Research Article

Geology, Mineralogy, Fluid Inclusion, and H–O–S–Pb Isotope Constraints on Ore Genesis of the Keyue Sb–Pb–Zn–Ag Deposit in Southern Tibet

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The Keyue deposit is a medium-sized deposit similar to the Zhaxikang deposit within the North Himalayan Metallogenic Belt (NHMB). The ore formation can be divided into Pb–Zn mineralization (stages 1 and 2), Sb–Ag mineralization (stages 3 and 4), and Sb–Hg mineralization (stages 5 and 6). The fluid inclusion data show that the first two pulses of mineralization have different characteristics, but both belong to the epithermal category (stage 2: 172.9–277.2°C, 7.4–17.0 wt% NaCl eq.; stages 3 and 4: 142.1–321.0°C, 2.7–17.96 wt% NaCl eq.). The H–O isotopic compositions of stages 3 and 4 quartz (δD_{V-SMOW} : –174‰––120‰, $\delta^{18}O_{H_2O}$: 1.59‰–11.34‰) are similar to those of stages 3 and 4 minerals (δD_{V-SMOW} : –165‰––150‰, $\delta^{18}O_{H_2O}$: 6.14‰–13.03‰), whereas they are different from stage 1 and 2 (δD_{V-SMOW} : –108.3‰––103.6‰, $\delta^{18}O_{H_2O}$: 1.92‰–3.82‰) and stage 5 and 6 (δD_{V-SMOW} : –165‰––138‰, $\delta^{18}O_{H_2O}$: –12.91‰–0.82‰) minerals from the Zhaxikang deposit. Additionally, stage 2 sulfides have $\delta^{34}S$ values of 5.4‰–11.2‰ that are similar to stage 2 sulfides in the Zhaxikang deposit (7.8‰–12.2‰), and these $\delta^{34}S$ values overlap those of many SEDEX-type deposits. The $\delta^{34}S$ values also show a decreasing trend from stage 2 through stages 3 and 4 to stage 5 in Keyue and Zhaxikang deposits, which may relate to the overprint by later mineralization events. The Pb isotopic data ($^{206}Pb/^{204}Pb$: 18.530–19.780, $^{207}Pb/^{204}Pb$: 15.674–15.939, and $^{208}Pb/^{204}Pb$: 38.618–40.559) show a significant crustal contribution. However, the minerals from different pulses of mineralization also exhibit slightly different Pb isotopic characteristics. These inferences from fluid inclusions and isotope are also demonstrated by geological and mineralogical evidence. Overall, the Keyue deposit is an epithermal deposit and has mainly experienced three pulses of mineralization.

1. Introduction

The North Himalayan Metallogenic Belt (NHMB), located in the most representative orogenic belt worldwide, is an important part of the Tethys-Himalaya metallogenic domain [1]. The NHMB is located in the eastern section of the North Himalayan Tectonic Belt (NH), and the main ore-bearing formations are a set of Late Triassic–Early Cretaceous flysch formations formed by turbidity sediment and carbonaceous–

siliceous–argillaceous rock series related to hydrothermal sedimentation [1, 2]. According to previous research [1–4], there are mainly three mineralization events within NHMB that generate a series of Sb, Sb–Au, Au, Pb–Zn (Ag), and Sb–Pb–Zn–Ag deposits (Figure 1). The first mineralization event is related to multiple seafloor volcanic events during a synsedimentary period (220–130 Ma; e.g., the first pulse of mineralization in the Zhaxikang Sb–Pb–Zn–Ag deposit); the second mineralization event is associated with a

FIGURE 1: (a) Tectonic framework of the Himalayan Terrane (modified from Yin [5] and Wang et al. [25]). (b) Regional geological map of the North Himalayan Metallogenic Belt (modified from Zheng et al. [1] and Wang et al. [25]).

metamorphic fluid system during the syn-collision period (60–42 Ma) of Indian and Eurasian plates that formed several orogenic Au–Sb deposits (e.g., Nianzha and Bangbu Au deposits); and the third mineralization event relates to the magmatic-hydrothermal activity during the postcollision period (25 Ma to present) and has formed some W–Sn, Pb–Zn (Ag), and Sb–Au deposits (e.g., Dongga W–Sn and Shalagang Sb deposits). The complex tectonic and metallogenic history makes the NHMB an area of great interest to the international community. Extensive research have been conducted in this region (e.g., [1–3, 5–9]); nevertheless, compared with other metallogenic belts in Tibet, the metallogeny of NHMB is still debated.

To date, the Zhaxikang deposit is the only super-large deposit identified within NHMB, which has the unique metallogenic element association of Sb–Pb–Zn–Ag. The Keyue deposit is a medium-sized deposit near the Zhaxikang deposit; there is only a fault zone separating them. They have similar metallogenic elements and mineral associations, orebody characteristics, ore paragenetic sequence, wall rocks, and so on [1, 10]. Thus, there may be a genetic relationship between these two deposits. On the other hand, the Sb–Pb–Zn–Ag metallogenic association is rarely reported even worldwide and only a few publications have been reported in other collision zones, for instance, the Coeur d’Alene mineral district in the Cordilleran orogen of northern Idaho

in the USA [11, 12] and the Rheinisches Schiefergebirge Sb–Pb–Zn(–Cu) veins in the Variscan orogen in northwest Germany that were suggested to result from overprinting of preexisting Pb–Zn veins by later mesothermal Sb veins [13, 14]. However, the genesis of this kind of deposits in NHMB is still controversial; the primary research was conducted on the Zhaxikang deposit. The current genetic models include a hot spring [6, 15], three magmatic hydrothermal fluids [16–18], a coarse-grained hydrothermal Pb–Zn vein overprinted by Sb-rich magmatic hydrothermal fluid [19], and two sedimentary exhalative (SEDEX) deposits overprinted by hydrothermal fluid [2, 20].

Here, based on the evidence from geology, mineralogy, elements, fluid inclusion, and H–O–S–Pb isotopes, we compare Keyue with Zhaxikang and discuss the genesis of the Keyue deposit. Our study has implications for understanding the mineralization and exploration of Sb–Pb–Zn–Ag deposits within NHMB.

2. Geological Setting

2.1. Regional Geology. The Himalayan Terrane, located between the Lhasa Terrane and the Indian Continent, is an important tectonic unit of the Cenozoic Himalayan–Tibetan orogen (Figure 1(a)) [21]. From north to south, the Himalayan Terrane is divided into the NH, the High

Himalayan Crystalline Rock Belt (HH), the Low Himalayan Fold Belt (LH), and the Sub-Himalayan Tectonic Belt (SH), respectively (Figure 1(a)) [22, 23]. These four tectonic belts are separated by four nearly EW-trending faults with the name of the South Tibet Detachment System (STDS), the Main Central Thrust (MCT), the Main Boundary Thrust (MBT), and the Main Frontal Thrust (MFT; Figure 1(a)) [5, 24].

The sedimentary sequence that includes the Late Precambrian to Devonian pre-rift, Carboniferous to Early Jurassic syn-rift, and Middle Jurassic to Cretaceous passive continental margin sediments, are recorded in NH and crop out in an EW and NWW trend [20]. The strata are composed of the Precambrian Laguigangri Group and a series of Upper Triassic, Jurassic, Lower Cretaceous, and Quaternary sediments [25]. A set of Late Triassic–Early Cretaceous flysch formations formed by turbidite deposits in neritic–bathyal environments is in dominance and crops out across the NH. This set of flysch formations host the majority of the Au–Sb–Pb–Zn–Ag deposits in the NHMB and consist of weak metamorphic slate that is intercalated with metamorphosed fine-grained sandstone, argillaceous limestone, micrite, and siliceous rock that is intercalated with volcanic rocks [2]. In addition, the Laguigangri Group containing schist, gneiss, and migmatite units crops out in the core of the Yelaxiangbo dome (Figure 1(b)), as well as some Quaternary sediments composed of gravel, sand gravel, sandy loam, clay, and ice boulder spread in the central and southern areas of the NH [2].

Two sets of faults both with multiple episodes of motion occur in the NH, and they are EW-trending and NS-trending, respectively. The older EW-trending faults cover a larger area and control the distribution of intermediate-acid magmatic rocks and ore deposits in the NH [2]. The Lazi–Qionduojiang, Rongbu–Gudui, and Luozha faults, as well as the STDS and numerous metamorphic core complexes, are all representative EW-trending faults (Figure 1(b)). In comparison, the younger NS-trending faults are also the important ore-controlling structures in the NH [19] and are considered as the result of east–west extension of the Qinghai–Tibet Plateau [26, 27]. These NS-trending faults are deemed to form from 25 Ma to now, especially during 18 to 4 Ma [28, 29]. Among these NS-trending faults, a series of rifts is considered to be associated with the older EW-trending faults [21, 22, 30, 31], which mainly include the Sangri–Cuona, Yadong–Gulu, Shenzha–Xietongmen, and Dangreyongcuo–Gucuo rift zones from east to west [32].

The Mesozoic and Cenozoic magmatism is recorded in the NH. From Late Triassic to the Early Cretaceous, the Mesozoic magmatism generated multiple suites of mafic–intermediate igneous rocks that include basaltic volcanic interlayers, dyke swarms, and subvolcanic dykes. The previous geochronological data reveal that the basic dyke swarms from different areas in the NH have SHRIMP U–Pb ages of 134.9 ± 1.8 Ma, 135.5 ± 2.1 Ma [33], and 138.0 ± 3.5 Ma [34], respectively. The SHRIMP U–Pb age of the gabbro is 155.8 Ma [35]. However, the genesis of these magmatic rocks is controversial. Tong et al. [34], Pan et al. [36], and Zhong et al. [37] regarded these basic dyke swarms as the result of

the late-stage massive expansion of the Neo-Tethys Ocean under the structural environment of the Himalayan passive continental margin intensive stretching and breaking-off, lithosphere extension-thinning, and asthenosphere upwelling. On the contrary, Zhu et al. [38] and Qiu et al. [39] suggested that these basic dyke swarms are the result of the interaction between mantle plume and lithospheric mantle material and form in the continental rift environment. The Cenozoic magmatism, considered to be the result of crustal thickening [40] related to the collision of the Indian Plate and the Eurasian Plate during the postcollision period (25 to 0 Ma) [41, 42], is characterized by the formation of monzogranite, leucogranite, diorite, porphyritic diorite, and aplite units [43, 44]. These Cenozoic intermediate–acidic intrusive masses distribute in the core of Ranba, Kangma, and Yelaxiangbo domes as well as the EW-trending faults in the form of batholith, laccolith, and dykes (Figure 1(b)).

2.2. Ore Deposit Geology. The Keyue deposit is located ~43 km west from Longzi County Town in NHMB, where it is near the Zhaxikang deposit (Figure 1(b)). This deposit has a reserve of 232,100 t Pb with an average grade of 3.00%, 172,648 t Zn with an average grade of 2.44%, 81,261 t Sb with an average grade of 1.15%, and 711.8 t Ag with an average of 100.72 g/t [45]. The majority of mineralization in the orefield is hosted by the Lower Jurassic Ridang formation that dips shallowly to the north with the dip angle of 10° – 20° . This formation is dominated by a set of epi-metamorphic marine clastic rocks that mainly consists of slate and some shale (Figure 2(a)) with few quartzose sandstone, calcareous sandstone, limestone, and tuff [45]. Some Middle Jurassic Zhela formations composed of limestone and dolomite with few phyllite rock, slate, and quartz siltstone that is intercalated with altered intermediate–basic volcanic rock, as well as Quaternary sediments distributed along valleys, also crop out in the orefield (Figure 2(c)) [10]. The intense magmatic and volcanic activities have generated a series of intermediate–basic and acidic magmatic rocks hosted by the Ridang Formation. Separately, the diabase is identified by drillhole and footrill in the central part of the orefield as dykes that emplaced into the Jurassic Ridang Formation (Figure 2(a)); the basalt usually occurs near the orebody in the form of consequent layer or shear layer distributing in slate and the contact position of slate and diabase [10, 45].

A series of faults and some folds developed in the Keyue orefield. These folds make the rocks within the strata deformed and metamorphic in different degrees [10]. Engineering and geological mapping projects of Huayu Mining Company [45] have identified two dominating faults (F1 and F2) that control the distribution of 7 orebodies within the orefield (Figure 2). The NS-striking F1 fault, with the length of 1600 m, width of 100 m, altitude of 265° – 295° , and dip angle of 50° – 70° , cut the Ridang Formation. In comparison, the smaller F2 fault also cut the Ridang Formation and is 500 m long and 1–15 m wide with the altitude of 110° – 120° and dip angle of 55° – 70° [45]. The orebodies are usually veined, stratiform, and lenticular with ramification in the depth. Combining with the observation of drillhole and

FIGURE 2: (a) Geological map of the Keyue Sb-Pb-Zn-Ag deposit (modified from Yang [10]); (b) cross-section along Exploration Line 44; (c) the schematic illustration of the internal structure of the Keyue deposits, with the vertical zonation, different alteration associations, and mineralization.

footrill, the orebodies have an obvious crack related to hydrothermal activity [10, 46]. Among these orebodies, orebody 1 controlled by fault F1 is the largest and richest one within the orefield, which hosts an overwhelming majority of the reserves (Figure 2) [45].

From altitude 4422 to 4722 m in orebody 1, the ore-forming elements of the Keyue Sb-Pb-Zn-Ag deposit are zoned from a lowermost Pb + Zn zone through the central

Ag-Sb (Pb + Zn) zone to an uppermost Sb (Hg) zone (Figure 2(c)), although there is no horizontal zoning [45, 46]. Additionally, various types of alteration associated with mineralization have occurred in the orefield [10, 45, 46], including (1) the carbonatization that is associated with Pb-Zn mineralization in the form of Mn-Fe carbonate veins (Figures 3(a) and 3(b)) and distribute together with the orebodies along the fault (Figure 2(c));

FIGURE 3: Hydrothermal alteration within the Keyue orefield. (a) Mn-Fe carbonate vein cut slate; (b) Mn-Fe carbonate in slate; (c) quartz veins cut slate; (d) the quartz that contains slate breccias and pyrite; (e) quartz vein cut altered rock; (f) sericitization. Mcar = Mn-Fe carbonate, Qtz = Quartz, Py = pyrite, Ser = sericite.

(2) the silicification that is associated with Sb mineralization and generally located in fault zones in the form of quartz veins, radiating quartz, and quartz druse (Figures 2(c), 3(c), and 3(d)); and (3) the weak sericite alteration (Figure 2(c)) that occurred in metabasalt and diabase near the upper plate of the orebody in the form of green spots (Figure 3(e)) with anomalous interference color under a microscope (Figure 3(f)).

3. Materials and Analytical Methods

We have done the field work in the Keyue orefield for more than 120 days in recent years, including the mapping, drillhole and footrill record compiling, and sampling. Around 550 ore and related rock samples have been collected from the drillhole, footrill, and dressing plant. Meanwhile, we also took more than 800 pictures for the geological phenomenon and samples. Besides the hand specimens' observation, 165 thin sections were also made for microscopic observation (around 300 photomicrographs have been taken) on a Zeiss AX 10 microscope with an AxioCam MRc 5 microscope camera system under plane polarized light, perpendicular polarized light, and reflected light. Combining these observations, the representative samples are selected for electron probe microanalysis (EPMA), scanning electron microanalysis (SEM), energy-dispersive spectroscopy (EDS), fluid inclusion, and H-O-S-Pb isotopic analyses.

3.1. EPMA and SEM-EDS. To determine the chemical compositions of sulfides and sulfosalt minerals, 105 finely polished sections were prepared for EPMA. The EPMA for 260 points in these sections was conducted on a JEOL JXA-8100 electron microprobe at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan. The electron microprobe was

operated under the condition of a 20 kV accelerating voltage, a 20 nA beam current, and a 5 μm spot diameter. The natural and synthetic standards were used to control the analytical quality, and the tested accuracy is better than 0.01%. The correction program supplied by the manufacturer is used for matrix corrections [47]. Based on the microscopic observation and EPMA, 20 points in five representative sections were selected for SEM-EDS analyses to study the mineral compositions, textures, coexisting relationships, and occurrence state of Ag. The SEM-EDS analyses were performed at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan, using a Quanta 450 FEG-SEM equipped with an SDD Inca X-Max 50 EDS system.

3.2. Fluid Inclusion. The petrography, microthermometry, and laser Raman spectrometry analyses of fluid inclusions (FIs) from 4 sphalerite, 2 Mn-Fe carbonate, and 9 quartz samples in different assemblages were carried out in the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan. The sample preparation for microthermometric measurement of FIs followed the procedures described in Shepherd et al. [48]. The microthermometry data were obtained using a Linkam THMS600 heating-freezing stage attached with a Zeiss microscope and related standard procedures, which has an enabled measurement within the range of -196 to 600°C. Liquid nitrogen and a thermal resistor were used for freezing and heating runs, respectively. The ice-melting temperatures (T_{m-ice}) and total homogenization temperatures ($T_{h-total}$) of fluid phases in FIs have been recorded during the measurements. During the initial stages of each heating run, the heating rate was maintained at 5°C per minute and then reduced to 0.1°C per minute when the temperature is approached to the phase change points.

Usually, the heating measurements were performed after freezing measurements. The densities of FIs were calculated using the FLINCOR procedure as in Brown and Lamb [49], and the salinities of aqueous (NaCl-H₂O) inclusions were calculated using the final melting temperatures of ice points [50]. In addition, a Renishaw MK1-1000 Laser Raman microspectrometer is used to determine the compositions of individual FIs in minerals, including vapor and liquid. The instrumental settings were kept constant during the analyses. An argon laser with a wavelength of 532 nm was used as the laser source at the power of 1000 MW. The spectral range fell between 1000 and 4000 cm⁻¹ for the analyses, and the spectral resolution was ± 2 cm⁻¹ with a beam size of 1 μ m.

3.3. H-O Isotopic Analyses. The H-O isotopic compositions of 12 quartz and 2 calcite samples from the Keyue deposit were measured on a MAT 253EM mass spectrometer at the Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing. For H isotopic analyses, the water from the fluid inclusion separates was collected by thermal decrepitation under vacuum at 500°C and then reduced over zinc at 400°C to generate H₂ that is released for mass spectrometry [51, 52]. As for O isotopes, oxygen was generated by the BrF₅ method the same as in Clayton and Mayeda [53], and then the resultant oxygen was converted to CO₂ by reaction with a graphite rod for the following measurement. The H-O isotopic values were reported relative to the V-SMOW standard, and the analytical errors are $\pm 2\text{‰}$ for δD and $\pm 0.2\text{‰}$ for $\delta^{18}O$.

3.4. S-Pb Isotopic Analyses. Nine sphalerite, five galena, three boulangerite, two chalcopyrite, two pyrite, and one stibnite samples were chosen for S isotopic analyses, and five galena, two boulangerite, and one stibnite samples were selected for Pb isotopic analyses. Separates of these minerals (40~80 mesh) were prepared by careful handpicking under a binocular microscope to achieve a purity more than 99.8%. Both the S-Pb isotopes were analyzed at the Analysis and Testing Research Center of the Nuclear Industry, Beijing Institute of Geology, Beijing, China.

For S isotopic analyses, a mixture of approximately 15 mg mineral separates and 150 mg Cu₂O was crushed into 200 mesh and heated to 980°C under a vacuum pressure of 0.02 Pa to convert sulfur to sulfur dioxide (SO₂) [54]. Then the generated SO₂ was measured on a Thermo Scientific Delta V Plus mass spectrometer. The S isotopic values were reported relative to the Canyon Diablo Troilite (V-CDT) standard, and the analytical uncertainties were better than $\pm 0.2\text{‰}$.

For Pb isotopic analyses, approximately 20 mg mineral separates were placed in 15 ml Teflon jars and the solids were dissolved in a mixture of HCl-HNO₃. After 24 h, the solutions were dried and 1 ml 6 N HCl was added, then the samples were dried again and dissolved in 1 ml 0.5 N HBr. After being centrifuged, lead was purified using anion exchange chromatography and collected in 1 ml 6 N HCl. At last, the dried samples were coated on a single rhenium filament by the classic H₃PO₄-silica gel method, and the Pb isotopic compositions were measured on a GV IsoProbe-T

thermal ionization mass spectrometer (TIMS). All the measured Pb isotopic values were corrected according to the values of NBS SRM 981 standards, and the measurement accuracy was better than 0.005% (2 σ).

4. Results

4.1. Mineralogy

4.1.1. Ore and Gangue Minerals. In the Keyue deposit, the ore minerals include sphalerite, galena, pyrite, arsenopyrite, chalcopyrite, tetrahedrite, freibergite, boulangerite, jamesonite, bournonite, and stibnite; the gangue minerals are mainly Mn-Fe carbonate, quartz, and calcite (Figures 4–6); and the supergenesis generates the minerals that prevalingly include ferrohydrite, sardinianite, valentinite, malachite, and siliceous sinter (Figure 7). The detailed characteristics of these minerals are as follows.

Mn-Fe carbonate is the most important gangue mineral within the orefield, and there are two types: (1) it occurs as fine-grained (<50 μ m) aggregates intergrown with fine-grained sulfides (sphalerite, pyrite, chalcopyrite, and arsenopyrite) to form the laminar and disseminated textures (Figures 4(a)–4(c)), and (2) it occurs as coarse-grained (3~5 mm) aggregates of overgrowing coarse-grained sphalerite, galena, chalcopyrite, and pyrite with banded and massive textures (Figures 4(d)–4(i) and 5(b)).

Sphalerite is the main Zn-bearing mineral within the orefield that shows black and brown colors. There are two types of sphalerite in the Keyue deposit: (1) the subhedral-xenomorphic fine-grained sphalerite (0.3~1 mm) coexisting with pyrite, arsenopyrite, and chalcopyrite to form the lamina hosted by Mn-Fe carbonate (Figures 4(a) and 4(b)) and (2) the subhedral-automorphic coarse-grained sphalerite intergrown with pyrite, chalcopyrite, galena, Mn-Fe carbonate, and quartz to form the banded, veined, and massive ores (Figures 4(d)–4(k) and 5(b)–5(d)), with grain size of 3~8 mm. According to the electron probe microanalysis (EPMA), sphalerite has Zn contents of 57.734%~64.645%, Fe contents of 2.189%~8.757%, and trace amounts of Au, Ga, Pb, Bi, Mn, and Cu (Table 1).

Galena is the dominating Pb-bearing mineral within the orefield and coexists with pyrite, sphalerite, and chalcopyrite hosted by Mn-Fe carbonate or quartz (Figures 4(a), 4(e)–4(l), and 4(p)). The medium- to coarse-grained galena is automorphic with the size of 0.5~8 mm. Meanwhile, galena is usually replaced by sulfosalt minerals (Figures 4(p) and 5(c)). The EPMA data show that galena has Pb contents of 81.641%~86.296% and Ag contents of 0.033%~1.166%, with trace amounts of Bi, Fe, Ni, Sb, and Cu (Table 1).

Pyrite is the most common Fe-bearing mineral within the orefield and is widely distributed. The subhedral-automorphic fine- to coarse-grained pyrite (0.3~5 mm) always coexists with galena, sphalerite, arsenopyrite, chalcopyrite, Mn-Fe carbonate, and quartz in the lamellar, disseminated, veined, and massive ores (Figures 4(a)–4(e), 4(i), 4(j), 4(l) and 5(b) and 5(c)). Pyrite contains 45.769%~46.565% Fe, 0.045%~0.352% Pb, and trace amounts of As, Ag, Bi, Cd, Co, Sb, Cu, Fe, and Zn (Table 1).

FIGURE 4: Continued.

FIGURE 4: Hand specimen photographs of representative samples from the Keyue Sb-Pb-Zn-Ag deposit. (a) Assemblage 1 lamellar sphalerite-pyrite-arsenopyrite and assemblage 2 massive and banded sphalerite-pyrite-galena hosted by Mn-Fe carbonate. (b) Assemblage 1 lamellar sphalerite-pyrite-arsenopyrite hosted by Mn-Fe carbonate, later assemblage 4 quartz-boulangerite veins cut the Mn-Fe carbonate; this sample also contains massive assemblage 4 quartz-boulangerite. (c) Assemblage 1 disseminated pyrite and chalcopyrite hosted by assemblage 1 Mn-Fe carbonate, later assemblage 4 quartz-boulangerite veins cut the Mn-Fe carbonate. (d) Banded assemblage 2 Mn-Fe carbonate-sphalerite-pyrite ore that contains some assemblage 3 quartz. (e) Massive assemblage 2 Mn-Fe carbonate-sphalerite-pyrite-galena ore. (f) Massive assemblage 2 coarse-grained sphalerite-galena-chalcopyrite ore. (g) Massive and banded assemblage 2 Mn-Fe carbonate-sphalerite-pyrite-galena ore. (h) Assemblage 2 coarse-grained galena-sphalerite-chalcopyrite. (i) Massive assemblage 2 Mn-Fe carbonate-sphalerite-chalcopyrite-pyrite-galena ore that is cut by a later assemblage 4 quartz-boulangerite vein. (j) Veined assemblage 3 quartz-sphalerite-galena-chalcopyrite ore that is cut by a later assemblage 4 quartz-boulangerite vein. (k) Assemblage 3 massive quartz-sphalerite-galena-chalcopyrite ore. (l) Assemblage 3 coarse-grained pyrite-chalcopyrite occurs in assemblage 3 quartz; this sample also contains minor assemblage 2 Mn-Fe carbonate. (m) Assemblage 3 massive quartz-chalcopyrite ore that contains some assemblage 4 quartz-bourbonite. (n) Assemblage 3 chalcopyrite replaced by assemblage 4 quartz-tetrahedrite-freibergite. (o) Assemblage 4 boulangerite and assemblage 3 chalcopyrite-quartz replace assemblage 2 Mn-Fe carbonate. (p) Veined assemblage 4 boulangerite-jamesonite replace assemblage 3 massive coarse-grained galena. (q) Massive assemblage 4 quartz-boulangerite-jamesonite ore. (r) Radial assemblage 5 stibnite hosted by assemblage 5 quartz. (s) Assemblage 5 stibnite replaced by assemblage 6 quartz-calcite vein. (t) Geyserite and valentinite formed by the supergenetic oxidation of assemblage 5 quartz-stibnite-cinnabar ore. Mcar1 = assemblage 1 fine-grained Mn-Fe carbonate; Apy1 = assemblage 1 lamellar arsenopyrite; Py1 = assemblage 1 lamellar pyrite; Sp1 = assemblage 1 lamellar sphalerite; Ccp1 = assemblage 1 chalcopyrite; Mcar2 = assemblage 2 coarse-grained Mn-Fe carbonate; Py2 = assemblage 2 pyrite; Sp2 = assemblage 2 sphalerite; Gn2 = assemblage 2 galena; Ccp2 = assemblage 2 chalcopyrite; Py3 = assemblage 3 pyrite; Sp3 = assemblage 3 sphalerite; Gn3 = assemblage 3 galena; Ccp3 = assemblage 3 chalcopyrite; Qtz3 = assemblage 3 quartz; Blr4 = assemblage 4 boulangerite; Jmt4 = assemblage 4 jamesonite; Bnn4 = assemblage 4 bourbonite; Ttr4 = assemblage 4 tetrahedrite; Fbt4 = assemblage 4 freibergite; Qtz4 = assemblage 4 quartz; Stb5 = assemblage 5 stibnite; Ci5 = assemblage 5 cinnabar; Qtz5 = assemblage 5 quartz; Cal6 = assemblage 6 calcite; Qtz6 = assemblage 6 quartz.

Arsenopyrite is another common Fe-bearing mineral within the orefield. The fine-grained arsenopyrite (0.1–0.5 mm) usually occurs in Mn-Fe carbonate or quartz intergrown with pyrite, sphalerite, and chalcopyrite in the form of automorphic and short columnar grains (Figures 4(a), 4(b), and 5(a)). Arsenopyrite is composed of 39.484%–43.610% As, 21.604%–23.421% S, 35.499%–36.146% Fe, and trace amounts of Au, Pb, Ag, In, Co, Sb, Cu, and Zn (Table 1).

Chalcopyrite is the prime Cu-bearing mineral within the orefield. The xenomorphic fine- to coarse-grained chalcopyrite (0.3–6 mm) coexisting with pyrite, galena, sphalerite, and arsenopyrite is hosted by Mn-Fe carbonate and quartz to form the disseminated, veined, and massive ores (Figures 4(c), 4(f), and 4(h)–4(o)). Chalcopyrite sometimes is replaced by sulfosalt minerals (Figures 4(m) and 4(n)). Based on the EPMA analyses, chalcopyrite has Cu contents of 33.332%–34.174%, Fe contents of 30.330%–30.456%, and Pb contents of 0.037%–0.148%. Trace amounts of As, Au, Ag, Bi, In, Co, and Zn are also present (Table 1).

Tetrahedrite and freibergite are dominating Ag-bearing minerals in the Keyue deposit. The xenomorphic tetrahedrite and freibergite usually coexist with bourbonite, boulangerite, jamesonite, chalcopyrite, and galena (Figures 4(n), 5(c), and 6). Freibergite has higher Ag (12.015%–27.015%), Fe (3.678%–6.259%), Sb (27.885%–28.067%), Cu (33.480%–

35.483%), and lower Zn (1.949%–3.435%) contents than tetrahedrite (Ag: 4.055%–6.933%; Fe: 3.858%–3.881%; Sb: 25.686%–27.363%; Cu: 18.975%–29.914%; and Zn: 3.342%–3.366%; Table 1), which reveals the substitution between Fe–Zn and Cu–Zn, as well as positive correlation between Ag–Fe and Ag–Cu. In addition, andorite is another Ag- and Sb-bearing mineral but is rarely found in the Keyue orefield; we can only find the stumpy andorite distributed in freibergite (Figure 6(d)).

Boulangerite and jamesonite are the important Pb- and Sb-bearing minerals in the Keyue deposit. The massive and needle-like boulangerite and jamesonite always occur in quartz (Figure 4(q)) intergrown with other sulfosalt minerals (Figures 6(d) and 6(e)). Boulangerite and jamesonite or the boulangerite-quartz veins sometimes replace and cut the earlier minerals (Figures 4(b), 4(c), 4(i), 4(j), 4(p), 4(q), and 5(d)). According to the EPMA data, boulangerite has higher Pb (53.979%–55.951%), lower Sb (24.083%–26.127%), and S (18.217%–19.096%) contents than jamesonite (Pb: 38.441%–40.001%; Sb: 33.733%–35.835%; and S: 21.757%–22.207%; Table 1). Meanwhile, boulangerite and jamesonite also contain minor amounts of Bi, Cd, Fe, Sn, Ni, and Cu.

Bourbonite is another Pb-, Cu-, and Sb-bearing mineral in the Keyue deposit. The subhedral-automorphic bourbonite is intergrown with tetrahedrite, freibergite, galena, and chalcopyrite that is hosted by quartz (Figures 4(m),

FIGURE 5: Photomicrographs of representative samples from the Keyue Sb-Pb-Zn-Ag deposit. (a) Assemblage 1 automorphic arsenopyrite. (b) Later formed assemblage 2 galena cut and replaced early formed sphalerite-pyrite-Mn-Fe carbonate. (c) Assemblage 4 tetrahedrite replaced assemblage 3 pyrite-sphalerite-galena-quartz. (d) Assemblage 4 boulangerite replaced assemblage 3 sphalerite-quartz. (e) Assemblage 5 quartz-stibnite vein cut the assemblage 4 boulangerite. (f) Assemblage 5 stibnite occurred among xenomorphic quartz grains. Abbreviations are the same as in Figure 4.

6(c), and 6(d)). Bournonite has Pb contents of 41.070%~42.890%, Sb contents of 23.673%~24.540%, Cu contents of 12.373%~13.533%, and minor amounts of Bi, Cd, Fe, and Zn (Table 1).

Stibnite is the main Sb-bearing mineral within the orefield and usually occurs in the upper part of the orebody. Stibnite coexists with quartz to form the veined and massive ores (Figures 4(r)–4(t) and 5(f)), and the stibnite-quartz veins sometimes cut the earlier boulangerite (Figure 5(e)). Stibnite contains 70.179%~70.3530% Sb, 28.400%~28.5340% S, and trace amounts of As, Pb, Cd, Sn, and Cu (Table 1). Meanwhile, cinnabar is the most important Hg-bearing mineral in Keyue orefield, and the fine-grained cinnabar (0.5~1 mm) aggregates coexist with stibnite and quartz (Figure 4(t)).

Quartz and calcite are also main gangue minerals within the orefield. The subhedral-xenomorphic coarse-grained (3~8 mm) quartz aggregates are in the form of quartz veins, radiating quartz, and quartz druse that coexist with sulfides and sulfosalt minerals (Figures 3(d), 4(i)–4(s), 5(c)–5(f), 6(a), and 6(b)). The coarse-grained (3~5 mm) calcite is usually intergrown with quartz to form the veins that cut and replace the early ores (Figure 4(s)).

The drusy and radial valentinite with yellow color and geyserite usually coexist with stibnite and cinnabar (Figures 4(t)), the green massive malachite is intergrown with chalcopryrite, the brown-black massive ferrosiderite occurs in the surface overgrowing Mn-Fe carbonate and

pyrite, and the white-grey sardinianite usually shows massive and nodular textures and coexist with galena.

4.1.2. Occurrence State of Ag in Ag-Bearing Minerals. The microscopic observation, EPMA, and back-scattering electron (BSE) microscopic research show that the main Ag-bearing minerals are tetrahedrite, freibergite, and andorite (Figures 4(n) and 6), which indicate that visible Ag is the dominating occurrence state of Ag in the Keyue deposit. Meanwhile, the BSE and X-ray mapping images from the EPMA, SEM, and EDS analyses reveal the following facts: (1) the border between the Ag-bearing and other minerals is very clear without transition region; (2) around the main Ag-bearing minerals, there are tiny Ag-bearing inclusions distributing in galena, with Ag-bearing inclusions differing in size and shape; and (3) there are no Ag-bearing inclusions present in other coexisting minerals, such as sphalerite and sulfosalt minerals (Figure 6). These facts suggest that the Ag-bearing inclusions are another occurrence state of visible Ag and relates to galena.

Furthermore, in some tiny areas ($<1\ \mu\text{m}$) where there are no Ag-bearing inclusions observed, the EPMA shows that there is Ag enrichment, which indicates that there is invisible Ag within sulfides in the Keyue deposit. There are two following invisible Ag types: (1) isomorphism lattice Ag: under high-temperature conditions, Ag and Sb enter into the mineral lattice by isomorphic substitution with Pb, and (2) submicroscopic Ag-bearing inclusions: under low-

FIGURE 6: The BSE images for primary Ag-bearing minerals and X-ray mapping images for Ag, Sb, Cu, and Pb elements in the Keyue Sb-Pb-Zn-Ag deposit. Abbreviations are the same as in Figure 4. Adt = andorite.

temperature conditions, Ag and Sb together form the sulfosalt minerals [55, 56]. In view of microthermometry research of fluid inclusions, the invisible Ag in galena should be mainly submicroscopic Ag-bearing inclusions.

Overall, the occurrence state of Ag in the Keyue deposit are prevailing in the form of visible Ag that can be divided into independent Ag-bearing minerals ($>50\mu\text{m}$; e.g., tetrahedrite, freibergite, and andorite) and Ag-bearing inclusions ($1\sim10\mu\text{m}$). By contrast, invisible Ag is much less and principally in the form of submicroscopic Ag-bearing inclusions.

4.2. Ore Paragenetic Sequence. Based on the detailed hand specimen and microscopic observations, six ore-forming assemblages of ore and gangue minerals and one supergene

assemblage have been recognized (Figure 7). The details are as follows.

Assemblage 1 is marked by Mn-Fe carbonate + sphalerite + pyrite + arsenopyrite + chalcopyrite $\pm$ galena. The fine-grained sphalerite, pyrite, chalcopyrite, and arsenopyrite occur in Mn-Fe carbonate to form the lamellar (Figures 4(a) and 4(b)) and disseminated (Figure 4(c)) ores.

Assemblage 2 is dominated by the development of Mn-Fe carbonate + galena + sphalerite + pyrite + chalcopyrite $\pm$ arsenopyrite. The more abundant and coarser-grained sulfides are hosted by coarse-grained Mn-Fe carbonate and slate. The ore textures of the assemblage 2 ores are mainly banded and massive (Figures 4(d)–4(i) and 5(b)). In some samples, the assemblage 2 minerals replace the assemblage 1 minerals (Figure 4(a)).

Stage Mineral	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Supergene stage
Mn-Fe carbonate	● ● ●	● ● ●					
Sphalerite	● ●	● ● ●	● ●				
Galena	●	● ● ●	● ●				
Pyrite	● ●	● ●	● ●				
Arsenopyrite	● ●	● ●	●				
Chalcopyrite	●	● ●	● ● ●				
Quartz			● ● ●	● ● ●	● ● ●	● ● ●	
Calcite			●			● ●	
Sericite			●		●		
Boulangerite				● ● ●			
Jamesonite				● ● ●			
Bournonite				● ●			
Freibergite				● ●			
Andorite				● ●			
Tetrahedrite				● ●			
Stibnite					● ● ●		
Cinnabar					● ●		
Ferrohydrite							● ●
Sardinianite							● ●
Valentinite							● ●
Malachite							● ●
Geyserite							● ●

Notes:

- ● ● Abundant
 ● ● Intermediate
 ● Minor

FIGURE 7: Ore paragenetic sequence within the Keyue Sb-Pb-Zn-Ag deposit.

Assemblage 3 is characterized by the formation of quartz ± calcite + pyrite + sphalerite + galena + chalcopyrite ± arsenopyrite without Mn-Fe carbonate and usually shows veined and massive textures (Figures 4(j)–4(l)). The quartz of assemblage 3 sometimes replaces the assemblage 2 minerals (Figure 4(d)).

Assemblage 4 is distinguished by quartz + antimony-lead-silver sulfosalt minerals that principally include boulangerite, jamesonite, bournonite, tetrahedrite, freibergite, and andorite. Assemblage 4 sulfosalt minerals replace (Figures 4(m)–4(p), 5(c), and 5(d)) and cut (Figures 4(b), 4(c), 4(i), and 4(j)) the minerals of assemblages 1, 2, and 3. We can also see the massive boulangerite and needle-like jamesonite (Figure 4(q)).

Assemblage 5 comprises quartz + stibnite + cinnabar. The elongated and radial stibnite is hosted by quartz (Figures 4(r), 4(s), and 5(f)) in this assemblage. The stibnite-quartz veins of assemblage 5 sometimes cut the assemblage 4 minerals (Figure 5(e)). In some ores, the massive stibnite and cinnabar experience the supergenetic oxidation to form the valentinite and siliceous sinter (Figure 4(t)).

Assemblage 6 is identified by quartz ± calcite without sulfides. This assemblage replaces the assemblages 1 to 5 ores (Figure 4(s)).

The supergene assemblage prevailing includes ferrohydrite, sardinianite, valentinite, malachite, and siliceous sinter (Figures 4(t) and 7).

4.3. Fluid Inclusion

4.3.1. Petrography

(1) *Genetic Types*. According to the relationship between FIs and host minerals, FIs are divided into three genetic types in the Keyue deposit: (1) primary FIs: the primary inclusions are the most developed FI type in the Keyue deposit, which usually randomly distribute in quartz and sphalerite crystal in the isolated form (Figures 8(a)–8(f) and 8(i)–8(l)) or orientatedly distribute in the Mn-Fe carbonate growth zoning in the filiform form (Figures 8(g) and 8(h)); (2) secondary FIs: the secondary inclusions are usually smaller than primary inclusions and are consistent in shape, which

TABLE 1: EPMA data for minerals from the Keyue deposit.

Sample number	Mineral	As	Au	S	Ga	Pb	Ag	Se	Bi	Mn	Cd	Fe	In	Co	Sn	Ni	Sb	Cu	Te	Zn	Total
2-3	Sp	—	0.038	33.431	0.004	0.130	—	—	0.027	—	0.019	2.864	—	—	—	0.003	—	0.068	—	63.907	100.491
3-4	Sp	—	0.011	33.353	—	0.085	—	—	0.042	—	0.051	3.999	—	—	—	0.015	—	0.184	—	62.565	100.305
4-1	Sp	0.004	0.126	33.414	—	0.038	—	—	—	—	0.032	2.189	—	—	—	0.011	0.049	0.029	—	64.162	100.054
4-2	Sp	—	—	33.215	—	0.053	—	—	—	—	0.005	2.343	—	—	—	—	0.002	0.147	—	64.234	99.999
5-3	Sp	0.009	0.044	33.298	—	0.079	—	—	0.032	—	0.033	4.007	0.051	—	—	—	—	0.140	—	62.291	99.984
5-2	Sp	—	—	33.640	—	0.122	—	—	0.095	—	0.019	6.070	—	—	—	—	0.029	1.145	—	59.236	100.356
6-3	Sp	0.039	0.033	33.731	0.023	0.216	—	—	0.004	—	—	2.439	—	—	—	0.006	0.003	—	—	64.645	101.139
1-2	Sp	0.011	0.076	33.281	0.007	0.091	—	—	0.043	—	—	4.983	0.049	—	—	0.007	—	0.012	—	61.894	100.454
7-4	Sp	—	—	33.294	—	0.098	—	—	0.012	0.146	0.024	—	4.041	—	0.033	0.012	0.012	0.091	0.018	60.844	98.625
8-4-1	Sp	—	0.016	33.314	—	0.078	0.614	0.008	0.143	0.035	0.032	3.193	—	0.006	—	—	1.181	1.838	—	60.154	100.612
8-4	Sp	0.032	—	33.749	0.030	—	—	—	—	0.017	0.031	3.852	—	0.022	—	—	—	0.037	0.019	63.290	101.079
11-4	Sp	0.056	0.005	33.242	0.053	—	—	0.005	0.030	0.021	0.005	3.561	—	0.001	—	0.006	0.009	0.012	—	63.570	100.576
11-3	Sp	0.019	—	33.816	0.067	0.191	—	0.037	—	0.046	—	5.486	—	0.012	—	0.012	0.008	—	—	61.554	101.248
28-1	Sp	—	0.049	33.358	0.097	0.055	—	0.071	0.03	0.004	0.004	3.063	—	0.028	0.268	—	0.044	0.906	—	—	98.591
33-1	Sp	—	0.060	33.514	—	0.046	—	0.005	0.017	0.029	0.043	4.077	—	—	0.031	—	—	—	—	62.878	100.700
35-1	Sp	—	0.005	33.014	—	—	—	—	0.049	0.025	—	2.784	—	—	0.247	0.018	0.034	0.326	—	62.991	99.493
15-2	Sp	0.042	0.113	33.627	0.103	0.074	—	—	0.015	0.068	0.045	8.757	—	0.004	—	—	0.046	0.051	0.050	57.734	100.727
34-3	Sp	0.013	0.044	33.194	0.004	0.098	—	0.008	0.119	0.055	0.019	3.704	—	0.056	—	0.158	—	—	0.003	61.905	99.380
2-2	Gn	—	—	13.308	—	85.553	0.095	—	0.335	—	—	0.027	—	—	—	—	0.246	0.012	—	0.026	99.602
3-1	Gn	—	—	13.464	—	84.717	0.139	—	0.213	—	—	0.031	—	—	—	0.022	0.217	0.029	—	—	98.832
3-2	Gn	—	—	13.536	0.042	84.604	0.033	—	0.132	—	—	0.018	—	—	—	—	0.126	0.008	—	—	98.499
3-3	Gn	—	—	13.407	—	85.522	0.093	—	0.282	—	—	0.012	—	—	—	0.011	0.205	—	—	—	99.532
5-1	Gn	—	—	13.486	0.020	84.577	0.091	—	0.312	—	—	0.04	—	—	—	—	0.189	0.014	—	—	98.729
5-3	Gn	—	—	13.451	—	83.778	0.092	—	0.164	—	—	0.071	—	—	—	—	0.165	—	—	—	97.721
5-2	Gn	—	—	13.540	—	85.395	0.139	—	0.210	—	—	0.031	—	—	—	0.012	0.309	0.031	—	—	99.667
1-1	Gn	—	—	13.488	—	84.989	0.172	0.011	0.524	—	—	0.038	—	—	—	—	0.065	—	—	—	99.287
1-3	Gn	—	—	13.426	—	85.184	0.131	0.004	0.547	—	—	0.024	—	0.038	—	0.013	0.151	0.230	—	0.020	99.768
7-3	Gn	—	—	13.582	0.030	85.306	0.109	—	0.289	—	—	0.031	—	—	—	0.014	0.204	0.005	0.067	0.009	99.646
7-4	Gn	—	—	13.649	—	84.767	0.038	—	0.38	0.001	—	—	—	—	—	0.001	0.220	0.010	0.013	0.030	99.109
18-2	Gn	—	—	13.491	—	84.491	0.180	0.025	0.779	0.018	—	0.076	—	—	0.008	—	0.009	0.173	0.072	0.471	99.793
18-3	Gn	—	—	13.381	0.003	82.832	0.747	0.005	2.044	—	—	0.171	—	—	—	0.016	—	0.308	0.001	—	99.508
24-1	Gn	—	—	13.545	—	84.609	0.167	—	0.330	—	—	0.036	—	0.007	—	0.021	0.212	—	0.057	0.012	98.996
28-1	Gn	—	—	13.489	—	86.296	0.044	—	0.416	—	—	—	—	—	—	—	0.111	0.016	0.101	0.031	100.504
32-2	Gn	—	—	13.564	—	81.641	1.166	0.131	2.873	—	—	0.016	—	—	—	0.034	0.010	—	0.030	—	99.465
15-4	Gn	—	—	13.596	0.020	85.520	0.131	—	0.373	0.012	—	0.012	—	—	—	—	0.142	—	0.074	—	99.880

TABLE 1: Continued.

Sample number	Mineral	As	Au	S	Ga	Pb	Ag	Se	Bi	Mn	Cd	Fe	In	Co	Sn	Ni	Sb	Cu	Te	Zn	Total
5-1	Py	—	0.079	53.193	—	0.046	0.023	—	0.046	—	0.020	46.336	—	—	—	0.014	0.017	0.017	—	0.019	99.810
8-3	Py	—	—	53.483	—	0.113	—	—	0.046	—	—	46.402	0.018	0.064	—	0.009	0.002	0.016	—	—	100.153
10-3	Py	0.713	—	52.769	0.012	0.093	—	—	0.039	—	0.040	46.235	—	0.074	—	0.020	—	0.021	0.003	0.027	100.046
10-4	Py	0.848	—	52.523	—	0.048	0.001	—	0.030	—	0.012	45.932	0.005	0.091	—	—	—	0.007	0.006	0.035	99.538
11-3	Py	0.928	0.062	51.566	—	0.134	0.023	—	0.054	—	0.034	45.769	—	0.085	—	—	0.051	0.011	—	0.048	98.765
21-1	Py	0.010	—	53.095	—	0.352	0.002	—	0.039	—	0.042	46.003	0.022	0.095	—	—	0.033	0.061	0.017	0.006	99.777
31-1	Py	0.017	—	53.437	—	0.045	0.018	0.019	0.111	—	—	46.565	—	0.069	—	—	—	0.014	0.016	0.013	100.324
3-4	Apy	41.307	—	22.467	—	0.025	0.024	—	0.067	—	—	35.648	—	—	—	—	0.350	0.016	—	0.327	100.231
5-1	Apy	39.484	0.040	23.421	—	—	—	—	—	—	—	36.146	0.010	—	—	—	0.557	0.012	—	0.027	99.697
5-3	Apy	40.065	0.115	22.722	—	0.119	0.010	—	—	—	0.013	36.100	0.034	—	—	0.003	0.042	0.020	—	—	99.243
10-4	Apy	42.373	—	22.559	—	0.122	0.010	—	0.031	0.029	—	35.499	0.026	0.068	—	—	—	—	—	0.023	100.740
31-1	Apy	43.610	0.093	21.604	—	0.055	0.021	—	—	0.017	—	35.633	0.065	0.065	—	0.023	0.004	0.003	—	0.024	101.217
14-2	Apy	40.798	0.069	22.586	—	0.112	—	—	—	—	0.013	35.735	—	0.056	—	—	0.020	—	—	0.025	99.414
7-2	Ccp	0.007	—	35.414	—	0.079	0.010	—	0.097	0.012	0.041	30.330	—	0.042	—	0.008	—	34.111	0.007	0.043	100.201
7-4	Ccp	—	0.040	34.923	0.017	0.127	0.007	—	0.050	—	0.008	29.901	0.037	0.030	—	—	0.005	33.332	—	0.065	98.542
8-4	Ccp	0.014	0.030	35.202	—	0.082	0.003	0.023	0.084	—	—	29.934	0.007	0.055	—	—	—	34.174	—	0.083	99.691
18-2	Ccp	0.047	0.025	35.068	0.024	0.037	0.054	—	0.028	0.015	—	30.404	0.006	0.038	—	—	—	33.993	—	0.048	99.787
18-3	Ccp	0.007	—	34.909	—	0.136	0.018	—	0.065	—	—	30.155	0.002	0.061	—	—	0.021	33.757	—	0.039	99.170
22-1	Ccp	0.004	—	34.719	—	0.046	—	—	0.021	—	—	30.297	0.003	0.057	—	0.012	0.004	33.684	—	0.112	98.959
31	Ccp	—	0.015	34.813	—	0.148	0.014	—	—	—	—	30.456	—	0.052	—	—	—	33.856	—	0.011	99.365
32-1	Ccp	—	0.039	35.141	—	0.109	—	0.004	0.062	—	0.050	30.303	0.029	0.045	0.023	0.003	0.040	34.081	—	0.076	100.005
22-1	Ttr	0.345	—	24.658	—	0.114	4.055	—	0.035	0.008	0.067	3.858	—	—	0.043	0.005	28.067	35.483	—	3.342	100.080
32-1	Ttr	0.252	0.114	24.963	0.003	0.017	6.933	—	0.037	0.002	0.024	3.881	—	0.029	—	—	27.885	33.480	—	3.366	100.986
1-3	Fbt	0.294	—	23.415	—	—	19.557	—	—	—	—	4.165	—	—	—	—	26.225	23.600	—	2.566	99.822
2-3	Fbt	0.232	—	23.289	—	—	19.808	—	0.111	—	0.191	4.330	—	—	—	—	25.686	23.849	—	2.326	99.822
2-3	Fbt	0.34	0.067	23.485	0.009	0.081	19.375	—	0.019	—	0.174	4.411	—	—	—	0.007	26.458	23.895	—	2.286	100.607
5-2	Fbt	0.27	0.005	22.979	0.006	0.054	21.461	—	—	—	0.247	3.678	—	—	—	—	26.167	22.402	—	3.017	100.286
8-4	Fbt	0.314	0.102	24.093	—	0.041	15.340	0.035	0.062	0.010	—	4.651	—	0.020	—	—	26.460	27.071	—	2.202	100.401
11-4	Fbt	0.261	0.053	24.121	0.006	0.002	15.592	0.048	0.015	—	—	4.457	—	—	—	—	27.191	27.196	—	2.418	101.360
18-3	Fbt	0.208	0.059	24.013	—	0.046	12.557	0.005	0.037	0.004	—	4.696	—	0.003	—	—	27.053	29.351	—	3.435	101.467
18-3	Fbt	0.249	—	24.314	—	0.055	12.015	—	0.025	0.001	—	4.322	—	—	—	0.026	27.363	29.914	—	3.425	101.709
21-1	Fbt	0.544	0.069	24.228	—	0.028	12.808	0.019	0.143	—	—	4.140	—	—	—	—	26.794	28.896	—	2.755	100.424
24-1	Fbt	0.114	0.094	22.765	0.055	0.078	27.015	—	—	0.013	—	6.259	—	0.028	—	0.006	26.564	18.975	—	—	101.966
28-1	Fbt	0.171	—	23.050	0.027	—	22.595	—	—	0.004	—	4.609	—	0.037	—	—	26.380	21.881	—	1.997	100.751
13-1	Fbt	0.210	—	23.858	—	0.097	17.547	—	—	0.011	—	4.632	—	0.005	—	0.014	26.962	25.832	—	2.289	101.457

TABLE 1: Continued.

Sample number	Mineral	As	Au	S	Ga	Pb	Ag	Se	Bi	Mn	Cd	Fe	In	Co	Sn	Ni	Sb	Cu	Te	Zn	Total
14-2	Fbt	0.212	0.072	23.447	—	0.080	21.079	—	—	0.019	—	4.742	—	0.027	—	—	26.926	22.981	—	1.949	101.534
15-4	Fbt	0.217	0.086	22.953	—	0.224	22.193	0.008	—	—	—	4.157	—	—	—	—	25.959	21.710	—	2.365	99.872
2-1	Blr	—	—	18.651	—	54.937	—	—	0.233	—	0.019	—	—	—	—	—	24.586	0.021	—	0.007	98.454
2-3	Blr	—	—	18.957	—	54.738	0.011	—	0.148	—	0.060	0.093	—	—	—	—	24.425	0.023	—	3.535	102.014
3-1	Blr	0.017	—	18.217	0.006	54.141	—	—	0.088	—	0.046	—	—	—	—	—	24.083	—	—	—	96.645
3-2	Blr	—	—	18.864	—	54.500	—	—	0.179	—	0.044	0.041	—	—	—	—	24.463	0.020	—	0.018	98.129
4-1	Blr	0.003	—	18.602	0.01	53.979	—	—	0.188	—	0.052	0.014	—	—	—	0.005	24.512	0.017	—	—	97.382
4-2	Blr	—	0.016	18.972	—	55.026	—	—	0.206	—	0.126	0.017	—	—	—	—	25.148	0.004	—	0.013	99.528
6-3-1	Blr	—	—	19.096	—	54.167	—	—	0.111	—	—	0.488	—	—	—	—	24.960	—	—	—	98.822
6-3	Blr	0.007	—	18.938	0.008	55.070	0.072	—	0.220	—	0.033	0.012	—	—	—	0.024	25.064	—	—	—	99.448
7-2	Blr	—	—	18.855	0.048	55.871	—	—	0.240	0.009	0.115	0.046	—	—	0.127	0.010	25.383	0.041	—	—	100.745
7-3	Blr	—	—	18.689	—	55.577	—	—	0.152	—	0.060	—	—	—	0.090	0.015	26.127	0.014	—	0.024	100.748
7-4	Blr	—	—	18.702	—	54.469	—	—	0.186	—	0.037	0.011	—	—	0.076	0.007	24.850	—	—	0.034	98.372
8-4	Blr	—	—	19.000	0.021	54.615	0.005	—	0.082	0.013	0.016	0.035	—	—	0.179	0.026	25.020	0.022	—	0.032	99.066
23-1	Blr	—	—	18.990	—	55.951	—	—	0.300	—	0.034	0.025	—	—	0.083	—	25.535	0.797	—	0.027	101.742
33-1	Blr	—	—	18.829	—	54.852	0.020	—	0.118	—	0.091	0.008	—	—	0.063	0.013	25.070	—	—	0.031	99.095
13-1	Blr	—	0.114	18.992	—	54.801	0.016	—	0.222	—	0.124	0.041	—	0.006	0.076	0.010	25.109	—	—	0.103	99.614
13-5	Blr	—	—	18.935	0.045	54.611	—	0.002	0.181	0.006	0.025	0.051	—	0.003	0.057	0.034	25.303	—	—	0.032	99.285
8-2	Jmt	—	—	21.913	0.054	40.001	—	—	0.247	0.109	0.023	2.639	—	0.021	0.171	0.003	34.138	0.023	—	0.051	99.393
8-3	Jmt	—	—	21.879	0.048	39.733	—	—	0.214	0.054	0.054	2.677	—	—	0.143	—	34.363	0.003	—	0.050	99.218
8-1-1	Jmt	—	—	22.019	—	38.441	—	0.002	0.115	0.142	0.111	2.619	—	0.019	0.124	0.006	33.733	0.005	—	—	97.336
8-1	Jmt	—	—	21.90	0.015	39.601	—	0.005	0.133	0.072	0.135	2.637	—	—	0.143	0.043	34.229	—	—	0.001	98.914
10-3	Jmt	0.002	—	21.757	0.013	39.076	0.101	—	0.143	0.097	0.094	2.652	—	—	0.176	—	35.713	0.071	—	0.042	99.937
10-4	Jmt	0.019	—	22.207	—	38.996	0.130	—	0.210	0.133	0.079	2.66	—	0.002	0.148	0.004	35.506	0.063	—	—	100.160
11-4	Jmt	—	—	21.972	0.023	39.342	—	0.020	0.187	0.062	0.105	2.715	0.007	—	0.198	0.005	34.933	0.017	—	0.006	99.592
11-3	Jmt	—	—	21.941	0.031	39.909	—	0.028	0.198	0.095	0.088	2.580	—	0.008	0.103	0.019	34.599	—	—	0.049	99.648
35-3	Jmt	—	—	21.983	—	39.380	0.268	0.012	0.126	0.028	0.082	2.660	—	0.007	0.177	0.024	35.835	0.034	—	0.076	100.690
13-1	Jmt	—	—	21.917	0.039	39.913	—	—	0.138	0.058	0.105	2.659	—	0.021	0.151	0.007	34.495	—	—	0.004	99.507
13-5	Jmt	0.004	—	21.881	—	39.654	—	0.029	0.113	0.040	0.089	2.748	—	—	0.168	0.002	34.543	0.017	—	—	99.288
3-1	Bnn	0.125	—	19.828	—	42.527	0.004	—	0.259	—	0.060	0.027	—	—	—	0.001	24.339	13.046	—	0.046	100.262
5-2	Bnn	0.124	—	19.225	—	41.070	0.010	—	0.109	—	0.020	0.182	—	—	—	0.018	23.716	13.262	—	0.116	97.852
1-1	Bnn	—	—	20.042	—	42.061	—	—	0.093	—	—	—	—	0.013	—	—	23.932	13.533	—	0.066	99.740
1-3	Bnn	0.049	—	19.905	—	41.608	—	—	0.226	—	—	0.040	—	0.009	—	0.014	23.965	13.241	—	0.014	99.071
18-2	Bnn	0.058	—	19.715	—	41.791	—	—	0.301	0.004	0.044	0.043	—	—	0.033	0.018	23.673	13.303	—	0.003	98.986
18-2-1	Bnn	—	—	20.030	0.046	42.235	—	0.015	0.500	0.006	0.068	0.039	—	—	0.003	—	24.212	13.150	—	0.599	100.903

TABLE 1: Continued.

Sample number	Mineral	As	Au	S	Ga	Pb	Ag	Se	Bi	Mn	Cd	Fe	In	Co	Sn	Ni	Sb	Cu	Te	Zn	Total
21-1	Bnn	0.015	—	19.991	—	41.646	0.006	0.032	0.160	—	0.045	0.008	—	0.001	0.089	—	24.540	13.409	—	0.003	99.945
22-1	Bnn	0.036	—	19.922	0.025	41.942	—	—	0.196	0.001	0.097	0.002	—	—	0.079	0.005	24.008	13.276	—	0.062	99.651
23-1	Bnn	0.070	—	19.945	0.012	42.335	0.006	0.007	0.142	—	0.026	0.007	—	—	0.081	—	24.409	13.235	—	0.111	100.386
23-1-1	Bnn	—	—	19.956	—	42.890	0.008	0.008	0.162	—	0.066	0.023	—	0.021	0.096	0.008	24.098	12.373	—	0.039	99.748
24-1	Bnn	0.097	—	20.036	—	41.541	—	—	0.249	—	0.033	—	—	0.003	0.075	0.011	24.305	13.444	—	0.006	99.800
27-1	Bnn	0.077	0.022	19.949	—	42.112	—	0.017	0.311	—	0.074	0.014	—	0.004	0.107	0.022	24.421	13.298	—	0.048	100.476
27-1-1	Bnn	—	—	19.934	—	42.808	0.012	—	0.422	—	0.135	—	—	—	0.091	—	24.214	13.337	—	0.029	100.982
27	Bnn	—	—	19.830	—	42.547	—	0.016	0.422	0.018	0.041	—	—	—	0.044	—	23.771	13.284	—	0.038	100.011
28-1	Bnn	0.116	—	20.034	—	42.004	—	—	0.114	0.013	0.060	0.033	—	—	0.072	0.038	24.252	13.375	—	0.028	100.139
32-1	Bnn	—	—	20.188	—	41.955	—	—	0.177	0.002	0.124	0.002	—	0.008	0.051	—	24.094	13.249	—	—	99.850
32-2	Bnn	0.057	—	19.830	—	42.433	—	—	0.383	0.001	0.091	0.030	—	0.012	0.104	0.040	24.200	13.347	—	0.024	100.552
15-4	Bnn	0.004	—	19.799	0.002	42.672	—	—	0.144	0.002	0.057	0.004	—	—	0.074	—	24.062	13.286	—	—	100.106
36-4	Stb	0.244	—	28.406	—	0.412	0.011	0.037	—	—	0.235	0.015	—	—	0.319	0.029	70.217	0.032	—	0.034	99.991
36-4-1	Stb	0.213	0.036	28.400	0.095	0.102	—	0.023	0.079	—	0.229	—	0.015	—	0.296	—	70.179	0.031	—	—	99.698
36-3	Stb	0.242	0.045	28.429	—	0.125	—	—	—	—	0.238	—	—	—	0.363	—	70.202	0.039	—	0.026	99.709
36-3	Stb	0.251	—	28.534	—	0.186	0.013	—	—	—	0.184	0.001	—	—	0.292	—	70.353	0.078	—	—	99.892

Note: the elemental content unit is %. Sp = sphalerite; Gn = galena; Py = pyrite; Apy = arsenopyrite; Ccp = chalcopyrite; Ttr = tetrahedrite; Fbt = freibergite; Blr = boulangerite; Jmt = jamesonite; Bnn = bornonite; Stb = stibnite.

FIGURE 8: Photomicrographs showing the types and characteristic features of fluid inclusions (FIs) at the Keyue Sb-Pb-Zn-Ag deposit. (a) Coexistence of the primary and secondary FIs that linearly distribute in assemblage 3 quartz. (b) The pseudosecondary FIs linearly distribute in assemblage 4 quartz. (c) The elliptic V-type FIs in assemblage 3 quartz. (d) The long-columnar C-type FIs in assemblage 3 quartz. (e) The irregular halite-bearing FIs in assemblage 4 quartz. (f) The elliptic G-type FIs in assemblage 3 quartz. (g) The rectangular L-type FIs in assemblage 1 Mn-Fe carbonate. (h) The rhombic L-type FIs in assemblage 2 Mn-Fe carbonate. (i) The L-type FIs isolatedly distribute in assemblage 5 quartz. (j) The long-columnar L-type FIs in assemblage 2 sphalerite. (k) The long-columnar L-type FI inclusions in assemblage 2 sphalerite. (l) The S-type FIs in assemblage 2 sphalerite. Abbreviations are the same as in Figure 5.

distribute in quartz in the filiform form (Figure 8(a)); and (3) pseudosecondary FIs: the shape of pseudosecondary FIs is similar to that of secondary FIs, and their compositions are consistent with primary FIs yet usually distribute in mineral crystal in the form of filiform assemblages (Figure 8(b)).

(2) *Phase Types*. Based on the observation of FI compositions and phases at room temperature (21°C), as well as phase

transitions during heating and cooling, there are four phase types of FIs which have been recognized in the Keyue deposit: (1) water FIs (W-type): the W-type FIs are the most common type in the Keyue deposit and are widespread in every ore-forming assemblages, which accounts for more than 90% of the total amount. The W-type FIs are usually black and consist of vapor and liquid phase water with minor reducing gases (e.g., CO₂). At room temperature (21°C), the W-type

TABLE 2: Microthermometric results of fluid inclusions from minerals in the Keyue deposit.

Sample number	Mineral	Genetic type	$T_{h, total}$ (°C)	$T_{m, ice}$ (°C)	Salinity (wt%)	Density (g/cm ³)
D41-1-2	Sp2	Primary	220.3~261.6 ($n = 30$)	-9.4~-5.6 ($n = 27$)	8.7~13.3 ($n = 27$)	0.86~0.92 ($n = 27$)
ZK3603-H8-1	Sp2	Primary	216.5~254.3 ($n = 30$)	-11.0~-4.7 ($n = 21$)	7.4~15.0 ($n = 21$)	0.86~0.93 ($n = 21$)
D41-1-1	Sp2	Primary	213.5~277.2 ($n = 25$)	-5.2~-13.1 ($n = 22$)	8.1~17.0 ($n = 22$)	0.86~0.96 ($n = 22$)
ZK805-H10-1	Sp2	Primary	172.9~241.5 ($n = 27$)	-12.7~-5.8 ($n = 26$)	8.9~16.6 ($n = 26$)	0.90~0.98 ($n = 26$)
Average			233.66 ($n = 112$)	-7.4 ($n = 96$)	10.97 ($n = 96$)	0.91 ($n = 96$)
ZK3603-397	Qtz3	Primary	188.7~245.9 ($n = 17$)	-6.7~-2.0 ($n = 12$)	3.4~10.1 ($n = 12$)	0.895~0.94 ($n = 12$)
D41-7-1	Qtz3	Primary	183.5~271.7 ($n = 30$)	-11.5~-1.9 ($n = 25$)	3.2~15.5 ($n = 25$)	0.84~1.02 ($n = 25$)
ZK4801-108-1	Qtz3	Primary	175.0~302.7 ($n = 38$)	-7.7~-4.1 ($n = 34$)	6.6~11.3 ($n = 34$)	0.79~0.96 ($n = 34$)
Average			229.13 ($n = 85$)	-5.8 ($n = 71$)	8.88 ($n = 71$)	0.90 ($n = 71$)
D41-1-2	Qtz4	primary	175.0~270.6 ($n = 15$)	-6.9~-5.1 ($n = 11$)	8.0~10.1 ($n = 11$)	0.84~0.94 ($n = 11$)
D41-4-2	Qtz4	primary	205.0~250.0 ($n = 29$)	-14.2~-2.0 ($n = 22$)	3.4~17.96 ($n = 22$)	0.84~0.98 ($n = 22$)
D41-1-1	Qtz4	primary	190.0~283.4 ($n = 14$)	-7.5~-3.7 ($n = 11$)	6.0~11.1 ($n = 11$)	0.81~0.94 ($n = 11$)
ZK805-H10-1	Qtz4	primary	188.7~321.0 ($n = 17$)	-8.9~-4.5 ($n = 16$)	7.2~12.7 ($n = 16$)	0.78~0.95 ($n = 16$)
D39-4-2	Qtz4	primary	142.1~232.3 ($n = 19$)	-9.7~-3.2 ($n = 17$)	5.3~13.6 ($n = 17$)	0.90~1.02 ($n = 17$)
D41-3-2	Qtz4	primary	172.6~252.0 ($n = 14$)	-5.8~-1.6 ($n = 11$)	2.7~8.9 ($n = 11$)	0.82~0.93 ($n = 11$)
Average			220.95 ($n = 108$)	-5.7 ($n = 88$)	8.69 ($n = 88$)	0.91 ($n = 88$)

Note: Sp2 = stage 2 sphalerite; Qtz3 = stage 3 quartz; Qtz4 = stage 4 quartz.

FIs can be divided into two subtypes according to the filling percentage of liquid phase: ① liquid-rich two-phase FIs (L-type; Figures 8(a), 8(b), and 8(i)–8(k)) have the liquid phase filling percentage around 60~95% and contain a tiny globose vapor phase wrapped in liquid phase; ② vapor-rich two-phase FIs (V-type; Figure 8(c)) have the liquid phase filling percentage of only 5~40% and are not abundant as L-type FIs in the Keyue deposit. (2) CO₂-bearing three-phase FIs (C-type): the C-type FIs slightly spread in assemblage 3 quartz and are composed of liquid phase, CO₂ liquid phase, and CO₂ vapor phase. The CO₂ vapor phase distributes in the CO₂ liquid phase in the form of tiny bubble and thump (Figure 8(d)). (3) Gas FIs (G-type): the G-type FIs with dead color are filled only by vapor phase, in round shape, and rarely develop in assemblage 3 quartz (Figure 8(f)). (4) Solid-bearing three-phase FIs (S-type): the S-type FIs rarely occur in assemblage 2 sphalerite and assemblage 4 quartz and consist of liquid phase, vapor phase, and daughter crystal, in which the liquid phase is in dominance (Figures 8(e) and 8(l)).

(3) *The Characteristic of FIs in Different Ore-Forming Assemblages.* The characteristics of FIs differ in different ore-forming assemblages. Assemblage 1: there are only minor amounts of FIs in Mn–Fe carbonate. The irregular, rectangular, and rhombic L-type FIs are dominated and isolatedly distribute with the size of 3~10 μm and liquid phase filling percentage of 70~90% (Figure 8(g)). Assemblage 2: in assemblage 2 Mn–Fe carbonate, the characteristic of FIs (Figure 8(h)) is similar to that of FIs in assemblage 1 Mn–Fe carbonate; however, assemblage 2 sphalerite develops many larger L-type (Figures 8(j) and 8(k)) and few S-type FIs (Figure 8(l)) with the size of 20~60 μm and long columnar, tubular, and rectangular shapes. Assemblage 3: assemblage 3 quartz develops lots of L-type (Figure 8(a)), a few

of V-type (Figure 8(c)) and G-type (Figure 8(f)), and few C-type (Figure 8(d)) FIs. These FIs distribute in isolation or assemblages and have irregular, tubular, elliptic, and negative crystal shapes with the size of 8~20 μm . Assemblage 4: the FIs in assemblage 4 quartz are less than those in assemblage 3 and are dominated by irregular, rectangular, elliptic, and negative crystal L-type FIs that distribute in isolation or assemblages with the size of 5~15 μm and liquid phase filling percentage of 70~90% (Figure 8(b)). Meanwhile, there are also some S-type FIs in assemblage 4 quartz (Figure 8(e)). Assemblage 5: assemblage 5 quartz only develops minor amounts of L-type FIs that isolatedly distribute in the shape of negative crystal and ellipse with the size of 4~12 μm and liquid phase filling percentage of 70~90% (Figure 8(i)).

4.3.2. Microthermometry. In view of the following facts, (1) the L-type FIs are in dominance, (2) the amounts and sizes of the FIs in assemblages 1 and 2 Mn–Fe carbonate and assemblage 5 quartz are relatively less and tiny, and (3) the primary FIs can constrain the characteristic of ore-forming fluid better; the microthermometry research are mainly trapped on 306 primary L-type FIs from 13 representative assemblage 2 sphalerite and assemblage 3 and 4 quartz samples. The results are listed in Table 2.

The L-type FIs in assemblage 2 sphalerite have homogenization temperatures of 172.9~277.2°C that concentrate on 230~250°C (Figure 9(a); average: 233.66°C; $n = 112$) and ice-melting temperatures of -13.1~-4.7°C (average: -7.4°C; $n = 96$), corresponding to salinities of 7.4~17.0 wt% NaCl eq. that concentrate on 10.0~13.0 wt% (Figure 9(b); calculated by equations from Hall et al. [57]; average: 10.97 wt% NaCl eq.; $n = 96$) and densities of 0.86~0.98 g/cm³ (calculated by equations from Liu and Duan [58]; average: 0.91 g/cm³; $n = 96$). The L-type FIs in assemblage 3 quartz have

FIGURE 9: Histograms of homogenization temperature and salinity of FIs in minerals of different assemblages from the Keyue Sb–Pb–Zn–Ag deposit: (a) and (b) assemblage 2 sphalerite; (c) and (d) assemblage 3 quartz; (e) and (f) Assemblage 4 quartz. Abbreviations are the same as in Figure 5.

homogenization temperatures ranging from 175.0 to 302.5°C that concentrate on 240–250°C (Figure 9(c); average: 229.13°C; $n = 85$) and ice-melting temperatures ranging from -11.5 to -1.9 °C (average: -5.8 °C; $n = 71$), which correspond to salinities ranging from 3.2 to 15.5 wt% NaCl eq. that concentrate on 8.0–9.0 wt% (Figure 9(d); average: 8.88 wt% NaCl eq.; $n = 71$) and densities ranging from 0.79 to 1.02 g/cm³ (average: 0.90 g/cm³; $n = 71$). The L-type FIs in assemblage 4 quartz show the homogenization temperatures varying from 142.1 to 321.0°C that concentrate on 220–240°C (Figure 9(e); average: 220.95°C; $n = 108$) and the ice-melting temperatures varying from -14.2 to -1.6 °C

(average: -5.7 °C; $n = 88$), with the calculated salinities that vary from 2.7 to 17.96 wt% NaCl eq. concentrating on 9.0–10.0 wt% (Figure 9(f); average: 8.69 wt% NaCl eq.; $n = 88$) and densities that vary from 0.78 to 1.02 g/cm³ (average: 0.91 g/cm³; $n = 88$).

4.3.3. Laser Raman Spectroscopy. The W-type, G-type, and C-type FIs in quartz and W-type FIs in Mn–Fe carbonate are selected for laser Raman microspectroscopic analyses, the size of these FIs is usually $\geq 10 \mu\text{m}$. All the results of individual FIs are shown in Figure 10. It can be generally recognized that H₂O dominates the liquid phase (Figures 10(b),

FIGURE 10: Continued.

FIGURE 10: Representative laser Raman spectra of FIs in the Keyue Sb-Pb-Zn-Ag deposit. (a) CO₂ spectra of vapor phase in the W-type FIs of assemblage 2 Mn-Fe carbonate; (b) H₂O spectra of liquid phase in the CO₂-bearing W-type FIs of assemblage 2 Mn-Fe carbonate; (c) CO₂ spectra of vapor phase in the CO₂-bearing W-type FIs of assemblage 3 quartz; (d) H₂O spectra of liquid phase in the CO₂-bearing W-type FIs of assemblage 3 quartz; (e) CO₂ spectra of vapor phase in the G-type FIs of assemblage 3 quartz; (f) CO₂ spectra of vapor phase in the C-type FIs of assemblage 3 quartz; (g) CO₂ spectra of vapor phase in the C-type FIs of assemblage 3 quartz; (h) H₂O spectra of liquid phase in the C-type FIs of assemblage 3 quartz; (i) CO₂ spectra of vapor phase in the CO₂-bearing W-type FIs of assemblage 4 quartz; (j) H₂O spectra of liquid phase in the CO₂-bearing W-type FIs of assemblage 4 quartz.

TABLE 3: The H-O isotopic data for minerals from the Keyue deposit.

Sample number	Mineral	δD_{V-SMOW} (‰)	$\delta^{18}O_{V-SMOW}$ (‰)	$\delta^{18}O_{H_2O}$ (‰)	$T_{h,total}$ (°C)	Description
ZK003-43	Cal3	-128	—	—	—	Stage 3 sphalerite-calcite.
ZK003-43	Cal3	-120	—	—	—	Stage 3 sphalerite-calcite.
D39-2	Qtz3	-157	15.7	2.86	183.1	Stage 3 quartz-sphalerite-pyrite vein.
D40-1	Qtz3	-125	21.1	11.34	233.65	Stage 3 quartz-sphalerite.
D40-1-1	Qtz3	-135	20.4	10.63	233.65	Stage 3 quartz-sphalerite.
D40-1-2	Qtz3	-153	20.7	10.94	233.65	Stage 3 quartz-sphalerite.
D41-8	Qtz3	-155	16.3	6.54	233.65	Stage 3 galena occurs in quartz druse.
ZK3603H3	Qtz3	-174	16.7	6.94	233.65	Stage 3 quartz-sphalerite
D41-4	Qtz3	-151	15.3	5.21	227.4	Stage 3 quartz-sphalerite-galena vein.
D41-3	Qtz4	-161	15.5	2.59	182.1	Stage 4 quartz-boulangerite vein.
D39-4	Qtz4	-165	15.6	2.69	182.1	Stage 4 quartz-boulangerite vein.
D39-4	Qtz4	-164	14.5	1.59	182.1	Stage 4 quartz-boulangerite vein.
4600-50	Qtz5	—	12.6	—	—	Stage 5 quartz-stibnite vein.
4600-50	Qtz5	—	14.3	—	—	Stage 5 quartz-stibnite vein

Note: Cal3 = stage 3 calcite; Qtz3 = stage 3 quartz; Qtz4 = stage 4 quartz; Qtz5 = stage 5 quartz.

10(d), 10(h), and 10(j)), while in the vapor phase, the Raman spectral apexes of H₂O and CO₂ can be observed except those of host minerals (quartz and calcite; Figures 10(a), 10(c), 10(e)–10(g), and 10(i)).

4.4. H-O-S-Pb Isotopes. All the H-O isotopic data are given in Table 3. The total δD_{V-SMOW} and $\delta^{18}O_{V-SMOW}$ values range from -174‰~-120‰ (average: -149‰, $n = 12$) and 12.6‰~21.1‰ (average: 16.56‰, $n = 12$), respectively. Separately, assemblage 3 calcite samples have δD_{V-SMOW} values of -120‰ and -128‰ (average: -124‰, $n = 2$), assemblage 3 quartz samples show δD_{V-SMOW} and $\delta^{18}O_{V-SMOW}$ values of -125‰~-174‰ (average: -150‰, $n = 7$) and 15.3‰~21.1‰ (average: 18.0‰, $n = 7$), assemblage 4 quartz samples exhibit δD_{V-SMOW} and $\delta^{18}O_{V-SMOW}$

values of -161‰~-165‰ (average: -163‰, $n = 3$) and 14.5‰~15.6‰ (average: 15.2‰, $n = 3$), and assemblage 5 quartz samples have $\delta^{18}O_{V-SMOW}$ values of 12.6‰~14.3‰ (average: 13.5‰, $n = 2$).

The S isotopic results of sulfides from the Keyue deposit are summarized in Table 4. The overall S isotopic variation range is from 4.9‰ to 11.2‰ with an average of 8.2‰ ($n = 22$). Among the sulfides, sphalerite samples have $\delta^{34}S_{CDT}$ ‰ values of 7.1‰~11.2‰ with an average of 10.0‰ ($n = 9$), galena samples cover the $\delta^{34}S_{CDT}$ ‰ values ranging 4.9‰~8.4‰ with an average of 6.7‰ ($n = 5$), pyrite samples have $\delta^{34}S_{CDT}$ ‰ values of 5.0‰ and 6.6‰ with an average of 5.8‰ ($n = 2$), chalcopyrite samples show $\delta^{34}S_{CDT}$ ‰ values of 6.4‰ and 7.0‰ with an average of 6.7‰ ($n = 2$), boulangerite samples exhibit $\delta^{34}S_{CDT}$ ‰ values

TABLE 4: The S isotopic data for sulfides from the Keyue deposit.

Sample number	Mineral	$\delta^{34}\text{S}_{\text{CDT}}\text{‰}$	Description
D41-2-4	Sp2	10.6	Stage 2 massive sphalerite–galena–chalcopyrite.
	Gn2	8.4	
ZK805-H8	Sp2	9.4	Stage 2 massive sphalerite–galena–chalcopyrite.
	Gn2	7.4	
Zk1604-H25	Gn2	5.4	Stage 2 massive sphalerite–galena–Mn–Fe carbonate cut by stage 4 quartz–boulangerite vein.
	Sp2	10.2	
	Blr4	6.6	
D41-3-1	Sp2	11.2	Stage 2 massive sphalerite cut by stage 4 quartz–boulangerite vein.
	Blr4	9.9	
D39-4-2	Sp2	11.2	Stage 2 massive sphalerite cut by stage 4 quartz–boulangerite vein.
	Blr4	7.4	
D40-2	Sp3	11.2	Stage 3 massive sphalerite–galena–chalcopyrite–galena; there are minor amounts of Mn–Fe carbonate left.
	Gn3	7.4	
D39-5-2	Gn3	4.9	Stage 3 massive sphalerite–galena–chalcopyrite cross-cut by quartz veins.
	Ccp3	6.4	
D40-1-2	Sp3	7.1	Stage 3 quartz–sphalerite.
D41-5	Sp3	9.6	Stage 3 massive quartz–sphalerite–chalcopyrite cut by stage 4 quartz–boulangerite vein.
	Ccp3	7.0	
ZK003-433-1	Sp3	9.9	Stage 3 sphalerite–calcite
D41-8	Py3	6.6	Stage 3 pyrite occurs in quartz; there are minor amounts of Mn–Fe carbonate left.
D41-7-1 (3)	Py3	5.0	Stage 3 quartz–pyrite–galena vein cut the Mn–Fe carbonate.
KY-1-1	Stb5	8.2	Stage 5 radial stibnite occurs in stage 5 quartz.

Note: Sp2 = stage 2 sphalerite; Gn2 = stage 2 galena; Sp3 = stage 3 sphalerite; Gn3 = stage 3 galena; Ccp3 = stage 3 chalcopyrite; Py3 = stage 3 pyrite; Blr4 = stage 4 boulangerite; Stb5 = stage 5 stibnite.

ranging from 6.6‰ to 9.9‰ with an average of 8.0‰ ($n = 3$), and the stibnite sample has the $\delta^{34}\text{S}_{\text{CDT}}\text{‰}$ value of 8.2‰ ($n = 1$) (Figure 11).

The Pb isotopic data of sulfides from the Keyue deposit are reported in Table 5. These sulfide samples give relative uniform Pb isotopic ratios of $^{206}\text{Pb}/^{204}\text{Pb} = 18.530\sim 19.780$ (average = 19.590, $n = 8$), $^{207}\text{Pb}/^{204}\text{Pb} = 15.674\sim 15.939$ (average = 15.849, $n = 8$), and $^{208}\text{Pb}/^{204}\text{Pb} = 38.618\sim 40.559$ (average = 40.155, $n = 8$). To be specific, five galena samples have $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of 19.709~19.765, $^{207}\text{Pb}/^{204}\text{Pb}$ ratios of 15.831~15.874, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of 40.247~40.395; two boulangerite samples exhibit the uniform $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of 19.771 and 19.780, $^{207}\text{Pb}/^{204}\text{Pb}$ ratios of 15.896 and 15.939, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of 40.423 and 40.559; and one stibnite sample shows the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio of 18.530, $^{207}\text{Pb}/^{204}\text{Pb}$ ratio of 15.674, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratio of 38.618.

5. Discussion

5.1. Geology, Mineralogy, and Element Characteristics. Based on the detailed field and petrological observations, as well as the cross-cutting relationships between minerals, the six ore-forming assemblages of ore and gangue minerals can represent six stages of ore formation from early to late

FIGURE 11: Frequency histogram plots of $\delta^{34}\text{S}$ values for sulfide minerals from the Keyue Sb–Pb–Zn–Ag deposit.

TABLE 5: The Pb isotopic data for sulfides from the Keyue deposit.

Sample number	Mineral	$^{206}\text{Pb}/^{204}\text{Pb}$	2σ	$^{207}\text{Pb}/^{204}\text{Pb}$	2σ	$^{208}\text{Pb}/^{204}\text{Pb}$	2σ	μ ($^{238}\text{U}/^{204}\text{Pb}$)
KY-1	Gn3	19.714	0.002	15.849	0.004	40.247	0.004	9.84
KY-2	Gn3	19.722	0.003	15.865	0.002	40.309	0.003	9.87
KY-3	Gn3	19.709	0.003	15.862	0.002	40.362	0.005	9.86
KY-4	Gn3	19.765	0.002	15.831	0.002	40.329	0.004	9.80
KY-5	Gn3	19.726	0.002	15.874	0.002	40.395	0.005	9.88
KY-6	Blr4	19.780	0.004	15.939	0.003	40.559	0.005	10.00
KY-7	Blr4	19.771	0.003	15.896	0.003	40.423	0.005	9.92
KY-8	Stb5	18.530	0.003	15.674	0.004	38.618	0.005	9.60

Note: Abbreviations are the same as in Table 4.

(Figure 7). These six stages are assigned to three clear pulses, and this ore paragenetic sequence in the Keyue deposit is similar to that in the Zhaxikang deposit [20, 25].

The first pulse is Pb–Zn mineralization which consists of stages 1 and 2. Stage 1 is the initial stage of ore formation, and stage 2 hosts majority of the Pb–Zn mineralization in the Keyue deposit. Although the net-veined, brecciated, concentric annular, and globular textures that are present in the Zhaxikang deposit are rarely found in the Keyue deposit, the lamellar (Figures 4(a) and 4(b)), disseminated (Figure 4(c)), banded, and massive (Figures 4(d)–4(i) and 5(b)) ore textures; the assemblages and mineralogy of Mn–Fe carbonate and sulfides; and the hydrothermal sedimentary ore-bearing rocks (Ridang Formation) [2] still reveal the submarine hydrothermal sediment (metasomatism) genesis of the first pulse of mineralization in the Keyue deposit [1, 2]. Meanwhile, in view of that the Ridang Formation also contains some marine volcanic rocks [1, 2], Pb–Zn mineralization may relate to the seafloor volcanism. The second pulse is Sb–Ag mineralization which includes stages 3 and 4. Stage 3 is the transitional period from the first pulse to the second pulse of mineralization and overprints the first pulse mineralization. Stage 4 hosts majority of the Sb–Ag mineralization and yields the ores with relatively high average Ag grades. Comparing with the Zhaxikang deposit, the Keyue deposit contains a higher amount of chalcopyrite in stage 3 and fewer kinds of sulfosalt minerals in stage 4. The third pulse is Sb–Hg mineralization which is composed of stages 5 and 6. Stage 5 hosts part of Sb and majority of Hg mineralization, and stage 6 represents the youngest stage of mineralization in the Keyue deposit. The veined, massive, needle-like, elongated, and radial ore textures; the assemblages and mineralogy of quartz–calcite–sulfide–sulfosalt minerals; and the visible Ag in tetrahedrite, freibergite, andorite, and Ag-bearing inclusions and the invisible Ag in the form of submicroscopic Ag-bearing inclusions all evidence the epithermal genesis of the second and third pulses of mineralization in the Keyue deposit, which may be related to the later magmatism [1, 2, 10, 19].

Comparing the geology, mineralogy, and ore paragenetic sequence of the Keyue and Zhaxikang deposits, the orebodies are all controlled by faults, the ore-bearing rocks are both Ridang formations, the mineralogy and ore paragenetic sequence of ore and gangue minerals are almost the same,

and there is only one regional fault that separates them. We infer that there is a genetic relationship between the Keyue and Zhaxikang deposits, and they have the same origins and experiences and the same mineralization events. On the other hand, both the orebodies in the Keyue and Zhaxikang deposits are controlled by faults, which do not present the typical pattern of SEDEX deposits that the bedded orebody occurs in the upper part and the veined orebody occurs in the lower part. Zheng et al. [1, 2] explained this phenomenon in Keyue and Zhaxikang deposits as follows: the location of ore-bearing faults is ancient hydrothermal vents, and due to the collision of the Indian and Eurasian plates, the Plateau Uplift makes the bedded orebody to be eroded, and the later tectogenesis forms the faults and destroys the orebodies to the present form. The fact that orebodies have an obvious crack related to hydrothermal activity is also a good evidence.

Additionally, the elemental characteristics of sulfides can also be used to distinguish the deposit type. For instances, Wen et al. [59] investigated several Pb–Zn deposits with different geneses in China and divided them into three systems according to Zn/Cd ratios: (1) high-temperature systems (porphyry, magmatic hydrothermal, skarn, and volcanic hosted massive sulfide- (VMS-) type deposits): 155~223; (2) low-temperature systems (Mississippi Valley-type (MVT) deposits): 17~201; and (3) exhalative systems: ① SEDEX-type deposits: 316~368 and ② seafloor hydrothermal sulfides: 211~510. The results indicate that the exhalative system usually has the highest Zn/Cd ratios. Calculated from the EPMA data, the Zn/Cd ratios of sphalerite range from 296 to 4402 in the Zhaxikang deposit [9, 20] and 1226 to 12,846 in the Keyue deposit (Table 1), which are both much higher than those of high- and low-temperature systems (Figure 12). However, these Zn/Cd ratios are also higher than those of exhalative systems, which could be related to the Cd element dispersion resulting from the overprint by second and third pulses of mineralization. Meanwhile, the Co/Ni ratios of pyrite are also an effective indicator for ore genesis: the Co/Ni ratio of pyrite related to volcanism is usually >1 and concentrates on 5~10, the Co/Ni ratio of sedimentogenic pyrite is <1, and the magmatic hydrothermal pyrite has Co/Ni ratios ranging from 1 to 5 [60–63]. As for the Keyue deposit, the Co/Ni ratios of pyrite range from 3.7 to 7.1 according to the EPMA data (Table 1), which indicates that

FIGURE 12: Diagram of Zn/Cd ratios versus Cd for sphalerite from the Keyue Sb–Pb–Zn–Ag deposit, compared with the Zhaxikang deposit (data cited from [9, 20]), as well as high-temperature (porphyry, magmatic hydrothermal, skarn, and VMS-type Pb–Zn deposit), low-temperature (MVT deposits), and exhalative systems (SEDEX-type Pb–Zn deposits and the seafloor hydrothermal sulfides; data cited from Wen et al. [59]).

pyrite could be influenced by volcanism and magmatism. The inferences from geology, mineralogy, and elemental characteristics are consistent.

5.2. FIs Evidence Implications for the Nature and Origin of Ore-Forming Fluids

5.2.1. Epithermal Genesis for the Keyue Deposit. Previous literatures [64, 65] suggest that FIs can provide a record of the ore-forming fluid system and trace the nature and genesis of original fluids. In the “temperature versus salinity” plot (Figure 13), the FI data almost fall into the epithermal deposits area. Meanwhile, when assuming a simple H_2O –NaCl system, the ore-forming pressure can be estimated by the “temperature versus density” plot [66]. Plotting the FI data of the Keyue deposit in the “temperature versus density” plot (Figure 14(a)), stages 2, 3, and 4 show the ore-forming pressure of 800~2000 bars, 500~1000 bars, and 300~1000 bars, respectively. To regard the average pressure gradient as $270 \times 105 \text{ Pa/km}$, the calculated mineralization depths of stages 2, 3, and 4 are 3.0~7.4 km, 1.9~5.6 km, and 1.1~3.7 km, respectively. The first pulse of mineralization has an obviously higher ore-forming pressure and deeper mineralization depth. From the above, the ore-forming fluids of the first and second pulses of mineralization show significantly different characteristics, which further support the existence of multiple pulses of mineralization in the Keyue deposit. Nevertheless, both the first and second pulses of mineralization belong to the epithermal category according to the calculated mineralization depths.

5.2.2. Comparison with Regional and Other Similar Deposits. For the Keyue deposit, minerals from the first pulse of mineralization mainly contain L-type FIs with few S-type

FIGURE 13: Diagram of homogenization temperature versus salinity for the fluid inclusions at the Keyue Sb–Pb–Zn–Ag deposit (modified from Wilkinson [75]).

FIs. This characteristic is similar to SEDEX and MVT deposits that mainly develop W-type FIs with few NaCl-bearing or CO_2 -bearing FIs [67]. The homogenization temperature, salinities, and densities of stage 2 sphalerite (Figures 9(a) and 9(b)) are similar to those of stage 2 minerals from the Zhaxikang deposit (Figure 14(b); homogenization temperature: 215~260°C, concentrate on 220~240°C; salinities: 8.9%~16.7%, concentrate on 12.0~15.0 wt%; and densities: $0.89\sim0.96 \text{ g/cm}^3$) [68]. Meanwhile, laser Raman spectroscopy and micropetrography of FIs reveal the presence of H_2O as the dominating vapor and liquid phases with some daughter minerals and minor CO_2 (Figures 8 and 10).

FIGURE 14: (a) The NaCl-H₂O system ρ -T-D diagram of the different stage fluids in the Keyue Sb-Pb-Zn-Ag deposit (modified from Chen et al. [67]). (b) The NaCl-H₂O system ρ -T-D diagram of the different stage fluids in the Zhaxikang Sb-Pb-Zn-Ag deposit (modified from Yu [68]).

These FI data suggest that the ore-forming fluid for the first pulse of mineralization is the low-temperature, low-medium salinity, and low-density H₂O-NaCl system containing CO₂. This is similar to the Red Dog (100~200°C and 14%~19%) and Tom (234~274°C and 2%~18%) SEDEX deposits, the ore-forming fluids of which are also of low temperature and low-medium salinity [69]. From the above, the FI data also support the submarine hydrothermal sediment (metasomatism) genesis of the first pulse of mineralization.

By comparison with the first pulse of mineralization, the second pulse of mineralization mainly contains the W-type FIs with few C-type, G-type, and S-type FIs. Meanwhile, according to laser Raman spectroscopy and micropetrography of FIs, the vapor and fluid phase of FIs are also dominated by H₂O with some daughter minerals and minor CO₂ (Figures 8 and 10), and the FIs show a more variable higher homogenization temperature (Figures 9(c) and 9(e)), slightly lower salinities (Figures 9(d) and 9(f)), and approximate densities (Figure 14 and Table 2). These FI data reveal that the ore-forming fluids for the second pulse of mineralization are the low-medium temperature, low-salinity, and low-density H₂O-NaCl system containing CO₂. Comparing the Keyue deposit with other regional deposits in NHMB, the stage 3 and 4 minerals from the Zhaxikang deposit (Figure 14) show little higher homogenization temperature (212~338.0, concentrate on 220~310°C), a little lower salinities (3.9~13.2 wt%, concentrate on 6.0~10.0 wt%), and similar densities (0.73~0.91 g/cm³) [68], whereas the Shalagang Sb deposit that is dominated by the stibnite-quartz ores has different FI characteristics (homogenization temperature: 134.9°C~221.9°C, concentrate on 160~190°C;

salinities: 1.65~7.25 wt%, concentrate on 5.0~6.0 wt%) [68]. These comparisons suggest that Sb mineralization for stibnite in the Shalagang deposit distinguishes from that for sulfosalt minerals in Keyue and Zhaxikang deposits.

As discussed in Section 5.1, there is a genetic relationship between the Keyue and Zhaxikang deposits, so when there is a lack of analytical data for minerals in the Keyue deposit, we can take the Zhaxikang deposit as an analogy. In the Zhaxikang deposit, from stages 3 and 4 to stages 5 and 6 (homogenization temperature: 210~317.0°C, concentrate on 230~270°C; salinities: 2.4~9.9 wt%, concentrate on 3.0~9.9 wt%), the homogenization temperature and salinities also show a decreasing trend and is more approximate to the Shalagang deposit. Meanwhile, the stibnite-quartz veins in Shalagang (ESR: 18.0 ± 1.8 ; zircon U-Pb: 23.6 ± 0.8) [1] and Zhaxikang (ESR: 18.3 ± 1.8 and 23.3 ± 2.3 ; $^{40}\text{Ar}/^{39}\text{Ar}$: 17.9 ± 0.5) [1] deposits have similar mineralization ages. These FIs and geochronology data indicate that the stage 5 and 6 stibnite-cinnabar-quartz-calcite assemblages in Zhaxikang and Keyue deposits may share the same origin with the stibnite-quartz veins in Shalagang. Nevertheless, we come to a conclusion in the previous paragraph that Sb mineralization for stibnite in the Shalagang deposit distinguishes from that for sulfosalt minerals in Keyue and Zhaxikang deposits, so the second and third pulses of mineralization may have different Sb origins.

On the other hand, the FI characteristics of the second and third pulses of mineralization in Keyue and Zhaxikang deposits are similar with those of quartz-stibnite-sulfosalt vein systems in the Variscan orogen in northwest Germany that have salinities of 1~11 wt% and homogenization

FIGURE 15: Diagram of δD versus $\delta^{18}O_{H_2O}$ for quartz from the Keyue Sb–Pb–Zn–Ag deposit, compared with Zhaxikang (data cited from Yang et al. [3], Meng et al. [6], Xie et al. [17], Li [76], and Zhang [77]), Shalagang, Mazhala, Zhegu, and Langkazi deposits (data cited from Yang et al. [3]) in NHMB.

temperatures of 133–389°C concentrated on 150–220°C [13]. Thus, the second and third pulses of mineralization of Keyue and Zhaxikang deposits may have similar genesis with deposits in the Variscan orogen in northwest Germany, which result from the overprinting of preexisting Pb–Zn veins by later mesothermal Sb veins related to later orogeny. Combining with the fact that the regional orogenic Sb–Au deposits mainly formed during the syn-collision period (60–42 Ma) [1], the second pulse of mineralization in Keyue and Zhaxikang deposits must relate to the regional orogeny during the syn-collision period, yet the third pulse of mineralization is most likely associated with the magmatic–hydrothermal activity during the postcollision period (25 Ma to now) [1].

Overall, the FI data indicate that the Keyue deposit is an epithermal deposit with three pulses of mineralization that may be associated to three regional mineralization events, which is in keeping with the inferences from geological, mineralogical, and element characteristics in Section 5.1.

5.3. Multiple Isotopes Constrain the Ore Genesis

5.3.1. H–O Isotopes. According to the H–O isotopic data, there is an increasing trend in δD_{V-SMOW} values and a decreasing trend in $\delta^{18}O_{V-SMOW}$ values from early to late stages. Meanwhile, combining with the measured $\delta^{18}O_{V-SMOW}$ values and homogenization temperatures of FIs ($T_{h-total}$), the $\delta^{18}O_{H_2O}$ values of ore-forming fluids are calculated by the theoretical equation of $1000 \ln \alpha_{quartz-H_2O} = 3.38 \times 10^6 T^{-2} - 3.40$ [70, 71]. Due to the lack of the $T_{h-total}$ data of stage 3 calcite and stage 5 quartz, the calculations are only aimed at stage 3 and 4 quartz samples. The calculated results also exhibit a decreasing trend in

$\delta^{18}O_{H_2O}$ values from stage 3 (2.86‰~11.34‰, average: 7.78‰, $n = 7$) to stage 4 (1.59‰~2.69‰, average: 2.29‰, $n = 3$). In the “ $\delta^{13}D_{V-SMOW}$ versus $\delta^{18}O_{H_2O}$ ” plot, stage 3 and 4 quartz from the Keyue deposit is similar to stage 3 and 4 quartz and calcite from the Zhaxikang deposit (Figure 15), which suggests that there may be a genetic relationship of these two deposits again. However, the H–O isotopic characteristics of stage 3 and 4 quartz and calcite from the Keyue and Zhaxikang deposits are significantly different from stage 1 and 2 Mn–Fe carbonate, as well as stage 5 and 6 quartz from the Zhaxikang deposit (Figure 15). This difference further proves the three pulses of mineralization in Keyue and Zhaxikang deposits as mentioned above in Sections 5.1 and 5.2.

Based on the geochronology evidence, the Shalagang Sb [1], Mazhala Au–Sb (ESR: 24.2 ± 2.4) [1], Zhegu Sb–Au (ESR: 18.4 ± 1.8 and 17.6 ± 1.8) [1], and Langkazi Au deposits [1] are all formed by the third regional mineralization event that relates to the magmatic–hydrothermal activity during the postcollision period (25 Ma to now) [1]. In the “ $\delta^{13}D_{V-SMOW}$ versus $\delta^{18}O_{H_2O}$ ” plot, the H–O isotopic compositions of these deposits are also influenced by the mixture of formation and magmatic water in different ratios (Figure 15). However, the H–O isotopic compositions of stage 5 and 6 quartz from the Zhaxikang deposit are obviously influenced by the mixture of formation and geothermal water; this may relate to the ore-forming depth. The stage 5 and 6 stibnite–cinnabar–quartz–calcite assemblages formed near the earth’s surface, so the magmatic water mixed with meteoric water to form the geothermal water. Meanwhile, the FI evidence shows that the second pulse of mineralization (stages 3 and 4) may relate to the regional orogeny during the syn-collision period, and the H–O isotopic characteristics of

stage 3 and 4 quartz from the Keyue deposit exhibit the influence by mixture of formation and magmatic and geothermal water, which not only demonstrates the magmatic activity contribution to the regional orogenic mineralization event during the syn-collision period (the second pulse of mineralization) but also confirms the overprint by the later geothermal water during the postcollision period (the third pulse of mineralization).

5.3.2. S–Pb Isotopes. There are mainly three sulfur sources in nature: (1) mantle sulfur: the $\delta^{34}\text{S}$ values are $0 \pm 3\%$, (2) seawater sulfur: the $\delta^{34}\text{S}$ values are around 20‰ (the values vary during different geological history periods), (3) the reduced sulfur in sediments: the $\delta^{34}\text{S}$ values are usually relatively light [72]. The stage 2 sulfides in the Keyue deposit have $\delta^{34}\text{S}$ values of 5.4‰–11.2‰, which are similar to those of stage 2 sulfides in the Zhaxikang deposit (7.8‰–12.2‰) [3, 9, 18, 73] and regional Ridang Formation (6.4‰–9.2‰; Figure 16(a)) [9]. Thus, the sulfur source for the first pulse of mineralization in Keyue and Zhaxikang deposits is compatible with mainly seawater sulfur mixing with some mantle sulfur. Meanwhile, the S isotopic compositions of stage 2 sulfides in Keyue and Zhaxikang deposits overlap the range of many SEDEX-type deposits that all have relatively heavy $\delta^{34}\text{S}$ values (Figure 16(b)). Nevertheless, the Red Dog (–37.2‰––16.4‰), Sullivan, HYC, and Dugald River SEDEX-type deposits show much lighter $\delta^{34}\text{S}$ values (Figure 16(b)), which may be due to the contribution of reduced sulfur in sediments and biogenic sulfur. Taking all of this evidence together, the first pulse of mineralization in the Keyue and Zhaxikang deposits could be related to the multiple seafloor volcanic events during the synsedimentary period (220–130 Ma) with the submarine hydrothermal sediment (metasomatism) genesis. Furthermore, the $\delta^{34}\text{S}$ values of sulfides in Keyue and Zhaxikang deposits show a decreasing trend with time (from stage 2 through stages 3 and 4 to stage 5; Figure 16(a)) and exhibit more contribution from mantle sulfur associated with magmatism [74] in stages 3 to 5, which may relate to the overprint by later mineralization events. This inference is in keeping with the fact that the deposits (Shalagan, Mazhala, Zhegu, and Langkazi deposits) may have formed in relation with the third regional mineralization event which relates to the magmatic–hydrothermal activity during the postcollision period having much lighter $\delta^{34}\text{S}$ values.

With regards to Pb isotopes, the Pb isotopic data of sulfides from the Keyue deposit have relatively uniform ranges, with $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of 18.530–19.780, $^{207}\text{Pb}/^{204}\text{Pb}$ ratios of 15.674–15.939, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of 38.618–40.559. In the “ $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ ” and “ $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ ” diagrams (Figure 17), most of the data points fall into the domain of the upper crust, rarely plotting in the orogenic belt area in the tectonic setting discrimination diagrams (Figures 17(a) and 17(b)); similarly, all the data points are located around the upper crust and orogenic belt evolution curves in the Pb isotopic growth curve diagrams (Figures 17(c) and 17(d)). To be specific, the Pb isotopic compositions of stage 3 and 4 galena and boulangerite from

the Keyue deposit are similar with those of stage 3 and 4 sulfides from the Zhaxikang deposit, which show that Pb is mainly sourced from the crust for the second pulse of mineralization in Keyue and Zhaxikang deposits. Meanwhile, most of the data points for stage 2 sphalerite from the Zhaxikang deposit fall into the Ocean island volcanic rock area (Figure 17(a)) and located below the orogenic belt curve (Figure 17(c)) in Pb isotopic diagrams, which proves the inference from S isotopes again that the first pulse of mineralization in Keyue and Zhaxikang deposits could be related to the multiple seafloor volcanic events during the synsedimentary period. Meanwhile, the Pb isotopic compositions of stage 5 stibnite in Keyue and Zhaxikang deposits are slightly different with those of earlier sulfides. Therefore, the Pb isotopic data also support the existence of three pulses of mineralization in Keyue and Zhaxikang deposits. Moreover, it is worth noting that sulfides share similar Pb isotopic characteristics with regional magmatic rocks and Ridang Formation, which also demonstrate the contribution from magmatism to the mineralization events in Keyue and Zhaxikang deposits.

In a word, the H–O–S–Pb isotopic evidence confirms the existence of three pulses of mineralization related to the three regional mineralization events again, which are in accord with the inferences from geology, mineralogy, elements, and FI evidence.

5.4. Ore-Forming Model. The ore-forming model synthesizes the geology, mineralogy, ore paragenetic sequence, elements, FIs, and H–O–S–Pb isotopes; the Keyue and Zhaxikang deposits have experienced three pulses of mineralization that may be associated with three regional mineralization events. The ore-forming model is as follows (Figure 18): (1) the first pulse of mineralization: during the synsedimentary period (220–130 Ma), under the influence of multiple seafloor volcanic events, the reducing environment in rifts and the adsorption of organic matter lead to the enrichment of metallogenic elements (e.g., Pb, Zn, Au, Ag, Mn, Fe, Ba, Ga, In, Tl, and B) in the Late Triassic–Early Cretaceous flysch formations formed by turbidity sediment and carbonaceous–siliceous–argillaceous rock series related to hydrothermal sedimentation, and the seafloor hydrothermal system circularly leached the metallogenic elements to form the first pulse of mineralization (stages 1 and 2) in Keyue and Zhaxikang deposits. (2) The second pulse of mineralization: during the syn-collision period (60–42 Ma) of the Indian–Eurasian plate, influenced by orogeny, the deep source mantle fluid formed by mantle exhaust and the CO_2 -bearing fluid formed by Lower crustal dehydration mixed and raised along the shear zone, with the contribution for ore-forming elements from magmatism to form a series of regional orogenic Au–Sb deposits. This mineralization event is related to the second pulse of mineralization (stages 3 and 4) and overprints the first pulse of mineralization in Keyue and Zhaxikang deposits. (3) Third pulse of mineralization: during the postcollision period (25 Ma to now), with the development of STDS, the metamorphic core complex, and the extensive emplacement of leucogranite, a series of W–Sn, Pb–Zn (Ag), and Sb–Au deposits developed in the

FIGURE 16: (a) The S isotopic compositions of sulfide minerals from the Keyue Sb-Pb-Zn-Ag deposit, compared with Zhaxikang (data cited from Yang et al. [3], Sun et al. [9], Zhou et al. [18], and Zhang [73]), Shalagang, Mazhala, Zhegu, and Langkazi deposits (data cited from Yang et al. [1]) in NHMB. (b) The S isotopic compositions of stage 2 sulfide minerals from the Keyue and Zhaxikang Sb-Pb-Zn-Ag deposits; the S isotopic compositions of sulfide minerals from typical SEDEX deposits all over the world are also plotted for comparison (modified from Leach et al. [78]).

region. This magmatic-hydrothermal mineralization event is associated with the third pulse of mineralization and also overprints the first and second pulses of mineralization in Keyue and Zhaxikang deposits. Moreover, the Plateau Uplift and complicated tectogenesis related to the collision of the Indian and Eurasian plates during the syn-collision and postcollision periods erode and destroy the early bedded Pb-Zn orebodies.

6. Conclusions

The geology, mineralogy, ore paragenetic sequence, elements, FIs, and H-O-S-Pb isotope evidence allow us to make the following conclusions:

- (1) There are six ore-forming assemblages of ore and gangue minerals that can represent six stages of ore

FIGURE 17: Diagrams of $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ showing the Pb isotopic compositions of sulfide minerals from the Keyue and Zhaxikang Sb-Pb-Zn-Ag deposits; reference evolution curves of Lower Crust, Upper Crust, Mantle, Orogenic Belt, and Ocean Island Volcanic Rocks are also displayed (modified from Zartman and Doe [79]). (a) $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ tectonic setting discrimination diagram; (b) $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ tectonic setting discrimination diagram; (c) $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ growth curve; (d) $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ growth curve.

formation from early to late, and these six stages are assigned to three clear pulses.

- (2) The occurrence states of Ag in the Keyue deposit are prevailing in the form of visible Ag that can be divided into independent Ag-bearing minerals and

Ag-bearing inclusions. The invisible Ag is much less and principally in the form of submicroscopic Ag-bearing inclusions.

- (3) The FIs in the Keyue deposit can be divided into three genetic (primary, secondary, and pseudosecondary)

FIGURE 18: The ore-forming model for three pulses of mineralization in the Keyue deposit.

and four phase (W-type, C-type, G-type, and S-type) types.

- (4) There is an increasing trend in δD_{V-SMOW} values, a decreasing trend in $\delta^{18}O_{V-SMOW}$ values, and a decreasing trend in $\delta^{34}S$ values from early to late stages. However, the Pb isotopic data have relatively uniform ranges.

- (5) The Keyue deposit is an epithermal deposit and has mainly experienced three pulses of mineralization that relates to the three regional mineralization events in NHMB.

- (6) There is a genetic relationship between the Keyue and Zhaxikang deposits, they have the same origins, and they experience the same mineralization events.

Data Availability

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

Conflicts of Interest

The authors declare that they do not have any commercial or associative interest that represents a conflict of interest in connection with the submitted work.

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References

- Y. Y. Zheng, X. Sun, L. M. Tian et al., "Mineralization, deposit type and metallogenic age of the gold antimony polymetallic belt in the eastern part of north Himalayan," *Geotectonica et Metallogenia*, vol. 38, no. 1, pp. 108–118, 2014.
- Y. Y. Zheng, M. Y. Liu, X. Sun et al., "Type, discovery process and significance of Zhaxikang antimony polymetallic ore deposit, Tibet," *Earth Science*, vol. 37, no. 5, pp. 1004–1014, 2012.
- Z. Yang, Z. Hou, X. Meng et al., "Post-collisional Sb and Au mineralization related to the south Tibetan detachment system, Himalayan orogen," *Ore Geology Reviews*, vol. 36, no. 1–3, pp. 194–212, 2009.
- G. M. Li, L. K. Zhang, Y. J. Jiao et al., "First discovery and implications of Cuonadong superlarge Be-W-Sn polymetallic deposit in Himalayan metallogenic belt, southern Tibet," *Mineral Deposits*, vol. 36, no. 4, pp. 1003–1008, 2017.
- A. Yin, "Cenozoic tectonic evolution of the Himalayan orogen as constrained by along-strike variation of structural geometry, exhumation history, and foreland sedimentation," *Earth-Science Reviews*, vol. 76, no. 1–2, pp. 1–131, 2006.
- X. J. Meng, Z. S. Yang, X. X. Qi, Z. Q. Hou, and Z. Q. Li, "Silicon-oxygen-hydrogen isotopic compositions of Zaxikang antimony polymetallic deposit in Southern Tibet and its responses to the ore-controlling structure," *Acta Petrologica Sinica*, vol. 24, no. 7, pp. 1649–1655, 2008.
- J. Fu, G. Li, G. Wang et al., "First field identification of the Cuonadong dome in southern Tibet: implications for EW extension of the North Himalayan gneiss dome," *International Journal of Earth Sciences*, vol. 106, no. 5, pp. 1581–1596, 2017.

- [8] J. Fu, G. Li, G. Wang et al., "Synchronous granite intrusion and E–W extension in the Cuonadong dome, southern Tibet, China: evidence from field observations and thermochronologic results," *International Journal of Earth Sciences*, vol. 107, no. 6, pp. 1–19, 2018.
- [9] X. Sun, Y. Zheng, F. Pirajno et al., "Geology, S–Pb isotopes, and $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of the Zhaxikang Sb–Pb–Zn–Ag deposit in Southern Tibet: implications for multiple mineralization events at Zhaxikang," *Mineralium Deposita*, vol. 53, no. 3, pp. 435–458, 2018.
- [10] W. T. Yang, *The Geologic Characteristics and Metallogenic Mechanism of Keyue Lead-Zinc Antimony Silver Deposit, Southern Tibet*, [M.S. Thesis], China University of Geoscience, Wuhan, China, 2015, Chapter 3.
- [11] G. Beaudoin, "Proterozoic Pb isotope evolution in the Belt–Purcell Basin; constraints from syngenetic and epigenetic sulfide deposits," *Economic Geology*, vol. 92, no. 3, pp. 343–350, 1997.
- [12] D. L. Leach, A. H. Hofstra, S. E. Church, L. W. Snee, R. B. Vaughn, and R. E. Zartman, "Evidence for Proterozoic and Late Cretaceous–early Tertiary ore-forming events in the Coeur d'Alene District, Idaho and Montana," *Economic Geology*, vol. 93, no. 3, pp. 347–359, 1998.
- [13] T. Wagner and N. J. Cook, "Late-Variscan antimony mineralization in the Rheinisches Schiefergebirge, NW Germany: evidence for stibnite precipitation by drastic cooling of high-temperature fluid systems," *Mineralium Deposita*, vol. 35, no. 2–3, pp. 206–222, 2000.
- [14] T. Wagner and J. Schneider, "Lead isotope systematics of vein-type antimony mineralization, Rheinisches Schiefergebirge, Germany: a case history of complex reaction and remobilization processes," *Mineralium Deposita*, vol. 37, no. 2, pp. 185–197, 2002.
- [15] J. F. Zhang, Y. Y. Zheng, G. Y. Zhang et al., "Genesis of Zhaxikang Pb–Zn–Sb–Ag deposit in northern Himalaya: constraints from multi-isotope geochemistry," *Earth Science*, vol. 35, pp. 1000–1010, 2010.
- [16] J. Duan, J. Tang, and B. Lin, "Zinc and lead isotope signatures of the Zhaxikang PbZn deposit, South Tibet: implications for the source of the ore-forming metals," *Ore Geology Reviews*, vol. 78, pp. 58–68, 2016.
- [17] Y. Xie, L. Li, B. Wang et al., "Genesis of the Zhaxikang epithermal Pb–Zn–Sb deposit in southern Tibet, China: evidence for a magmatic link," *Ore Geology Reviews*, vol. 80, pp. 891–909, 2017.
- [18] Q. Zhou, W. Li, C. Qing et al., "Origin and tectonic implications of the Zhaxikang Pb–Zn–Sb–Ag deposit in northern Himalaya: evidence from structures, Re–Os–Pb–S isotopes, and fluid inclusions," *Mineralium Deposita*, vol. 53, no. 4, pp. 585–600, 2018.
- [19] W. Liang, Z. Hou, Z. Yang et al., "Remobilization and overprinting in the Zhaxikang Pb–Zn–Ag–Sb polymetal ore deposit, Southern Tibet: implications for its metallogenesis," *Acta Petrologica Sinica*, vol. 29, no. 11, pp. 3828–3842, 2013.
- [20] D. Wang, Y. Zheng, R. Mathur, and S. Wu, "The Fe–Zn isotopic characteristics and fractionation models: implications for the genesis of the Zhaxikang Sb–Pb–Zn–Ag deposit in Southern Tibet," *Geofluids*, vol. 2018, Article ID 2197891, 23 pages, 2018.
- [21] A. Yin and T. M. Harrison, "Geologic evolution of the Himalayan–Tibetan orogen," *Annual Review of Earth and Planetary Sciences*, vol. 28, no. 1, pp. 211–280, 2000.
- [22] T. M. Harrison, P. Copeland, W. S. F. Kidd, and A. Yin, "Raising Tibet," *Science*, vol. 255, no. 5052, pp. 1663–1670, 1992.
- [23] J. Lee, B. R. Hacker, W. S. Dinklage et al., "Evolution of the Kangmar dome, southern Tibet: structural, petrologic, and thermochronologic constraints," *Tectonics*, vol. 19, no. 5, pp. 872–895, 2000.
- [24] A. Yin, "Mode of Cenozoic east–west extension in Tibet suggesting a common origin of rifts in Asia during the Indo-Asian collision," *Journal of Geophysical Research: Solid Earth*, vol. 105, no. B9, pp. 21745–21759, 2000.
- [25] D. Wang, X. Sun, Y. Zheng et al., "Two pulses of mineralization and genesis of the Zhaxikang Sb–Pb–Zn–Ag deposit in southern Tibet: constraints from Fe–Zn isotopes," *Ore Geology Reviews*, vol. 84, pp. 347–363, 2017.
- [26] M. Coleman and K. Hodges, "Evidence for Tibetan plateau uplift before 14 Myr ago from a new minimum age for east–west extension," *Nature*, vol. 374, no. 6517, pp. 49–52, 1995.
- [27] P. Kapp, M. Taylor, D. Stockli, and L. Ding, "Development of active low-angle normal fault systems during orogenic collapse: insight from Tibet," *Geology*, vol. 36, no. 1, pp. 7–10, 2008.
- [28] A. Yin, P. A. Kapp, M. A. Murphy et al., "Significant Late Neogene east–west extension in northern Tibet," *Geology*, vol. 27, no. 9, pp. 787–790, 1999.
- [29] H. Williams, S. Turner, S. Kelley, and N. Harris, "Age and composition of dikes in southern Tibet: new constraints on the timing of east–west extension and its relationship to postcollisional volcanism," *Geology*, vol. 29, no. 4, pp. 339–342, 2001.
- [30] R. Armijo, P. Tapponnier, J. L. Mercier, and T. L. Han, "Quaternary extension in southern Tibet: field observations and tectonic implications," *Journal of Geophysical Research*, vol. 91, no. B14, pp. 13803–13872, 1986.
- [31] P. England and G. Houseman, "Extension during continental convergence, with application to the Tibetan Plateau," *Journal of Geophysical Research*, vol. 94, no. B12, pp. 17561–17579, 1989.
- [32] Z. Q. Li, Z. Q. Hou, and F. J. Nie, "Characteristic and distribution of the partial melting layers in the upper crust: evidence from active hydrothermal fluid in the South Tibet," *Acta Geologica Sinica*, vol. 79, no. 1, pp. 69–77, 2005.
- [33] S. H. Jiang, F. Nie, P. Q. Hu, Y. Liu, and X. Lai, "Geochemical characteristics of the mafic dyke swarms in South Tibet," *Acta Geologica Sinica*, vol. 81, no. 1, pp. 60–71, 2007.
- [34] J. S. Tong, J. Liu, H. M. Zhong, J. Xia, R. K. Lu, and Y. H. Li, "Zircon U–Pb dating and geochemistry of mafic dike swarms in the Lhozag area, southern Tibet, China, and their tectonic implications," *Geological Bulletin of China*, vol. 26, no. 12, pp. 1654–1664, 2007.
- [35] Q. T. Bian and L. Ding, "Discovery of the Zhegucuo Au(As)-bearing fine granular quartz diorite in the eastern Tethyan Himalayan Belt and its significance," *Acta Petrologica Sinica*, vol. 22, pp. 977–988, 2006.
- [36] G. T. Pan, L. Q. Wang, and D. C. Zhu, "Thoughts on some important scientific problems in regional geological survey of the Qinghai–Tibet plateau," *Regional Geology of China*, vol. 23, pp. 12–19, 2004.
- [37] H. Zhong, J. Xia, J. Tong, R. Lu, Y. Li, and S. Xu, "New results and major progress in regional geological survey of the Lhozag County Sheet," *Regional Geology of China*, vol. 23, pp. 451–457, 2004.

- [38] D.-C. Zhu, S.-L. Chung, X.-X. Mo et al., "The 132 Ma Comei-Bunbury large igneous province: remnants identified in present-day southeastern Tibet and southwestern Australia," *Geology*, vol. 37, no. 7, pp. 583–586, 2009.
- [39] B. B. Qiu, D. C. Zhu, Z. D. Zhao, and L. Q. Wang, "The westward extension of Comei fragmented large igneous province in southern Tibet and its implications," *Acta Petrologica Sinica*, vol. 26, no. 7, pp. 2207–2216, 2010.
- [40] M. P. Searle, R. R. Parrish, K. V. Hodges, A. Hurford, M. W. Ayres, and M. J. Whitehouse, "Shisha Pangma leucogranite, South Tibetan Himalaya: field relations, geochemistry, age, origin and emplacement," *Journal of Geology*, vol. 105, no. 3, pp. 295–318, 1997.
- [41] T. M. Harrison, P. Copeland, W. S. F. Kidd, and O. M. Lovera, "Activation of the Nyainqentanghla shear zone: implications for uplift of the southern Tibetan plateau," *Tectonics*, vol. 14, no. 3, pp. 658–676, 1995.
- [42] Z. Hou, S. Tian, Z. Yuan et al., "The Himalayan collision zone carbonatites in western Sichuan, SW China: petrogenesis, mantle source and tectonic implication," *Earth and Planetary Science Letters*, vol. 244, no. 1–2, pp. 234–250, 2006.
- [43] F. J. Nie, P. Hu, S. H. Jiang, Z. Q. Li, and Y. Liu, "Type and temporal-spatial distribution of gold and antimony deposits (prospects) in Southern Tibet, China," *Acta Geological Sinica-English Edition*, vol. 79, no. 3, pp. 374–384, 2005.
- [44] L. Zeng, L. E. Gao, C. Dong, and S. Tang, "High-pressure melting of metapelite and the formation of Ca-rich granitic melts in the Namche Barwa massif, southern Tibet," *Gondwana Research*, vol. 21, no. 1, pp. 138–151, 2012.
- [45] X. G. Zhang and D. W. Ciren, *The Census Report of the Keyue Sb-Pb-Zn-Ag Deposit in Southern Tibet*, Census Report, Huayu Mining Company, 2012, Chapter 3 and 4.
- [46] N. A. W. Gyatso, *The Geological and Geochemical Characteristics of Keyue Lead-Zinc Antimony Silver Deposit, Southern Tibet*, [M.S. Thesis], China University of Geoscience, Wuhan, China, 2015, Chapter 3.
- [47] V. N. Korolyuk, Y. G. Lavrent'ev, L. V. Usova, and E. N. Nigmatulina, "Some features of X-ray registration using a JXA-8100 electron-probe microanalyzer," *Journal of Analytical Chemistry*, vol. 65, no. 3, pp. 249–254, 2010.
- [48] T. J. Shepherd, A. H. Rankin, and D. Alderton, *A Practical Guide to Fluid Inclusion Studies*, Blackie & Son, Glasgow, UK, 1985.
- [49] P. E. Brown and W. M. Lamb, "P-V-T properties of fluids in the system $\text{H}_2\text{O} \pm \text{CO}_2 \pm \text{NaCl}$: New graphical presentations and implications for fluid inclusion studies," *Geochimica et Cosmochimica Acta*, vol. 53, no. 6, pp. 1209–1221, 1989.
- [50] R. J. Bodnar, "Revised equation and table for determining the freezing point depression of H_2O -NaCl solutions," *Geochimica et Cosmochimica Acta*, vol. 57, no. 3, pp. 683–684, 1993.
- [51] M. L. Coleman, T. J. Shepherd, J. J. Durham, J. E. Rouse, and G. R. Moore, "Reduction of water with zinc for hydrogen isotope analysis," *Analytical Chemistry*, vol. 54, no. 6, pp. 993–995, 1982.
- [52] H. B. Liu, G. S. Jin, J. J. Li et al., "Determination of stable isotope composition in uranium geological samples," *World Nuclear Geoscience*, vol. 30, no. 3, pp. 174–179, 2013.
- [53] R. N. Clayton and T. K. Mayeda, "The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis," *Geochimica et Cosmochimica Acta*, vol. 27, no. 1, pp. 43–52, 1963.
- [54] B. W. Robinson and M. Kusakabe, "Quantitative preparation of sulfur dioxide, for sulfur-34/sulfur-32 analyses, from sulfides by combustion with cuprous oxide," *Analytical Chemistry*, vol. 47, no. 7, pp. 1179–1181, 2002.
- [55] T. G. Sharp and P. R. Buseck, "The distribution of Ag and Sb in galena: inclusions versus solid solution," *American Mineralogist*, vol. 78, no. 1–2, pp. 85–95, 1993.
- [56] P. Costagliola, F. Di Benedetto, M. Benvenuti et al., "Chemical speciation of Ag in galena by EPR spectroscopy," *American Mineralogist*, vol. 88, no. 8–9, pp. 1345–1350, 2003.
- [57] D. L. Hall, S. M. Sterner, and R. J. Bodnar, "Freezing point depression of NaCl-KCl- H_2O solutions," *Economic Geology*, vol. 83, no. 1, pp. 197–202, 1988.
- [58] B. Liu and G. X. Duan, "The density and isochoric formulae for NaCl- H_2O fluid inclusions (salinity ≤ 25 wt%) and their applications," *Acta Mineralogica Sinica*, vol. 7, no. 4, pp. 345–352, 1987.
- [59] H. Wen, C. Zhu, Y. Zhang, C. Cloquet, H. Fan, and S. Fu, "Zn/Cd ratios and cadmium isotope evidence for the classification of lead-zinc deposits," *Scientific Reports*, vol. 6, no. 1, article 25273, 2016.
- [60] G. Loftus-Hills and M. Solomon, "Cobalt, nickel and selenium in sulphides as indicators of ore genesis," *Mineralium Deposita*, vol. 2, no. 3, pp. 228–242, 1967.
- [61] A. Bralía, G. Sabatini, and F. Troja, "A revaluation of the Co/Ni ratio in pyrite as geochemical tool in ore genesis problems," *Mineralium Deposita*, vol. 14, no. 3, pp. 353–374, 1979.
- [62] B. A. Brill, "Trace-element contents and partitioning of elements in ore minerals from the CSA Cu-Pb-Zn deposit, Australia, and implications for ore genesis," *The Canadian Mineralogist*, vol. 27, no. 2, pp. 263–274, 1989.
- [63] H. B. Li and F. Z. Zeng, "The pyrite's typomorphic characteristics in gold deposit," *Contributions to Geology and Mineral Resources Research*, vol. 20, no. 3, pp. 199–203, 2005.
- [64] T. Ulrich, D. Günther, and C. A. Heinrich, "Gold concentrations of magmatic brines and the metal budget of porphyry copper deposits," *Nature*, vol. 399, no. 6737, pp. 676–679, 1999.
- [65] F. Pirajno, *Hydrothermal Processes and Mineral Systems*, Springer, Berlin, 2009.
- [66] E. Roedder, *Composition of Fluid Inclusions: Reviews of World Literature*, US Government Printing Office, 1972.
- [67] Y. J. Chen, P. Ni, H. D. Fan et al., "Diagnostic fluid inclusions of different types hydrothermal gold deposits," *Acta Petrologica Sinica*, vol. 23, no. 9, pp. 2085–2108, 2007.
- [68] M. Yu, *Characteristics of Ore Geology and Ore-Forming Fluid in the Zhaxikang Sb-Pb-Zn-Ag Deposit, Southern Tibet, China*, [M.S. Thesis], China University of Geoscience, Beijing, China, 2015, Chapter 4.
- [69] D. L. Leach, E. Marsh, P. Emsbo, C. S. Rombach, K. D. Kelley, and M. Anthony, "Nature of hydrothermal fluids at the shale-hosted red dog Zn-Pb-Ag deposits, Brooks Range, Alaska," *Economic Geology*, vol. 99, no. 7, pp. 1449–1480, 2004.
- [70] R. N. Clayton, J. R. O'Neil, and T. K. Mayeda, "Oxygen isotope exchange between quartz and water," *Journal of Geophysical Research*, vol. 77, no. 17, pp. 3057–3067, 1972.
- [71] K. F. Qiu, R. D. Taylor, Y. H. Song, H. C. Yu, K. R. Song, and N. Li, "Geologic and geochemical insights into the formation of the Taiyangshan porphyry copper-molybdenum deposit,

- Western Qinling Orogenic Belt, China,” *Gondwana Research*, vol. 35, pp. 40–58, 2016.
- [72] H. R. Rollinson, “A terrane interpretation of the Archaean Limpopo Belt,” *Geological Magazine*, vol. 130, no. 6, pp. 755–765, 1993.
- [73] J. F. Zhang, *The Genesis Study of Zhaxikang Lead Zinc Antimony Silver Deposit, North Himalayan*, [M.S. Thesis], China University of Geoscience, Wuhan, China, 2010, Chapter 4.
- [74] K. F. Qiu, E. Marsh, H. C. Yu et al., “Fluid and metal sources of the Wenquan porphyry molybdenum deposit, western Qinling, NW China,” *Ore Geology Reviews*, vol. 86, pp. 459–473, 2017.
- [75] J. J. Wilkinson, “Fluid inclusions in hydrothermal ore deposits,” *Lithos*, vol. 55, no. 1–4, pp. 229–272, 2001.
- [76] G. Q. Li, *Element and Isotope Geochemistry of the Zhaxikang Sb–Pb–Zn Polymetallic Deposit, Tibet*, [M.S. thesis], China University of Geoscience, Beijing, China, 2010, Chapter 5.
- [77] S. K. Zhang, *Geology and Geochemistry Characteristics of Zhaxikang Antimony Polymetallic Deposits, Southern Tibet*, [M.S. Thesis], China University of Geoscience, Beijing, China, 2013, Chapter 5.
- [78] D. L. Leach, D. F. Sangster, K. D. Kelley, R. L. Ross, G. Garven, and C. R. Allen, “Sediment-hosted Pb–Zn deposits: a global perspective,” *Economic Geology*, vol. 100, pp. 561–608, 2005.
- [79] R. E. Zartman and B. R. Doe, “Plumbotectonics—the model,” *Tectonophysics*, vol. 75, no. 1–2, pp. 135–162, 1981.