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

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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 NWW- 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, H$_2$O–CO$_2$, and daughter mineral-bearing inclusions. The fluid inclusions of the early stage are mainly liquid-rich, gas-rich, and H$_2$O–CO$_2$ types, with a small number containing daughter minerals. Cumulatively, the types have homogenization temperatures, densities, and salinities of 304 °C to 438 °C, 0.35 to 1.37 g/cm$^3$, and 0.8 wt.% to 44.6 wt.% NaCl eqv., respectively. Inclusions of the middle stage are mainly liquid-rich and gas-rich types, with a small amount of H$_2$O–CO$_2$ and daughter mineral-bearing types; their homogenization temperatures, densities, and salinities vary from 242°C to 297 °C, 0.71 to 1.44 g/cm$^3$, 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 °C to 238 °C, 0.81 to 0.90 g/cm$^3$, and 0.2 wt.% to 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 H$_2$O–NaCl–CO$_2$±CH$_4$ system. The $\delta^{18}$O$_{\text{water}}$ values calculated for ore-bearing quartz vary from −13.4‰ to −9.1‰, and the $\delta D_{\text{V-SMOW}}$ 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 $\delta^{34}$S$_{\text{V-CDT}}$ values range
from 1.2‰ to 8.4‰. The \( ^{206}\text{Pb} / ^{204}\text{Pb} \), \( ^{207}\text{Pb} / ^{204}\text{Pb} \), and \( ^{208}\text{Pb} / ^{204}\text{Pb} \) 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 \( ^{87}\text{Sr} / ^{86}\text{Sr} \) 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.

**Keywords:** Sulfide Rb–Sr dating; Fluid inclusion; H–O–S–Pb isotopes; Low-sulfidation epithermal Pb–Zn–Ag deposit; Jiawula; Inner Mongolia; Northern Great Xing'an Range

### 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., Wunugetushan, 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 et al., 2010), host rock features and mineral paragenesis (Qin et al., 1999; Sheng and Fu, 1999; Chen et al., 2008), genetic classification (Yang et al., 2009; Nie et al., 2011), and fluid inclusions properties (Wu et al., 2007, 2010; Shuang et al., 2009; Zhai et al., 2010). But reliable ore-forming ages for the Pb–Zn–Ag deposits have not been reported. Furthermore, sources for the ore-forming materials and genetic classification of the Pb–Zn–Ag deposits are also controversial. Zhao and Zhang (1997) and Sheng and Fu (1999) reported a K–Ar age of 133–110 Ma and a single grain zircon U–Pb age of 139.2 Ma, respectively, for quartz monzonite porphyry that is spatially related to the Jiawula deposit. However, these ages have a wide range and cannot directly represent the age of mineralization. As for sources of the ore-forming materials, Shuang et al. (2009) pointed out that the ore-forming materials were mainly from the crust, but Zhai et al. (2013) considered that they were mainly from the mantle. The Pb–Zn–Ag deposits have mainly been classified as one of two genetic types of deposits: medium–low temperature hydrothermal vein-type deposits (Pan and Sun, 1992; Zhao and Zhang, 1997; Wu et al., 2010; Zhai et al., 2010) and low-sulfidation epithermal deposits (Zhao and Wu, 2002; Qi et al., 2005). In this paper, we present new sulfide Rb–Sr ages, analyses of fluid inclusions, and H–O–S–Pb isotopes. The purpose of this study is to classify the deposit type, determine the mineralization age, reveal the characteristics of the ore-forming fluids and their evolution, and discuss the sources of ore-forming fluids
and metals of the Jiawula deposit. We also incorporate our results with previous studies to probe the ore-forming geodynamic setting of these Pb–Zn–Ag deposits in the Manzhouli area and provide a new metallogenic model for the Jiawula deposit.

2. Regional Geology

The Manzhouli region is located in the southeastern margin of the Argun orogenic belt, also referred to as the Argun massif, which belongs to the eastern segment of the Sayan–Central Mongolia–Argun orogenic belt. The NE-trending Argun orogenic belt is one of the key tectonic units in northeastern China and is bounded by the Mesozoic Mongolia–Okhotsk suture to the northwest and the Derbugan fault to the southeast (Fig. 1a). This orogenic belt experienced a complicated tectonic evolution involving at least six major geological events since the Neoproterozoic: (1) Middle–late Neoproterozoic to Early Cambrian, development of a geosyncline and deposition of marine basalt, andesite, dacite, mudstone, siltstone, and carbonate of the Xinghuadukou Group, marine sandstone, siltstone, carbonate, dacite, and rhyolite of the Jiageda Formation, and marine carbonate, sandstone, siltstone, and mudstone of the Argunhe Formation (Wu et al., 2012); (2) Late Neoproterozoic to early Palaeozoic Khanka orogeny resulted in amalgamation of the Argun block and the Vitim–Stanovoy block, which was located at the southwestern edge of the Siberian Craton, forming the Argun orogenic belt (Ge et al., 2005; Wu et al., 2005; 2012); (3) Early Palaeozoic amalgamation of the above units with the Central Mongolia block to the southwest along the Kelulun fault (Li et al., 2004); (4) Late
Paleozoic, subduction of the Paleo-Asian Oceanic plate beneath the Siberia Craton and the formation of Mongol–Okhotsk back-arc basin. At this time, the Argun block separated from the Siberian Craton again and formed the basement of island-arc terranes between the Paleo-Asian and Mongol–Okhotsk Oceans; (5) Early Mesozoic subduction of the Mongol–Okhotsk Ocean basin towards both the north and south resulted in formation of calc–alkaline granitoids and related porphyry Cu–Mo deposits in the Argun orogenic belt (e.g., Wunugetushan, Babayi, and Badaguan); and (6) Collision of the Mongol–North China continent with the Siberian Craton, resulting in closure of the Mongol–Okhotsk ocean basin in the late Middle Jurassic (Sorokin et al., 2004). Subsequently, the Argun area evolved into a post-collisional setting during Late Jurassic–Early Cretaceous, characterized by a large number of intermediate–acidic volcanic rocks with minor granitic intrusions, leading to the large-scale Pb–Zn–Ag mineralization of the Argun metallogenic belt (Wu et al., 2007).

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 Baiyingaolao, Meiletu,
and Damoguaihe 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 Baiyingaolao Formation consists of dacite, rhyolite, and tuff; the Meiletu Formation is composed of basalt and andesite; and the Damoguaihe 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 magmatisim can be divided into the Late Hercynian, Indosinian, Early Yanshanian, and Late Yanshanian periods (Wu et al., 2010). The Hercynian granitoids, consisting of dominatly granite, granodiorite, and monzogranite, 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 monzogranite, 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 monzogranite, 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 reserves 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 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 main silver-bearing minerals are argentite, native silver, freibergite, and hessite. The gangue minerals are mainly quartz and calcite. The ores mainly comprise xenomorphic granular, euhedral–subhedral granular, exsolution, poikilitic, intergrowth, and intersertal textures (Fig. 3a–c). 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 as bands 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 percent 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 $\pm 1\%$, 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 $0.710236\pm0.000007$ (2σ mean), which coincides well with the published value of $0.710258\pm0.000002$ (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 percent 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) H$_2$O-CO$_2$ inclusions: Fluid salinities were calculated from the final melting temperatures of CO$_2$ 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 FIs 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–galena–sphalerite 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 veins of the middle stage; and (5) NJ9-1 and NJ9-2 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

\[ a_{\text{quartz-water}} = (3.38 \times 10^6)T^{-2} - 3.40, \]

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 δ¹⁸O_w 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 minutes at a temperature of 1100°C (Robinson and Kusakabe, 1975). After purification, SO2 was transferred to the sample tube and the S-isotopic ratio $^{34}S/^{32}S$ was measured on the mass spectrometer of a Finnigan MAT 251 instrument. The lead isotopic composition was measured using a GV IsoProbe-T multi-collector thermal ionization mass spectrometer. The $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios had a precision better than 0.005% (2σ). The Pb-isotopic analyses are reported with respect to Pb standard reference NBS-981 values (Todt et al., 1993): $^{206}\text{Pb}/^{204}\text{Pb} = 16.934\pm 0.007$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.486\pm 0.012$, and $^{208}\text{Pb}/^{204}\text{Pb} = 36.673\pm 0.033$, 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 $^{87}\text{Rb}/^{86}\text{Sr}$ vary from 0.0723 to 11.29, with an average of 4.5102, and the isotope ratios of $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71265 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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:

(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 occur along transcrystalline microfractures in quartz crystals of the early and middle stages, accounting for 25% of the total number of inclusions (Fig. 5a and b).

(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 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).

(3) H₂O-CO₂ inclusions (C type): These inclusions are oval or polygon-shaped, generally 7 to 30 μm in diameter. The CO₂ phases account for 40–60% of the total volume of inclusions, and the CO₂-vapor phase accounts for 60–70% of total CO₂ phase at room temperature. This type, accounting for 10% of the total number of inclusions, is distributed as isolated in quartz of the early and middle stages (Fig. 5c).

(4) Daughter mineral-bearing inclusions (S type): Inclusions of this type are relatively rare and occur as isolated inclusions in quartz of the early and middle stages. These fluid inclusions are oval-shaped with diameters of 6–10 μm and contain bubbles generally accounting for 15–25% of the total volume. They usually contain one daughter mineral. These daughter minerals are all light blue and cube-shaped, implying that they are halite (Fig. 5b). Inclusions of this type account for 5% of the total number of inclusions.

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.

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 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 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, 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 are estimated to be 35.6 wt.% and 36.8 wt.% NaCl eqv., and the fluid densities are 1.44 g/cm³ (Table 2; 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 °C to –0.1 °C, with salinities of 0.2–1.9 wt.% NaCl eqv.; the inclusions homogenized into the liquid phase at temperatures of 181–238 °C, and the fluid densities are 0.81–0.90 g/cm³ (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 CO₂ and CH₄ with a small amount of H₂O (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 H₂O (Fig. 7b, d, f). In addition, the gas phase of some
WL-type inclusions from the middle stage contains mainly CH₄ (Fig. 7e). In general, from early to late, the CO₂ and CH₄ contents of the ore-forming fluids gradually decrease, evolving from an early H₂O–NaCl–CO₂–CH₄ system through a middle H₂O–NaCl–CO₂±CH₄ system into a late H₂O–NaCl system, with ore-forming fluids generally having affinities to an H₂O–NaCl±CO₂±CH₄ 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).

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 paleodepths 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 δD values of −141.0‰, δ18O quartz values of −4.0‰ to −4.5‰, and δ18O water values of −9.7‰ to −9.2‰, respectively; the δD, δ18O quartz, and δ18O water values of 11 samples from the middle stage range from −166‰ to −133‰, −5.5‰ to −1.2‰, and −13.4‰ to −9.1‰, respectively; and the δD, δ18O quartz, and δ18O water values of two samples from the late stage are −145‰, −2.2‰ to −1.6‰, and −13.3‰ to −12.7‰, 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 δ18O water–δD 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 (‰) 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 $^{206}$Pb/$^{204}$Pb, $^{207}$Pb/$^{204}$Pb, and $^{208}$Pb/$^{204}$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 $^{206}$Pb/$^{204}$Pb, $^{207}$Pb/$^{204}$Pb, and $^{208}$Pb/$^{204}$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 $^{206}$Pb/$^{204}$Pb, $^{207}$Pb/$^{204}$Pb, and $^{208}$Pb/$^{204}$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 $^{206}$Pb/$^{204}$Pb versus $^{207}$Pb/$^{204}$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 $^{206}$Pb/$^{204}$Pb versus $^{208}$Pb/$^{204}$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 ($^{87}\text{Sr}/^{86}\text{Sr}$) and different ($^{87}\text{Rb}/^{86}\text{Sr}$) (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 $^{40}\text{Ar}/^{39}\text{Ar}$ 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 mainly occurred in two periods: (1) Late Triassic–Early Jurassic porphyry Cu–Mo deposits; and (2) Late Jurassic–Early
Cretaceous Cu–Zn–Sn skarn, hydrothermal vein-type Pb–Zn–Ag, and epithermal Ag (Au–Cu) deposits.


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 H$_2$O–NaCl–CO$_2$–CH$_4$ 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 eqv (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 CO$_2$-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 eqv (Fig. 11), which is also consistent with fluid immiscibility during the main stage. Although petrographic studies did not indicate the presence of CH$_4$-bearing inclusions, laser Raman spectroscopy revealed significant CH$_4$ in the WL-type inclusions, and thus the middle stage ore-forming fluid belongs to an H$_2$O–NaCl–CO$_2$±CH$_4$ system.
There are only WL-type aqueous inclusions in the late stage. The fluids are characterized by relatively low homogenization temperatures between 181 °C and 238 °C, low salinity from 0.2 wt.% to 1.9 wt.% NaCl eqv (Fig. 11), and low density ranging from 0.81 to 0.90 g/cm³. Laser Raman spectroscopy identified only H₂O, confirming that the late stage comprised an H₂O–NaCl 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 \( \delta^1D \) and \( \delta^{18}O_{\text{water}} \) 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 (\( \delta^{34}S_2 \)), oxygen fugacity (\( f_{O_2} \)), pH, ionic strength, and temperature. Sulfur isotopic composition of hydrothermal sulfides depends not only on the \( \delta^{34}S \) 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, \( H_2S \) was dominant in the hydrothermal system during ore formation, and pyrite, sphalerite, galena, and chalcopyrite were deposited in an environment with low \( f_{O_2} \) and low pH. Under equilibrium conditions, when the hydrothermal system is
dominated by H₂S with low fO₂ and low pH, the values of δ³⁴SΣ, δ³⁴SH₂S, and δ³⁴Spyrite 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 δ³⁴Spy > δ³⁴Ssp > δ³⁴Sgn, suggesting that the different sulfide minerals had been in equilibrium (Ohmoto, 1986; Wu et al., 2014). In this paper, we use the δ³⁴SH₂S values to represent the total S isotope composition of the hydrothermal system and to trace the source of S. The δ³⁴SH₂S values were calculated with the equation:

\[ \delta^{34}S_{H2S} = \delta^{34}S_i - A_i (10^6 \times T^{-2}) \]

where i stands for different sulfides; Aᵢ value 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 δ³⁴SH₂S value. The δ³⁴SH₂S 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, 1979).

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 versus ²⁰⁷Pb/²⁰⁴Pb diagram (Fig. 10a), the data points are projected primarily toward the area between the orogenic belt and mantle evolution lines; in the ²⁰⁶Pb/²⁰⁴Pb versus ²⁰⁸Pb/²⁰⁴Pb diagram (Fig. 10b), almost all of the projected data points are located in the field of the orogenic belt evolution line. The μ 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 $^{87}$Sr/$^{86}$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 ($^{87}$Sr/$^{86}$Sr)$_i$ values are between 0.712381 and 0.712770, with an average of 0.712641, which are lower than the continental crust average $^{87}$Sr/$^{86}$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 CO₂ 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- to low temperature, low salinity, and low density and are dominated by meteoric water with a small amount 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, hydromicazation, illitization, carbonation, chloritization, and kaolinization. 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 northwesterly 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 deposit, 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-collision 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-collision 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 orebodies. 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, which may have been caused by hydrothermal fluid boiling. The resulting low-sulfidation epithermal Pb–Zn–Ag deposits were deposited at a depth of 0.8–2.0 km, forming deposits such as Jiawula and Chaganbulagen. Finally, as the hydrothermal fluids continued to move upward, and additional meteoric water was added to the hydrothermal system, the Erentaolegai low-sulfidation epithermal Ag deposit was formed (Fig. 12).
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 H$_2$O–NaCl–CO$_2$±CH$_4$ 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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References


Robinson, B.W., Kusakabe, M., 1975. Quantitative preparation of sulfur dioxide, for
$^{34}\text{S} / ^{32}\text{S}$ analyses, from sulfides by combustion with cuprous oxide. Analytical Chemistry 47, 1179–1181.


Geologica Sinica 88, 558–569.


**Figure Captions**

Fig. 1. Regional geological map of the Manzhouli area, Inner Mongolia, showing (a) geotectonic units and (b) locations of major deposits/occurrences (modified from Zhao and Zhang, 1997; Ge et al. 2007; Wu et al. 2010). 1, Erentaolegi low-sulfidation epithermal Ag deposit; 2, Wuqigenwula vein-type Pb–Zn–Ag occurrence; 3, Jiawula vein-type Pb–Zn–Ag deposit; 4, Chaganbulagen vein-type Pb–Zn–Ag deposit; 5, Erdengwula low-sulfidation epithermal Ag occurrence; 6, Bayanhaolei high-sulfidation epithermal Cu–Au–Ag occurrence; 7, Wunugetushan porphyry Cu–Mo deposit; 8, Halasheng vein-type Pb–Zn deposit; 9, Changling porphyry Cu–Mo occurrence; 10, Longling skarn Cu–Zn–Sn occurrence; 11, Toudaojing porphyry Cu–Mo deposit; 12, Babai porphyry Cu–Mo deposit; 13, Badaguan porphyry Cu–Mo deposit; 14, Daba high-sulfidation epithermal Cu–Au–Ag occurrence; I, Derbugan fault; II, Argunhe–Hulun fault; III, Hanigou fault; IV, Muhar
fault; V, Jiawula–Chaganbulagen fault.

Fig. 2. Geological map of the Jiawula ore district.

Fig. 3. Representative photos of ores from the Jiawula deposit: (a) chalcopyrite surrounding pyrite, developing a poikilitic texture under reflected light; (b) chalcopyrite occurring as emulsion droplet within sphalerite, forming an exsolution texture under reflected light; (c) pyrite associated with pyrrhotite, forming an intergrowth texture under reflected light; (d) massive ore; (e) vein ore; (f) disseminated ore; (g) quartz–galena vein from the middle stage crosscutting quartz–pyrite–pyrrhotite vein of the early stage; (h) quartz–pyrite–galena–sphalerite ore of the middle stage; (i) quartz vein of the late stage crosscutting Pb–Zn ore of the middle stage. Cp, chalcopyrite; Gn, galena; Po, pyrrhotite; Py, pyrite; Sp, sphalerite.

Fig. 4. Rb–Sr isochrons for the Jiawula Pb–Zn–Ag deposit for (a) sphalerite, (b) pyrite, and (c) sphalerite and pyrite.

Fig. 5. Photomicrographs of representative fluid inclusions in quartz crystals from the Jiawula deposit: (a) gas-rich, liquid-rich, and secondary inclusions of the quartz–pyrrhotite–pyrite–chalcopyrite stage; (b) daughter mineral-bearing inclusions of the quartz–pyrite–galena–sphalerite stage; (c) H$_2$O–CO$_2$ inclusions of the quartz–pyrite–galena–sphalerite stage; (d) liquid-rich inclusions of the quartz–pyrite
stage; $L_{\text{H}_2\text{O}}$, liquid phase $\text{H}_2\text{O}$; $V_{\text{H}_2\text{O}}$, vapor phase $\text{H}_2\text{O}$; $L_{\text{CO}_2}$, liquid phase carbon dioxide; $V_{\text{CO}_2}$, vapor phase carbon dioxide; Ih, halite.

Fig. 6. Histograms of salinities and homogenization temperatures for fluid inclusions from the Jiawula deposit.

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) WG-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.

Fig. 8. $\delta^D$ versus $\delta^{18}\text{O}_{\text{water}}$ diagram of the Jiawula deposit (after Sheppard, 1977).

Fig. 9. Histogram of sulfur isotope data for the Jiawula deposit.

Fig. 10. Diagram of lead isotopic compositions of the Jiawula deposit (base map from Zartman and Doe, 1981).

Fig. 11. Diagram of homogenization temperature versus salinity of fluid inclusions in the Jiawula deposit.
Fig. 12. Metallogenic model of the lode Pb–Zn–Ag deposits in the Manzhouli area (modified from Wu et al., 2008).

Tables

Table 1 Rb–Sr isotopic analyses of sphalerite and pyrite from the Jiawula Pb–Zn–Ag deposit.

Table 2 Microthermometry data of the fluid inclusions from the Jiawula deposit.

Notes: \( V \), volume fraction of gas phase in the total volume; \( T_{m, \, \text{CO}_2} \), melting temperature of CO\(_2\) ice; \( T_{m, \, \text{clath}} \), melting temperature of clathrate; \( T_{\text{h, \, CO}_2} \), partial homogenization temperature of CO\(_2\); \( T_{m, \, \text{ice}} \), final ice-melting temperature; \( T_{\text{h}} \), total homogenization temperature.

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

Table 4 Sulfur and lead isotope compositions of sulfides from the Jiawula deposit.

Notes: \( \mu = \frac{^{238}\text{U}}{^{206}\text{Pb}} \), \( \omega = \frac{^{232}\text{Th}}{^{204}\text{Pb}} \), the age for calculating the values of \( \mu \) and \( \omega \) is 143Ma.
Table 1 Rb–Sr isotopic analyses of sphalerite and pyrite from the Jiawula Pb–Zn–Ag deposit.

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<th>Sample</th>
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<th>Sr (ppm)</th>
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Table 2 Microthermometry data of the fluid inclusions from the Jiawula deposit.

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Notes: V, volume fraction of gas phase in the total volume of inclusion; $T_{\text{m, CO}_2}$, melting temperature of CO$_2$ ice; $T_{\text{m, clath}}$, melting temperature of clathrate; $T_{\text{h, CO}_2}$, partial homogenization temperature of CO$_2$; $T_{\text{m, ice}}$, final ice-melting temperature; $T_{\text{h}}$, total homogenization temperature.
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Table 4 Sulfur and lead isotope compositions of sulfides from the Jiawula deposit.

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<th>²⁰⁷Pb/²⁰⁴Pb (2σ)</th>
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<td>38.094±0.004</td>
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<td>35.0</td>
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<td>2.6</td>
<td>4.7</td>
<td>18.328±0.002</td>
<td>15.536±0.002</td>
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<td>9.4</td>
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<td>3.4</td>
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<td>38.177±0.004</td>
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Notes: μ = ²³⁸U/²⁰⁴Pb, ω = ²³²Th/²⁰⁴Pb, the age for calculating the values of μ and ω is 143Ma.

Research highlights

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

The ore-forming fluids are medium–low temperature and variable salinity fluids.

The ore-forming fluids are mainly meteoric water with minor magmatic water.

The ore-forming materials mainly came from the Mesozoic magma.

The deposit is a low-sulfidation epithermal Pb–Zn–Ag deposit.