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ORIGINAL ARTICLE

An experimental study on metal precipitation driven by fluid mixing: implications for genesis of carbonate-hosted lead–zinc ore deposits

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Abstract A type of carbonate-hosted lead–zinc (Pb–Zn) ore deposits, known as Mississippi Valley Type (MVT) deposits, constitutes an important category of lead–zinc ore deposits. Previous studies proposed a fluid-mixing model to account for metal precipitation mechanism of the MVT ore deposits, in which fluids with metal-chloride complexes happen to mix with fluids with reduced sulfur, producing metal sulfide deposition. In this hypothesis, however, the detailed chemical kinetic process of mixing reactions, and especially the controlling factors on the metal precipitation are not yet clearly stated. In this paper, a series of mixing experiments under ambient temperature and pressure conditions were conducted to simulate the fluid mixing process, by titrating the metal-chloride solutions, doping with or without dolomite, and using NaHS solution. Experimental results, combined with the thermodynamic calculations, suggest that H_2S, rather than HS^- or S^{2-}, dominated the reactions of Pb and/or Zn precipitation during the fluid mixing process, in which metal precipitation was influenced by the stability of metal complexes and the pH. Given the constant concentrations of metal and total S in fluids, the pH was a primary factor controlling the Pb and/or Zn metal precipitation. This is because neutralizing or neutralized processes for the ore-forming fluids can cause instabilities of Pb and/or Zn chloride complexes and re-distribution of sulfur species, and thus can facilitate the hydrolysis of Pb and Zn ions and precipitation of sulfides. Therefore, a weakly acidic to neutral fluid environment is most favorable for the precipitation of Pb and Zn sulfides associated with the carbonate-hosted Pb–Zn deposits.

Keywords Metal precipitation · Fluid mixing · Sulfur species · MVT lead–zinc ore deposits · Carbonate-hosted lead–zinc deposits

1 Introduction

Fluid mixing is considered to play an important role in the formation of various hydrothermal ore deposits, such as the Carlin-type gold deposits in the Jerritt Canyon, Nevada (Cooke 1996; Hofstra et al. 1988), Creede polymetallic vein deposits, Colorado (Henley 1984; Henley et al. 1984; Plumlee 1994), Mississippi Valley-type lead–zinc ore deposits (Anderson 1975; Leach et al. 2005; Plumlee et al. 1994), epithermal deposits in the Pacific Rim (Jiang et al. 2004), Olympic Dam-type Cu–U–Au deposits (Fang and Li 2014; Haynes et al. 1995), and porphyry copper–

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molybdenum–gold deposits (Fan et al. 2001; Li and Liu 2002). An important reason is that fluid mixing can effectively facilitate the precipitation and mineralization of ore-forming metal elements (Leach et al. 2005; Reed 2006; Reed and Spycher 1985). Therefore, studies on fluid mixing process can considerably promote better understanding of the genesis of large and giant hydrothermal ore deposits.

Fluid mixing is the most favorable genesis model for the formation of Mississippi Valley Type (MVT) Pb–Zn ore deposits (Anderson 1975; Beales 1975; Beales and Jackson 1966), besides sulfate reduction model (Anderson 1973, 1991; Barton 1967), and reduced sulfur model (Anderson 1973, 1975) (Table 1). A pioneering study from Beales and Jackson (1966) on the Pine Point Pb–Zn ore deposit, Canada, proposed the first fluid mixing model. In the model, some kind of chloride complex-bearing fluid originated from a distal basin migrated into the metallogenic area, and mixed with local H_2S-bearing fluid, resulting in the precipitation of metals and deposition of sulfides. Corbella et al. (2004) demonstrated that fluid mixing is an efficient way to produce the MVT ore deposit and associated carbonate dissolution. In recent years, this model received increasing support from studies on ore field structures (Brown 1970; Ohle 1985), isotopes (Bottrell et al. 2001), homogenization temperature, and salinity of fluid inclusions (Kesler et al. 1997; Leach et al. 1993), halogen and inert gases (Grandia et al. 2003; Kendrick et al. 2002), and numerical simulations (Anderson and Garven 1987; Appold and Garven 2000; Corbella et al. 2004; Plumlee et al. 1994; Reed 2006; Reed and Spycher 1985). A general understanding is that during the fluid mixing process Pb and/or Zn ions chemically react with reduced sulfur species in the fluids, producing sulfide precipitation. In a hydrothermal system, however, reduced sulfur could occur in the form of H_2S, S^{2-}, S_3^-, or HS^- (Manning 2011; Pokrovski and Dubrovinsky 2011; Tossell 2012). Which form of reduced sulfur dominates the metal precipitation of the MVT Pb–Zn ore deposits and is involved dynamic process during the metal precipitation is still unclear.

In this paper, we conduct a series of fluid mixing experiments at ambient temperature and pressure conditions, through titrating Pb and/or Zn-bearing chloride solutions with sulfur-bearing solution. We also used the experimental results, combined with the thermodynamic calculations, to depict the detailed chemical kinetic process of mixing reactions, the geochemical pathways on metal precipitation associated to the carbonate-hosted Pb–Zn deposits, and the main controlling factors on the metal precipitation.

2 Experimental methods

2.1 Starting materials

Solution preparation was operated at the hydrothermal laboratory of the high-temperature and high-pressure experimental platform in the Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences. Three kinds of Pb and/or Zn chloride solutions, as well as a NaHS solution, were made up to be the analogues of initial metal chloride-containing and sulfur-bearing fluids, respectively. Lead and/or zinc chloride solutions prepared for the experiments are as follows: (1) 0.01 mol/L $ZnCl_2$ and 1 mol/L NaCl; (2) 0.0005 mol/L $PbCl_2$ and 1 mol/L NaCl; and (3) 0.01 mol/L $ZnCl_2$, 0.0005 mol/L $PbCl_2$, 0.002 mol/L $CaCl_2$, 0.002 mol/L $MgCl_2$, and 1 mol/L NaCl. Lead and zinc concentrations in all three initial solutions are approximately 100 ppm and 650 ppm, respectively. These values are quite similar to the Lead and zinc concentrations in ore-forming fluids of the MVT Pb–Zn ore deposits (Carpenter et al. 1974; Czamanske et al. 1963; Pinckney and Haffty 1970; Stoffell et al. 2008; Yardley 2005). Initial NaHS solutions are various at the concentrations of 0.0002, 0.002, 0.001, 0.01, 0.02, and 0.1 mol/L. All reagents used

Table 1 Representative models for the migration and deposition of sulfides in the MVT deposits

Model type	Migration process	Precipitation mechanism
Fluid mixing models (two kinds of fluids)	A fluid with very little reduced sulfurs carries metals into the depositional site, and mixes with the other one with abundant reduced sulfurs	Mixing of metal-rich fluid with reduced sulfur-rich fluid; Mixing of metal-rich fluid with local H_2S gas reservoir
Local sulfate reduction model (single fluid)	A fluid carries metals and sulfates into the depositional site	Sulfates are reduced by the reactions with local methane or other organic matters
Reduced sulfur model (single fluid)	An acidic fluid carries metals and reduced sulfurs into the depositional site at temperatures of > 200 °C	Decrease in temperature or pressure; change in pH; dilution; wall–rock interaction; addition of reduced sulfur

during the preparation process of initial solutions are of analytical purity and the water used was deionized.

To facilitate the observation of sulfide precipitates produced during fluid mixing process, a dolomite, the most common host rocks for carbonate-hosted Pb–Zn ore deposits (Gerdemann and Myers 1972; Gregg 1985; Han et al. 2007; Lyle 1977; Rowan 1987; Sass-Gustkiewicz and Dzulyński 1998; Zhang et al. 2009), was also prepared. The dolomite sample was fresh and fine-grained. It was collected from the Lower Carboniferous Baizuo Formation, located in the Huize Mining Area of Yunnan Province, China. The dolomite consisted of more than 80% dolomite and minor calcite, with a great quantity of Ca, Mg, Fe, Mn and other trace elements (Fraser et al. 1989; Jazi et al. 2017). The sample was firstly crushed and then powdered in an agate mortar to 40 mesh in dimension.

2.2 Experimental strategy and procedure

Given that MVT Pb–Zn ore deposits are the product of regional or sub-continental scale hydrothermal processes which have nothing to do with magmas (Leach et al. 1993, 2001, 2005; Stoffell et al. 2008; Sverjensky 1986). They form at very low pressure and temperature conditions, for instance, mainly at 50–200 °C and within 100 MPa (Banks and Russell 1992; Grandia et al. 2003; Gratz and Misra 1987; Leach et al. 1996, 2004, 2005; Marie and Kesler 2000; Roedder 1977; Samson and Russell 1987; Savard et al. 2000). At these conditions, stabilities of Pb and Zn chloride complexes are seldom affected by the pressure and temperature (Fig. 1). Because of this, we designed a series of mixing experiments under ambient temperature and pressure conditions to simulate the fluid mixing process, by titrating metal-chloride solutions, doping with or without dolomite, and using NaHS solution. On the basis of these experimental results, we can extrapolate chemical kinetic processes to the conditions related to the MVT Pb–Zn ore deposits.

The experiments were designed in two groups, fluid-mixing experiments and fluid–rock reaction experiments. All of the experiments were performed at the hydrothermal laboratory high-temperature and high-pressure experimental platform in the GIG.

(1) *Fluid-mixing experiments* were conducted through a method of titrating Pb and/or Zn chloride solutions with sulfur-bearing solutions, including three sets of parallel experiments as follows:

    1. *Mixing of solutions containing Zn and NaHS* 10 mL of the prepared Zn chloride solution was placed in a 50 mL plastic vial. Hydrochloric acid or sodium hydroxide was added to adjust solution acidity to pH = 2.09, 2.70, 3.76, 5.00, and 5.80. The solutions with different pH values were titrated using 0.002 mol/L NaHS solution.
    2. *Mixing of solutions containing Pb and NaHS* 10 mL of the prepared Pb chloride solution was placed in a 50 mL plastic vial. Hydrochloric acid or sodium hydroxide was added to adjust solution acidity to pH = 1.38, 2.38, 2.42, 3.00, 3.20, 4.00, 5.00, and 6.00. The solutions with different pH values were titrated using 0.0002 mol/L NaHS solution.
    3. *Mixing of solutions containing Pb–Zn and NaHS* 10 mL of the prepared Pb–Zn chloride solution was placed in a 50 mL plastic vial. Hydrochloric acid or sodium hydroxide was added to adjust solution acidity to pH = 1.66, 2.40, 3.32, and

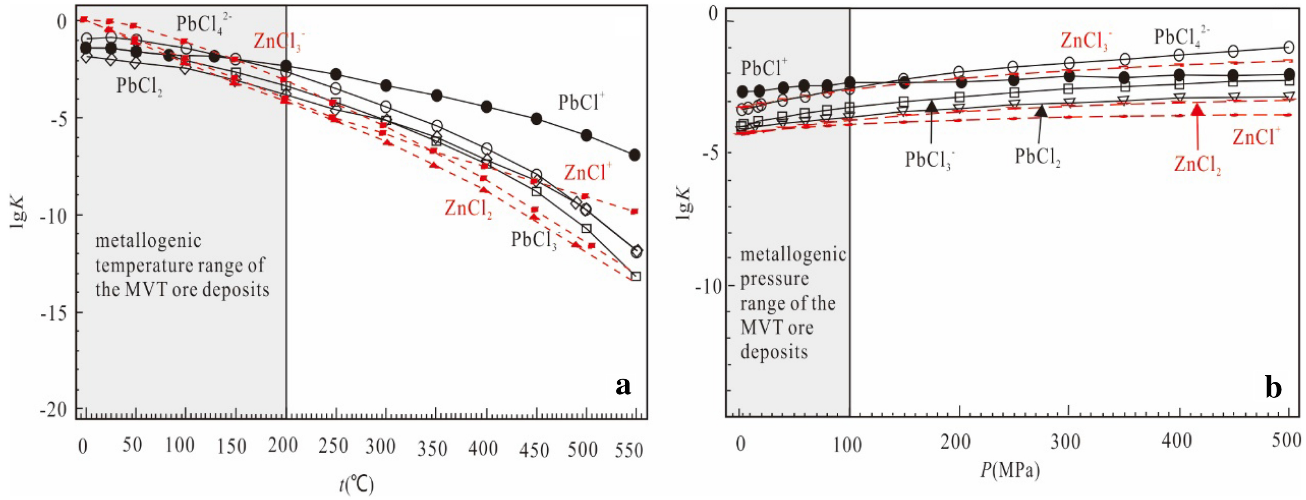

Fig. 1 Stabilities of base metal-chloride complexes, modified from Reed (2006). **a** $t - \log K$ diagram of the base metal-chloride complexes (P = 80.0 MPa); **b** $P - \log K$ diagram of the base metal-chloride complexes (t = 200 °C)

3.90. The solutions with different pH values were titrated using 0.002 mol/L NaHS solution.

During slow titration of the NaHS solutions into the Pb–Zn chloride solutions, continuous shaking of the plastic vial was necessary to prevent the precipitates from local oversaturation of NaHS and to speed up chemical reactions. Meanwhile, we kept close watch on the precipitation processes from the solution mixtures. Once the precipitates were observed, an excess amount of NaHS solution was rapidly added into the mixtures. During the procedure above, the pH value was measured at different steps. Finally, the solid precipitates and residue solutions in the plastic vial were separated from each other by filtration for XRD and ICPMS analysis, respectively.

(2) *Fluid–rock reaction experiments* were carried out through titrating NaHS solution into the Pb–Zn chloride solutions doping with 2 g of 40-mesh fine-grained dolomite powder collected from the Huize Mining Area, China. The purpose of these experiments was to observe the role of wall rock on metal precipitation during the fluid mixing process. Considering that the pH value of the solutions in these experiments could be varied due to the disequilibrated fluid–rock reaction, it therefore cannot truly reflect the chemical kinetics of the fluid mixing process. So, the pH values of the solutions were no longer measured. After the titration, the solid phases were separated from the solutions, by filtration and dry for electron microprobe analysis.

2.3 Analytical methods

pH measurements of solutions were performed in the GIG hydrothermal laboratory by a FiveEasy™ pH meter manufactured by Mettler-Toledo International, Inc. Calibrations using a prepared buffer solution (GGJ-119). Calibration was carried out before each pH measurement.

XRD and EPMA analyses were finished in the test center of the South China University of Technology. The equipment used for XRD analysis is the D8ADVANCE diffractometer manufactured by Bruker Corporation, Germany. The analytical conditions are as follows: wavelength of incident ray is 0.15418 nm; tube pressure and flow were 40 kV and 40 mA, respectively; scanning range, step length, and speed are 5°–90°, 0.02°, and 19.2 s/step, respectively; and the slit was DS 0.5° RS 8 mm (corresponding to a LynxExe array detector). For the EPMA analysis, the EPMA-1600 manufactured by Shimadzu Corporation, Japan was employed, together with the Genesis energy spectrometer manufactured by EDAX Inc., the United States. The experimental conditions are as follows: acceleration voltage was 2.0 kV, resolution of secondary electrons was 6 nm, X-ray detection angle was 52.5°, and energy resolution is 120 eV.

3 Experimental results

3.1 Titration curve for fluid mixing experiments

In the fluid mixing experiments, with the addition of NaHS solutions into various initial pH metal chloride solutions, the pH values of all the mixed solutions increased slowly. Once the titration amount of NaHS solution was enough to deposit all the Pb and/or Zn ions, the pH values clearly declined (Table A. 1, Fig. 2). For example, in experiment Hh-3, 0.002 mol/L NaHS solution was titrated into the Zn chloride solution with an initial pH value of 3.76. With the increase of titration volumes of NaHS solution from 3.50 to 14.00 mL, the pH value of mixed solutions changed from 3.88 to 4.05. When the titration volume of NaHS solution reached 60.00 mL, however, the pH value of mixed solutions declined to 2.53. This tendency occurs in not only for single Pb or Zn chloride solutions, but also complex Pb–Zn chloride solutions as well (Fig. 2).

During the titration, precipitates could not be observed until the titration amount of NaHS solution was large enough (Table A. 1, Fig. 2). Usually the lower pH values of the initial metal-bearing solutions had, the more NaHS solution was needed to produce initial precipitates (Table A. 1, Fig. 3). For example, in the experiment of Hh-3, 0.002 mol/L NaHS solution was titrated into the Zn chloride solution with an initial pH value of 3.76. While the titration volume of NaHS solution reached 1.50 mL, no obvious precipitates could be observed, and the pH value of mixed solutions became to be a little higher, i.e. 3.80. Till the NaHS solution was added up to 3.50 mL, precipitates were indeed observed for the first time. By contrast, in the experiment of Hh-4, it needs at least 6.00 mL 0.002 mol/L NaHS solution to produce obvious precipitates with an initial pH value of 2.70.

Comparing with Zn chloride solutions, Pb or Pb–Zn chloride solutions with similar initial pH value need much less 0.002 mol/L NaHS solution to produce obvious precipitates, as shown in Fig. 3. For example, 3.50 mL 0.002 mol/L NaHS solution was titrated into the Zn chloride solution with initial pH value of 3.76 and thus can produce obvious precipitates. However, as for Pb chloride solution with initial pH value of 4.00 and Pb–Zn chloride solution with initial pH value of 3.90, the titration volumes of NaHS solution needed were 0.80 mL and 0.20 mL, respectively. Considering that the initial pH values of metal-bearing chloride solutions were similar and the concentration of titrated NaHS solution was also constant,

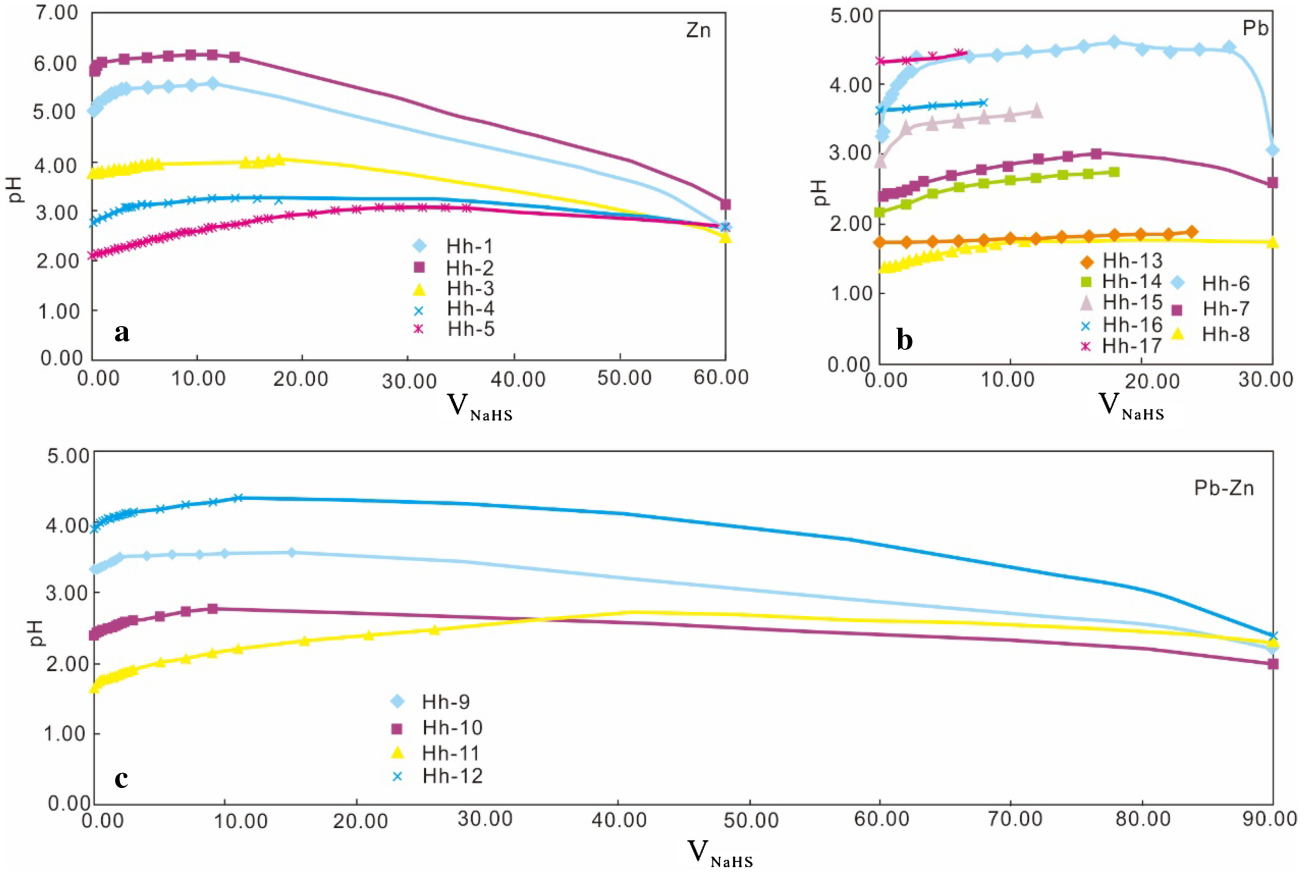

Fig. 2 Titration curves for NaHS solution into various initial pH metal-bearing solutions. **a** Titration curves for NaHS solution into Zn-bearing solutions with various initial pH; **b** titration curves for NaHS solution into Pb-bearing solutions with various initial pH; **c** titration curves for NaHS solution into Pb and Zn-bearing solutions with various initial pH. In these experiments, with the addition of NaHS solutions into metal chloride solutions, the pH values of all the mixed solutions increase up slowly; After the titrated amount of NaHS solution is enough to make all the Pb and/or Zn ions precipitate, the pH values decline notably

such a difference most likely results from initial metal concentration difference and discrepant geochemical behavior between Pb and Zn.

3.2 Precipitates produced by fluid–rock reaction experiments

Experiments on titrating NaHS solution into the Pb–Zn chloride solutions doping with 2 g of 40-mesh fine-grained dolomite powder demonstrate that a large amount of sulfide precipitates can be formed. As shown in Fig. 4, large numbers of nanoscale precipitates were found on the surface of the dolomites. EDS spectrum analysis on these precipitates indicates that the main components of these precipitates are Pb, Zn, and S (Table 1, Fig. 4). Furthermore, XRD analysis of these solid precipitates show that they mainly consisted of galena and/or sphalerite (Fig. 5).

4 Discussion

4.1 Species and distributions of sulfur in the hydrothermal fluids related to the MVT Pb–Zn ore deposits

In the fluid mixing model on the formation of carbonate-hosted MVT Pb–Zn ore deposits, it is usually thought that reduced sulfur species in the fluids dominate the metal precipitation (Anderson 1975; Beales and Jackson 1966; Corbella et al. 2004; Giordano 2002; Giordano and Barnes 1981; Leach et al. 2005, 2006; Reed 2006). In a hydrothermal system, reduced sulfur can occur in the forms of H_2S, S^{2-}, S_3^-, or HS^- (Manning 2011; Pokrovski and Dubrovinsky 2011; Tossell 2012). The free radical S_3^- is dominant when temperatures are above 250 °C, especially at 350 °C and 0.5 GPa (Pokrovski and Dubrovinsky 2011; Tossell 2012). Considering that the MVT Pb–Zn ore deposits mainly form at temperatures of no more than 200 °C and pressures of no more than 0.1 GPa (Basuki

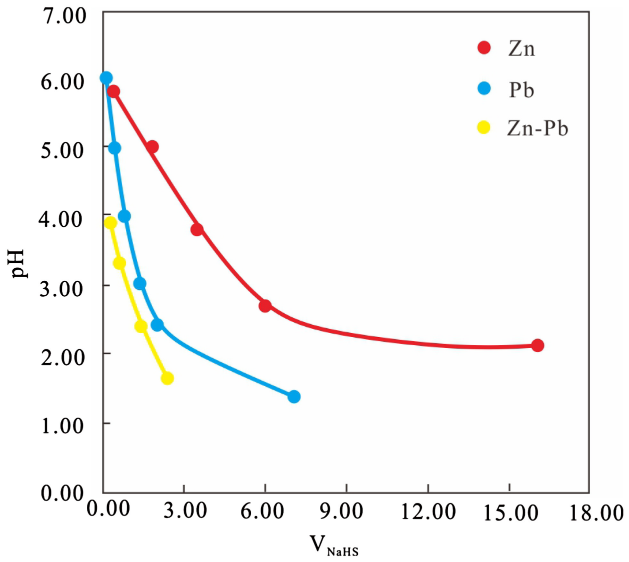

Fig. 3 Relationship between the initial pH values of metal-bearing solutions and the smallest volumes of NaHS solution needed to produce observable precipitates. The lower the initial pH values of the metal-bearing solutions are, the more the titration volumes of NaHS solution to produce initial precipitates need

2002; Conliffe et al. 2013; Han et al. 2016; Leach et al. 2005; Wilkinson 2001), S_3^- radical cannot act as a dominant sulfur species in the Pb–Zn metallogenic hydrothermal fluids. Therefore, during the fluid mixing processes related to the MVT Pb–Zn ore deposits, H_2S, S^{2-}, and HS^- are the potential dominant species. Based on sulfur's chemical equilibriums in the hydrothermal system and thermodynamic data (Lin et al. 1985), calculated pH-logf_{O2} phase diagrams of sulfur at 298 K and 523 K show that H_2S and S^{2-} are stable at acidic and strongly basic pH conditions, respectively, while the stability field of HS^- lies between them (Fig. 6). Note that higher temperature compresses the stability field of HS^-, thus the boundary between HS^- and H_2S consequently changes from the pH values of about 7.0–7.7. It suggests that at high temperatures H_2S can be fairly stable up to neutral pH conditions. Thus, it provides the theoretical basis for extrapolating our experimental results at ambient conditions to that of higher temperatures and pressures (Table 2).

Given that NaHS is a kind of salt with strongly alkaline cation and weakly acidic anion (Oxtoby et al. 2012; Petrucci and Harwood 1977), in an aqueous solution, its weakly acidic anion is easily hydrolyzed (Oxtoby et al. 2012; Petrucci and Harwood 1977), as shown in the Eq. (1), resulting in the formation of a kind of weak basic solution:

$$HS^- + H_2O \rightleftharpoons H_2S(aq) + OH^-. \quad (1)$$

Meanwhile, the weakly acidic anion can also dissociate to form a kind of weak acidic solution. The dissociation reaction equation is as follows:

$$HS^- \rightleftharpoons S^{2-} + H^+ \quad (2)$$

Directions of the Eq.s (1) and (2) are dependent on the acidity or basicity of hydrothermal fluids (Oxtoby et al. 2012; Petrucci and Harwood 1977). The acidic environment forwards the Eq. (1), while the basic one is favorable for the Eq. (2). Previous studies have demonstrated that the MVT Pb–Zn ore deposits were usually formed in the acidic or neutral hydrothermal fluids (Banks et al. 2002; Emsbo 2000; Grandia et al. 2003; Leach et al. 2005), suggesting the Eq. (1) as a dominant reaction to control the proportions of H_2S and HS^- during the formation of the MVT Pb–Zn ore deposits. In our fluid mixing experiments, the low initial pH values of metal-containing chloride solutions are in favor of the progress of the Eq. (1). This can explain the first increase of the pH values of mixed solutions in all of the fluid mixing experiments (Fig. 2), and is also in agreement that H_2S is stable in the acidic–neutral fluids (Fig. 6).

Temperature and pH can influence not only the stability fields of H_2S and HS^- in the hydrothermal fluids, but also the distribution proportions of them. Under the acidic conditions and at room temperature, the proportion of H_2S on reduced sulfur is close to 100% (Fig. 7). This is the main reason why most studies supposed that H_2S dominates the precipitation of Pb and Zn during fluids mixing for the genesis model of MVT Pb–Zn ore deposits (Anderson 1975; Beales and Jackson 1966; Corbella et al. 2004; Leach et al. 2005, 2006; Reed 2006). However, our calculations show that although higher temperatures can make the stability field of HS^- compressed into the basic domain (Fig. 6), it can also promote the distribution of a proportion of HS^- in the acidic hydrothermal fluids. As shown in Fig. 7, at 473 K and pH of $\sim$ 5.5 conditions the proportion of HS^- has increased up to 10%, and while the pH is up to 6 the proportion of HS^- is more than 20%. This may not be negligible for the fluid mixing model for the genesis of the MVT Pb–Zn ore deposits.

4.2 Geochemical pathways on metal precipitation during the fluid mixing processes associated to the carbonate-hosted Pb–Zn deposits

In the fluid mixing model related to the carbonate-hosted Pb–Zn deposits, metal precipitation and deposition is usually attributed to the mixing of a sulfur-deficient but metal chloride-rich fluid with another reduced sulfur-rich (i.e. H_2S and/or HS^-) at the site of host carbonate (Anderson 1975; Beales 1975; Beales and Jackson 1966).

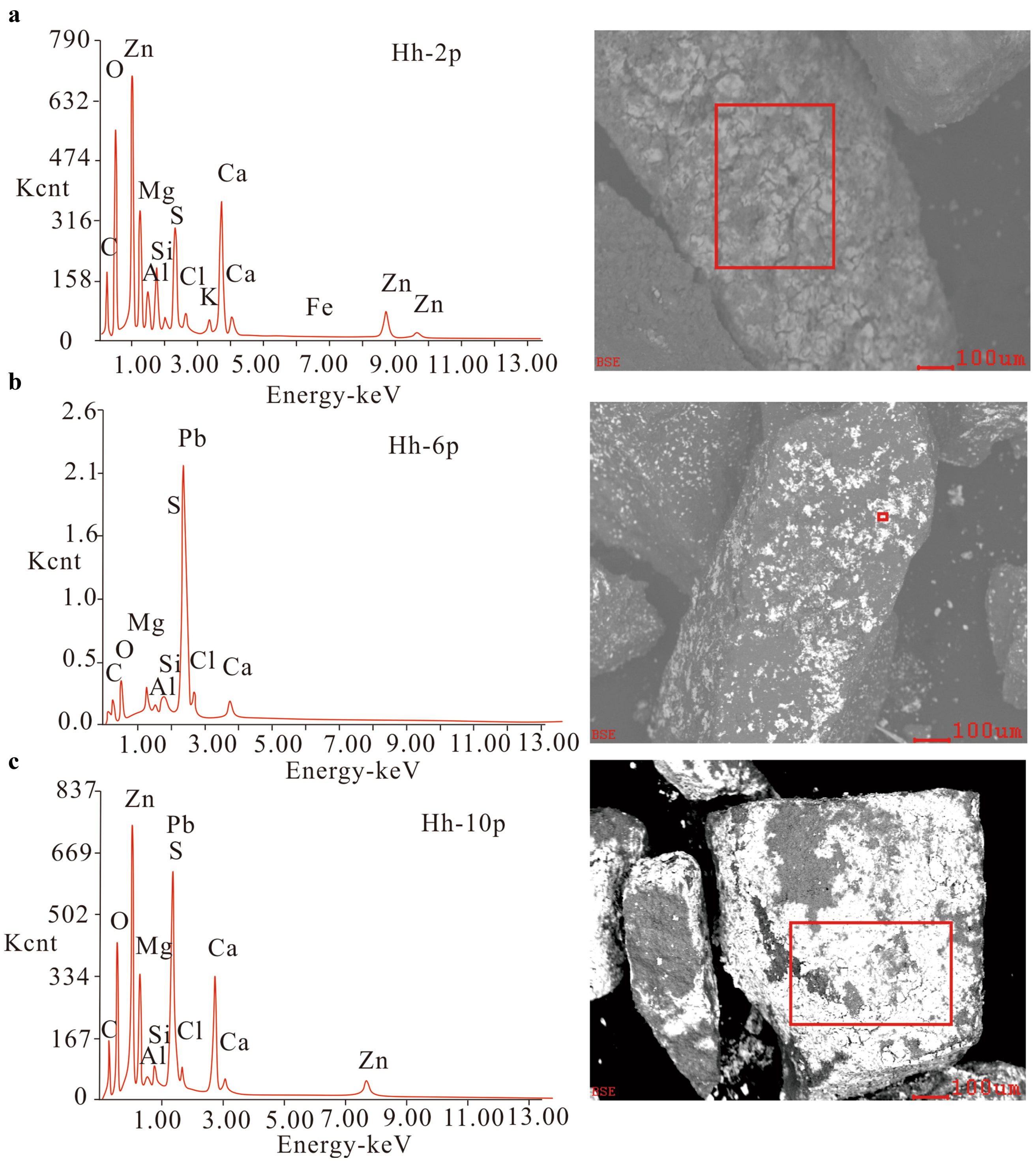

Fig. 4 EPMA spectra and photomicrograph of precipitates from fluid–rock reaction experiments. **a** Sample of Hh-2p; **b** sample of Hh-6p; **c** sample of Hh-10p. The results indicate that the main components of these precipitates are Pb, Zn, and S

There are, therefore, two kinds of main pathways to account for the mixing (Fig. 8), through (1) topographically-driven, reduced S-rich fluid continually flowing into the site of host carbonate which has been largely percolated by metal chloride fluid, such as the Huize Pb–Zn ore deposits, southwestern China (Zhang et al. 2014b), or (2) Pb–Zn chloride ore fluid migrating into the carbonate sequences filled with local reduced S-rich

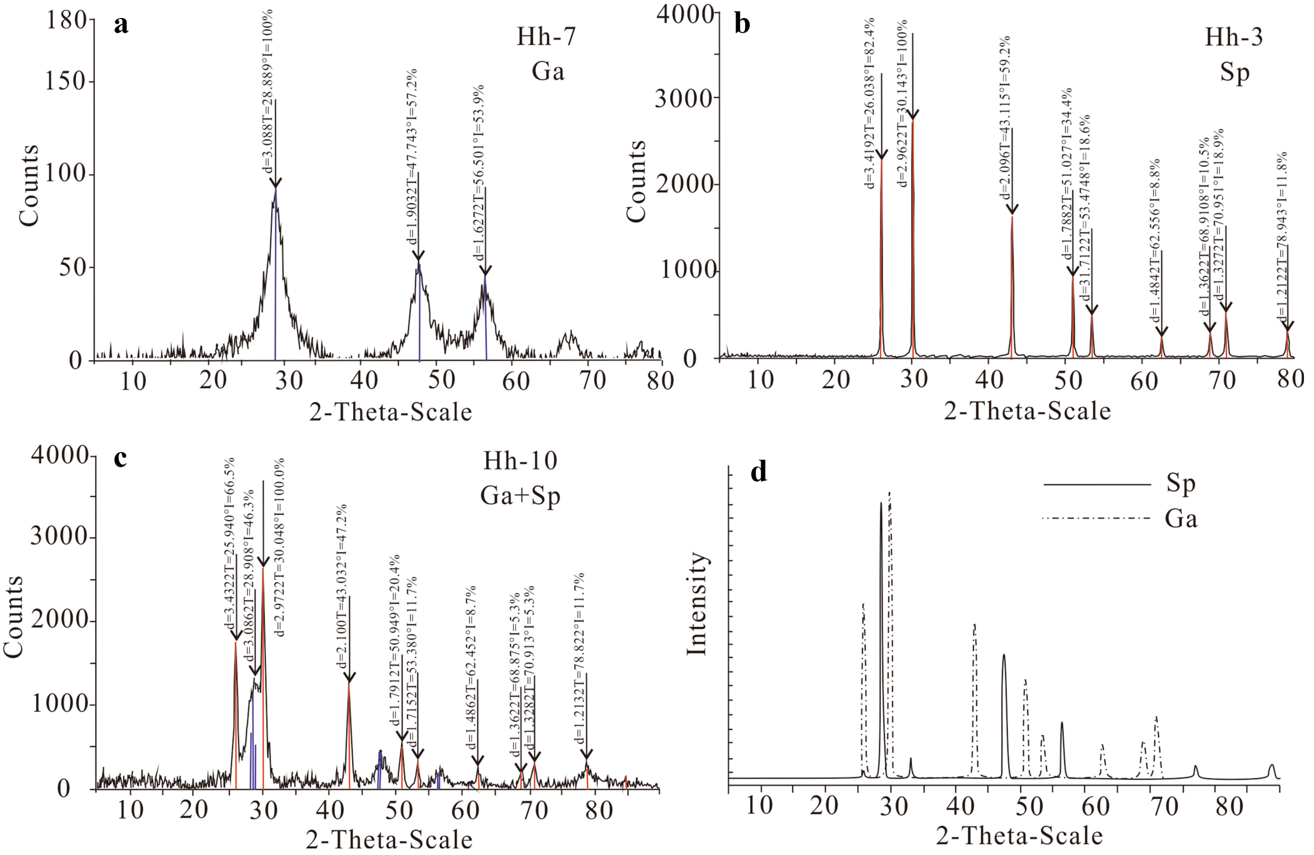

Fig. 5 XRD analysis spectra of precipitates from fluid–rock reaction experiments, demonstrating the growth of sulfide on the surface of dolomite. **a** Sample of Hh-3 showing the precipitates as sphalerite; **b** sample of Hh-7 showing the precipitates as galena; **c** sample of Hh-10 showing the precipitates as sphalerite and galena; **d** standard XRD spectrum of sphalerite and galena, data from http://rruff.info. Mineral abbreviation: Ga-galena, Sp-sphalerite

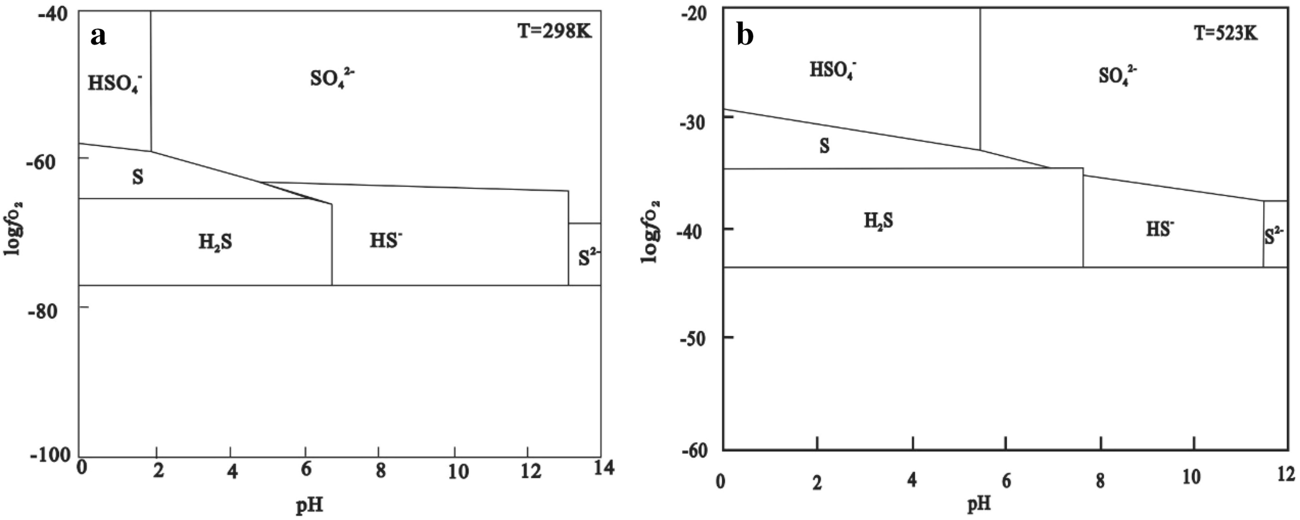

Fig. 6 pH-log$f(O_2)$ phase diagram of S in the hydrothermal system at various temperatures. The complete calculation method is presented in Online Appendix A. H_2S dominates for pH below 7, HS^- between 7 and 13, S^{2-} above 12 at T = 298 K. The pH range for H_2S stability was offset towards alkalinity by 1.0 units with the temperature changing from 298 to 473 K

fluid, for instance, the Northern Arkansas MVT Pb–Zn deposits, North American (Wilkinson et al. 2009), and the Pine Point Pb–Zn ore deposit, Canada (Beales and Jackson 1966). During the fluid mixing, geochemical

Table 2 The results of EDS spectrum analysis on precipitates

Sample no.	Pb	Zn	S	C	O	Ca	Mg	Si	Al	Cl
Hh-1 p		28.18	8.95	16.55	18.17	10.3	6.17	3.08	2.15	3.09
Hh-2 p		31.51	6.22	14.35	17.87	13.2	6.19	2.93	2.04	1.16
Hh-3 p		33.38	10.5	13.96	14.93	10.15	5.28	2.57	1.75	2.82
Hh-4 p		28.6	8.46	15.76	18.82	11.74	6.66	3.34	2.31	0.44
Hh-5 p		27.54	8.88	15.06	19.16	12.69	7.29	3.12	2.37	0.6
Hh-6 p	62.35		8.28	10.28	7.98	4.04	2.2	1.39	0.73	2.75
Hh-7 p	37.78		5.89	11.69	19.39	11.59	5.68	3.21	2.09	1.41
Hh-8 p	36.31		4.8	11.59	20.16	11.45	5.66	3.85	2.45	0.82
Hh-9 p	17.32	46.41	24.33							11.94
Hh-10 p	11.04	40.42	17.57	12.51	6.51	7.43	3.08			1.44
Hh-11 p	11.43	21.79	8.86	15.66	17.85	14.43	8.39	0.45		1.14
Hh-12 p	8.23	28.1	11.21	14.3	14.02	14.05	7.07	0.99	0.56	1.47

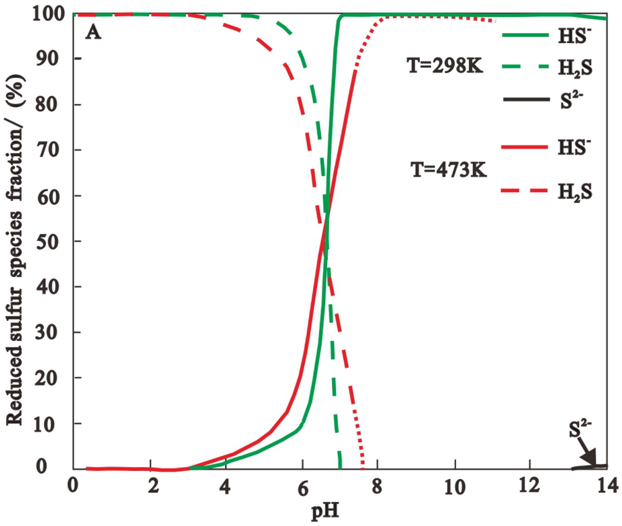

Fig. 7 Sulfur species fraction versus solution pH at T = 298 K and 473 K, respectively, the curve of T = 473 K modified from Reed (2006). Concentrations of H_2S, HS^-, S^{2-}as functions of pH (Bjerrum plot) calculated from Online Appendix C. When T = 298 K, at pH ≤ 4, the sulfur in the solution mainly exists as H_2S; at pH ≥ 7, the sulfur in the solution is mainly presented as HS^-; $4 < \text{pH} < 7$, H_2S and HS^- coexists. As the temperature increases, the dominant field of H_2S moves to the right about one pH unit

reactions causing metal precipitation are considerably different.

Given that metal chloride complexes are more stable in an acidic fluid and at high temperature (And et al. 2003; Reed 2006; Seward 1984; Seward and Barnes 1997; Tagirov et al. 2007a, b; Tagirov and Seward 2010), in the first main pathway (Fig. 8a), metal-chloride-rich ore fluids with low pH values percolate into the site of host carbonate, easily resulting in instabilities of metal chloride complexes due to Pb and Zn hydrolysis according to:

$$Me^{2+} + 2H_2O \leftrightarrow Me(OH)_2 + 2H^+. \tag{3}$$

Dehydration of the hydrolyzed hydroxide products can take the form:

$$Me(OH)_2 \rightarrow MeO \downarrow + H_2O. \tag{4}$$

Equation (3) supplies a large amount of hydrogen ions to dissolve the host carbonate, resulting in massive alteration and even karsting (Pirajno 1992) and formation of secondary carbonate minerals (Misra 2000). Because of exhaustion of hydrogen ions, the ore fluids become closely neutral (Robb 2005); this causes Eq. (1) in the reverse direction and thus forming more HS^- in the fluids, when reduced sulfur-rich fluids come to mix in the site of host carbonate. Considering that sulfide usually has the smallest solubility product constant (Reed 2006) and the solubility of galena and sphalerite in a NaCl system under various conditions is very low (less than 1 ppm) (Barrett and Anderson 1982, 1988; Daskalakis and Helz 1993; Hayashi et al. 1990; Hennig 1971; Melent'Yev et al. 1969), those hydroxides and oxides of Pb and Zn in fluids or on the surface of carbonate can easily transform into sulfides, according to:

$$Me(OH)_2 + H_2S(aq) \rightarrow MeS \downarrow + 2H_2O, \tag{5}$$

$$MeO(s) + H_2S(aq) \rightarrow MeS \downarrow + H_2O. \tag{6}$$

Or,

$$Me(OH)_2 + HS^- \rightarrow MeS \downarrow + 2H_2O + OH^-, \tag{7}$$

$$MeO(s) + HS^- \rightarrow MeS \downarrow + OH^-. \tag{8}$$

The transformation from hydroxides and/or oxides to sulfides could plausibly interpret the formation of sulfide zonation in the carbonate-hosted Pb–Zn deposits, such as the Huize, Zhaotong and some other Pb–Zn ore deposits, southwestern China (Zhang et al. 2014a, b).

Compared to the first main pathway for the fluid mixing, the other main pathway does not involve in multiple metal depositions (Fig. 8b). During the influx of reduced sulfur-

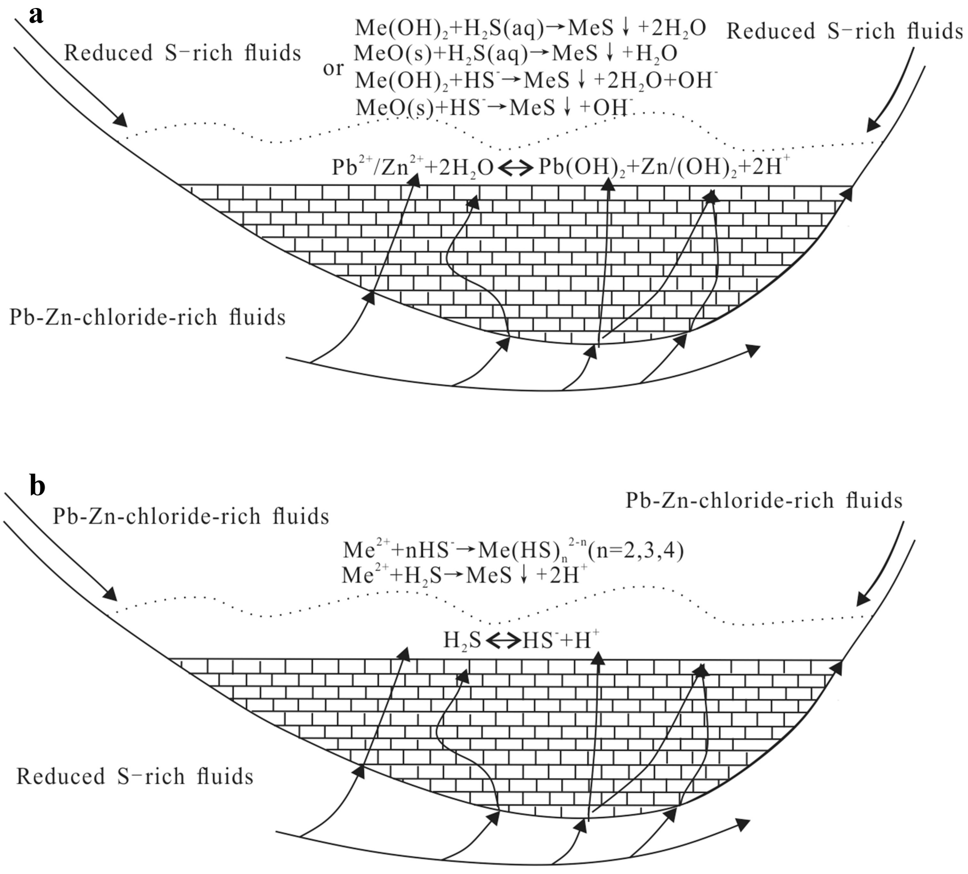

Fig. 8 Model diagrams on two kinds of fluid mixing processes associated to carbonate-hosted MVT Pb–Zn deposits. Me represents the Pb and Zn metal ions

rich fluids into the carbonate sequences, the distribution of S species in ore fluids is controlled by Eq. (1) or:

$$H_2S \rightleftharpoons HS^- + H^+. \tag{9}$$

Due to the occurrence of the host carbonate, hydrogen ions are consumed and consequently, the fluid is neutral or weakly alkaline (Anderson 1997). In this kind of fluid, both H_2S and HS^- are the dominant species (Fig. 7). Considering that Pb and Zn bisulfide complexes are stable in low temperature, neutral to alkaline, low salinity solutions (Akinfiev and Tagirov 2014; Bourcier and Barnes 1987; Giordano and Barnes 1979; Zhong et al. 2015) in the form:

$$Me^{2+} + nHS^- \rightleftharpoons Me(HS)_n^{2-n} \quad (\mathrm{n} = 2,\ 3,\ 4) \tag{10}$$

metal precipitation cannot happen by the reaction:

$$Me^{2+} + HS^- \rightarrow MeS \downarrow + H^+ \tag{11}$$

When metal-chloride-rich ore fluids are injected into the site of host carbonate and the neutralized or weakly alkaline S-rich fluids, Pb and Zn chloride complexes are unstable, some of which are transformed into bisulfide complexes according to the Eq. (10), some react directly with H_2S in the fluids:

$$Me^{2+} + H_2S \rightarrow MeS \downarrow + 2H^+. \tag{12}$$

For Eqs. (10) and (12), it is not likely that Pb and Zn ions hydrolyze because of sufficient sulfur occurring in the mixing fluids, which is different from the first geochemical pathway. Meanwhile, because H_2S in the fluids are consumed during sulfide deposition by Eq. (12), it leads to unstable Pb and Zn bisulfide complexes and thus releases partial HS^- to form H_2S, till reaching the equilibrium among the sulfur species, metal ions, and bisulfide complexes.

The true scenario on the fluid mixing associated with the carbonate-hosted Pb–Zn deposits is most likely attributed to successive geochemical processes involving not only the first main pathway but the second one. It probably depends on the paleogeographic and tectonic features on the deposition site (Anderson 1975; Corbella et al. 2004; Leach et al. 2005). However, while considering metal precipitation, the first pathway can make the metal deposition reach its maximum size, probably forming a series of larger size and higher-grade ore deposits than the second one.

4.3 Control factors on metal precipitation reaction during the fluid mixing

It is well known that decrease in temperature and change in the properties or composition of the ore fluid can significantly promote metal precipitation during hydrothermal processes (Fan et al. 2001; Reed 2006; Seward and Barnes 1997). As mentioned above, the MVT-type Pb–Zn deposits usually form at very low pressure and temperature conditions (Banks and Russell 1992; Ganino and Arndt 2012; Grandia et al. 2003; Leach et al. 1996, 2005; Marie and Kesler 2000; Savard et al. 2000). Instabilities of metal complexes and thus metal precipitation are seldom affected by temperature. Although the processes can change the properties or composition of the ore fluids such as increasing the sulfur concentration, fluid oxidation and mixing with groundwater (Seward and Barnes 1997), they are difficult to control during our fluid mixing experiments.

Interestingly, when the NaHS solution was titrated into the metal chloride solution the pH value of the mixed solutions became higher and no precipitates were observed until the titration volume was large enough (Fig. 2). This implies that the reactions between metal ions and sulfur species were indeed influenced by the environmental pH and the stability of metal complex. Given that HS^- reacts directly with metal ions according to the Eq. (11), released hydrogen ions should promote the acidity of the fluids while precipitates are observed. On the contrary, the low pH primarily leads to sulfur species transformation from HS^- to H_2S according to the Eq. (1), releasing OH^- to neutralize the fluids. With the neutralization of the fluids, metal chloride complexes are increasingly unstable (Reed 2006), which consequently makes bisulfide complexation and sulfide precipitation happen. Because Eq. (12) produce not only the sulfide precipitations but also hydrogen ions, massive metal precipitation is usually accompanied by the release of hydrogen ions. This distinctly interprets the decline of the pH values at the final stages of our fluid mixing experiments (Fig. 2).

Another interesting observation is that when the initial pH value of the metal chloride solution is approximately 6 drops of NaHS solution titrating, which can immediately produce precipitates (Figs. 2, 3). It no doubt suggests that metal precipitation is much easier to happen at weakly acidic–neutral conditions. At these conditions, on the one hand, metal chloride complexes were less stable (Reed 2006), some of which were replaced by the bisulfide complexes following the Eq. (10); on the other hand, most of HS^- are transformed into H_2S according to the Eq. (1). Therefore, they cause most Pb and Zn ions react directly with H_2S in the ore fluids according to Eq. (12) to produce precipitates.

Given that a weakly acidic–neutral condition is likely to be the most favorable to form Pb–Zn ore deposits, the host carbonate thus plays a crucial role to adjust the environmental pH. In many MVT Pb–Zn ore deposits the ore bodies occur as cement among the carbonate breccia fragments (Anderson and Garven 1987; Sverjensky 1986). This suggests that the ore fluids migrate into and completely react with the carbonate sequences, consequently resulting in their neutralization. During or after this process, released hydrogen ions dissolved the carbonate and thus lead to later precipitation of calcite and dolomite. Therefore, whatever the pathway for the fluid mixing is the first model or the second one, the environmental pH was neutralizing or neutralized before the metal precipitation. This key process caused instabilities of Pb and Zn chloride complexes and re-distribution of sulfur species, and thus facilitated the hydrolysis of Pb and Zn ions and precipitation of sulfides, such as galena, sphalerite and so on.

Besides the above, the nature of low solubility product for sulfide also makes Pb/Zn precipitation happen easily. Previous experiments have demonstrated that the solubility of galena and sphalerite under different temperature, NaCl concentration, and pH conditions was less than 1 ppm, even at temperatures of up to 300 °C (Ewald and Hladky 1980; Barrett and Anderson 1988). Given that the solubility products of PbS and ZnS at 25 °C are K_{sp} (PbS) = 1.3×10^{-36} and K_{sp} (ZnS) = 1.6×10^{-24}, the salt effect was minimal and can be ignored. Therefore, the solubility product of galena and sphalerite in pure water can be used to study the respective precipitation situation of the two metals.

In our experiments, since the NaHS solution was titrated slowly into a large amount of metal-containing solution, the common ion effects caused by the relative excess of metal ions should promote the formation of Pb/Zn precipitates at the first stage. However, because the solubility of the sulfide precipitates was very small, the coordination effect can be not considered, the acid effect is therefore significant during the whole experiments, as described in Sect. 4.2.

5 Conclusion

On the basis of a series of mixing experiments under ambient temperature and pressure conditions on titrating NaHS solution into metal-chloride solutions doping with or without dolomite, we found that metal precipitation during the fluid mixing was influenced by the stability of metal complex and the environmental pH. Because metal chloride complex is stable in an acidic fluids and metal bisulfide complex is in favor of neutral-alkaline environments, sulfur species, the initial pH of ore fluids and the environment pH during metal precipitation govern the stabilities of metal complexes. Therefore, the environment pH was a primary factor controlling the Pb and/or Zn metal precipitation during the fluid mixing associated with the carbonate-hosted Pb–Zn ore deposits.

Thermodynamic calculations on the pH-logf_{O2} and the pH-x diagram from 25 to 250 °C show that although higher temperatures can make the stability field of H_2S expand from acidic to weakly alkaline domain and correspondingly compress the stability field of HS^- from weakly acidic to weakly alkaline domain, it also can promote the distribution proportion of HS^- in the acidic–neutral hydrothermal fluids. Combined with our fluid mixing experimental results, we think that a weakly acidic–neutral condition is likely to be the most favorable condition to form Pb–Zn ore deposits, in which carbonate plays a crucial role in adjusting the environmental pH. Neutralization of the environmental pH driven by the carbonate-ore fluid interaction promote instabilities of Pb and Zn chloride complexes and re-distribution of sulfur species, and thus facilitates the hydrolysis of Pb and Zn ions and precipitation of sulfides. During the fluid mixing reactions H_2S, rather than HS^- or S^{2-} in the solutions, dominates the reactions of Pb and/or Zn precipitation.

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References

Akinfiev NN, Tagirov BR (2014) Zn in hydrothermal systems: thermodynamic description of hydroxide, chloride, and hydrosulfide complexes. Geochem Int 52:197–214

And DJH, Brodholt JP, Sherman DM (2003) Zinc complexation in hydrothermal chloride brines: results from ab initio molecular dynamics calculations. J Phys Chem A 107:614–619

Anderson GM (1973) The hydrothermal transport and deposition of galena and sphalerite near 100 °C. Econ Geol 68:480–492

Anderson GM (1975) Precipitation of Mississippi Valley-type ores. Econ Geol 70:937–942

Anderson GM (1991) Organic maturation and ore precipitation in southeast Missouri. Econ Geol 86:909–926

Anderson CB (1997) Understanding carbonate equilibria by measuring alkalinity in experimental and natural systems. J Geosci Educ 50:389–403

Anderson GM, Garven G (1987) Sulfate-sulfide-carbonate associations in Mississippi valley-type lead–zinc deposits. Econ Geol 82:482–488

Appold MS, Garven G (2000) Reactive flow models of ore formation in the southeast Missouri district. Econ Geol 95:1605–1626

Banks DA, Russell MJ (1992) Fluid mixing during ore deposition at the Tynagh base-metal deposit, Ireland. Eur J Miner 4:921–931

Banks DA, Boyce AJ, Samson IM (2002) Constraints on the origins of fluids forming Irish Zn–Pb–Ba deposits: evidence from the composition of fluid inclusions. Econ Geol 97:471–480

Barrett TJ, Anderson GM (1982) The solubility of sphalerite and galena in NaCl brines. Econ Geol 77:1923–1933

Barrett TJ, Anderson GM (1988) The solubility of sphalerite and galena in 1–5 m NaCl solutions to 300 °C. Geochim Cosmochim Acta 52:813–820

Barton PBJ (1967) Possible role of organic matter in the precipitation of the Mississippi Valley ores. Econ Geol 3:371–377

Basuki NI (2002) A review of fluid inclusion temperatures and salinities in Mississippi Valley-type Zn–Pb deposits: identifying thresholds for metal transport. Explor Min Geol 11:1–17

Beales FW (1975) Precipitation mechanisms for Mississippi valley-type ore deposits; a reply. Econ Geol 70:943–948

Beales FW, Jackson SA (1966) Precipitation of lead–zinc ores in carbonate reservoirs as illustrated by Pine Point ore field, Canada. Inst Min Metall B 75:278–285

Bottrell SH, Crowley S, Self C (2001) Invasion of a karst aquifer by hydrothermal fluids: evidence from stable isotopic compositions of cave mineralization. Geofluids 1:103–121

Bourcier WL, Barnes HL (1987) Ore solution chemistry: VII. Stabilities of chloride and bisulphide complexes of zinc to 350 °C. Econ Geol 82:1839–1863

Brown JS (1970) Mississippi valley type lead-zinc ores. Miner Deposita 5:103–119

Carpenter AB, Trout ML, Pickett EE (1974) Preliminary report on the origin and chemical evolution of lead-and zinc-rich oil field brines in central Mississippi. Econ Geol 69:1191–1206

Conliffe J, Wilton D, Blamey N, Archibald SM (2013) Paleoproterozoic Mississippi Valley type Pb–Zn mineralization in the Ramah Group, Northern Labrador: stable isotope, fluid inclusion and quantitative fluid inclusion gas analyses. Chem Geol 362:211–223

Cooke DR (1996) Epithermal gold mineralization, Acupan, Baguio District, Philippines; geology, mineralization, alteration, and the thermochemical environment of ore deposition. Econ Geol 91:243–272

Corbella M, Ayora C, Cardellach E (2004) Hydrothermal mixing, carbonate dissolution and sulfide precipitation in Mississippi Valley-type deposits. Miner Deposita 39:344–357

Czamanske GK, Roedder E, Burns FC (1963) Neutron activation analysis of fluid inclusions for copper, manganese, and zinc. Science 140:401–403

Daskalakis KD, Helz GR (1993) The solubility of sphalerite (ZnS) in sulfidic solutions at 25 °C and 1 atm pressure. Geochim Cosmochim Acta 57:4923–4931

Emsbo P (2000) Gold in sedex deposits. SEG Rev 13:427–437

Ewald AH, Hladky G (1980) Solubility measurements on sphalerite. CSIRO Div Miner Inv Rep 136:68

Fan HR, Groves DI, Mikucki EJ, McNaughton NJ (2001) Fluid mixing in the generation of Nevoria gold mineralization in the Southern Cross greenstone belt, Western Australia. Miner Depos 20:37–43

Fang WX, Li JX (2014) Metallogenic regulations, controlling factors, and evolutions of iron oxide copper and gold deposits in Chile. Adv Earth Sci 29:1011–1024

Fraser DG, Feltham D, Whiteman M (1989) High-resolution scanning proton microprobe studies of micron-scale trace element zoning in a secondary dolomite: implications for studies of redox behaviour in dolomites. Sediment Geol 65:223–232

Ganino C, Arndt N (2012) Metals and society: an introduction to economic geology. Springer, Berlin

Gerdemann PE, Myers HE (1972) Relationships of carbonate facies patterns to ore distribution and to ore genesis in the southeast Missouri lead district. Econ Geol 67:426–433

Giordano TH (2002) Transport of Pb and Zn by carboxylate complexes in basinal ore fluids and related petroleum-field brines at 100 C: the influence of pH and oxygen fugacity. Geochem Trans 3:56

Giordano TH, Barnes HL (1979) Ore solution chemistry VI; PbS solubility in bisulfide solutions to 300 °C. Econ Geol 74:1637–1646

Giordano TH, Barnes HL (1981) Lead transport in Mississippi Valley-type ore solutions. Econ Geol 76:2200–2211

Grandia F, Canals A, Cardellach E, Banks DA, Perona J (2003) Origin of ore-forming brines in sediment-hosted Zn-Pb deposits of the Basque-Cantabrian Basin, Northern Spain. Econ Geol 98:1397–1411

Gratz JF, Misra KC (1987) Fluid inclusion study of the Gordonsville zinc deposit, central Tennessee. Econ Geol 82:1790–1804

Gregg JM (1985) Regional epigenetic dolomitization in the Bonneterre Dolomite (Cambrian), southeastern Missouri. Geology 13:503

Han RS, Liu CQ, Huang ZL, Chen J, Ma DY, Lei L, Ma GS (2007) Geological features and origin of the Huize carbonate-hosted Zn–Pb–(Ag) District, Yunnan, South China. Ore Geol Rev 31:360–383

Han RS, Li B, Ni P, Qiu WL, Wang XD, Wang TG (2016) Infrared micro-thermometry of fluid inclusions in sphalerite and geological significance of the huize super-large Zn–Pb–(Ge–Ag) deposit, Yunnan Province. J Jilin Univ Earth Sci Ed 46:91–104

Hayashi K, Sugaki A, Kitakaze A (1990) Solubility of sphalerite in aqueous sulfide solutions at temperatures between 25 and 240 °C. Geochim Cosmochim Acta 54:715–725

Haynes DW, Cross KC, Bills RT, Reed MH (1995) Olympic Dam ore genesis; a fluid-mixing model. Econ Geol 90:281–307

Henley RW (1984) The geothermal framework of epithermal deposits. In: Berger BR, Bethke PM (eds) Geology and geochemistry of epithermal system: society of economic geologists. Rev Econ Geol, vol 2, pp 1–24

Henley RW, Truesdell AH, Barton PB Jr, Whitney JA (1984) Fluid mineral equilibria in hydrothermal systems. Rev Econ Geol 1:267

Hennig W (1971) Löslichkeit von Zinkblende unter hydrothermalen Bedingungen im System ZnS-NaC1-H_2O. Neues Jahrb Mineralogie Abh 116:61–79

Hofstra AH, Northrop HR, Rye RO, Landis GP, Birak DJ (1988) Origin of sediment-hosted disseminated gold deposits by fluid mixing: Evidence from jasperoids in the Jerritt Canyon gold district, Nevada, USA. In: Bicentennial gold '88, geological society of Australia, oral programme, vol 22, pp 284–289

Jazi MA, Karimpour MH, Shafaroudi AM (2017) Nakhlak carbonate-hosted Pb (Ag) deposit, Isfahan province, Iran: a geological, mineralogical, geochemical, fluid inclusion, and sulfur isotope study. Ore Geol Rev 80:27–47

Jiang SH, Nie FJ, Yi Z, Peng HU (2004) The latest advances in the research of epithermal deposits. Earth Sci Front 11:401–411

Kendrick MA, Burgess R, Pattrick RAD, Turner G (2002) Hydrothemal fluid origins in a flourite-rich Mississippi Valley-type district: combined noble gas (He, Ar, Kr) and halogen (CI, Br, I) analysis of fluid inclusions from the South Pennine ore field, United Kingdom. Econ Geol 97:435–451

Kesler SE, Friedman GM, Krstic D (1997) Mississippi valley-type mineralization in the Silurian paleoaquifer, central Appalachians. Chem Geol 138:127–134

Leach DL, Rowan EL, Shelton KL, Bauer RM, Gregg JM (1993) Fluid-inclusion studies of regionally extensive epigenetic dolomites, Bonneterre Dolomite (Cambrian), southeast Missouri: evidence of multiple fluids during dolomitization and lead-zinc mineralization: alternative interpretation and reply. Geol Soc Am Bull 105:968–978

Leach DD, Viets JG, Kozłowski A, Kibitlewski S (1996) Geology, geochemistry, and genesis of the Silesia-Cracow zinc–lead district, southern Poland. Econ Geol 4:144–170

Leach DL, Bradley D, Lewchuk MT, Symons DT, Marsily GD, Brannon J (2001) Mississippi Valley-type lead–zinc deposits through geological time: implications from recent age-dating research. Miner Deposita 36:711–740

Leach DL, Marsh E, Emsbo P, Rombach CS, Kelley KD, Anthony M (2004) Nature of hydrothermal fluids at the shale-hosted red dog Zn–Pb–Ag deposits, Brooks Range, Alaska. Econ Geol 99:1449–1480

Leach DL, Sangster DF, Kelley KD, Large RR, Garven G, Allen CR, Gutzmer J, Walters S (2005) Sediment-hosted lead-zinc deposits: a global perspective. Econ Geol 100:561–607

Leach D, Macquar JC, Lagneau V, Leventhal J, Emsbo P, Premo W (2006) Precipitation of lead–zinc ores in the Mississippi Valley-type deposit at Trèves, Cévennes region of southern France. Geofluids 6:24–44

Li XJ, Liu W (2002) Fluid inclusion and stable isotope constraints on the genesis of the Mazhuangshan gold deposit, eastern Tianshan Mountains of China. Acta Petrol Sin 18:551–558

Lin CX, Bai ZH, Zhang ZR (1985) The thermodynamic manual book of minerals and related compounds. Science Press, Beijing

Lyle JR (1977) Petrography and carbonate diagenesis of the Bonneterre Formation in the Viburnum Trend area, southeast Missouri. Econ Geol 72:420–434

Manning CE (2011) Sulfur surprises in deep geological fluids. Science 331:1018–1019

Marie JS, Kesler SE (2000) Iron-rich and iron-poor Mississippi Valley-type mineralization, Metaline District, Washington. Econ Geol 95:1091–1106

Melent'Yev BN, Ivanenko VV, Pamfilova LA (1969) Solubility of some ore-forming sulfides under hydrothermal conditions. Geochem Internet 6:416–460

Misra KC (2000) Mississippi Valley-type (MVT) zinc–lead deposits. Springer, Dordrecht

Ohle EL (1985) Breccias in Mississippi Valley-type deposits. Econ Geol 80:1736–1752

Oxtoby DW, Gillis HP, Campion A (2012) Principles of modern chemistry, 7th edn, Cengage learning, New York.

Petrucci RH, Harwood WS (1977) General chemistry: principles and modern applications. Macmillan, New York

Pinckney DM, Haffty J (1970) Content of zinc and copper in some fluid inclusions from the Cave-in-Rock District, southern Illinois. Econ Geol 65:451–458

Pirajno F (1992) Hydrothermal mineral deposits. Springer, Berlin

Plumlee GS (1994) Fluid chemistry evolution and mineral deposition in the main-stage Creede epithermal system. Econ Geol Bull Soc Econ Geol 89:1860–1882

Plumlee GS, Leach DL, Hofstra AH, Landis GP, Rowan EL, Viets JG (1994) Chemical reaction path modeling of ore deposition in Mississippi Valley-type Pb-Zn deposits of the Ozark region, US midcontinent. Econ Geol 90:1346–1349

Pokrovski GS, Dubrovinsky LS (2011) The S3-ion is stable in geological fluids at elevated temperatures and pressures. Science 331:1052–1054

Reed MH (2006) Sulfide mineral precipitation from hydrothermal fluids. Rev Mineral Geochem 61:609–631

Reed MH, Spycher NF (1985) Boiling, cooling, and oxidation in epithermal systems: a numerical modeling approach. Rev Econ Geol 61:249–272

Robb L (2005) Introduction to ore-forming processes. Blackwell Publishing, Oxford

Roedder E (1977) Fluid inclusion studies of ore deposits in the Viburnum Trend, Southeast Missouri. Econ Geol 72:474–479

Rowan EL (1987) Homogenization temperatures and salinities of fluid inclusions from the Viburnum Trend, Southeast Missouri, and the northern Arkansas zinc distict. Endoscopy 30:69–87

Samson IM, Russell MJ (1987) Genesis of the Silvermines zinc–lead-barite deposit, Ireland; fluid inclusion and stable isotope evidence. Econ Geol 82:371–394

Sass-Gustkiewicz M, Dzulyński S (1998) On the origin of strata-bound Zn–Pb ores in the Upper Silesia, Poland. Ann Soc Geol Pol 68:267–278

Savard MM, Chi G, Sami T, Williams-Jones AE, Leigh K (2000) Fluid inclusion and carbon, oxygen, and strontium isotope study of the Polaris Mississippi Valley-type Zn–Pb deposit, Canadian Arctic Archipelago: implications for ore genesis. Miner Deposita 35:495–510

Seward TM (1984) The formation of lead (II) chloride complexes to 300 °C: a spectrophotometric study. Geochim Cosmochim Acta 48:121–134

Seward TM, Barne HL (1997) Metal transport by hydrothermal ore fluids. In: Barnes HL (ed) Geochemistry of hydrothermal ore deposits, Wiley, New York, pp 435–486

Stoffell B, Appold MS, Wilkinson JJ, Mcclean NA, Jeffries TE (2008) Geochemistry and evolution of Mississippi Valley-type mineralizing brines from the Tri-State and northern Arkansas districts determined by LA-ICP-MS microanalysis of fluid inclusions. Econ Geol 103:1411–1435

Sverjensky DA (1986) Genesis of Mississippi Valley-type lead–zinc desposits. Annu Rev Earth Planet Sci 14:177

Tagirov BR, Seward TM (2010) Hydrosulfide/sulfide complexes of zinc to 250 °C and the thermodynamic properties of sphalerite. Chem Geol 269:301–311

Tagirov B, Zotov A, Schott J, Suleimenov O, Koroleva L (2007a) A potentiometric study of the stability of aqueous yttrium–acetate complexes from 25 to 175 °C and 1–1000 bar. Geochim Cosmochim Acta 71:1689–1708

Tagirov BR, Suleimenov OM, Seward TM (2007b) Zinc complexation in aqueous sulfide solutions: determination of the stoichiometry and stability of complexes via ZnS (cr) solubility measurements at 100 °C and 150 bars. Geochim Cosmochim Acta 71:4942–4953

Tossell JA (2012) Calculation of the properties of the S3—radical anion and its complexes with Cu+ in aqueous solution. Geochim Cosmochim Acta 95:79–92

Wilkinson JJ (2001) Fluid inclusions in hydrothermal ore deposits. Lithos 55:229–272

Wilkinson JJ, Stoffell B, Wilkinson CC, Jeffries TE, Appold MS (2009) Anomalously metal-rich fluids form hydrothermal ore deposits. Science 323:764–767

Yardley BWD (2005) Metal concentrations in crustal fluids and their relationship to ore formation. Econ Geol 100:613–632

Zhang CQ, Jinjie YU, Mao JW, Rui ZY (2009) Advances in the study of Mississippi Valley-type deposits. Miner Depos 28:195–210

Zhang Y, Han R, Wei P, Qiu W (2014a) Thermodynamic study on paragenesis and separation of lead and zinc-taking the Zhaotong Pb–Zn deposit in Northeastern Yunnan, China as a case. Acta Geol Sin 88:247–248

Zhang Y, Han R, Wu P, Zhou G, Wei P, Qiu W (2014b) The restrictions of fO2 and fS2 for lead–zinc paragenesis and separation of the Zhaotong Huize-type Pb–Zn deposit in Northeast Yunnan, China. Geotecton Et Metallog 38:898–907

Zhong R, Brugger J, Chen Y, Li W (2015) Contrasting regimes of Cu, Zn and Pb transport in ore-forming hydrothermal fluids. Chem Geol 395:154–164