



# Geological, rare earth elemental and isotopic constraints on the origin of the Banbanqiao Zn–Pb deposit, southwest China



Bo Li <sup>a,b,c</sup>, Jia-Xi Zhou <sup>a,b,\*</sup>, Zhi-Long Huang <sup>a</sup>, Zai-Fei Yan <sup>a</sup>, Guang-Ping Bao <sup>a</sup>, Hai-Rui Sun <sup>a</sup>

<sup>a</sup> State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China

<sup>b</sup> Department of Land Resources Engineering, Kunming University of Science and Technology, Kunming 650093, China

<sup>c</sup> Kunming Prospecting Design Institute of China Nonferrous Metals Industry, Yunnan Copper Industry (Group) Co. Ltd., Kunming 650051, China

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## ABSTRACT

The newly discovered Banbanqiao Zn–Pb deposit in the southeastern part of the Sichuan–Yunnan–Guizhou (SYG) Pb–Zn metallogenic province is located on the western Yangtze Block, southwest China. Ore bodies of the Banbanqiao deposit are stratiform type, host in dolomitic limestone and dolostone of the Lower Carboniferous Dapu Formation and occur within the NNE-trending Banbanqiao anticline. More than 1.5 million tonnes (Mt) Zn–Pb ores at grades of 0.26–10.32 wt.% Pb and 0.81–28.8 wt.% Zn have been controlled until now.  $\delta^{13}\text{C}_{\text{PDB}}$  and  $\delta^{18}\text{O}_{\text{SMOW}}$  values of calcite separates range from  $-2.8\text{‰}$  to  $-0.7\text{‰}$  (average  $-1.1\text{‰}$ ) and  $+14.1\text{‰}$  to  $+17.0\text{‰}$  (average  $+15.5\text{‰}$ ), respectively. The  $\delta^{13}\text{C}_{\text{PDB}}$  values are similar to those of marine carbonate rocks, but higher than those of mantle and significantly different from those of sedimentary organic matter. However, the  $\delta^{18}\text{O}_{\text{SMOW}}$  values are among those of mantle, marine carbonate rocks and sedimentary organic matter.  $\delta^{34}\text{S}_{\text{CDT}}$  values of sulfide separates range from  $+3.2\text{‰}$  to  $+9.9\text{‰}$  (average  $+6.5\text{‰}$ ), unlike mantle-derived sulfur ( $0 \pm 3\text{‰}$ ), whilst lower than evaporites ( $+22\text{‰}$  to  $+28\text{‰}$ ) within host strata.  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  values of country shale and dolostone whole-rock samples are 18.47, 15.66 and 38.70, and 18.44–18.60, 15.66–15.85 and 38.70–39.14, respectively. Sulfide separates have  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  values ranging from 18.03 to 18.73, 15.65 to 15.78 and 38.15 to 39.14, respectively. These Pb isotopic data indicate a clearly crustal source of Pb in the plot of  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$ . Total REE ( $\Sigma\text{REE}$ ) contents of country shale and dolostone whole-rock samples are 2.63 ppm and 0.72–86.2 ppm with  $\delta\text{Eu}$  values are 2.79 and 0.34–0.70, respectively. Pyrite, sphalerite, galena and calcite samples have  $\Sigma\text{REE}$  contents of 5.3–36.4 ppm, 0.29–3.39 ppm, 0.52 ppm and 22.0–41.1 ppm, respectively, and  $\delta\text{Eu}$  values of 0.64–0.86, 0.94–2.86, 0.32 and 0.21–0.45, respectively. These rare earth elemental and isotopic data suggest that the REE, C and S in the ore-forming fluids of the Banbanqiao deposit were mainly originated from the carbonate host rocks, while the Pb and O were primarily derived from radiogenic Pb- and  $^{18}\text{O}$ -depleted sources, which are most likely to be the underlying Proterozoic basement rocks. Studies on the geology, rare earth elements and isotope geochemistry indicate that the Banbanqiao deposit is a carbonate-hosted, stratiform, anticline-controlled, epigenetic and high grade Zn–Pb deposit formed by elemental compositions of mixed origin, and is a typical SYG-type deposit in the western Yangtze Block, southwest China.

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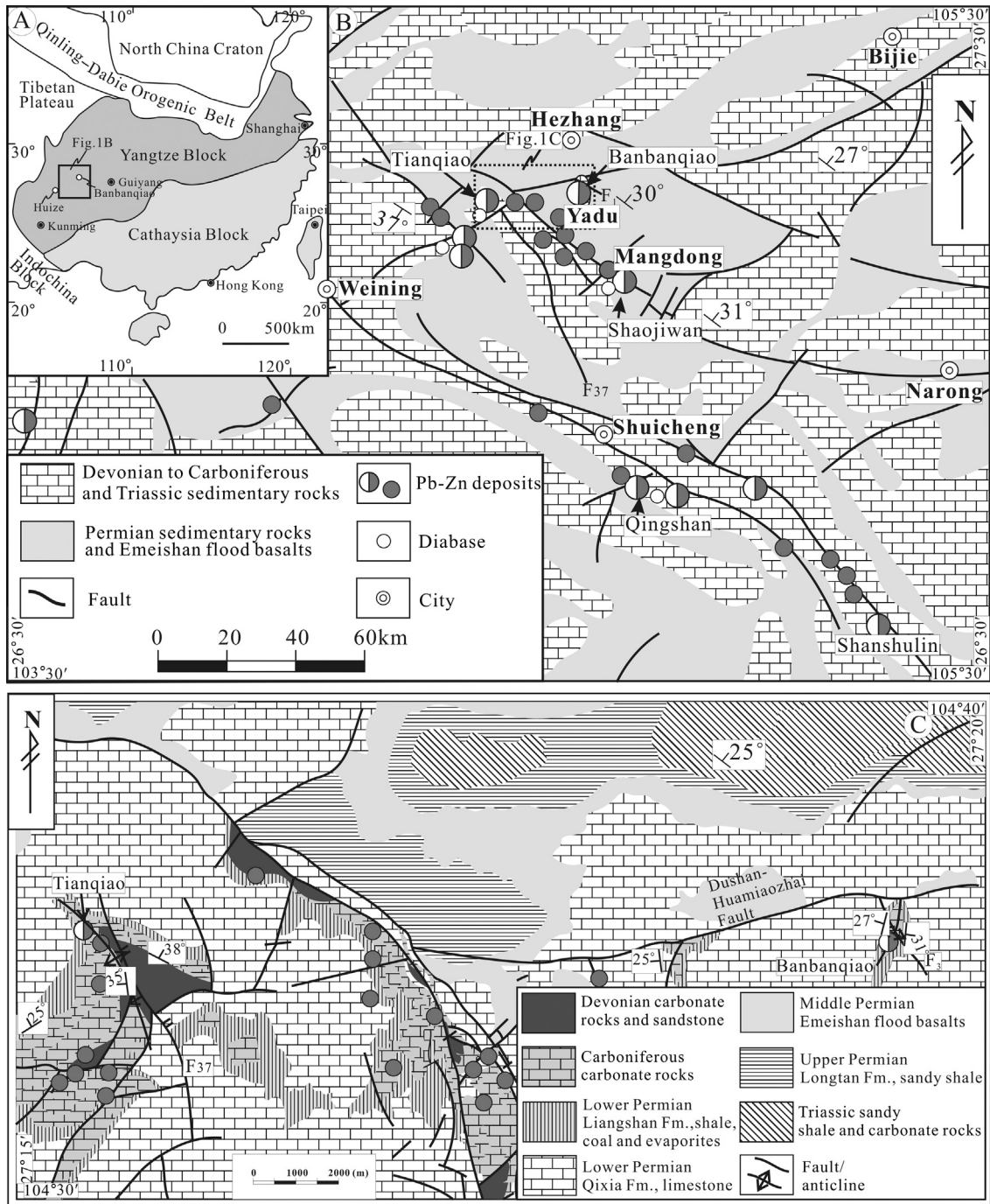
## 1. Introduction

The Sichuan–Yunnan–Guizhou (SYG) Pb–Zn metallogenic province contains 408 known Pb–Zn deposits with total more than 200 million tons Pb–Zn ores at average grade of 5 wt.% Pb and 10 wt.% Zn (Liu and Lin, 1999; Zhou et al., 2013a,b). Tectonically, this province is located on the western Yangtze Block, southwest

\* Corresponding author at: State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China.

E-mail address: [zhoujiaxi@vip.gyig.ac.cn](mailto:zhoujiaxi@vip.gyig.ac.cn) (J.-X. Zhou).

China (Fig. 1A; Zheng and Wang, 1991; Cromie et al., 1996; Zhou et al., 2001; Han et al., 2007; Huang et al., 2010), where multiple orogenic events occurred (e.g., Zaw et al., 2007; Hu and Zhou, 2012; Pirajno, 2013). Studies have demonstrated that the Pb–Zn deposits in the SYG province have some similar features, including: (i) host in carbonate rocks of Sinian (Neoproterozoic Ediacaran) to Permian, (ii) occur within thrust fault and/or fold structures, (iii) high grade of Pb + Zn ( $>15$  wt.%), (iv) spatially associated with the Permian Emeishan flood basalts (ca.  $\sim 260$  Ma), and (v) ore bodies mainly formed at 222–192 Ma, much younger than the Emeishan basalts (e.g., Zheng and Wang, 1991; Liu and Lin, 1999;



**Fig. 1.** (A) Tectonic setting map of South China. (B) Geological map of the southeastern Sichuan–Yunnan–Guizhou (SYG) Pb–Zn metallogenic province (after Zhou et al., 2013a). (C) Geological detailed map of the Tianqiao to Banbanqiao Pb–Zn ore fields (after Zhou et al., 2014a).

Deng et al., 2000; Hu and Zhou, 2012; Zhou et al., 2002a, 2013c,d, 2014a,b, 2015; Zhang et al., 2015). However, the sources of ore-forming elements and ore genesis of these Pb–Zn deposits in the SYG province have long been a matter of debate, although many research papers have published. For example, Chen (1986) considered that the elements were sourced from the carbonate host rocks, whereas Zhou et al. (2001) thought that the elements were derived from the Precambrian igneous rocks. Recently, Zhou et al. (2013a, 2014a, 2015) suggested that the Paleozoic ore-hosting carbonate rocks, Proterozoic basement rocks and Permian Emeishan flood basalts together provide the ore-forming elements for these deposits in the SYG province. On the other hand, although the most

of these Pb–Zn deposits in the SYG province are clearly epigenetic, different opinions have been proposed on the ore genesis of them. These hypotheses include: (i) the Mississippi Valley-type (MVT) deposit related to basin brine (Zheng and Wang, 1991; Zhou et al., 2001; Wu et al., 2013; Zhang et al., 2015), (ii) the Permian Emeishan mantle plume-related deposit (Xie, 1963; Huang et al., 2003, 2010; Xu et al., 2014), and (iii) the unique SYG-type deposit that are different from the typical MVT deposit (Bai et al., 2013; Zhou et al., 2013a–c, 2014b). Recently, studies of Cd, Ge and Zn isotopes (Zhu et al., 2013; Zhou et al., 2014a,b; Meng et al., 2015), and *in situ* trace elements of sphalerite (Ye et al., 2011) have indicated that the ore genesis of these Pb–Zn deposits in the SYG province is

complex and cannot easily be determined. Therefore, more case studies to help us understand the giant Pb–Zn mineralization in the SYG province.

The Banbanqiao deposit, a newly discovered Zn–Pb deposit, is located in the southeastern part of the SYG province (Zhou et al., 2014a). This deposit is not controlled by NW-trending regional ore-controlling structures (e.g. Yadu–Mangdong and Weining–Shuicheng) in northwest Guizhou province (Fig. 1A), but occurs within NNE-trending Banbanqiao anticline (Fig. 1B). We have reported some Zn–S and Pb isotopic data of the Banbanqiao deposit in previous study (Zhou et al., 2014a) and found that it has lower S and Pb isotopic values than those of the deposits occurred along the NW-trending regional faults (such as Shanshulin, Qingshan, Shaojiwan and Tianqiao) (Zhou et al., 2013a–c, 2014b), maybe represent different formation mechanism or ore-forming condition. Additionally, with the deepening of the exploration, we find that the Banbanqiao deposit has some other unique geological characteristics, including (i) hosts in carbonate rocks of Lower Carboniferous Dapu Formation, (ii) occurs as stratiform type within axis of Banbanqiao brachy anticline, (iii) the disseminated texture predominates, (iv) high Zn/(Zn + Pb) ratios (0.8–0.9), (v) simple mineralogy and weak wall rock alteration, and (vi) Lower Permian Liangshan Formation shale circle around (Figs. 1B and 2).

REE and C–O–S–Pb isotopes are powerful tools for tracing the source of the ore-forming elements (e.g., Zheng and Wang, 1991; Carr et al., 1995; Huston et al., 1995; Ohmoto and Goldhaber, 1997; Badrzadeh et al., 2011; Zhou et al., 2001, 2011, 2014a,b; Palinkaš et al., 2013; Pass et al., 2014). C–O–S and Pb isotopes have been widely used in previous studies for these Pb–Zn deposits in the SYG province (e.g., Zhou et al., 2001; Huang et al., 2003; Han et al., 2007; Li et al., 2007a; Zhou et al., 2013a, 2014a, 2015), whereas the studies of REE are limited (Huang et al., 2010; Zhou et al., 2011). Therefore, the Banbanqiao Zn–Pb deposit is used as case study in this paper, by analyzing REE contents of sulfide and calcite separates, and country shale and dolostone whole-rock samples, together with new C–O isotopic data and additional S–Pb isotopic data, the authors discuss the origin of the ore-forming elements, and propose a model that can account for the formation of Zn–Pb sulfide ores and provide new information for understanding the cause of a huge amount of base metals enriched in the SYG province.

## 2. Geological background

### 2.1. Regional geology

The Yangtze Block is composed of Archean to Proterozoic basement and Paleozoic to Mesozoic cover sequence (Liu and Lin, 1999; Zhou et al., 2002b). In the northern part of the Yangtze Block, sparse metamorphic rocks represent crystalline basement (Qiu et al., 2000; Hu and Zhou, 2012), whereas the Meso- to Neo-Proterozoic volcanic-sedimentary sequence represents folded basement in the western part (Yan et al., 2003; Sun et al., 2009; Zhao et al., 2010). The cover sequence of the western Yangtze Block consists mainly of Paleozoic and lower Mesozoic shallow marine sedimentary rocks, and Jurassic to Cenozoic terrestrial sediments (Liu and Lin, 1999; Yan et al., 2003; Huang et al., 2010). In the western Yangtze Block, the Permian mantle plume-derived Emeishan large igneous province (ca. ~260 Ma) covering an area of 250,000 km<sup>2</sup> (e.g., Chung and Jahn, 1995; Zhou et al., 2002b). This igneous province is dominantly composed of Emeishan flood basalts (Fig. 1B and C). During late Permian to early Jurassic, the western Yangtze Block collided with the Yidun arc resulting in the closure of the Paleo-Tethys Ocean. This event is known as the Indosinian (257–205 Ma) Orogeny (e.g., Han et al., 2007; Reid et al., 2007; Zhou et al., 2013a,d), and main thrust faults and folds

in the western Yangtze Block related to it were affected by the later Yanshanian (205–65 Ma) and Himalayan (65–0 Ma) Orogeny (Zaw et al., 2007; Hu and Zhou, 2012; Pirajno, 2013).

More than 400 Pb–Zn deposits hosted in Neo-Proterozoic to Lower Permian carbonate rocks have been found in the western Yangtze Block (Liu and Lin, 1999). These deposits distribute in a large triangular area of 170,000 km<sup>2</sup> in SW Sichuan, NE Yunnan and NW Guizhou provinces (Zhou et al., 2013a; Xu et al., 2014; Zhang et al., 2015). This triangular area forms the famous SYG Pb–Zn metallogenic province (e.g., Liu and Lin, 1999; Zhou et al., 2001; Han et al., 2007; Huang et al., 2010; Zhou et al., 2013a, 2014a). Among these deposits, the Huize world-class Zn–Pb–Ge deposit (Fig. 1A) contains more than 5 Mt Zn–Pb metal reserves (Han et al., 2007; Zhou et al., 2013a). NS- and NE-trending faults are well developed in the western part of the SYG province (Liu and Lin, 1999; Han et al., 2007; Zhou et al., 2015), whereas NW-trending faults are dominant in the eastern part (Fig. 1B; Zhou et al., 2013a). It is obvious that these faults strictly control the distribution of Pb–Zn deposit in the SYG province (Fig. 1B and C; Han et al., 2007; Zhou et al., 2013b, 2014b, 2015; Zhang et al., 2015). Gypsum-bearing evaporites are widespread in the Cambrian to Triassic sedimentary rocks (Liu and Lin, 1999; Han et al., 2007) and are very important sulfur sources for the Pb–Zn deposits in the SYG province. The southeastern part of the SYG province, where the Banbanqiao deposit situated, has no Proterozoic basement rocks exposure and the cover sequence includes Devonian to Triassic sedimentary rocks (Fig. 1B) and the Permian Emeishan flood basalts (Fig. 1C). More than 100 Pb–Zn deposits have been found in this region, which hosted in dolomitic limestone and dolostone of Devonian to Lower Permian, and occurred along the main NW- and NE-striking structures (Fig. 1B and C). Most of the typical Pb–Zn deposits (such as Shanshulin, Qingshan, Shaojiwan and Tianqiao) in this region related to the NW-trending thrust faults and fold structures (Fig. 1B; Zhou et al., 2013e), whereas the newly found Banbanqiao Zn–Pb deposit situated in the NNE-trending fold structure (Figs. 1C and 2; Zhou et al., 2014a).

Geochronological studies in the SYG province have reported the calcite Sm–Nd isotopic ages of 222 ± 14 Ma (Li et al., 2007b) and 196 ± 13 Ma (Zhou et al., 2013d) for the Huize and Maozu deposits, respectively, and fluorite Sm–Nd age of 201.1 ± 2.9 Ma (Mao et al., 2012; Zhang et al., 2015) for the Jinshachang deposit. Sphalerite Rb–Sr ages for the Paoma, Tianqiao, Jinshachang and Lehong deposits are 200.1 ± 4.0 Ma (Lin et al., 2010), 191.9 ± 6.9 Ma (Zhou et al., 2013a), 206.8 ± 3.7 Ma (Zhou et al., 2015) and 200.9 ± 2.3 Ma (Mao et al., 2012). Thus, these typical Pb–Zn deposits in the SYG province formed at 222–192 Ma (Zhou et al., 2015).

### 2.2. Geology of the Banbanqiao ore deposit

#### 2.2.1. Stratigraphy and lithology

In the Banbanqiao deposit area, the degree of geological work is relatively low in the past, with the deepening of the exploration, the strata were reclassified (Fig. 2). The Lower Carboniferous Dapu Formation was divided out from the previous decided Upper Carboniferous Huanglong–Maping Formation (Zhou et al., 2014a). Therefore, the exposed rocks include Lower Carboniferous Dapu Formation dolostone and dolomitic limestone, Upper Carboniferous Huanglong Formation dolostone and limestone. The Zn–Pb ore bodies of the Banbanqiao deposit are hosted by the dolomitic limestone and dolostone of the Lower Carboniferous Dapu Formation (Figs. 2 and 3). Overlying Carboniferous rocks are shale and coal of the Lower Permian Liangshan Formation, and limestone of Lower Permian Qixia Formation, all of which are overlain by the Middle Permian Emeishan basalts. Organic matter is widely distributed in the Lower Permian Liangshan Formation shale and coal.

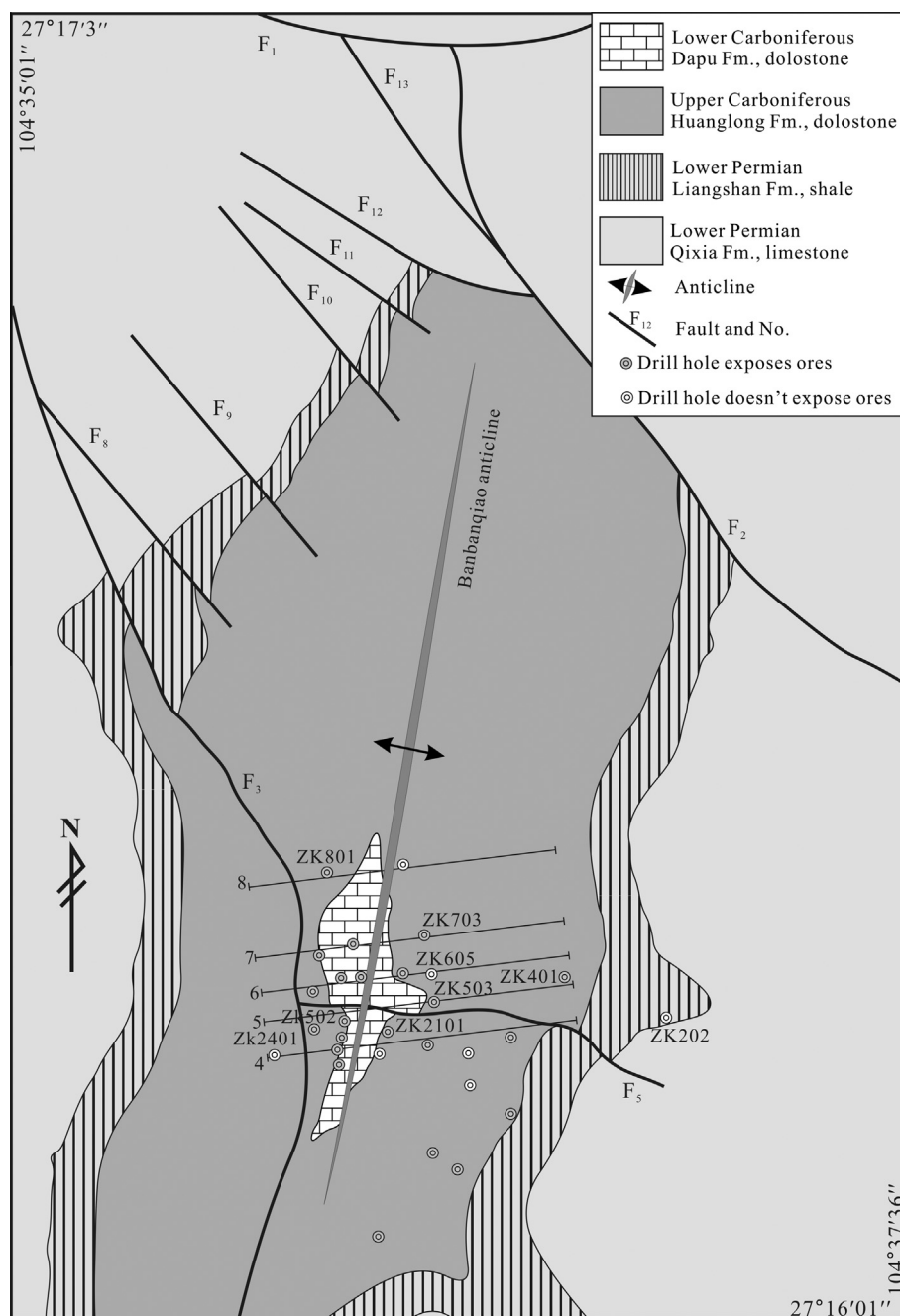


Fig. 2. Geological map of the Banbanqiao Zn–Pb deposit (after Zhou et al., 2014a).

### 2.2.2. Structure

Fault and fold structures in the Banbanqiao Zn–Pb deposit area are developed, including EW-trending Dushan–Huamianzhai thrust fault ( $F_1$ ), series of NW-trending normal faults and NNE-trending Banbanqiao anticline (Figs. 1C, 2, and 3). The Dushan–Huamianzhai thrust fault ( $F_1$ ) with dip angles between  $40^\circ$  and  $70^\circ$  is a regional structure that controls the distribution of Pb–Zn deposits in the studied area (Fig. 1B and C). In the Banbanqiao district, the NW-trending normal fault ( $F_3$ ) has dip angles between  $45^\circ$  and  $85^\circ$ , and controls the occurrence of Zn–Pb ore bodies. The Lower Carboniferous Dapu Formation, Upper Carboniferous Huanglong Formation and Lower Permian Liangshan Formation strata form the Banbanqiao brachy anticline structure

(Figs. 1C and 2). Ore bodies occur within axis of the Banbanqiao anticline (Fig. 3).

### 2.2.3. Ore body

Ore bodies in the Banbanqiao deposit are predominated by stratiform type (Fig. 3). There are three ore bodies have been found in the Banbanqiao deposit area, of which the No. II ore body is the largest. This ore body is stratiform, and occurs along the NW-trending normal fault ( $F_3$ ) and within axis of the Banbanqiao brachy anticline (Fig. 3). Ore bodies in the Banbanqiao deposit contains more than 1.5 million tons Zn–Pb ores at grades of 0.26 wt.% to 10.32 wt.% Pb and 0.81 wt.% to 28.8 wt.% Zn, with high Zn/Pb ratios mostly

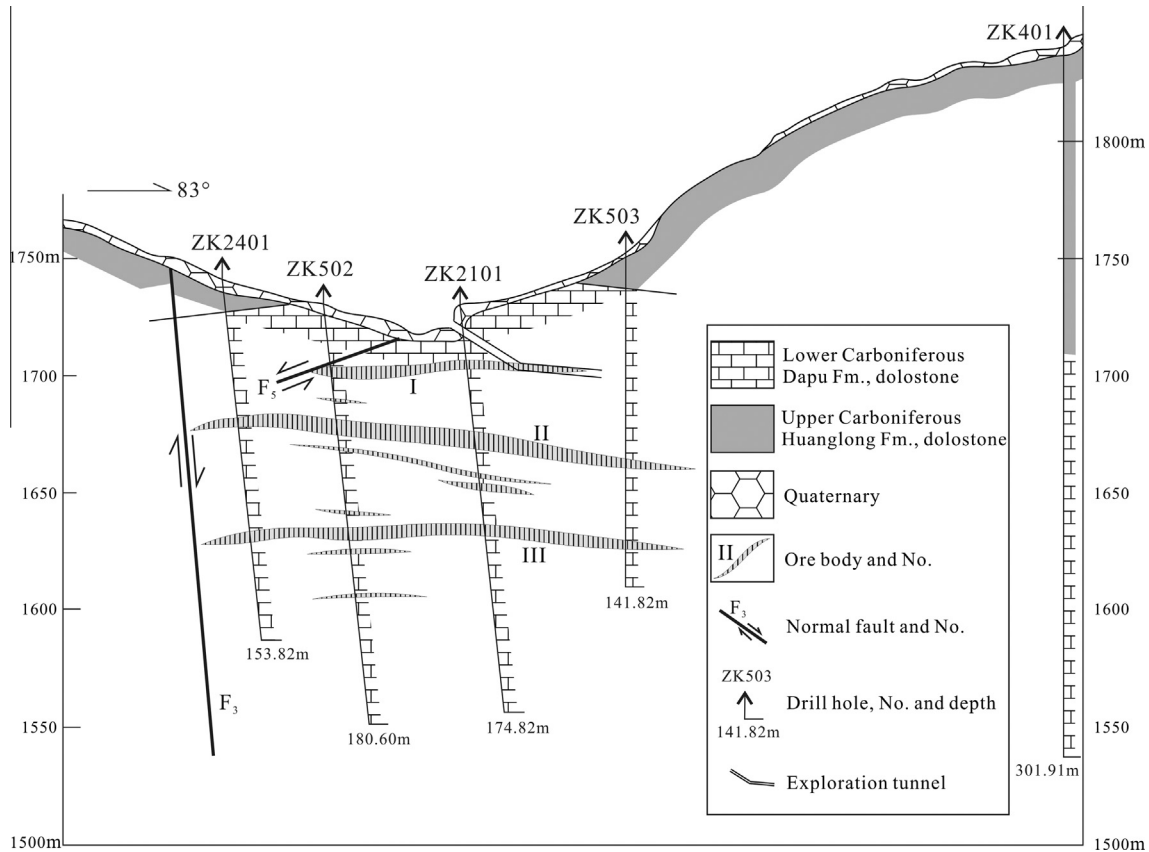


Fig. 3. Cross section of No. 5 exploration line in the Banbanqiao Pb–Zn deposit that shows shape of ore body, wall rocks and anticline (after Zhou et al., 2014a).

ranging from 4 to 12. Ores also contain major elements of S and Fe, and minor to trace elements of Cd, Ge and Ga (Zhou et al., 2014a).

#### 2.2.4. Texture and structure of ores

Ores in the Banbanqiao Zn–Pb deposit underwent hydrothermal and supergene oxidizing processes (Zhou et al., 2014a). Therefore, there are oxidized and unaltered sulfide ores along with a mixture of these two types. Unaltered sulfide ores consist of sphalerite, pyrite, galena, calcite and dolomite. Oxidized and mixed ores have extremely complex mineral assemblages include smithsonite, limonite, cerussite, and sulfide and carbonate minerals. Within the unaltered sulfide ore zones, structures are composed of disseminated (Fig. 4A and E), massive (Fig. 4B and C), brecciated (Fig. 4D), vein (Fig. 4F) and banded, and textures consist of anhedral to euhedral granular (Fig. 5C, D, and F), metasomatic (Fig. 5A, B, and F), filling (Fig. 5D and E), and crush pressure shadows (Fig. 5D).

#### 2.2.5. Mineral paragenesis

Based on crosscutting, overgrowth and replacement relationships, the hydrothermal period can be divided into two stages, including the sulfide–carbonate and the carbonate stages. In the sulfide–carbonate stage, the mineral assemblages include (i) pyrite + sphalerite + calcite (Fig. 4A, D, and F), (ii) pyrite + sphalerite + galena + calcite (Fig. 4C) and (iii) sphalerite + galena + calcite (Fig. 4B and E). Details about mineral paragenesis are listed in Table 1.

#### 2.2.6. Wall rock alteration

Like other Pb–Zn deposits in the southeast SYG province, wall rock alteration types of the Banbanqiao Zn–Pb deposit are simple and mainly include: (i) dolomite, (ii) Fe–Mn carbonates, and (iii)

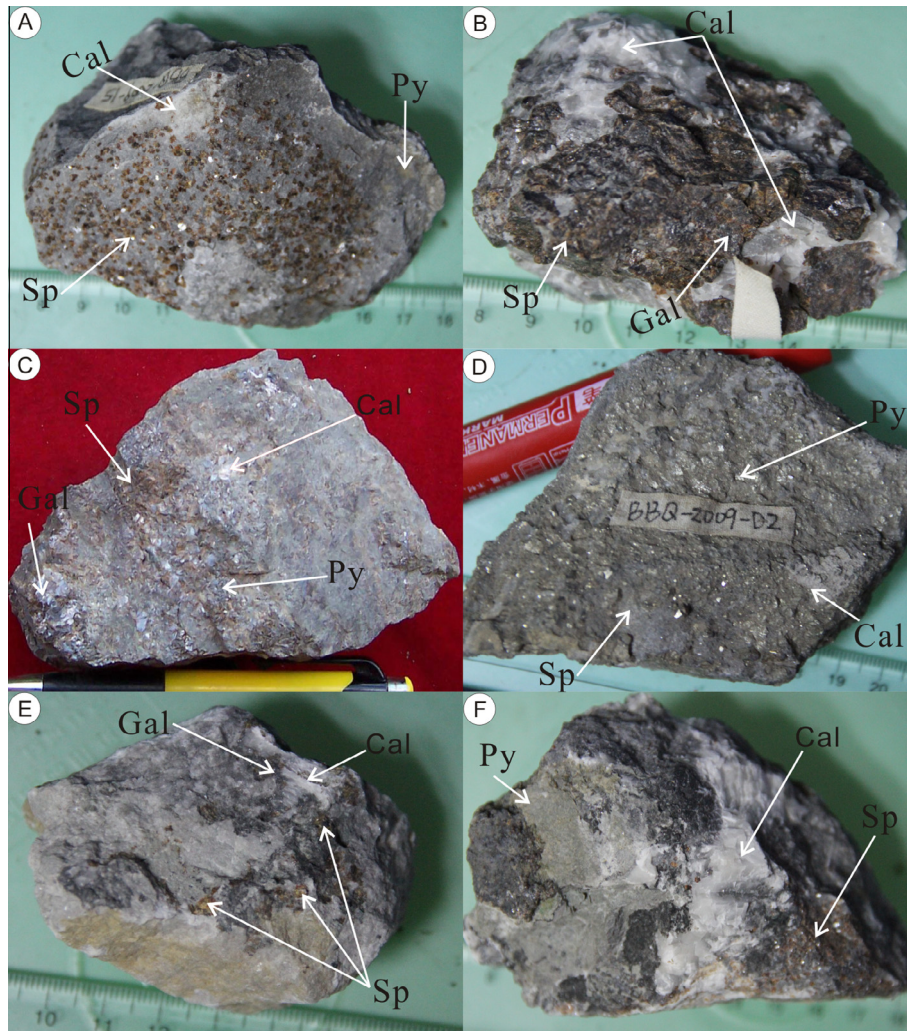
zones of gossan consisting of iron and aluminum oxides and hydroxides. Dolomitization enhances rock brittleness and cause crack opening for Pb–Zn mineralization. Fe–Mn carbonatization resulted in light brown, maroon and puce Fe (Mn)-bearing dolomite and is closely associated with Pb–Zn mineralization. Gossan coexists with Pb–Zn sulfide ores on the space and is usually located in the upper levels of Pb–Zn mineralization zone. The intensity of gossan formation is directly related to Pb–Zn mineralization (Zhou et al., 2014a).

### 3. Analytical methods

Fourteen representative sulfide ore hand specimens from drill holes and exploration tunnels were collected. Pyrite, sphalerite, galena and calcite were hand picked from these samples using a binocular microscope and analyzed for REE, and C, O, S and Pb isotopes. Additionally, one whole-rock sample of Lower Permian Liangshan Formation shale and eight whole-rock samples of Lower Carboniferous Dapu Formation dolostone were collected for REE and Pb isotopes.

#### 3.1. Carbon and Oxygen isotope analysis

C and O isotopes' analysis was completed at the State Key Laboratory of Environmental Geochemistry, Chinese Academy of Sciences, by using a Finnigan MAT-253 mass spectrometer. Calcite reacts with 100% phosphoric acid ( $H_3PO_4$ ) to produce  $CO_2$ . The analytical precisions ( $2\sigma_m$ ) are  $\pm 0.3\%$  for  $\delta^{13}C$  value and  $\pm 0.6\%$  for  $\delta^{18}O$  value. C and O isotopic compositions are reported relative to Vienna Pee Dee Belemnite (V-PDB).  $\delta^{18}O_{SMOW} = 1.03086 \times \delta^{18}O_{PDB} + 30.86$  (Friedman and O'Neil, 1977).



**Fig. 4.** Photos of ore types and mineral assemblages in the Banbanqiao deposit. (A) Euhedral granular sphalerite (Sp) with massive pyrite (Py) and patchy calcite (Cal). (B) Patchy and vein Cal with massive Sp and granular galena (Gal). (C) Massive and veined Sp with granular pyrite and patchy Cal. (D) Euhedral granular Py with massive Sp and patchy Cal. (E) Granular Sp with patchy Cal and fine-grained Gal. (F) Vein Cal with massive Sp and Py.

### 3.2. Sulfur isotope analysis

Sulfur isotopes' analysis was carried out by using the Element Analyzer (EA) method on a Continuous Flow Isotope Ratio Mass Spectrometry at the State Key Laboratory of Environment Geochemistry, Chinese Academy of Sciences. GBW 04415 and GBW 04414  $\text{Ag}_2\text{S}$  were used as the external standards and Vienna Canyon Diablo Troilite (V-CDT) was the referent standard. Analytical accuracy is  $\pm 0.2\%$  ( $2\sigma_m$ ).

### 3.3. Lead isotope analysis

Pb isotopes' analysis was carried out using the GV IsoProbe-T thermal ionization mass spectrometer (TIMS) at the Beijing Institute of Uranium Geology. The analytical procedures involved dissolution of samples using HF and  $\text{HClO}_4$  in crucibles, followed by basic anion exchange resin to purify the Pb. Analytical results for the standard NBS 981 are  $^{208}\text{Pb}/^{206}\text{Pb} = 36.612 \pm 0.005$  ( $2\sigma_m$ ),  $^{207}\text{Pb}/^{206}\text{Pb} = 15.458 \pm 0.004$  ( $2\sigma_m$ ) and  $^{206}\text{Pb}/^{204}\text{Pb} = 16.935 \pm 0.003$  ( $2\sigma_m$ ).

### 3.4. REE analysis

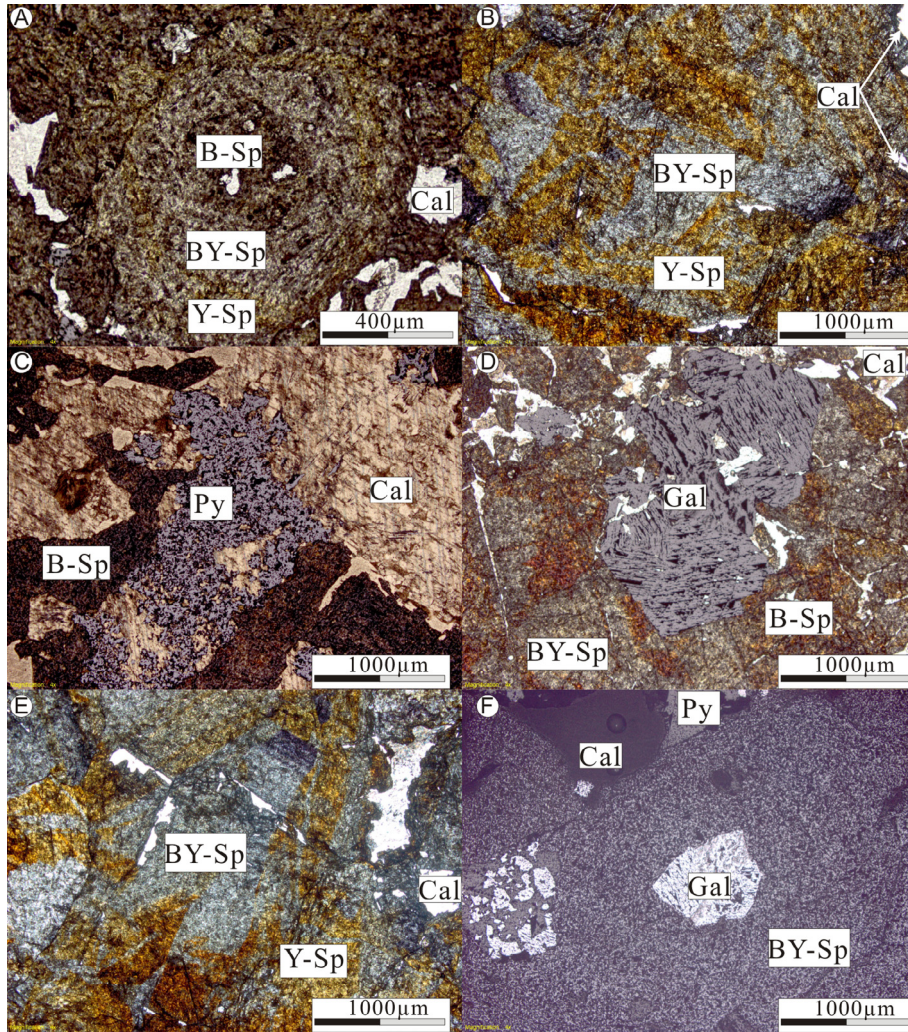
Dissolution of sulfide and calcite separates, and shale and dolostone whole-rock samples was completed in the State Key

Laboratory of Ore Deposit Geochemistry, Chinese Academy of Sciences, and then REE contents of sulfide separates were analyzed using an ELAN DRC-e ICP-MS at the Beijing Institute of Uranium Geology, and calcite separates and whole-rock samples were analyzed using an ELAN DRC-e Q-ICP-MS, at the State Key Laboratory of Ore Deposit Geochemistry, Chinese Academy of Sciences. A detailed analytical procedure for REE analysis is available in Qi et al. (2000). Relative analytical error for REE is better than 5% ( $2\sigma_m$ ).

## 4. Analytical results

### 4.1. Carbon and Oxygen isotopic compositions

C–O isotopic compositions of calcite separates from sulfide ore samples are listed in Table 2 and plotted in Fig. 6. The  $\delta^{13}\text{C}_{\text{PDB}}$  and  $\delta^{18}\text{O}_{\text{SMOW}}$  values of nine calcite separates range from  $-2.8\%$  to  $-0.7\%$  (mean  $-1.1\%$ ) and  $+14.1\%$  to  $+17.0\%$  (mean  $+15.5\%$ ), respectively. Compared with the well-known Huize (Huang et al., 2010) and Tianqiao (Zhou et al., 2013a) deposits in the SYG province, calcite separates from the Banbanqiao deposit have higher  $\delta^{13}\text{C}_{\text{PDB}}$  values, but lower  $\delta^{18}\text{O}_{\text{SMOW}}$  values (Fig. 6).



**Fig. 5.** Photos of microscopic structures for sulfide ores in the Banbanqiao deposit. (A) Patchy calcite (Cal) within brown sphalerite (B-Sp), and B-Sp within brown–yellow sphalerite (BY-Sp), which enclosed in yellow sphalerite (Y-Sp). (B) BY-Sp enclosed in Y-Sp within. (C) B-Sp with pyrite (Py) and Cal. (D) Early Cal enclosed in galena (Gal) and BY-Sp, and Gal within B-Sp and BY-Sp. (E) Cal within Gal and BY-Sp, and BY-Sp enclosed in Y-Sp. (F) Gal within BY-Sp, and BY-Sp coexisting with Cal and Py. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 1**  
Mineral paragenesis in the Banbanqiao deposit.

| Period             | Hydrothermal      |                     |                | Supergene |
|--------------------|-------------------|---------------------|----------------|-----------|
| Stage              | Sulfide–carbonate |                     | Carbonate      | Oxidized  |
| Mineral assemblage | Sp + Py + Cal     | Sp + Py + Gal + Cal | Sp + Gal + Cal | Dol + Cal |
| Sp                 | ■                 |                     |                |           |
| Py                 | ■                 |                     |                |           |
| Gal                | ■                 |                     |                |           |
| Dol                |                   |                     |                | ■         |
| Cal                | ■                 |                     |                |           |
| Lim                |                   |                     |                | ■         |
| Cer                |                   |                     |                | ■         |

Sp, sphalerite; Py, pyrite; Gal, galena; Cal, calcite; Dol, dolomite; Lim, limonite; Cer, Cerussite. — Less; ■ More.

#### 4.2. Sulfur isotopic compositions

$\delta^{34}\text{S}_{\text{CDT}}$  values of sulfide separates from sulfide ore samples are shown in Table 3 and plotted in Fig. 7. All sulfide separates have  $\delta^{34}\text{S}_{\text{CDT}}$  values ranging from +3.2‰ to +9.9‰ (mean +6.5‰,  $n = 21$ ), of which pyrite, sphalerite and galena samples have  $\delta^{34}\text{S}_{\text{CDT}}$  values ranging from +8.8‰ to +9.9‰ (mean +9.5‰,  $n = 5$ ),

+3.9‰ to +9.0‰ (mean +6.4‰,  $n = 11$ ), and +3.2‰ to +4.8‰ (mean +3.9‰,  $n = 5$ ), respectively. It is clear that from pyrite to sphalerite, and then to galena, the  $\delta^{34}\text{S}_{\text{CDT}}$  values are decreasing, reflecting sulfur isotope equilibrium fractionation. Sulfide separates from the Banbanqiao deposit have lower  $\delta^{34}\text{S}_{\text{CDT}}$  values (Fig. 7) than those of the Tianqiao (Zhou et al., 2013a), Shaojiwan (Zhou et al., 2013b), Qingshan (Zhou et al., 2013c) and Shanshulin

**Table 2**  
C–O isotopic compositions of calcite separate.

| No.  | Object  | $\delta^{13}\text{C}_{\text{PDB}}/\text{‰}$ | $2\sigma_m$ | $\delta^{18}\text{O}_{\text{PDB}}/\text{‰}$ | $2\sigma_m$ | $\delta^{18}\text{O}_{\text{SMOW}}/\text{‰}$ | $\delta^{18}\text{O}_{\text{H}_2\text{O}}/\text{‰}$ |
|------|---------|---|-------------|---|-------------|--|---|
| B06  | Calcite | −1.2  | 0.1         | −14.1                                       | 0.2         | +16.3  | +6.8  |
| B08  | Calcite | −2.8  | 0.2         | −13.5                                       | 0.2         | +17.0  | +7.5  |
| B09  | Calcite | −1.2  | 0.2         | −14.1                                       | 0.2         | +16.3  | +6.8  |
| B10  | Calcite | −0.8  | 0.1         | −16.0                                       | 0.2         | +14.4  | +4.9  |
| B15  | Calcite | −0.8  | 0.1         | −15.1                                       | 0.1         | +15.3  | +5.8  |
| B17  | Calcite | −1.0  | 0.1         | −14.8                                       | 0.2         | +15.6  | +6.1  |
| B18  | Calcite | −0.7  | 0.1         | −14.1                                       | 0.2         | +16.3  | +6.8  |
| B21  | Calcite | −0.7  | 0.1         | −16.3                                       | 0.1         | +14.1  | +4.6  |
| B924 | Calcite | −0.8  | 0.1         | −16.0                                       | 0.2         | +14.4  | +4.9  |

$$\delta^{18}\text{O}_{\text{SMOW}} = 1.03086 \times \delta^{18}\text{O}_{\text{PDB}} + 30.86 \text{ (Friedman and O'Neil, 1977); } \Delta^{18}\text{O}_{\text{Cal-H}_2\text{O}} = \delta^{18}\text{O}_{\text{Cal}} - \delta^{18}\text{S}_{\text{H}_2\text{O}} = 2.78 \times 10^6 / (t + 273.15)^2 - 2.89, t = 200 \text{ °C (Zheng and Chen, 2000).}$$

(Zhou et al., 2014b) deposits in the southeastern part of the SYG province (Fig. 1B), whereas similar to those of the Huize deposit in the central part of the SYG province (Fig. 1A; Han et al., 2007).

#### 4.3. Lead isotopic compositions

Lead isotopic compositions of whole-rock and sulfide separate samples are listed in Table 4 and shown in Fig. 8. Twelve sulfide separate samples have  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios between 18.029 and 18.726 (average 18.283),  $^{207}\text{Pb}/^{204}\text{Pb}$  ratios between 15.651 and 15.784 (average 15.687) and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios between 38.145 and 39.138 (average 38.425). The  $^{238}\text{U}/^{204}\text{Pb}$  ( $\mu$ ) values range from 9.60 to 9.81 (average 9.65). Eight dolostone whole-rock samples have  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios ranging from 18.436 to 18.602 (average 18.519),  $^{207}\text{Pb}/^{204}\text{Pb}$  ratios ranging from 15.663 to 15.850 (average 15.754) and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios ranging from 38.703 to 39.140 (average 38.842). The  $\mu$  values range from 9.58 to 9.94 (average 9.76). One shale whole-rock sample has  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratio of 18.467, 15.656 and 38.704. The  $\mu$  value is 9.57. It is obvious that most sulfide samples have lower radiogenic Pb than those of country whole-rock (Fig. 8A and B).

#### 4.4. REE contents

REE contents of country whole-rock, sulfide and calcite separate samples are listed in Table 5 and shown in Fig. 9. One shale

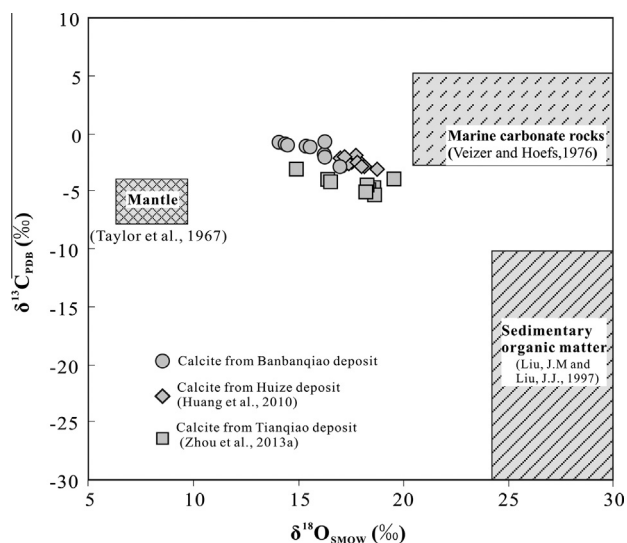
whole-rock sample has total REE ( $\Sigma\text{REE}$ , excluding Y) content of 2.63 ppm,  $\delta\text{Eu}$  value of 2.79 and La/Yb<sub>N</sub> ratio of 2.86. Eight dolostone whole-rock samples have (i) total REE contents ranging from 0.72 ppm to 86.2 ppm (average 27.4 ppm), (ii)  $\delta\text{Eu}$  values ranging from 0.34 to 0.70 (average 0.56), and (iii) La/Yb<sub>N</sub> ratios ranging from 1.92 to 6.76 (average 4.70). Twelve sulfide separate samples have  $\Sigma\text{REE}$  contents ranging from 0.29 ppm to 36.4 ppm (average 4.27 ppm),  $\delta\text{Eu}$  values ranging from 0.32 to 2.86 (average 1.72) and La/Yb<sub>N</sub> ratios ranging from 0.4 to 27.24 (average 7.46). These sulfide samples are distinguished by: (i) two pyrite separates have  $\Sigma\text{REE}$  contents ranging from 5.27 ppm to 36.4 ppm,  $\delta\text{Eu}$  values between 0.64 and 0.86 and La/Yb<sub>N</sub> ratios of 1.67–10.49, (ii) nine sphalerite separates have  $\Sigma\text{REE}$  contents ranging from 0.39 to 3.39 ppm,  $\delta\text{Eu}$  values ranging from 0.94 to 2.86 and La/Yb<sub>N</sub> ratios ranging from 0.4 to 12.26, and (iii) one galena separate has  $\Sigma\text{REE}$  content of 0.52 ppm,  $\delta\text{Eu}$  value of 0.32 and La/Yb<sub>N</sub> ratio of 27.24. Two calcite separate have  $\Sigma\text{REE}$  contents ranging from 22.0 to 41.1 ppm,  $\delta\text{Eu}$  values between 0.21 and 0.45 and La/Yb<sub>N</sub> ratios of 5.54–8.42. Obviously, calcite and pyrite separates have higher REE contents than those of sphalerite and galena. In addition, it is clear that the pyrite, calcite and galena separates have negative Eu anomaly, whereas almost all the sphalerite separates have positive Eu anomaly.

## 5. Discussions

### 5.1. Origin of ore-forming elements

#### 5.1.1. Constraints from C–O isotopes

Generally, there are three principal sources of C in hydrothermal fluids: (i) mantle, (ii) marine carbonate rocks, and (iii) sedimentary organic matter (Taylor et al., 1967; Veizer and Hoefs, 1976; Demény and Harangi, 1996; Liu and Liu, 1997; Demény et al., 1998). The  $\delta^{13}\text{C}_{\text{PDB}}$  values for mantle, marine carbonate and



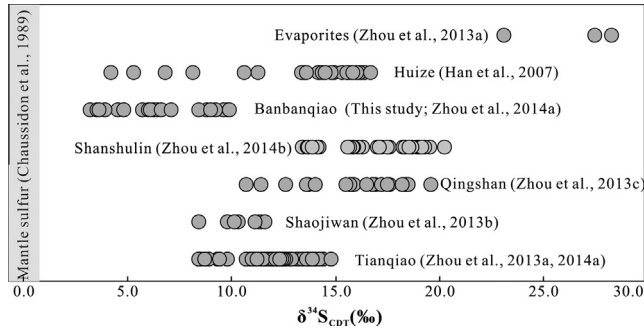
**Fig. 6.** Plot of  $\delta^{13}\text{C}_{\text{PDB}}$  vs.  $\delta^{18}\text{O}_{\text{SMOW}}$  values. The  $\delta^{13}\text{C}_{\text{PDB}}$  and  $\delta^{18}\text{O}_{\text{SMOW}}$  values for calcite separates from the Banbanqiao deposit compared with mantle, marine carbonate rocks and sedimentary organic matter, and those from the Huize and Tianqiao deposits.

**Table 3**  
Sulfur isotopic compositions of sulfide separate.

| No. | $\delta^{34}\text{S}_{\text{CDT}}/\text{‰}$ ( $2\sigma_m$ ) |            |            | T (°C) |
|-----|---|------------|------------|--------|
|     | Pyrite  | Sphalerite | Galena     |        |
| B02 | +8.8 ± 0.1  | +5.7 ± 0.1 |            | 224    |
| B04 |   | +6.2 ± 0.2 | +3.2 ± 0.1 |        |
| B06 | +9.8 ± 0.2  |            | +4.5 ± 0.1 | 163    |
| B08 |   | +8.4 ± 0.1 |            | 271    |
| B09 | +9.6 ± 0.1  | +6.4 ± 0.1 | +3.5 ± 0.1 |        |
| B10 |   | +6.0 ± 0.1 |            | 271    |
| B15 |   | +3.9 ± 0.2 | +3.6 ± 0.2 |        |
| B17 |   | +6.1 ± 0.1 |            | 271    |
| B18 | +9.2 ± 0.2  | +6.6 ± 0.2 |            |        |
| B20 |   | +4.8 ± 0.2 |            | 147    |
| B21 |   | +9.0 ± 0.1 | +4.8 ± 0.1 |        |

$$\Delta^{34}\text{S}_{\text{Sp-Gal}} = \delta^{34}\text{S}_{\text{Sp}} - \delta^{34}\text{S}_{\text{Gal}} = 0.74 \times 10^6 / (t + 273.15)^2 \text{ (Czamanske and Rye, 1974).}$$





**Fig. 7.** Sulfur isotopic compositions histogram for the Banbanqiao deposit. The  $\delta^{34}\text{S}_{\text{CDT}}$  values for the Banbanqiao deposit compared with mantle-derived sulfur and evaporites, and the Huize, Tianqiao, Shaojiwan, Qingshan and Shanshulin deposits in the SYG province.

organic matter range from  $-4.0\text{‰}$  to  $-8.0\text{‰}$  (Taylor et al., 1967),  $-4.0\text{‰}$  to  $+4.0\text{‰}$  (Veizer and Hoefs, 1976), and  $-30.0\text{‰}$  to  $-10.0\text{‰}$  (Liu and Liu, 1997), respectively. Calcite separates from the Banbanqiao deposit have  $\delta^{13}\text{C}_{\text{PDB}}$  values higher than those of mantle and organic matters, but similar to those of marine carbonate (Fig. 6). This indicates that mantle and organic matter did not contribute significant quantities of C to the hydrothermal fluids, and so the C in the ore-forming fluids was likely provided by the carbonate host rocks, similar to other carbonate-hosted Pb–Zn deposits in the studied region (Zhou et al., 2013a, 2014b, 2015). The  $\delta^{18}\text{O}_{\text{SMOW}}$  values of calcite separates from the Banbanqiao deposit are higher than those of mantle ( $+6.0\text{‰}$  to  $+10.0\text{‰}$ ; Taylor et al., 1967), but lower than those of marine carbonate rocks ( $\delta^{18}\text{O}_{\text{SMOW}} = +20.0\text{‰}$  to  $+30.0\text{‰}$ ; Veizer and Hoefs, 1976) and sedimentary organic matter ( $\delta^{18}\text{O}_{\text{SMOW}} = +24.0\text{‰}$  to  $+35.0\text{‰}$ ; Liu and Liu, 1997). The calculated  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values of the hydrothermal fluids range from  $+4.6\text{‰}$  to  $+7.5\text{‰}$  based on oxygen isotope equilibrium fractionation equation between calcite and water ( $\Delta^{18}\text{O}_{\text{Cal-H}_2\text{O}} = \delta^{18}\text{O}_{\text{Cal}} - \delta^{18}\text{O}_{\text{H}_2\text{O}} = 2.78 \times 10^6 / (t + 273.15)^2 - 2.89$ ,  $t = 200\text{ °C}$ ; Zheng and Chen, 2000), which are similar to those of mantle-derived O (Demény and Harangi, 1996; Demény et al., 1998). In the plot of  $\delta^{13}\text{C}_{\text{PDB}}$  vs.  $\delta^{18}\text{O}_{\text{SMOW}}$  values (Fig. 5A), all calcite

separates from the Banbanqiao deposit plotted in the field between mantle and marine carbonate rocks, but away from those of sedimentary organic matter. These suggest that the ore-forming fluids were  $^{18}\text{O}$ -depleted compared with the carbonate host rocks and were likely to be derived from a mixed source region (the mantle-derived O in Emeishan basalts and dissolved O from the carbonate host rocks). Calcite separates from the Huize (Huang et al., 2010) and Tianqiao (Zhou et al., 2013a) deposits have  $\delta^{13}\text{C}_{\text{PDB}}$  values lower than those of the Banbanqiao deposit suggests more C in the formers were derived from mantle (Huang et al., 2010) and/or organic material (Zhou et al., 2013a).

### 5.1.2. Implications from S isotopes

Sulfide ores in the Banbanqiao deposit have simple sulfur-bearing minerals assemblage of galena, sphalerite and pyrite, but lack sulfate (Zhou et al., 2014a). Since sulfate minerals are not present in the Banbanqiao deposit, the equilibrium–disequilibrium constraints between sulfide minerals pairs such as pyrite–sphalerite and sphalerite–galena that deposited contemporaneously have the most significance. The  $\delta^{34}\text{S}$  values' differences between nine sulfide minerals pairs from the same hand specimen ranging  $+2.5\text{‰}$  to  $+4.2\text{‰}$ , and the relations of  $\delta^{34}\text{S}_{\text{pyrite}} > \delta^{34}\text{S}_{\text{sphalerite}}$  and  $\delta^{34}\text{S}_{\text{sphalerite}} > \delta^{34}\text{S}_{\text{galena}}$  for these pairs suggests that sulfide precipitated under sulfur isotope equilibrium fractionation. The observed fractionation for five sphalerite–galena pairs in the Banbanqiao Zn–Pb deposit corresponds to mineral formation temperatures (Czamanske and Rye, 1974) of  $147\text{--}271\text{ °C}$  (Table 3). Studies have demonstrated that in low oxidation state sulfur isotopic compositions of sulfide minerals (especially pyrite) approximately represent the  $\delta^{34}\text{S}$  values of the hydrothermal fluids (e.g., Ohmoto, 1972; Ohmoto et al., 1990; Dixon and Davidson, 1996; Seal, 2006; Basuki et al., 2008; Pass et al., 2014). Pyrite from the Banbanqiao deposit has  $\delta^{34}\text{S}_{\text{CDT}}$  values ranging from  $+8.8\text{‰}$  to  $+9.9\text{‰}$  (mean  $+9.5\text{‰}$ ), unlike mantle-derived sulfur ( $0 \pm 3\text{‰}$ ; Chaussidon et al., 1989). Sulfate-bearing evaporites in Permian strata (Fig. 7) have  $\delta^{34}\text{S}_{\text{CDT}}$  values ranging from  $+22\text{‰}$  to  $+28\text{‰}$  (Zhou et al., 2014a), within the range of Cambrian to Triassic seawater ( $+15\text{‰}$  to  $+35\text{‰}$ ; Claypool et al., 1980). Thermal chemical reduction of sulfate to sulfide can lower  $\delta^{34}\text{S}$  values up to  $+15\text{‰}$  (e.g., Ohmoto et al., 1990; Ohmoto and Goldhaber, 1997; Basuki et al., 2008; Pass et al., 2014) such that the reduced sulfur in sulfide ores interpreted to be the products of evaporites within the Permian strata by thermal chemical sulfate reduction (TSR). The metallogenic temperatures range from  $147\text{ °C}$  to  $271\text{ °C}$  (Table 3), excluding bacterial sulfate reduction, which would result in a larger sulfur isotope fractionation. Therefore, S in the hydrothermal fluids was mainly sourced from evaporites by TSR with a limited influence of mantle-derived S as suggested by O isotopic data above.

### 5.1.3. Constrained by Pb isotopes

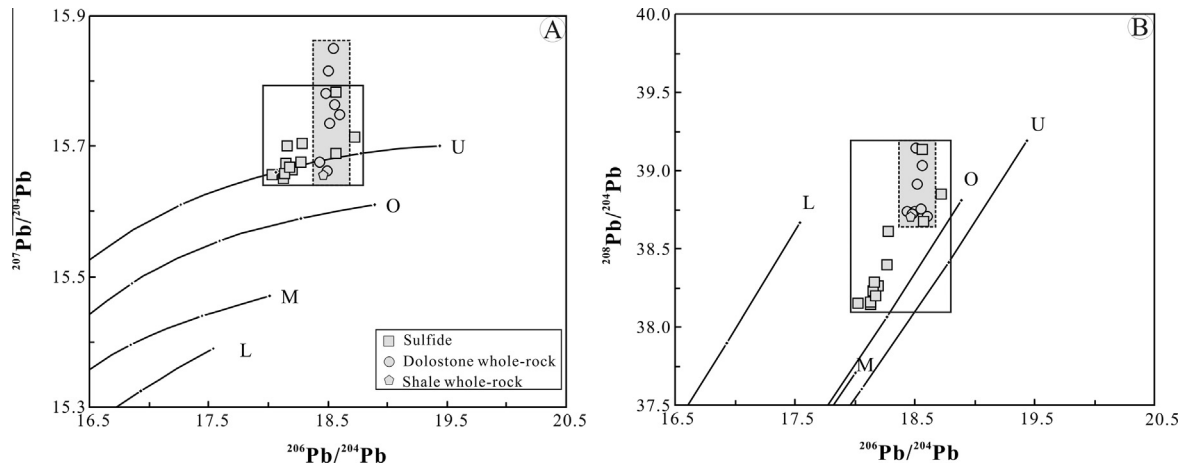
Because some Pb isotopes are radiogenic, the Pb isotopic ratios need to be corrected to a consistent age in order to make comparisons between different phases. Sulfides have very low U and Th contents, hence the radiogenic Pb of sulfides after their formation is negligible and no age correction is needed, whereas the Pb isotopes in the whole-rock are needed. (e.g., Carr et al., 1995; Muchez et al., 2005; Pass et al., 2014; Zhou et al., 2014b). Previous studies have demonstrated that these typical Pb–Zn deposits in the SYG province formed at  $\sim 200\text{ Ma}$ , which is used for correcting the Pb isotope of whole-rock. In the diagram of  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios (Fig. 8A), all the sulfides and country whole-rock samples plot in the upper crust lead average evolution curve (Zartman and Doe, 1981). In the plot of  $^{208}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios (Fig. 8B), they are plotted near to the orogenic belt lead average evolution curve (Zartman and

**Table 4**  
Pb isotopic compositions of country whole-rock and sulfide separate.

| No.  | Object     | $^{206}\text{Pb}/^{204}\text{Pb}^a$<br>( $2\sigma_m$ ) | $^{207}\text{Pb}/^{204}\text{Pb}^a$<br>( $2\sigma_m$ ) | $^{208}\text{Pb}/^{204}\text{Pb}^a$<br>( $2\sigma_m$ ) | $\mu^b$ |
|------|------------|--|--|--|---------|
| B903 | Shale      | $18.467 \pm 0.002$                                     | $15.656 \pm 0.003$                                     | $38.704 \pm 0.004$                                     | 9.57    |
| B904 | Dolostone  | $18.436 \pm 0.004$                                     | $15.675 \pm 0.002$                                     | $38.736 \pm 0.005$                                     | 9.61    |
| B905 | Dolostone  | $18.558 \pm 0.005$                                     | $15.763 \pm 0.003$                                     | $39.030 \pm 0.007$                                     | 9.77    |
| B908 | Dolostone  | $18.497 \pm 0.003$                                     | $15.663 \pm 0.002$                                     | $38.735 \pm 0.006$                                     | 9.58    |
| B912 | Dolostone  | $18.551 \pm 0.002$                                     | $15.850 \pm 0.003$                                     | $38.756 \pm 0.005$                                     | 9.94    |
| B913 | Dolostone  | $18.602 \pm 0.002$                                     | $15.748 \pm 0.002$                                     | $38.703 \pm 0.006$                                     | 9.73    |
| B920 | Dolostone  | $18.517 \pm 0.002$                                     | $15.735 \pm 0.003$                                     | $38.913 \pm 0.004$                                     | 9.72    |
| B923 | Dolostone  | $18.509 \pm 0.002$                                     | $15.816 \pm 0.003$                                     | $39.140 \pm 0.006$                                     | 9.88    |
| B925 | Dolostone  | $18.483 \pm 0.002$                                     | $15.782 \pm 0.003$                                     | $38.720 \pm 0.005$                                     | 9.82    |
| B03  | Pyrite     | $18.571 \pm 0.001$                                     | $15.689 \pm 0.001$                                     | $38.675 \pm 0.003$                                     | 9.62    |
| B06  | Pyrite     | $18.280 \pm 0.001$                                     | $15.705 \pm 0.001$                                     | $38.609 \pm 0.002$                                     | 9.69    |
| B05  | Sphalerite | $18.130 \pm 0.001$                                     | $15.651 \pm 0.002$                                     | $38.145 \pm 0.002$                                     | 9.64    |
| B08  | Sphalerite | $18.200 \pm 0.001$                                     | $15.665 \pm 0.001$                                     | $38.261 \pm 0.002$                                     | 9.63    |
| B09  | Sphalerite | $18.153 \pm 0.002$                                     | $15.674 \pm 0.001$                                     | $38.229 \pm 0.001$                                     | 9.69    |
| B15  | Sphalerite | $18.133 \pm 0.001$                                     | $15.658 \pm 0.001$                                     | $38.161 \pm 0.001$                                     | 9.61    |
| B17  | Sphalerite | $18.270 \pm 0.001$                                     | $15.676 \pm 0.002$                                     | $38.393 \pm 0.002$                                     | 9.62    |
| B18  | Sphalerite | $18.176 \pm 0.002$                                     | $15.668 \pm 0.001$                                     | $38.201 \pm 0.002$                                     | 9.60    |
| B20  | Sphalerite | $18.726 \pm 0.001$                                     | $15.715 \pm 0.001$                                     | $38.850 \pm 0.003$                                     | 9.62    |
| B21  | Sphalerite | $18.029 \pm 0.001$                                     | $15.656 \pm 0.002$                                     | $38.154 \pm 0.001$                                     | 9.63    |
| B924 | Sphalerite | $18.159 \pm 0.001$                                     | $15.701 \pm 0.001$                                     | $38.286 \pm 0.003$                                     | 9.66    |
| B10  | Galena     | $18.564 \pm 0.002$                                     | $15.784 \pm 0.003$                                     | $39.138 \pm 0.007$                                     | 9.81    |

<sup>a</sup> Age-corrected (200 Ma).

<sup>b</sup>  $\mu = ^{238}\text{U}/^{204}\text{Pb}$ .



**Fig. 8.** Plots of  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  (A) and  $^{208}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  (B) ratios for sulfides and wall rocks. Trends for the Upper Crust (U), Orogen belt (O), Mantle (M) and Lower Crust (L) are taken from Zartman and Doe (1981).

**Table 5**

REE contents (ppm) of country whole-rock, and sulfide and calcite separate.

| No.  | Object     | La    | Ce    | Pr    | Nd    | Sm    | Eu    | Gd    | Tb    | Dy    | Ho    | Er    | Tm    | Yb    | Lu    | $\Sigma\text{REE}$ | $\delta\text{Eu}$ | $(\text{La}/\text{Yb})_N$ |
|------|------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------------------|-------------------|---------------------------|
| B903 | Shale      | 0.424 | 0.773 | 0.093 | 0.445 | 0.102 | 0.124 | 0.180 | 0.027 | 0.163 | 0.039 | 0.126 | 0.018 | 0.100 | 0.017 | 2.63               | 2.79              | 2.86                      |
| B904 | Dolostone  | 10.1  | 14.9  | 2.16  | 8.09  | 1.58  | 0.357 | 1.89  | 0.263 | 1.49  | 0.340 | 1.02  | 0.159 | 1.070 | 0.165 | 43.6               | 0.63              | 6.36                      |
| B905 | Dolostone  | 0.384 | 0.457 | 0.079 | 0.346 | 0.065 | 0.017 | 0.088 | 0.018 | 0.105 | 0.026 | 0.073 | 0.011 | 0.076 | 0.014 | 1.76               | 0.68              | 3.43                      |
| B908 | Dolostone  | 3.41  | 4.90  | 0.689 | 3.14  | 0.784 | 0.172 | 1.054 | 0.147 | 0.828 | 0.188 | 0.442 | 0.063 | 0.340 | 0.052 | 16.2               | 0.58              | 6.76                      |
| B912 | Dolostone  | 0.711 | 0.774 | 0.124 | 0.471 | 0.111 | 0.028 | 0.167 | 0.026 | 0.159 | 0.034 | 0.097 | 0.013 | 0.075 | 0.011 | 2.80               | 0.63              | 6.43                      |
| B913 | Dolostone  | 0.954 | 0.954 | 0.147 | 0.601 | 0.145 | 0.030 | 0.216 | 0.034 | 0.196 | 0.048 | 0.143 | 0.022 | 0.110 | 0.021 | 3.62               | 0.51              | 5.85                      |
| B923 | Dolostone  | 14.7  | 25.9  | 2.56  | 7.54  | 1.14  | 0.208 | 2.20  | 0.307 | 2.801 | 0.753 | 2.40  | 0.401 | 3.36  | 0.509 | 64.8               | 0.40              | 2.95                      |
| B925 | Dolostone  | 21.0  | 36.2  | 3.55  | 9.95  | 1.37  | 0.210 | 2.54  | 0.437 | 2.950 | 0.788 | 2.57  | 0.458 | 3.61  | 0.579 | 86.2               | 0.34              | 3.92                      |
| B920 | Dolostone  | 0.132 | 0.206 | 0.023 | 0.103 | 0.029 | 0.008 | 0.043 | 0.007 | 0.054 | 0.010 | 0.048 | 0.006 | 0.046 | 0.007 | 0.72               | 0.70              | 1.92                      |
| B03  | Pyrite     | 3.26  | 13.7  | 1.58  | 7.49  | 1.54  | 0.328 | 1.61  | 0.402 | 2.58  | 0.466 | 1.64  | 0.225 | 1.32  | 0.217 | 36.4               | 0.64              | 1.67                      |
| B06  | Pyrite     | 1.12  | 2.07  | 0.263 | 0.884 | 0.292 | 0.057 | 0.142 | 0.04  | 0.166 | 0.028 | 0.109 | 0.019 | 0.072 | 0.012 | 5.27               | 0.86              | 10.49                     |
| B05  | Sphalerite | 0.069 | 0.06  | 0.012 | 0.085 | 0.143 | 0.032 | 0.018 | 0.002 | 0.006 | 0.002 | 0.007 | 0.001 | 0.004 | 0.001 | 0.44               | 1.93              | 11.63                     |
| B08  | Sphalerite | 0.208 | 0.489 | 0.052 | 0.226 | 0.129 | 0.059 | 0.077 | 0.018 | 0.106 | 0.014 | 0.049 | 0.008 | 0.059 | 0.010 | 1.50               | 1.81              | 2.38                      |
| B09  | Sphalerite | 0.353 | 0.888 | 0.152 | 0.922 | 0.338 | 0.074 | 0.170 | 0.044 | 0.208 | 0.043 | 0.076 | 0.018 | 0.087 | 0.013 | 3.39               | 0.94              | 2.74                      |
| B15  | Sphalerite | 0.082 | 0.079 | 0.006 | 0.149 | 0.096 | 0.025 | 0.009 | 0.001 | 0.006 | 0.003 | 0.007 | 0.003 | 0.017 | 0.003 | 0.49               | 2.60              | 3.25                      |
| B17  | Sphalerite | 0.049 | 0.05  | 0.011 | 0.125 | 0.061 | 0.009 | 0.003 | 0.002 | 0.008 | 0.003 | 0.006 | 0.003 | 0.013 | 0.002 | 0.35               | 2.03              | 2.54                      |
| B18  | Sphalerite | 0.291 | 0.427 | 0.052 | 0.224 | 0.076 | 0.054 | 0.044 | 0.002 | 0.030 | 0.004 | 0.009 | 0.005 | 0.016 | 0.002 | 1.24               | 2.86              | 12.26                     |
| B20  | Sphalerite | 0.003 | 0.011 | 0.032 | 0.123 | 0.061 | 0.016 | 0.011 | 0.003 | 0.011 | 0.005 | 0.007 | 0.001 | 0.005 | 0.001 | 0.29               | 1.89              | 0.40                      |
| B21  | Sphalerite | 0.189 | 0.163 | 0.018 | 0.139 | 0.100 | 0.029 | 0.013 | 0.003 | 0.029 | 0.004 | 0.017 | 0.002 | 0.019 | 0.002 | 0.73               | 2.46              | 6.71                      |
| B924 | Sphalerite | 0.255 | 0.142 | 0.017 | 0.107 | 0.036 | 0.022 | 0.023 | 0.003 | 0.026 | 0.004 | 0.011 | 0.004 | 0.021 | 0.002 | 0.67               | 2.34              | 8.19                      |
| B10  | Galena     | 0.202 | 0.149 | 0.018 | 0.088 | 0.021 | 0.002 | 0.017 | 0.002 | 0.007 | 0.002 | 0.005 | 0.001 | 0.005 | 0.001 | 0.52               | 0.32              | 27.24                     |
| B02  | Calcite    | 4.12  | 10.1  | 2.01  | 10.9  | 4.07  | 0.601 | 4.01  | 0.492 | 2.61  | 0.504 | 1.01  | 0.087 | 0.501 | 0.033 | 41.1               | 0.45              | 5.54                      |
| B10  | Calcite    | 2.31  | 6.54  | 1.05  | 6.21  | 1.98  | 0.132 | 1.85  | 0.201 | 1.03  | 0.114 | 0.373 | 0.027 | 0.185 | 0.031 | 22.0               | 0.21              | 8.42                      |

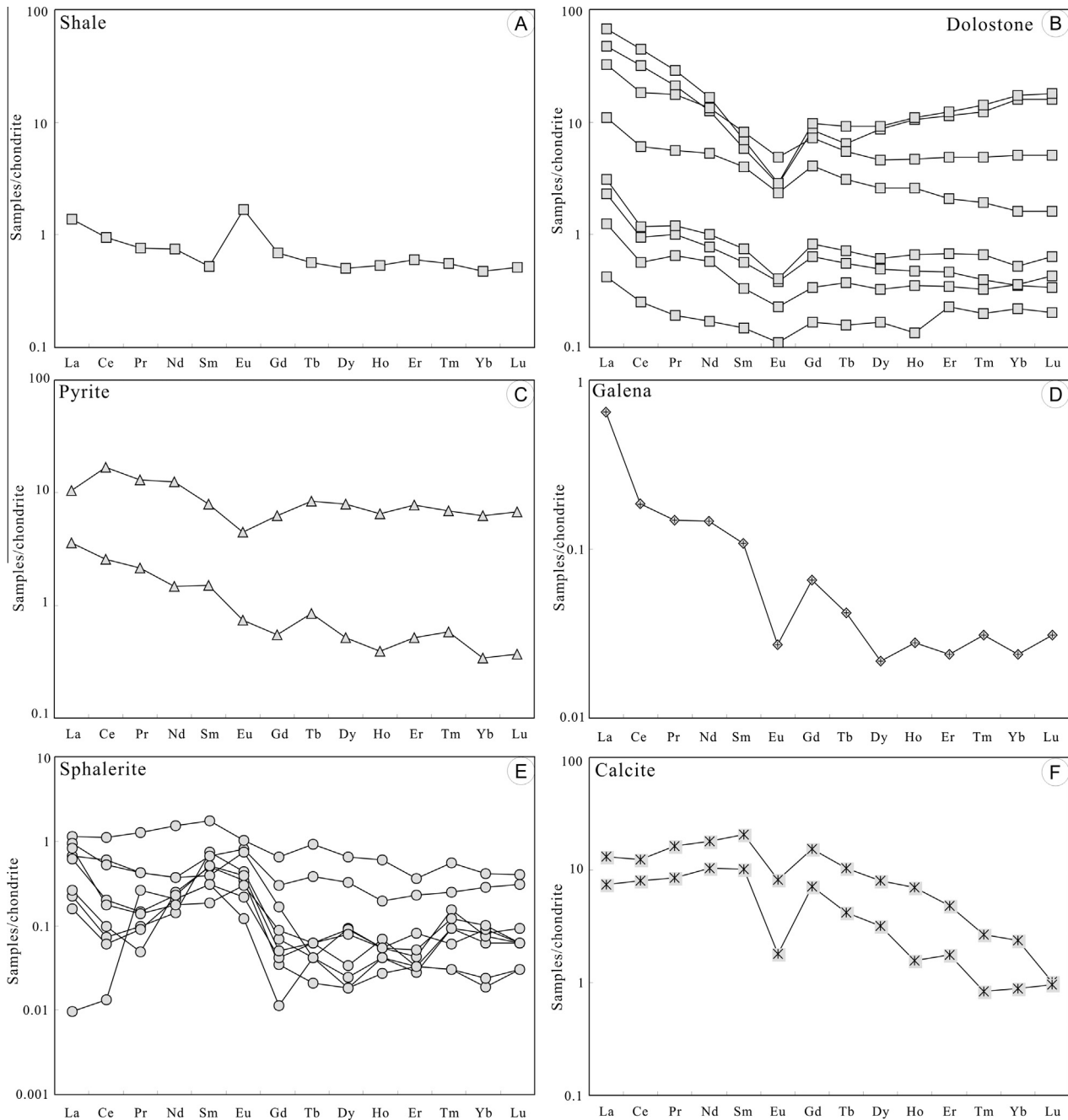
$$\delta\text{Eu} = \text{Eu}/\text{Eu}^* - \text{Eu}_N/0.5(\text{Sm}_N + \text{Gd}_N)$$

Doe, 1981). Additionally, all the sulfides and country whole-rock samples have  $\mu$  values (Table 4) within the range of crust. All these observations suggest that the Pb of sulfide ores and country rocks in the Banbanqiao deposit area has a crustal source. On the other hand, it is clear that country whole-rock samples have more radiogenic Pb than sulfides (Fig. 8A and B), suggesting that the country rocks are not the main source of Pb in the hydrothermal fluids. Previous studies have indicated that the Proterozoic basement rocks were one of the most important sources in the SYG province (e.g., Zheng and Wang, 1991; Han et al., 2007; Zhou et al., 2013a, 2014a). The Pb isotope data of the Banbanqiao deposit within the range of the basement rocks (Zhou et al., 2014a), so the majority of Pb sourced from the basements.

#### 5.1.4. Implications of rare earth elements

Rare earth elements (REE) aid in determining the origin of the ore-forming elements (e.g., Huston et al., 1995; Huang et al., 2010; Zhou et al., 2011; Souissi et al., 2013). The total REE contents

of pyrite and calcite are significantly higher than those of sphalerite and galena (Table 5), and the sulfide ores mainly consists of pyrite, sphalerite, galena and calcite, so the  $\Sigma\text{REE}$  of calcite and pyrite can approximately represent the  $\Sigma\text{REE}$  of the hydrothermal fluids (Zhou et al., 2011; Souissi et al., 2013). In the REE chondrite-normalized patterns (Fig. 9), pyrite (Fig. 9C) and calcite (Fig. 9F) samples have similar patterns to those of the hosting dolostone (Fig. 9B), but are different from those of shale (Fig. 9A). This indicates that REE in the hydrothermal solutions were likely to be sourced from the carbonate host rocks. Additionally, the  $\text{Eu}/\text{Eu}^*$  values of pyrite and calcite ( $\delta\text{Eu} = 0.21\text{--}0.86$ ) are significantly lower than 1, indicating that the hydrothermal fluids were Eu-depleted or derived from Eu-depleted source region. The Liangshan Formation shale whole-rock sample has positive Eu anomaly ( $\delta\text{Eu} = 2.79$ ), whereas the Dapu Formation dolostone whole-rock samples have negative Eu anomaly ( $\delta\text{Eu} = 0.34\text{--}0.70$ ). This also suggests that REE in the ore-forming fluids were likely derived from the carbonate host rocks.

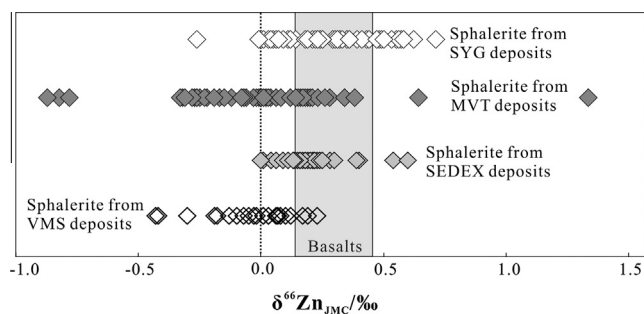


**Fig. 9.** (A–F) Chondrite-normalized REE patterns (Boynton, 1984). (A) REE pattern for shale. (B) REE patterns for dolostone. (C) REE patterns for pyrite. (D) REE pattern for galena. (E) REE patterns for sphalerite. (F) REE patterns for calcite.

## 5.2. Ore genesis

Isotope geochronology studies have suggested that the Pb–Zn mineralization in the SYG province occurred during 222–192 Ma in response to the closure of the Paleo-Tethys Ocean (Li et al., 2007b; Lin et al., 2010; Mao et al., 2012; Zhou et al., 2013a,d, 2015; Zhang et al., 2015), which is known as the Indosinian Orogeny (Hu and Zhou, 2012; Zhou et al., 2013a,d; Zhang et al., 2015). These deposits in the western Yangtze Block have been affected by multiple orogenic events after the Indosinian Orogeny (e.g., Zaw et al., 2007; Hu and Zhou, 2012). It is clear that most of these Pb–Zn deposits in the SYG province are epigenetic, but origin of them is complex and cannot easily determined, as suggested by Cd, Ge and Zn isotopes (Fig. 10; Zhu et al., 2013;

Zhou et al., 2014a,b; Meng et al., 2015). For example, although the ages (222–192 Ma) of Pb–Zn deposits is much younger than the mantle-derived Emeishan basalts (Ca. ~260 Ma; Zhou et al., 2002b), it has been suggested that the basalts provided ore-forming thermal dynamic and parts of metallogenic materials (such as O and S) for the deposits (Xie, 1963; Huang et al., 2010; Bai et al., 2013; Xu et al., 2014; Zhou et al., 2014a, 2014b; Zhang et al., 2015; Section 5.1). The Pb–Zn deposits in the SYG province can be comparable to typical MVT-type deposits (e.g., Leach et al., 2001, 2005, 2010; Muecher et al., 2005; Oliver, 1986, 1992; Pirajno, 2009, 2013) in terms of geological setting, ore-bearing rocks and source related to basin brine (Zheng and Wang, 1991; Zhou et al., 2001; Wu et al., 2013; Zhang et al., 2015). However, these deposits display a set of characteristics that contrast with



**Fig. 10.** Comparison of Zn isotopic compositions between sphalerite from SYG deposits and Pb–Zn deposits of MVT, SEDEX and VMS types (after Zhou et al., 2014b).

those of typical MVT-type deposits, including ore-controlled thrust faults and fold structures (convergent geodynamic setting), high grade of Pb + Zn (>15 wt.%), complex sources (carbonate host rocks, Emeishan basalts and basement rocks; see Section 5.1) of ore-forming elements, moderate temperature (150–270 °C), medium to low salinity (<15 wt.% NaCl), weak wall rock alteration and the lack of collapse breccias (e.g., Han et al., 2007; Bai et al., 2013; Zhou et al., 2011, 2013a, 2014b; Xu et al., 2014). Therefore, the Banbanqiao deposit is a carbonate-hosted, stratiform, anticline-controlled, epigenetic and high grade Zn–Pb deposit formed by elemental compositions of mixed origin, and is a typical SYG-type deposit in the western Yangtze Block, southwest China (Zhou et al., 2013a, 2014b, 2015). The mineralization process is similar to that of brine-related deposits elsewhere, including extraction of ore-forming elements from all kinds of rocks by convective circulation of hydrothermal fluids, and then they mixed with sulfate ion- and organic matter-bearing cool water and subsequent reduction of  $\text{SO}_4^{2-}$  to  $\text{S}^{2-}$  and precipitation of these elements in favorable structural and lithological units (Hu and Zhou, 2012; Zhou et al., 2014b).

## 6. Conclusions

Ore bodies in the Banbanqiao deposit occur within axis of NNE-trending Banbanqiao anticline. C–O–S–Pb isotopes and REE suggest: (i) C in the hydrothermal fluids was the dissolved product of the carbonate host rocks, (ii) O in the ore-forming fluids was derived from a mixed source of mantle-derived O in Emeishan basalts and dissolved O from the carbonate host rocks, (iii) S in the ore-forming solutions was sourced from evaporites by TSR with a limited influence of mantle-derived S, (iv) Pb in the hydrothermal fluids was originated from a mixed source of the basement rocks and the carbonate host rocks, and (v) REE in the hydrothermal fluids were sourced from the carbonate host rocks. The fluids' mixing is an important mechanism for the Banbanqiao sulfide formation. Ore genesis of the Banbanqiao deposit is different from the typical MVT-type deposit, it is a carbonate-hosted, stratiform, anticline-controlled, epigenetic and high grade Zn–Pb deposit formed by elemental compositions of mixed origin, and is a typical SYG-type deposit.

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