

Original Article

Noble Gas and Stable Isotopic Constraints on the Origin of the Ag–Cu Polymetallic Ore Deposits in the Baiyangping Area, Yunnan Province, SW China

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Abstract

The Lanping basin, Yunnan province, SW China, is located at the juncture of the Eurasian and Indian Plates in the eastern part of the Tibetan Plateau. The Lanping basin, in the Sanjiang Tethyan metallogenic province, is a significant Cu–Ag–Zn–Pb mineralized belt in China that includes the largest sandstone-hosted Zn–Pb deposit in the world, the Jinding deposit, as well as several Ag–Cu deposits (the Baiyangping and Jinman deposits). These deposits, with total reserves of over 16.0 Mt Pb + Zn, 0.6 Mt Cu, and 7,000 t Ag, are mainly hosted in Meso-Cenozoic clastic rocks and are dominantly controlled by two Cenozoic thrust systems developed in the western and eastern segments of the basin. The Baiyangping, Babaoshan, and Hetaoqing ore deposits are representative of the epithermal base metal deposits in the Lanping basin. The microthermometric data show that the ore-forming fluids for these deposits were low temperature (110–180 °C) and had bimodal distribution of salinity at moderate and mid to high salinities (approximately 2–8 wt.% and 18–26 wt.% NaCl equivalent). The C and O isotope data indicate that the ore-forming fluids were related to hot basin brines. We present new He and Ar isotope data on volatiles released from fluid inclusions contained in sulfides and in barite in these three deposits. ³He/⁴He ratios of the ore-forming fluids are 0.01 to 0.14 R/Ra with a mean of 0.07 Ra (where R is the ³He/⁴He ratio and Ra is the ratio for atmospheric helium). This mean value is intermediate to typical ³He/⁴He ratios for the crust (R/Ra = 0.01 to 0.05) and the ratio for air-saturated water (R/Ra = 1). The mean ratio is also significantly lower than the ratios found for mantle-derived fluids (R/Ra = 6 to 9). The ⁴⁰Ar/³⁶Ar ratios of the ore-forming fluids range from 298 to 382 with a mean of 323. This value is slightly higher than that for the air-saturated water (295.5). The ³He/⁴He ratios of fluids from the fluid inclusions imply that the ore-forming fluid for the Baiyangping, Babaoshan, and Hetaoqing deposits was derived from the crust and that any mantle-derived He was negligible. The content of the radiogenic Ar ranges between 0.2 to 20.4%, and the proportion of air-derived ⁴⁰Ar averages 94.1%. This indicates that atmospheric Ar was important in the formation of these deposits but that some radiogenic ⁴⁰Ar was derived from crustal rocks. Based on these observations coupled with other geochemical evidence, we suggest that the ore-forming fluids responsible for the formation of the Ag–Cu–Pb–Zn polymetallic ore deposits in the Baiyangping area of the Lanping basin were mainly derived from crustal fluids. The fluids may have mixed with some amount of air-saturated water, but there was no significant involvement of mantle-derived fluids.

Keywords: He–Ar and C–O isotopes, fluid inclusions, ore-forming fluid, Ag–Cu polymetallic deposits, Baiyangping ore cluster.

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1. Introduction

The Lanping basin is located at the juncture of the Eurasian and Indian plates in the eastern Tibetan Plateau. The basin is compressed between the Lancangjiang River suture to the west and Jinshajiang–Ailaoshan suture to the east. The Lanping basin is a significant Pb–Zn–Cu–Ag mineralization belt in the Sanjiang Tethyan metallogenic province in China which hosts numerous economically significant deposits (Xue *et al.*, 2002, 2003, 2007; He *et al.*, 2005, 2009; Zhao, 2006; Zhang *et al.*, 2013; Feng *et al.*, 2014; Zou *et al.*, 2015). A number of Cenozoic base metal deposits occur in this basin including the largest sandstone-hosted Pb–Zn deposit in the world, the Jinding deposit, with reserves of 200 Mt ore grading 6.08% Zn and 1.29% Pb. Several Ag–Cu–Pb–Zn–Co deposits, including the Baiyangping and Jinman deposits, are located in the northern part of the basin (Tian, 1997; Chen *et al.*, 2000, 2004; Xue *et al.*, 2003, 2007; Zhang *et al.*, 2013; Zou *et al.*, 2015). These deposits, hosting total reserves of over 16.0 Mt Pb+Zn, 0.6 Mt Cu, and 7,000 t Ag, are hosted by Meso-Cenozoic mottled clastic rocks, and are dominantly controlled by the post-Paleocene thrust systems related to the Indo-Asian collision (He *et al.*, 2004; Xu & Zhou, 2004; Zhang *et al.*, 2013).

The Baiyangping area, which hosts many Ag–Cu ore deposits, is an important polymetallic ore deposit district (Tian, 1997; Gong *et al.*, 2000; Liu *et al.*, 2004; Li *et al.*, 2005). The district has reserves of 4,600 t at 178 g/t Ag, 0.38 Mt at 1.45% Cu, 0.43 Mt at 5.15% Pb, 0.36 Mt at 5.02% Zn, and 1,444 t at 0.08% Co (Tian, 1997; He *et al.*, 2004; Zhao, 2006). A number of scientific studies have been conducted on these deposits since their discovery. Xue *et al.* (2007) and He *et al.* (2009) studied the geology and geochemistry of the deposits, Xue *et al.* (2003); He *et al.* (2004), Li and Song, (2006), and Wang *et al.* (2011) performed radiogenic isotope dating and studied the stable isotopes, and Hou *et al.* (2008) studied the ore-forming environment. Despite these previous detailed investigations, no consensus on ore genesis has been reached and one of the most important reasons for this lack of consensus is controversy over the source of the ore fluids. The focus of the debate for the deposits in the Baiyangping area is whether mantle-derived fluids were involved in any way in the ore-forming processes. Most of the previous geochemical studies have proposed that all of the ore-forming components were from the Lanping basin (Hou *et al.*, 2008; Liu *et al.*, 2004; He *et al.*, 2005, 2009; Zou *et al.*, 2015), but some studies

have argued that the ore-forming fluids were a mixture of fluids derived from organic matter, basal brines, and fluids from mantle-derived magmatic sources (Chen *et al.*, 2000, 2004; Xue *et al.*, 2003; Xue *et al.*, 2010; Feng *et al.*, 2014).

The isotopic composition of noble gases is the ideal constituent to discriminate between fluids of meteoric, crustal, or mantle origin. This is possible because the isotopic compositions of the noble gases from the different sources are quite different. In addition, the noble gases are chemically inert and their isotopes remain essentially unchanged during most geological processes. This means they can record the original source of the geological fluids. The isotopic compositions of noble gases, such as He and Ar, have been used by many investigators to provide insights into fluid processes (Turner & Stuart, 1992; Stuart *et al.*, 1994a, 1995; Hu *et al.*, 1998a, 1998b, 2004, 2009, 2012; Burnard *et al.*, 1999; Mao *et al.*, 2003; Moura *et al.*, 2014; Day *et al.*, 2015; Zhu & Peng, 2015). In this study, we present the results of a systematic investigation of geology, fluid inclusions, and isotope geochemistry to determine whether mantle-derived fluids were involved in the ore-forming process. We also attempt to decipher the origin of the fluids that formed the Baiyangping polymetallic Ag–Cu ore deposits.

2. Geological setting

The Lanping basin is located in the eastern Indo-Asian collision zone, a prominent NS-trending topographic feature in south China (Fig. 1). Tectonically, this basin is an intra-continental basin developed within the Lanping–Simao micro-plate, a micro-plate between the Yangtze Plate to the east and the Tibet–Yunnan Plate to the west. The Lanping–Simao micro-plate is bounded by the Lancangjiang regional fault to the west and by the Jinshajiang–Ailaoshan fault to the east (Hou *et al.*, 2008; Xue *et al.*, 2003, 2007; Zhao, 2006; He *et al.*, 2009). Proterozoic metamorphic rocks (sericite schist, marble, and gneiss), which form the basement of the Lanping basin are exposed along both fault zones at the margins of the basin. The Mesozoic sedimentary strata in the basin mainly consist of the Upper Triassic Sanhedong Formation of carbonates, the Middle Jurassic Huakaizuo Formation of carbonate-bearing sandstone and carbonaceous shale and slate, and the Lower Cretaceous Jingxing Formation, terrestrial clastic sediments. The Cenozoic strata are dominated by

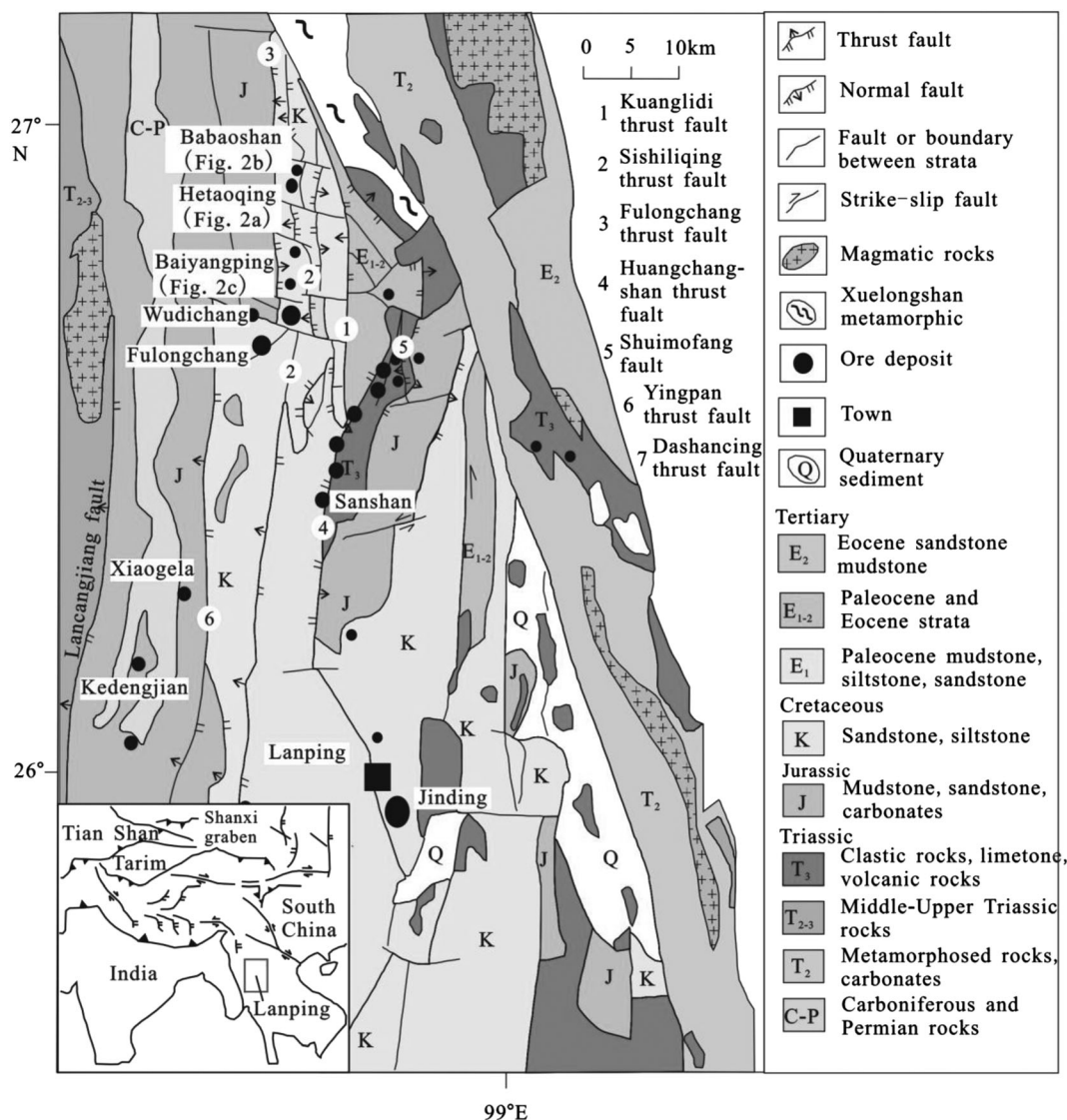


Fig. 1 Geologic map of the northern part of the Lanping basin showing the location of important epithermal Ag–Cu polymetallic ore deposits (modified after Xue *et al.*, 2007).

lacustrine clastic sediments including siltstone, mudstone, sandstone, and conglomerate. The outcrops of Himalayan igneous rocks are mostly restricted to the margins of the Lanping basin. A few small plutons such as the Zhuopan, Huanglianpu, and Weishan plutons occur inside the basin. These plutons are composed of quartz syenite, granitic porphyry, assyntite (nepheline syenite), and essexite (alkali gabbro) (Dong *et al.*, 2005; Zhao, 2006). Trans-lithosphere faults occur at the margins of the basin and trans-crustal faults at the center of the basin (Xue *et al.*, 2002; Hou *et al.*, 2008). The basin has been affected by several tectonic events such as

rifting during the Indo-Chinese epoch, compression during the Yanshanian epoch and, finally, strike-slip extension during the Himalayan epoch (He *et al.*, 2009; Hou, 2010).

As a result of the Indo-Asian collision, two large-scale Cenozoic thrust-nappe systems developed in the Lanping basin. They are separated by a NE-trending axial fault. The thrust-nappe systems appear to have controlled the spatial distribution of many Cenozoic Ag–Cu polymetallic deposits in the region. Vein-type Cu–Ag deposits and epithermal Ag–Cu polymetallic deposits occur mainly in the western thrust-nappe

system, whereas epithermal Cu–Ag polymetallic deposits mainly occur in the eastern thrust-nappe system (Chen *et al.*, 2000; Zhao, 2006; He *et al.*, 2009; Hou, 2010; Zhang *et al.*, 2013).

The Baiyangping Ag–Cu–Co deposit, Babaoshan Ag–Cu deposit and Hetaoqing Cu deposit (Table 1) are in the northern part of the Lanping basin, part of the western thrust-nappe system (also called the western metallogenic belt). The western metallogenic belt has traditionally been referred to as the “western ore zone of the Baiyangping district” by local geologists (He *et al.*, 2009). In addition to the Baiyangping, Babaoshan, and Hetaoqing deposits, other important epithermal Ag-bearing polymetallic deposits in this belt include the Fulongchang, and Wudichang deposits (Fig. 1). The western metallogenic belt is about 15 km long and 1.2–3 km wide. In this area there are three sets of faults: the N–S striking Sishiliqing thrust fault (F₂), its second-order NE-striking faults (F₆–F₉ and F₁₂), and the approximately E–W striking strike-slip faults (F₃–F₄ and F₁₁) (Fig. 2a–c). These faults occur between the sandstone and carbonaceous slate of the Huakaizuo Formation or within the sandstones of the Lower Cretaceous Jingxing Formation.

The ore deposits in this region are mainly hosted in terrestrial-marine sedimentary rocks that have experienced low-grade metamorphism. These include quartz sandstone, siltstone, and mudstone of the Lower Cretaceous Jingxing Formation in addition to mottled clastic rocks, schist, sandy slates, and siliceous mudstone of the Middle Jurassic Huakaizuo Formation.

Fractured rock and fault gouge also hosts mineralization (Fig. 2a–c). Orebodies occur in the NE- and nearly E–W-trending second-order fault zones or on both sides of the faults. The faults generally dip SE at 43° to 87°. Common alterations in the host rocks include carbonate alteration, baritization, pyritization, and silicification (Chen *et al.*, 2000, 2004; He *et al.*, 2005). Ore occurs as open-space fillings and cement and mainly occurs as veins, lenses, and stratiform orebodies. Ore minerals include tennantite, chalcopyrite, Ag-bearing tetrahedrite, cobaltite, argentite, kongsbergite, bornite, chalcocite, pyrite, and cinnabar. Gangue minerals include calcite, barite, ankerite, siderite, and minor quartz. Ore types are dominated by network, veinlet, and brecciated types, and ore textures are mainly granular, fissured, metasomatic textures (Tian, 1997; Zhao, 2006; He *et al.*, 2009).

3. Distribution and characteristics of mineral deposits

3.1. The Baiyangping Ag–Cu–Co deposit

The Baiyangping deposit is an important deposit in the Lanping basin. It is located in the central section of the western metallogenic belt in the northwest part of the Lanping basin, about 30 km northwest of Jinding (Fig. 1). It contains metal reserves of about 2,000 t Ag, 0.12 Mt Cu and over 1,400 t Co, with grades of from 7.5 to 2,438 g/t Ag, 0.05 to 8.16% Cu, and 0.006 to 0.42% Co (Table 1; Tian, 1997).

Table 1 Summary of geological and mineralogical features of three important epithermal Ag–Cu polymetallic ore deposits in the Baiyangping area

| Deposit | Economic metals | Wall rock | Structural control | Sulfide assemblages | Mineralization style |
|-------------|-----------------|--|--|-----------------------------|--|
| Hetaoqing | Cu | Lower Cretaceous quartz sandstone and siltstone | ~E–W-striking strike-slip fault | Cp, Te, Py, Cc, Bo | Barite veins in extensional sites |
| Babaoshan | Cu–Ag | Lower Cretaceous quartz sandstone; Jurassic mudstone, siltstone, sandstone, and carbonates | ~E–W-striking strike-slip fault | Cp, Te, Cc, Arg, Ko, Py, Ci | Barite veins and breccias |
| Baiyangping | Cu–Ag–Co | Lower Cretaceous quartz sandstone, mudstone and siltstone | NE-striking second-order fault related to a N–S-striking thrust fault; the front zone in the western thrust-nappe system | Te, Py, Cp, Cob, Fre, Arg | Calcite network veins, minor wall rock mineralization, |

Ore mineral abbreviations: Arg, argentite; Bo, bornite; Cc, chalcocite; Ci, cinnabar; Cob, cobaltite; Cp, chalcopyrite; Fre, freibergite; Ko, kongsbergite; Py, pyrite; Te, tennantite.

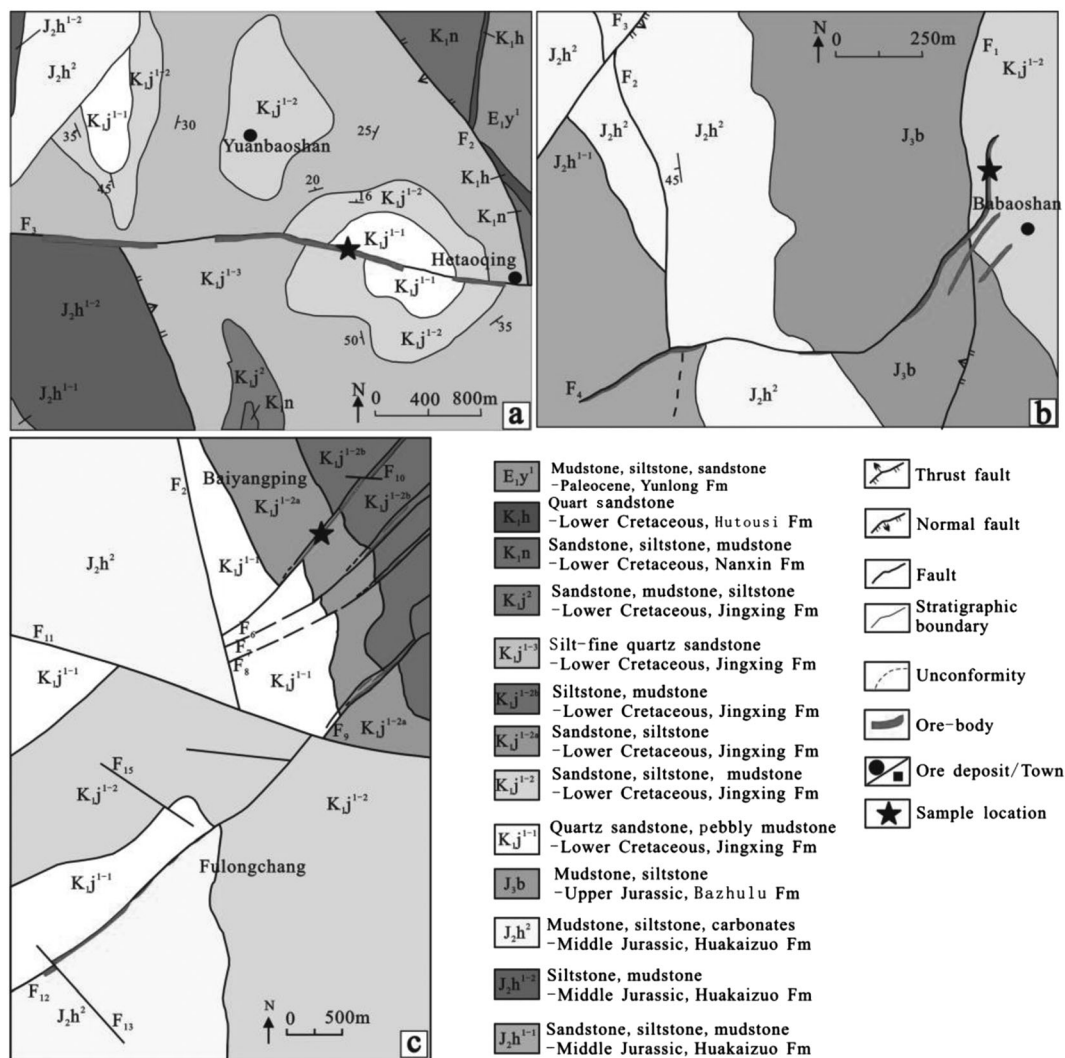


Fig. 2 Simplified geologic maps of portions of the Baiyangping area showing the geology and structures near major Ag–Cu–Co deposits. a) Map of the Hetaoqing Cu deposit (simplified from Yunnan Geological Survey, 2003). b) Map of the Babaoshan Ag–Cu deposit (modified from Su *et al.*, 2004). c) Map of the Baiyangping Ag–Cu–Co deposit. (modified from Xue *et al.*, 2007).

At the scale of an ore zone, three groups of faults can be distinguished, including the N–S striking Sishiliqing thrust fault (F_{12}) and its second-order NE-striking faults (F_6 – F_9 , F_{12}), and the approximately E–W strike-slip fault F_{11} (Fig. 2c). These faults mainly occur in the sandstone of the Lower Cretaceous Jingxing Formation or in the mudstone of the Huakaizuo Formation. The faults probably resulted from regional eastward thrusting (Tian, 1997; Chen *et al.*, 2000, 2004; Hou *et al.*, 2008).

The orebodies are mainly hosted by the sandstones, siltstones, and mudstones of the Cretaceous Jinxing

Formation (K_{1j}) although ore also occurs in siliceous mudstone of the Middle Jurassic Huakaizuo Formation (J_{2h}). The ore at Baiyangping is dominantly open-space filling and cement and ore occurs in veinlets, networks, and breccia structures. Ore minerals include tetrahedrite, arsenian tetrahedrite, sphalerite, galena, chalcopyrite, bornite, pyrite, cobaltite, and minor argentite (Fig. 3a and b). Silver is present as argentite with minor amounts in tetrahedrite. Cu is mainly present in tetrahedrite, which occurs as euhedral to anhedral grains, commonly coexisting with chalcopyrite (Xue *et al.*, 2003, 2007; Zhao, 2006; He *et al.*, 2009). Gangue

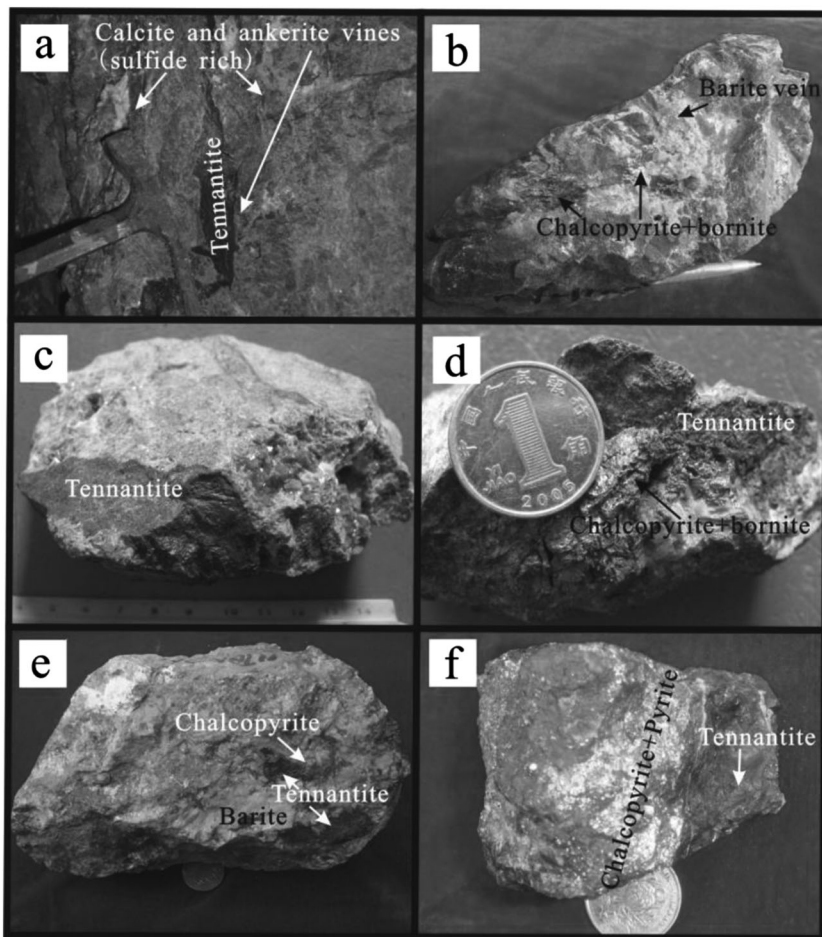


Fig. 3 Photographs of hand specimens showing relationships of hydrothermal minerals in the Baiyangping, Babaoshan, and Hetaoqing ore deposits. a) Calcite and ankerite vein containing tennantite. b) Barite vein containing chalcopyrite and bornite. c) Tennantite veinlet. d) Calcite vein containing chalcopyrite, bornite, and tetrahedrite. e) Barite vein containing tennantite, chalcopyrite, and bornite. f) Chalcopyrite–pyrite–tennantite assemblage.

minerals include calcite, barite, ankerite, siderite, and minor quartz.

3.2. The Babaoshan Ag–Cu deposit

The Babaoshan Ag–Cu deposit is located in the northern part of the western metallogenic belt (Fig. 1). When this manuscript was written, the deposit was known to contain reserves of more than 500 t Ag and around 0.1 Mt Cu, with grades from 29 to 250 g/t Ag, and 1.6 to 19.4% Cu (Su *et al.*, 2004). The property has not been fully explored. The Babaoshan orebodies occur in, from NE to SW, the Upper Jurassic Baoxiangsi Formation (J₃b), the Lower Cretaceous Jingxing Formation (K₁j) and the Middle Jurassic Huakaizuo Formation (J₂h) (Fig. 2b). Orebodies are mainly hosted by J₃b quartz sandstone and siltstone and to a lesser extent by J₂h siliceous mudstone and K₁j sandstone, siltstone, and mudstone. Ore minerals are dominated by

tetrahedrite, Ag-bearing tetrahedrite, argentite, chalcopyrite, bornite, chalcocite, and native silver. Most of the silver is in Ag-bearing tetrahedrite with only minor amounts in argentite and native silver (Fig. 3c and d). Gangue minerals include calcite, ankerite, barite, and minor sericite. The wall rock alteration associated with mineralization is characterized by weak silicification and carbonatization, which mainly produce siliceous rocks and veins of calcite and dolomite with minor siderite. The orebodies are dominated by sulfide-bearing calcite veins, although disseminated ore in altered wall rocks is also common (Su *et al.*, 2004; Zhao, 2006).

3.3. The Hetaoqing Cu deposit

The Hetaoqing Cu deposit is located in the northern part of the western metallogenic belt (Fig. 1). It has reserves of 55,304 t of contained copper and an average grade of 1.68% Cu (unpublished data). The main ore

hosting strata are the Middle Jurassic Huakaizuo Formation and the Lower Cretaceous Jingxing Formation sandstone, siltstone, and mudstones. The orebodies occurring as veins, lenses, and semi-layered and irregular bodies (Fig. 2a). The dominant ore veins show open-space filling structure (Zhao, 2006). Ore minerals include tennantite, chalcocite, chalcopyrite, bornite, and pyrite. Gangue minerals consist of calcite, celestite, siderite, dolomite, barite, and minor fluorite (Fig. 3e and f). Alteration of the host rocks is dominated by dolomitization, carbonatization, and silicification. Alteration mineral assemblages are simple and consist of pyrite, barite, fluorite, calcite, celestite, and dolomite (Zhao, 2006).

4. Fluid inclusion studies

Previous studies have produced a large number of microthermometric determinations from fluid inclusions in the Baiyangping deposit (Zeng, 2007; He *et al.*, 2009; Xue *et al.*, 2010). Here we report new microthermometric data for fluid inclusions from the Babaoshan and the Hetaoqing deposits. Samples selected included calcites associated with copper-bearing sulfides from the Babaoshan deposit and barites that coexisted with copper-bearing sulfides from the Hetaoqing deposit.

Fluid inclusion microthermometry was performed at the Institute of Geochemistry, Chinese Academy of Sciences in Guiyang, China. Microthermometric analyses were carried out on a Linkam THMSG 600 programmable heating–freezing stage attached to a Leica microscope. The equipment was calibrated using synthetic fluid inclusions. Estimated accuracy is about $\pm 0.2^\circ$ below 50°C and $\pm 2^\circ$ for temperatures above 100°C (Su *et al.*, 2009).

4.1. Fluid inclusion petrography

Fluid inclusions have been found in calcite from the Babaoshan deposit and barite from the Hetaoqing deposit. The fluid inclusions present relatively regular shapes (ellipsoidal, amygdaloidal, and negative crystal shapes), and commonly range in size from 5 to $14\ \mu\text{m}$ in maximum dimension (Fig. 4). A few secondary fluid inclusions in healed fractures are present but were not studied. The fluid inclusions studied were present as isolated inclusions, were distributed in clusters, or were present along growth zones; all are considered to be primary or pseudosecondary inclusions.

Based on their phase assemblages at room temperature, fluid inclusions in hydrothermal minerals can be categorized into two types. Type A inclusions are composed of only a liquid aqueous solution (LH_2O ; Fig. 4a). Type B inclusions are composed of a liquid aqueous solution plus water vapor ($\text{LH}_2\text{O} + \text{VH}_2\text{O}$; Fig. 4a–d).

In the samples we studied, type B inclusions are more abundant than the type A and the two types of fluid inclusions generally appear separately. The Type B inclusions are about 70 to 90% filled by liquid phase (Fig. 4a–d).

4.2. Microthermometric measurements

Microthermometric data for inclusions from the Baiyangping area are summarized in Table 2. At these Ag–Cu–Pb–Zn deposits, the homogenization temperatures (T_h) for aqueous inclusions range from 105 to 287°C and the salinities range from 1.9 to 24.6 wt.% NaCl equivalent (Xue *et al.*, 2010). The microthermometric data show that the ore-forming fluids for these deposits were low temperature (peak values at 110 to 180°C) (Fig. 5a) and had two peaks at moderate and mid-high salinities (peak values at approximately 2 to 8 wt.% and 18 to 26 wt.% NaCl equivalent) (Fig. 5b) (Xue *et al.*, 2010).

5. Isotope geochemistry

5.1. Analytical techniques

Microscopic observation identified 10 representative calcites associated with ore-bearing sulfides that were selected for analysis. Samples selected included seven calcites associated with copper-bearing sulfides from the Baiyangping deposit and three calcites that coexisted with copper-bearing sulfides from the Hetaoqing deposit. All samples were crushed, sieved, and finally calcite grains were handpicked under a binocular microscope to a purity of $>99\%$. The C and O isotopic compositions of calcite were determined on a Finnigan MAT 251 mass spectrometer at the Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang. Additional details of analytical procedures can be found in Liu *et al.* (2004). The resulting C and O isotope compositions are reported using standard V-PDB for carbon and V-SMOW for oxygen isotopes. Total uncertainties were estimated to be better than $\pm 0.2\%$ for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ at the 1σ level.

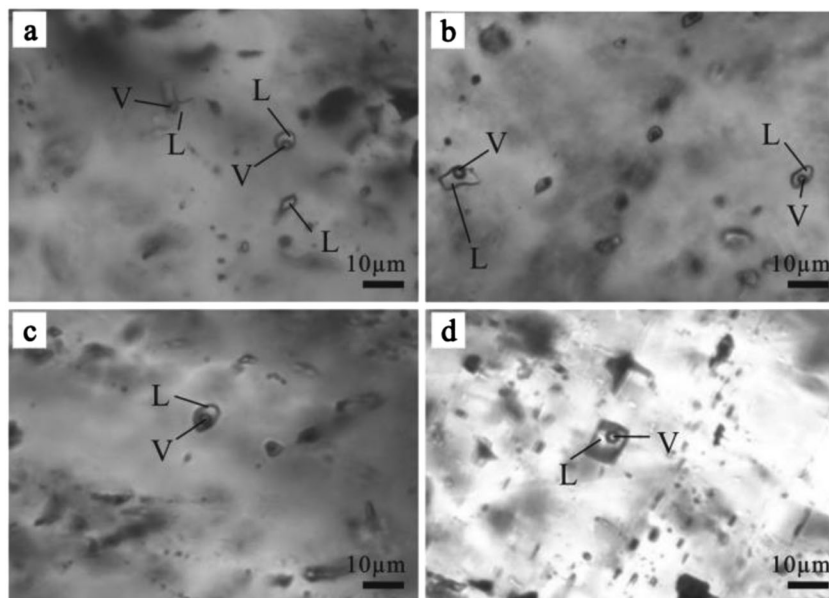


Fig. 4 Photomicrographs of fluid inclusion types in the Babaoshan and Hetaoqing ore deposits. a) Type B inclusions and a few type A inclusions in calcite. b) A series of type A inclusions occurring together in calcite. c) Type B inclusions in barite. d) Type B inclusions in barite.

Table 2 Summary of microthermometric data for fluid inclusions contained in ore minerals from mines in the Baiyangping area

| Mine | Mineral | T_h (°C) | T_{ice} (°C) | Salinity (wt.% NaCl eq.) | References |
|-------------|------------|------------|----------------|--------------------------|--------------------------|
| Baiyangping | Calcite | 122–238 | –7.6––1.1 | 1.9–11.2 | Zeng (2007) |
| | Sphalerite | 105–155 | –26.1––14.4 | 18.1–24.6 | Xue <i>et al.</i> (2010) |
| | Calcite | 117–282 | –18.2––1.1 | 1.9–21.1 | Xue <i>et al.</i> (2010) |
| Hetaoqing | Barite | 128–287 | –19.9––2.8 | 4.3–22.3 | This work |
| Babaoshan | Calcite | 107–185 | –25.4––2.3 | 3.9–24.4 | This work |

T_h , total homogenization temperature of inclusions; T_{ice} , freezing temperature.

Samples of sulfide (pyrite, tennantite, and chalcopyrite) and barite formed during the ore-forming stage were collected from underground mine workings at the Baiyangping, Babaoshan, and Hetaoqing ore deposits to study the noble gas isotopes. The coarse crystals of sulfide and barite were first crushed and then handpicked under a binocular microscope to a purity of > 99%. An all metal extraction line and mass spectrometer (GV 5400). The sensitivities of GV5400 for He and Ar were 3.9725×10^{-4} A/Torr (1 Torr = 1.33×10^2 Pa) and 1.1018×10^{-3} A/Torr, respectively, and the resolutions for High Mass Faraday and Multiplier were 228.1 and 628.3, respectively (Hu *et al.*, 2012). The gases from the fluid inclusions in sulfide and barite were measured at the noble gas mass spectrometry laboratory of the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang.

The helium and argon isotope compositions were analyzed by bulk extraction of fluids using the *invacuo*

crushing method. This method can reduce the effects from radiogenic isotopes produced *in situ* and from adsorbed atmospheric gases, overcoming problems due to the low blank. In addition, the relatively large volumes of fluid extracted, relative to laser extraction methods, allow for greater analytical precision. The volatile extraction and analytical procedures are similar to those of Burnard *et al.* (1997) and Stuart *et al.* (1994a, b, 1995). The samples were ultrasonically cleaned in acetone for 20 min before loading into the online *invacuo* crushing devices. Approximately 500 to 1000 mg of mineral grains 0.5 to 1.5 mm in size were loaded into a screw-type crusher. The samples were baked at a temperature of 120 to 150 °C with the ultra-high vacuum system for 24 h to remove adhered atmospheric contaminants. At the same time, the gas extraction system was kept under a high vacuum. The gases from fluid inclusions were released by sequentially crushing the samples in high-vacuum conditions (10^{-8} Torr), and then loading into the gas

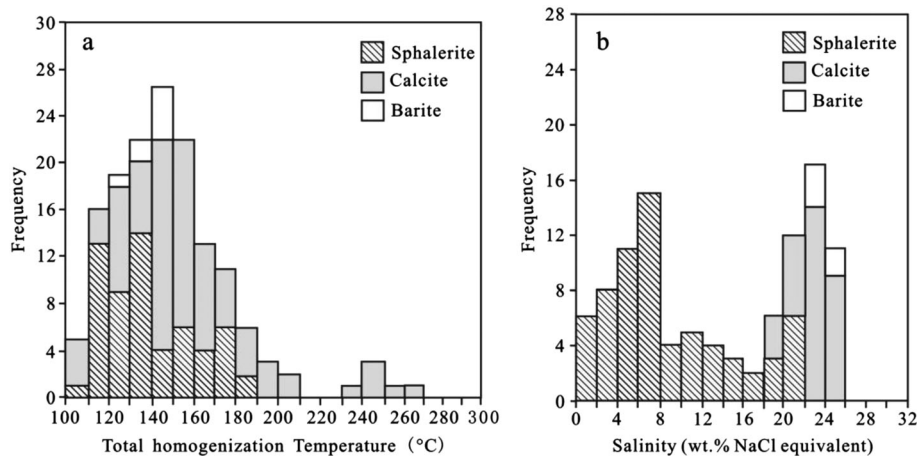


Fig. 5 Histograms of microthermometric data for fluid inclusions from Ag–Cu–Pb–Zn ore deposits in the Baiyangping area. a) Total homogenization temperature; b) Salinities.

purification systems in order to purify the released gases. Ar was sequestered in an activated charcoal cold finger at liquid N₂ temperature (−196 °C), then separated from the helium. He and Ar isotopes and abundances were analyzed separately on the GV 5400 mass spectrometer. Gas abundances were determined by peak-height comparison with known amounts of standard air from an air bottle. He and Ar abundances and isotopic ratios were calibrated against pipettes of 0.1 cm³ STP air (5.2 × 10^{−7} cm³ STP ⁴He and 9.3 × 10^{−4} cm³ STP ⁴⁰Ar). Procedural blanks were < 2 × 10^{−10} cm³ STP ⁴He and (2–4) × 10^{−10} cm³ STP ⁴⁰Ar and constituted < 1% of analyses. The blank is too low to affect calibration of the abundance measurement.

5.2. Results

5.2.1. C and O isotopes

The results of the carbon and oxygen isotopic analyses of calcite from the Baiyangping and Hetaoqing ore deposits of this study as well as the isotopic compositions determined by Liu *et al.* (2004) are presented in Table 3 and Figure 6. The $\delta^{13}\text{C}$ values range from −5.1 to 0.7‰ (average −2.7‰), and the $\delta^{18}\text{O}$ values range from 0.2‰ to 20.3‰ (average 12.2‰). These samples have a relatively narrow range of $\delta^{13}\text{C}$ values but a much wider range of $\delta^{18}\text{O}$ values.

5.2.2. Noble Gas isotopes

Analytical results for He and Ar isotopic compositions in gases from fluid inclusions in sulfides and barite

Table 3 Carbon and oxygen isotopic compositions of hydrothermal calcite from the Baiyangping and Hetaoqing deposits

| Sample no. | Mineral | $\delta^{13}\text{C}_{\text{PDB}}\text{‰}$ | $\delta^{18}\text{O}_{\text{SMOW}}\text{‰}$ |
|--|---------|--|---|
| Hetaoqing deposit | | | |
| HTQ10-17 | Calcite | -3.7 | 6.3 |
| HTQ10-26 | Calcite | -5.1 | 14.0 |
| HTQ10-35 | Calcite | -4.0 | 13.1 |
| Baiyangping deposit | | | |
| BYH10-07 | Calcite | -3.0 | 15.0 |
| BYH10-16 | Calcite | -2.1 | 17.3 |
| BYH10-17 | Calcite | -2.4 | 14.0 |
| BYH10-19 | Calcite | -2.3 | 17.3 |
| BYH10-46 | Calcite | -1.5 | 18.6 |
| BYH10-53 | Calcite | 0.7 | 19.7 |
| BYH10-70 | Calcite | -2.2 | 7.5 |
| Baiyangping deposit (After Liu <i>et al.</i> , 2004) | | | |
| HX-24 | Calcite | -1.9 | 0.9 |
| HX-25-1 | Calcite | -2.3 | 1.1 |
| HX-26 | Calcite | -1.1 | 1.3 |
| HX-27 | Calcite | -1.9 | 0.2 |
| HX-30 | Calcite | -0.5 | 0.2 |
| HX-48 | Calcite | -3.6 | 20.3 |
| H-78 | Calcite | -3.1 | 16.3 |
| H-79-2 | Calcite | -3.1 | 15.8 |
| H-85 | Calcite | -3.0 | 15.1 |
| H-84 | Calcite | -4.2 | 18.2 |

from the Hetaoqing, Babaoshan, and Baiyangping deposits are tabulated in Table 4 along with their isotopic ratios. The concentrations of ⁴⁰Ar range from 28.38 to 315.61 × 10^{−8} cm³ STP ⁴⁰Ar/g, and ⁴He concentrations are 1.91 to 258.75 × 10^{−8} cm³ STP ⁴He/g. The large variations in the noble gas isotopic concentrations measured may reflect differences in fluid inclusion

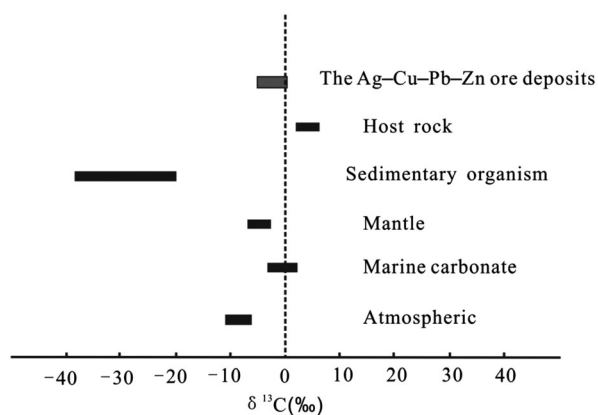


Fig. 6 Graph showing the range of carbon isotope compositions in calcite from the Baiyangping and Hetaoqing deposits compared with carbon isotopes in different geologic environments.

abundances in the samples. $^3\text{He}/^4\text{He}$ ratios range from 0.01 to 0.14 R/Ra (Ra represents the $^3\text{He}/^4\text{He}$ ratio of air, 1.39×10^{-6}), and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios range from 296.06 and 381.65. $^3\text{He}/^4\text{He}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of fluid inclusions from the Baiyangping deposit are 0.03 to 0.05 Ra and 298.00 to 299.65. $^3\text{He}/^4\text{He}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of fluid inclusions from the Babaoshan Ag-Cu deposit are 0.05 to 0.14 Ra and 299.88 to 307.52; $^3\text{He}/^4\text{He}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of fluid inclusions from the Hetaoqing Cu deposit are 0.01 to 0.10 Ra and 318.28 to 381.65. This shows that there are minor differences in the isotope ratios of He and Ar in the fluid inclusions in samples from the different deposits.

6. Discussion

6.1. Reliability and representativeness of the data and the effects of isotope fractionation

Samples of sulfide and barite analyzed in this study are well crystallized euhedral grains without any obvious subsequent deformation. Fluid inclusion studies of ore-bearing calcite and barite veins revealed that the trapped fluids were, at least in ore-bearing calcite and barite, predominantly primary. This suggests that the fluids extracted from the sulfides were probably related to hydrothermal mineralization. The sulfides we analyzed were well-formed euhedral grains collected from underground mines that had not been modified since they were formed. They were thus well sealed and provided a very good sample of the noble gases

originally present (Trull *et al.*, 1991; Baptiste & Fouquet, 1996). Fluid inclusions in these sulfides and barite can be very valuable in preserving information concerning the physical and chemical conditions of ore formation.

The effects of diffusion and fractionation on noble gas isotopes in fluid inclusions caused by the physical properties of the host minerals have concerned geochemists for many years. In general, physical diffusion of He isotopes occurs most easily (Wilkinson, 2001). Olivine and sulfides have good sealing ability, and among the sulfides, pyrite has the highest sealing ability and a very low diffusion coefficient (Trull *et al.*, 1991; Baptiste & Fouquet, 1996). Although some quantity of helium would be lost from the inclusions after the fluids were trapped in any mineral, the fractionation of helium isotopes is not significant during the loss process and the $^3\text{He}/^4\text{He}$ ratio remains unaffected (Ballentine & Burnard, 2002; Hu *et al.*, 2004). Therefore, when using $^3\text{He}/^4\text{He}$ ratios (as opposed to simple He abundance), we do not need to consider the effect of He loss. Argon can be well preserved in fluid inclusions in most minerals (Trull *et al.*, 1991). Moreover, research indicates that when using the *in vacuo* vacuum crushing method to extract noble gases from the samples, the crushing will not fractionate the isotopes and also will not cause radiogenic ^4He and ^{40}Ar to be released from the crystal lattices of host minerals (Stuart *et al.*, 1994b; Burnard *et al.*, 1999).

Zou *et al.* (2015) obtained mineralization ages of between 30 and 27 my for the Ag-Cu ore deposits in the Baiyangping area. In addition, with inclusion-trapped He (and Ar) unlikely to be extensively lost within ~ 100 my (Burnard *et al.*, 1999; Hu *et al.*, 2004). Therefore, the loss of He and Ar is relatively limited and cannot induce notable influence on the He and Ar isotopic compositions (Stuart *et al.*, 1994a). In addition, trace element analyses showed the average Li, U, and Th concentrations of the chalcopyrite were 0.10, 0.01 and $0.05 \mu\text{g} \cdot \text{g}^{-1}$, respectively; the average Li, U and Th concentrations of the tennantite were 1.43, 0.09 and $0.10 \mu\text{g} \cdot \text{g}^{-1}$, respectively (unpublished data). These analytical results mean that the contents of U, Th, K, and Li are very low and these elements are not able to produce measurable quantities of radiogenic daughter products in the host minerals. Therefore *in situ* ^4He production is essentially zero and can have almost no influence on the isotopic compositions (Craig & Lupton, 1976; Kendrick *et al.*, 2001).

The atmospheric He contribution can be determined from the $F^4\text{He}$ values, $F^4\text{He}$ being the $^4\text{He}/^{36}\text{Ar}$ ratio of the sample relative to the same isotopic ratio in the

Table 4 He and Ar isotopic compositions of inclusion-trapped fluid in sulfide and barite from the Baiyangping, Hetaoqing, and Babaoshan Ag–Cu polymetallic ore deposits

| Sample No. | Minerals | Crushing number | Weight [†] (g) | $^4\text{He}^{\dagger} (10^{-8} \text{ cm}^3 \text{ stp})$ | $^{40}\text{Ar}^{\dagger} (10^{-8} \text{ cm}^3 \text{ stp})$ | R(Ra) | $^{40}\text{Ar}/^{36}\text{Ar}$ | $^{40}\text{Ar}^*/^{4}\text{He}$ | $^4\text{He} (10^{-8} \text{ cm}^3 \text{ stp g}^{-1})$ | $^{40}\text{Ar} (10^{-8} \text{ cm}^3 \text{ stp g}^{-1})$ | F ⁴ He |
|------------|--------------|--------------------|-------------------------|--|---|---------------|---------------------------------|----------------------------------|---|--|-------------------|
| HTQ10-1 | pyrite | 1 | 107.33 ± 0.092 | 15.75 ± 0.002 | 0.01 ± 0.000 | 370.56 ± 2.93 | 0.030 | | | | 15260 |
| | | 2 | 30.74 ± 0.012 | n | 0.01 ± 0.001 | | | | | | |
| | | Total ^c | 0.5336 | 138.07 ± 0.093 | 15.75 ± 0.002 | 0.01 ± 0.001 | 370.56 ± 5.79 | 0.023 | 258.75 | 29.51 | 19629 |
| HTQ10-5 | chalcopyrite | 1 | 0.3086 | 2.70 ± 0.002 | 9.60 ± 0.002 | 0.01 ± 0.001 | 334.49 ± 5.79 | 0.414 | 8.75 | 31.10 | 569 |
| HTQ10-6a | barite | 1 | 0.2218 | 4.56 ± 0.004 | 7.78 ± 0.002 | 0.11 ± 0.006 | 339.53 ± 7.18 | 0.221 | 20.58 | 35.06 | 1204 |
| HTQ10-6b | tennantite | 1 | 7.78 ± 0.003 | 22.8 ± 0.009 | 0.08 ± 0.004 | 318.28 ± 2.67 | 0.210 | | | | 656 |
| | | 2 | 2.90 ± 0.002 | 6.32 ± 0.004 | 0.10 ± 0.009 | 381.65 ± 9.73 | 0.491 | | | | 1061 |
| | | Total ^c | 0.3437 | 10.68 ± 0.004 | 29.1 ± 0.010 | 0.08 ± 0.010 | 330.17 ± 4.52 | 0.286 | 31.09 | 84.72 | 732 |
| BBS10-1 | tennantite | 1 | 6.55 ± 0.002 | 35.7 ± 0.004 | 0.14 ± 0.005 | 303.25 ± 1.22 | 0.139 | | | | 336 |
| | | 2 | 3.63 ± 0.003 | 15.1 ± 0.003 | 0.14 ± 0.007 | 307.52 ± 3.66 | 0.163 | | | | 446 |
| | | Total ^c | 0.4825 | 10.17 ± 0.003 | 50.8 ± 0.005 | 0.14 ± 0.009 | 304.50 ± 1.85 | 0.148 | 21.08 | 105.38 | 368 |
| BBS11-6 | pyrite | 1 | 0.3045 | 0.78 ± 0.012 | 8.70 ± 0.015 | 0.05 ± 0.010 | 302.12 ± 13.71 | 0.245 | 2.55 | 28.58 | 163 |
| BBS11-17 | pyrite | 1 | 0.2065 | 0.39 ± 0.006 | 5.86 ± 0.034 | 0.10 ± 0.015 | 299.88 ± 19.55 | 0.217 | 1.91 | 28.38 | 122 |
| BYP11-5 | tennantite | 1 | 0.1813 | 4.03 ± 0.062 | 57.22 ± 0.335 | 0.05 ± 0.005 | 296.06 ± 2.92 | 0.027 | 22.22 | 315.61 | 126 |
| BYP11-9 | tennantite | 1 | 0.3864 | 4.98 ± 0.076 | 29.81 ± 0.175 | 0.04 ± 0.003 | 299.65 ± 4.41 | 0.083 | 12.90 | 77.14 | 303 |
| BYP11-15-1 | tennantite | 1 | 0.1584 | 3.37 ± 0.052 | 22.23 ± 0.130 | 0.03 ± 0.003 | 298.20 ± 5.32 | 0.060 | 21.30 | 140.32 | 273 |
| | | 1 | 0.2998 | 4.84 ± 0.074 | 47.78 ± 0.280 | 0.04 ± 0.004 | 298.00 ± 326 | 0.083 | 16.14 | 159.37 | 182 |

[†]Sample weights are the <100 μm fraction after crushing. [‡]Errors quoted are at the 1σ confidence level; totals are the sums of all crushes. n, under determination limit. Ra, ³He/⁴He ratio of air; ⁴⁰Ar* refers to the excess Ar.

atmosphere (Kendrick *et al.*, 2001; Landis & Hofstra, 2012). The samples we studied have $F^4\text{He}$ values ranging from 122 to 19,629 (Table 4), obviously much higher than one. This means that the contribution of atmospheric He to the fluids that formed these Ag–Cu deposits was negligible.

It should be mentioned that post-crystallization production of ^3He within a mineral can take place by the interaction of cosmic rays with certain nuclei. However, this process is limited to depth of 1.5 m from the Earth's surface and the samples we analyzed were all collected from underground mine workings. The production of cosmogenic ^3He can be ignored (Burnard *et al.*, 1999).

Because the ore deposits are relatively young (<30 my), the *in situ* contribution of ^4He by the ore mineral themselves was essentially zero and in addition, we believe that the secondary processes discussed have not changed the $^3\text{He}/^4\text{He}$ and $^{36}\text{Ar}/^{40}\text{Ar}$ ratios. The He and Ar isotopic values measured from the fluid inclusions in sulfides and barite roughly represent the initial He and Ar isotopic compositions of the primary ore-forming fluids.

6.2. Sources of ore fluids

The ore-forming fluids responsible for these Ag–Cu polymetallic deposits left only aqueous inclusions behind. There are essentially no CO_2 -bearing inclusions (Xu *et al.*, 2004; Xue *et al.*, 2010). The ore-forming fluids of the Hetaoqing, Babaoshan and Baiyangping deposits were low temperature and moderate to mid-high salinity fluids, fluids similar to those from Mississippi Valley-type (MVT) and sedimentary exhalative type (SEDEX) deposits (He *et al.*, 2009; Xue *et al.*, 2010). He *et al.* (2009) proposed that regional basinal brines were widely developed in the Lanping basin and these brines were relatively low temperature and high salinity. Therefore, we suggest these basin brines as the main source for the ore-forming fluids responsible for the Ag–Cu mineralization. This suggestion is supported by the hydrogen and oxygen isotopic compositions of these Ag–Cu deposits (Gong *et al.*, 2000; Wang *et al.*, 2011) and the isotopic compositions also indicated that the water in the ore-forming fluids were mainly of meteoric origin. Compared to typical basinal brines, some fluid inclusions in the deposits yield relatively low salinities (<10 wt.% NaCl equivalent; Fig. 7). This could result from fluid mixing between meteoric water and basin brines.

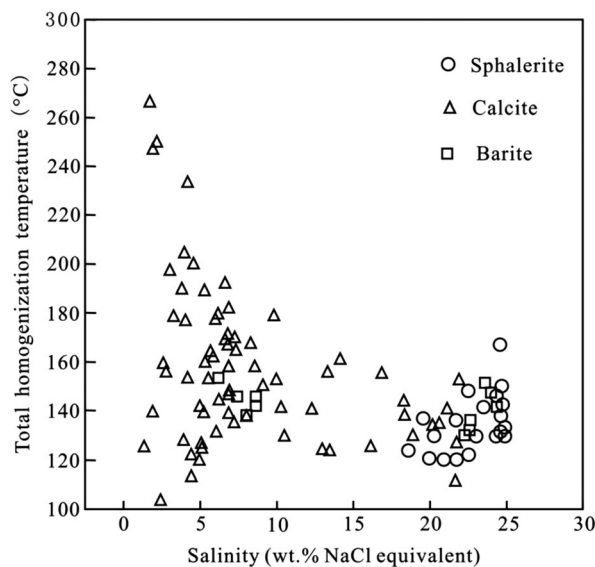


Fig. 7 Plot of homogenization temperature (T_h) vs. salinity for fluid inclusions from Ag–Cu–Pb–Zn ore deposits in the Baiyangping area. Basinal brine values after Xue *et al.* (2006).

Carbon and oxygen isotope compositions in these polymetallic deposits generally have a relatively narrow range of $\delta^{13}\text{C}$ values but a much wider range of $\delta^{18}\text{O}$ values (Table 3). In general, the $\delta^{13}\text{C}$ values of carbonates should be equal to, or higher than, that of the associated reducing ore-forming fluids (Ohmoto, 1972). The $\delta^{13}\text{C}$ values we measured range from -5.1 to 0.7‰ (average of -2.7‰), values between those associated with mantle and marine sources (Table 3; Fig. 6). This indicates the involvement of marine carbonates with mantle/magmatic fluids within the basin as a source of carbon. The presences of hydrocarbon-rich inclusions in gangue minerals from other Pb–Zn–Cu deposit in the Lanping basin (like the Jinding deposit; Xue *et al.*, 2002, 2007) suggest that the source of the ore-forming fluid was probably basinal brines.

The noble gases contained in inclusion-trapped fluid are likely to be a combination of three potential noble gas sources, each with distinct noble gas elemental and isotopic compositions. These sources are: (i) Air-saturated water (ASW), such as meteoric fluids or marine water ($^3\text{He}/^4\text{He} = 1.39 \times 10^{-6} \equiv 1 \text{ R/Ra}$ and $^{40}\text{Ar}/^{36}\text{Ar} = 295.5$). (ii) Mantle noble gases ($^3\text{He}/^4\text{He}$ ratios of $6-9 \text{ R/Ra}$ and $^{40}\text{Ar}/^{36}\text{Ar} > 40,000$, (Burnard *et al.*, 1999)). (iii) Noble gases produced in the crust ($^3\text{He}/^4\text{He}$ ratios $\leq 0.1 \text{ R/Ra}$ (Andrews, 1985) and $^{40}\text{Ar}/^{36}\text{Ar} \geq 45,000$ (Fontes *et al.*, 1991)). Note that the

difference in $^3\text{He}/^4\text{He}$ ratios between the crust and mantle gases is approximately three orders of magnitude. Therefore, even if the crustal fluid has been mixed with a trace amount of mantle-derived fluid, these can be distinguished easily from the helium isotopes.

As shown in Table 4, $^3\text{He}/^4\text{He}$ ratios in different minerals from the Baiyangping, Babaoshan, and Hetaoqing hydrothermal fluids are relatively uniform, from 0.01–0.14 Ra. These values are all significantly lower than mantle values, but quite consistent with typical crustal values (0.01–0.05). The relatively low R/Ra values of all the deposits in this study indicate that crustal fluids were important in the formation of the Ag–Cu polymetallic deposits of the Baiyangping area. The measured $^{40}\text{Ar}/^{36}\text{Ar}$ values range from 298.0 to 381.7 (mean 322.8), similar to the atmospheric value of 295.5. This indicates that the ore-forming fluid was some form of air-saturated water, possibly meteoric water or connate water.

In Figure 8, most of the data points are scattered between the ASW and the crustal-derived field and all points have $^3\text{He}/^4\text{He}$ ratios far from the mantle-derived field. Similarly, from Figure 9, we can see that the data points for the Baiyangping, Hetaoqing, and Babaoshan deposits are all close to the field of the crustal fluid component in $^{40}\text{Ar}/^{36}\text{Ar}$ space. The isotopic ratios of the fluids we measured clearly have crustal affinities, indicating that the ore fluids were derived predominantly from the crust without any significant interfusion of mantle fluids.

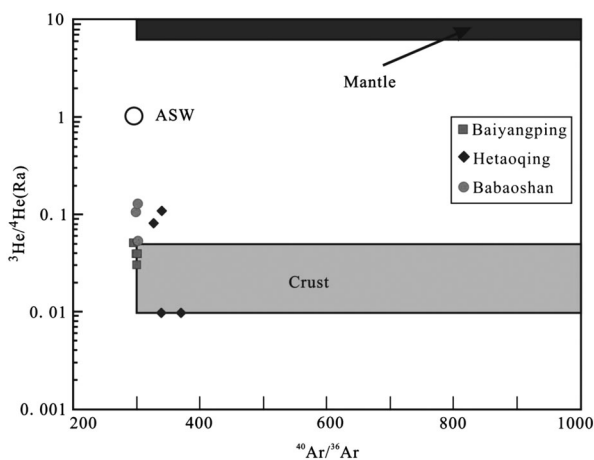


Fig. 8 Plot of $^3\text{He}/^4\text{He}$ (Ra) vs. $^{40}\text{Ar}/^{36}\text{Ar}$ ratios in gases from fluid inclusions from the Ag–Cu polymetallic deposits in the Baiyangping area.

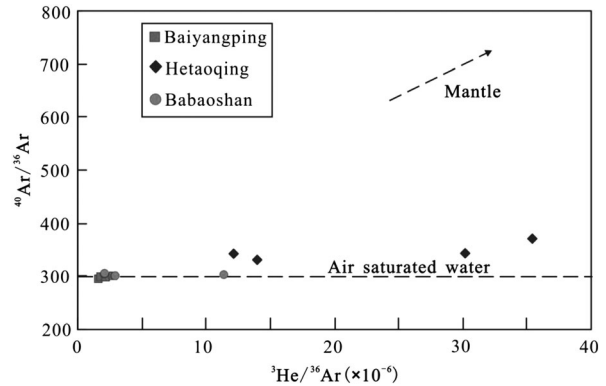


Fig. 9 Plot of $^3\text{He}/^{36}\text{Ar}$ vs. $^{40}\text{Ar}/^{36}\text{Ar}$ for gases from fluid inclusions from the Ag–Cu polymetallic deposits in the Baiyangping area.

The $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of all the samples are slightly higher than that of the atmosphere (295.5), indicating that there is some excess radiogenic ^{40}Ar in the samples (excess radiogenic ^{40}Ar , that is non-atmospheric ^{40}Ar , is denoted as $^{40}\text{Ar}^*$). The proportion of $^{40}\text{Ar}^*$ can be estimated by the measured $^{40}\text{Ar}/^{36}\text{Ar}$ values according to the following equation (Kendrick *et al.*, 2001):

$$^{40}\text{Ar}^* \% = \frac{(^{40}\text{Ar})_{\text{sample}} - 295.5}{(^{40}\text{Ar}/^{36}\text{Ar})_{\text{sample}}} \times 100.$$

The estimated concentrations of $^{40}\text{Ar}^*$ range from 0.2 to 20.4%, and the proportion of air-derived ^{40}Ar averages 94.1%. This indicates that atmospheric Ar was dominant in the fluids that formed these deposits and that the radiogenic ^{40}Ar present was derived from crustal rocks.

The noble gas data from the Baiyangping, Hetaoqing, and Babaoshan deposits place important new constraints on the conditions of ore formation both for these three deposits and, by inference, for deposits throughout much of the Baiyangping area. As stated above, the ore-forming fluids of the Baiyangping area were derived predominantly from the crust. This conclusion is also supported by the following: (i) Our data indicate that the ore-forming fluids were related to hot basin brines; (ii) Hydrogen and oxygen isotope data suggest that the ore-forming fluids mainly derive from meteoric water (He *et al.*, 2009); (iii) sulfur and lead isotope data (Xu *et al.*, 2004; Xue *et al.*, 2007; Zou *et al.*, 2012) suggest that the

metallogenic materials deposited in the Baiyangping area mainly come from the crustal basement rock and the strata within the basin with no contribution from the mantle.

7. Conclusions

This study undertook a comprehensive analyses of the geology, fluid inclusions, and C, H, O, He, and Ar isotopic geochemistry of the Ag–Cu polymetallic ore deposits in the Baiyangping area of the Lanping basin.

The $^3\text{He}/^4\text{He}$ ratios in all of the fluid inclusion gases studied range from 0.01 to 0.14 R/Ra, all significantly lower than the mantle values but consistent with typical crustal values (0.01–0.05 R/Ra). The measured $^{40}\text{Ar}/^{36}\text{Ar}$ values range from 298.00 to 381.65, slightly greater than the atmospheric value of 295.5. This indicates the presence of a significant proportion of radiogenic ^{40}Ar of mantle or crustal origin.

We suggest that the ore-forming fluids were mainly derived from crustal fluid. It may have mixed with small amounts of air-saturated water, but there was no considerable involvement of mantle-derived fluid.

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