressed pellets.

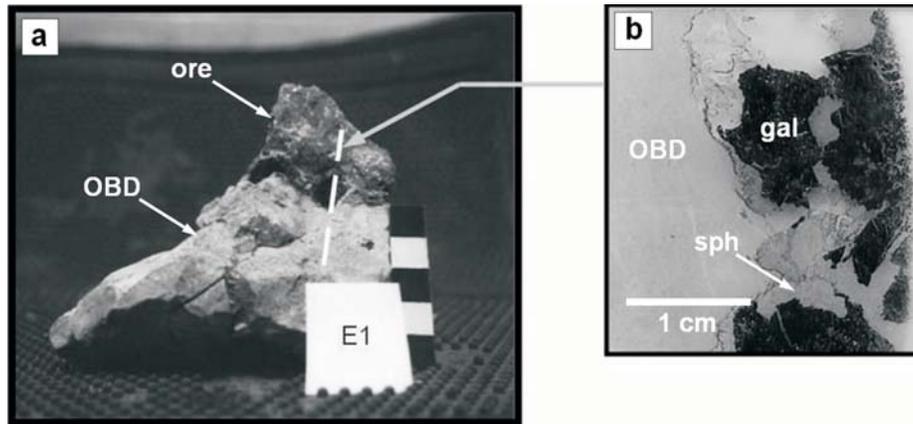


Fig. 1. (a) Sample taken from the boundary between the OBD and the ore body (scale – 5 cm).
 (b) Thin section along direction highlighted.
 Symbols: gal – galena, sph – sphalerite, OBD – the Ore Bearing Dolomite

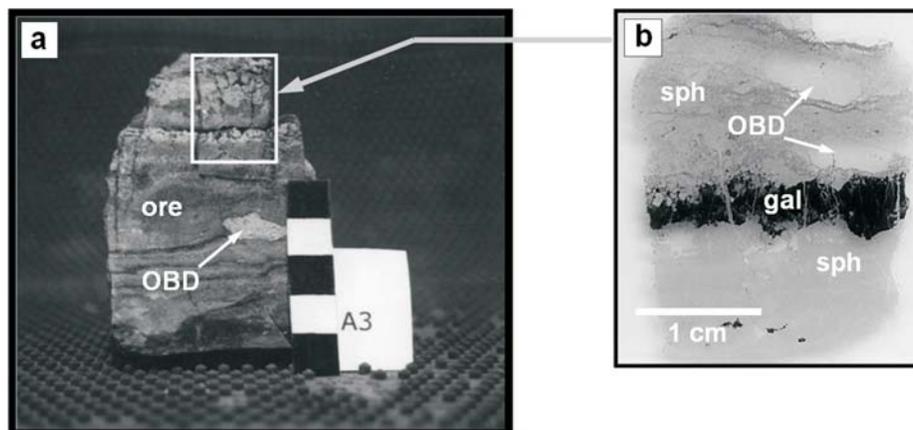


Fig. 2. (a) Sample taken from the boundary between the OBD and the ore body (scale – 5 cm).
 (b) Thin section prepared parallel to the cut.
 Symbols: gal – galena, sph – sphalerite, OBD – the Ore Bearing Dolomite

3. Results

The most important oxidized Pb mineral in the samples is cerussite. Anglesite is also present but in much smaller amounts and only in specific microenvironments. Two types of cerussite occurrence in galena have been recorded:

Type 1 In-situ galena replacement:

- a – microcrystalline cerussite replacing galena crystals along their cleavages, locally accompanied by anglesite,
- b – cerussite replacing galena crystals massively from their edges.

Type 2 MacrocrySTALLINE cerussite filling fractures and cavities.

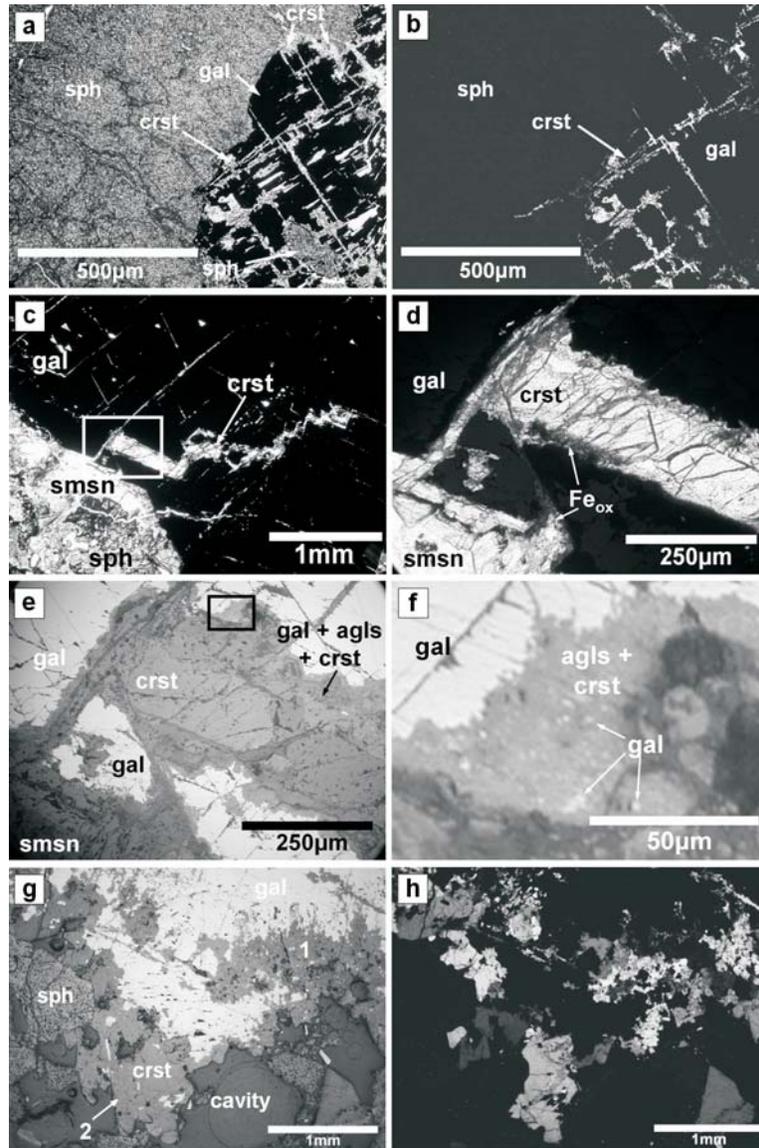


Fig. 3. Photomicrographs of different types of cerussite. (a) and (b) Cerussite Type 1a. Veinlets of cerussite replacing galena along sulphide cleavages. Note cerussite veinlets continuing into sphalerite (upper right). (c) and (d) Infilled fracture in galena at the contact with partially oxidized sphalerite. Dilated cleavage fracture in galena filled with Type 2 cerussite. Smithsonite locally replaces sphalerite. Note local concentrations of Fe (hydroxy)oxides (white rectangle locates images d and e). (e) and (f) Aggregates of galena, cerussite and anglesite, in contact with cerussite and smithsonite, at the galena crystal margins. Coarse-crystalline cerussite (Type 2) fills dilated fracture (black rectangle in e locates image f). (g) and (h) Cerussite of Type 1b. Galena replaced by cerussite. 1 – fine-crystalline cerussite, 2 – coarse-crystalline cerussite. Type of photographs: (a) transmitted light, 1N, (b) transmitted light, XN, (c) transmitted light, 1N, (d) transmitted light, 1N, (e) reflected light, 1N, (f) reflected light, 1N, (g) reflected light, 1N, (h) transmitted light, XN. Symbols: agls – anglesite, crst – cerussite, Fe_{ox} – iron (hydroxy)oxides, gal – galena, smsn – smithsonite, sph – sphalerite

Type 1a cerussite, occurring as very fine crystalline aggregates with individual crystallites of several μm , replaces galena crystals along their cleavages (Fig. 3a, b). The intensity of this process varies. In some cases, thin irregular veinlets of cerussite emanating from galena crystals penetrate sphalerite for distances of several μm to even hundreds of μm (Fig. 3a, b). Very fine crystalline aggregates of cerussite mixed with galena and anglesite may be present on the boundary between Type 2 cerussite and galena (Fig. 3e, f). Due to the presence of finely-dispersed galena remnants, these aggregates are non-transparent in transmitted light. Similar aggregates occur on the edges of galena at its contact with cavities and with other minerals, e.g. sphalerite or smithsonite. In some cases, local concentrations of Fe-(hydroxy)oxides also occur at the boundaries of this type of cerussite (Fig. 3d).

Type 1b cerussite replacing galena massively from its edges occurs typically close to cavities (Fig. 3g, h). It occurs in two different forms, fine-crystalline ($< 10 \mu\text{m}$ in size) and coarse-crystalline ($> 200 \mu\text{m}$). Galena remnants occur in both although they are more common in the fine-crystalline form.

Type 2 cerussite infilling open fractures in galena occurs as coarsely-crystalline aggregates (Fig. 3c, d, e) in which individual crystals may reach 100–200 μm in size. Typically, there are no galena remnants inside these aggregates.

Characteristically, oxidized galena commonly coexists with non-oxidized sphalerite. This relationship is observed only if these two sulphides are in direct contact (e.g. Fig. 3a, b). In such cases, a typical superficial cover of the galena-oxidation products as described by Źabiński (1960) is not formed. In the absence of such direct contacts, sphalerite is commonly oxidized and galena is usually cut or covered by cerussite (e.g. Fig. 3g).

4. Discussion

4.1. Mechanism of oxidation of galena in direct contact with sphalerite

Co-occurrences (intergrowths) of non-altered sphalerite and oxidized galena (Fig. 3a, b) can be evaluated in the terms of galvanic coupling between two sulphides. A coupling model was also used by Źabiński (1960) to explain the increased rate of Zn and Pb sulphide oxidation in a coupling with iron sulphides. However, to the best of our knowledge, such a model has not previously been used to explain the fact that different sulphides might not have been oxidized in comparison to others in the Zn-Pb deposits of Upper Silesia.

Galvanic coupling can be described in terms of the rest potentials of particular electrodes. Such an electrode consists of sulphide mineral surrounded by a solution. The potentials are measured by comparison with a standard hydrogen electrode just after putting them into the solution (Sato 1960). The reasons for this are that the potential of sulphide electrodes changes with time and that it is difficult to reach equilibrium, even after several weeks in some cases (Sato 1960). Solutions that have been used to calculate rest potentials vary among different authors because they have tried to obtain potentials that compare most closely to different environments, e.g. of different pHs. However, the comparison of rest potentials measured by any given author can be reliable because each used the same solution for each electrode (Table 1).

TABLE 1

Rest potentials obtained by different authors in a coupling with hydrogen electrode [V]

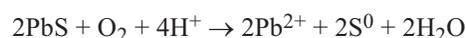
	Won (1967)	Karavaiko (1985)	da Silva et al. (2003)
Pyrite	–	0.60	–
Sphalerite	~0.2	0.23	0.372
Galena	~0.1	–	0.325

The higher the potential of an electrode, the less susceptible to oxidation the electrode is. If a coupling is formed, the electrode with a lower rest potential is oxidized while that with the higher rest potential is passivated. Passivation means that the electrode will remain unchanged during the oxidation of the other. Thus, on the basis of the measured rest potentials of given sulphides, the course of oxidation in couplings made of these minerals can be predicted. For example, when sphalerite is in direct contact with galena, only the latter will substantially oxidize because it has a lower rest potential. On the other hand, if sphalerite is in a coupling with pyrite, the iron sulphide will not oxidize whereas the sphalerite will be heavily oxidized.

Thus, if sphalerite is in direct contact with galena, galvanic couplings should be considered rather than the relative solubility and stability of particular oxide minerals of lead and zinc. In such an assemblage, the following reactions are considered to occur on particular sulphides:



In the coupling, the following reaction occurs (Fig. 4a):



The difference between potentials in the coupling consequently becomes less with the progress of reaction on particular electrodes; therefore, the reaction should stop after some time. Moreover, if there is no solution with oxidants around the sulphides, the reaction will not progress either.

Galena which is not in direct contact with other sulphides (Fig. 4b) will be covered by its oxidized minerals after some time and further oxidation will be blocked as a result (Fig. 4c). This process, widely described in the literature, is termed galena armouring (Reichert, Borg 2008). If sphalerite loses direct contact with galena, substantial amounts of oxidized zinc minerals should form while galena will remain only slightly changed along its edges. After a period of time, sphalerite and other sulphides (e.g. pyrite, marcasite) can be fully replaced by their oxidation products while galena, remaining covered by its oxidized minerals, will be only partially oxidized (Fig. 4c).

The proposed model could explain the substantial oxidation of galena coexisting with almost unchanged pyrite and sphalerite as noted above (see Cabala 1996, 2001). If sulphide minerals in ore bodies are intergrown, oxidation should be governed by the galvanic properties of the

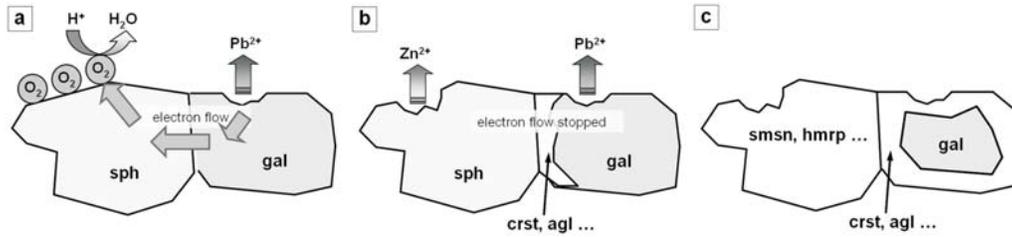


Fig. 4. Sequence of steps leading to the formation of different mineral assemblages.
 (a) Galvanic coupling made between galena and sphalerite. (b) Decay of galvanic coupling.
 (c) Further oxidation governed by solubility and relative stability of Zn and Pb oxide minerals.
 agl – anglesite, gal – galena, hmrp – hemimorphite, smsn – smithsonite, sph – sphalerite

relevant ore minerals. On the other hand, where the ore involves sulphides dispersed in carbonates, oxidation is thought to be governed by other factors such as: a) the susceptibility of sulphides to oxidizing agents, b) the relative solubilities and macroscopic properties (e.g. surface areas) of the oxidized minerals, c) the affinity of bacteria towards the surface of different sulphides and their resistance to toxic elements liberated from sulphides undergoing oxidation.

4.2. The role of ferric (III) iron in the oxidation of galena

The substantial quantities of iron (hydroxy)oxides seen around Type 1a aggregates (Fig. 3d and 5a) suggest that iron could influence galena oxidation and the subsequent formation of oxidized lead minerals. This hypothesis is supported by the observation that apart from oxygen, ferric ions have been found to be important oxidation agents (Herbert 1999) as follows:



At a pH of less than 3.5, iron stays in solution whereas, at a higher pH which is typical for carbonates, Fe^{3+} hydrolyses and precipitates as $\text{Fe}(\text{OH})_3$ which subsequently transforms into iron oxides/hydroxides. The ferric ions are no longer in solution and therefore cannot serve as oxidizing agents. However, locally, the pH may be lowered below 3.5 where FeS_2 oxidizes along with the liberation of hydrogen ions. Thus, in the vicinity of iron sulphides being oxidized, the ferric ion can still be an important oxidizing agent. Ferrous ions that are produced in reaction (1) may be further oxidized either inorganically by O_2 or by bacteria (e.g. Espejo et al. 1988; Jensen, Webb 1995): $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ and galena oxidation continue. There are extensive experimental and environmental studies on the oxidation of ores by bacteria confirming their role (e.g. Herbert 1999; Tributsch 2001).

In the investigated samples, ferric ions must have come from the oxidation of iron sulphides close by because of their restricted mobility in carbonates. Therefore, the pH might have been only locally and temporarily lowered (Fig. 5b). Iron oxides/hydroxides must have precipitated during and/or after the formation of Type 1a cerussite but before the Type 2 variety. This observation suggests that pH changes linked to iron oxide/hydroxide formation were rather local and temporal.

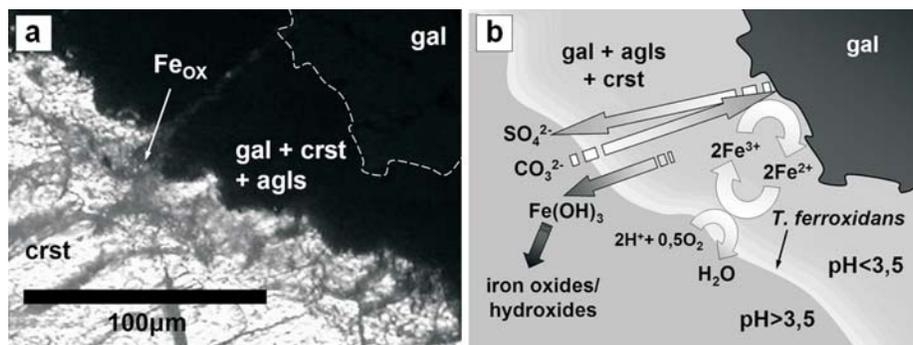
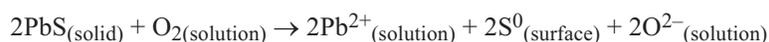


Fig. 5. (a) Contact between aggregate of anglesite, cerussite and galena with coarse-crystalline cerussite. Ferric (hydro)oxides are visible (transmitted light, 1N). (b) Schematic representation of galena oxidation involving bacteria and ferric/ferrous ions. Two possible microenvironments of different pH are marked. Inside Type 1a aggregate, carbonate ions are expected to diffuse towards galena surface whilst a proportion of sulphate ions diffuse in the opposite direction. Symbols: agls – anglesite, crst – cerussite, Fe_{ox} – iron (hydroxy)oxides, gal – galena

4.3. Geochemical parameters of cerussite and anglesite formation

Based on the scarcity of anglesite among the products of galena oxidation, Kuźniar (1928, 1932) proposed the direct oxidation of galena to cerussite without any intermediate sulphate step. Żabiński (1960) considered this hypothesis to be improbable because the reaction $2PbS + Ca(HCO_3)_2 \rightarrow 2PbCO_3 + Ca(SH)_2$ seemed unlikely. However, in the light of recent improvements in the understanding of sulphide oxidation, a direct formation of cerussite from galena should be re-examined.

The initial step of galena oxidation involves the liberation of Pb^{2+} from the sulphide surface as is confirmed by elevated amounts of sulphur species on the galena surface after slight oxidation (Buckley, Woods 1996). This reaction can be described as follows (after Sato 1960):



As the lead ions move into the solution, further oxidation of the sulphur forms thiosulphate $S_2O_3^{2-}$, $S_4O_6^{2-}$, sulphite SO_3^{2-} and, finally, sulphates SO_4^{2-} that also go into solution (Herbert 1999). Thus, the galena oxidation can be viewed as two separate processes. The formation of lead carbonate or sulphate depends on the relative mineral solubilities which reflect SO_4^{2-} activity, CO_2 partial pressures and pH (Fig. 6, after Reichert, Borg 2008).

CO_2 partial pressures vary in ore deposits as there are several known sources of carbon dioxide: atmosphere, biological processes and carbonate host rocks (Reichert, Borg 2008). Gaseous CO_2 equilibrates with dissolved CO_2 which then forms carbonic acid (H_2CO_3) which, in turn, dissociates to CO_3^{2-} which reacts with lead ions to form cerussite ($Pb^{2+} + CO_3^{2-} \rightarrow PbCO_3$). The activity of SO_4^{2-} may also depend on other factors, e.g. the relationship between the rate of sulphide oxidation and the removal of oxidation products and the supply of sulphate ions from the oxidation of other sulphides nearby.

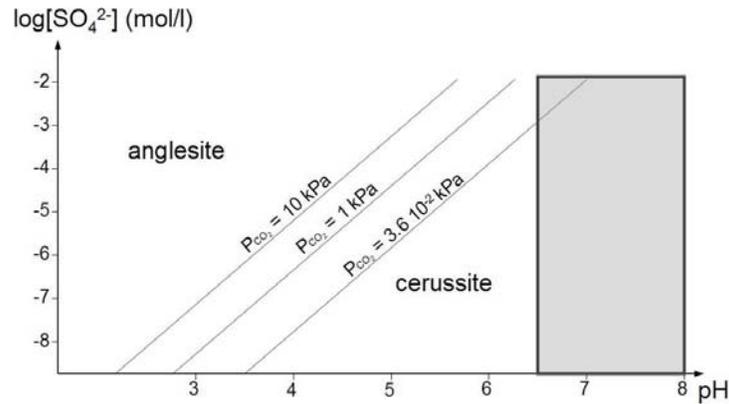


Fig. 6. Components that restrain solubility of Pb in solutions of different pH, different CO₂(g) partial pressures and different amounts of SO₄²⁻ represented as activity (mol/dm³). Modified after Reichert, Borg (2008). Grey rectangle represents pH conditions typical of a carbonate environment

In limestone/dolostone environments, some constraints on the activity of H⁺ ions can be assumed; the pH value is typically ca 7–8 (e.g. Al-Ruwaih 2001). Galena oxidation (PbS + 2O₂ → Pb²⁺ + SO₄²⁻) does not lead to solution acidification. In this case, the hydrolysis of water can be ignored as water hydrolyses (Pb²⁺ + H₂O ↔ PbOH⁺ + H⁺) only slightly in the presence of lead ions (Cotton et al. 2002). Thus, pH does not change significantly as lead sulphide oxidizes. The influence of zinc sulphide oxidation on pH is also negligible. In that pH range, the activity of CO₃²⁻ is only a slight influence on the stability of cerussite; lead carbonate is preferentially formed (Fig. 6).

On the other hand, the Upper Silesian Zn-Pb deposits are rich in iron sulphides (e.g. Kucha 2003). Pyrite and marcasite liberate hydrogen ions during oxidation (FeS₂ + H₂O + 7/2 O₂ → Fe²⁺ + 2 SO₄²⁻ + 2 H⁺), acidifying surrounding solutions. The pH can drop to as little as 1, as Źabiński (1964) found in the pyrite-rich area of the Bolesław Quarry. However, the carbonates associated with the Upper Silesian Zn-Pb deposits have the potential to neutralise these acids:



The pH can be buffered to ca 6.5–7.0 (e.g. Dold 2005). Sulphate ions reacting with limestone cause gypsum precipitation and, thereby, the lowering of SO₄²⁻ activity. (Reichert, Borg 2008). The direct formation of anglesite is only possible when the activity of SO₄²⁻ ions is relatively high and the pH low (Fig. 6). The weathering of Pb sulphide does not cause such an acidification. However, in the micro-environments around oxidized iron sulphides, falling pH may facilitate anglesite formation. The anglesite may then be replaced by cerussite (PbSO₄ + CO₃²⁻ → PbCO₃ + SO₄²⁻) when, with pH increasing and SO₄²⁻ activity decreasing, cerussite becomes more stable mineral (Sangameshwar, Barnes 1983).

4.4. Formation of oxidized lead minerals

Detailed thin-section investigations indicate that the direct oxidation of galena to lead carbonate is the most probable explanation for many of the observed cerussite occurrences.

In Type 1a, only lead carbonate, without even traces of anglesite, infills cleavage fractures in galena (Fig. 3a, b). The microcrystalline character of this form indicates that no recrystallization of an earlier oxidized mineral occurred. Therefore, cerussite must have been the primary filling of the fractures.

In Type 1b, the relationship with the primary sulphide is unclear as the cerussite could have recrystallized. The larger sizes and euhedral shapes of crystals in contact with finely-crystalline cerussite suggest so (Fig. 3g, h). The galena remnants indicate that this cerussite formed during the replacement of primary sulphide. The fact that these massive replacements of galena contain no anglesite, even in small galena pockets, indicates that direct oxidation of galena to lead carbonate is also most probable in this case.

In the coarsely-crystalline Type 2 cerussite, the genetic relationship with primary lead sulphide is difficult to determine. The absence of galena remnants as in Type 1 and sharp boundaries suggest that this cerussite crystallized directly from solution.

A more complex situation arises where Type 1a cerussite is in contact with Type 2. In these cases, two separate steps of lead-oxide formation can be deduced (Fig. 7). It is suggested that the first step of cerussite formation (Type 1a) took place as the galena was fractured (Fig. 7.1),

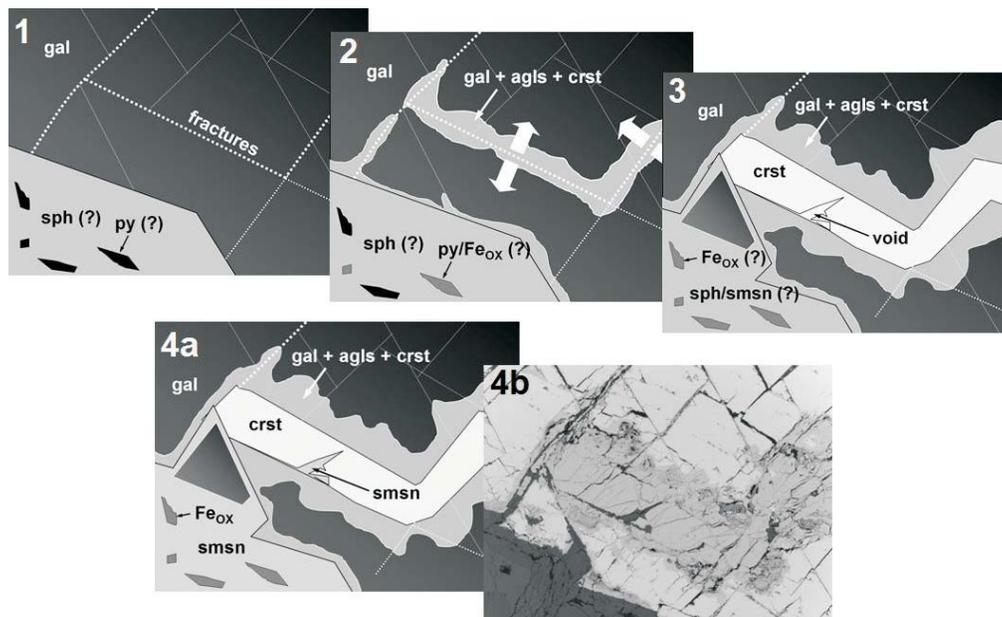


Fig. 7. Stages leading to the formation of Type 1a cerussite at the contact with Type 2 cerussite. (1) Formation of fractures. (2) Formation of aggregates of anglesite, cerussite with remnants of galena, fracture expansion, oxidation of neighbouring pyrite. (3) Infilling of open fractures by coarse crystalline cerussite. (4a) Smithsonite replaces sphalerite(?) and infills voids. (4b) Final stage as observed in samples, SEM-BSE image. Symbols: agls – anglesite, crst – cerussite, Fe_{ox} – iron (hydroxy)oxides, gal – galena, py – pyrite, smsn – smithsonite, sph – sphalerite

but before the fractures were fully opened (Fig. 7.2). The presence of anglesite within Type 1a leads to the conclusion that lead sulphate precipitated either because the SO_4^{2-} activity was adequately high or the pH low enough. The latter possibility is more probable as, in the vicinity, iron sulphides were undergoing oxidation, what is confirmed by the presence of iron (hydro)oxides close to, and on, the Type 1a aggregates (Fig. 3d), and of Fe-sulphides remnants in some of these oxides. Moreover, oxidized iron sulphides can also provide additional sulphate ions to further facilitate sulphate formation. These textures confirm earlier observations by Żabiński (1960) who found anglesite in the environs of iron sulphides. After the fractures opened, the second stage began – some of the opened fractures were filled with the coarse crystalline Type 2 cerussite (Fig. 7.3). Afterwards or concurrently, nearby sphalerite might have undergone oxidation and oxidized zinc minerals formed as shown in Fig. 7.4a, b.

5. Conclusions

The coexistence of substantially oxidized galena and non-altered sphalerite can be understood when the galvanic couplings between the two sulphides are considered. Such a coupling only occurs when the two sulphides are in direct contact. When they are, galena will undergo preferential oxidation. When direct contact is lacking or is blocked by oxidation products, the galvanic coupling also decays. In such cases, sulphide oxidation is governed by other factors, e.g. the stability of sulphides and their respective oxidized minerals, the solubility of metal ions or the affinities of bacteria with sulphide surfaces.

In carbonate environments, lead sulphide can be easily oxidized directly to cerussite. A mechanism involving the oxidation of galena through an intermediate sulphate should also be considered in discussions on the genesis of oxidized lead minerals. Where FeS_2 undergoes oxidation in the vicinity of galena, lower pH and the presence of ferric ions become important oxidation agents leading to anglesite formation.

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