



# Tracing the ore-formation history of the shear-zone-controlled Huogeqi Cu–Pb–Zn deposit in Inner Mongolia, northern China, using H, O, S, and Fe isotopes



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## ABSTRACT

The original ore-fluid of the Huogeqi Cu–Pb–Zn deposit in Inner Mongolia, northern China, was enriched in heavy oxygen isotopes with  $\delta^{18}\text{O}$  values ranging from 9.9 to 11.4 per mil, which is characteristic of the metamorphic devolatilization of pelitic rocks. The  $\delta\text{D}$  values determined by direct measurement of syn-ore hydrothermal tremolite range from  $-116$  to  $-82$  per mil, lying between the domains of typical metamorphic fluid and meteoric water, which is in equilibrium with organic matter. Oxygen and hydrogen isotope ratios indicate that the ore-fluid was derived from deep-sourced metamorphic fluid and interacted with organic-rich shale during fluid migration, which is consistent with the fluid evolution history revealed by a previous fluid inclusion study. Sulfides in the deposit are characteristically enriched in heavy S isotopes, with an average  $\delta^{34}\text{S}$  value of  $13.4 \pm 6.2$  per mil ( $1\sigma$ ,  $n = 103$ ). The S-isotope ratios are identical to stratabound sulfides generated through the non-bacterial reduction of Neoproterozoic marine sulfate (with  $\delta^{34}\text{S}$  values of  $\sim 17$  per mil). Previous studies on lead isotopes of sulfides revealed that the ore-forming metals (Cu, Pb, and Zn) at the Huogeqi deposit were also remobilized from a stratabound source. This source was syngenetically elevated in its Cu-, Pb-, and Zn-sulfide content as a result of submarine hydrothermal activities forming sulfide-rich layers within a rift tectonic setting. The Fe isotope ratios for sulfides are consistent with those of an intercalated iron-formation within the ore-hosting rocks, suggesting that the Fe in the sulfides was derived from local host rocks during sulfide precipitation and the Fe-rich rocks are favorable lithological units for high-grade mineralization. The heterogeneous sources of ore-fluid, S, ore-forming metals, and Fe are explained by a multistage genetic model, which is supported by the geological characteristic of the deposit. The enriched sulfides were subsequently remobilized and enriched by metamorphic devolatilization during the Permian and Triassic periods. The metamorphic ore-fluid ascended along a shear zone and interacted with organic-rich shale. Sulfides eventually precipitated within the shear zone at a shallower crustal level, especially where the shear zone intersected Fe-rich host rocks. This multistage genetic model has implications for mineral exploration. Greenschist to amphibolite facies terranes containing thick Neoproterozoic rift sequences are ideal regions for potential Cu–Pb–Zn mineralization. In particular, intercalated volcanic rocks within the rift sequences are indicative of high heat-flow and are ideal for the development of submarine hydrothermal systems. The primary structures hosting mineralization and ore shoots in the Huogeqi area are jogs in the shear zones. In addition, Fe-rich lithological units, such as iron-formations, are ideal hosts for high-grade ore.

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## 1. Introduction

The Huogeqi deposit in the Langshan area of western Inner Mongolia has reserves of 0.71 Mt grading 1.35% Cu, 0.97 Mt grading 1.49% Pb, and 0.78 Mt grading 1.46% Zn (Huang et al., 2001), and contains up to 0.1 g/t of Au (Huo, 2011). Although the deposit has been explored and mined

since 1958, its genesis has remained unclear. Models include a syngenetic submarine exhalative setting (mainly based on the fact that the Cu–Pb–Zn orebodies are hosted by rift-related sequences and show intimate spatial relations with layered iron-formation). The geochemical characteristics (e.g. S and Pb isotopes) of the deposit are also typical of submarine exhalative systems (Wang and Yang, 1993; Yu et al., 1993; Geng, 1997; Jin et al., 1997; Fei et al., 2004; Peng et al., 2006, 2007; Zhu et al., 2006). Alternatively, an epigenetic model has been proposed on the basis of the observation that Cu–Pb–Zn mineralization is structurally controlled by deformed and faulted host rocks

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(Niu et al., 1991; Ren et al., 1992; Yang, 1998; Zhang and Wang, 2001, 2002). Others have suggested that the deposit has characteristics of orogenic-type mineralization and have proposed that it was formed by remobilization of submarine exhalative sulfides during Late Paleozoic orogeny (Chen et al., 2004, 2007b, 2009a; Chen, 2006; Pirajno, 2009). Our studies on ore fabrics and fluid inclusions also indicate that the mineralization is shear-zone-controlled and the ore-fluid had a metamorphic origin (Zhong et al., 2012, 2013).

In this study, the enigmatic ore-formation history of the Huogeqi deposit is reconstructed using conventional (H, O, and S) and non-traditional (Fe) stable isotopes to constrain the sources of aqueous fluids, sulfur, and iron in the ore-forming system. Both syngenetic and epigenetic geological processes are modeled in this study for a better understanding of the ore-forming process. A multistage genetic model is proposed on the basis of a synthesis of stable isotope data, geological features and previous geochronological results, lead isotope ratios, and fluid inclusion studies. Finally, the indicators of mineral exploration are discussed on the basis of the multistage genetic model.

## 2. Geological setting

The Lang Mountains (Langshan) in the northwest corner of the North China Craton (NCC) is dominated by greenschist to amphibolite facies rift sequences assigned to the Langshan Group, which includes metasedimentary schist, shale, quartzite and marble, intercalated with felsic and mafic metavolcanic rocks (Peng et al., 2007; Zhai et al., 2008). These sequences were deposited on Archean high-grade metamorphosed rocks in the NCC during Meso- to Neo-proterozoic rifting events in and around the craton (Lu et al., 2002; Zhai and Santosh, 2013).

The Langshan Group was previously interpreted as Mesoproterozoic rift sequences (Lu et al., 2002); however, recent zircon U–Pb geochronological studies on metasedimentary rocks (<1100 Ma; Gong, 2014) and intercalated volcanic rocks (867–805 Ma; Peng et al., 2010) constrain the depositional age to the Neoproterozoic.

Carboniferous to Triassic (321–228 Ma) intermediate to granitic plutons intrude the Langshan Group (Fig. 1; Pi et al., 2010; Liu, 2012; Wang et al., 2012; Wu et al., 2013). During this period, the northern margin of the NCC was reactivated during tectonic activity along the Paleo-Asian Ocean to the north. This reactivation was marked by widespread magmatism, metamorphism, and deformation. It is still unclear whether the Paleo-Asian Ocean finally closed in the Devonian or in the late Permian–Early Triassic (Sengor and Natal'in, 1996; Chen, 2002; Xiao et al., 2003; Chen et al., 2007a; Chen et al., 2009b; Zhang et al., 2009; Xu et al., 2013). In the former model, the closure of the ocean took place during the Devonian, followed by the formation of a limited intracratonic oceanic basin in a post-collisional setting, which was finally closed under a compressional environment by Early–Middle Triassic times (Chu et al., 2013). The latter model emphasizes that the northern NCC was an Andean-like active continental margin during the Carboniferous–Permian, and the late Permian to Triassic magmatism was related to the final closure of the Paleo-Asian Ocean. Both models include compressional tectonics during the late Permian and Early Triassic following the final closure of either a newly formed oceanic basin or the Paleo-Asian Ocean. This is consistent with the recognized continuous thrust fault activities between 270 and 190 Ma along the northern margin of the craton (Wang et al., 2013).

Northeast-trending thrusts developed throughout the Langshan area, resulting in strong folding and mylonitization of the Langshan Group (Fig. 1). The thrusts dip southeast in the north slope of the Lang Mountains and dip northwest in the south slope, forming back-thrusts associated with a northwest–southeast compressional tectonic setting (Fig. 1). The age of late Permian and Early Triassic thrusting is constrained between  $237 \pm 3$  and  $213 \pm 2$  Ma by  $^{39}\text{Ar}/^{40}\text{Ar}$  dating of muscovite separated from mylonite (Gao, 2010).

The Huogeqi Cu–Pb–Zn deposit is located at the north side of the Lang Mountains, adjacent to a southeast-dipping thrust fault (Fig. 1). Neoproterozoic amphibolite-facies units assigned to the Langshan Group host the deposit. The group in the area includes quartzite, almandine–biotite schist, andalusite–biotite schist, two-mica schist, and diopside–tremolite marble. The metasedimentary sequences are interlayered with deformed amphibolite units, which are interpreted as metamorphosed basaltic volcanic rocks (Fig. 2; Zhu et al., 2006). Furthermore, an intercalated iron-formation consisting of magnetite, Fe-rich amphibole, and siderite hosts Cu–Pb–Zn orebodies in the area. These Fe-rich host rocks were hydrothermally altered to pyrite and pyrrhotite near mineralized veins.

The Langshan Group is typically mylonitized in the Huogeqi mining area. Orebodies in the area are generally concordant with the mylonitic foliation along jogs in the shear foliation (Fig. 2). The orebodies extend for up to 1500 m along strike, exceed 1200 m down-dip, and are tens of meters thick. They consistently dip at angles of  $65^\circ$ – $80^\circ$  (Fig. 3). Cu–Pb–Zn sulfides are present parallel to shear bands, resulting in the typical banded and laminated mineralization style (Fig. 4A). Disseminated and quartz-vein-type mineralization is also common at Huogeqi. In addition, sulfide-bearing microfractures exhibit characteristics of shear deformation in a brittle–ductile manner and locally crosscut the mylonitic foliation (Zhong et al., 2012).

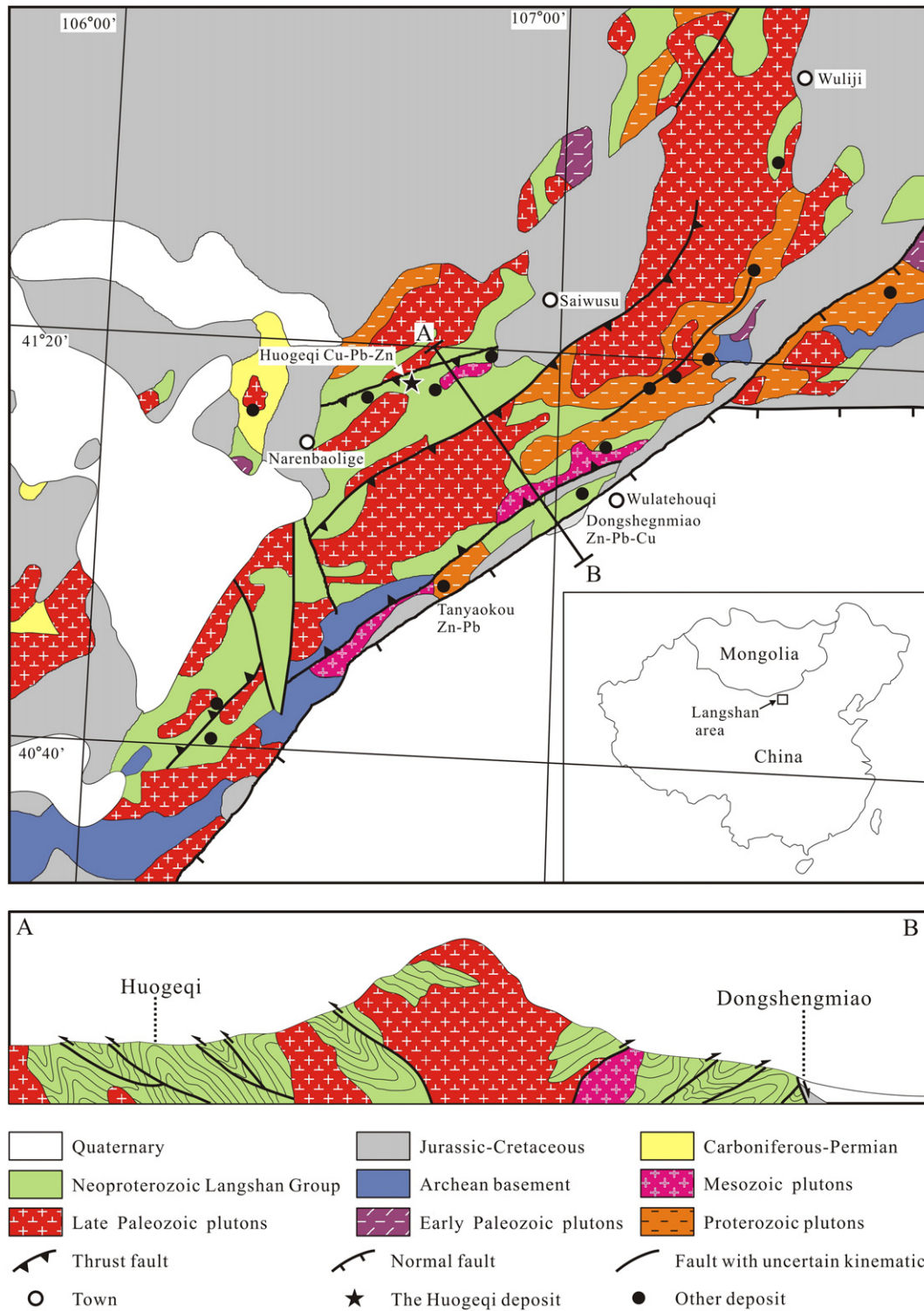
Ore minerals in the Huogeqi deposit include chalcopyrite, galena, sphalerite, pyrrhotite, and pyrite (Fig. 4B), with minor amounts of arsenopyrite, breithauptine, costibite, gudmundite, and native bismuth. Syn-ore hydrothermal gangue minerals include quartz, tremolite, epidote, chlorite, biotite, muscovite and minor spessartine, which is a typical greenschist-facies assemblage produced in the ore-forming environment. Fluid inclusion microthermometer suggests that the ore-forming temperature was  $364^\circ \pm 41^\circ\text{C}$  ( $1\sigma$ ,  $n = 57$ ) and chlorite geothermometer similarly suggests an ore-forming temperature of  $362^\circ \pm 26^\circ\text{C}$  ( $1\sigma$ ,  $n = 9$ ; Zhong et al., 2013), which are consistent with greenschist facies temperatures. Peak metamorphic was at almandine–amphibolite facies, as indicated by the presence of minerals such as almandine, plagioclase, pyroxene and biotite, which are locally replaced by sulfides and accompanying shear-zone hosted hydrothermal Cu–Pb–Zn mineralization (Zhong et al., 2014). The mineralization has a metamorphic origin and post-dates the peak metamorphism of the host rocks. The ore-fluid is mesothermal,  $\text{CH}_4$ -rich, and its low-salinity are characteristic of the equilibrium between deep-sourced metamorphic fluids and organic-rich carbonaceous shale (Zhong et al., 2013).

As a result of the “deep and later” nature of active orogenic belts (Goldfarb et al., 2005), the metamorphic ore-fluid was derived from the devolatilization of an under-thrust rock pile at depth. The fluid subsequently migrated upward and deposited Cu–Pb–Zn sulfides at higher crustal levels during regional uplift and retrograde metamorphism. Consequently, mineralization associated with the metamorphic fluid was during retrograde metamorphism of immediate host rocks.

A  $^{39}\text{Ar}/^{40}\text{Ar}$  geochronological study reveals that ca. 240 Ma Cu–Pb–Zn mineralization took place after amphibolite facies metamorphism during ca. 271 Ma, which is consistent with the post-peak mineralization deduced from petrographic observations by Zhong et al. (in press).

## 3. Sampling and analytical methods

Syn-ore hydrothermal tremolite was separated from high-grade ore for oxygen and hydrogen isotopic analysis to ascertain the isotopic characteristics of the mineralizing fluid. The tremolite grains form veinlets and are intergrown with sulfides in addition to being surrounded by them (Fig. 4C). This indicates that the tremolite and sulfide are coeval. Furthermore, sulfide inclusions were ubiquitous in the tremolite, verifying the syn-ore nature of the tremolite. Both oxygen and hydrogen isotope ratios were directly determined for the tremolite samples. Sulfide minerals such as pyrite, pyrrhotite, chalcopyrite, galena, and sphalerite



**Fig. 1.** Geological map of the Langshan area in western Inner Mongolia (the upper part, modified from Peng et al., 2007). The sketch of the cross section is after Hu and Niu (1992), based on a synthesis of several geological sections across the Langshan area.

were separated from the ore (Fig. 4A, B, D). These minerals were analyzed for their sulfur isotope ratios. The  $\delta^{57}\text{Fe}$  values were measured for Fe-bearing sulfides (pyrite, pyrrhotite, and chalcopyrite) and magnetite obtained from the iron-formation host rocks to help determine the Fe source of the sulfides.

Hydrogen and oxygen isotopes were measured at the Institute of Mineral Resources, Chinese Academy of Geological Sciences. Tremolite samples were heated and the extracted  $\text{H}_2\text{O}$  was collected and reduced

by Cr at a high temperature for isotopic measurement. Oxygen isotopes of tremolite were analyzed using the  $\text{BrF}_5$  method to obtain  $\text{CO}_2$ , as documented by Clayton and Mayeda (1963). The measurements of hydrogen and oxygen isotopic composition were obtained using a MAT-253 EM mass spectrometer. The analytical uncertainty was  $\pm 0.2\%$  for oxygen and  $\pm 2\%$  for hydrogen.

Sulfur isotope measurements were performed at the Institute of Mineral Resources, Chinese Academy of Geological Sciences. All the

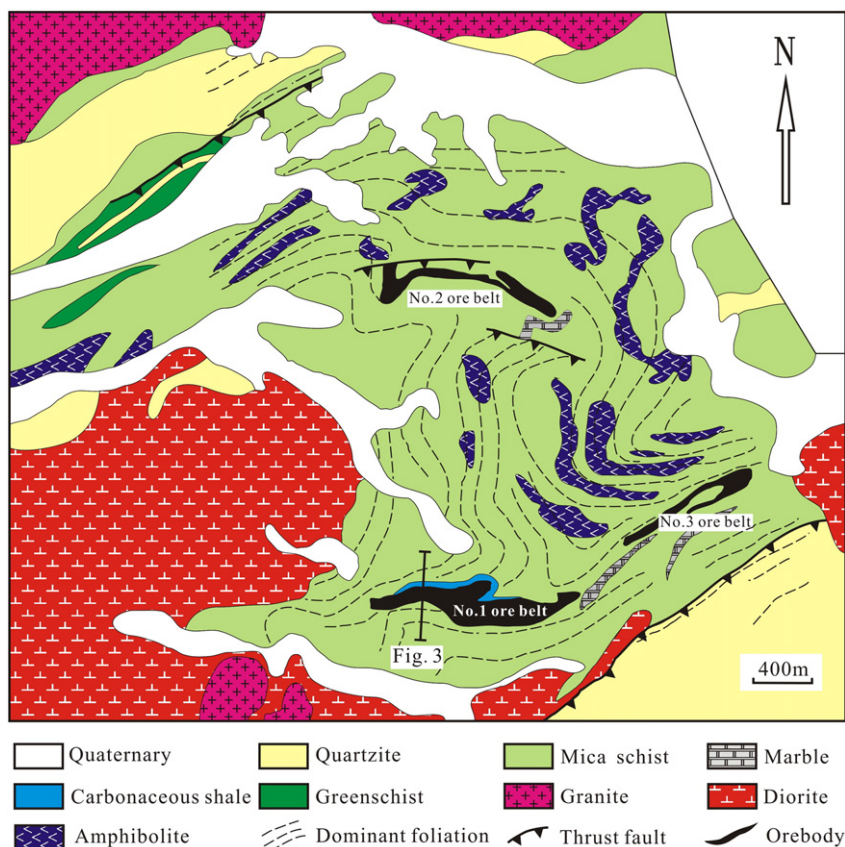


Fig. 2. Geological map of the Huogeqi deposit (modified after Zhang and Wang, 2001, 2002).

sulfide samples were reacted with  $\text{Cu}_2\text{O}$  powder to produce  $\text{SO}_2$ , and the  $\text{SO}_2$  isotope ratios were measured using a MAT-233 mass spectrometer.

Iron isotope ratios were analyzed at the Institute of Geology, Chinese Academy of Geological Sciences. After ultrasonic cleaning in purified water, Fe-bearing minerals were completely dissolved in acid to ensure purification. The Fe isotope ratios of the purified solutions were measured using a Nu Instruments multiple-collector plasma source mass spectrometer. Zhu et al. (2002) and Wang et al. (2011) document details of the Fe isotope measurement method used.

Stable isotopic data are reported as deviations of the isotopic ratio of a sample relative to the Vienna SMOW standard for oxygen and hydrogen, Canyon Diablo Troilite (CDT) for sulfur, and reference material IRMM-14 for iron.

## 4. Stable isotope compositions

### 4.1. Oxygen and hydrogen isotopes

The oxygen and hydrogen isotope ratios for tremolite from the Huogeqi deposit range from 10.4 to 10.6 per mil and from  $-82.1$  to  $-116.1$  per mil, respectively (Table 1). The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of ore-fluids are calculated to be in equilibrium with tremolite are 11.2 to 11.4 per mil and  $-94.4$  to  $-60.4$  per mil, respectively (Fig. 5). This is based on the tremolite–water fractionation equations from Zheng (1993) and Graham et al. (1984), assuming mineral precipitation at  $360^\circ\text{C}$  (see above). This data and previously published H–O isotopic data of two mineralized quartz veins obtained by Yang (1998) from fluid inclusions in quartz from the deposit are included in Table 1 (Fig. 5). The measured  $\delta^{18}\text{O}$  values of two quartz samples are 15.5 and 16.2 per mil and that of the equilibrated ore-fluid are calculated to be 9.9 and 10.6 per mil, respectively, using the quartz–water fractionation equation by Clayton et al. (1972) at  $360^\circ\text{C}$ . The  $\delta^{18}\text{O}$  values for fluid

inclusions from the two quartz samples are  $-115$  and  $-144$  per mil, respectively (Table 1).

### 4.2. Sulfur isotopes

Sulfur isotope ratios for 26 samples of sulfide minerals were measured in this study, yielding  $\delta^{34}\text{S}$  values consistent with the previously published isotopic data (77 measurements) compiled by Wang and Yang (1993) (Fig. 6). Since there is no systematic difference between the new and previous results, all of the 103 isotopic values were used for data processing (Table 2).

Sulfides exhibit a wide variation in sulfur isotopic compositions, ranging from  $-3.5$  to 26.3 per mil; however, they are generally isotopically heavy with an average  $\delta^{34}\text{S}$  value of 13.4 per mil ( $1\sigma$ ,  $n = 103$ ). The vast majority of analyzed sulfides (87.4%) have  $\delta^{34}\text{S}$  values higher than 7 per mil.

The  $\delta^{34}\text{S}$  values of different sulfide minerals decrease in the following order: pyrrhotite > sphalerite > chalcopyrite > pyrite > galena (Table 2). This is generally consistent with the series expected in an isotopically equilibrated system comprising multiphase sulfides. An exception is pyrite, which precipitated earlier than and in disequilibrium with other sulfides (Zhong et al., 2012). If pyrite was in equilibrium with pyrrhotite, its  $\delta^{34}\text{S}$  value of 15.7 per mil would be higher than the measured average value of 12.0 per mil by 3.7 per mil, calculated using the pyrite–pyrrhotite fractionation equation of Ohmoto and Rye (1979) at  $360^\circ\text{C}$ . The small amount (3.7 per mil) of isotopic depletion of pyrite agrees with the reduced ore-fluid having a low  $\text{SO}_4^{2-}/\text{H}_2\text{S}$  ratio (see below), which could have resulted in a slight depletion of early sulfide compared to the ambient ore-fluid and other sulfide minerals that formed subsequently (Ohmoto and Rye, 1979).

With the exception of pyrite, the differences between sulfide minerals are theoretically compatible with the sulfur isotope fractionation factors. For example, the isotopic fractionation between sphalerite and

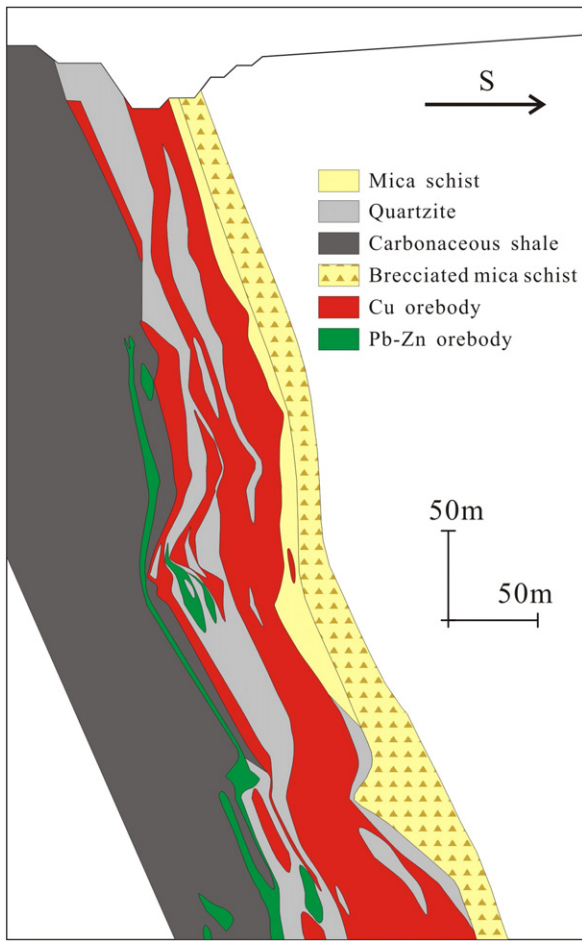


Fig. 3. A cross section of orebodies at Huogeqi.

galena is calculated as 2.0 per mil at 360 °C using the sphalerite–galena fractionation equation of Ohmoto and Rye (1979), and the difference based on the measured values is 1.3 per mil (Table 2). Similarly, the measured isotopic fractionations of pyrrhotite–galena (3.0 per mil) and chalcopyrite–galena (1.0 per mil) are also close to the calculated values (2.0 and 1.7 per mil, respectively) at 360 °C (Table 2). This indicates that the sulfides were generally in equilibrium with each other (except for pyrite) at medium temperature, which is consistent with the fact that they precipitated from a homogeneous mesothermal fluid.

#### 4.3. Iron isotopes

Both hydrothermal Cu ore and iron-formation from the mineralized Langshan Group were selected for iron isotope studies. Two magnetite samples from the iron-formation have  $\delta^{57}\text{Fe}$  values of  $-11.9$  and  $-2.5$  per mil. Pyrite, pyrrhotite, and chalcopyrite separated from Cu ore were analyzed, yielding  $\delta^{57}\text{Fe}$  values ranging from  $-2.14$  to  $0.07$  per mil, averaging  $-0.96 \pm 0.96$  per mil ( $n = 15$ ). Pyrite has the greatest range of Fe isotope values between  $-2.14$  and  $0.07$  per mil ( $n = 6$ ); however, the vast majority of the pyrite samples ( $n = 5$ ) have  $\delta^{57}\text{Fe}$  values of  $> -1.00$  per mil ( $-0.69 \pm 0.43$  on average,  $1\sigma$ ,  $n = 5$ ), except for one sample with an extremely light Fe isotope ratio of  $-2.14$  per mil. Pyrrhotite is the most isotopically depleted sulfide of all the minerals studied with  $\delta^{57}\text{Fe}$  values ranging from  $-1.84$  to  $-1.01$  per mil (averaging  $-1.23 \pm 0.62$  per mil,  $1\sigma$ ,  $n = 7$ ). Two samples of chalcopyrite are relatively enriched in heavy Fe isotopes, with  $\delta^{57}\text{Fe}$  values of  $-0.20$  and  $0.06$  per mil (Fig. 7; Table 3).

### 5. Constraints on the sources of ore-forming materials

#### 5.1. Source of ore-fluids

Oxygen and hydrogen isotopes are good indicators of the source and evolutionary history of ore-fluids. The mineralized fluid at Huogeqi was enriched in heavy oxygen isotopes, which is diagnostic of metamorphic

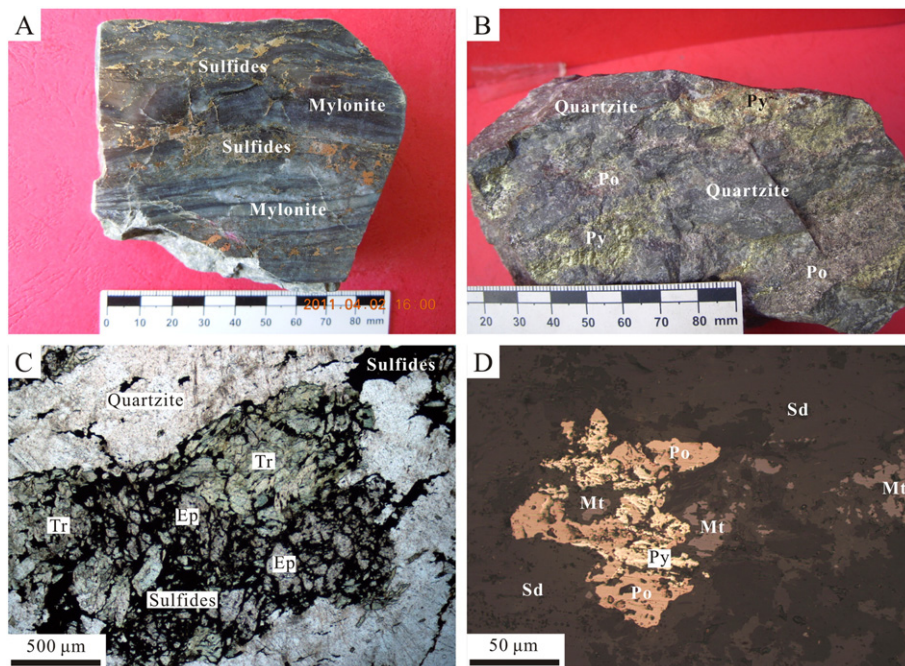


Fig. 4. Petrographic characteristic of ore zones at the Huogeqi deposit: (A) hand-specimen of mylonite-hosted ore, note that sulfides are generally parallel to the mylonitic foliation; (B) hand-specimen of quartzite-hosted ore composed mainly of pyrite and pyrrhotite; (C) sulfide veinlets and accompanying syn-ore tremolite and epidote under plane-polarized light; and (D) iron formation composed of magnetite and siderite was hydrothermally altered, and magnetite porphyroblast was replaced by pyrite and pyrrhotite under reflected light.

**Table 1**  
Oxygen and hydrogen isotope data.

Sample type	Analyzed mineral	$\delta^{18}\text{O}$ (‰)		$\delta\text{D}$ (‰)		Source
		Mineral	Water	Mineral	Water	
Disseminated Cu ore	Tremolite	10.6	11.4 <sup>a</sup>	−108.1	−86.4 <sup>a</sup>	This study
Disseminated Cu ore	Tremolite	10.4	11.2 <sup>a</sup>	−82.1	−60.4 <sup>a</sup>	This study
Disseminated Cu ore	Tremolite	10.5	11.3 <sup>a</sup>	−116.1	−94.4 <sup>a</sup>	This study
Mineralized quartz vein	Quartz	16.17	10.6 <sup>a</sup>	–	−115 <sup>b</sup>	Yang (1998)
Mineralized quartz vein	Quartz	15.47	9.9 <sup>a</sup>	–	−144 <sup>b</sup>	Yang (1998)

<sup>a</sup> Calculated based on the isotope ratios of minerals that in equilibrium with ore-fluid.

<sup>b</sup> Direct measurement of fluid inclusion water.

fluids that are in equilibrium with pelitic metasedimentary rocks (Fig. 5; Goldfarb et al., 1991). Such isotopically heavy ore-fluids are characteristic of orogenic gold deposits, wherein mineralization is due to metamorphic devolatilization (Fig. 5; Goldfarb et al., 2005). The  $^{18}\text{O}$ -rich nature of the ore-fluid is incompatible with the submarine exhalative model for the Huoqeqi deposit (Peng et al., 2007), because this model infers modified seawater as the major component of ore-fluids. Such fluids can have isotopic ratios similar to those of seawater, as observed in VMS deposits (Fig. 5; Ohmoto and Rye, 1974; Tornos, 2006). Extensive fluid-assisted modifications and remobilization during metamorphism and deformation might result in the isotopic re-equilibration of syngenetic orebodies (Marshall and Spry, 2000). This possibility, however, is inconsistent with the fact that the Cu–Pb–Zn sulfides at the deposit are generally strain-free and non-deformed. Furthermore, the post-peak nature of the sulfides suggests that the ambient host rocks were dry during mineralization.

The hydrogen isotope ratios reported by Yang (1998) for Huoqeqi were obtained by measuring fluid inclusions extracted from quartz. However, because of the large abundance of secondary inclusions in sheared veins at the deposit, a large proportion of meteoric water unrelated to ore formation would have been obtained during fluid extraction, resulting in measured  $\delta\text{D}$  values lower than those of primary ore-fluids (Fig. 5). In this scenario, the direct measurement of syn-ore hydrous minerals such as tremolite can better reflect the hydrogen isotope ratios of ore-fluids (Goldfarb et al., 1991). With this in consideration,  $\delta\text{D}$

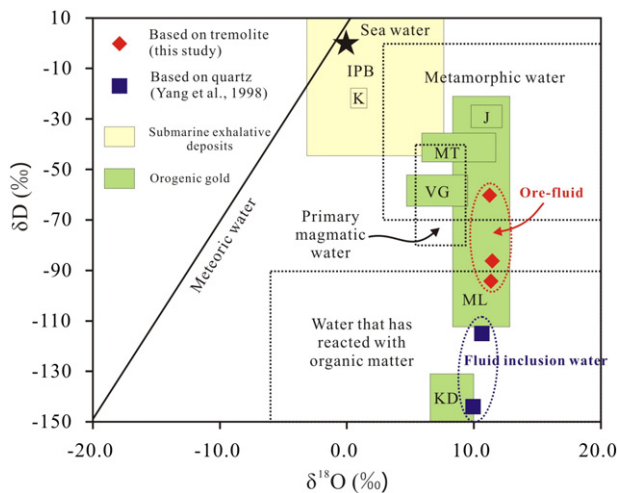
values measured directly from the tremolite (−94.4 to −60.4 per mil) provide more precise information regarding the primary nature of the ore-fluids (Table 1; Fig. 5). Compared with common metamorphic fluids, ore-fluid at Huoqeqi was more depleted in deuterium, lying between the domains of typical metamorphic fluids and water that reacts with organic matter. This might result from isotopic equilibrium between a metamorphic fluid and organic-rich shale during fluid migration, which is confirmed by the presence of  $\text{CH}_4$  in ore-fluids and phase equilibrium in the C–H–O system (Zhong et al., 2013).

## 5.2. Source of sulfur

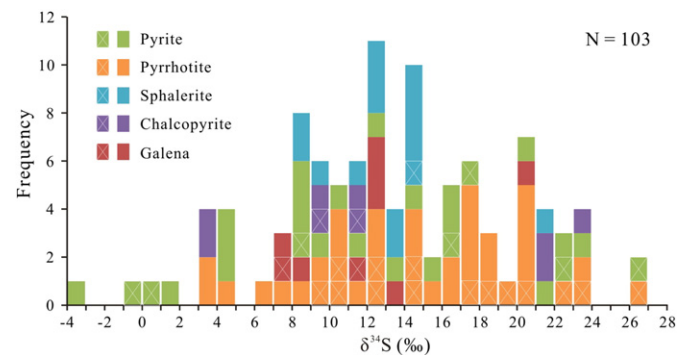
The widespread presence of pyrrhotite (Fig. 4B), absence of sulfate minerals, and large abundance of  $\text{CH}_4$  in fluid inclusions demonstrate that the ore-fluid forming Huoqeqi was reduced and  $\text{H}_2\text{S}$  in the fluid was significantly predominated over  $\text{SO}_4^{2-}$ . In a fluid with a very low  $\text{SO}_4^{2-}/\text{H}_2\text{S}$  ratio, isotopic fractionation between sulfides and the bulk S of the ore-fluid is insignificant. Thus, the sulfur isotope ratios of sulfides can directly reflect the isotopic composition of the ore-fluid and consequently the source region for the sulfur (Ohmoto and Rye, 1979).

The very heavy sulfur isotope values of sulfides ( $13.4 \pm 6.2$  per mil on average) at Huoqeqi are identical to those of  $\text{H}_2\text{S}$  derived from the non-bacterial reduction of marine sulfate, which rules out magmatic rocks as a source of sulfur (Ohmoto and Rye, 1979). Considering the reduction of Neoproterozoic seawater sulfate with a  $\delta^{34}\text{S}$  value of ~17 per mil (Huston, 1999), the sulfur isotopic composition of the source region can be interpreted to be due to the thermochemical reduction of sulfate by either organic matter or Fe(II)-bearing minerals on or beneath the seafloor (Ohmoto and Rye, 1979). Both mechanisms require a warm (>80 °C; reduction by organic matter) or hot (>250 °C; reduction by Fe minerals) environment near the seafloor and indicate marine sulfate as the ultimate sulfur source. Consequently, the sulfur was initially derived from a submarine hydrothermal system and subsequently remobilized by hydrothermal fluids during metamorphism.

The presence of a submarine hydrothermal system as a source of ore-forming material is also demonstrated by previously published



**Fig. 5.** Plots of  $\delta^{18}\text{O}$  versus  $\delta\text{D}$  for samples from Huoqeqi. The composition of the ore-fluid (red diamonds) is based on measurements of oxygen and hydrogen from syn-ore tremolite. The composition of the fluid inclusion is presented as purple triangles, which is more depleted in deuterium due to the involvement of secondary fluid inclusions (see text for details). The isotopic compositions of orogenic gold deposits are after Goldfarb et al. (2005); and the compositions of submarine exhalative deposits are from Ohmoto and Rye (1974; Kuroko) and Tornos (2006; Iberian Pyrite Belt). The  $\delta^{18}\text{O}$ - $\delta\text{D}$  field natural waters with different origins are after Taylor (1974) and Sheppard (1986). Abbreviations: Py = pyrite, Po = pyrrhotite, Tr = tremolite, Ep = epidote, Mt = magnetite, Sd = siderite, J = Juneau; MT = Meguma Terrane; VG = Victorian Goldfields; ML = Mother Lode; KD = Klondike; K = Kuroko; IPB = Iberian Pyrite Belt.



**Fig. 6.** Histogram of  $\delta^{34}\text{S}$  values of sulfides from Huoqeqi. The bars without pattern are data obtained in this study, and bars with white crosses are from the compilation by Wang and Yang (1993).

**Table 2**

$\delta^{34}\text{S}$  values of sulfides, including both new results of this study and published data compiled by Wang and Yang (1993).

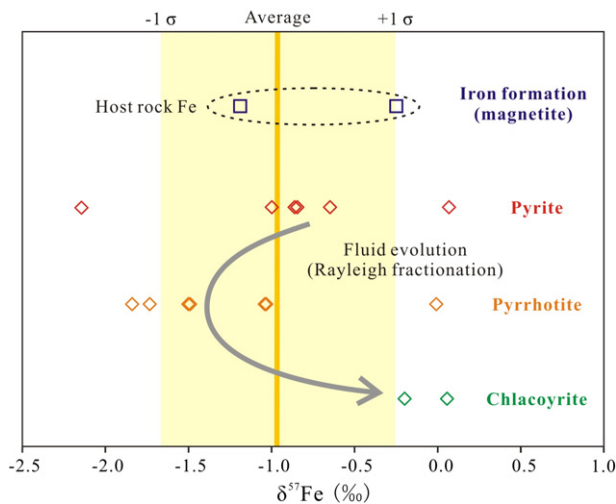
Mineral	Range (‰)	Average $\pm 1\sigma$ (‰)	Number
Pyrite	−3.5–26.1	12.0 $\pm$ 7.9	28
Pyrrhotite	3.5–26.3	14.9 $\pm$ 5.6	42
Sphalerite	8.5–21.5	13.1 $\pm$ 3.2	15
Chalcopyrite	3.5–23.5	12.9 $\pm$ 7.6	9
Galena	7.2–20.5	11.8 $\pm$ 4.0	9

lead isotopic compositions of sulfides for the study area, which are poor in radiogenic lead and consistently have two-stage lead model ages of ca. 1000 to 900 Ma (Li et al., 1986; Yu et al., 1993; Zhu et al., 2006). This is consistent with the depositional age of the rift succession in the Neoproterozoic Langshan Group. The lead isotope ratios indicate that the ore-forming metals (Cu, Pb, and Zn) were also remobilized from a pre-enriched stratabound source within the Neoproterozoic units. The intercalated volcanic rocks dated at ca. 867–805 Ma by Peng et al. (2010) indicate a high-heat-flow environment during rifting, which was favorable for the development of submarine ore-forming systems.

### 5.3. Source of iron

The Fe isotopic composition of sulfides acts as a good indicator for the source of iron in sulfides. To constrain more precisely the source of iron, the isotopic systematics for magnetite from the ore-hosting iron-formation at Huogeqi was investigated, which are depleted in heavy Fe isotopes and has negative  $\delta^{57}\text{Fe}$  values. Although only two  $\delta^{57}\text{Fe}$  values are reported in this study, the generally negative Fe isotope values for the iron-formation at Huogeqi have been demonstrated by a systematic isotopic study by Xiangkun Zhu and Chuang Bao (personal communication). The iron-formation at Huogeqi is more depleted than most banded iron-formation globally and the majority characteristically has positive  $\delta^{57}\text{Fe}$  values (Wang et al., 2012).

The two iron-formation samples from Huogeqi yielded a  $\delta^{57}\text{Fe}$  range of −1.19 to −0.25 per mil, which is generally consistent with the  $1\sigma$  Fe isotope range of −1.66 to −0.25 per mil for bulk sulfides (Fig. 7). This indicates that the majority of the iron in the sulfides was derived from the rocks hosting the mineralization, which have been suggested in previous studies (Zhong et al., 2012, 2014). Evidence include: (1) sulfidation of magnetite observed at the contact between syn-tectonic veins and iron-formation (Fig. 4D), suggesting the



**Fig. 7.** The  $\delta^{57}\text{Fe}$  values of sulfides as well as magnetite from ore-hosting iron formation, as shown is the average of  $\delta^{57}\text{Fe}$  values of sulfides with  $1\sigma$  standard deviation. The gray arrow shows the evolution Fe isotopes of sulfides due to Rayleigh fractionation.

**Table 3**

Iron isotope data.

Sample	Mineral	$\delta^{57}\text{Fe}$ (‰)	$1\sigma$ (‰)	$\delta^{56}\text{Fe}$ (‰)	$1\sigma$ (‰)
Cu ore	Pyrite	−0.92	0.03	−0.61	0.09
Cu ore	Pyrite	−0.86	0.09	−0.62	0.03
Cu ore	Pyrite	0.07	0.09	0.03	0.00
Cu ore	Pyrite	−0.73	0.11	−0.51	0.04
Cu ore	Pyrite	−1.00	0.04	−0.63	0.09
Cu ore	Pyrite	−2.14	0.14	−1.43	0.11
Cu ore	Pyrrhotite	−1.73	0.04	−1.20	0.01
Cu ore	Pyrrhotite	−1.04	0.03	−0.73	0.06
Cu ore	Pyrrhotite	−1.03	0.10	−0.70	0.05
Cu ore	Pyrrhotite	−0.01	0.05	0.00	0.07
Cu ore	Pyrrhotite	−1.49	0.05	−1.01	0.04
Cu ore	Pyrrhotite	−1.84	0.09	−1.23	0.02
Cu ore	Pyrrhotite	−1.50	0.06	−0.98	0.06
Cu ore	Chalcopyrite	0.06	0.03	0.08	0.03
Cu ore	Chalcopyrite	−0.20	0.03	−0.15	0.05
Iron formation	Magnetite	−1.19	0.04	−0.86	0.06
Iron formation	Magnetite	−0.25	0.02	−0.17	0.04

formation of pyrite and pyrrhotite from the interaction between Fe in host rocks and  $\text{H}_2\text{S}$  in aqueous solutions (see Fig. 6c of Zhong et al. (2012)); (2) chalcopyrite is preferentially present in Fe-rich host rocks (e.g. diopside-rich marble) rather than in Fe-poor quartzite, suggesting that Fe in silicates also provides a favorable sink for chalcopyrite precipitation (see Fig. 6c, d of Zhong et al. (2014)); (3) flow-through thermodynamic modeling indicated that Fe-rich lithological units are ideal hosts for high-grade sulfide ore and for intensive sulfidation of the host rock with a consequently dramatic drop in  $\text{H}_2\text{S}$  activity in the mineralized fluid (Zhong et al., 2014). Thus, pyrite, pyrrhotite, and chalcopyrite were commonly deposited because of interactions between deep-sourced S (−Cu)-bearing fluids and Fe being derived from local host rocks. Fe-rich host rocks (e.g. iron-formations) are ideal traps for sulfide precipitation and Cu mineralization.

The variation in Fe-isotopic composition in different sulfides can be accounted for by isotopic fractionation during mineral precipitation. Fe(II) should have considerably predominated over Fe(III) in the highly reduced ore-fluid at Huogeqi (see above), therefore the fractionation involving Fe(III) species is not considered to be significant. Pyrite precipitated earlier than other sulfides and is enriched in heavy Fe relative to dissolved Fe in the ambient solution by a  $\delta^{57}\text{Fe}$  fractionation as high as  $\sim 1.46$  per mil at 350 °C (Syverson et al., 2013). This indicates that most of the early pyrite would have been isotopically heavier than the bulk ore-fluid; the isotope value of which is represented by the average value for all of the sulfide samples (Fig. 7). As a result of the precipitation of isotopically heavy pyrite, the dissolved Fe in the ore-fluid would have become progressively depleted in heavy Fe (i.e. Rayleigh fractionation), causing a considerable variation in the Fe isotope ratios for the sulfides (Fig. 7). This isotopic evolutionary trend was reversed when pyrrhotite became a major sulfide phase. On the basis of experiments on isotopic fractionation between synthetic FeS crystals and aqueous Fe in a reducing solution, FeS is shown to be more depleted in heavy isotopes than dissolved Fe ( $\Delta^{57}\text{Fe}_{\text{Fe(II)}-\text{FeS}} = \sim 1.3$  per mil; Butler et al., 2005). This accounts for the generally lower  $\delta^{57}\text{Fe}$  value of pyrrhotite with respect to pyrite (Fig. 7). The precipitation of pyrrhotite following pyrite would then result in an increase in the  $\delta^{57}\text{Fe}$  value for dissolved Fe in the residual ore-fluid. Most chalcopyrite was formed during late-stage pyrrhotite precipitation, with some precipitating after pyrrhotite (Zhong et al., 2012). Chalcopyrite was generated in the isotopically heavy residual fluid after massive pyrrhotite had already precipitated and is therefore characterized by high  $\delta^{57}\text{Fe}$  values (Fig. 7). As pyrrhotite is a more common sulfide than pyrite at Huogeqi (Fig. 4c), a simple mass-balance effect would eventually result in a residual fluid with a  $\delta^{57}\text{Fe}$  value higher than that of the initial ore-fluid. The systematic variation in Fe isotopes is consistent with the paragenesis of sulfide minerals and provides further support for the epigenetic model for the Huogeqi deposit.

## 6. Discussion

### 6.1. Ore-formation history

The long-running controversy regarding whether the Huogeqi deposit is of syngenetic or epigenetic origin is mainly because of the deposit's mixed syngenetic and epigenetic characteristics. On one hand, the ore fabrics clearly indicate that the Cu–Pb–Zn mineralization is structurally controlled in shears that postdate peak metamorphism (Zhong et al., 2012). In particular, the consistent post-peak metamorphic signatures of hydrothermal sulfides rule out the possibility that a massive sulfide deposit was remobilized in situ during metamorphism, considering that metamorphic fluid was absent during the retrograde stage. On the other hand, some of the geochemical features (e.g. S and Pb isotopes) for the sulfides are identical with those from submarine hydrothermal ore-forming systems. In addition, the coexistence of Cu–Pb–Zn sulfides and an iron-formation – the latter was undoubtedly formed during sedimentary or diagenetic processes near the seafloor – led some researchers to conclude that the Cu–Pb–Zn mineralization is syngenetic (Chen, 2009). These paradoxical, geological, and geochemical characteristics and intimate spatial relation between the iron-formation and sulfide orebodies can be understood from a systematic study of stable isotopes, which provide good pointers to the origin of ore-fluids, sulfur, and metals.

Heterogeneous sources for the mineralization are indicated in this study by: (1) the ore-fluid was derived from metamorphic devolatilization; (2) sulfur and ore-forming metals were remobilized from a deep-seated stratabound source that was pre-enriched in metals during submarine hydrothermal activity; and (3) Fe in the sulfides was locally derived through the interaction between S(–Cu)-bearing ore-fluids and Fe-rich host rocks such as the iron-formation (Fig. 8). These results agree closely with the previous results of fluid inclusion studies and petrographic observations by Zhong et al. (2012, 2013).

The heterogeneous origin of aqueous fluid, S, and metals at Huogeqi is accounted for by the deposit's multistage genetic history (Fig. 8). During the Neoproterozoic, Cu–Pb–Zn–S pre-enrichment took place in a submarine hydrothermal system, accompanied by the deposition

rocks in a rift setting, forming sedimentary or volcanic rocks with considerable abundance of sulfides. These sulfides were subsequently remobilized by metamorphic devolatilization and accompanying shear deformation during the Permian and Triassic. The metal- and S-bearing ore-fluid ascended along a shear zone and interacted with organic-rich shale during fluid migration, forming the CH<sub>4</sub>–H<sub>2</sub>O ore-fluid. Aqueous S and Cu carried by the mineralized fluid interacted with Fe from the host rocks at the depositional site, resulting in the precipitation of Fe-bearing sulfides. The precipitation of large amounts of pyrite and pyrrhotite would have led to a dramatic decrease in the activity of reduced S in the fluid. Our recent thermodynamic model revealed that Cu mainly dissolves as a hydrosulfide CuHS<sub>aq</sub> complex in a sulfide-saturated, reduced, and low-salinity fluid under the pressure–temperature conditions at Huogeqi (Zhong et al., 2015a, in press). In this scenario, a decrease in the concentration of reduced sulfur, which is the major ligand of Cu complexation, would destabilize aqueous Cu-hydrosulfide complexes in the fluid and subsequently lead to the precipitation of chalcopyrite. Therefore, Fe in the host rocks provided a favorable sink for sulfide precipitation and high-grade mineralization.

### 6.2. Implications for mineral exploration

Syngenetic and epigenetic processes were critical in the formation of the Huogeqi deposit, therefore the multistage genetic model has practical implications for mineral exploration. Neoproterozoic syngenetic pre-enrichment process is a favorable geological background for redeposition of sulfides from fluids during metamorphism, in which case epigenetic mineralization is expected in areas with thick Neoproterozoic rift sequences. In particular, intercalated metavolcanic rocks are indicators of high heat-flow during rifting and consequently are ideal locations for submarine hydrothermal activities.

Metamorphism and deformation are key processes controlling both mineral precipitation and structures affecting orebodies. As a result, the present nature of mineralization share many similarities with orogenic-type gold and base metal deposits (Goldfarb et al., 2005; Li et al., 2007, 2008; Zhang et al., 2012; Zheng et al., 2012, 2014, 2015). Pre-enriched rift rocks metamorphosed at greenschist to amphibolite facies under a favorable pressure–temperature regime are commonly and extensively devolatilized and subject to metal remobilization (Tomkins, 2010). Structures in shear-zone-controlled deposits are the primary geological feature controlling mineralization and the most significant target for mineral exploration. As shown in Fig. 2, Cu–Pb–Zn orebodies are present in jogs along a shear zone in the Huogeqi area, which marks dilatational zones during shearing; shears are subject to the flow of numerous ore-fluids circulating through surrounding rocks. Therefore, orebodies are potentially present in areas with significant changes in strikes along a shear zone. The structurally controlled mineralization is evidenced by recent results of mineral exploration, which shows that most Cu and Pb–Zn occurrences in the Langshan area are distributed along major thrust and strike-slip faults (see Figs. 1 and 3 of Li et al., 2013). A secondary geological unit controlling mineralization is the Fe-rich lithological units of host rocks. Iron exchange between the ore-fluid and host rock, Fe-rich rocks such as iron-formation and diopside-rich marble are favorable sites for the deposition of massive sulfides. High-grade Cu–Pb–Zn ores are expected where shear zones intersect interlayered iron-formations or diopside-rich marble beds.

## 7. Conclusions

The Huogeqi ore-fluid had a metamorphic origin and was in equilibrium with organic-rich shale. Sulfur was remobilized during metamorphism from stratabound sulfides deposited during submarine hydrothermal activities. This suggests a syngenetic pre-enrichment process was operating during the development of Neoproterozoic rift-related rocks. The iron in the sulfides was derived from the

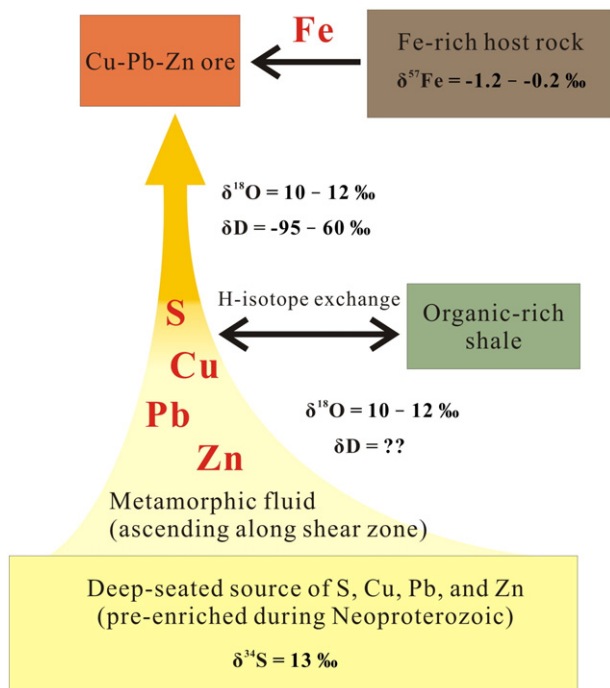


Fig. 8. A sketch showing the sources and isotopic nature of ore-fluid, S, ore-forming metals and Fe at the Huogeqi deposit.



local rocks during sulfide precipitation, suggesting that Fe-rich host rocks are favorable sinks for mineralization.

A multistage genetic model is proposed here, for the formation of the Huoqeqi deposit during remobilization of deep-seated stratabound sulfides during metamorphism. In this model, the Cu–Pb–Zn mineralization was proximally remobilized and deposited in jogs along shear zones.

Shear-zone-controlled Cu–Pb–Zn deposits are expected to be present in areas with thick sequences of greenschist–amphibolite facies rift rocks, especially where intercalated metavolcanic rocks are present. Shears are the primary geological structure controlling mineralization, and jogs in shear zones are good sites for ore–fluid concentration. In addition, Fe-rich layers are ideal hosts for high-grade mineralization.

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