



# Microscale sulfur isotopic compositions of sulfide minerals from the Jinding Zn–Pb deposit, Yunnan Province, Southwest China<sup>☆</sup>



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## ARTICLE INFO

### Article history:

Received 8 March 2013

Received in revised form 19 July 2013

Accepted 23 July 2013

Available online 25 August 2013

### Keywords:

Sulfur isotopes

Sulfide minerals

Jinding

Zn–Pb deposit

Southwest China

## ABSTRACT

The Jinding Zn–Pb deposit, located in the Lanping basin in Northwest Yunnan Province, is the largest Zn–Pb deposit in China, and also probably the youngest sediment-hosted super giant Zn–Pb deposit in the world. Its genesis differs from the well-known major types of sediment-hosted Zn–Pb deposits. Based on mineral paragenesis and textures, there are two stages of mineralization: stage 1 that is typically characterized by fine-grained sulfide minerals (galena, sphalerite, pyrite and marcasite) disseminated in sandstones of the Lower Cretaceous Jingxing Formation (K<sub>1j</sub>), and massive sulfides in limestone breccias of the Paleocene Yunlong Formation (E<sub>1y</sub>); and stage 2 which mainly occurs as coarse-grained galena veins crosscutting stage 1 sulfides, and minor amounts of colloform sphalerite intergrown with galena. In situ sulfur isotopic analyses of galena, sphalerite and pyrite were determined by secondary ion mass spectrometry (SIMS), and showed highly variable  $\delta^{34}\text{S}$  values (–42.1‰–7.7‰) of different ore types. Stage 1 mineralization has  $\delta^{34}\text{S}$  values from –42.1‰ to –10.2‰ with the majority ranging from –26‰ to –14‰. Stage 2 mineralization has higher  $\delta^{34}\text{S}$  values (–8.3‰–7.7‰). Combined with the geological settings and mineral paragenesis, the sulfur isotopic data presented here suggest multiple sulfur sources (biogenic sulfur + evaporites) and formation mechanisms for reduced sulfur (H<sub>2</sub>S). H<sub>2</sub>S responsible for stage 1 sulfide precipitation was associated with bacterial sulfate reduction (BSR). However, H<sub>2</sub>S of stage 2 was likely derived from thermochemical sulfate reduction (TSR). The most reasonable scenario for the stage 1 mineralization is a metal-bearing brine mixing with an H<sub>2</sub>S-rich fluid, thereby causing rapid sulfide precipitation. Till the stage 2, the ore-forming fluid shifted to the meteoric water that infiltrated and reacted with evaporitic rocks, leached metals and transported them as sulfate- or sulfite-complexes to the Jinding dome where the oxidized sulfur was reduced by organic matters to H<sub>2</sub>S, leading to precipitation of metal sulfides. In contrast to other sulfide deposits in the Lanping basin, biogenic sulfur might have played a key role in the mineralization process, especially during the early stage of formation of the Jinding Zn–Pb deposit.

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## 1. Introduction

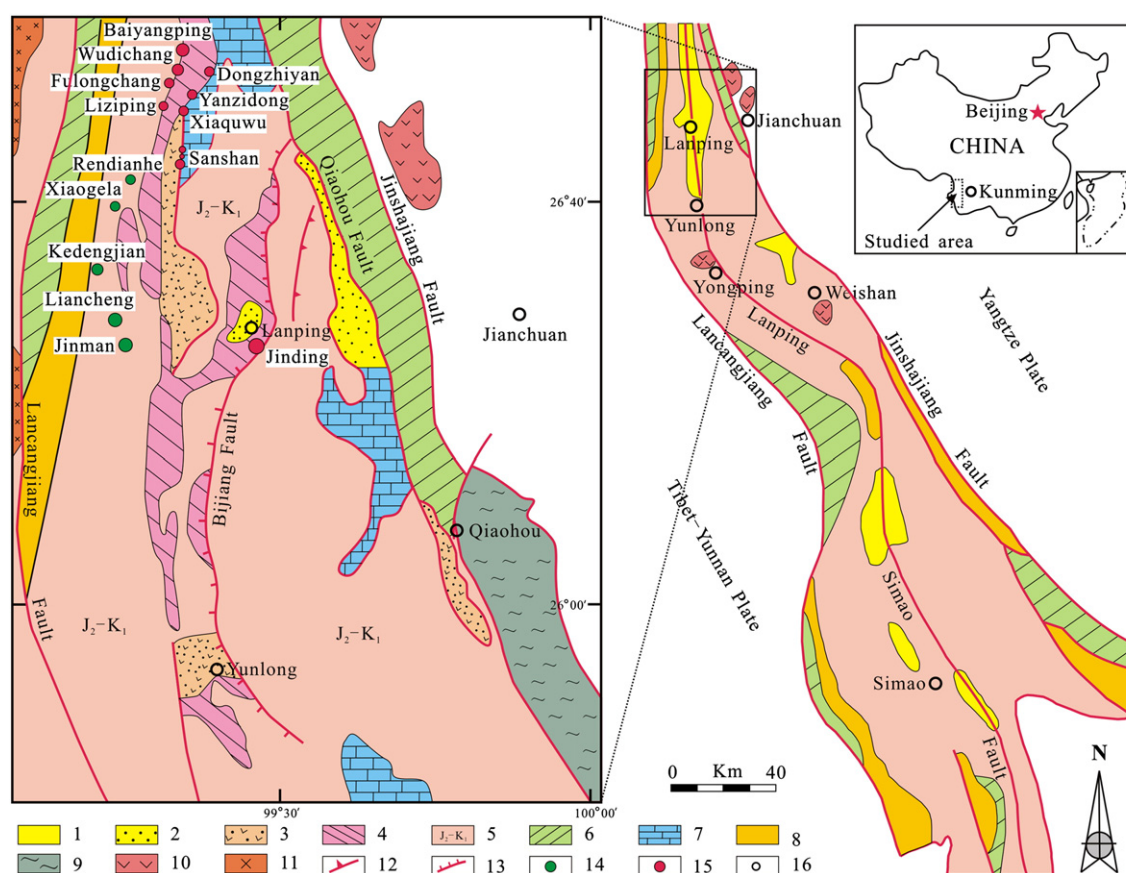
Numerous sediment-hosted base metal deposits are located in the Tuotuohe, Yushu, Changdu, and Lanping basins in the Sangjiang area along the northeastern margin of Tibetan plateau, Southwest China. Particularly in the Lanping basin, there are a lot of significant economic sediment-hosted Zn–Pb–Cu–Ag deposits, like the Jinding super giant Zn–Pb deposit (Shi et al., 1983; Qin and Zhu, 1991; Luo et al., 1994; Li and Kyle, 1997; Kyle and Li, 2002; Xue et al., 2007a; Tang et al., 2011), the Baiyangping Zn–Pb–Ag–Cu concentrated district (Chen et al., 2000; Gong et al., 2000; Yang et al., 2003; Liu et al., 2010; Feng et al.,

2011), and the Jinman Cu deposit (Yan and Li, 1997; Ji and Li, 1998; Liu et al., 2001; Gao et al., 2006; Zhang and Wen, 2012) (Fig. 1). These deposits formed in the highly deformed Paleogene foreland basin within an active collisional setting (Hou et al., 2006, 2007; Xue et al., 2007a; Hou and Cook, 2009). The emplacement of these sulfide deposits is strictly constrained by the Cenozoic thrust fault systems related to Indo-Asian continental collision (Xu and Li, 2003; L.Q. He et al., 2004; Xu and Zhou, 2004). These large thrust nappe-controlling sediment-hosted base metal deposits in the compressional regime distinguish from the major types of sediment-hosted base metal deposits recognized in the world, including Sedimentary Exhalative-type (SEDEX) Zn–Pb deposits, Mississippi Valley-type (MVT) Zn–Pb deposits, Sandstone-type (SST) Pb–Zn deposits and Sandstone-type (SSC) Cu deposits (Misra, 2000; Leach et al., 2005; He et al., 2009; Wang et al., 2009). The SEDEX deposits are generally considered to form in the continental rifting environments (Basuki and Spooner, 2004), in contrast to the

<sup>☆</sup> This article belongs to the Special Issue on Orogenesis and metallogenesis in the Sanjiang Tethyan Domain.

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**Fig. 1.** Sketch geological map of the Lanping–Simao basin in western Yunnan, China, with enlargement of the Lanping basin showing the main mineralized zones. 1—Cenozoic clastic rocks. 2—Miocene sandstone, mudstone and conglomerates. 3—Eocene–Oligocene sandstone and conglomerates. 4—Paleocene Yunlong Formation. 5—Middle Jurassic–Lower Cretaceous silicic clasts. 6—Middle–Upper Triassic volcanics, silicic clasts and carbonate. 7—Upper Triassic limestones. 8—Paleozoic metamorphic flysch. 9—Precambrian–Devonian metamorphic rocks. 10—Neogene alkali rocks and trachytes. 11—Yanshanian diorites and quartz diorites. 12—Overthrusting fault. 13—Growth fault. 14—Cu mineralized zone. 15—Pb–Zn mineralized zone. 16—City. Modified after Zhao (2006) and Xue et al. (2007a).

MVT deposits that usually occur in the orogenic foreland basins (Bradley and Leach, 2003) or intracontinental rifting basins (Clendenin and Duane, 1990; Sangster, 1990). The SST deposits are hosted in mature marine quartz-rich sandstones in prolonged stable geological settings (Bjorlykke and Sangster, 1981), whereas, the SSC deposits form within the red sandstones (Misra, 2000). Therefore, studies of the Zn–Pb–Cu–Ag deposits in southwestern China provide good opportunities to study the base-metal ore-forming systems in the continental collisional orogenic settings (He et al., 2009).

The Jinding deposit is the largest Zn–Pb deposit in China, and also probably the youngest sediment-hosted super giant Zn–Pb deposit in the world (Xue et al., 2000, 2007a; Khin et al., 2007). It consists of approximately 220 Mt base metals, covering a surface area of about 8 km<sup>2</sup> (Third Geological Team, 1984), which were estimated about 317 × 10<sup>4</sup> m<sup>3</sup> reduced sulfur (H<sub>2</sub>S) involved in the mineralization (Gao et al., 2008). The deposit, hosted in the siliciclastic strata of Early Cretaceous and Paleocene, is characterized by simple mineralogy, fine-grained ore textures and involvement of basinal brines in the mineralization (Qin and Zhu, 1991; Li, 1998; Kyle and Li, 2002; Chi et al., 2007). The genesis of the deposit has been a subject of debate and controversy since the 1980s. Previous studies have proposed two contrasting genetic models: (1) syngenetic origin with the emphasis on the mineralization during the syndepositional period (Shi et al., 1983; Bai et al., 1985; Zhao, 1989; Qin and Zhu, 1991; Luo et al., 1994; Hu et al., 1998), and (2) epigenetic origin focusing on late hydrothermal superimposition or modification (Gao, 1989; Hu, 1989a; Li and Kyle, 1997; Kyle and Li, 2002; Xue et al., 2007a). These studies used the conventional bulk-grain analytical techniques for sulfur isotopic analysis and reported  $\delta^{34}\text{S}_{\text{V-CDT}}$  values of sulfide minerals from the Jinding Zn–Pb

deposit that ranged from −30.4‰ to −1.8‰. Based on these values, Zhao (1989), and Zhou and Zhou (1992) suggested multiple sulfur sources of evaporites and mantle-derived sulfur. However, Ye et al. (1992), Xue et al. (2002) and Gao et al. (2008) suggested that the source of sulfur was evaporites in the Lanping basin, and reduced sulfur might be derived from bacterial sulfate reduction (BSR) and thermochemical sulfate reduction (TSR). Because sampling techniques such as micro-drilling or mineral separation greatly exceeds the scale of texture variations ( $\mu\text{m}$ ) in sulfide minerals, it is difficult to obtain pure minerals of the same generation for sulfur isotopic analysis by classical methods. Therefore, previously reported  $\delta^{34}\text{S}$  values of sulfides from the Jinding deposit likely represented average values of different mineralization stages, which made the sources of the sulfur and mechanisms of sulfide precipitation, difficult to interpret.

While analysis of mg-quantities of material is routine for both stable and radiogenic isotopic analyses, important geologic features such as zoned minerals and micro-scale alteration phases require in situ measurements at the micron scale (e.g., Reed, 1990; Neal et al., 1995). The secondary ion mass spectrometry (SIMS) is capable of performing in situ measurements with ca. 10  $\mu\text{m}$  resolution and progress has been made in developing precise and accurate methods for the isotopic analysis using this instrument (McKeegan, 1987; Reed, 1989; Neal et al., 1995; Riciputi et al., 1998; Ireland, 2004; Kozdon et al., 2010). Many studies have shown unique advantages of in situ analysis for sulfur isotopes of microscale intracrystals in understanding the detailed mineralizing processes that cannot be resolved from bulk  $\delta^{34}\text{S}$  values (Delouie et al., 1986; Layne et al., 1991; McKibben and Eldridge, 1995; Peevler et al., 2003; Ferrini et al., 2010; Drake et al., 2013). However, SIMS was chosen in this study to determine in situ sulfur isotopes of sulfide

minerals from different mineralization stages of the Jinding Zn–Pb deposit, which could effectively avoid mixed sulfur isotopic information introduced by the conventional sulfur isotopic analysis used before. In situ measurements of sulfur isotope enable us to discuss the sources of sulfur and formation mechanisms of reduced sulfur of different mineralization stages, and finally conclude the genetic history of the Jinding deposit.

## 2. Geological settings

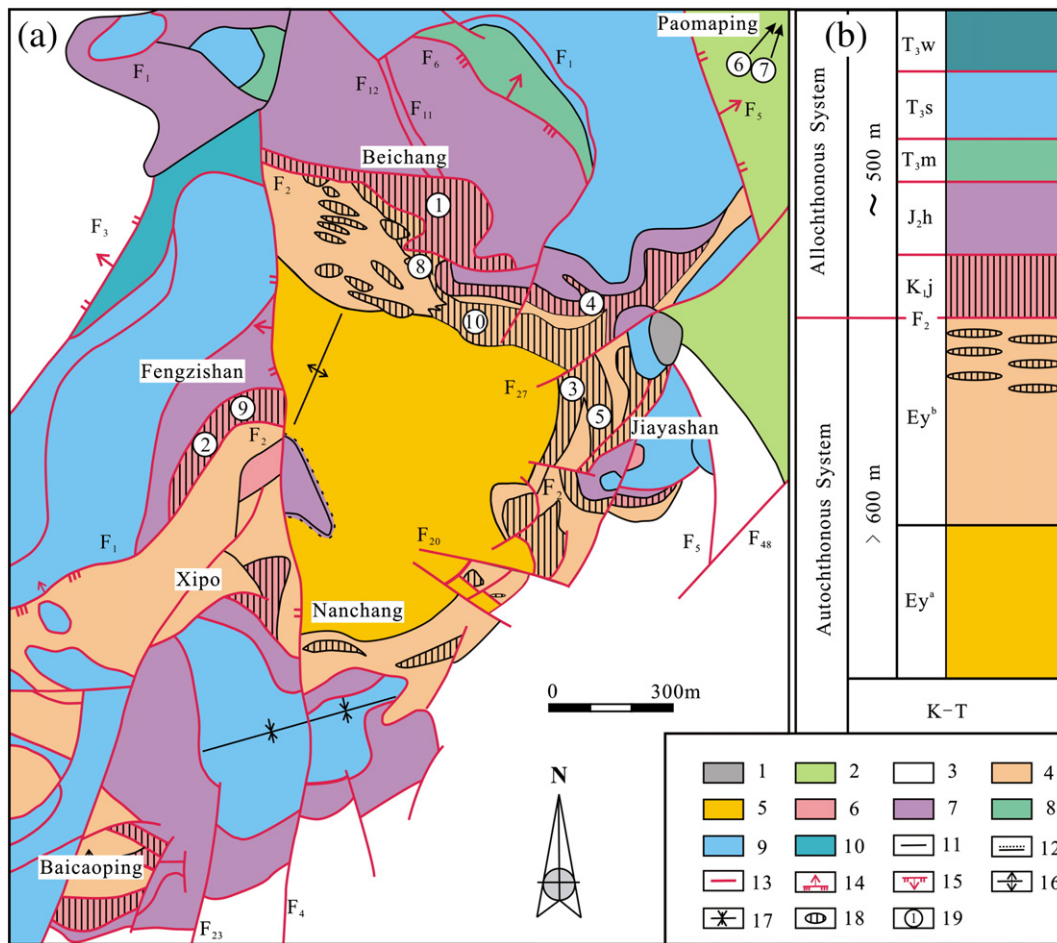
### 2.1. Regional geology

The Sanjiang area, defined by the Jinshajiang–Ailaoshan, Lancangjiang and Nujiang shear zones in the southwestern China, has experienced the multi-episodes of ocean–continental subduction in the Tethys Period and the continental–continental collision in Cenozoic; various ore deposits formed in the ocean growth and subduction environment, as well as the transition stage from the main collision to late collision, and Cenozoic collision induced the formation of porphyry Cu–Au deposits, sediment-hosted Pb–Zn–Ag–Cu deposits and orogenic Au deposits (Deng et al., 2010, 2012).

The Lanping–Simao basin, known as part of Sanjiang fold-and-thrust belt, is a north–northwest-trending intracontinental basin developed on the Changdu–Lanping–Simao microplate between the Tibet–Yunnan

plate west of the Lancangjiang fault and the Yangtze plate east of the Jinshajiang–Ailaoshan fault (Fig. 1) (Yin et al., 1990). The Yangtze plate, Tibet–Yunnan plate and the Changdu–Lanping–Simao microplate initially departed from Gondwana and collaged to Eurasia during the Late Paleozoic and Early Mesozoic (Sengor, 1985; Chen et al., 1995; Scotese, 2000; Veevers, 2006, 2009; Metcalfe, 2011; Yu et al., 2012; Lehmann et al., 2013). In the Late Paleozoic, the Changdu–Lanping–Simao microplate was separated by oceans (Jinshajiang Paleo-Tethyan Ocean to the east and Lancangjiang Paleo-Tethyan Ocean to the west) from the Yangtze plate and Tibet–Yunnan plate (Feng, 2002; Tao et al., 2002; Metcalfe, 2006; Xue et al., 2007a; Jian et al., 2009; Metcalfe, 2011). When the Paleo-Tethyan Ocean was closed in the Late Permian or Early Triassic, the Lancangjiang and Jinshajiang oceanic plates subducted eastward and westward beneath the microplate, respectively, leading to a conjunction of the Yangtze plate, Tibet–Yunnan plate and the clamping microplate (Luo et al., 1994; Jin et al., 2003). Then, the Lanping–Simao basin, based on the Paleo-Tethyan basement, started an intracontinental evolution which approximately included Late Triassic rifting, Jurassic–Cretaceous depression, and Paleogene foreland basin (Yin and Harrison, 2000; Wang et al., 2001; Spurlin et al., 2005; Li et al., 2006; He et al., 2009).

The metamorphic basement of the Lanping–Simao basin consists of Proterozoic and Paleozoic strata, which are mainly distributed along the margins of the basin (Xue et al., 2007a). Inside the basin, it was



**Fig. 2.** (a) Map of the geology and structures associated with the Jinding Zn–Pb deposit (Third Geological Team, 1984) and (b) schematic stratigraphic column in the Jinding deposit. 1–Pleistocene gravel and sand (QP). 2–Paleocene Guolang Formation (Eg), muddy siltstone intergrown with fine sandstone. 3–Paleocene Yunlong Formation (Ey<sup>2</sup>), conglomerates entraining gypsum and siltstone. 4–Paleocene Yunlong Formation (Ey<sup>3</sup>), gypsum-bearing limestone breccia and siltstone. 5–Paleocene Yunlong Formation (Ey<sup>1</sup>), fine sandstone and siltstone containing limestone blocks. 6–Lower Cretaceous Jingxing Formation (K<sub>1j</sub>), sandstone and sandy limestone breccia. 7–Middle Jurassic Huakaizuo Formation (J<sub>2h</sub>), silty mudstone, siltstone and fine sandstone. 8–Upper Triassic Maichuqing Formation (T<sub>3m</sub>), silty mudstone. 9–Upper Triassic Sanhedong Formation (T<sub>3s</sub>), calcareous mudstone, firestone- or bitumen-bearing dolomitic limestone. 10–Upper Triassic Waigucun Formation (T<sub>3w</sub>), muddy siltstone. 11–Geological boundary. 12–Unconformable boundary. 13–Ambiguous fault. 14–Thrust fault. 15–Normal fault. 16–Anticline axes. 17–Syncline axes. 18–Zn–Pb ores. 19–Sample location.



mainly filled with the Mesozoic–Cenozoic strata, comprising Late Triassic marine clastics, carbonates and sandy mudstones, Jurassic marine–terrestrial red clastics and minor carbonates, Cretaceous shallow lake-facies red clastics, and Cenozoic siliciclastics (Mu et al., 1999; Zhong et al., 2000; Liao and Chen, 2005). At least six horizons of evaporites, dominated by gypsum with minor halite, and occasionally also sylvite, with a local total thickness of over 2 km, have mainly been recognized in Middle–Upper Triassic, Middle–Upper Jurassic and Paleocene sediments (Gao, 1989; Xue et al., 2007a; He et al., 2009).

Over 100 Pb–Zn–Ag–Cu deposits or occurrences are located in the Lanping basin, most of which are concentrated in the northern segment of the basin and spatially classified into four ore belts (Jinman Cu belt, Baiyangping Pb–Zn–Ag–Cu belt, Sanshan Pb–Zn belt and Jinding Zn–Pb deposit) (Hou et al., 2006; He et al., 2009). These deposits are commonly hosted in the Mesozoic–Cenozoic siliciclastics, and controlled by the Cenozoic thrust fault structures (Wang et al., 2001; Hou et al., 2006, 2008). Besides, the local continental crust uplifting, associated with India–Eurasian continental collisional compression, might produce the dome structure which provided favorable space for metal precipitation (Xue et al., 2002). Cenozoic magmatic rocks (68–23 Ma) are dominantly exposed along the margins of the basin, except a few outcrops inside the basin (e.g., Zhuopan intrusives in Yongping County) (Zhang et al., 2000; Hou et al., 2003; Xue et al., 2003; Liu et al., 2006).

## 2.2. Deposit-scale geology

The Jinding Zn–Pb deposit, consisting of Paomaping, Beichang, Jiayashan, Fengzishan, Nanchang, Xipo and Baicaoping ore blocks (Fig. 2a), is located at the eastern wing of Gaoping–Laomujing syncline and to the west of Pijiang fault (part of the Lanping–Simao fault, Luo et al., 1994). The strata include rocks of both the autochthonous and the overlying allochthonous systems as a result of regional westward over-thrusting. The allochthonous system containing Upper Triassic Waigucun, Sanhedong and Maichuqing Formations, Middle Jurassic Huakaizuo Formation and Lower Cretaceous Jingxing Formation, is juxtaposed over the autochthonous system consisting of Paleocene Yunlong Formation and the Mesozoic strata (Fig. 2b). The Jinding deposit is hosted within a tectonic dome, approximately 3 km long and 2.5 km wide with a NNE-trending axis. The autochthon comprises the core of the dome, and is surrounded by the allochthon. Two systems are separated by the overthrust fault (F<sub>2</sub>). Sulfide ores, chiefly occurring as sheet-like, stratoid or lenticular ores controlled by lithofacies and structures, are hosted in the limestone breccias of Paleocene Yunlong Formation and the overlying sandstones of Early Cretaceous Jingxing Formation (Fig. 3) (Third Geological Team, 1984; Luo et al., 1994). Abundant sulfates (such as gypsum, celestite and barite) discontinuously occur in the vicinity of the sulfide ores. Organic matters are wide-spread in the ore field, and occur as bitumen and fossil oil fillings in the fractures and dissolution cavities of ores, and organic fluid inclusions discovered in transparent and non-transparent minerals (Fu, 2004; Xue et al., 2007a). Hu (1989b) reported that both ore-bearing strata and non ore-bearing strata (Triassic limestones) in the Jinding deposit showed much higher contents of organic matters (mean 3.55% and 1.99%, respectively) than similar sediments (<0.5% for carbonate rocks, and 0.05% for sandstones) in regional area.

The deposit has had a complex fluid history. However, sulfide mineralization can be grouped into two stages based on mineral paragenesis and textures (Fig. 4).

**Stage 1 mineralization** Stage 1 sulfides can be further subdivided into two sub-types: (1) fine-grained disseminated in sandstones and (2) massive or as veins in limestone breccias. The relationship between these two sub-types is difficult to distinguish, because they are hosted in different rock units, (1) within the upper ore-bearing layer of

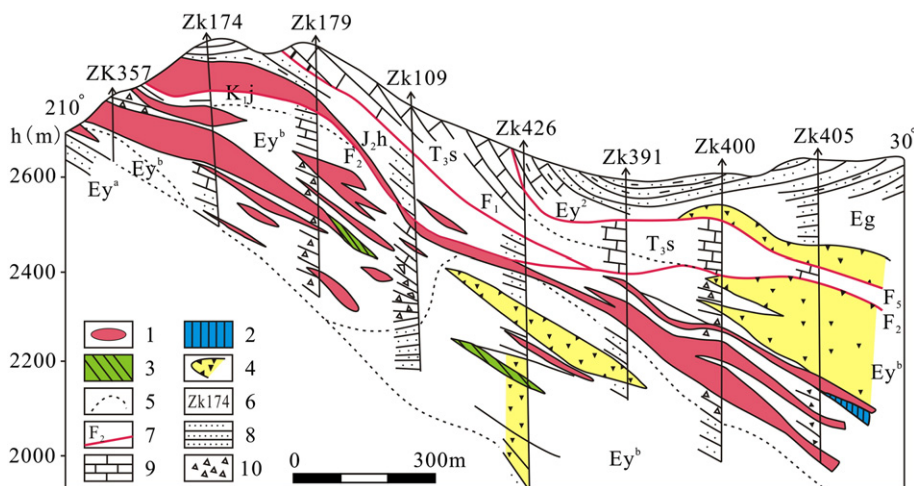
Lower Cretaceous Jingxing Formation quartz sandstones and (2) within the lower counterpart of Paleocene Yunlong Formation limestone breccias. Stage 1 is characterized by extensive Zn mineralization. The (1) sub-type ores display quartz, feldspar and calcite, sphalerite, pyrite (sometime marcasite), and galena as dominant mineral components (Figs. 5a, 6a, b). Sulfide minerals occur as fine-grained (0.05–0.03 mm) disseminated mineralization, together with diagenetic calcite cements, detrital quartz and feldspar. The (2) sub-type ores are characterized by a simple mineral assemblage of sphalerite, galena, pyrite and calcite hosted in limestone breccias (Fig. 5b, c, e).

**Stage 2 mineralization** This stage of mineralization is mainly characterized by the late coarse-grained galena veins (up to 3 cm in width) crosscutting stage 1 sulfide mineralization (Figs. 5e, 6c, f), and, minor colloform sphalerite intergrown with vein galena hosted by limestone breccias (Figs. 5f, 6g). Colloform sphalerite shows concentric ring structures and is surrounded by galena. This texture is similar to sulfides that were interpreted to have formed from late metal-rich colloidal solution (Third Geological Team, 1984; Zhao, 2006; Zeng, 2007). Barite occurs with stage 2 galena (Fig. 6d, f).

## 3. Samples and analytical methods

Ten polished thin sections were prepared from hand specimens sampled from Paomaping, Beichang, Jiayashan and Fengzishan districts. Mineralogical and textural relationships within the samples were characterized using both optical and scanning electron microscopy (SEM). Thin sections were examined in transmitted and reflected light using a polarizing microscope. Then, these sections were carbon coated, to create a conductive surface, prior to analysis using a Cambridge Stereoscan 120 scanning electron microscope (SEM) at the University of Manitoba (Canada). The SEM is equipped with a back-scattered electron detector as well as an energy dispersive X-ray spectroscopy detector which was used to further characterize the textures present within the samples and for qualitative chemical characterization of the minerals. The rectangular thin sections were cut into 25 millimeter diameter round thin sections, to fit the SIMS sample holders. The round thin sections were cleaned and gold coated (200 Å thick). For sulfur isotope analysis, a 1.8 nA primary beam of Cs<sup>+</sup> was accelerated (+10 kV) onto the sample surface with a sputtering diameter of 25 μm. The instrument operated at a 200 V sample offset for sulfur, –10 kV secondary accelerating voltage and at mass resolving power of 350. For detailed description of operating conditions see Riciputi et al. (1998). Ions were detected with an ETP electron multiplier coupled with and ion-counting system and an overall dead time of 34 ns. <sup>32</sup>S<sup>–</sup> and <sup>34</sup>S<sup>–</sup> were detected sequentially by switching the magnetic field. A typical analysis lasted 6 min, comprising 50 cycles of analysis.

During the measurement process by SIMS, an intrinsic mass dependent bias is introduced, which is referred to as instrumental mass fractionation (IMF) and typically favors the low mass isotope. The greatest contributor to the IMF is the ionization process, which depends most strongly upon sample characteristics (i.e., chemical composition). This is referred to as compositionally dependent fractionation or “matrix effects” (e.g., Riciputi et al., 1998). Therefore, accurate isotopic SIMS analysis requires that IMF be corrected for by standardizing the IMF using mineral standards that are compositionally similar to the unknown. SIMS results from the standard are compared to its accepted isotopic composition in



**Fig. 3.** Geological section of Beichang–Paomaping ore blocks in the Jinding Zn–Pb deposit. 1–Pb–Zn ore. 2–Pyrite ore. 3–Celestite ore. 4–Gypsum ore. 5–Strata boundary. 6–Drilling No. 7–Numbered faults. 8–Siltstone. 9–Limestone. 10–Limestone breccias. Other stratigraphic markers are similar to those in Fig. 2.

order to calculate a correction factor that is applied to the unknowns measured during the same analysis session (e.g. Leshin et al., 1998).

The standards used in this study were large, homogeneous sulfide grains from the Balmat mine, New York (Crowe and Vaughan, 1996). These standards are pyrite with a  $\delta^{34}\text{S}$  of +15.1‰ ( $\pm 0.3\%$ ), sphalerite (+14.0‰  $\pm 0.3\%$ ) and galena (+15.6‰  $\pm 0.3\%$ ) with the overall spot-to-spot analytical precision of ~0.4‰. Data is reported in the conventional  $\delta$ -notation relative to the Vienna-Canyon Diablo Troilite (V-CDT) standard. Sulfur isotope analyses consisting of 21 spots on pyrite, 37 spots on galena and 48 spots on sphalerite from diverse mineralization types are summarized in Table 1 with examples in Fig. 6.

**4. Results**

The results showed a much wider range of  $\delta^{34}\text{S}$  values from –42.1‰ to 7.7‰, than previously published sulfur isotopic data (–30.4‰ to –1.8‰) produced by bulk analysis (Ye et al., 1992; Zhou and Zhou, 1992). In this paper, we were able to correlate our in situ,

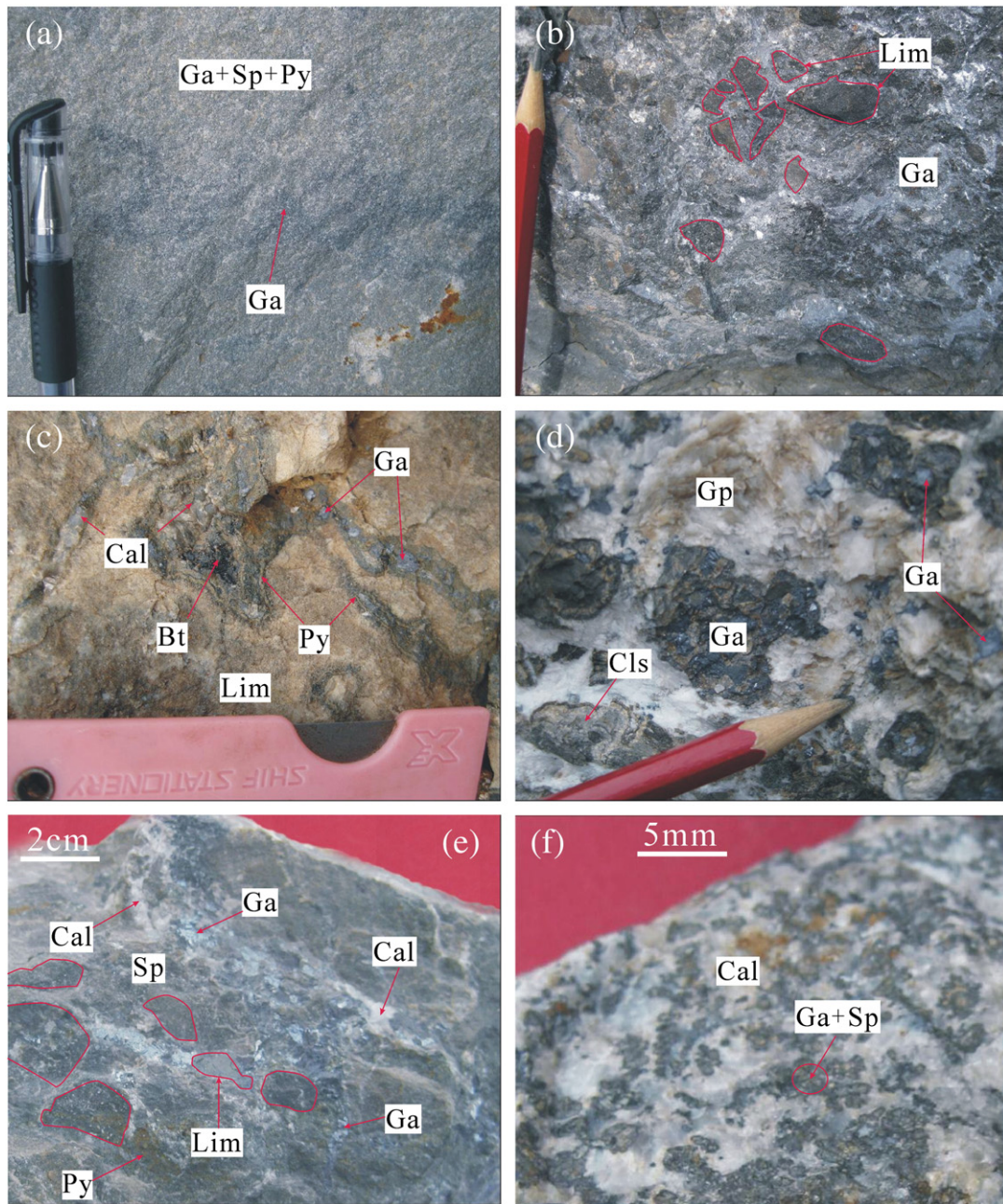
micro-analytical, sulfur isotopic data with distinct generations of sulfides and textures (Figs. 7 and 8). Stage 1 sulfides showed the overall  $\delta^{34}\text{S}$  values ranging from –42.1‰ to –10.2‰ (Fig. 7a). Fine-grained disseminated sulfides hosted in sandstones showed a wide  $\delta^{34}\text{S}$  range from –42.1‰ to –10.4‰, whereas massive sulfides hosted in limestone breccias had a narrow range of  $\delta^{34}\text{S}$  values from –28.6‰ to –10.2‰. Sulfides of stage 2 had higher  $\delta^{34}\text{S}$  values from –8.4‰ to 7.7‰ (Fig. 7b).

Fig. 8 showed the variation in  $\delta^{34}\text{S}$  values for different sulfide minerals from the Jinding Zn–Pb deposit. Stage 1 pyrite had  $\delta^{34}\text{S}$  values from –26.9‰ to –12.6‰, similar to coeval galena (–39.6‰ to –10.2‰) and sphalerite (–42.1‰ to –10.4‰). Stage 2 galena had  $\delta^{34}\text{S}$  values from –8.4‰ to 7.7‰, whereas stage 2 sphalerite had  $\delta^{34}\text{S}$  values from –8.3‰ to 2.9‰. Different ore blocks in the Jinding deposit displayed a wide range of  $\delta^{34}\text{S}$  values of sulfide minerals, especially in the Beichang and Fenzgishan blocks. Some extremely negative  $\delta^{34}\text{S}$  values (<–30‰) were found in the stage 1 sulfides from the Fenzgishan block, which had been less reported for the Jinding deposit.

MINERAL	Stage 1 mineralization		Stage 2 mineralization
	Disseminated mineralization	Massive or vein mineralization	Vein galena and colloform sphalerite
Pyrite	▬ ▬ ▬ ▬	▬ ▬ ▬ ▬	
Marcacite	▬ ▬ ▬ ▬		
Sphalerite			▬ ▬ ▬ ▬
Galena	▬ ▬ ▬ ▬	▬ ▬	
Calcite	▬ ▬	▬ ▬ ▬ ▬	▬ ▬ ▬ ▬
Celestite			▬ ▬
Barite			▬ ▬ ▬ ▬
Quartz	▬ ▬ ▬ ▬		
Gypsum			▬ ▬
Organics	▬ ▬	▬ ▬	▬ ▬

**Fig. 4.** Simplified paragenetic sequence of major sulfides and gangue minerals from the Jinding Zn–Pb deposit. Stages are defined primarily by sulfide associations and textural variations at the thin section scale. Solid bars represent the distribution of major minerals within a given stage; four broken bars represent minor occurrences; two broken bars represent trace occurrences.





**Fig. 5.** Mineralization types from the Jinding Zn–Pb deposit. (a) Disseminated sulfides of stage 1 in sandstone are crosscut by the galena vein of stage 2. (b) Massive galena of stage 2 cements limestone breccias. (c) Sulfide vein consisting of galena and pyrite of stage 2 fills in the fractures between breccias, and is intergrown with organics (bitumen) and calcite. (d) Coarse-grained galena of stage 2 is intergrown with celestite and gypsum. (e) Coarse-grained galena vein of stage 2 crosscuts massive sphalerite of stage 1 in limestone breccias. (f) Limestone-hosted ore shows colloform sphalerite and galena of stage 2. Abbreviations: Bt—bitumen, Cal—calcite, Cls—celestite, Ga—galena, Gp—gypsum, Lim—limestone breccias, Py—pyrite, Sp—sphalerite.

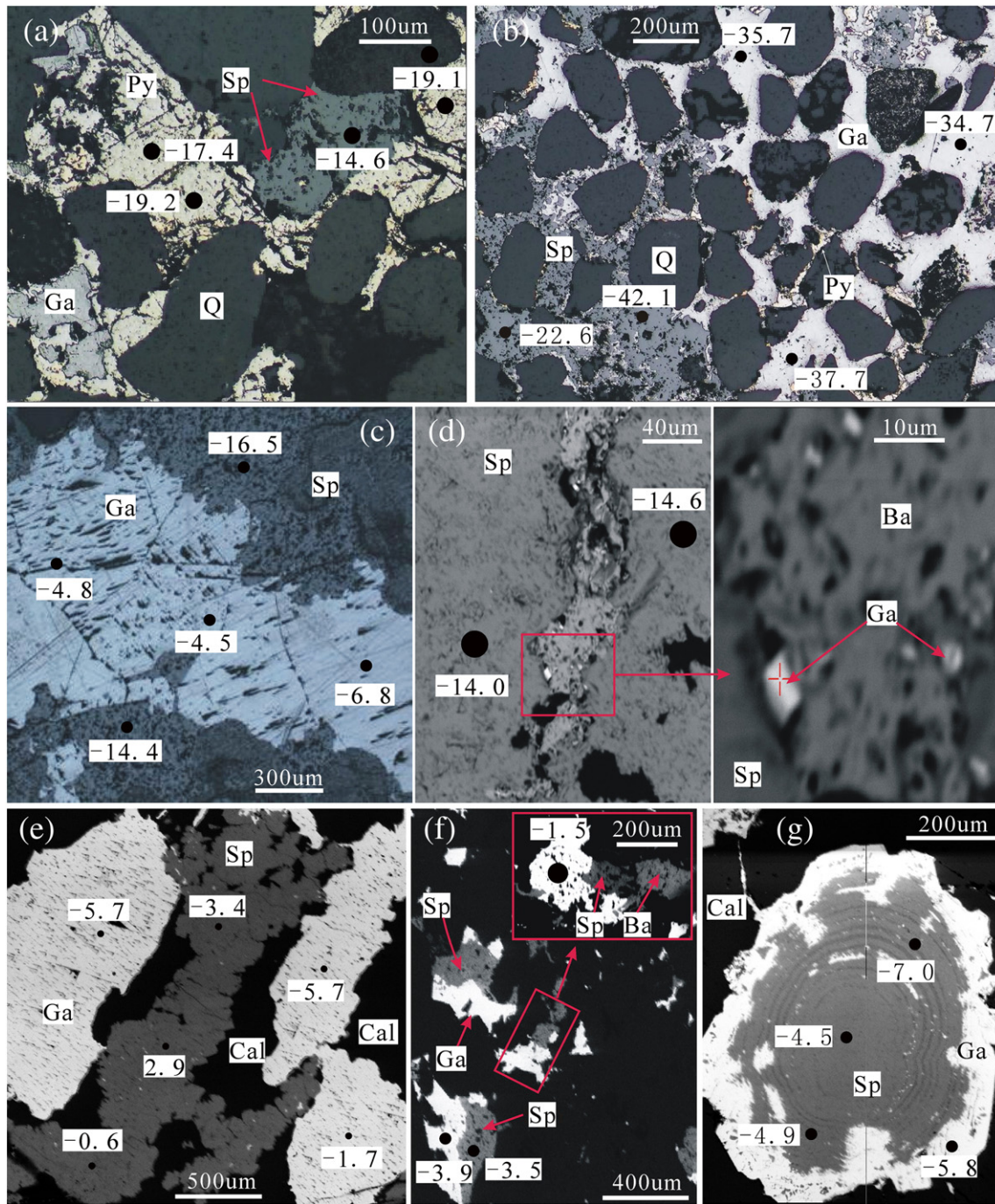
## 5. Discussions

The sulfur isotopes ( $\delta^{34}\text{S}$ ) of ore deposits are generally able to place important constraints on the nature of the ore-forming fluid, and the genetic processes for mineralization (e.g., sources of reduced sulfur, mechanisms for sulfate reduction, and related physico-chemical conditions) (Jørgensen, 1979; Ohmoto and Rye, 1979; Ohmoto, 1992; Basuki et al., 2008; Wagner et al., 2010). The most striking characteristics of sulfur isotopes from the Jinding Zn–Pb deposit are the highly variable and low  $\delta^{34}\text{S}$  values for stage 1 sulfide minerals and the relatively higher  $\delta^{34}\text{S}$  values for stage 2 sulfide minerals (Figs. 7 and 8).

### 5.1. Source(s) of sulfur and sulfate reduction mechanisms

Numerous studies (Sakai, 1968; Ohmoto, 1972; Peevler et al., 2003; Ferrini et al., 2010) have shown that there are several factors that could affect the sulfur isotopic composition of sulfide minerals. These factors include temperature, pH and  $f_{\text{O}_2}$  of the fluid, as well as the  $\delta^{34}\text{S}$  value of the  $\text{H}_2\text{S}$  responsible for precipitating sulfide minerals. Because sulfur isotopic fractionation between the reduced sulfur species in solution such as  $\text{H}_2\text{S}$  and sulfide minerals (like  $\text{FeS}_2$ ,  $\text{ZnS}$  and  $\text{PbS}$ ) at low temperatures ( $<350^\circ\text{C}$ ) is very small (Peevler et al., 2003), the large range in  $\delta^{34}\text{S}$  values of sulfides from the Jinding deposit is impossible to be





**Fig. 6.** Photomicrographs in reflected light and back-scattered electron images showing representative textures of mineral associations of different mineralization stages and  $\delta^{34}\text{S}_{\text{V-CDT}}$  values of sulfide minerals. (a) Galena, sphalerite and pyrite of stage 1 occur interstitial to quartz in sandstone. (b) Stage 1 sulfide cements in sandstones. (c) Coarse-grained galena vein of stage 2 crosscuts the massive sphalerite of stage 1 in limestone breccias. (d) The vein of stage 2 is composed of barite and galena (inset), which crosscuts the massive sphalerite of stage 1 in limestone breccias. (e) Coarse-grained sphalerite and galena of stage 2 in sandstones. (f) Galena-dominated sulfide vein of stage 2 consists of sphalerite and barite (inset) in sandstones. (g) Colloform sphalerite of stage 2 shows zonal textures intergrown with galena in limestone breccias. Abbreviations: Ba—barite, Cal—calcite, Ga—galena, Py—pyrite, Q—quartz, Sp—sphalerite.

caused by changes in fluid temperature. In addition, within the stability field of pyrite, not even significant changes in pH and  $f_{\text{O}_2}$  would produce the large range in  $\delta^{34}\text{S}$  values observed (Ohmoto, 1972). Therefore, the large range in  $\delta^{34}\text{S}$  values from the Jinding deposit is likely caused by changes in the  $\delta^{34}\text{S}$  value of  $\text{H}_2\text{S}$  in solution when sulfide minerals precipitated.

Several potential sulfur sources may possibly be involved in hydrothermal mineralization, including mantle sulfur ( $\sum \delta^{34}\text{S} = 0\text{‰}$ ), oceanic sulfate ( $\sum \delta^{34}\text{S} = -20\text{‰}$ ), and biogenic sulfur with greatly varied negative  $\delta^{34}\text{S}$  values (Ohmoto and Rye, 1979). In general, we cannot judge the source of sulfur in hydrothermal solution only by the  $\delta^{34}\text{S}$

values of hydrothermal minerals, but should take full account of the physico-chemical conditions of the ore-forming solutions (Ohmoto, 1972). Given that stage 1 mineral assemblage usually shows pyrite, sphalerite, galena and calcite (Fig. 4) that might form in low  $f_{\text{O}_2}$  and low pH conditions (Luo et al., 1994), the  $\delta^{34}\text{S}$  values of sulfides are approximately equal to the  $\sum \delta^{34}\text{S}$  value of the ore-forming fluid. By contrast, stage 1 shows the typical feature of biogenic sulfur that is generally associated with bacterial sulfate reduction (BSR) (Fig. 9). However, barite began to be present in the stage 2 mineral association, indicating that the  $f_{\text{O}_2}$  became high in the ore-forming fluid. In this case, the  $\delta^{34}\text{S}$  values of barite are roughly equivalent to the  $\sum \delta^{34}\text{S}$  value of

**Table 1**  
Short descriptions and sulfur isotopes data ( $\delta^{34}\text{S}_{\text{V-CDT}} \text{‰}$ ) of sulfide minerals.

Sample no.	Location	Spot no.	Mineral	$\delta^{34}\text{S}_{\text{V-CDT}} \text{‰}$	$2\sigma \text{‰}$	Sample no.	Location	Spot no.	Mineral	$\delta^{34}\text{S}_{\text{V-CDT}} \text{‰}$	$2\sigma \text{‰}$
Stage 1: disseminated sulfides in sandstone (n = 17)						Stage 1: massive sulfides in limestone breccia (n = 2)					
①	Beichang	1	Pyrite	-22.3	0.9	⑦	Beichang	1	Pyrite	-18.0	0.7
		2	Pyrite	-19.3	0.9			2	Pyrite	-16.3	0.6
		3	Pyrite	-12.6	0.9	Stage 1: sulfide vein in limestone breccia (n = 14)					
		4	Pyrite	-17.1	0.9	⑧	Beichang	1	Galena	-14.7	0.8
		5	Pyrite	-22.4	0.9			2	Galena	-18.8	0.8
		6	Pyrite	-17.4	0.9			3	Galena	-25.2	0.8
		7	Pyrite	-19.2	0.7			4	Galena	-12.7	0.8
		8	Pyrite	-19.1	0.7			5	Galena	-10.2	0.8
		1	Sphalerite	-10.4	0.7			1	Sphalerite	-13.2	0.9
		2	Sphalerite	-17.5	0.7			2	Sphalerite	-23.8	0.9
		3	Sphalerite	-19.3	0.7			3	Sphalerite	-13.2	0.9
		4	Sphalerite	-14.4	0.7			4	Sphalerite	-16.9	0.9
		5	Sphalerite	-14.6	0.7			1	Pyrite	-14.9	0.7
		1	Galena	-15.5	0.8			2	Pyrite	-17.3	0.7
		2	Galena	-10.5	0.8			3	Pyrite	-12.7	0.7
		3	Galena	-15.0	0.8			4	Pyrite	-15.5	0.7
		4	Galena	-12.0	0.8			5	Pyrite	-13.2	0.7
Stage 1: disseminated sulfides in sandstone (n = 17)						Stage 2: sulfide vein in sandstone (n = 10)					
②	Fengzishan	1	Pyrite	-26.9	0.6	⑨	Fengzishan	1	Sphalerite	-6.0	0.6
		2	Pyrite	-24.4	0.7			2	Sphalerite	-4.1	0.6
		3	Pyrite	-26.2	0.7			3	Sphalerite	-3.5	0.6
		4	Pyrite	-26.0	0.7			4	Sphalerite	-5.5	0.6
		5	Pyrite	-25.3	0.7			5	Sphalerite	-5.2	0.6
		6	Pyrite	-24.9	0.7			1	Galena	-7.2	0.8
		1	Sphalerite	-40.3	0.7			2	Galena	-7.2	0.8
		2	Sphalerite	-34.4	0.7			3	Galena	-3.9	0.8
		3	Sphalerite	-42.1	0.7			4	Galena	-6.7	0.8
		4	Sphalerite	-22.6	0.7			5	Galena	-1.5	0.8
		5	Sphalerite	-34.9	0.7	Stage 2: sulfide vein in sandstone (n = 6)					
		1	Galena	-34.7	0.8	④	Beichang	1	Sphalerite	-3.4	0.7
		2	Galena	-36.1	0.8			2	Sphalerite	2.9	0.7
		3	Galena	-35.7	0.8			3	Sphalerite	-0.6	0.7
		4	Galena	-29.2	0.8			1	Galena	-1.7	0.8
		5	Galena	-39.6	0.8			2	Galena	-5.7	0.8
		6	Galena	-37.7	0.8			3	Galena	-5.9	0.8
Stage 1: massive sulfides in sandstone (n = 6)						Stage 2: galena vein in limestone breccia (n = 2)					
③	Jiayashan	1	Sphalerite	-20.3	0.7	⑦	Paomaping	1	Galena	-6.9	1.2
		2	Sphalerite	-27.5	0.7			2	Galena	-8.4	1.2
		3	Sphalerite	-20.7	0.7	Stage 2: galena vein in limestone breccia (n = 4)					
		1	Galena	-28.6	0.8	⑧	Beichang	1	Galena	-6.8	1.2
		2	Galena	-23.7	0.8			2	Galena	-4.5	1.2
		3	Galena	-11.4	0.8			3	Galena	-4.8	1.2
				4	Galena			-7.2	1.2		
Stage 1: massive sulfides in sandstone (n = 2)						Stage 2: colloform sulfides in limestone breccia (n = 15)					
④	Beichang	1	Sphalerite	-16.0	0.7	⑩	Beichang	1	Sphalerite	-7.3	0.9
		2	Sphalerite	-11.0	0.7			2	Sphalerite	-8.3	0.9
Stage 1: massive sulfides in limestone breccia (n = 5)								3	Sphalerite	-7.3	0.9
⑤	Paomaping	1	Sphalerite	-12.3	0.7			4	Sphalerite	-5.7	0.9
		2	Sphalerite	-14.0	0.7			5	Sphalerite	-5.8	0.9
		3	Sphalerite	-14.1	0.7			6	Sphalerite	-6.8	0.9
		4	Sphalerite	-13.7	0.7			7	Sphalerite	-6.7	0.9
		5	Sphalerite	-14.6	0.7			8	Sphalerite	-6.9	0.9
Stage 1: massive sulfides in limestone breccia (n = 2)								9	Sphalerite	-5.7	0.9
⑥	Paomaping	1	Galena	-23.1	1.2			10	Sphalerite	-4.9	0.9
		2	Galena	-21.3	1.2			11	Sphalerite	-4.5	0.9
Stage 1: massive sulfides in limestone breccia (n = 4)								12	Sphalerite	-7.0	0.9
⑦	Beichang	1	Sphalerite	-16.5	0.7			1	Galena	-8.3	0.8
		2	Sphalerite	-14.4	0.7			2	Galena	-5.8	0.8
		3	Sphalerite	-16.5	0.7			3	Galena	7.7	0.8
		4	Sphalerite	-23.5	0.7						

the ore-forming fluid, far more than  $\delta^{34}\text{S}$  values of sulfides. Luo et al. (1994) reported the  $\delta^{34}\text{S}$  values of barite associated with stage 2 mineralization were in the range from 11.2‰ to 16.3‰, similar to those (10.8‰–15.7‰) of evaporites in the Lanping basin (Zhang and Wen, 2012). Therefore, these evaporitic rocks likely acted as the source of sulfur for stage 2 mineralization, and the reduced sulfur ( $\text{H}_2\text{S}$ ) was produced by means of sulfate reduction.

Stage 1 sulfides show the most varied and negative  $\delta^{34}\text{S}$  values, suggesting that  $\text{H}_2\text{S}$  was derived from BSR mechanism. The BSR mechanism is the most efficient means for causing a large fractionation between  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{S}$  at low temperatures (Chen et al., 1994; Habicht

et al., 1998). The sulfur isotope fractionation between  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{S}$  caused by BSR is reported to be between 4‰ and 46‰, with an average of 21‰ (Canfield and Teske, 1996; Habicht et al., 1998). Moreover, an extreme fractionation (~46‰) would be obtained only if at a slow rate during BSR process (Rees, 1973). Due to irreversibility, the BSR reaction usually brings about large sulfur isotopic fractionation with biogenic sulfur circulating in nature (Chen et al., 1994). This process generally causes a fractionation of less than 46‰ (Chang et al., 2007). However, part of  $\delta^{34}\text{S}$  data of sulfides (-42.1‰ to -30‰) from the Jinding deposit show larger fractionations from evaporites, similar to those of sulfides in modern oceanic sediments or euxinic waters



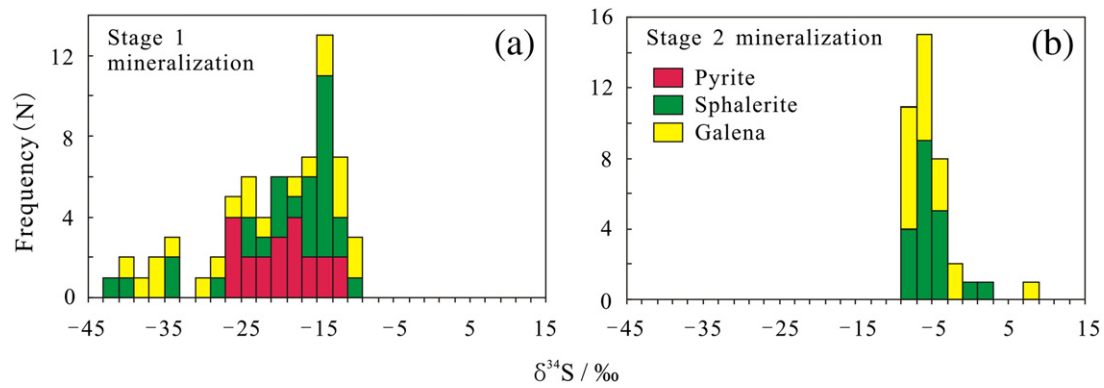


Fig. 7. Histograms displaying sulfur isotopic compositions of sulfide minerals from different mineralization stages.

which are considered as a result of bacterial sulfate reduction combined with disproportionation of intermediate sulfur species (like  $\text{S}^0$ ,  $\text{S}^{2-}\text{O}_3^{2-}$  and  $\text{SO}_3^{2-}$ ) (Canfield and Thamdrup, 1994; Canfield and Teske, 1996; Habicht et al., 1998). In general, the process of bacteria involved disproportionation can cause a fractionation, up to 7‰ to 11‰, within both

lacustrine and marine sulfur cycle, which leads to an enrichment of  $^{32}\text{S}$  in sediments (Canfield and Thamdrup, 1994; Canfield and Teske, 1996; Cypionka et al., 1998; Habicht et al., 1998). When the pre-existing sulfides associated with bacterial sulfate reduction was oxidized to elemental sulfur ( $\text{S}^0$ ), the  $\text{S}^0$  was microbially disproportionated by

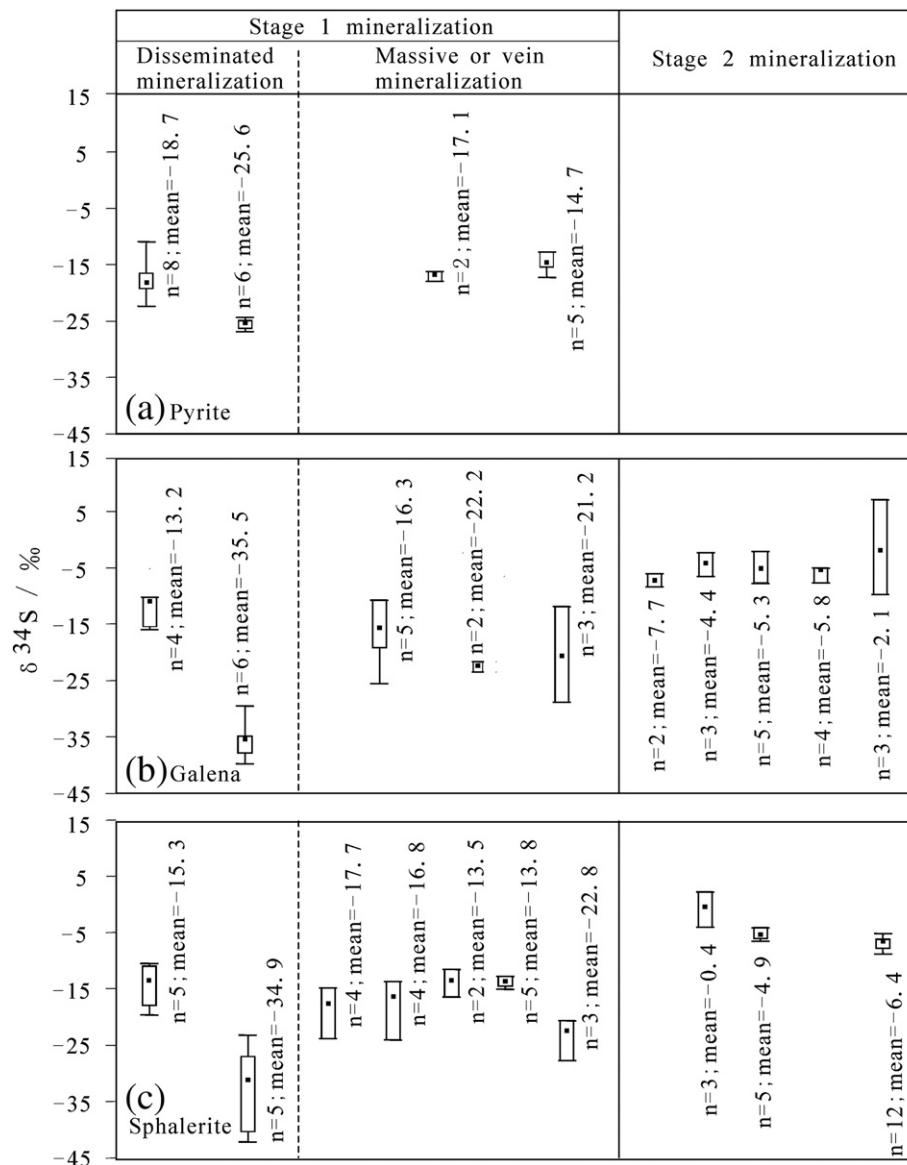
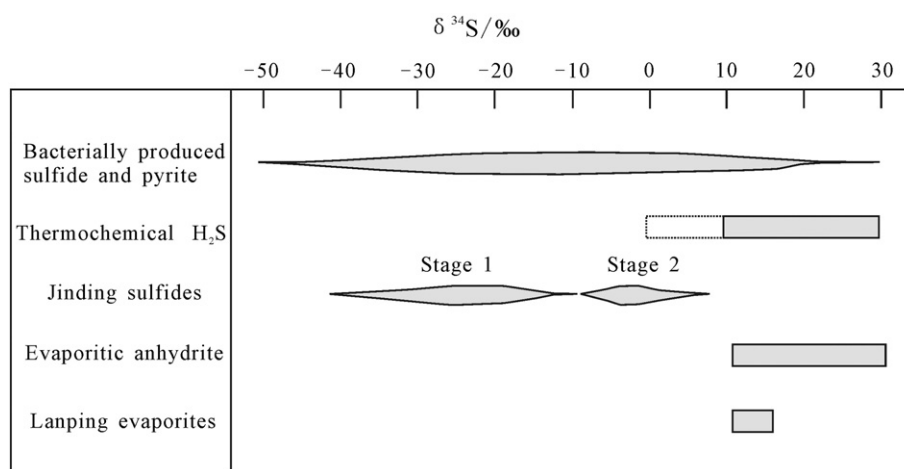


Fig. 8. Box plots showing variations in sulfur isotopic composition of sulfide minerals from stage 1 and 2 mineralization. Number of analyses for each stage or type, and mean value are indicated next to each box plot. The line represents the range of sulfur isotopes, vertical bar is 25% to 75% range, and the filled square is the mean value.



**Fig. 9.** Sulfur isotopic compositions of sulfides from the Jinding deposit, comparing with the typical ranges for naturally occurring sulfur isotopes from BSR and TSR mechanisms. Modified after Warren (1999).

the chemolithotrophic bacterial metabolism to sulfate and sulfide, as follows:  $4S^0 + 4H_2O \rightarrow SO_4^{2-} + 3H_2O + 2H^+$ , accompanied by relatively large sulfur isotopic fractionation (Thamdrup et al., 1993). So the cycle repeated, it would produce more  $^{34}S$ -depleted sulfides than was formed directly by bacterial sulfate reduction (Chang et al., 2007). This mechanism could be used to interpret the extremely  $^{34}S$ -depleted sulfides in stage 1 from the Jinding deposit. However, BSR characteristically occurs at temperatures of less than 60 °C to 80 °C (Machel and Foght, 2000; Machel, 2001), although occasionally it has been found to occur up to 110 °C at some modern hydrothermal vents (Jørgensen et al., 1992). These temperatures are far lower than the mineralizing temperatures of 115–234 °C from fluid inclusions in stage 1 sphalerite (Zeng, 2007). Therefore, BSR could have happened in non-mineralizing sites or before mineralization (Leach et al., 2005). Then, reduced sulfur could be transported from the primary origin to the Jinding dome where it formed a reducing gas cap, which could rapidly precipitate sulfides when it mixed with a metal-bearing fluid.

The feature of the  $\delta^{34}S$  values of stage 2 sulfides indicates that  $H_2S$  might be derived either from bacterial sulfate reduction (BSR), or thermochemical sulfate reduction (TSR), or both, comparing with the typical ranges for naturally occurring sulfur isotopes under BSR and TSR mechanisms (Fig. 9). If the system remains closed to  $SO_4^{2-}$  but open to  $H_2S$  (i.e., sulfate reduction proceeds at a faster rate than sulfate supply, but open to  $H_2S$  in the sense that  $H_2S$  is fixed instantaneously as sulfide minerals, or removed), precipitation of  $^{32}S$ -enriched sulfides would drive the composition of the remaining sulfate to higher ( $^{34}S$ -enriched) values. During the initial stages of sulfide, BSR process could have produced highly fractionated sulfur and sulfides with very low  $\delta^{34}S$  values ( $< -20\%$ ). As the system evolved, the sulfur reservoir became closed to  $SO_4^{2-}$  but open to  $H_2S$ . Under this condition the  $\delta^{34}S$  ( $H_2S$ ) would increase with increasing degree of sulfate reduction. Consequently, the  $\delta^{34}S$  of the accumulated sulfides would also increase with increasing degree of sulfate reduction. Thus, Rayleigh fractionation of sulfur isotope can explain the increasing  $\delta^{34}S$  values of stage 2 sulfides. However, the relationship of mineral cutting suggests two separate mineralizing events for stage 1 and stage 2. The intra-crystalline variation of  $\delta^{34}S$  values is usually very small, inconsistent with that of BSR process in a closed system (Peevler et al., 2003; Drake et al., 2013). Even though the BSR process for stage 1 could last to the stage 2, from the point of view of mass conservation some sulfur-bearing compounds with extraordinary  $^{34}S$  enrichment should be found in the Jinding deposit, but it wasn't. In addition, some sulfate minerals (like barite, celestite and anhydrite) precipitated temporally with stage 2 sulfides, which argued that it wasn't possible to keep the system closed to  $SO_4^{2-}$  during the stage 2 period. Consequently, the BSR mechanism in the system closed

to  $SO_4^{2-}$  but open to  $H_2S$  will be excluded as the means of  $H_2S$  production in stage 2.

Alternatively, the  $\delta^{34}S$  variations of stage 2 sulfides could also be interpreted by thermochemical sulfate reduction (TSR) that may cause a fractionation of  $\sim 0$  to  $20\%$  (Kiyosu and Krouse, 1990; Machel et al., 1995) at relatively higher temperatures ( $>80$  °C to 100 °C, Orr, 1974; Machel et al., 1995; Machel, 2001). The possibility of TSR reaction occurring at the Jinding deposit could be assessed by considering the following aspects: (1) thermal regime of 80 °C or higher caused by geothermal gradation, or heated by hot mineralizing fluid over long time (Luo et al., 1994; Wen et al., 1995); (2) sufficient  $SO_4^{2-}$  anions provided by dissolution of evaporites in the Lanping basin (Xue et al., 2007a; He et al., 2009); and (3) reductants such as solid organic bitumen, petroleum sulfur or methane from the fossil-oil reservoir (Chang and Zhang, 2003; Guo et al., 2003; Fu et al., 2005; Xue et al., 2007b, 2009; Gao et al., 2012). Because multiple evaporitic horizons of the different epochs recognized in the Lanping basin could provide  $SO_4^{2-}$  to the hydrothermal system, the  $\delta^{34}S$  values of sulfates dissolved in the fluid were in a relatively large range from 10.8‰ to 15.7‰ (Zhang and Wen, 2012). In view of sulfur isotopic fractionation ( $\Delta\delta^{34}S_{SO_4^{2-}H_2S} < 20\%$ ) caused by TSR process, the resulted  $\delta^{34}S$  values of sulfides will locate within the range from  $-9.2\%$  to  $4.3\%$ , approximately overlapping with those ( $-8.4\%$ – $7.7\%$ ) of stage 2 sulfides from the Jinding deposit.

## 5.2. Mechanism of mineralization of the Jinding deposit

Three general models have been proposed to account for the transport and deposition of base metal sulfides, namely mixing model, sulfate reduction model and reduced sulfur model, in the sediment-hosted base metal deposits (Sverjensky, 1981; Anderson and MacQueen, 1982). The mixing model implies the coexistence of two fluids, one of which is the ore-forming fluid containing dissolved metals (usually thought of as chloride complexes of zinc and lead), but the other could be an  $H_2S$ -containing fluid of which  $H_2S$  is mainly derived from bacterial sulfate reduction. The two fluids transport to the site of the deposition and mix that leads to sulfide precipitation (Anderson, 1973; Beales, 1975; Anderson, 1983, 1991, 2008). The mixing model is especially applied to the MVT deposits where abundant evaporites develop. Because acid is produced during sulfide precipitation due to fluid mixing ( $H_2S_{aq} + Zn^{2+} \rightarrow ZnS_s + 2H^+$ , Merce et al., 2004), the mixing model can interpret widespread presence of carbonatization and dissolution collapse breccias (Anderson, 1983). The Jinding Zn–Pb deposit is macro-morphologically divided into the upper stratiform or tabular sandstone-type ores, and the lower lentoid or tubular limestone breccia-type ores. Similar distribution of ore bodies in the MVT deposits has been described and interpreted as a result of a



reduced gas phase control (Anderson, 2008). From the point of view of sulfur isotopic fractionation, such greatly varied negative  $\delta^{34}\text{S}$  values of stage 1 sulfides could solely be associated with bacterial sulfate reduction. The pre-existing bacteriogenic sulfur might be transported to form a reduced gas cap in the Jinding dome.  $\text{H}_2\text{S}$  provided by the gas cap in the presence of available metals would result in rapid precipitation of sulfide minerals with a very fine-grained texture, as is a common texture of stage 1 sulfides in the Jinding deposit.

Sulfate reduction model means base metals and oxidized sulfur ( $\text{SO}_4^{2-}$ ) are transported by the same fluid to the site of deposition where the oxidized sulfur is reduced to  $\text{H}_2\text{S}$  by organic matter causing the precipitation of sulfides (Olson, 1984; Garven, 1985). Given the presence of a great amount of barite and celestite in the stage 2 mineralization, it is inferred that the content of  $\text{SO}_4^{2-}$  in the fluid should be high. Luo et al. (1994) studied the H–O isotopes of late celestite and considered the ore-forming fluid had shifted to meteoric water in the stage 2 mineralization. During the infiltration process of the meteoric water, the fluid reacted with the evaporitic rocks and dissolved sulfates. Then, it leached metals from the wall rocks and transported them as sulfate- or sulfite-complexes to the Jinding dome where the oxidized sulfur was reduced to  $\text{H}_2\text{S}$  by organic matters. Usually, various kinds of organic matter, such as kerogen, light oil, hydrocarbon gases, heavy oil, bitumen with different occurrences and maturation, and oil-and-methane-inclusions in calcite and celestite have been observed, which suggest ever an ancient oil-gas reservoir in the Jinding dome (Xue et al., 2006, 2009). If methane was provided, reaction with sulfate in ore solution would be slow, resulting in precipitation of well-formed crystals as metals were present (Anderson, 2008). This mechanism might account for coarse-grained occurrence of galena in stage 2.

Base metals and reduced sulfur are transported in the same fluid at low pH, and precipitation is caused by an increase in pH, cooling, or a reduction in salinity due to dilution, which is referred to as the reduced sulfur model (Helgeson, 1969; Anderson, 1973; Sverjensky, 1981). Under the condition of  $<200^\circ\text{C}$ , it is extremely difficult for  $\text{H}_2\text{S}$  to coexist with metals in the oilfield water. The reduced sulfur model is generally applied to the deposits that have neither evaporites nor traces of sulfate reduction. In any case, the mechanism seems improbable for the Jinding deposit, where the ore-forming fluid would have to

maintain a low pH, even if traveling through terrestrial alkaline red clastic rocks.

The Jinding deposit was considered to be formed at 33 to 28 Ma (Wang et al., 2009), temporally corresponding to the late-collisional transition stage of India–Asian continental collision that meant the stress regime in Sanjiang region shifted from collisional compression to strike-slip (Hou and Cook, 2009). At that time, crustal compression and shortening in the Lanping area reached a climax and started to relax. Under this tectonic setting, mantle-derived magmas emplaced upward and formed alkali intrusions which might provide the heat energy to drive the hydrothermal system (Wang et al., 2009). Some geophysical and geological progresses suggested igneous intrusions might hide underneath the Jinding deposit (Ge et al., 1999; Zhang et al., 2000). Therefore, we can approximately conclude the hydrothermal mineralizing process of the Jinding deposit. Because of continued India–Asian collision, the surrounding orogenic belt lifted relative to the Paleogene foreland basins in the eastern and northern margins of the Tibetan plateau, and strong compression resulted in the thrusting of these basins. In the Lanping basin, the fluid generated from the orogen migrated laterally along gently-dipping detachment faults of the thrust systems toward the basin and evolved into metal-bearing fluid through interaction with country rocks. The metal-bearing fluid migrated vertically along major thrust faults ( $F_2$ ) and finally deposited sulfide minerals when it came across the  $\text{H}_2\text{S}$ -rich fluid, of which  $\text{H}_2\text{S}$  was derived from BSR for stage 1 mineralization in the open spaces induced by thrust-nappe structures at shallow levels. During the stage 2 mineralization, the meteoric water infiltrated and reacted with evaporitic rocks, and then it leached metals and transported them as sulfate- or sulfite-complexes to the Jinding dome where the oxidized sulfur was reduced by organic matters to  $\text{H}_2\text{S}$ , leading to sulfide precipitation.

### 5.3. Comparison with other sulfide deposits in the Lanping basin

The sulfur isotopic compositions of sulfides from the Jinding Zn–Pb deposit are compared with  $\delta^{34}\text{S}$  values of other sulfide deposits (Jinman Cu ore belt, Baiyangping Ag–Cu–Pb–Zn ore belt and Sanshan Pb–Zn ore belt) in the Lanping basin (Fig. 10). The  $\delta^{34}\text{S}$  values of sulfides from the Jinman Cu ore belt vary from  $-23\%$  to  $12\%$ , with the peak ranging

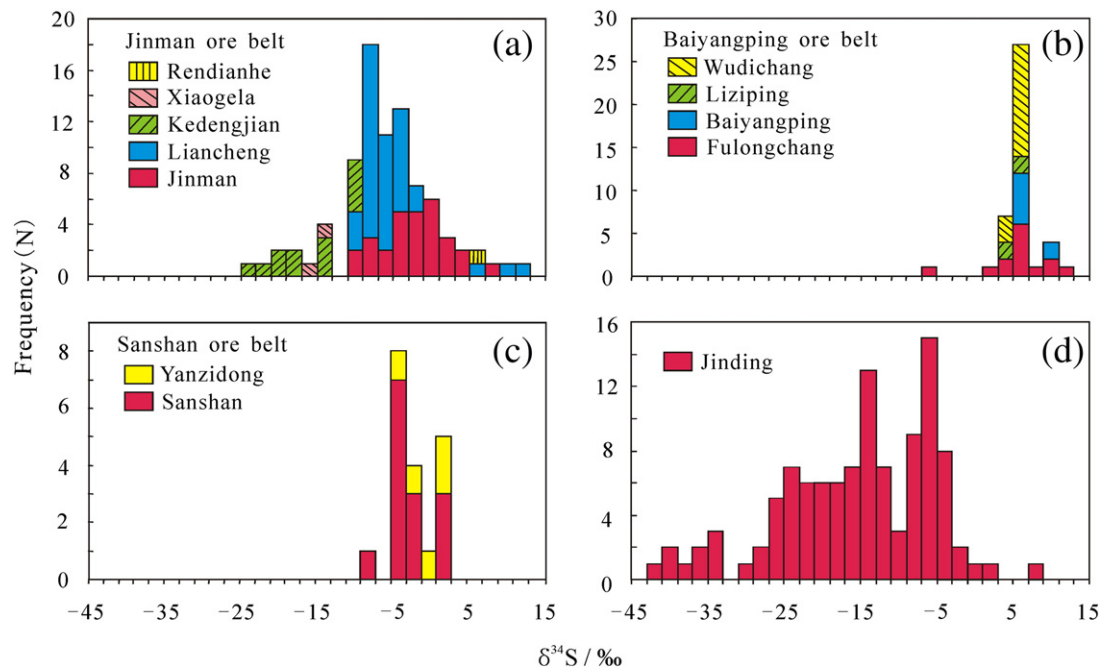


Fig. 10. Histograms showing the sulfur isotopic composition of sulfide minerals from several deposits in the Lanping basin. Sulfur isotopic data of the deposits, except Jinding, were measured by the conventional analytical method.

from  $-8\%$  to  $-2\%$  (Ji and Li, 1998; Li, 2002; Zhao, 2006; Zhang and Wen, 2012; and reference therein). Baiyangping ore belt has  $\delta^{34}\text{S}$  values that range from  $+3\%$  to  $+7\%$  (Wei, 2001; Wang and He, 2003; Li et al., 2005; Wang et al., 2011). Sanshan ore belt displays  $\delta^{34}\text{S}$  values varying from  $-7.3\%$  to  $2.1\%$  with the peak ranging from  $-5\%$  to  $+1\%$  (M.Q. He et al., 2004; Zhao, 2006). Previous studies proposed that the sulfur was mainly derived from a mantle source, not excluding the contribution of biogenic sulfur to individual deposit (Ji and Li, 1998; Li, 2002; M.Q. He et al., 2004; Zhao, 2006). However, this view was also questioned by some researchers who suggested the sulfur might be resulted from sulfate reduction (Wang et al., 2011; Zhang and Wen, 2012). By contrast, the Jinding deposit shows the absolutely dominant numbers of greatly varied negative  $\delta^{34}\text{S}$  values of sulfide minerals. The overall lower  $\delta^{34}\text{S}$  values of sulfides distinguish the Jinding deposit from other sulfide deposits located in the Lanping basin, which indicates that biogenic sulfur might have played a key role in the mineralization of the Jinding Zn–Pb deposit.

## 6. Conclusions

We have used the secondary ion mass spectrometry (SIMS) to determine the sulfur isotopic compositions of sulfide minerals from different mineralization stages in the Jinding Zn–Pb deposit. In situ sulfur isotopic analyses of sulfide minerals show the widest range and lowest  $\delta^{34}\text{S}$  values ( $-42.1\%$  to  $-30\%$ ) ever reported for the Jinding deposit. Stage 1 has  $\delta^{34}\text{S}$  values from  $-42.1\%$  to  $-10.2\%$  with the majority ranging from  $-26\%$  to  $-14\%$ , suggesting a biogenic sulfur source associated with bacterial sulfate reduction. Stage 2 has higher  $\delta^{34}\text{S}$  values between  $-8.3\%$  and  $7.7\%$  that indicates reduced sulfur was likely produced by thermochemical sulfate reduction. By contrast, biogenic sulfur might have played a key role in the mineralization process, especially during the early stage of formation of the Jinding Zn–Pb deposit.

The most reasonable scenario for the stage 1 mineralization is a metal-bearing brine mixing with an  $\text{H}_2\text{S}$ -rich fluid, thereby causing rapid sulfide precipitation. Till the stage 2, the ore-forming fluid shifted to the meteoric water that infiltrated and reacted with evaporitic rocks, leached metals and transported them as sulfate- or sulfite-complexes to the Jinding dome where the oxidized sulfur was reduced by organic matters to  $\text{H}_2\text{S}$ , leading to precipitation of metal sulfides.

## Acknowledgments

The research was supported by the National Basic Research Program (No. 2009CB421005), a NSERC Discovery grant to Fayek and the CRC program, the strategy surveys program of the tri-Rare metal resources of China (No. 12120113078200), and the 12th Five-Year Plan Project of State Key Laboratory of Ore-deposit Geochemistry, Chinese Academy of Sciences (SKLOGD-ZY125-03). We thank Dr. Ravinder Sidhu (Canada) for her assistance in SEM analysis and Breana Hashman for her help with SIMS analysis. Further thanks are due to Dr. Feiyue Wang and Ph.D student Jincheng Luo for their help during the SIMS analysis in Canada.

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