Fluid inclusions and isotopic characteristics of the Jiawula Pb–Zn–Ag deposit, Inner Mongolia, China

Tiegang Li, Guang Wu, Jun Liu, Yanqing Hu, Yunfu Zhang, Dafeng Luo, Zhihao Mao

Abstract

The large Jiawula Pb–Zn–Ag deposit is located in the Derbugan metallogenic belt of the northern Great Xing’an Range. The vein style orebodies of the deposit occur along NW to NNW-trending fault zones. The ore-forming process at the deposit can be divided into three stages: an early quartz–pyrite–pyrrhotite–chalcopyrite stage, a middle quartz–carbonate–pyrite–galena–sphalerite stage, and a late quartz–carbonate–pyrite stage. Sulfide Rb–Sr dating indicates that the Jiawula deposit formed at ca. 143–142 Ma. Four types of fluid inclusions have been distinguished in quartz veins including liquid-rich, gas-rich, H2O–CO2, and daughter mineral-bearing inclusions. The fluid inclusions of the early stage are mainly liquid-rich, gas-rich, and H2O–CO2 types, with a small amount containing daughter minerals. Cumulatively, the types have homogenization temperatures, densities, and salinities of 304–438 °C, 0.35–1.37 g/cm³, and 0.8–44.6 wt.% NaCl eqv., respectively. Inclusions of the middle stage are mainly liquid-rich and gas-rich types, with a small amount of H2O–CO2 and daughter mineral-bearing types; their homogenization temperatures, densities, and salinities vary from 242 °C to 297 °C, 0.71 to 1.44 g/cm³, and 0.4 wt.% to 36.8 wt.% NaCl eqv., respectively. The late stage only comprises liquid-rich inclusions with homogenization temperatures, densities, and salinities of 181–238 °C, 0.81–0.90 g/cm³, and 0.2–1.9 wt.% NaCl eqv., respectively. The ore-forming fluids of the Jiawula deposit are generally characterized by moderate temperature and low salinity and density, and belong to an H2O–NaCl–CO2 system. The δ18Owater values calculated for ore-bearing quartz vary from −13.4‰ to −9.1‰, and the δDwater values from bulk extraction of fluid inclusion waters vary from −166‰ to −133‰, suggesting that the ore-forming fluids mainly consist of meteoric water with a small amount of magmatic water. The δ34S values range from 1.2‰ to 8.4‰. The 206Pb/204Pb, 207Pb/204Pb, and 208Pb/204Pb values of the ore minerals are in the ranges of 18.319–18.377, 15.499–15.596, and 38.094–38.314, respectively. Initial 87Sr/86Sr ratios of sulfides range from 0.712381 to 0.712770. The data for the S, Pb, and Sr isotopic systems indicate that the ore-forming metals and sulfur came from Mesozoic magma. The Jiawula deposit is a low-sulfidation epithermal Pb–Zn–Ag deposit, and fluid boiling is the dominant mechanism for the deposition of ore-forming materials.

1. Introduction

The Manzhouli area, located in the northeastern part of Inner Mongolia, bordering Mongolia to the west and Russia to the north (Fig. 1a), is one of the most important Pb–Zn–Ag metallogenic regions in China. To date, a great number of economically important porphyry Cu–Mo deposits (e.g., Wungetushan, Badaguan, and Babayi), medium–low temperature hydrothermal vein-type Pb–Zn–Ag deposits (e.g., Jiawula and Chaganbulagen), and low-sulfidation epithermal Ag deposits (e.g., Erentaolegai) have been discovered (Wu et al., 2010; Liu et al., 2014). In addition, a few Cu–Zn–Sn skarns (e.g., Longling) and numerous high-sulfidation epithermal Cu–Au (Ag) mineral occurrences (e.g., Bayanhaolei and Daba) have also been discovered in this area (Fig. 1b). Previous studies in this area have mainly described geological characteristics of typical deposits (Qi et al., 2005; Zeng, 2010), host rock features and mineral paragenesis (Qin et al., 1999; Sheng and...
Pre-Mesozoic strata, consisting of rocks of the Neoproterozoic Jiageda and Sinian–Lower Cambrian Argunhe Formations, are sporadically distributed in the Manzhouli area. The Jiageda Formation consists of sericite-quartz schist, quartzite, sandstone, slate, rhyolitic tuff, and marble, whereas the Argunhe Formation mainly comprises marble, with a small amount of sericite-quartz schist and metasandstone. The Mesozoic strata are widely distributed and subdivided, from bottom to top, into the Middle Jurassic Wanbao and Tamulangou Formations, Upper Jurassic Manketouebo and Manitu Formations, and Lower Cretaceous Baiyanggaola, Meiletu, and Damogualia Formations. The Wanbao Formation is composed of continental conglomerate, sandy conglomerate, sandstone, and thin pelitic siltstone with coal seams; the Tamulangou Formation consists of andesite and basaltic andesite; the Manketouebo Formation is mainly made of rhyolite; the Manitu Formation is composed of andesite and dacite; the Baiyanggaola Formation consists of dacite, rhyolite, and tuff; the Meiletu Formation is composed of basalt and andesite; and the Damogualia Formation comprises conglomerate, sandstone, and shale with coal seams (Meng et al., 2011). Fault and folds are well-developed in the Manzhouli area. The faults are mainly NW- and NE-trending. The NE-trending faults are represented by the Derbugan fault and controlled the distribution of a NE-trending uplift and depression. Many porphyry Cu–Mo and hydrothermal vein-type Pb–Zn–Ag deposits occurred in the uplifts, along the northwestern side of the Derbugan fault, forming the NE-striking Derbugan metallogenic belt. The NW-trending faults mainly include the Badaguan, Hanigou, and Muhar faults, and they control the distribution of NW-trending smaller belts of mineralization. The pre-Mesozoic folds are mainly NE-striking and are characterized by tight and even reversed form, whereas the Mesozoic folds commonly show open shapes with short axes, forming dome and basin patterns. Widespread volcanic structures are superimposed on the older regional structures. Regional magmatism can be divided into the Late Hercynian, Indosinian, Early Yanshanian, and Late Yanshanian periods (Wu et al., 2010). The Hercynian granitoids, consisting of dominantly granite, granodiorite, and monzonogranite, occur as batholiths or stocks, with K–Ar isotope ages of 271–262 Ma (Zhao and Zhang, 1997). The Indosinian granitoids, consisting of dominantly monzogranite and syenogranite, with a small amount of granodiorite, occur as batholiths, with Rb–Sr isochron ages varying from 225 to 211 Ma (Qin et al., 1998). The Early Yanshanian granitoids, consisting of biotite granite, granodiorite, and monzonogranite, occur as batholiths or stocks, with K–Ar isotope ages of 177–138 Ma (Zhao and Zhang, 1997) and are related to porphyry Cu–Mo mineralization (Wu et al., 2010). The Late Yanshanian granitoids, mainly comprising granite porphyry, quartz porphyry, and quartz monzonogranite, occur as apophyses or stocks, with K–Ar isotope ages ranging from 138 to 93 Ma (Qin et al., 1995) and are related to the Pb–Zn–Ag mineralization (Wu et al., 2010).

3. Ore deposit geology

The Jiawula deposit is located 150 km southwest of Manzhouli City, Inner Mongolia. The deposit, discovered in 1985, contains proven resources of 259,769 tons Pb, 386,616 tons Zn, 29,619 tons Cu, and 950 tons Ag, with average grades of 2.86% Pb, 3.98% Zn, 0.39% Cu, and 117 g/t Ag (Wu et al., 2010). The Jiawula deposit has been mined since 1995. The exposed strata in the Jiawula deposit are Middle Jurassic continental conglomerate and sandstone of the Wanbao Formation, Middle Jurassic andesite and basaltic andesite of the Tamulangou

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Formation, Late Jurassic rhyolite of the Manketouebo Formation, Late Jurassic andesite and dacite of the Manitu Formation, Early Cretaceous dacite, rhyolite and tuff of the Baiyingaolao Formation, and Early Cretaceous basalt of the Meiletu Formation. The intrusive rocks in the Jiawula deposit are mainly composed of the Late Hercynian granitoids and Late Yanshanian orthophyre, quartz porphyry, quartz monzonite porphyry, and feldspar porphyry. The NW- to NWW-striking Jiawula–Chaganbulagen fault is the major fault in the Jiawula area. Other NWW-, NW-, and NNW-trending faults have a genetic relationship with volcanic features, form a fan-shaped fault system that spreads from southeast to northwest, and control the distribution of orebodies at the Jiawula deposit (Fig. 2).

The Jiawula deposit consists of more than 40 orebodies occurring as veins. These orebodies strike 330–350° W and dip 42° to 70° SW. The main orebodies of the Jiawula deposit are the No. 1, No. 2, No. 3, No. 4, and No. 12 veins (Fig. 2). All of the orebodies occur in the NWW-, NW-, and NNW-trending fault zones. Among these orebodies, the No. 2 orebody is the largest, being more than 2000 m long and 0.36 to 14.98 m thick with an average thickness of 3.87 m. Average grades are 124 g/t Ag, 2.65% Pb, 4.24% Zn, and 0.30% Cu, respectively. The ore minerals are mainly galena, sphalerite, pyrite, chalcopyrite, pyrrhotite, arsenopyrite, and magnetite (Fig. 3). The xenomorphic granular pyrite (0.3–0.8 mm) is distributed in crystals of chalcopyrite, developing a poikilitic texture.
Fig. 3a). Exsolution blebs of chalcopyrite (15–25 μm) occur in crystals of sphalerite (Fig. 3b). The euhedral–subhedral pyrite (0.5–2.0 mm) and pyrrhotite (0.6–2.5 mm) grains are intergrown (Fig. 3c). Xenomorphic chalcopyrite (0.2–0.5 mm) is distributed in intercrystalline pyrite and/or pyrrhotite crystals, developing an intersertal texture (Fig. 3c). The structures of the ores can be massive, granular, brecciated, disseminated, vein, or veinlet (Fig. 3d–f). The alteration assemblage includes quartz, carbonate, illite, hydromuscovite, chlorite, kaolinite, sericite, and fluorite, occurring in the ore-bearing faults and pervasive alteration of nearby wallrocks. The dominant alteration related to the Pb–Zn–Ag mineralization is a quartz, carbonate, illite, and hydromuscovite assemblage. Crosscutting relationships in the veins (Fig. 3g–i) indicates the ore paragenesis of the Jiawula deposit can be divided into three stages: (1) early quartz–pyrite–pyrrhotite–chalcopyrite stage; (2) middle quartz–carbonate–pyrite–galena–sphalerite stage; and (3) late quartz–carbonate–pyrite stage. Of these three stages, the middle stage is the main mineralizing event.

4. Sampling and analytical methods

4.1. Sulfide Rb–Sr isotopes

The Rb and Sr isotopic analyses of 13 samples (including six pyrite and seven sphalerite samples), separated from ten ore samples from the main ore-forming stage in orebody No. 2 of the Jiawula Pb–Zn–Ag deposit, were performed on a VG 354 mass spectrometer with five collectors at the Center of Modern Analysis, Nanjing University. Of these ten samples: (1) samples NJ9-3, NJ9-4, and NJ9-5 were collected at the 420-m level and are massive Pb–Zn–Ag ores; (2) samples NJ9-6, NJ9-7, and NJ9-9, collected at the 390-m level, are massive Pb–Zn–Ag ores with pyrite; (3) samples NJ9-10, NJ9-11, and NJ9-12 were collected at the 390-m level and are disseminated Pb–Zn–Ag ores with abundant pyrite; and (4) sample NJ52, collected at the 390-m level, is massive Pb–Zn–Ag ore.

Approximately 100 mg of hand-picked sample (40–60 mesh size fraction) was used for each analysis. The sample separates were
soaked in 10% acetic acid to remove any remaining limestone or calcite, then repeatedly rinsed and ultrasonically cleaned in deionized water, dried, and weighed. The minerals were then crushed to 200–400 mesh in 0.5 ml clean deionized water by means of a boron–carbide mortar and pestle and leached with water to remove and sample any fluid inclusions. The resulting leachates were separated from the residual sulfide by repeated centrifuging and rinsing with deionized water. It is difficult to eliminate the influence of secondary fluid inclusions in the sulfide samples (Nakai et al., 1990, 1993; Brannon et al., 1992; Yin et al., 2009) and to extract synthetic fluid inclusions completely with lower total procedural blanks. The ages only constrained by means of Rb–Sr dating of sulfide residues are very precise (Nakai et al., 1990, 1993; Brannon et al., 1992; Yin et al., 2009; Tian et al., 2014), so we did not analyze the leachate. The sulfide residues were analyzed using the methods described by Nakai et al. (1993) and Wang et al. (2007). The $^{87}\text{Rb}/^{86}\text{Sr}$ analytical error is ±1%, and $^{87}\text{Sr}/^{86}\text{Sr}$ analytical error is 0.01–0.005%. Total procedure blanks for Rb–Sr dating of sulfide residues are very precise (Nakai et al., 1990, 1993; Brannon et al., 1992; Yin et al., 2009; Tian et al., 2014), so we did not analyze the leachate.

The sulfide residues were analyzed using the methods described by Nakai et al. (1993) and Wang et al. (2007). The $^{87}\text{Rb}/^{86}\text{Sr}$ analytical error is ±1%, and $^{87}\text{Sr}/^{86}\text{Sr}$ analytical error is 0.01–0.005%. Total procedure blanks for Rb and Sr were <20 pg and <50 pg, respectively. During the course of the analyses, the average measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for standard sample NBS987 was 0.710236 ± 0.000007 (2σ mean), which coincides well with the published value of 0.710258 ± 0.000002 (Nakai et al., 1993). All Sr isotopic compositions were corrected for mass fractionation to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. The isochron ages were calculated with the ISOPLOT program (Ludwig, 1998). The errors indicated for ages and initial isotopic ratios are expressed at the 95% confidence limits. The decay constant used in the age calculation for $^{87}\text{Rb}$ is $1.42 \times 10^{-11}/\text{a}^{-1}$.

### 4.2. Fluid inclusion microthermometry and laser Raman spectroscopy

Nine samples were selected for fluid inclusion analyses, including two samples of the early stage, five samples of the middle stage, and two samples of the late stage. The samples of the early stage, collected from orebody No. 2 at the 390-m level, are quartz–pyrrhotite–pyrite–chalcopyrite veins. Two samples from the middle stage were collected from orebody No. 1 at the 450-m level and are quartz–galena–sphalerite veins. The remaining three samples of the middle stage were collected from orebody No. 2 at the 390-m level and are quartz–galena–sphalerite–pyrite veins. The two samples of the late stage, collected from orebody No. 2 at the 540-m level, are quartz–pyrite veins. Microthermometric measurements were conducted using a Linkam THMSG 600 heating–freezing stage mounted on an Olympus BX-50 microscope at the China University of Geosciences, Beijing. The estimated accuracies of the freezing and heating measurements were ±0.1 °C from −100 °C to 25 °C, ±1 °C from 25 °C to 400 °C, and ±2 °C above 400 °C, respectively. Fluid salinity and density were calculated using different equations depending on the types of fluid inclusions as described below (Roedder, 1984; Lu et al., 2004):

1. **Aqueous two-phase inclusions:** Fluid salinities were calculated from ice-melting temperatures using the equation of Bodnar (1993). Fluid densities were calculated with the equation of Liu and Duan (1987).
(2) Fluid inclusions: Fluid salinities were calculated from the final melting temperatures of CO₂ clathrate with the equation of Collins (1979). The densities were obtained from the phase diagrams of Shepherd et al. (1985).

(3) Daughter mineral-bearing inclusions: Salinities were calculated from the daughter mineral-melting temperatures with the equation of Hall et al. (1988). The densities were calculated by using the equation of Liu (2001).

Volatile compositions of single Fls were identified by using a Renishaw inVia laser Raman probe at the MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences (CAGS). The wavelength of the Ar⁺ laser was 514.5 nm and the beam size is 1 μm. The spectrum was measured from 100 to 4500 cm⁻¹ and the acquisition time was 20 s. The spectrum resolution was ±2 cm⁻¹. Instrumental setting was kept constant during all analyses.

4.3. H–O–S–Pb isotopes

Fifteen quartz samples from the early, middle, and late stages were analyzed for O (quartz) and H (fluid inclusions) isotopes. Samples include (1) NJ-65 and NJ-73 were collected from orebody No. 2 at the 390-m level and are quartz–pyrite–pyrrhotite–chalcopyrite veins of the early stage; (2) NJ-11, NJ-13, NJ-14, NJ-15, and NJ-17, collected from orebody No. 1 at the 450-m level, are quartz–pyrite–pyrrhotite veins of the middle stage; (3) NJ-53, NJ-55, NJ-56, and NJ-57 were collected from orebody No. 2 at the 390-m level and are quartz–galena–sphalerite–pyrite veins of the middle stage; (4) NJ-70 and NJ-77, collected from orebody No. 3 at the 475-m level, are quartz–galena–sphalerite–pyrite veins of the middle stage; and (5) NJ-9-1 and NJ-9-2 were collected from orebody No. 2 at the 540-m level and are quartz–pyrite veins of the late stage. The H–O isotope analyses were accomplished at the MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, CAGS, using a Finnigan MAT253 mass spectrometer.

The accuracy of the O isotope analysis is better than ±0.2‰, and that of the H isotope analysis is better than ±2‰ (Mao et al., 2008). The δ¹⁸O of water was calculated from the O isotopes of quartz by using the fractionation equation 10001n³⁰⁸Owater = (3.38 × 10⁻⁶)T² – 3.40, where T is the temperature in degrees kelvin (Clayton et al., 1972), and the average fluid inclusion temperature of each stage was used to calculate the δ¹⁸Owater value.

The sulfur and lead isotope composition of three pyrite, four galena, and three sphalerite grains, separated from seven ore samples from the middle stage of the Jiawula deposit, were measured at the Analytical Laboratory of the Beijing Research Institute of Uranium Geology. Of these seven samples, (1) NJ-9, NJ-10, and NJ-12 were collected from orebody No. 1 at the 450-m level and are massive Pb–Zn–Ag ores; (2) NJ-19, collected from orebody No. 2 at the 420-m level, is massive Pb–Zn–Ag ore with pyrite; (3) NJ-69 was collected from orebody No. 3 at the 475-m level and is massive Pb–Zn–Ag ore; and (4) NJ-72 and NJ-74, collected from orebody No. 2 at the 390-m level, are massive Pb–Zn–Ag ores with abundant pyrite.

For sulfur isotope analysis, each sample was weighed to 15 mg, mixed with CuO powder, placed in a vacuum quartz tube, and allowed to react for 15 min at a temperature of 1100 °C (Robinson and Kusakabe, 1975). After purification, SO₂ was transferred to the sample tube and the S-isotopic ratio ³⁴S/³²S was measured on the mass spectrometer of a Finnigan MAT 251 instrument. The lead isotopic composition was measured using a GV IsoProbe-T multicollector thermal ionization mass spectrometer. The ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁶Pb ratios had a precision better than 0.005% (2σ). The Pb-isotopic analyses are reported with respect to Pb standard reference NBS-981 values (Todd et al., 1993): ²⁰⁶Pb/²⁰⁴Pb = 19.34 ± 0.007, ²⁰⁷Pb/²⁰⁶Pb = 15.486 ± 0.012, and ²⁰⁸Pb/²⁰⁶Pb = 36.673 ± 0.033, respectively.

5. Analytical results

5.1. Sulfide Rb–Sr age

The Rb and Sr isotopic data for samples from the quartz–pyrite–galena–sphalerite stage in the Jiawula deposit are presented in Table 1. The Rb and Sr concentrations of 13 sulfide samples range from 0.1034 to 7.367 ppm and 1.301 to 7.148 ppm, respectively. The isotope ratios of ⁸⁷Rb/⁸⁶Sr vary from 0.0723 to 11.29, with an average of 4.5102, and the isotope ratios of ⁸⁷Sr/⁸⁶Sr range from 0.7128 to 0.7356, averaging 0.7218. Seven sphalerite samples yield a Rb–Sr isochron age of 143.0 ± 2.0 Ma, with an initial ⁸⁷Sr/⁸⁶Sr range of 0.71265 ± 0.007, and an MSWD of 3.2 (Fig. 4a). A Rb–Sr isochron age of 142.0 ± 3.0 Ma is defined by six pyrite samples, with an initial ⁸⁷Sr/⁸⁶Sr ratio of 0.71267 and an MSWD of 5.7 (Fig. 4b). The 13 sulfide samples give a Rb–Sr isochron age of 142.7 ± 1.3 Ma, with an initial ⁸⁷Sr/⁸⁶Sr ratio of 0.71266 and an MSWD of 3.8 (Fig. 4c). These results indicate that the Jiawula deposit was formed at ca. 143–142 Ma.

5.2. Fluid inclusion study

5.2.1. Petrography

Based on characteristics at and below room temperature, phase transitions during heating, and the results of laser Raman spectroscopy, the fluid inclusions in the Jiawula deposit are divided into the following four major types:

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stage</th>
<th>Mineral</th>
<th>Rb (ppm)</th>
<th>Sr (ppm)</th>
<th>⁸⁷Rb/⁸⁶Sr</th>
<th>⁸⁷Sr/⁸⁶Sr (2σ)</th>
<th>⁸⁷Sr/⁸⁶Sr (2σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NJ-9-3</td>
<td>Main ore-forming stage</td>
<td>Sphalerite</td>
<td>2.439</td>
<td>1.428</td>
<td>2.069</td>
<td>0.716972 ± 0.000004</td>
<td>0.712764</td>
</tr>
<tr>
<td>NJ-9-4</td>
<td>Main ore-forming stage</td>
<td>Sphalerite</td>
<td>3.487</td>
<td>1.753</td>
<td>5.862</td>
<td>0.724464 ± 0.000007</td>
<td>0.712544</td>
</tr>
<tr>
<td>NJ-9-5</td>
<td>Main ore-forming stage</td>
<td>Sphalerite</td>
<td>4.012</td>
<td>1.625</td>
<td>7.281</td>
<td>0.727566 ± 0.000005</td>
<td>0.712770</td>
</tr>
<tr>
<td>NJ-9-6</td>
<td>Main ore-forming stage</td>
<td>Sphalerite</td>
<td>4.307</td>
<td>3.813</td>
<td>3.313</td>
<td>0.719333 ± 0.000006</td>
<td>0.712549</td>
</tr>
<tr>
<td>NJ-9-7</td>
<td>Main ore-forming stage</td>
<td>Sphalerite</td>
<td>4.982</td>
<td>1.301</td>
<td>11.29</td>
<td>0.735598 ± 0.000004</td>
<td>0.712684</td>
</tr>
<tr>
<td>NJ-9-8</td>
<td>Main ore-forming stage</td>
<td>Sphalerite</td>
<td>1.952</td>
<td>7.148</td>
<td>0.8056</td>
<td>0.714279 ± 0.000005</td>
<td>0.712711</td>
</tr>
<tr>
<td>NJ-9-9</td>
<td>Main ore-forming stage</td>
<td>Sphalerite</td>
<td>0.0723</td>
<td>6.436</td>
<td>0.0723</td>
<td>0.731475 ± 0.000004</td>
<td>0.712673</td>
</tr>
</tbody>
</table>
(1) Liquid-rich inclusions (WL type): These inclusions are oval, elongated, and irregular, with diameters of 2–40 μm, although mainly 5–15 μm, and contain bubbles typically accounting for 10–30% of the total volume. They homogenize to liquid when heated. Inclusions of this type account for approximately 40% of the total number of inclusions and are distributed in isolation in quartz of every stage (Fig. 5a, b, and d). The secondary liquid-rich type inclusions generally are smaller in size than the primary inclusions, and are distributed in isolation in quartz of every stage. These fluid inclusions were homogenized to vapor when heated. Inclusions of this type comprise approximately 20% of the total number of inclusions and are randomly distributed in isolation or occur as clusters throughout the quartz crystals of the early and middle stages (Fig. 5a).

(2) Gas-rich inclusions (WG type): These are oval-shaped inclusions with diameters of 5–15 μm, mainly about 10 μm, and have bubbles usually accounting for 55–85% of the total volume. These fluid inclusions were homogenized to vapor at temperatures of 26.8–30.4 °C, corresponding to salinities of 2.6–7.3 wt.% NaCl eqv. The C-type fluid inclusions range from 304–368 °C and have fluid densities ranging from 0.55 to 0.78 g/cm³. The final ice melting temperatures of WL-type fluid inclusions range from −4.6 °C to −1.5 °C, corresponding to salinities of 2.6–7.3 wt.% NaCl eqv. The WG-type fluid inclusions homogenized into liquid at temperatures of 329–438 °C, with salinities ranging from 0.35 to 0.64 g/cm³. The CO₂-melting temperatures of C-type fluid inclusions range from −62.4 °C to −59.0 °C, and the melting temperatures of clathrate are 8.5–9.6 °C, corresponding to the salinities of 0.8–3.2 wt.% NaCl eqv. The microthermometric results and calculated salinities and densities are shown in Table 2 and Fig. 6. Below, we summarize the results from each hydrothermal stage.

Fluid inclusions in early stage quartz: The final ice melting temperatures of WL-type fluid inclusions range from −4.6 °C to −1.5 °C, corresponding to salinities of 2.6–7.3 wt.% NaCl eqv. The WG-type fluid inclusions homogenized into the liquid phase at temperatures of 304–368 °C and have fluid densities ranging from 0.55 to 0.78 g/cm³. The final ice melting temperatures of WG-type fluid inclusions are from −2.3 °C to −1.6 °C, with salinities from 2.7 to 3.9 wt.% NaCl eqv. The fluid inclusions homogenized into the gas phase at temperatures of 329–438 °C and have fluid densities ranging from 0.35 to 0.64 g/cm³. The CO₂ melting temperatures of C-type fluid inclusions range from −62.4 °C to −59.0 °C, and the melting temperatures of clathrate are 8.5–9.6 °C, corresponding to the salinities of 0.8–3.2 wt.% NaCl eqv. The homogenization temperatures of the CO₂ phase are 26.8–30.4 °C. Some of the C-type fluid inclusions homogenized to liquid CO₂, and the others to vapor CO₂, with a range of final homogenization temperatures from 337 °C to 393 °C; the fluid densities are 0.55–0.64 g/cm³. The vapor phase in the two S-type inclusions homogenized into the liquid phase between 253 °C and 270 °C, and the final disappearance temperatures for halite daughter minerals was 365 °C and 373 °C. The salinities are estimated to be 44.6 wt.% and 43.8 wt.% NaCl eqv., and the fluid densities are 1.36 g/cm³ and 1.37 g/cm³ (Table 2 and Fig. 6a and b).

Fluid inclusions in quartz of the middle stage: The final ice melting temperatures of WL-type inclusions range from −2.5 °C to −0.2 °C, with salinities of 0.4–4.2 wt.% NaCl eqv. The inclusions homogenized into the liquid phase at temperatures of 242–297 °C, and the fluid densities range from 0.71 to 0.83 g/cm³. The final ice melting temperatures of WG-type inclusions vary from −0.3 °C to −0.2 °C, with salinities of 0.4–0.5 wt.% NaCl eqv.; the inclusions homogenized into the vapor phase at temperatures of 276 °C to 281 °C, and the fluid densities are 0.74–0.75 g/cm³. The CO₂ melting temperatures of the C-type inclusions range from −60.5 °C to −59.0 °C, and the melting temperatures of clathrate are 8.9–9.3 °C, corresponding to salinities of 1.4–2.2 wt.% NaCl eqv. The C-type inclusions homogenized to liquid CO₂ at temperatures of 28.6–29.5 °C, and had final homogenization temperatures that range from 265 °C to 268 °C; the fluid densities are 0.76–0.77 g/cm³. Vapor to liquid homogenization temperatures for S-type inclusions are 215 °C and 220 °C, the halite daughter minerals in the two inclusions dissolved at 264 °C and 282 °C; the salinities.

5.2.2. Microthermometry

The microthermometric results and calculated salinities and densities are shown in Table 2 and Fig. 6. Below, we summarize the results from each hydrothermal stage.
are estimated to be 35.6 wt.% and 36.8 wt.% NaCl equiv., and the fluid densities are 1.44 g/cm$^3$ (Table 2 and Fig. 6c and d).

Fluid inclusions in quartz of the late stage: The final ice melting temperatures of WL-type inclusions range from $1.1^\circ$C to $0.1^\circ$C, with salinities of 0.2–1.9 wt.% NaCl equiv.; the inclusions homogenized into the liquid phase at temperatures of 181–238 $^\circ$C, and the fluid densities are 0.81–0.90 g/cm$^3$ (Table 2; Fig. 6e and f).

5.2.3. Laser Raman spectra

The results of representative laser Raman spectroscopic analyses are shown in Fig. 7. The gas phase components for C-type fluid inclusions in early and middle stage quartz are mainly CO$_2$ and CH$_4$ with a small amount of H$_2$O (Fig. 7a and c). The gas phase component for WL- and WG-type inclusions in quartz of the early, middle, and late stages is mainly H$_2$O (Fig. 7b, d, and f). In addition, the gas phase of some WL-type inclusions from the middle stage contains mainly CH$_4$ (Fig. 7e). In general, from early to late, the CO$_2$ and CH$_4$ contents of the ore-forming fluids gradually decrease, evolving from an early H$_2$O–NaCl–CO$_2$–CH$_4$ system through a middle H$_2$O–NaCl–CO$_2$±CH$_4$ system into a late H$_2$O–NaCl system, with ore-forming fluids generally having affinities to an H$_2$O–NaCl ± CO$_2$±CH$_4$ system.

5.2.4. Trapping pressure of fluid inclusions and ore-forming depth

Fluid inclusions may provide data for the trapping pressure and resultant depth estimates (Roedder and Bodnar, 1980; Shepherd et al., 1985; Brown and Hagemann, 1995). The homogenization temperatures of inclusions estimate minimum fluid trapping temperatures, which then require a pressure correction to estimate actual trapping temperatures (Roedder, 1984). However, when fluid immiscibility or boiling is documented, no corrections for pressure are required, and the homogenization temperatures represent the trapping temperatures of the fluids. Estimates of the trapping pressure can be obtained only if an independent estimate of trapping temperature is known or if the inclusions were trapped under immiscible conditions (Roedder and Bodnar, 1980; Shepherd et al., 1985; Brown and Hagemann, 1995; Liu et al., 2014).

---

Table 2

Microthermometry data of the fluid inclusions from the Jiawula deposit.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Type</th>
<th>Size (µm)</th>
<th>V (vol.%)</th>
<th>Number</th>
<th>$T_{m,\text{ice}}$ (°C)</th>
<th>$T_{m,\text{CO}_2}$ (°C)</th>
<th>$T_{m,\text{clath}}$ (°C)</th>
<th>$T_{h,\text{CO}_2}$ (°C)</th>
<th>$T_{h}$ (°C)</th>
<th>Salinity (% NaCl equiv.)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early</td>
<td>WL</td>
<td>6–15</td>
<td>10–30</td>
<td>15</td>
<td>$-1.5$ to $-4.6$</td>
<td>$304$–$368$</td>
<td>$2.6$–$7.3$</td>
<td>$0.55$–$0.78$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>WG</td>
<td>6–16</td>
<td>55–80</td>
<td>10</td>
<td>$-1.6$ to $-2.3$</td>
<td>$329$–$438$</td>
<td>$2.7$–$3.9$</td>
<td>$0.35$–$0.64$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>5–20</td>
<td>45–65</td>
<td>10</td>
<td>$-59$ to $-62.4$</td>
<td>$337$–$393$</td>
<td>$0.8$–$3.2$</td>
<td>$0.55$–$0.64$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>4–18</td>
<td>20–24</td>
<td>2</td>
<td>$365$–$373$</td>
<td>$43.8$–$44.6$</td>
<td>$1.36$–$1.37$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Middle</td>
<td>WL</td>
<td>6–12</td>
<td>10–30</td>
<td>43</td>
<td>$-0.2$ to $-2.5$</td>
<td>$242$–$297$</td>
<td>$0.4$–$4.2$</td>
<td>$0.71$–$0.83$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>WG</td>
<td>6–18</td>
<td>60–85</td>
<td>2</td>
<td>$-0.2$ to $-0.3$</td>
<td>$276$–$281$</td>
<td>$0.4$–$0.5$</td>
<td>$0.74$–$0.75$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>5–14</td>
<td>15–20</td>
<td>2</td>
<td>$-60.5$ to $-59.0$</td>
<td>$265$–$268$</td>
<td>$1.4$–$2.2$</td>
<td>$0.76$–$0.77$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>6–18</td>
<td>2</td>
<td>1</td>
<td>$264$–$282$</td>
<td>$35.6$–$36.8$</td>
<td>$1.44$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Late</td>
<td>WL</td>
<td>5–20</td>
<td>10–30</td>
<td>23</td>
<td>$-0.1$ to $-1.1$</td>
<td>$191$–$238$</td>
<td>$0.2$–$1.9$</td>
<td>$0.81$–$0.90$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: V, volume fraction of gas phase in the total volume of inclusion; $T_{m,\text{CO}_2}$, melting temperature of CO$_2$ ice; $T_{m,\text{clath}}$, melting temperature of clathrate; $T_{h,\text{CO}_2}$, partial homogenization temperature of CO$_2$; $T_{m,\text{ice}}$, final ice-melting temperature; $T_{h}$, total homogenization temperature.
Immiscibility or phase separation in fluid inclusions assemblages was found in quartz from the early and middle stages in the Jiawula deposit. Thus, trapping pressures were estimated based on the quartz fluid inclusion data from the early and middle stages by using the FLINCOR software of Brown (1989) and the equation of Bowers and Helgeson (1983). Using the data for the C-type inclusions, we obtained trapping pressures of 340–690 bars for the early stage and 550–560 bars for the middle stage; for the WL-type inclusions, we obtained trapping pressures of 110–290 bars for the early stage and 80–180 bars for the middle stage. Considering pressure for most fault-controlled deposits fluctuates between lithostatic and hydrostatic conditions, we estimated the ore-forming depth using lithostatic pressure for the C-type inclusions and hydrostatic pressure for the WL-type inclusions. Results suggest that the paleo-depths vary from 1.1 to 2.9 km for the early stage and 0.8 to 2.0 km for the middle stage that is the main ore stage.

5.3. Isotope data

5.3.1. Hydrogen–oxygen isotopes

The analytical results for oxygen isotopes in 15 quartz samples and hydrogen isotopes in fluid inclusions of 15 quartz samples from the Jiawula deposit are shown in Table 3. Of these, two samples from the early stage have $\delta^D$ values of $-141.0\%e$, $\delta^{18}O_{\text{quartz}}$ values of $-4.0\%e$ to $-4.5\%e$, and $\delta^{18}O_{\text{water}}$ values of $-9.7\%e$ to $-9.2\%e$, respectively; the $\delta^D$, $\delta^{18}O_{\text{quartz}}$, and $\delta^{18}O_{\text{water}}$ values of 11 samples from the middle stage range from $-166\%e$ to $-133\%e$, $-5.5\%e$ to $-1.2\%e$, and $-13.4\%e$ to $-9.1\%e$, respectively; and the $\delta^D$, $\delta^{18}O_{\text{quartz}}$, and $\delta^{18}O_{\text{water}}$ values of two samples from the late stage are $-145\%e$, $-2.2\%e$ to $-1.6\%e$, and $-13.3\%e$ to $-12.7\%e$, respectively. All of these samples plot between the magmatic water box and meteoric water line, with most data near the meteoric water line in the $\delta^{18}O_{\text{water}}$–$\delta^D$ diagram of Sheppard (1977) (Fig. 8).

5.3.2. Sulfur isotopes

Sulfur isotopic compositions for three pyrite samples, three sphalerite samples, and four galena samples from the main ore-forming stage of the Jiawula deposit are shown in Table 4 and Fig. 9. The $\delta^{34}S(\%e)$ values range from 4.1 to 8.4 for pyrite, 3.4 to 4.4 for sphalerite, and 1.2 to 2.6 for galena. These $S$ isotopic results, with low positive $\delta^{34}S$ values, suggest that the $S$ source for the Jiawula deposit was mainly magmatic.

5.3.3. Lead isotopes

Lead isotopic compositions for three pyrite samples, three sphalerite samples, and four galena samples from the main ore-forming stage of the Jiawula deposit are shown in Table 4 and Fig. 10. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios for three pyrite samples vary from 18.319 to 18.358, 15.529 to 15.593, and 38.101 to 38.306, respectively. The ratios of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ for four galena samples vary from 18.320 to 18.377, 15.499 to 15.596, and 38.094 to 38.314, respectively. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios for three sphalerite samples range from 18.338 to 18.363, 15.544 to 15.579, and 38.177 to 38.262, respectively. In the $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ diagrams of Zartman and Doe (1981) (Fig. 10a), the Pb isotopic compositions of the Jiawula deposit are projected in the area between the orogenic belt and the mantle evolution line; in the $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ diagrams (Fig. 10b), all of the projected data points are located on the orogenic belt line or its vicinity.

6. Discussion

6.1. Mineralization age

Ore-forming ages in some recent studies have been obtained by using the Rb–Sr isotope system of ore minerals, such as sphalerite, or gangue minerals, such as fluorite, which are related to mineralization (Nakai et al., 1990; Brannon et al., 1992; Tretbar et al., 2000; Yang and Zhou, 2001; Zhang et al., 2008; Zheng et al., 2013). The hydrothermal minerals for Rb–Sr isochron dating must satisfy the conditions of being genetically related and contemporaneous with ore, isotopically closed, and having the same ($^{87}\text{Sr}/^{86}\text{Sr}$)}
Fig. 7. Laser Raman spectra of fluid inclusions from the Jiawula deposit: (a) C-type fluid inclusions of the early stage; (b) WL-type fluid inclusions of the early stage; (c) C-type fluid inclusions of the middle stage; (d) WC-type fluid inclusions of the middle stage; (e) WL-type fluid inclusions of the middle stage; (f) WL-type fluid inclusions of the late stage.

Table 3
H and O isotopic compositions (‰ V-SMOW) of the Jiawula deposit.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stage</th>
<th>Mineral</th>
<th>$T_b$ (°C)</th>
<th>$\delta D$</th>
<th>$\delta ^{18}O_{\text{quartz}}$</th>
<th>$\delta ^{18}O_{\text{water}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NJ-65</td>
<td>Early stage</td>
<td>Quartz</td>
<td>353</td>
<td>-141</td>
<td>-4.5</td>
<td>-9.7</td>
</tr>
<tr>
<td>NJ-73</td>
<td>Early stage</td>
<td>Quartz</td>
<td>353</td>
<td>-141</td>
<td>-4.0</td>
<td>-9.2</td>
</tr>
<tr>
<td>NJ-11</td>
<td>Middle stage</td>
<td>Quartz</td>
<td>271</td>
<td>-155</td>
<td>-4.6</td>
<td>-12.5</td>
</tr>
<tr>
<td>NJ-13</td>
<td>Middle stage</td>
<td>Quartz</td>
<td>271</td>
<td>-142</td>
<td>-4.8</td>
<td>-12.7</td>
</tr>
<tr>
<td>NJ-14</td>
<td>Middle stage</td>
<td>Quartz</td>
<td>271</td>
<td>-133</td>
<td>-5.5</td>
<td>-13.4</td>
</tr>
<tr>
<td>NJ-15</td>
<td>Middle stage</td>
<td>Quartz</td>
<td>271</td>
<td>-160</td>
<td>-5.0</td>
<td>-12.9</td>
</tr>
<tr>
<td>NJ-17</td>
<td>Middle stage</td>
<td>Quartz</td>
<td>271</td>
<td>-134</td>
<td>-4.7</td>
<td>-12.6</td>
</tr>
<tr>
<td>NJ-53</td>
<td>Middle stage</td>
<td>Quartz</td>
<td>271</td>
<td>-133</td>
<td>-5.2</td>
<td>-13.1</td>
</tr>
<tr>
<td>NJ-55</td>
<td>Middle stage</td>
<td>Quartz</td>
<td>271</td>
<td>-143</td>
<td>-4.9</td>
<td>-12.8</td>
</tr>
<tr>
<td>NJ-56</td>
<td>Middle stage</td>
<td>Quartz</td>
<td>271</td>
<td>-147</td>
<td>-4.8</td>
<td>-12.7</td>
</tr>
<tr>
<td>NJ-57</td>
<td>Middle stage</td>
<td>Quartz</td>
<td>271</td>
<td>-161</td>
<td>-4.2</td>
<td>-12.1</td>
</tr>
<tr>
<td>NJ-70</td>
<td>Middle stage</td>
<td>Quartz</td>
<td>271</td>
<td>-166</td>
<td>-4.9</td>
<td>-12.8</td>
</tr>
<tr>
<td>NJ-77</td>
<td>Middle stage</td>
<td>Quartz</td>
<td>271</td>
<td>-133</td>
<td>-1.2</td>
<td>-9.1</td>
</tr>
<tr>
<td>NJ9-1</td>
<td>Late stage</td>
<td>Quartz</td>
<td>209</td>
<td>-145</td>
<td>-2.2</td>
<td>-13.3</td>
</tr>
<tr>
<td>NJ9-2</td>
<td>Late stage</td>
<td>Quartz</td>
<td>209</td>
<td>-145</td>
<td>-1.6</td>
<td>-12.7</td>
</tr>
</tbody>
</table>

Fig. 8. $\delta D$ versus $\delta ^{18}O_{\text{water}}$ diagram of the Jiawula deposit (after Sheppard, 1977).
and different \( \frac{87Rb}{86Sr} \) (Li et al., 2002). Well-crystallized ore minerals in massive ores, which have no obvious fractures, were selected for this present study. Results from our Rb–Sr isochron dating indicate an age of 143.0 ± 2.0 Ma for seven sphalerite samples, an age of 142.0 ± 3.0 Ma for six pyrite samples, and an age of 142.7 ± 1.3 Ma for seven sphalerite and six pyrite samples. The results are consistent within the error range and represent the ore-forming age of the Jiawula deposit.

The Derbugan metallogenic belt is characterized by porphyry Cu–Mo, hydrothermal vein-type Pb–Zn–Ag, and epithermal Ag (Au–Cu) deposits (Wu et al., 2010). For the Wunugetushan porphyry Cu–Mo deposit, Qin et al. (1999) obtained a single grain zircon U–Pb age of 183.3 ± 0.6 Ma and a whole rock Rb–Sr isochron age of 183.9 ± 1.0 Ma for emplacement of the monzonite granite porphyry intrusion, whereas Chen et al. (2011) obtained an \( 40Ar/39Ar \) age of 179.0 ± 1.9 Ma for the porphyry emplacement. Also at the Wunugetushan deposit, Qin et al. (1999) reported a K–Ar age of 183.5 ± 1.7 Ma for a sericite sample from altered rocks, Chen et al. (2011) defined ore formation from a molybdenite Re–Os date of 177.6 ± 4.5 Ma, and Li et al. (2012) reported a molybdenite Re–Os isochron age of 178.0 ± 10 Ma. Chen (2010) obtained a zircon LA–ICP–MS U–Pb age of 229.6 ± 2.0 Ma for a quartz diorite porphyry intrusion occurring in the Taipingchuan porphyry Cu–Mo deposit, which is located in the northern part of the Derbugan metallogenic belt. Chen et al. (2010) reported a zircon LA–ICP–MS U–Pb age of 202 ± 5.7 Ma for the granodiorite porphyry and a Re–Os isochron age of 203.6 ± 4.6 Ma for molybdenite from the Taipingchuan porphyry Cu–Mo deposit.

The age of mineralization in our study area is notably younger than that of the above magmatic-hydrothermal systems elsewhere in the metallogenic belt. Previous ages for quartz monzonite porphyry in the Jiawula–Chaganbulagen ore field of 133–110 Ma had been reported (Pan and Sun, 1992; Qin et al., 1995; Zhao and Zhang, 1997) prior to our study, and Sheng and Fu (1999) reported a single grain zircon U–Pb age of 139.2 Ma for the quartz monzonite porphyry. Li et al. (1994) reported a Rb–Sr isochron age of 120 Ma for the quartz porphyry at the Erentaolegai epithermal deposit.

Considering the Rb–Sr isochron age obtained by us in this study and other geochronological data obtained by previous workers, we conclude that important mineralization in the Derbugan metallogenic belt is younger than that of the above magmatic-hydrothermal systems elsewhere in the metallogenic belt. Previous ages for quartz monzonite porphyry in the Jiawula–Chaganbulagen ore field of 133–110 Ma had been reported (Pan and Sun, 1992; Qin et al., 1995; Zhao and Zhang, 1997) prior to our study, and Sheng and Fu (1999) reported a single grain zircon U–Pb age of 139.2 Ma for the quartz monzonite porphyry. Li et al. (1994) reported a Rb–Sr isochron age of 120 Ma for the quartz porphyry at the Erentaolegai epithermal deposit.

### Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stage</th>
<th>Mineral</th>
<th>( \delta^{34}S_{CDT} ) (‰)</th>
<th>( \delta^{34}S_{H2S} ) (‰)</th>
<th>( 206\text{Pb}/204\text{Pb} ) (2σ)</th>
<th>( 207\text{Pb}/204\text{Pb} ) (2σ)</th>
<th>( 208\text{Pb}/204\text{Pb} ) (2σ)</th>
<th>( \mu )</th>
<th>( \omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NJ-19</td>
<td>Middle stage</td>
<td>Pyrite</td>
<td>4.1</td>
<td>2.8</td>
<td>18.358 ± 0.001</td>
<td>15.593 ± 0.001</td>
<td>38.306 ± 0.003</td>
<td>9.5</td>
<td>36.2</td>
</tr>
<tr>
<td>NJ-72</td>
<td>Middle stage</td>
<td>Pyrite</td>
<td>5.5</td>
<td>4.2</td>
<td>18.333 ± 0.002</td>
<td>15.545 ± 0.002</td>
<td>38.154 ± 0.006</td>
<td>9.4</td>
<td>35.3</td>
</tr>
<tr>
<td>NJ-74</td>
<td>Middle stage</td>
<td>Pyrite</td>
<td>8.4</td>
<td>7.1</td>
<td>18.319 ± 0.002</td>
<td>15.529 ± 0.002</td>
<td>38.101 ± 0.004</td>
<td>9.3</td>
<td>35.0</td>
</tr>
<tr>
<td>NJ-9</td>
<td>Middle stage</td>
<td>Galena</td>
<td>2.6</td>
<td>4.7</td>
<td>18.377 ± 0.002</td>
<td>15.596 ± 0.002</td>
<td>38.314 ± 0.004</td>
<td>9.3</td>
<td>35.2</td>
</tr>
<tr>
<td>NJ-10</td>
<td>Middle stage</td>
<td>Galena</td>
<td>1.2</td>
<td>3.3</td>
<td>18.320 ± 0.002</td>
<td>15.499 ± 0.002</td>
<td>38.194 ± 0.004</td>
<td>9.3</td>
<td>35.1</td>
</tr>
<tr>
<td>NJ-69</td>
<td>Middle stage</td>
<td>Galena</td>
<td>2.6</td>
<td>4.7</td>
<td>18.328 ± 0.002</td>
<td>15.536 ± 0.002</td>
<td>38.134 ± 0.004</td>
<td>9.4</td>
<td>35.1</td>
</tr>
<tr>
<td>NJ-9</td>
<td>Middle stage</td>
<td>Sphalerite</td>
<td>3.4</td>
<td>3.1</td>
<td>18.352 ± 0.002</td>
<td>15.565 ± 0.002</td>
<td>38.211 ± 0.005</td>
<td>9.4</td>
<td>35.6</td>
</tr>
<tr>
<td>NJ-12</td>
<td>Middle stage</td>
<td>Sphalerite</td>
<td>4.4</td>
<td>4.1</td>
<td>18.363 ± 0.001</td>
<td>15.579 ± 0.001</td>
<td>38.262 ± 0.003</td>
<td>9.4</td>
<td>35.9</td>
</tr>
<tr>
<td>NJ-69</td>
<td>Middle stage</td>
<td>Sphalerite</td>
<td>3.7</td>
<td>3.3</td>
<td>18.338 ± 0.002</td>
<td>15.544 ± 0.002</td>
<td>38.177 ± 0.004</td>
<td>9.4</td>
<td>35.3</td>
</tr>
</tbody>
</table>

Notes: \( \mu = \frac{238U}{204Pb} \) and \( \omega = \frac{232Th}{204Pb} \).

Fluid inclusions of the early stage are water-rich aqueous, gas-rich aqueous, and aqueous-carbonic, as well as a few with halite daughter minerals. The H₂O–NaCl–CO₂–CH₄ fluids are characterized by high homogenization temperatures between 304 °C and 438 °C and large fluctuations in salinity between 0.8 wt.% and 44.6 wt.% NaCl equiv (Fig. 11). Fluid immiscibility can be inferred from the coexistence of water-rich, gas-rich, and aqueous-carbonic inclusions in fluid inclusion assemblages that homogenized at similar temperatures and with contrasting salinities (Lu et al., 2004; Liu et al., 2014). Therefore, we speculate that the fluids of the early stage were likely produced by immiscibility in a single fluid that initially was at a temperature >438 °C, was CO₂-bearing, and had a medium- to low-salinity.

Fluid inclusions in the middle stage are mainly water-rich type WL inclusions, although with uncommon types WG, C, S. The ore-forming fluids were of moderate temperature, varying from 242 °C to 297 °C, and showed a large variation in salinity, from 0.4 to 36.8 wt.% NaCl equiv (Fig. 11), which is also consistent with fluid immiscibility during the main stage. Although petrographic studies did not indicate the presence of CH₄-bearing inclusions, laser Raman spectroscopy revealed significant CH₄ in the WL-type inclusions, and thus the middle stage ore-forming fluid belongs to an H₂O–NaCl–CO₂ ± CH₄ system.

From the early stage to the middle stage, and then to the late stage, the temperature of the hydrothermal fluids gradually decreases. Likewise, there is a decrease in salinity from the early stage to the late stage (Fig. 11).

In summary, the fluids of the early stage in the Jiawula deposit were high-temperature, with variable salinity, and CO₂-bearing; the fluids of the main ore-forming stage were moderate temperature, also variable in salinity, relatively low density, and were H₂O–NaCl–CO₂ ± CH₄ in composition; and the fluids of the late stage were low temperature, low salinity, low density, and lacked CO₂. Fluid immiscibility characterized the early and middle stages. The temperature and salinity of the hydrothermal fluids gradually decreased from the early, through the middle, and to the late stage.

6.3. Source of ore-forming fluid and materials

6.3.1. Source of ore-forming fluid

The δD values range from −166‰ to −133‰, and the δ¹⁸Owater values vary from −13.4‰ to −9.1‰. These values lie between the magmatic water field and meteoric water line, but are mainly close to the meteoric water line in the δ¹⁸Owater–δD diagram (Fig. 8). This indicates that a significant component of meteoric water characterized the hydrothermal system, but perhaps also late magmatic exsolution was also important (Rye, 1993; Ouyang et al., 2014). Taylor (1974) believed that mixing between magmatic and meteoric water may be a plausible explanation for the type of low δD and δ¹⁸Owater values reported here. Consequently, we conclude that the ore-forming fluids of the Jiawula deposit are of mixed magmatic and meteoric water origin. Previous studies on ore-forming fluids of the Chaganbulagen and Jiawula Pb–Zn–Ag deposits in this area (Wu et al., 2010; Zhai et al., 2013) also indicated that the ore-forming hydrothermal fluids were mainly from meteoric and magmatic water.

6.3.2. Source of sulfur and ore-forming metals

The isotope composition of sulfides from hydrothermal deposits is a function of total S isotopic compositions (δ³⁴S), oxygen fugacity (fO₂), pH, ionic strength, and temperature. Sulfur isotopic composition of hydrothermal sulfides depends not only on the δ³⁴S value of source materials, but also on the physicochemical condition of the ore-forming fluid (Ohmoto, 1972). Therefore, determining the total S isotopic composition of the hydrothermal fluids during sulfide precipitation is essential for defining the S source. The sulfide assemblage at the Jiawula deposit is dominated by pyrite, sphalerite, galena, and chalcopyrite, and no sulfate minerals have been detected. Thus, H₂S was dominant in the hydrothermal system during ore formation, and pyrite, sphalerite, galena, and chalcopyrite were deposited in an environment with low fO₂ and low pH. Under equilibrium conditions, when the hydrothermal system is dominated by H₂S with low fO₂ and low pH, the values of δ³⁴S₁, δ³⁴S₂, and δ³⁴S₃ are approximately the same (Wu et al., 2014). The average δ³⁴S values of pyrite, sphalerite, and galena for the Jiawula deposit are 6.0‰, 3.8‰, and 1.9‰, respectively. These are in general agreement with the equilibrium sequence of δ³⁴S₁ > δ³⁴S₂ > δ³⁴S₃, suggesting that the different sulfide minerals had been in equilibrium (Ohmoto, 1986; Wu et al., 2014). In this paper, we use the δ³⁴S₁ values to represent the total S isotope composition of the hydrothermal system and to trace the source of S. The δ³⁴S₁ values were calculated with the equation:

$$\delta^{34}S_{1} = \delta^{34}S_{i} - A_{i}(10^{3} \times T^{-2})$$

where i stands for different sulfides; Aᵢ is 0.4 for pyrite, 0.1 for sphalerite, and −0.63 for galena, respectively; T is the temperature in degrees kelvin (Xu et al., 1993); and the average fluid inclusion temperature from the middle stage was used to calculate the δ³⁴S₁ value. The δ³⁴S₁ values vary from 2.8‰ to 7.1‰ (Table 4) and are slightly higher than that of the meteorite S, indicating sulfur in the Jiawula deposit was mainly derived from magmatic and sedimentary sources (Ohmoto and Rye, 1975).

The Pb isotope data are useful geochemical tracers and can indicate crustal evolution, a source of lead, and thus deposit genesis (Lu et al., 2000). In the 206Pb/204Pb vs. 207Pb/204Pb diagram (Fig. 10a), the data points are projected primarily toward the area...
between the orogenic belt and mantle evolution lines; in the $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 10b), almost all of the projected data points are located in the field of the orogenic belt evolution line. The $\mu$ values in the mantle and crust are 8.92 and 9.58, respectively (Doe and Zartman, 1979). The $\mu$ values of metal sulfides from the Jiawula deposit are between 9.3 and 9.5, which are obviously higher than the range of 8–9 in the mantle and slightly lower than 9.58 in the crust (Doe and Zartman, 1979), implying that Pb was mainly derived from the crust, with also a mantle contribution.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are commonly used to trace the source of material and any crust or mantle contamination of magmatic and deep fluids (Hou et al., 2006). The $^{87}\text{Sr}/^{86}\text{Sr}$ values are between 0.712381 and 0.712770, with an average of 0.712641, which are lower than the continental crust average $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.719 (Sun, 2001) and higher than the mantle initial value of 0.704 (Faure, 1986). We interpret this to suggest that the Sr was mainly derived from the continental crust, but with a small amount of mantle input.

6.4. Mechanism of mineral deposition and genetic model

6.4.1. Mechanism of mineral deposition

Ore-forming hydrothermal fluids generally transport metals in complexes with aqueous Cl$^-$ and HS$^-$ (Barnes, 1979). The mechanisms leading to the precipitation of metals from Cl$^-$ and/or HS$^-$ complexes include the following (Barnes, 1979; Ramboz et al., 1982; Robb, 2004; Chi and Xue, 2011): (1) temperature decrease, (2) pressure decrease, (3) phase separation, (4) fluid mixing/dilution, and (5) fluid/rock interaction causing pH and Eh shifts.

As described in Section 6.2, fluids of the early and middle stages in the Jiawula deposit are both immiscible. We conclude that ascending hydrothermal fluids, due to sudden reduce pressure, took place boiling, giving rise to fluid immiscibility. Boiling resulted in escape of a large number of volatile components, causing the strong changes of physicochemical condition of hydrothermal fluids. For example, escape of CO$_2$ component can cause fluid pH value increase and oxygen fugacity decrease. The above changes of physicochemical condition destroyed the stability of the complexes, leading to the precipitation of metals from the complexes. Therefore, fluid boiling is the dominant mechanism for the deposition of ore-forming materials in the Jiawula deposit.

6.4.2. Model of mineralization

The Pb–Zn–Ag deposits located in the Derbugan metallogenic belt, northern Great Xing'an Range, were generally defined as medium–low temperature hydrothermal vein-type deposits based on mineralization temperatures of 176–367 °C obtained by fluid inclusion microthermometry (Pan and Sun, 1992; Zhao and Zhang, 1997; Wu et al., 2010; Zhai et al., 2010) or low-sulfidation epithermal deposits according to mineral assemblage, wall-rock alteration type, and mineralization environment (Zhao and Wu, 2002; Qi et al., 2005). Our new data from fluid inclusion study in this work indicate that the ore-forming fluids of the Jiawula deposit are characterized by moderate–low temperature, low salinity, and low density and are dominated by meteoric water with a small amount of
of magmatic water. The ore minerals of the deposit are mainly galena, sphalerite, pyrite, chalcopyrite, pyrrhotite, and arsenopyrite; the main alteration types include silicification, sericitization, hydromicasization, illitization, carbonation, chloritization, and kaolinitization. Moreover, The Jiawula Pb–Zn–Ag deposit has a close temporal–spatial relationship with Mesozoic volcanic and subvolcanic rocks, and its orebodies are controlled by faults and/or radial fractures of volcanic edifices. Both geological and geochemical characteristics above are similar to those of many low-sulfidation epithermal deposits (Heald et al., 1987; Hedenquist, 1994). Therefore, we propose that the Jiawula deposit as well as other vein-type Pb–Zn–Ag deposits occurring in the Derbugan metallogenic belt is a low-sulfidation epithermal deposit.

Studies of the Late Jurassic to Early Cretaceous Pb–Zn–Ag deposits in the Derbugan metallogenic belt have suggested they formed in a tectonic setting similar to that of those deposits occurring in the southern part of the Great Xing’an Range. This was a back-arc extensional setting, which resulted from the northwestward subduction of the Pacific plate beneath the eastern part of the Eurasia continent (Ge et al., 2007; She et al., 2009, 2012). The types of mineral deposits are different in the Derbugan and Great Xing’an Range metallogenic belts, the former being of low-sulfidation epithermal deposits, which is related to volcanic–subvolcanic hydrothermal activity, and the latter being of magmatic hydrothermal type, which is related to granitic intrusive rocks (Mao et al., 2013; Ouyang et al., 2013a). We infer that the Late Jurassic–Early Cretaceous vein-type Pb–Zn–Ag deposits in the Derbugan metallogenic belt were most likely formed in a post–collisional extensional environment after the Mongol–Okhotsk ocean closure. Latest Middle Jurassic nappes are widely distributed in the upper Heilongjiang basin, but Early Cretaceous strike–slip structures and massif escape document a post–collisional event (Li et al., 2004; Wu et al., 2005, 2008; Ouyang et al., 2013b).

Considering the geological and geochemical features and tectonic setting, as well as porphyry Mo mineralization recently discovered within a monzogranite porphyry, which is located 1.5 km southeast of the Jiawula deposit (Mao et al., 2013), we propose a mineralization model for these vein-type Pb–Zn–Ag deposits in the Manzhouli area. During the Late Jurassic–Early Cretaceous, the study area was in a post–collisional extensional environment, and the extension resulted in lithospheric delamination, asthenosphere upwelling, and crust–mantle interaction. This caused extensive volcanism and emplacement of subvolcanic rocks and felsic porphyry intrusions. The molybdenum-rich subvolcanic porphyry Mo mineralization was first formed. Subsequently, lead-, zinc-, and silver-rich subvolcanic hydrothermal fluids moved upward along the pre-existing faults and/or radial fractures of volcanic edifices and unmixed, due to changing physicochemical conditions, along the pre-existing faults and/or radial fractures of volcanic edifices.

7. Conclusions

(1) The sulfide Rb–Sr isochron age of the Jiawula deposit is ca. 143–142 Ma.

(2) The ore-forming fluids of the Jiawula deposit are characterized by moderate temperature, variable salinity, low density, and an H2O–NaCl–CO2 ± CH4 composition.

(3) The ore-forming fluids of the Jiawula deposit consist mainly of meteoric water with a small amount of magmatic water, and the ore-forming materials mainly came from the Mesozoic magma.

(4) The Jiawula deposit is a low-sulfidation epithermal deposit, and fluid boiling is the dominant mechanism for the deposition of ore-forming materials.

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