How carbonate dissolution facilitates sediment-hosted Zn-Pb mineralization

Weihua Liu*, Sam C. Spinks, Matthew Glenn, Colin MacRae and Mark A. Pearce
CSIRO Mineral Resources, Clayton, Victoria 3168, Australia

ABSTRACT

Most of the world’s Zn and Pb is extracted from sediment-hosted Zn-Pb deposits. The Zn-Pb deposits hosted in carbonate rocks are hypothesized to form by mixing of acidic metal-bearing brines with reduced sulfur-bearing fluids while dissolving sedimentary carbonate. To test the role of carbonate in this process, we conducted hydrothermal experiments simulating ore formation by reacting Zn + Pb + Ba-bearing brines with H₂S and SO₄²⁻ produced by native sulfur, with and without carbonate minerals (calcite or dolomite crystals), at 200 °C and water-saturated pressure. Sphalerite, galena, and barite (or anhydrite) crystals formed only when carbonate was present in the experiment, accompanied by carbonate dissolution. The textures of sphalerite clusters are similar to those observed in ancient and modern hydrothermal deposits. Thermodynamic modeling at 150 °C and 250 °C demonstrates that mixing of metal-rich brines and H₂S causes most of the Zn in solution to precipitate as sphalerite only when carbonate dissolution occurs to buffer the pH, consistent with the experimental observations. The need for a pH buffer increases with increasing temperature, and different pH buffers may play a role for different deposit types. We propose that carbonate-buffered fluid mixing is a critical process for forming post-sedimentary Zn ± Pb ± Ba deposits in sedimentary carbonate rocks.

INTRODUCTION

Sediment-hosted Zn-Pb deposits, such as Mississippi Valley-type (MVT), Irish-type, and sedimentary exhalative (SEDEX) (e.g., Large et al., 2005; Leach et al., 2005; Wilkinson, 2014), are the most important Zn and Pb resources globally. Different ore-genesis models have been proposed for different classes of these deposits: Large et al. (1998, 2005) proposed a syn-sedimentary–exhalative origin for the giant HYC deposits (McArthur River, Australia), while Perkins and Bell (1998) and Spinks et al. (2021) identified key features of post-sedimentary mineralization and carbonate replacement by metal sulfide minerals. A carbonate replacement model is proposed for the Irish-type (e.g., Wilkinson, 2014; Wilkinson and Hitzman, 2015) and MVT-type deposits (e.g., Corbella et al., 2004). Kelley et al. (2004) also argued that sphalerite and barite in the giant Anarraq Zn deposit in the Red Dog district, Alaska (USA), also formed via carbonate replacement.

Ore-genesis models for Zn-Pb deposits in sedimentary carbonate rocks have been proposed for many decades (e.g., Jackson and Beales, 1967; Anderson, 1975, Anderson and Garven, 1987; Cooke et al., 2000) and have been used to explain field observations (e.g., Leach et al., 2005; Wilkinson, 2014) and as a basis for reactive transport modeling (e.g., Garven et al., 1999; Corbella et al., 2004); however, experimental studies have mainly focused on the solubility of Zn-Pb sulfide minerals and stability of aqueous Zn and Pb complexes (e.g., Ruaya and Seward, 1986; Bourcier and Barnes, 1987; Barrett and Anderson, 1988; Tagtrog and Seward, 2010; Mei et al., 2015, 2016; Etschmann et al., 2018, 2019; Sanz-Robinson and Williams-Jones, 2019). Recently, room-temperature titration experiments by Zhang et al. (2019a, 2019b) suggested that hydrolysis is the key factor for Zn-Pb sulfide precipitation, and Zhang et al. (2021) emphasized that pH change is the primary mechanism for Zn-Pb sulfide deposition up to 150 °C; however, the role of carbonate replacement has not yet been closely examined experimentally.

Our study elucidates the chemical processes that control the formation of Zn-Pb deposits in carbonate rocks using experimental and thermodynamic modeling techniques, focusing on the role of carbonate in the deposition of Zn-Pb sulfide minerals from hydrothermal fluids.

METHODS

Sodium-chloride brines with different pH and concentrations of Zn, Pb, Ba, Ca, and Mg were reacted with native sulfur with and without carbonate (calcite or dolomite) crystals at 200 °C (for solution composition, see Table S1 in the Supplemental Material). We chose native sulfur (S) because it disproportionates to H₂S and SO₄²⁻ in water at elevated temperatures (Ellis and Giggenbach, 1971), providing reduced sulfur and also conveniently buffering the redox state of the solution near the sulfate-sulfide boundary. The solid reaction products were characterized using scanning electron microscopy (SEM), electron probe microanalysis (EPMA), electron backscatter diffraction (EBSD), and cathodoluminescence (CL; e.g., MacRae et al., 2013). We investigated experimental reactions and fluid mixing of metal-bearing brine with H₂S using thermodynamic modeling. Details of the experimental and modeling methods are described in the Supplemental Material.

RESULTS

The backscattered electron (BSE), EPMA, CL, and EBSD images of solid reaction products for representative samples are shown in Figures 1–3. Solutions of Zn²⁺ + NaCl reacted with sulfur, calcite (samples R5-3, R5-4; Figs. 1A and 1B), and dolomite (sample R3; Fig. 1C) to produce sphalerite and anhydrite with coincident dissolution of carbonate. The sphalerite grew in spheroidal clusters tens of hundreds of micrometers in diameter (Fig. 1A), with angular crystals as large as 2 µm in size (Fig. 1B).

*E-mail: weihua.liu@csiro.au

© 2021 The Authors. Gold Open Access: This paper is published under the terms of the CC-BY license.

1 Supplemental Material. Details of the experiments, analysis, and modeling. Please visit https://doi.org/10.1130/GEOL.S.14903352 to access the supplemental material, and contact editing@geosociety.org with any questions.
The globular sphalerite on 03 November 2021 by guest downloaded from http://pubs.geoscienceworld.org/gsa/geology/article-pdf/49/11/1363/5437492/g49056.1.pdf

Some galena and barite crystals dissolved and barite and sphalerite clusters (Fig. 2C–E) Mg-calcite and sphalerite forming a shell around a partially dissolved calcite crystal in sample R11-1. (F) Growth of sphalerite clusters and galena on anhydrite crystals. For sample compositions, see Table S1 (see footnote 1). anh—anhdyrite; sp—sphalerite; cal—calcite; Mg-cal—magnesia calcite; ga—galena.

Solutions of Zn$^{2+}$ + Mg$^{2+}$ + Ca$^{2+}$ + NaCl reacted with S and calcite (sample R11-1) to produce sphalerite and anhydrite as well as Mg-calcite crystals with partial dissolution of the calcite. The Mg-calcite and sphalerite crystals grew in a shell around the dissolving calcite crystal (Figs. 1D and 1E). Sphalerite clusters and galena also grew on the anhydrite crystals when Pb$^{2+}$ was added (Fig. 1F). Adding Ba$^{2+}$ to the initial solution caused barite formation instead of anhydrite, with sphalerite clusters growing on larger, angular barite crystals (sample R16-1; Fig. 2A).

Solutions of Zn$^{2+}$ + Ba$^{2+}$ + Pb$^{2+}$ + Mg$^{2+}$ + Ca$^{2+}$ + NaCl, when reacted with S and calcite (samples R12-5 and R17-1) and dolomite (sample R17-3) also caused carbonate dissolution and sulfide and barite precipitation. Some barite redissolved as the sphalerite clusters grew on and around the crystals (Figs. 2A and 2E). Cubic and octahedral galena crystals grew around the barite and sphalerite crystals (Figs. 2C and 2F). Some galena and barite crystals dissolved and seeded the growth of sphalerite (Figs. 2C–2E and 3).

Close examination of the sphalerite clusters showed fine structural zonation from the center of the cluster to the rim, as shown in Figures 3A–3F. Major mineral phases identified in these figures are identified using EPMA (Fig. 3A), quantitative spot microanalysis (Table S2; spots marked in Figs. 3A and 3B), and EBSD (Fig. 3F). The globular sphalerite clusters showed ring-like growth zones (BSE in Fig. 3B; CL in Fig. 3C). These zones contain nanocrystals of a globular, equiaxed-type morphology with nanoporosity (Figs. 3D and 3E). The coarse crystals around the rim of the cluster showed the strongest CL emission. By contrast, the growth zones in the center of the clusters showed some CL emission indicating a crystalline phase but at a reduced level, suggesting that the crystal size is extremely small (<~100 nm). The EBSD phase map (Fig. 3F) shows that sphalerite clusters have diffraction patterns only in the coarser crystals around the rim of the clusters.

The experimental products of a non-acidified solution (sample R11-1; Table S1) are like the acidified ones. Comparison experiments with identical starting compositions of metal-bearing brines were reacted with S but did not contain carbonates. No Zn or Pb sulfide precipitation was observed in those experiments, and the inductively coupled plasma–optical emission spectrometry (ICP-OES) analysis showed most of the Zn stayed in solution (Table S4). The solution also turned more acidic (pH = 0.6–1) than the initial solution (Table S1).

Thermodynamic modeling of the reaction products for the experimental systems is generally consistent with the observed mineral assemblages, pH, and composition of the resultant solutions (Table S4). An example (sample R12-5) is demonstrated in the Supplemental Material (Fig. S1).

DISCUSSION AND CONCLUSION

Ore Textures

The globular textures of the sphalerite clusters observed in our experiments are very similar to those observed in seafloor hydrothermal systems (Hu et al., 2019; Glenn et al., 2020) as well as the colloform textures observed in MVT ores (Roedder, 1968; Leach et al., 2005, 2010) and Irish-type ores (Hitzman et al., 2002). In those ores, there are multiple depositional layers and more replacement features than in our experimental products, which most likely indicates multiple episodes of carbonate dissolution and ore deposition within a compact subsurface environment. While sulfide deposition occurred in our experiments in a closed and spatially unrestricted system, complexity in mineralogy, grain size, and mineral chemistry still develops (Figs. 1–3).
Role of Carbonates

Our experiments demonstrate that the carbonates play a key role in facilitating sphalerite and galena precipitation from the mixture of Zn-Pb-bearing brine and H$_2$S. The role of carbonate is to sequester H$^+$ (increase solution pH) through carbonate dissolution to sustain sphalerite and galena precipitation:

\[
\text{ZnCl}_4^{2-} + 2\text{H}_2\text{S}(	ext{aq}) = \text{ZnS}_2\text{sphalerite} + 4\text{Cl}^{-} + 2\text{H}^+ \quad (1)
\]

\[
\text{PbCl}_4^{2-} + 2\text{H}_2\text{S}(	ext{aq}) = \text{PbS}_2\text{galena} + 3\text{Cl}^{-} + 2\text{H}^+ \quad (2)
\]

\[
\text{CaCO}_3\text{calcite} + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^- \quad (3)
\]

Different carbonate species (dolomite or calcite) do not affect this fundamental process because Zn-Pb ± Ba mineral assemblages always formed in our experiments with similar features, which indicates that the role of carbonate is a simple process of dissolution to take up H$^+$ produced by sulfide precipitation (Equations 1 and 2). The equilibrium constants (logK) of Zn-Pb sulfide deposition (Equations 1 and 2) notably decrease with increasing temperatures (Table S3; logK values were calculated based on Mei et al. [2015] and Etschmann et al. [2018]): e.g., from 5.3 at 25 °C to −3.5 at 250 °C for Equation 1, and from 6.0 at 25 °C to −2.4 at 250 °C for Equation 2. This trend indicates that although the sphalerite may precipitate by reacting with reduced sulfur without carbonate at room temperature (Zhang et al., 2019a), the need for a pH buffer to enhance Zn-Pb sulfide precipitation (Equations 1 and 2) increases vastly with increasing temperatures.

To further test the role of carbonate in the deposition of Zn-Pb sulfide minerals, we modeled fluid mixing of a Zn-Pb-Ba-bearing, sulfur-poor brine (1000 ppm Zn, 200 ppm Pb, and 500 ppm Ba) with H$_2$S at two pH values of 2 and 5.5, and with and without dolomite, at 150 °C and 250 °C (Figs. 4A–4D). These two temperatures were chosen to be the same as in the log f$_{O_2}$-pH (f$_{O_2}$—oxygen fugacity) diagrams of Cooke et al. (2000). See the Supplemental Material for the choice of ore fluid composition, thermodynamic models, and result data (Table S5).

All the mixing reactions that start from point 1 and point 2 in the sulfate-stable region proceed to the sulfate-stable area (Figs. 4B and 4D). Without carbonate, the reaction paths (marked red) reach acidic pH (point 3 in Figs. 4B and 4D) independent of the starting pH of 2 or 5.5 after 0.2 m H$_2$S being reacted. Figures 4A and 4C show that most of the Zn and Ba remain in solution with the final concentration increasing with temperature. At 150 °C, 88% of Zn, 99% of Ba, and 15% of Pb remain in solution when the starting pH is 2; and 65% of Zn, 99% of Ba, and 11% of Pb remain in solution when the starting pH is 5.5 (Fig. 4A). At 250 °C and starting pH of 2, 99%...
of Zn, Pb, and Ba remain in solution, and when starting pH is 5.5, 99% of Zn and Ba and 39% of Pb remain in solution (Fig. 4C).

In contrast, when carbonate is present, most of the Zn and Pb in solution precipitates in all scenarios (Fig. 4, blue reaction paths toward point 4), with the final concentrations of 0.01–0.5 ppm Zn and 0.2–0.9 ppm Pb left in solution. At 250 °C, a significant concentration of Ba stays in solution due to a lack of sulfate when the reaction path proceeds toward reduced conditions. The reaction paths from point 3 to point 4 in Figures 4B and 4D indicate that under reducing conditions, carbonate also enhances metal-sulfide precipitation.

The modeling results show that a simple mixing of Zn-bearing (~1000 ppm Zn) brines with H₂S of as much as 0.2 m under acidic or near-neutral pH conditions would not effectively precipitate sphalerite at 150–250 °C. This is because the partial precipitation of sphalerite decreases the fluid pH and stops the ore deposition due to the high solubility of sphalerite in acid solutions, as shown in Cooke et al. (2000) and Spinks et al. (2021). The much higher degree of galena precipitation in the carbonate-free experiments is due to the lower solubility of galena compared to sphalerite (e.g., Etschmann et al., 2018). Thus, galena deposition is likely to be less dependent on a pH buffer than sphalerite. Also, metal hydrolysis (Zhang et al., 2019a, 2019b) is unnecessary because reaction paths are wholly within the predominant field of Zn and Pb chloride complexes and sulfate minerals (Figs. 4B and 4D).

Implications for Ore Formation

Our results verify the long-standing hypothesis of Zn-Pb ore-formation via fluid-mixing of metal-bearing brine and reduced sulfur by Jackson and Beales (1967) and Anderson (1975). Further, we have demonstrated how sphalerite, galena, and barite form from the interaction of a single metal-rich ore fluid with reduced sulfur when facilitated by the dissolution of carbonate buffering the pH of the solution.

There are limitations in applying our experimental and modeling results to ore deposits. Firstly, at high ratios of H₂S/metal concentrations and/or at low temperatures (ambient to ~100 °C) where solubility of sphalerite is low, the precipitation of metal-sulfide minerals without a carbonate buffer is likely. The logK values for sphalerite deposition (Equation 1) indicate this, and it has been observed by Zhang et al. (2019a, 2019b). Secondly, the acidic fluids generated by sulfide deposition may be continually replaced by newly arriving ore fluid, negating the need for a pH buffer. Thirdly, this study does not consider other chemical processes for ore formation (e.g., cooling, fluid mixing with pore water, and ore fluids reacting with organic matter) that can operate in different geological settings where carbonate rock is absent (e.g., some sandstone-hosted Pb-Zn deposits), or that several factors could play in concert to cause ore deposition. Nevertheless, carbonate-buffered fluid mixing is likely a critical mechanism for the formation of post-sedimentary Zn-Pb ± Ba deposits in carbonate rocks and in carbonate-hosted polymetallic sulfide deposits (e.g., Knorsch et al., 2020). These findings demonstrate the importance of the presence of carbonate in sediment-hosted base-metal mineral systems, showing that accounting for carbonate should be an essential part of any mineral systems-based exploration targeting approach.

ACKNOWLEDGMENTS

Research funding is from the Australian Commonwealth Scientific and Industrial Research Organisation (CSIRO) and the Australian Research Council (grant LE130100087). We thank S. Schmid and C. Siegel for their helpful comments. Special thanks to J. Menuge, two anonymous reviewers, and editor G. Dickens for their constructive reviews.
REFERENCES CITED

Anderson, G.M., 1975, Precipitation of Mississippi Valley–type ores: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 70, p. 937–942, https://doi.org/10.2113/gsecongeo.70.5.937.

Anderson, G.M., and Garven, G., 1987, Sulfate–sulfide-carbonate associations in Mississippi Valley–type lead–zinc deposits: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 82, p. 482–488, https://doi.org/10.2113/gsecongeo.82.2.482.

Barrett, T.J., and Anderson, G.M., 1988, The solubility of sphalerite and galena in 1–5 m NaCl solutions to 300°C: Geochimica et Cosmochimica Acta, v. 52, p. 813–820, https://doi.org/10.1016/0016-7037(88)90353-5.

Bourcier, W.L., and Barnes, H.L., 1987, Ore solution chemistry: VII, Stabilities of chloride and bisulfide complexes of zinc to 350 degrees C: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 82, p. 1839–1863, https://doi.org/10.2113/gsecongeo.82.7.1839.

Corbella, M., Ayora, C., and Cardellach, E., 2004, Hydrothermal mixing, carbonate dissolution and sulfide precipitation in Mississippi Valley–type deposits: Mineralium Deposita, v. 39, p. 344–357, https://doi.org/10.1007/s00126-004-0412-5.

Cooke, D.R., Bull, S.W., Large, R.R., and McLeod, P.J., 2000, The importance of oxidized brines for the formation of Australian Proterozoic stratiform sediment–hosted Pb-Zn (sedex) deposits: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 95, p. 1–17, https://doi.org/10.2113/gsecongeo.95.1.1.

Figure 4. Calculated Zn, Pb, and Ba concentrations as a result of mixing Zn-Pb-Ba-bearing, sulfur-poor brine with 0.2 m H₂S(aq), with and without presence of dolomite at water-saturated pressure and 150 °C (A) and 250 °C (C). Initial fluid compositions in 1 kg water: NaCl = 3 m, Zn²⁺ = 1000 ppm, Pb²⁺ = 200 ppm, and SO₄²⁻ = 1 × 10⁻⁵ m; starting pH of 2.0 (point 1) and 5.5 (point 2); starting log fO₂ (fO₂—oxygen fugacity) of −35 at 150 °C, and −28 at 250 °C. Changes of pH and log fO₂ of reaction paths are plotted in log fO₂-pH diagrams (B and D) that show stability fields of Zn and sulfur species when ΣS is 0.2 m (arrows indicate reaction direction).
