Research Article

Precipitation Reaction Mechanisms of Mineral Deposits Simulated with a Fluid Mixing Model

Yan Zhang,1 Runsheng Han,1 Xing Ding,2,3 Yurong Wang,2 and Pingtang Wei4

1Kunming University of Science and Technology, Southwest Geological Survey, Geological Survey Center for Non-ferrous Mineral Resources, Kunming 650093, China
2State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
3CAS Center for Excellence in Tibetan Plateau Earth Sciences, Beijing 100101, China
4Kunming Geological Prospecting Institute, China Metallurgical Geological Bureau, Kunming 650024, China

Correspondence should be addressed to Runsheng Han; 554670042@qq.com

Received 16 September 2020; Revised 31 December 2020; Accepted 23 January 2021; Published 22 February 2021

Academic Editor: Giovanni Mongelli

Copyright © 2021 Yan Zhang et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Nonmagmatic, carbonate-hosted epigenetic hydrothermal Pb–Zn deposits similar to those at the Huize Pb–Zn Mine are widespread across the Sichuan–Yunnan–Guizhou (SYG) polymetallic province. The precipitation mechanisms of these geologically intriguing deposits are an area of interest for many researchers. To simulate the underlying precipitation reaction mechanisms and dynamics of each aspect, a fluid mixing model for metal sulfide precipitation was used in a series of experiments, where solutions that contain Pb/Zn chloride complexes and sulfide were subjected to pH changes, water-rock reactions, and dilutions. Based on the results of these experiments, thermodynamic phase diagrams, and other experimental findings, a fluid mixing genetic model was developed for SYG Pb–Zn deposits, and this model was used to analyze the mechanisms of metal sulfide precipitation. The results indicate that acidic fluids in the form of chloride complexes transported Pb and Zn, whereas sulfide exists in the form of H2S within these fluids. The precipitation of metal sulfides occurs when these fluids undergo changes in pH, water-rock reactions, or isothermal dilution. The pH changes were found to be the most effective method for the induction of sulfide precipitation, followed by dilution and then water-rock reactions. The formation of sulfide precipitates due to pH changes, water-rock reactions, and dilution can be attributed to a single mechanism, i.e., changes in the pH of the fluid. Therefore, changes in pH are the primary mechanism of sulfide precipitation.

1. Introduction

Since the 1990s, there have been numerous studies on the Pb–Zn deposits in the Sichuan–Yunnan–Guizhou (SYG) polymetallic region, which are typified by the Huize Pb–Zn deposit. These studies have yielded several important discoveries regarding the geological background of this region and the geological features of its deposits [1–7], most notably in terms of the deposit geochemistry [4, 8–16], the structure of the ore field [4, 5, 7], and the genesis of these deposits [1, 2, 4, 8, 11, 17]. Based on the unique geological characteristics of the mineral deposits in the SYG region (i.e., the high-grade ore, the tremendous scale of their metal reserves and large size of a single orebody, the large number of associated components, the significant depth of the orebodies, the high mineralization temperature, the elevated alteration strength, and the evident mineral assemblage zoning), Han et al. [5, 18] proposed that the nonmagmatic, carbonate-hosted epigenetic hydrothermal Pb–Zn deposits can be divided into two “end-members,” i.e., Mississippi Valley-type (MVT) and Huize-type (HZT) Pb–Zn deposits.

The mechanisms of sulfide precipitation in the Huize Pb–Zn deposit are as follows:

(1) Fluid Mixing. Based on C–O isotopic analysis, Huang et al. [11, 19–21] concluded that fluid mixing is a critical
process for mineralization. Luo et al. [22] proposed that fluid mixing is the main mechanism for metal precipitation; these insights were based on the findings of previous fluid inclusion studies. By analyzing Sr isotopic compositions and fluid inclusions, Zhang et al. [23–25] concluded that fluid mixing and boiling are the primary causes of sulfide precipitation.

(2) Boiling. Han et al. [5, 26, 27] proposed that decompression boiling is one of the most important mechanisms for Pb/Zn enrichment and mineralization. 

(3) pH Changes. Zhou [28], Yan [29], and Zhong et al. [30] all agree that changes in the pH are the primary cause of sulfide precipitation.

In summary, the mechanisms of sulfide precipitation have been investigated via fluid inclusion studies, as well as trace element and isotopic tracing methods. However, the findings of these studies have not been validated by complementary methods, such that the evolution process of the mineralization fluids has yet to be fully elucidated because of the experimental limitations of such studies. Based on the findings of previous geological studies and other research data, Zhang et al. [15, 16, 31–33] conducted a series of fluid inclusion studies, isotopic analyses, thermodynamic analyses, and mineralization experiments at ambient temperature and pressure. Based on their observations, they concluded that fluid mixing is the primary mechanism for metal sulfide precipitation from hydrothermal fluids in the Huize Pb–Zn deposit.

Zhang et al. [31] performed a series of mixing experiments at ambient temperature and pressure, where NaHS was titrated into metal chloride solutions (with and without dolomite rocks); they found that metal precipitation during fluid mixing depends on the stability of the metal complexes involved in this process and the pH of the mixing environment. The environmental pH, in particular, is the primary determining factor for metal precipitation during fluid mixing. The aforementioned mixing process is a process that couples pH changes, water-rock interactions, and dilution, where the subprocesses, mechanisms, and results of this process have already been studied and discussed in significant detail [31, 32]. However, when the pH changes, water-rock interactions and dilutions occur in isolation. Thus, the exact chemical reactions that lead to metal precipitation in the form of sulfide complexes have yet to be identified, and little is known about the dynamics of their chemical reactions or the factors that control the rate and occurrence of these chemical reactions. Nonetheless, with regard to the standalone effects of pH changes, water-rock interactions, and dilutions, we can assume that the following process occurs: when subsurface fluids migrate in massive quantities over long distances, the metal-bearing fluid extracts small amounts of sulfide throughout this process. As the fluid is acidic and the sulfide concentration is insufficient to induce precipitation, the chloride complexes of Pb and Zn are much more stable than their sulfur–hydrogen counterparts under these conditions. Therefore, Pb/Zn and sulfides exist within the mineralization fluid as chloride complexes and H₂S, respectively. However, if a change occurs in the physical and chemical conditions of the fluid, the Pb/Zn chloride complexes become unstable and the Pb/Zn elements bind to the sulfides instead, which in turn leads to their precipitation as metal sulfides. In this study, a series of geochemistry experiments were performed, where solutions that contain Pb/Zn chloride complexes and sulfide were subjected to pH changes, water-rock reactions, and dilution. Based on the results of these experiments, thermodynamic phase diagrams, and other experimental data, a fluid mixing genetic model for SYG Pb–Zn deposits was developed to elucidate the reaction mechanisms by which metal element precipitation occurs in these deposits.

2. Materials and Methods

2.1. Preparation of the Solutions and Specimens. Carpenter et al. [34] first measured the metal concentration of basin brines from an MVT deposit. They analyzed the oil field brines of tens of deposits from the Gulf Coast and observed Pb and Zn concentrations up to 111 and 575 ppm, respectively. In a review of sedimentary basins around the world, Yardley [35] reported observations of Pb and Zn concentrations of up to 100 ppm and several hundred ppm in crustal fluids. A few early studies on the MVT deposits from the Cave-in-Rock district of southern Illinois also detected high metal concentrations in fluid inclusions from these deposits [36, 37]. Czamanske et al. [36] observed Zn concentrations greater than 500 ppm in fluorite fluid inclusions, whereas Pinckney and Haffty [37] reported Zn concentrations between 10 and 1040 ppm in the fluid inclusions of various crystals. In general, the age of mineralization correlates with the metal concentration of the accompanying fluid inclusions (with higher metal concentrations in early-stage mineralization material), but these concentrations are highly variable. Stoffell et al. [38] used laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to analyze the metal concentrations of single fluid inclusions from MVT deposits in northern Arkansas and the Tri-State district. They found that the Pb and Zn concentrations of these fluid inclusions range between 0.7 and 95 ppm and 0.2 and 400 ppm, respectively. The highest metal concentrations in both of these districts were found in sphalerite-hosted inclusions. The Zn concentrations of quartz- and calcite-hosted inclusions from these districts range from 0.1 to 34 ppm. Based on LA-ICP-MS analyses of the Pb concentration of fluid inclusions from the MVT deposits of northern Arkansas and the Zn/Pb ratio of their basin brines, Wilkinson et al. [39] estimated that the Zn concentration of these fluid inclusions may be as high as 3000 ppm. The metal concentrations they observed in sphalerite-hosted inclusions were more than two orders of magnitude greater than those of cogenetic gangue-hosted inclusions.

In this study, Pb/Zn solutions were prepared with a Pb concentration of 100 ppm and Zn concentration of 500 ppm. Let \( b = \omega M \rho / 1000 \), where \( b \) is the moality, \( \omega \) is the mass concentration, \( \rho \) is the density, and \( M \) is the molar mass. Inputting \( \omega \rho_p = 100, M_{Pb} = 207.2, \omega \rho_z = 500, M_{Zn} = 65.41 \), and \( \rho = 1 \) into this equation yields \( b_{Pb} = 0.00048 \) mol/
kg and $b_{Zn} = 0.0076$ mol/kg. To simplify the calculations, the values of $b_{Pb}$ and $b_{Zn}$ were rounded to 0.0005 mol/kg and 0.01 mol/kg, which correspond to the mass concentrations of 103.6 and 654.1 ppm, respectively.

High-oxidation-state metal ions, such as Fe$^{3+}$ and Al$^{3+}$, undergo intense hydrolysis reactions in aqueous solutions. Similarly, divalent metal ions, such as Fe$^{2+}$, Cu$^{2+}$, Pb$^{2+}$, and Zn$^{2+}$, may also be hydrolyzed to a certain extent. As the precipitation of metal sulfides is directly determined by the solution pH, it also poses the greatest hindrance to element transport. Therefore, during the preparation of the Pb/Zn solutions, their pH must be carefully controlled to prevent cationic hydrolysis (Table 1). According to Le Chatelier’s principle, increasing the H$^+$ concentration (acidifying the solution) will shift the reaction equilibrium to the left (see Table 1). Hence, metal hydrolysis can be prevented by acidifying the solution.

The stability constant of metal chloride complexes is at least four orders of magnitude greater than that of metal hydroxide complexes (Table 2). Therefore, the former is much more stable than the latter. White flocculent precipitates appear immediately if a 2.5 mol/L ZnCl$_2$ solution is much more stable than the latter. White hydroxide complexes (Table 2). Therefore, the former is least four orders of magnitude greater than that of metal

An aqueous solution of 2.922, 0.0277, and 0.0508 g of analytical grade NaCl, CaCl$_2$, and MgCl$_2$, respectively, were added to a beaker that was previously washed with deionized water, followed by the addition of approximately 100 mL of deionized water. The solution was stirred thoroughly using a stirring rod. Then, 0.3408 g of ZnCl$_2$, and 0.0348 g of PbCl$_2$ were added to the salt solution. To prevent Pb and Zn hydrolysis, a few drops of HCl were added to reduce the solution pH to <2. This also ensured that precipitation would not occur during NaHS titration. A total of 25 mL of 0.001 mol/kg NaHS was added to another beaker, and this solution was diluted to 100 mL. A pipette was used to titrate NaHS into the previously prepared Pb/Zn salt solution while it was stirred continuously. After the addition of NaHS, the solution was transferred to a 250 mL volumetric flask. Deionized water was used to wash the previously used beaker and glass rod, and the wash was then transferred to the volumetric flask. Finally, the solution was brought up to 250 mL in the volumetric flask and shaken thoroughly. In this solution, $b_{PbCl2} = 0.0005$ mol/kg, $b_{ZnCl2} = 0.01$ mol/kg, $b_{NaCl} = 2$ mol/kg, $b_{CaCl2} = 0.002$ mol/kg, and $b_{MgCl2} = 0.002$ mol/kg.

Before preparing mixed solution (c), experiments were carried out to ensure that no precipitates, even in minuscule amounts, would occur when the pH was less than 2. The specific process was as follows. To prevent Pb and Zn hydrolysis, a few drops of HCl were added to change the solution pH, and a pH meter was used to measure the pH. A pipette was used to titrate NaHS into the previously prepared Pb/Zn salt solution while it was stirred continuously. Finally, water was added for a final solution volume of 250 mL in the volumetric flask. These solutions were sent to the ALS Laboratory Group for measurements of the Pb and Zn concentrations. The test showed that when the pH was less than 2, $\omega_{Pb} = 104 – 110$ ppm and $\omega_{Zn} = 665 – 675$ ppm, which were within the allowable error range of the calculated value (103.6 and 654.1 ppm). When the pH value was higher than 3, the measured value was clearly lower than the calculated value, which indicates that precipitates were produced during the preparation process of the solution. Therefore, it was concluded that when the pH is less than 2, the addition of the NaHS solution does not lead to the production of precipitates.

All of the reagents used in the preparation process were of analytical grade, and all of the water used in this experiment was ultrapure deionized water.

2.2. Experimental Schemes and Methods. The following processes were simulated in this study: simple pH changes, water-rock reactions, and isothermal dilution (simple dilution, dilution after short-lived water-rock interactions, and dilution after extensive water-rock interactions). These simulations are described in detail below:

(1) pH Changes. 20 mL of mixed solution (c) was poured into a small plastic bottle, and HCl and NaOH were used to adjust
As it is possible for different types of dilution to occur during a single geological process, we designed a variety of processes to observe the precipitation that occurs in the natural world, tectonic stress fields often transport fluids with varying compositions, properties, and temperatures/pressures into the same space, where dilution is ever-present throughout this process. Dilution processes may be either isothermal or nonisothermal, depending on the temperature differences between the reacting fluids (because the experiments required to study nonisothermal dilution and the mechanisms of this process are extremely complex, and nonisothermal dilution will be addressed in another paper). Isothermal dilution includes simple dilution, dilution after short-lived water-rock interactions, and dilution after extensive water-rock interactions, where each of these subprocesses corresponds to a distinct geological process. Although this simplified model of dilution does not encompass all of the processes that occur in nature, it still covers the most important dilution pathways. Most natural dilution processes can be described by one of these subprocesses or some combination of subprocesses.

### Table 2: Stability constants of metal inorganic complexes (25°C).

| Ligands | Metal ion | Number of ligands (n) | log β_n |
|---------|-----------|-----------------------|---------|
| Cl^-    | Pb^{2+}   | 1, 2, 3               | 1.42, 2.23, 3.23 |
|         | Zn^{2+}   | 1, 2, 3               | 0.43, 0.61, 0.53, 0.20 |
|         | Pb^{3+}   | 1, 2, 3               | 7.82, 10.85, 14.58 |
|         | Zn^{2+}   | 1, 2, 3               | 4.40, 11.30, 14.14, 17.66 |

β_n is the cumulative stability constant.

### Table 1: Main chemical reactions of Pb and Zn in the NaCl solution.

| No. | Reaction equation | No. | Reaction equation |
|-----|------------------|-----|------------------|
| 1   | Zn^{2+} + H_2O ^= ZnOH^+ + H^+ | 11  | Pb^{2+} + H_2O ^= PbOH^+ + H^+ |
| 2   | Zn^{2+} + 2H_2O ^= Zn(OH)_2 + 2H^+ | 12  | Pb^{2+} + 2H_2O ^= Pb(OH)_2 + 2H^+ |
| 3   | Zn^{2+} + 3H_2O ^= Zn(OH)_3^- + 3H^+ | 13  | Pb^{2+} + 3H_2O ^= Pb(OH)_3^- + 3H^+ |
| 4   | Zn^{2+} + 4H_2O ^= Zn(OH)_4^- + 4H^+ | 14  | PbCl_2 + 2NaCl ^= Na_2PbCl_3^- + 3Cl^- |
| 5   | ZnCl_2 + 2NaCl ^= Na_2ZnCl_3^+ + 3Cl^- | 15  | PbCl_2 + 2NaCl ^= Na_2PbCl_3^- + 2Cl^- |
| 6   | ZnCl_2 + 2NaCl ^= Na_2ZnCl_4^- + 2Cl^- | 16  | PbCl_2 + 2NaCl ^= Na_2PbCl_4^- + Cl^- |
| 7   | ZnCl_2 + 2NaCl ^= Na_2ZnCl_3^+ + Cl^- | 17  | PbCl_2 + 2NaCl ^= Na_2PbCl_4^- + Cl^- |
| 8   | ZnCl_2 + 2NaCl ^= Na_2ZnCl_4^- | 18  | PbCl_2 + 2NaCl ^= Na_2PbCl_4^- |

(2) Water-Rock Reactions. Water-rock reactions were simulated by observing the reaction between mixed solution ① (a metal chloride complex system with a set quantity of NaHS) and dolomite at varying temperatures (25, 50, 75, 100, and 150°C). Mixed solution ① was used as the control for this experiment. The water-rock interaction experiments performed by Zhang et al. [32] using mixed solution ① indicated that the water-rock reactions reach equilibrium after 48 h. Hence, all of the water-rock reaction experiments in this study were performed with a reaction time of 48 h. With regard to the experimental method, 10 mL of mixed solution ① or ② was decanted into a 20 mL sealed centrifuge tube (or a polychlorofluorocarbon- (PTFE-) lined Morey vessel) to which 0.5 g of 40-mesh dolomite was added. The mixture was then placed in a thermostatic bath (50 and 75°C) or muffle furnace (100 and 150°C). After the mixture was allowed to react for two days, it was removed from the reaction vessel and then centrifuged and filtered. The supernatant was sent to the ALS Laboratory Group for measurements of the Pb and Zn concentrations. The 25°C experiment was performed at ambient temperature, while the 50 and 75°C experiments were performed in a thermostatic bath. The 100 and 150°C experiments were performed in a muffle furnace using the PTFE-lined Morey vessel as the reaction vessel.

### Figure 1: pH – log a_{Zn^{2+}} diagram.

These solutions to different levels of acidity. The pH value of the prepared mixed solution ① was 1.81, and the experimental pH ranged from 1 to 10, for which 0.3 mol/L HCl was added when necessary to obtain the experimental solution with a pH of 1. To ensure the addition of the least amount of NaOH as possible, a series of different concentrations of NaOH (CNaOH = 0.0000001 – 0.1 mol/L) were used. After pH adjustment, the mixture was centrifuged and filtered. The supernatant was sent to the ALS Laboratory Group for measurements of the Pb and Zn concentrations via ICP-MS analyses, and the control was a sample whose acidity was not adjusted.

(2) Water-Rock Reactions. Water-rock reactions were simulated by observing the reaction between mixed solution ① (a metal chloride complex system with a set quantity of NaHS) and dolomite at varying temperatures (25, 50, 75, 100, and 150°C). Mixed solution ① was used as the control for this experiment. The water-rock interaction experiments performed by Zhang et al. [32] using mixed solution ① indicated that the water-rock reactions reach equilibrium after 48 h. Hence, all of the water-rock reaction experiments in this study were performed with a reaction time of 48 h. With regard to the experimental method, 10 mL of mixed solution ① or ② was decanted into a 20 mL sealed centrifuge tube (or a polychlorofluorocarbon- (PTFE-) lined Morey vessel) to which 0.5 g of 40-mesh dolomite was added. The mixture was then placed in a thermostatic bath (50 and 75°C) or muffle furnace (100 and 150°C). After the mixture was allowed to react for two days, it was removed from the reaction vessel and then centrifuged and filtered. The supernatant was sent to the ALS Laboratory Group for measurements of the Pb and Zn concentrations. The 25°C experiment was performed at ambient temperature, while the 50 and 75°C experiments were performed in a thermostatic bath. The 100 and 150°C experiments were performed in a muffle furnace using the PTFE-lined Morey vessel as the reaction vessel.

(3) Isothermal Dilution. In the natural world, tectonic stress fields often transport fluids with varying compositions, properties, and temperatures/pressures into the same space, where dilution is ever-present throughout this process. Dilution processes may be either isothermal or nonisothermal, depending on the temperature differences between the reacting fluids (because the experiments required to study nonisothermal dilution and the mechanisms of this process are extremely complex, and nonisothermal dilution will be addressed in another paper). Isothermal dilution includes simple dilution, dilution after short-lived water-rock interactions, and dilution after extensive water-rock interactions, where each of these subprocesses corresponds to a distinct geological process. Although this simplified model of dilution does not encompass all of the processes that occur in nature, it still covers the most important dilution pathways. Most natural dilution processes can be described by one of these subprocesses or some combination of subprocesses.

As it is possible for different types of dilution to occur during a single geological process, we designed a variety of processes to observe the precipitation that occurs in the
presence/absence of host rocks with different diluents, dilution volumes, and reaction times. The procedures used in this experiment were as follows.

A total of 10 mL of mixed solution was decanted into a 50 mL plastic bottle, and the following steps were implemented:

1. A pH meter was used to measure pH, the pH of the solution prior to dilution. Then, 10 or 20 mL of pure water or 2 mol/L NaCl was used to dilute the solution.
2. A pH meter was used to measure pH, the pH of the solution prior to adding the dolomite. Next, 0.2000 g of 40-mesh dolomite was added to the solution, and pH was measured after the solution was left overnight. The solution was then diluted with 10 or 20 mL of pure water or 2 mol/L NaCl.
3. A pH meter was used to measure pH, the pH of the solution prior to adding the dolomite. Another 0.2000 g of 40-mesh dolomite was added to the solution, and pH was measured after 10 min. Another 10 or 20 mL of pure water or 2 mol/L NaCl was added to dilute the solution.

We measured pH after the dilution; the solution was filtered and centrifuged, and the supernatant was sent to the ALS Laboratory Group for measurements of the Pb and Zn concentrations. Procedures (1), (2), and (3) were meant to approximate the following geological processes:

1. The dilution of metal-carrying fluids by 1- or 2-fold their volume in atmospheric precipitation or brine while the fluids were still moving.
2. The dilution of metal-carrying fluids that entered the mineralization space and thoroughly reacted with dolomite host rocks by 1- or 2-fold their volume in atmospheric precipitation or brine.
3. The dilution of metal-carrying fluids that entered the mineralization space and reacted with dolomite host rocks for a brief period (10 min) by 1- or 2-fold their volume in atmospheric precipitation or brine.

2.3. Analytical Methods. In the experiment, we used ICP-MS to measure the lead and zinc content in the blank and the supernatant, and the precipitation amount was obtained by subtracting the content of the supernatant from that of the blank.

The solutions were sent to the ALS Laboratory Group for measurements of the Pb and Zn concentrations. The pH measurements were performed at the Laboratory for High-Temperature and High-Pressure Hydrothermal Experiments of the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, and the electron probe microanalyzer (EPMA) measurements were carried out at the Analysis and Testing Center of the South China University of Technology.

The pH meter used in our experiments was a Mettler Toledo pH meter, and the pH meter was calibrated at three points every day by using freshly prepared buffer solutions (GGJ-119).

The EPMA used in these experiments was a Shimadzu EPMA-1600 (Japan), which was equipped with an EDAX Genesis energy-dispersive spectrometer (USA). The parameters of the EPMA measurements were as follows: acceleration voltage of 2.0 kV, secondary electron image resolution of 6 nm, X-ray take-off angle of 52.5°, and energy resolution of 120 eV.

3. Results

3.1. pH Changes. In this experiment, only a few drops of HCl or NaOH were used to adjust the pH of the Pb/Zn solution, which had a volume of 20 mL. Therefore, the dilution caused by HCl or NaOH addition was negligible, and it may be assumed that any precipitation that occurred in this experiment was purely caused by pH changes. The EPMA results show that precipitation can be caused by simply altering the pH of mixed solution, and the precipitates were identified as sulfides of Pb and Zn (Table 3 and Figure 2). In Table 4 and Figure 2, we can observe that the increase in pH significantly promoted the precipitation of Pb and Zn sulfides. Precipitation began to occur at pH > 4, where the precipitation rates of Pb and Zn were 85% and 35%, respectively, when pH > 6. At pH = 7.7, the precipitation rates of Pb and Zn were both 98%. These results are consistent with the findings of Zhang et al. [31] on the mechanisms of Pb and Zn sulfide precipitation during the fluid mixing process, i.e., an increase in pH promotes sulfide precipitation. These experimental results also agree with the results of the CHEM-XPT simulations performed by Reed [40] (Figures 3(c) and 3(d)).

3.2. Water-Rock Reactions. The rate of Pb and Zn precipitation gradually increased with temperature. In the group without NaHS addition, the precipitates included Pb(OH)\(_2\) and Zn(OH)\(_2\) (Reactions (7) and (8)). In the group with NaHS addition, Pb(OH)\(_2\) and Zn(OH)\(_2\) precipitates formed as intermediaries because the solubility products of PbS and ZnS were much lower than those of Pb(OH)\(_2\) and Zn(OH)\(_2\). However, if there was a sufficient supply of sulfide, all of the precipitates were converted into sulfides (Reactions (3)–(6) or (7)–(11)). The precipitation rate of the NaHS-containing group (approximately 35% at 150°C) was slightly higher than that of the group without NaHS at all points, whose Pb and Zn precipitation rates at 150°C were approximately 32% and 25%, respectively (Table 5 and Figure 4).

As there was no visible decrease in the solution in the centrifuge tube before and after the experiment (≤75°C), which indicates that the cover of the centrifuge tube effectively prevented the evaporation of the solution, other methods were not considered for sealing; however, this issue will need to be seriously considered in later experiments at higher temperatures.

3.3. Effects of Fluid Dilution. The results of the dilution experiment (Tables 6 and 7 and Figures 5–7) demonstrate that fluid dilution can induce Pb/Zn sulfide precipitation. As
dilution reduces the concentration of the solution, it follows from Le Chatelier’s principle that \( H_2S \) will become increasingly ionized, which then increases the pH of the solution. This destabilizes the Pb/Zn chloride complexes and triggers the formation of sulfide precipitates. The addition of dolomite increases the pH of the solution through water-rock reactions, and it was observed in XS-14 and XS-15 that some precipitates were formed by the water-rock reaction itself (note: these were Pb/Zn sulfides, not Pb/Zn hydroxides). This occurred because the solubility product of sulfides is much smaller than that of hydroxides, such that the reaction will tend towards the formation of more stable compounds. When pure water or NaCl solution was added to dilute the solution, the precipitates formed by dilution supplemented the precipitates formed by water-rock reactions.

In view of the three geological processes that were meant to be simulated by this experiment, the following conclusions can be drawn:

1. Pure dilution always results in Pb/Zn precipitation rates of approximately 53%–56%, regardless of the diluent (atmospheric precipitation or brine) or volume of dilution (1- or 2-fold the solution volume).

### Table 3: EPMA test results.

| Sample no. | Pb wt. % | Pb At. % | Zn wt. % | Zn At. % | S wt. % | S At. % | C wt. % | C At. % | O wt. % | O At. % | Ca wt. % | Ca At. % | Mg wt. % | Mg At. % |
|------------|----------|----------|----------|----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 0724-6     | 9.32     | 1.4      | 37.57    | 17.85    | 15.25   | 14.77   | 13.04   | 13.04   | 8.83    | 17.13   | 9.4     | 7.28    | 5.11    | 6.54    |

| Sample no. | Si wt. % | Si At. % | Al wt. % | Al At. % | Cl wt. % | Cl At. % | K wt. % | K At. % | Fe wt. % | Fe At. % | P wt. % | P At. % | Ti wt. % | Ti At. % |
|------------|----------|----------|----------|----------|----------|----------|---------|---------|----------|----------|---------|---------|----------|---------|
| 0724-6     | —        | —        | —        | —        | 1.49     | 1.3      | —       | —       | —        | —        | —       | —       | —        | —       |

*Figure 2: Electron probe patterns of 0724-5 and 0724-7.*
(2) In case the metal-carrying fluid enters the mineralization space and only interacts briefly with the dolomite, dilution with an equal volume of pure water or NaCl brine yields the same result as in (1). However, dilution with twice the solution volume causes the effects of water-rock reactions and dilution to stack with each other, which increases the precipitation rate to approximately 70%.

(3) If the metal-carrying fluid is allowed to react extensively with the dolomite host rock after entering the mineralization space, dilution with an equal volume of pure water or NaCl brine increases the precipitation rate of Pb to ~70%. However, the Zn precipitation rate is still the same as that in (1). Dilution with twice the solution volume causes the effects of dilution and water-rock reactions to combine, thus increasing the Pb and Zn precipitation rate to approximately 80 and 70%, respectively.

In summary, simple dilution does induce precipitation to a certain extent. However, dilution induces precipitation much more effectively after the metal-carrying fluid has reacted extensively with its host rocks in the mineralization space. As the diluent and metal-carrying fluid are unlikely to simultaneously reach the mineralization space, this scenario is a more realistic representation of actual geological processes.

4. Discussion

4.1. Sulfide Precipitation and Changes in the Fluid pH. As NaHS is a strong base and weak acid [41, 42], its weak acid anions are easily hydrolyzed in aqueous solutions [41, 42] (see Reaction (1)) to form a weakly alkaline solution, as follows:

\[ \text{HS}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{S(aq)} + \text{OH}^- \] (1)

Additionally, the weak acid anions can dissociate to form a weakly acidic solution, as follows:

\[ \text{HS}^- \rightleftharpoons \text{S}^2^- + \text{H}^+ \] (2)

Reaction (1) occurs under acidic conditions, whereas basic conditions are conducive for Reaction (2) [41, 42]. As the pH of mixed solution ② was less than 4, Reaction (1) was the main reaction that controlled the ratio of H₂S to HS⁻. During the experiment, the dropwise addition of HCl reduced the pH of the solution, thus causing the sulfides and Pb/Zn to exist as H₂S and stable chloride complexes, respectively, in the solution. Dropwise NaOH addition increased the pH, which then caused the sulfides to exist as H₂S, HS⁻, and S²⁻ in pH-dependent ratios [31]. The Pb/Zn chloride complexes gradually became less stable as the solution developed a basic environment, which induced Pb and Zn to bind with sulfides, as shown in the reactions below (this occurred until all of the Pb and Zn precipitated from the solution):

\[ \text{Na}_2\text{MeCl}_{2+n} = \text{Me}^{2+} + 2\text{Cl}^- + 2\text{NaCl} \quad (n = 1, 2, 3, 4) \] (3)

\[ \text{Me}^{2+} + \text{H}_2\text{S} \rightarrow \text{MeS}_n + 2\text{H}^+ \] (4)

\[ \text{Me}^{2+} + \text{HS}^- \rightarrow \text{MeS}_n + \text{H}^+ \] (5)

\[ \text{Me}^{2+} + \text{S}^2^- \rightarrow \text{MeS}_n \] (6)

In the water-rock interaction experiment, both experimental groups exhibited precipitation due to pH increases that were in turn induced by water-rock reactions. In the NaHS-containing group, the Pb/Zn chloride complexes were destabilized by the increase in pH, which led to the formation of sulfide precipitates. In the group without NaHS addition, the increase in pH induced Pb/Zn hydrolysis, which led to the formation of hydroxide precipitates. The reaction by
which pH changes induced hydroxide formation (as an intermediary for sulfide formation) is as follows:

\[ \text{Me}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Me(OH)}_2 + 2\text{H}^+ \]  

The hydroxides then undergo a dehydration reaction to form oxides:

\[ \text{Me(OH)}_2 \rightarrow \text{MeO} + \text{H}_2\text{O} \]  

The Pb/Zn hydroxides and oxides in the fluids or on the surface of carbonate rocks are easily converted into sulfides, as shown in the following equations [43]:

\[ \text{Me(OH)}_2 + \text{H}_2\text{S(aq)} \rightarrow \text{MeS} + 2\text{H}_2\text{O}, \]

\[ \text{MeO(s)} + \text{H}_2\text{S(aq)} \rightarrow \text{MeS} + \text{H}_2\text{O}. \]  

Alternatively,

\[ \text{Me(OH)}_2 + \text{HS}^- \rightarrow \text{MeS} + 2\text{H}_2\text{O} + \text{OH}^-, \]

\[ \text{MeO(s)} + \text{HS}^- \rightarrow \text{MeS} + \text{OH}^- . \]  

Pb and Zn are much more likely to undergo hydrolysis at high temperatures and pressures, but the tendency of Pb and Zn hydroxides to redissolve into the solution makes it difficult to measure their hydrolysis constants. Although the sample did undergo partial redissolution at

---

**Figure 3**: Effects of pH changes on Pb–Zn precipitation (c and d according to Reed [40]). (a, b) Effects of pH changes on Pb and Zn precipitation when the acidity of mixed solution ② was adjusted. (a) Concentration vs. pH. (b) Precipitation rate vs. pH. (c, d) Computational simulations of the effects of pH changes, where NaOH was added to an acidic fluid (1 mol NaCl, initially) with aqueous Pb and Zn to increase its pH from 0.8 to 7 at \( T = 200^\circ\text{C} \). (c) Minerals. (d) Total concentrations of the aqueous components.
each temperature during the aforementioned experiment during the water-rock reactions, our observations indicate that Pb/Zn hydrolysis becomes more acute with increasing temperatures.

Dilution essentially changes the pH of the solution to a pH range that is more amenable for the precipitation of Pb/Zn sulfides. In summary, changes in the pH of the metal-carrying fluid were found to be the primary cause of sulfide precipitation in all of the experiments that were performed in this study. This includes the pH change experiments, as well as the water-rock interaction and dilution experiments that superficially appeared to be independent of pH.

4.2 Differences between the Sulfide Precipitation Mechanisms of MVT and HZT Deposits. The present data show that the pH values of basin brines for a typical MVT deposit range between 5 and 6 [44]. At these pH values, the chloride complexes of Pb and Zn are likely to be insoluble [33, 44–50], where some of the Pb and Zn will precipitate as Pb(OH)\(_2\) and Zn(OH)\(_2\) [32]. Therefore, it is impossible for the basin brines of the MVT deposits to carry high concentrations of mineralizing metals. When fluids carrying metal chloride complexes enter a mineralizing space, water-rock interactions occur owing to the presence of carbonate strata. This depletes the H\(^+\) of the fluid and increases its pH, thus rendering it a neutral or weakly basic solution [51]. If the fluid

| Sample no. | Test value rate (ppm) | Pb Precipitation (ppm) | Precipitation rate (%) | Test value rate (ppm) | Zn Precipitation (ppm) | Precipitation rate (%) | Dolomite mass (g) | Solution type | Temperature |
|------------|----------------------|------------------------|------------------------|----------------------|------------------------|------------------------|------------------|--------------|-------------|
| Sb-16      | 77.2                 | 32.3                   | 29.5                   | 623                  | 95                     | 13.2                   | 0.5037           | ③           | 25°C        |
| Sb-17      | 87.4                 | 22.1                   | 20.2                   | 594                  | 81                     | 12.0                   | 0.5023           | ③           | ③          |
| Sb-18      | 75.3                 | 34.2                   | 31.2                   | 567                  | 151                    | 21.0                   | 0.5036           | ③           | 50°C        |
| Sb-19      | 79.1                 | 30.4                   | 27.8                   | 532                  | 143                    | 21.2                   | 0.5033           | ③           | ③          |
| Sb-20      | 74.9                 | 34.6                   | 31.6                   | 547                  | 171                    | 23.8                   | 0.5024           | ③           | ③          |
| Sb-21      | 75.5                 | 34.0                   | 31.1                   | 523                  | 152                    | 22.5                   | 0.5047           | ③           | 75°C        |
| Sb-22      | 72.4                 | 37.1                   | 33.9                   | 538                  | 180                    | 25.1                   | 0.5015           | ③           | ③          |
| Sb-23      | 74.4                 | 35.1                   | 32.1                   | 518                  | 157                    | 23.3                   | 0.5033           | ③           | 100°C       |
| Sb-24      | 70.9                 | 38.6                   | 35.3                   | 547                  | 171                    | 33.7                   | 0.5047           | ③           | 150°C       |
| Sb-25      | 73.8                 | 35.7                   | 32.6                   | 507                  | 168                    | 24.9                   | 0.5058           | ③           | ③          |
| 0720-1     | 109.5                | —                      | —                      | 675                  | —                      | —                      | —                | Blank        |
| XS-13      | 109.5                | —                      | —                      | 718                  | —                      | —                      | —                | Blank        |

Note: 0720-1 is blank for mixed solution ① and XS-13 is blank for mixed liquid ②.

Figure 4: Temperature-precipitation rate diagram for the water-rock interactions.
| No. | Sample no. | Test value (ppm) | Pb Precipitation (ppm) | Precipitation rate (%) | Test value (ppm) | Zn Precipitation (ppm) | Precipitation rate (%) | Surrounding rock | Diluting fluid | Volume | pH₀ | pH₁ | pH₂ |
|-----|------------|------------------|------------------------|------------------------|------------------|------------------------|------------------------|-------------------|---------------|---------|------|------|------|
| 1   | XS-1       | 49.4             | 60.1                   | 54.9                   | 327              | 391.0                  | 54.5                   | —                 | Pure water    | 10 mL   | 1.81 | —   | 2.48 |
| 2   | XS-2       | 51.3             | 58.2                   | 53.2                   | 334              | 384.0                  | 53.5                   | —                 | Pure water    | 20 mL   | 1.81 | —   | 2.4  |
| 3   | XS-3       | 50.7             | 58.8                   | 53.7                   | 327              | 391.0                  | 54.5                   | —                 | 2 mol/L NaCl  | 10 mL   | 1.81 | —   | 2.19 |
| 4   | XS-4       | 45.7             | 63.8                   | 58.3                   | 322              | 396.0                  | 55.2                   | —                 | 2 mol/L NaCl  | 20 mL   | 1.81 | —   | 2.35 |
| 5   | XS-5       | 34.0             | 75.5                   | 68.9                   | 325              | 393.0                  | 54.7                   | Add dolomite for the night | Pure water    | 10 mL   | 1.81 | 5.3 | 5.71 |
| 6   | XS-6       | 21.8             | 87.7                   | 80.1                   | 207              | 511.0                  | 71.2                   | Add dolomite for the night | Pure water    | 20 mL   | 1.81 | 5.5 | 5.76 |
| 7   | XS-7       | 35.5             | 74.0                   | 67.6                   | 322              | 396.0                  | 55.2                   | Add dolomite for the night | 2 mol/L NaCl  | 10 mL   | 1.81 | 5.45 | 6.18 |
| 8   | XS-8       | 23.2             | 86.3                   | 78.8                   | 203              | 515.0                  | 71.7                   | Add dolomite for the night | 2 mol/L NaCl  | 20 mL   | 1.81 | 5.49 | 6.24 |
| 9   | XS-9       | 44.6             | 64.9                   | 59.3                   | 338              | 380.0                  | 52.9                   | Add dolomite for 10 min | Pure water    | 10 mL   | 1.81 | 1.81 | 4.15 |
| 10  | XS-10      | 28.6             | 80.9                   | 73.9                   | 219              | 499.0                  | 69.5                   | Add dolomite for 10 min | Pure water    | 20 mL   | 1.81 | 1.81 | 4.33 |
| 11  | XS-11      | 45.9             | 63.6                   | 58.1                   | 326              | 392.0                  | 54.6                   | Add dolomite for 10 min | 2 mol/L NaCl  | 10 mL   | 1.81 | 1.81 | 4.24 |
| 12  | XS-12      | 35.7             | 73.8                   | 67.4                   | 232              | 486                    | 67.6                   | Add dolomite for 10 min | 2 mol/L NaCl  | 20 mL   | 1.81 | 1.81 | 4.32 |
| 13  | XS-13 (blank) | 109.5           | 0.0                    | 0.0                    | 718              | 0.0                    | 0.0                    | Blank            | —             | —       | 1.81 | 1.81 | 1.81 |
| 14  | XS-14      | 69.1             | 40.4                   | 36.9                   | 644              | 74.0                   | 10.3                   | Add dolomite for the night | —             | —       | 1.81 | 1.81 | 5.4 |
| 15  | XS-15      | 92.3             | 17.2                   | 15.7                   | 696              | 22.0                   | 3.1                    | Add dolomite for 10 min | —             | —       | 1.81 | 1.81 | 4.23 |
contains small amounts of sulfide (i.e., the scenario that was simulated in this study) or mixes with another sulfide-containing fluid [31], H₂S and HS⁻ species will be present in the fluid [31]. As mentioned previously, the fluid will simultaneously undergo pH changes, water-rock interactions, dilution, and mixing; notably, the sulfide complexes of Pb and Zn are more stable at low temperatures, neutral-to-basic pH levels, and low salinity levels [52–56]:

\[
\text{Me}^{2+} + n\text{HS}^- \rightleftharpoons \text{Me}([\text{HS}]_{2-n}^n) \quad (n = 2, 3, 4). \tag{12}
\]

At this point, the metal precipitation reaction (Reaction (6)) cannot occur, and the chloride complexes of Pb and Zn in the fluid become unstable. Some of these complexes turn into sulfur–hydrogen complexes (Reaction (12)) while the other portion reacts directly with the H₂S and HS⁻ in the fluid to form sulfide precipitates (Reactions (4) and (5)). This process gradually depletes the H₂S species in the fluid, which destabilizes the Pb/Zn sulfur–hydrogen complexes. These complexes then release some of their HS⁻ to form H₂S, which continues until an equilibrium is reached among the S species, metal ions, and sulfur–hydrogen complexes.

As MVT basin brines do not contain high metal concentrations and have high initial pH levels, a small change in their physical and chemical conditions is sufficient to bring their pH levels to a range that is amenable for Pb/Zn sulfide precipitation. This explains why low-grade disseminated ores

### Table 7: EPMA test results.

| Sample no. | Pb wt.% | Pb At.% | Zn wt.% | Zn At.% | S wt.% | S At.% | C wt.% | C At.% | O wt.% | O At.% | Ca wt.% | Ca At.% | Mg wt.% | Mg At.% |
|------------|---------|---------|---------|---------|-------|-------|-------|-------|-------|-------|--------|--------|--------|--------|
| XS-4       | 18.75   | 3.04    | 33.57   | 17.28   | 15.15 | 15.89 | 12.2  | 34.18 | 8.04  | 16.9  | 6.66   | 5.59   | 4.07   | 5.63   |
| XS-6       | 5.66    | 0.61    | 11.93   | 4.06    | 4.15  | 2.88  | 17.26 | 31.97 | 26.8  | 37.26 | 22.34  | 12.4   | 11.61  | 10.62  |
| XS-8       | —       | —       | —       | —       | —     | —     | —     | —     | —     | —     | —      | —      | —      | —      |
| XS-10      | 2.49    | 0.32    | 33.38   | 13.79   | 10.5  | 8.84  | 13.96 | 31.4  | 14.93 | 25.21 | 10.15  | 6.84   | 5.28   | 5.86   |
| XS-12      | 1.01    | 0.12    | 24      | 9.14    | 6.59  | 5.12  | 11.79 | 24.43 | 21.4  | 33.31 | 12.82  | 7.96   | 6.89   | 7.05   |

| Sample no. | Si wt.% | Si At.% | Al wt.% | Al At.% | Cl wt.% | Cl At.% | K wt.% | K At.% | Fe wt.% | Fe At.% | P wt.% | P At.% | Ti wt.% | Ti At.% |
|------------|---------|---------|---------|---------|---------|---------|-------|-------|--------|--------|-------|-------|--------|--------|
| XS-4       | —       | —       | —       | —       | 1.57    | 1.49    | —     | —     | —      | —      | —     | —     | —      | —      |
| XS-6       | 0.26    | 0.2     | —       | —       | —       | —       | —     | —     | —      | —      | —     | —     | —      | —      |
| XS-8       | 3.05    | 2.13    | 2.03    | 1.47    | —       | —       | 1.47  | 0.73  | —      | —      | —     | —     | —      | —      |
| XS-10      | 3.72    | 3.14    | 2.47    | 2.17    | 0.8     | 0.54    | 1.13  | 0.69  | —      | —      | —     | —     | —      | —      |
| XS-12      | 6.79    | 6.02    | 4.76    | 4.39    | 1.02    | 0.71    | 2.27  | 1.44  | 0.67   | 0.3    | —     | —     | —      | —      |

XS-13 is a control solution with no additions or alterations, and XS-14 is a control solution that was filtered, but not diluted after dolomite was added and left overnight in the solution. XS-15 is a control, where the solution was filtered, but not diluted after dolomite was added and left for 10 min in the solution.
are easily formed by the MVT basin brines. Furthermore, as these fluids are present in enormous quantities, they will naturally form large deposits and mineral districts.

In contrast, the ore-forming fluids of the HZT deposits are usually quite acidic (pH < 3.6) [15, 25, 57]. This minimizes Pb/Zn hydrolysis and enhances Pb/Zn solubility (each unit decrease in pH is known to cause a geometric increase in the metal concentration [33]). Therefore, a fluid of this type can carry enormous amounts of metal over long distances, during which the metals may coexist in an aqueous state with some amount of H₂S (such as in mixed solution (3)). As these fluids have a low initial pH, a large change in their physical and chemical conditions (especially pH) is necessary to trigger precipitation. Therefore, these fluids will be able to extract mineral-forming substances as they migrate through the earth, which will ultimately become highly concentrated,
slurry-like ore-forming fluids that precipitate dense, block-like Pb/Zn ores. This is generally beneficial for the formation of high-grade ores and orebodies. The strong dilation of the fluid is also conducive to the formation of highly enriched and thick orebodies.

5. Conclusions

The results of this study indicate that, within a fluid whose Pb/Zn and sulfide contents exist as chloride complexes and H₂S, respectively, sulfide precipitation can be induced by subjecting this fluid to pH changes, water-rock reactions, or isothermal dilution. The most effective method for triggering the precipitation of sulfides from such a fluid is a change in pH, followed by dilution and then water-rock interactions. Water-rock interactions and dilution both induce precipitation by shifting the pH of the fluid into a range that is amenable for Pb/Zn sulfide precipitation.

Although the aforementioned insights were obtained from experiments performed at low temperatures and pressures, these conditions partially resemble the mineralization temperatures and pressures of nonmaggmatic, carbonate-hosted epigenetic Pb/Zn deposits. Nonetheless, a change in the pressure and temperature will alter the threshold for large-scale Pb/Zn hydrolysis reactions and the dynamics of water-rock interactions. In our next study, we will perform systematic experiments to study the effects of mineralization temperatures and pressures using a high-temperature/high-pressure experimental apparatus to obtain more realistic experimental data on the mechanisms of metal sulfide precipitation.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts.

Acknowledgments

This study was supported jointly by the National Natural Science Foundation of China (grant numbers 41802089, 41572060, and U1133602), the Ten Thousand Talent
Program of Yunnan Province (grant number YNWR-QNB)-2019-157), the Projects for Yunnan Engineering Laboratory of Mineral Resources Prediction and Evaluation (2012), and the Yunnan and Kunming University of Science and Technology Postdoctoral Sustentation Fund.

References

[1] J. R. Xie, A Discussion on the Deposits Classify, Science Press, 1964.
[2] G. C. Tu, Geochemistry of Strata-Bound Ore Deposits in China, Science Press, 1984.
[3] C. Q. Zhang, S. P. Wu, H. M. Li, F. Liu, B. J. Guo, and D. R. Gao, “Distribution, characteristics and genesis of Mississippi Valley-type lead-zinc deposits in Sichuan-Yunnan-Guizhou area,” Mineral Deposits, vol. 24, no. 3, pp. 336–348, 2005.
[4] R. S. Han, J. Chen, Z. L. Huang et al., Dynamics of Tectonic Ore-Forming Process and Localization-Prognosis of Concealed Orebodies: As Exemplified by the Huize Surper-Large Zn-Pb-(Ag-Ge) District, Yunnan, Science Press, 2006.
[5] R. S. Han, Y. Z. Hu, X. K. Wang et al., “Mineralization model of rich Ge-Ag-bearing Zn-Pb poly metallic deposit concentrated district in Northeastern Yunnan, China,” Acta Geologica Sinica, vol. 86, no. 2, pp. 280–293, 2012.
[6] C. Q. Zhang, Z. Y. Rui, Y. C. Cheng, D. H. Wang, Z. H. Chen, and D. B. Lou, “The main successive strategic bases of resources for Pb-Zn deposits in China,” Geology in China, vol. 40, no. 1, pp. 248–272, 2013.
[7] R. S. Han, F. Wang, Y. Z. Hu et al., “Metallogenic tectonic dynamics and chronology constrains on the Huize-typ (HZT) germanium-rich silver-zinc-lead deposits,” Geotectonica et Metallogenia, vol. 38, no. 4, pp. 758–771, 2014.
[8] H. C. Liu and W. D. Lin, Metallogenic Rules of Zn-Pb-(Ag) Deposits in Northeastern Yunnan, Yunnan University Publishing House, 1999.
[9] J. Z. Wang, C. Y. Li, Z. Q. Li, and J. J. Liu, “The geological setting, characters and origin of Mississippi Valley-type Pb-Zn deposits in Sichuan and Yunnan Provinces,” Geology-Geochemistry, vol. 29, no. 2, pp. 41–45, 2001.
[10] G. C. Tu, “Two unique mineralization areas in southwest China,” Bulletin of Mineralogy, Petrology and Geochemistry, vol. 22, pp. 1-2, 2002.
[11] Z. L. Huang, J. Chen, and R. S. Han, Geochemistry and Ore Genesis of Huize Super-Large Lead-Zinc Deposit, Yunnan Province, Concurrently Discuss the Relationship Between Emeishan Basalt and Lead-Zinc Deposits, Geological Publishing House, 2004.
[12] W. B. Li, Z. L. Huang, J. Chen, C. Xu, T. Guan, and M. D. Yin, “Sulfur isotopes and rare-earth elements geochemistry of the giant Huize Zn-Pb deposit in Yunnan Province,” Acta Geologica Sinica, vol. 78, no. 4, pp. 507–518, 2004.
[13] R. S. Han, C. Q. Liu, Z. L. Huang et al., “Geological features and origin of the Huize carbonate-hosted Zn-Pb-(Ag) district, Yunnan,” Ore Geology Reviews, vol. 31, pp. 360–383, 2007.
[14] R. S. Han, C. Q. Liu, J. M. Carranza et al., “REE geochemistry of altered fault tektontes of Huize-type Zn-Pb-(Ge-Ag) deposit, Yunnan Province, China,” Geochemistry: Exploration, Environment, Analysis, vol. 12, pp. 127–146, 2012.
[15] Y. Zhang, R. Han, P. Wei, and W. Qiu, “Fluid inclusion features and physiochemical conditions of the Kuangshanchang Pb-Zn deposit, Huize, Yunnan Province,” Journal of Jilin University, vol. 47, no. 3, pp. 719–733, 2017.
[16] Y. Zhang, R. Han, P. Wei, and L. Wang, “Identification of two types of metallogenic fluids in the ultra-large Huize Pb-Zn deposit, SW China,” Geoﬂuids, vol. 2017, Article ID 6345810, 22 pages, 2017.
[17] C. Q. Zhang, The Genetic Model of Mississippi Valley Type Deposit in the Boundary Area of Sichuan, Yunnan and Guizhou Province, China, Chinese Academy of Geological Sciences, Beijing, China, 2008.
[18] R. S. Han, Y. Zhang, F. Wang, P. Wu, W. L. Qiu, and W. Y. Li, The Metallogenic Mechanism and Localization-Prognosis of Concealed Orebodies in Rich Zn-Pb-(Ge) Deposits at Northeastern Yunnan Deposit Concentration District, SW China, Science Press, 2019.
[19] Z. L. Huang, W. B. Li, J. Chen et al., “Carbon and oxygen isotope constraints on mantle fluid involvement in the mineralization of the Huize super-large Pb-Zn deposits, Yunnan Province, China,” Journal of Geochemical Exploration, vol. 78–79, no. 3, pp. 637–642, 2003.
[20] Z. L. Huang, X. B. Li, M. F. Zhou, W. B. Li, and Z. G. Jin, “REE and C-O isotopic geochemistry of calcites from the world-class Huize Pb-Zn deposits, Yunnan, China: implications for the ore genesis,” Acta Geologica Sinica - English Edition, vol. 84, no. 3, pp. 597–613, 2010.
[21] Z. L. Huang, J. Chen, R. S. Han et al., “REE geochemistry of calcite-a gangue mineral in the Huize ore deposit, Yunnan,” Acta Mieralogica Sinica, vol. 21, no. 4, pp. 659–666, 2001.
[22] D. F. Luo, Z. L. Huang, F. Wang, J. X. Zhou, and X. B. Li, “Mechanism of transportation and precipitation of mineralization elements in the Huize super-large Pb-Zn deposit, Yunnan Province, China,” Acta Mieralogica Sinica, vol. 32, no. 2, pp. 288–293, 2012.
[23] Z. L. Zhang, Z. L. Huang, B. Rao, T. Guan, and Z. F. Yan, “The sources of ore-forming fluid in the Huize lead–zinc ore deposits: evidences for water-rock reaction,” Journal of Jilin University, vol. 35, no. 5, pp. 587–592, 2005.
[24] Z. L. Zhang, Characteristics and Sources of Ore-Forming Fluids in Huize Pb-Zn Deposit, Yunnan Province: Evidence from Fluid Inclusion and Water Rock Reaction Experiments, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China, 2006.
[25] Z. L. Zhang, Z. L. Huang, B. Rao, T. Guan, and Z. F. Yan, “Are lead sulphides and zinc sulphides of lead-zinc ore deposits precipitated from acidic solutions? A discussion on the ore-forming fluid of Huize lead-zinc ore deposit, Yunnan province,” Acta Mieralogica Sinica, vol. 26, no. 1, pp. 53–58, 2006.
[26] R. S. Han, C. Q. Liu, Z. L. Huang et al., “Fluid inclusions of calcite and sources of ore-forming fluids in the Huize Zn-Pb-(Ag-Ge) district, Yunnan, China,” Acta Geologica Sinica - English Edition, vol. 78, no. 2, pp. 583–591, 2004.
[27] R. S. Han, H. J. Zou, B. Hu, Y. Z. Hu, and C. D. Xue, “Features of fluid inclusions and sources of ore-forming fluid in the Maoping carbonate-hosted Zn-Pb-(Ag-Ge) deposit, Yunnan, China,” Acta Petrologica Sinica, vol. 23, no. 9, pp. 2109–2118, 2007.
[28] C. Zhou, “The source of mineralizing metals, geochemical characterization of ore-forming solution, and metallogenetic mechanism of Qilingchang Pb-Zn deposit, Northeastern Yunnan province, China,” Bulletin of Mineralogy, Petrology and Geochemistry, vol. 17, no. 1, pp. 34–36, 1998.
[29] X. R. Yan, *Metallogenic Model and Prediction of Huize Pb-Zn Deposit*, Kunming University of Science and Technology, Kunming, Georgia Institute of Science and Technology, Kunming, China, 2007.

[30] K. H. Zhong, W. Liao, M. Y. Song, and Y. Q. Zhang, "Discussion on sulfur isotope of Huize Pb—Zn deposit in Yunnan, China," *Journal of Chengdu University of Technology*, vol. 40, no. 2, pp. 130–138, 2013.

[31] Y. Zhang, R. S. Han, X. Ding, J. J. He, and Y. R. Wang, "An experimental study on metal precipitation driven by fluid mixing: Implications for genesis of carbonate-hosted lead–zinc ore deposits," *Geochemistry*, vol. 38, no. 2, pp. 202–215, 2019.

[32] Y. Zhang, R. S. Han, X. Ding, Y. R. Wang, and P. T. Wei, "Experimental study on fluid migration mechanism related to Pb-Zn super-enrichment: Implications to mineralisation mechanisms of the Pb-Zn deposits in the Sichuan-Yunnan–Guizhou, SW China," *Ore Geology Reviews*, vol. 114, no. 103110, pp. 1–19, 2019.

[33] Y. Zhang, R. S. Han, and P. T. Wei, "The order of sphalerite and galena precipitation: a case study from lead-zinc deposits in Southwest China," *Journal of Central South University*, vol. 27, pp. 288–310, 2020.

[34] A. B. Carpenter, M. L. Trout, and E. E. Pickett, "Preliminary report on the origin and chemical evolution of lead-and zinc-rich oil field brines in Central Mississippi," *Economic Geology*, vol. 69, no. 8, pp. 1191–1206, 1974.

[35] B. W. D. Yardley, "Metal concentrations in crustal fluids and their relationship to ore formation," *Economic Geology*, vol. 100, no. 4, pp. 633–632, 2005.

[36] G. K. Czamanske, E. Roedder, and F. C. Burns, "Neutron activation analysis of fluid inclusions for copper, manganese, and zinc," *Science*, vol. 140, no. 3565, pp. 401–403, 1963.

[37] D. M. Pinckney and J. Haffley, "Content of zinc and copper in some fluid inclusions from the Cave-in-Rock District Southern Illinois," *Economic Geology*, vol. 65, no. 4, pp. 451–458, 1970.

[38] B. Stoffell, M. S. Appold, J. J. Wilkinson, N. A. Mclean, and T. E. Jeffries, "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," *Economic Geology*, vol. 103, no. 7, pp. 1411–1435, 2008.

[39] J. J. Wilkinson, B. Stoffell, C. C. Wilkinson, T. E. Jeffries, and M. S. Appold, "Anomalously metal-rich fluids form hydrothermal ore deposits," *Science*, vol. 323, no. 5915, pp. 764–767, 2009.

[40] M. H. Reed, "Sulfide mineral precipitation from hydrothermal fluids," *Reviews in Mineralogy and Geochemistry*, vol. 61, no. 3, pp. 95–109, 2006.

[41] R. H. Petrucci and W. S. Harwood, *General Chemistry: Principles and Modern Applications*, Macmillan, 1977.

[42] D. W. Oxtoby, H. P. Gillis, and A. Campion, *Principles of Modern Chemistry*, Thomson Higher Education, 7th edition, 2012.

[43] J. Y. Cao, B. B. Lu, B. Ma, and S. Y. Li, "Reviews on the villcination and flotation of oxidized lead—zinc ores," *Multipurpose Utilization of Mineral Resources*, vol. 2, pp. 17–21, 2016.

[44] D. L. Leach, D. F. Sangster, K. D. Kelley et al., "Sediment-hosted lead-zinc deposits: a global perspective," *Economic Geology*, vol. 100, pp. 561–607, 2005.

[45] G. M. Anderson, *Some Geochemical Aspects of Sulfide Precipitation in Carbonate Rocks*, G. Kisvarsanyi, S. K. Grant, W. P. Pratt, and J. W. Koenig, Eds., *International Conference of MVT Lead-Zinc Deposits*, 1983, pp. 61–76, University of Missouri Rolla, Rolla, MO, USA, 1983.