

# Homogeneous Zn isotopic compositions in the Maozu Zn-Pb ore deposit in Yunnan Province, southwestern China

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## ABSTRACT

The Sichuan-Yunnan-Guizhou (SYG) metallogenic province, southwestern Yangtze Block, is one of the most important Zn-Pb repositories in China, with more than 200 million tons (Mt) of Zn-Pb ores. The source regions for the regional Zn-Pb mineralization in the SYG are still controversial, mostly in regard to the Emeishan flood basalts, basement rocks and host rocks. The Maozu Zn-Pb deposit is geographically close to the SYG center, which could also indicate that it is closer to the regional Zn-bearing fluid center than those deposits along the SYG margin. However, the origin of the ore-forming Zn in the Maozu deposit has not been constrained until now. In this study, the Zn and S isotopic compositions and Fe and Cd concentrations of the sphalerite from the Maozu deposit are investigated to evaluate the Zn isotopic fractionation during sphalerite precipitation, the source regions of the ore-forming zinc and sulfur, and the center of the regional Zn-bearing fluid system. It is suggested that the Zn isotopic fractionation between the sphalerite and original fluid during sphalerite precipitation could be limited due to the striking decrease in the temperature of the incoming fluid. The Zn isotopic variation of the sphalerite from four mining levels in the Maozu deposit is really small ( $-0.06$  to  $+0.23\text{‰}$ ), which could be attributed to heterogeneous Zn isotopic compositions in original incoming fluid rather than Zn isotopic fractionation during sphalerite deposition. As such, in the Maozu deposit, the Zn isotopic compositions of original hydrothermal fluid could approximately be represented by the Zn isotopic signals documented in sphalerite ( $-0.06$  to  $+0.23\text{‰}$ ). We found that the Zn isotopic signatures of incoming fluid are largely overlapped with those of the basement rocks ( $+0.10$  to  $+0.34\text{‰}$ ), signifying that the ore-forming Zn could be predominantly sourced from the basement rocks. However, in the Maozu deposit, the ore-forming sulfur is most likely derived from the sulfur-bearing evaporates hosted in the country rocks via thermochemical sulfate reduction (TSR). The contrasting sources of ore-forming zinc and sulfur suggest the mixing of Zn-bearing fluid from the basement rocks and sulfur-bearing fluid from the host rocks, which could be responsible for the sharp decrease in the temperature of the incoming fluid in the Maozu deposit. Combined with the results of previous studies, the integrally lower Zn isotopic compositions of sphalerite in the Maozu deposit compared to those deposits along the SYG margin may demonstrate that the Maozu deposit is closer to the regional Zn-bearing fluid center. If this is the case, Zn isotopes could be an effective proxy to trace the Zn source of Zn-enriched ore deposits and to identify the regional Zn-bearing fluid center of Zn-enriched metallogenic provinces.

## 1. Introduction

The Sichuan-Yunnan-Guizhou (SYG) metallogenic province is an important component of the giant South China low-temperature metallogenic domain (Hu et al., 2017a, b). More than 400 Zn-Pb ore deposits occur in the SYG mineralization region, with total Zn + Pb

reserves of ~200 Mt (Liu and Lin, 1999; Zhou et al., 2013). Most of these deposits, such as the Maozu deposit, have been considered comparable to typical Mississippi Valley-type (MVT) deposits, in terms of tectonic setting, type of host rocks, and younger age than the host rocks for mineralization (Wang et al., 2003; Han et al., 2007; Zhou et al., 2013; Xiong et al., 2018). The source region for the regional Zn-Pb

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mineralization in the SYG remains controversial, despite the many investigations that have been conducted. All of these deposits are spatially coexistent with the Permian Emeishan flood basalts (~260 Ma; Zhou et al., 2002), triggering much controversy on the relationship between the regional mineralization and Emeishan basalts (Huang et al., 2003; Zhou et al., 2018). In addition, geological and geochemical evidence also point out that the Mesoproterozoic to lower Ediacaran basements and upper Ediacaran to Paleozoic sedimentary rocks are two other potential source regions (Liu and Lin, 1999; Zhou et al., 2001; Huang et al., 2003; Han et al., 2007; Zhou et al., 2014b, 2018). In the SYG, studies with respect to Zn source have been conducted in the Shanshulin, Tianqiao, Banbanqiao, Tianbaoshan and Wusihe deposits (Zhou et al., 2014a, b; He et al., 2015; Zhou et al., 2018; Zhu et al., 2018). However, these conducted studies did not make a consensus in regard to the regional Zn source, with arguments among the Emeishan basalts, basement rocks and host rocks. Additionally, these studies only focused on a single deposit along the SYG margin, without providing implications for the center of the regional Zn-bearing fluid system. In the Maozu deposit, Zn is the dominant ore-forming element, whereas the origin of ore-forming Zn has not been constrained until now. Geographically, the Maozu Zn-Pb deposit is very close to the SYG center, which could also suggest that the Maozu deposit is closer to the regional Zn-bearing fluid center than those deposits along the SYG margin.

The Zn isotopic fractionation mechanisms during sphalerite precipitation and the magnitude of fractionation between sphalerite and fluid have previously been well-studied (e.g., Mason et al., 2005; Wilkinson et al., 2005; Kelley et al., 2009; Gagnevin et al., 2012; Pašava et al., 2014; Zhou et al., 2014a, b; Gao et al., 2017). The extent of Zn isotopic fractionation between the sphalerite and original fluid during sphalerite deposition is commonly significant, triggering widely varying  $\delta^{66}\text{Zn}$  values in sphalerite (~0.8‰ variation; Wilkinson et al., 2005; Pašava et al., 2014; Zhou et al., 2014a, b). In this situation, it is difficult to reconstruct the Zn isotopic compositions of the original hydrothermal fluid via the Zn isotopic signatures recorded in precipitated sphalerite in a single ore deposit. Note that, however, the original hydrothermal fluids do not have entirely homogeneous Zn isotopic compositions, generally corresponding to a Zn isotopic variation of ~0.2‰ (John et al., 2008; Gagnevin et al., 2012). Therefore, a small Zn isotopic variation (~0.2‰) in sphalerite could just be due to the succession of the Zn isotopic variation in the original fluid, rather than the Zn isotopic fractionation of sphalerite with hydrothermal fluid. If the Zn isotopic compositions of the original hydrothermal fluid can be well reconstructed, tracing the Zn source of the ore-forming fluid through Zn isotopic system is effective and feasible (Wilkinson et al., 2005; Duan et al., 2016). Moreover, Zn isotopic fractionation could also occur during the regional fluid migration, resulting in gradually increasing Zn isotopic compositions in fluid away from the center of the Zn-bearing fluid system (Wilkinson et al., 2005; Kelley et al., 2009). Therefore, Zn isotopic system could also potentially be applied to trace the possible pathway of fluid migration and to identify the possible center of the regional hydrothermal system. In this study, the Zn and S isotopic compositions of sphalerite are investigated to trace the sources of the ore-forming zinc and sulfur in the Maozu deposit. Combined with the results of previous studies, we seek to confirm that whether the Maozu deposit is closer to the center of the regional Zn-bearing hydrothermal system compared to the other marginal deposits in the SYG.

## 2. Geological setting

### 2.1. Regional geology

The Yangtze Block, which is part of the South China Block, is bounded by the Tibetan Plateau to the west, Qinling Orogenic Belt to the north, and Cathysia Block to the south (Fig. 1A). The SYG polymetallic metallogenic province, with a triangular coverage area of ~170,000 km<sup>2</sup> (Zhou et al., 2014a, b), is tectonically located in the

southwestern margin of the Yangtze Craton (Fig. 1A). The Mesoproterozoic to lower Ediacaran basement complexes and upper Ediacaran to Cenozoic cover sequences constitute the southwestern Yangtze Block (Zhou et al., 2001; Hu et al., 2017a, b; Xiong et al., 2018). The Mesoproterozoic to lower Ediacaran basements comprise phyllites, graywackes, volcanic rocks, and minor carbonates (Zhou et al., 2001; Zhou et al., 2014b; Xiong et al., 2018). The cover sequences consist of upper Ediacaran to Permian marine and Mesozoic to Cenozoic continental sedimentary rocks, mainly including carbonates, evaporates, black shales, and clastic rocks (Yan et al., 2003; Zhou et al., 2014b). The Ediacaran Dengying Formation is the most important ore-hosting strata in the SYG, accounting for over 75% of the Zn-Pb reserves (Guan and Li, 1999; Chen, 2015), in which the orebodies of deposits are generally strata-bound within the strata (Xiong et al., 2018). Many economic Zn-Pb deposits, such as the Wusihe, Tianbaoshan, Tianqiao, Banbanqiao, Shanshulin, and Maozu deposits, are distributed along the Anninghe, Xiaojiang, Mile-Shizong, and Ziyun-Yadu regional fractures and their secondary faults (Fig. 1B). The well-developed and interlaced fault structures control the migration of regional ore-forming fluids, and a series of thrust-fold systems are the primary ore-hosting structures in the SYG (Zhang et al., 2015; Xiong et al., 2018). In the southwestern Yangtze Block, the Permian Emeishan flood basalts cover an area of more than 250,000 km<sup>2</sup> (~260 Ma; Zhou et al., 2002), spatially overlying the Zn-Pb deposits hosted in the Ediacaran to Permian sedimentary rocks (Han et al., 2007; Zhou et al., 2014a, b).

### 2.2. Deposit geology

The Maozu deposit is geographically located in the north-central SYG (Fig. 1B). The strata exposed in the Maozu ore field, from lower to upper stratigraphy, are the Ediacaran carbonates; Cambrian black shales, sandstones, and carbonates; Permian Emeishan basalts; and Mesozoic to Cenozoic continental sedimentary rocks (Zhou et al., 2013). Therein, the Ediacaran Dengying Formation carbonates (mainly dolostone) are the primary ore-hosting strata in the Maozu deposit (Fig. 2). Structurally, the orebodies in the Maozu deposit are controlled by several tectonic systems of faults and folds (i.e., the Maozu, Changpo and Dadong faults and the Changpo, Ganshulin, Baika, and Hongfadong folds; Fig. 2). These fault systems, which act as conduits for hydrothermal fluids, control the migration of deep fluids, and the fold systems provide space for the incoming fluids (He et al., 2006). The Permian Emeishan basalts are distributed in the northwestern Maozu ore field, which is well isolated with the Zn-Pb mineralization via the Maozu thrust-fault (Fig. 2A). The orebodies can be classified into two layers based on the different hosting positions in the Dengying Formation (Fig. 2B). Four orebodies from the upper part of the Dengying Formation account for ~85% of the Zn-Pb reserves, and five orebodies from the lower part of the Dengying Formation account for ~14% of the Zn-Pb reserves (Liu, 2009; Zhou et al., 2013). These orebodies yield a total Zn-Pb reserve of 2.4 Mt, with average grades of 6.04 wt% Zn and 1.91 wt% Pb (Liu, 2009). The ore minerals include sphalerite and galena, and the gangue minerals comprise pyrite, dolomite, quartz, calcite, and fluorite. The sphalerite is characterized by a granular texture and massive, disseminated and veined structures (Fig. 3). The alteration types of the host rock principally include dolomitization, calcitization, pyritization, and ferritization, in which the dolomitization and calcitization are closely associated with Zn-Pb mineralization (Zhou et al., 2013).

## 3. Samples and analytical methods

### 3.1. Samples

Eight representative sphalerite samples were collected from four mining levels in the Maozu deposit, which covers two orebody layers hosted in different locations in the Dengying Formation (Figs. 2 and 3).

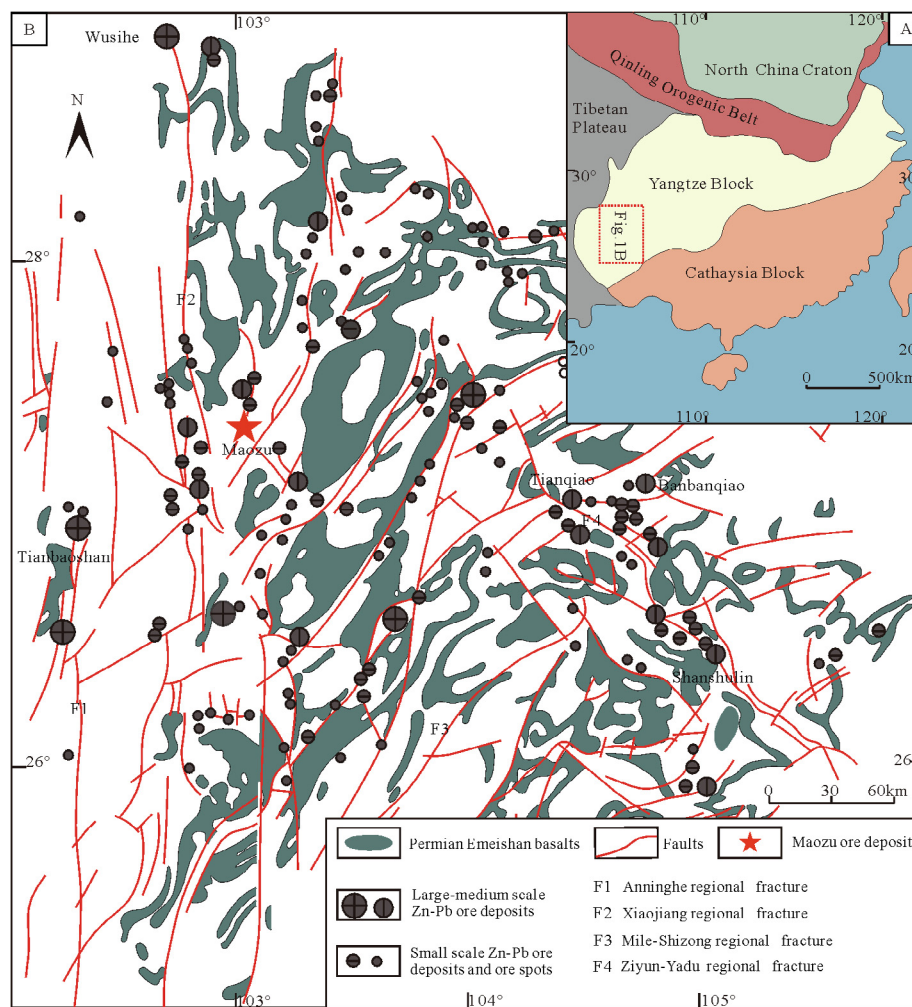


Fig. 1. Map of the tectonic framework of South China (A); regional geological map of the Sichuan-Yunnan-Guizhou Zn-Pb metallogenic province (B) that shows the distribution of major faults, basalts and Zn-Pb ore deposits (modified from He et al., 2015).

MZ-3 and MZ-7 were obtained from the 1350# adit with disseminated and massive structures, respectively (Fig. 3A and B). MZ-17 was collected from the 1380# adit with a disseminated structure (Fig. C). MZ-20 and MZ-26 were collected from the 1400# adit with massive and veined structures, respectively (Fig. D and E). MZ-49, MZ-51, and MZ-62 were obtained from the 1550# adit with massive and veined structures, respectively (Fig. F, G and H). One host rock sample was collected from the 1350# adit, and the other five host rock samples were collected from an outcrop within the Maozu ore field (N27.35°, E102.99°). Five basement samples were sampled from the outcrop out of the Maozu ore-field (N26.11°, E103.04° and N26.09°, E103.02°). All of the sphalerite powder used for analyses were sampled using the Micro-Drill Sampling System (MSS) at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. The tungsten steel used for the MSS has a diameter of 0.5 mm, which can greatly avoid the contamination of host rocks.

### 3.2. Methods

Sphalerites, carbonates, and Si-bearing basement rocks were digested using HNO<sub>3</sub> (15 mol/L), HCl (6 mol/L), and HNO<sub>3</sub> (15 mol/L) + HF (23 mol/L), respectively, at 120 °C for 24 h. Sample solutions were evaporated to dryness and then digested in 2 ml of 2 N HCl. Elemental Zn was purified from other matrix elements using anion exchange chromatography (AGPM-1) as reported by Tang et al. (2006). Zn isotopic ratios were measured using Nu Plasma MC-ICP-MS under

low-resolution mode at the Key Laboratory of Isotope Geology, Department of Land and Resources, Institute of Geology, Chinese Academy of Geological Sciences. Mass discrimination effects were corrected using combined sample-standard bracketing (SSB) (Li et al., 2008; Zhou et al., 2014a, b). The accuracy and reproducibility of analyses were assessed via replicate analyses of the international standards BHVO-2 (basalt), which yielded an average  $\delta^{66}\text{Zn}$  value of  $0.3 \pm 0.04\text{‰}$  ( $2\sigma$ ,  $n = 6$ ). Each result reflected the mean value over N number of repeats, and all results are reported relative to the Lyon JMC 3-0749L Zn standard (Maréchal et al., 1999) based on the difference between the IRMM3702 and JMC Lyon Zn solution ( $\Delta^{66}\text{Zn}_{\text{IRMM3702-JMC Lyon}} = 0.30\text{‰}$ ; Moeller et al., 2012; Samanta et al., 2016).

Sulfur isotopic analyses were conducted using a Thermo Flash 2000 at the State Key Laboratory of Resource Utilization and Environmental Restoration, Institute of Geographic Science and Natural Resources Research, Chinese Academy of Sciences. IAEA-S-1 (Ag<sub>2</sub>S;  $\delta^{34}\text{S} = -0.3 \pm 0.16\text{‰}$ ,  $n = 6$ ) was used as the external standards. The relative errors ( $2\sigma$ ) are better than 0.1‰ based on the replication of standard materials. Sulfur isotopic compositions are reported relative to the Canyon Diablo Troilite (CDT).

The concentrations of Zn, Fe, and Cd in sphalerite were measured using a PinAAcle 900F atomic absorption spectrometer at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. The measurements of concentrations of Zn, Fe and Cd in basement rocks and host rocks were conducted using the method of ME-MS61r at the ALS Chemex (Guangzhou) Company

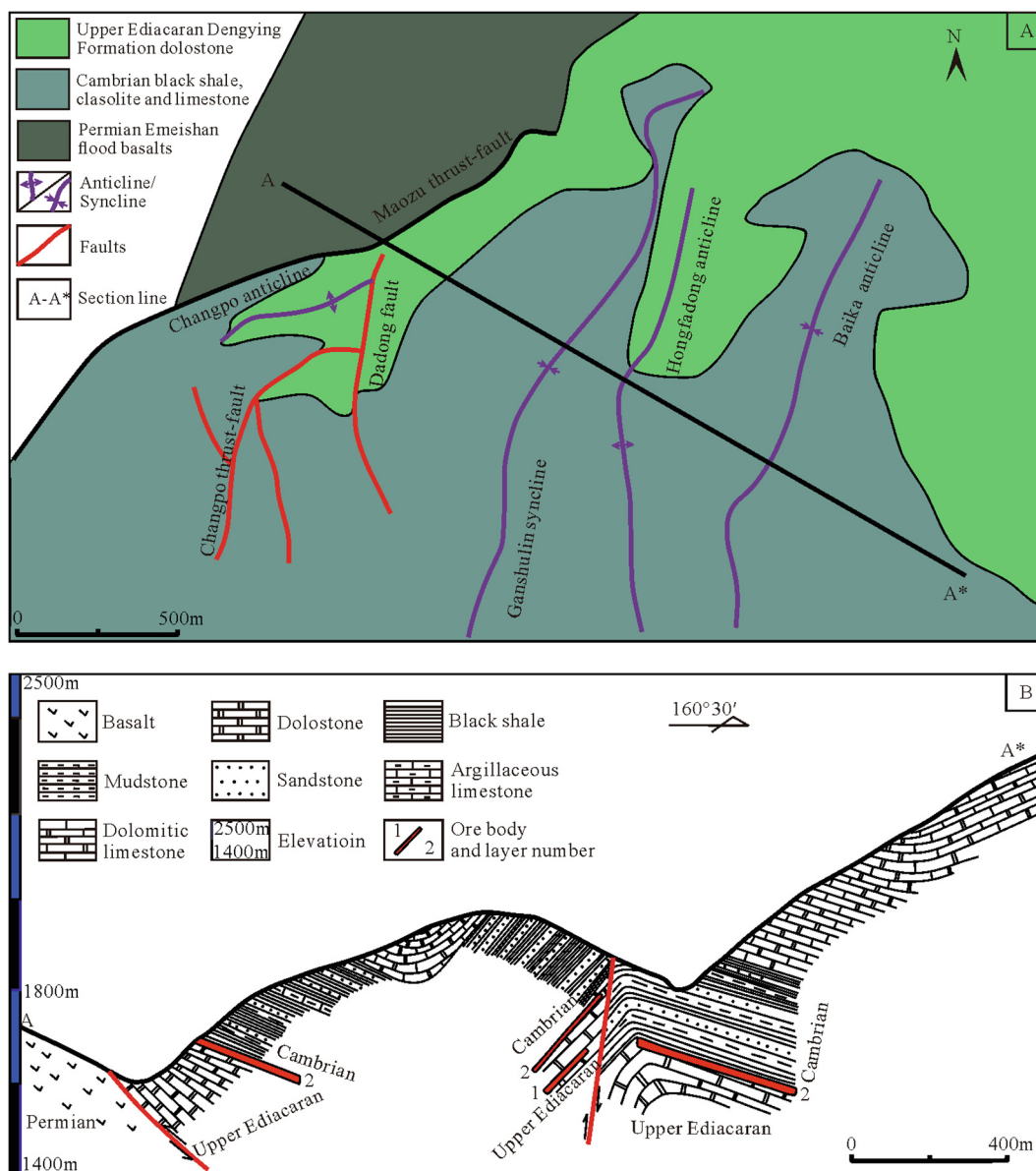


Fig. 2. Geological map of the Maozu ore deposit, showing the major exposed strata and ore-controlling structures (modified from Zhou et al., 2013).

Limited. The relative error of the Zn, Fe, and Cd concentrations is less than 5% (28). In addition, utilizing  $Fe_{(ppm)}/Zn_{(‰)}$  and  $Cd_{(ppm)}/Zn_{(‰)}$  to correct the Fe and Cd contents in the sphalerite could diminish the interference of the incorporation of different proportions of host rocks.

#### 4. Results

The Zn and S isotopic compositions and Zn, Fe and Cd concentrations of the sphalerite from the Maozu Zn-Pb deposit are exhibited in Table 1. The Zn isotopic variation of the sphalerite from four mining levels in the deposit is really small ( $-0.06$  to  $+0.23‰$ ) without obvious spatial evolution (Fig. 4). The Fe and Cd contents in the sphalerite, presented as  $Fe_{(ppm)}/Zn_{(‰)}$  and  $Cd_{(ppm)}/Zn_{(‰)}$ , also do not yield any regular variations (Fig. 4). Moreover, four micro-drilled sphalerite samples from two specimens in the same 1400# adit nearly cover the entire range of the Fe and Cd contents variations of all sphalerite samples (Figs. 4 and 5). The sulfur isotopic compositions of sphalerite in the Maozu deposit vary from 12.9 to 17.3‰. Moreover, the Zn and S isotopic compositions of sphalerite from the Maozu deposit are decoupled (Fig. 6).

#### 5. Discussion

##### 5.1. Zn isotopic fractionation during sphalerite precipitation suggested in previous studies

Before using the Zn isotopic compositions of sphalerite to trace the source of ore-forming fluid, the magnitude of the Zn isotopic fractionation between the sphalerite and fluid during sphalerite precipitation should be evaluated. Previous studies have demonstrated that several mechanisms during fluid evolution could result in Zn isotopic fractionation between sphalerite and the hydrothermal fluid, including the changes in temperature (Mason et al., 2005; Toutain et al., 2008), changes in pH and Zn complex speciation (Pašava et al., 2014) and Rayleigh fractionation (e.g., Wilkinson et al., 2005; Kelley et al., 2009; Gagnevin et al., 2012; Zhou et al., 2014a, b; Gao et al., 2017). An experiment demonstrated that temperature variations of 30–50 °C have no effect on Zn isotopic fractionation during smithsonite precipitation from Zn-chloride and Zn-nitrate solutions (Maréchal and Sheppard, 2002). Moreover, there is no obvious correlation between Zn isotopic compositions and temperatures in sphalerite from the Irish Midlands

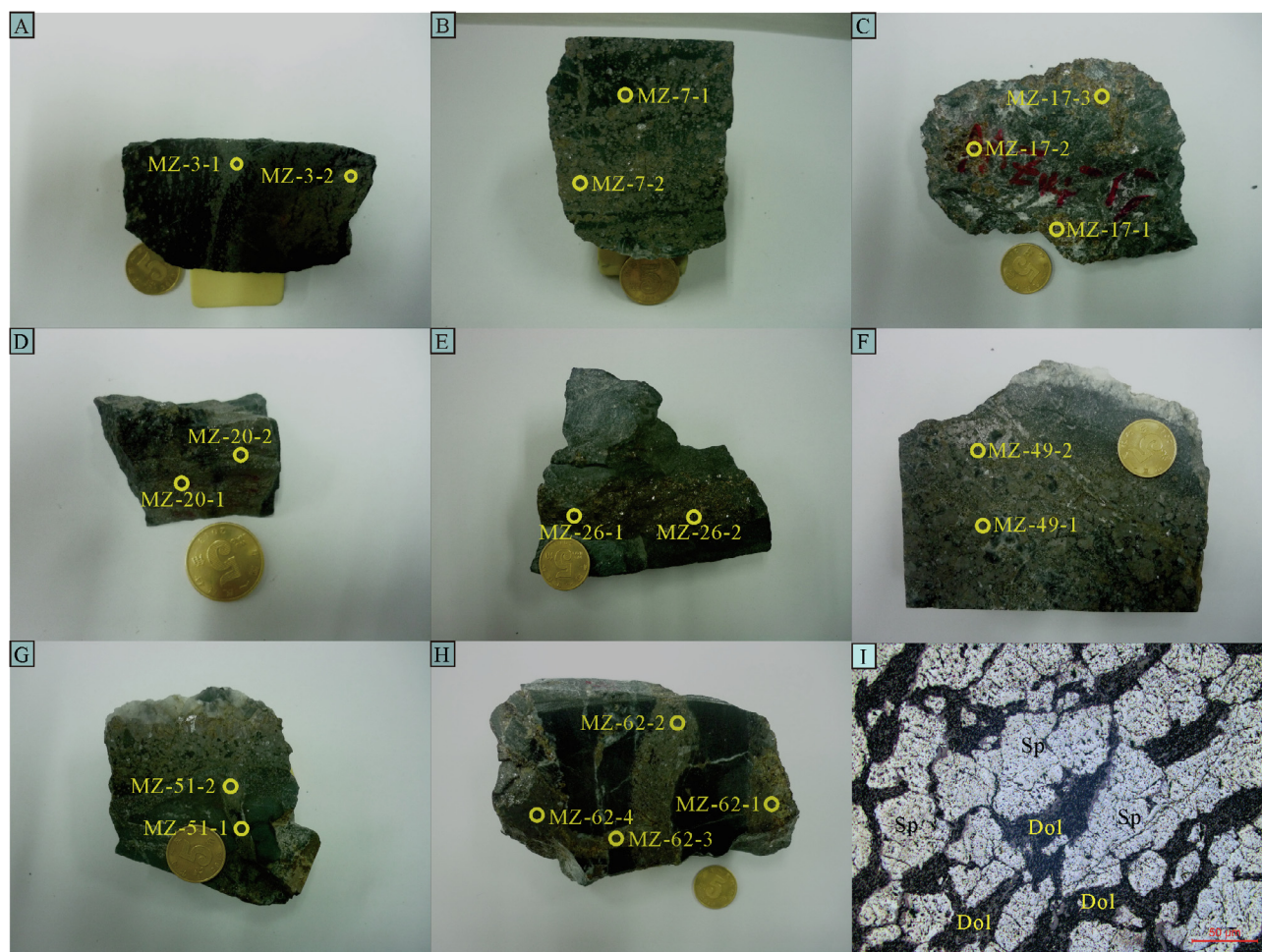


Fig. 3. A–H: specimen images of sphalerite ores from the Maozu deposit, showing micro-drilled positions of MZ-3 (A), MZ-7 (B), MZ-17 (C), MZ-20 (D), MZ-26 (E), MZ-49 (F), MZ-51 (G), and MZ-62 (H); I: microphotograph of MZ-3 showing the fine granular texture of sphalerite; Sp = sphalerite, Dol = dolomite.

ore filed ( $R^2 = 0.011$ ), where the temperature conditions of each sphalerite have been well-constrained (60–250 °C; Wilkinson et al., 2005). These observations indicate that the influence of temperature gradients on Zn isotope fractionation is negligible when the temperatures are lower than 300 °C (Maréchal and Sheppard, 2002; Wilkinson et al., 2005; Zhou et al., 2014a, b). The homogenization temperatures of fluid inclusions in hydrothermal minerals from the Maozu deposit vary from 153 to 282 °C (Liu and Lin, 1999; He et al., 2006), indicating that the changes in temperature are not expected to be responsible for the Zn isotopic variations in sphalerite from the Maozu deposit. The theoretical calculation showed that Zn isotopic fractionation between sulfides and solutions controlled by pH and Zn complex speciation could be significant (Fujii et al., 2011). For instance, they proposed that Zn associated with carbonate speciation can be isotopically 1.0‰ heavier than parent solution with ~7.5 pH condition, and that Zn isotopic compositions in sulfides can drop by at least 0.6‰ relative to parent solution with pH > 9. Pašava et al. (2014) also stated that the changes in pH and Zn complex species could be responsible for the extremely negative and varied  $\delta^{66}\text{Zn}$  values in natural sphalerites (Fig. 7; from –0.80 to –0.01‰ at La Florida and from –0.75 to +0.24‰ at Picos de Europa, Spain). Nevertheless, the  $\delta^{66}\text{Zn}$  values in sphalerite from the Maozu deposit are mostly positive and cluster within a narrow range, which suggests that the changes in pH and Zn complex speciation are not dominant controls for the Zn isotopic variation of sphalerite in this deposit (Fig. 7).

The Zn isotopic compositions of sphalerite from the Maozu deposit do not show any spatial evolution among the four mining levels (Fig. 4),

unlike Rayleigh fractionation that yields obvious spatial variation of  $\delta^{66}\text{Zn}$  in sphalerite within a single orebody (Gao et al., 2017). Previous studies have shown that dominant Rayleigh fractionation generally produces ~0.8‰ variation of  $\delta^{66}\text{Zn}$  in sphalerite at a deposit scale (Fig. 7). For example, in the SYG, Rayleigh fractionation yield Zn isotopic variation in sphalerite from –0.26 to +0.58‰ and +0.07 to +0.71‰ at the Tianqiao and Banbanqiao Zn–Pb deposits, respectively (Zhou et al., 2014b), which are also reported from an Irish ore field (–0.17 to +0.64‰, Wilkinson et al., 2005). However, the Zn isotopic compositions in sphalerite from the Maozu deposit cluster within a narrow range (–0.06 to +0.23‰), which contrasts with the Zn isotopic variation dominated by Rayleigh fractionation (Fig. 7). Moreover, Rayleigh fractionation would result in increasing  $\delta^{66}\text{Zn}$  values in sphalerite from the early to late stages (Archer et al., 2004; Zhou et al., 2014a, b), during which the increasing  $\delta^{66}\text{Zn}$  values should be mirrored by decreasing Fe and increasing Cd concentrations due to Fe and Cd are preferentially precipitated at the early and late stages, respectively (John et al., 2008; Kelley et al., 2009; Liu et al., 2012). However, the Zn isotopic ratios and Fe and Cd concentrations in sphalerite from the Maozu deposit do not display any correlation (Fig. 4). More clearly, in the 1400# adit, despite yielding extremely similar Zn isotopic ratios (MZ-20-2 and MZ-26-2; MZ-20-1 and MZ-26-1), all four of these micro-drilled sphalerites exhibit entirely distinct character of Fe and Cd concentrations from each other (Fig. 5). The absence of correlation between the Zn isotopic ratios and Fe–Cd concentration in sphalerite also suggests that Rayleigh fractionation could not be important for the Zn isotopic variation of sphalerite in the Maozu deposit.

**Table 1**

The Zn-S isotopic compositions and Zn-Fe-Cd contents in sphalerites, host rocks, and basement rocks.

Nos.	Positions	Mineral	Zn (wt%)	Fe (wt%)	Cd (ppm)	$\delta^{66}\text{Zn}$ (‰)	2 $\sigma$	$\delta^{34}\text{S}$ (‰)
MZ-3-1	1350#	Sphalerite	51.84	6.82	1227	0.04	0.02	16.7
MZ-3-2	1350#	Sphalerite	47.53	5.37	993	0.14	0.05	17.3
MZ-7-1	1350#	Sphalerite	52.27	6.53	1004	0.12	0.03	15.4
MZ-7-2	1350#	Sphalerite	44.90	6.47	829	0.23	0.03	14.7
MZ-17-1	1380#	Sphalerite	49.23	8.36	1169	-0.05	0.07	13.0
MZ-17-2	1380#	Sphalerite	52.28	6.18	1169	-0.02	0.09	13.2
MZ-17-3	1380#	Sphalerite	53.24	7.24	1171	-0.06	0.00	12.
MZ-20-1	1400#	Sphalerite	47.42	19.80	1267	0.18	0.08	16.8
MZ-20-2	1400#	Sphalerite	45.39	6.92	1249	0.03	0.01	16.7
MZ-26-1	1400#	Sphalerite	36.02	5.74	493	0.17	0.01	14.5
MZ-26-2	1400#	Sphalerite	21.65	10.56	280	0.06	0.07	14.1
MZ-49-1	1550#	Sphalerite	54.22	6.34	897	0.02	0.04	13.8
MZ-49-2	1550#	Sphalerite	31.23	16.68	547	-0.04	0.04	14.2
MZ-51-1	1550#	Sphalerite	51.05	6.49	1083	0.20	0.00	13.6
MZ-51-2	1550#	Sphalerite	51.42	4.63	1146	-0.01	0.08	13.4
MZ-62-1	1550#	Sphalerite	59.65	6.81	1142	0.11	0.02	13.4
MZ-62-2	1550#	Sphalerite	49.79	3.83	1524	0.08	0.03	13.6
MZ-62-3	1550#	Sphalerite	49.67	10.42	991	0.11	0.00	13.8
MZ-62-4	1550#	Sphalerite	55.79	7.95	1191	0.17	0.06	13.7
Nos.	Positions	Host rocks	Zn (ppm)	Fe (wt%)	Cd (ppm)	$\delta^{66}\text{Zn}$ (‰)	2 $\sigma$	$\delta^{34}\text{S}$ (‰)
MZ-31	1350#	Carbonates	43,400	0.35	169.50	0.09	0.03	-
MZ-5	outcrop	Carbonates	43	2.96	0.08	0.31	0.01	-
MZ-8	outcrop	Carbonates	43	0.06	0.29	0.32	0.01	-
MZ-13	outcrop	Carbonates	27	0.19	0.04	-0.03	0.04	-
MZ-15	outcrop	Carbonates	17	0.12	0.04	0.04	0.04	-
MZ-16	outcrop	Carbonates	23	0.10	0.06	0.41	0.07	-
Nos.	Positions	Basement rocks	Zn (ppm)	Fe (wt%)	Cd (ppm)	$\delta^{66}\text{Zn}$ (‰)	2 $\sigma$	$\delta^{34}\text{S}$ (‰)
WC-1	outcrop	Carbonates	3	2.01	0.04	0.21	0.04	-
HS-4	outcrop	Carbonates	24	0.79	0.07	0.10	0.04	-
TBS16-2	outcrop	Graywackes	61	4.57	0.02	0.30	0.04	-
Td1900-8	outcrop	Phyllites	115	2.03	0.24	0.15	0.05	-
Td1900-3	outcrop	Phyllites	199	4.95	0.37	0.34	0.05	-

Note: “-” mean not measured.

Considering the above three mechanisms that could trigger Zn isotopic fractionation between sphalerite and fluid are not important, we propose that the Zn isotopic fractionation between the sphalerite and hydrothermal fluid could be limited during sphalerite deposition in the Maozu deposit.

### 5.2. Mechanisms for the limited Zn isotopic fractionation during deposition processes

The presence of isotopically unfractionated Zn between the sphalerite and original hydrothermal fluid has been reported from two sphalerite specimens in the Irish Navan deposit (Gagnevin et al., 2012). Three possible explanations have been suggested as follows: 1) the much slower growth of sphalerite allows isotopic re-equilibration with the fluid; 2) the very limited rate of input of hydrothermal fluid during sphalerite precipitation; and 3) a striking decrease in temperature diminishes the extent of kinetic fractionation.

The Zn isotopic equilibrium fractionation between chalcopyrite and sphalerite in the stockwork mineralization region from the Alexandrinka VHMS deposit has been reported to correspond to ~300 °C temperature conditions (Mason et al., 2005). Theoretically, isotopic equilibrium fractionation is a function of temperature, with larger fractionation generated at lower temperatures (Urey, 1947; Fujii et al., 2011). However, both experimental and natural studies suggested that Zn isotopic fractionation is independent with temperatures when the temperature conditions are lower than 300 °C (Maréchal and Sheppard, 2002; Wilkinson et al., 2005). This may indicate that Zn isotopic equilibrium is difficult to achieve when the temperature conditions are lower than 300 °C. In the Maozu deposit, the ore-forming temperature conditions have been evaluated as < 300 °C (Liu and Lin, 1999; He et al., 2006), under which achieving Zn isotopic equilibrium could not be expected. Meanwhile, the sulfur isotopic compositions of

sulfide from the Maozu deposit also do not strictly follow an equilibrium fractionation order of pyrite > sphalerite > galena (Fig. 8; Tatsumi, 1965; Ohmoto, 1986). In addition, the assumption of a very slow input of fluid is plausible at the Irish Navan deposit, based on the common presence of colloform and zoned textures in sphalerite specimens (Gagnevin et al., 2012). However, sphalerite samples from the Maozu deposit are characterized by a fine granular texture (Fig. 3I), which is distinct from the Irish Navan deposit. Consequently, the much slower growth of sphalerite as well as the very slow input of hydrothermal fluid cannot be supported in the Maozu deposit.

A striking decline in temperature probably occurred in the Maozu deposit based on the integrally homogeneous Fe and Cd concentrations in the sphalerite (Fig. 4). Previous studies have demonstrated that Fe is preferentially precipitated during early stages under relatively high-temperature conditions, both in an experiment (Seewald and Seyfried, 1990) and in the natural hydrothermal systems (John et al., 2008; Kelley et al., 2009; Liu et al., 2012). Conversely, Cd is inclined to substitute for Zn in sphalerite during late stages under relatively low-temperature conditions (Liu et al., 2012; Wen et al., 2016). Therefore, the Fe and Cd concentrations in sphalerite could reflect the relative temperature conditions of sphalerite precipitation. However, in the Maozu deposit, the sphalerites collected from four mining levels, suggesting different ore-forming environments, mostly yield indistinguishable Fe and Cd contents without any regular variation (Fig. 4). Moreover, the four micro-drilled sphalerites from the same 1400# adit, suggesting similar ore-forming environments, almost cover the entire variation range of Fe and Cd contents in all of the sphalerite samples (Figs. 4 and 5). These observations indicate that the temperature of the incoming hydrothermal fluid did not gradually decrease during sphalerite precipitation and thus that Fe and Cd cannot function as temperature proxies. The striking decline in temperature is also supported by the fine granular texture of sphalerite (diameter = ~50 μm; Fig. 3I).

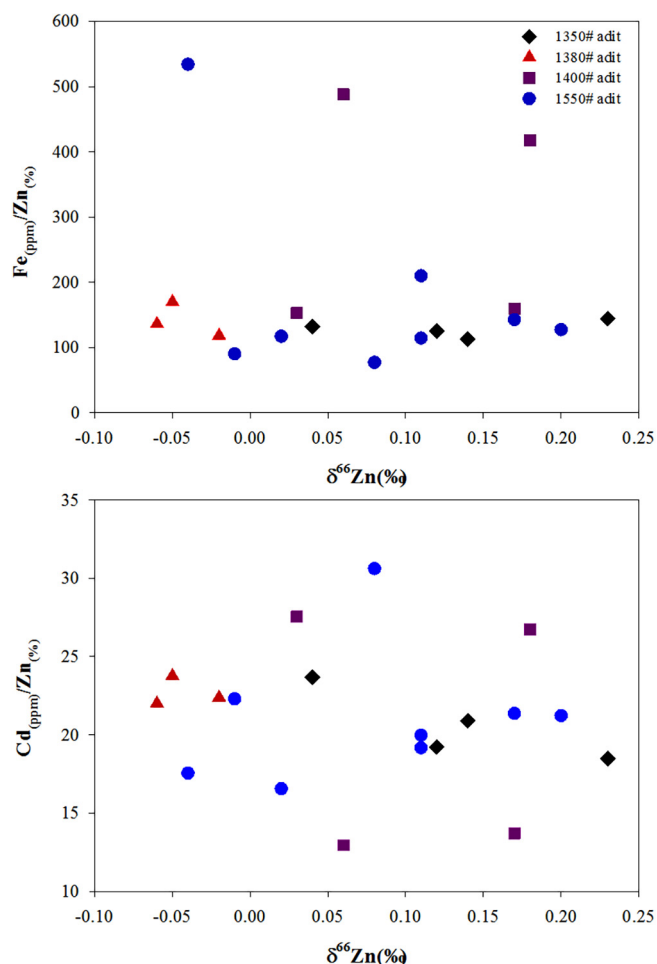


Fig. 4. Zn isotopic ratios plotted against Fe and Cd concentrations in sphalerite from four mining levels in the Maozu deposit, the different four adits could represent different ore-forming environments.

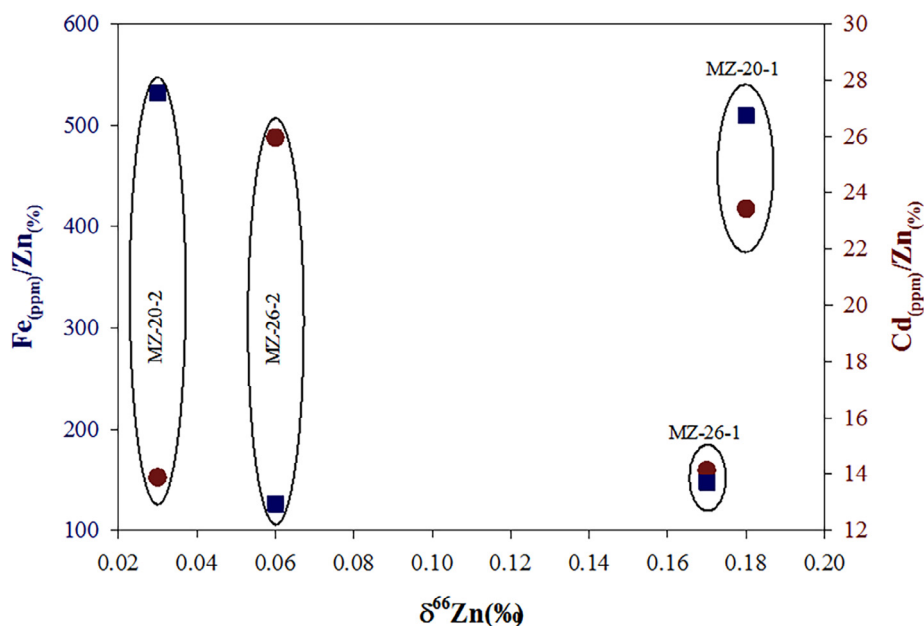


Fig. 5. Zn isotopic ratios plotted against Fe and Cd concentrations in sphalerite from the 1400# adit, the same adit could represent a similar ore-forming environment.

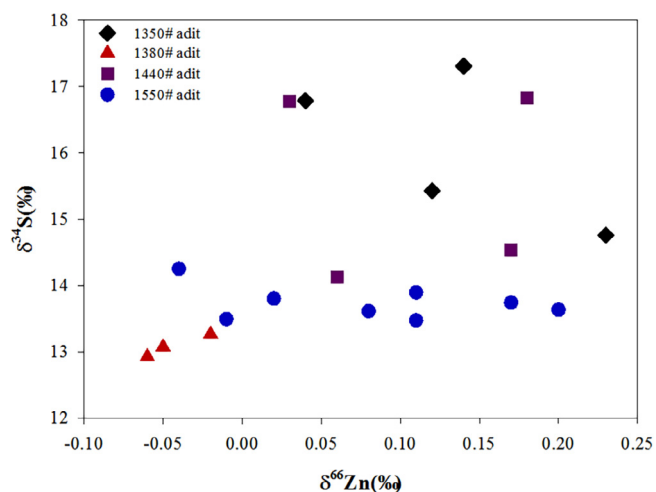
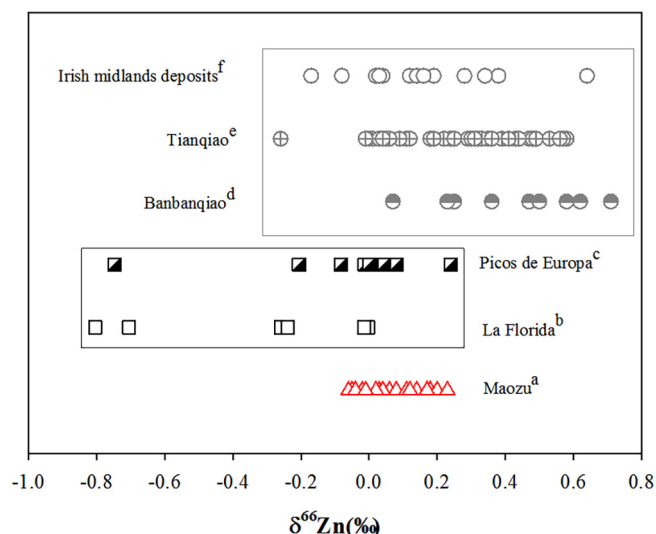


Fig. 6. Sulfur isotopic compositions plotted against zinc isotopic compositions in sphalerite from the Maozu deposit, showing the sulfur isotopic variations between the four mining levels and the decoupled correlation between the Zn and S isotopic ratios in the sphalerite.

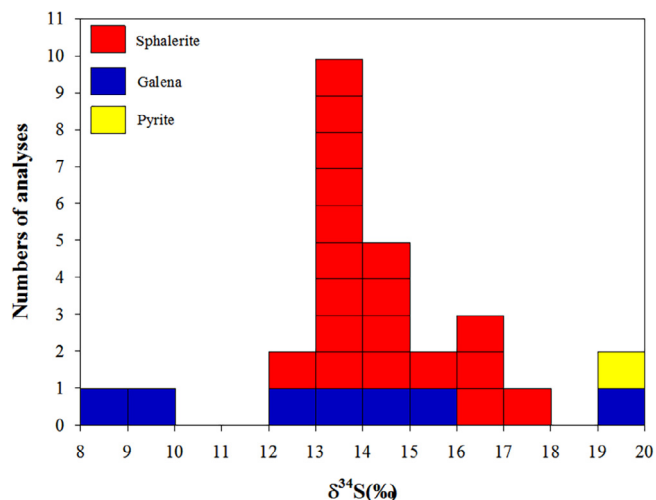
Therefore, the sharp decline in temperature of the incoming fluid is suggested to be responsible for the limited isotopic fractionation of Zn between the sphalerite and original hydrothermal fluid.

### 5.3. Source-controlled Zn isotopic variation

Considering that the Zn isotopic fractionation between sphalerite and hydrothermal fluid is limited, the  $\delta^{66}\text{Zn}$  values of the sphalerite could approximately represent the Zn isotopic signals of the incoming hydrothermal fluid ( $-0.06$  to  $+0.23\text{‰}$ ). Previous studies have suggested that the Emeishan basalts, host rocks, and basement rocks are three possible sources for the regional Zn-Pb mineralization in the SYG (Liu and Lin, 1999; Zhou et al., 2001; Huang et al., 2003; Han et al., 2007; Zhou et al., 2014b, 2018). A leaching experiment of sphalerite at room temperature showed that Zn isotopic fractionation only happens at initial stage ( $^{66}\text{Zn}_{\text{eluent-sphalerite}} = 0.2\text{‰}$ ) and the Zn isotopic differences between eluent and sphalerite would disappear rapidly when



**Fig. 7.** Zn isotopic variations in sphalerite controlled by different precipitation mechanisms at a deposit scale. Black square data reflect changes in the pH and Zn complex speciation of fluid; Grey circle data reflect Rayleigh fractionation. Red triangle data are the Zn isotopic variations in the Maozu deposit, which contrast with the changes in pH and Zn complex speciation and Rayleigh fractionation. Data sources: a (this study), b and c (Pašava et al., 2014), d and e (Zhou et al., 2014b), and f (Wilkinson et al., 2005).



**Fig. 8.** Sulfur isotopic compositions histogram of sulfides from the Maozu deposit, showing that the sulfides do not follow the equilibrium fractionation order of pyrite > sphalerite > galena. Data sources: sphalerite (this study), and galena and pyrite (Liu and Lin, 1999; Zhou et al., 2013).

0.2% Zn was eluted (Fernandez and Borrok, 2009). This experiment could indicate the Zn isotopic fractionation during leaching rocks are not important, especially during abundant Zn extraction in an ore-forming process. The Zn isotopic compositions of the Emeishan basalts have been reported to range from +0.30 to +0.44‰ (Zhou et al., 2014a, b), corresponding to those of basalts worldwide (+0.32 ± 0.16‰; Wang and Zhu, 2010). Considering that the integral Zn isotopic signal of basalts is much higher than that of all sphalerites (+0.08‰ on average), the Emeishan basalts could not be expected to provide major Zn metals for the Maozu deposit. The Zn isotopic compositions of host carbonates could be largely varied, as indicated by the available data from this and previous studies (−0.24 to +0.41‰; He et al., 2015; Zhou et al., 2014a). Previous studies also indicated that Phanerozoic carbonates are characterized by heavy Zn isotopic compositions. For instances: both modern biogenic carbonates and Permian-

Triassic boundary carbonates show heavy Zn isotopic compositions (mean = ~0.91‰; Pichat et al., 2003; Liu et al., 2016). Therefore, it is possible that Zn isotopic compositions of host carbonates are largely varied but dominantly heavy, although heavier Zn isotopic compositions (> 0.41‰) of host carbonates were not determined in this region due to limited data (n = 14). Recently, the Maozu deposit has been suggested an ore-forming age of 196 ± 13 Ma (Zhou et al., 2013), when huge Phanerozoic carbonates characterized by heavy Zn isotopic composition have deposited. However, the sphalerite from the Maozu deposit exhibits light Zn isotopic composition with a narrow variation range. This suggests that the host carbonates also could not be a major Zn source for the Maozu deposit, despite that minor contribution of Zn from host rocks is possible. Five basement samples, including carbonates, graywackes, and phyllites, yield low δ<sup>66</sup>Zn values from +0.10 to +0.34‰. Similarly, the basements of an Irish ore field, where the rock assemblage (mainly graywackes and volcanic rocks) is similar to here, also have been reported to have light Zn isotopic compositions (+0.00 to +0.18‰; Wilkinson et al., 2005; Gagnevin et al., 2012). It is possible that the basements in this region are characterized by light Zn isotopic composition with a narrow variation range (+0.10 to +0.34‰). Therefore, we prone to believe that the Zn metals in the Maozu deposit could have been predominantly sourced from the basement rocks, similar to the Pb and Sr in this deposit (Zhou et al., 2013; Zheng et al., 2015).

Therefore, the small Zn isotopic variations in sphalerite from the Maozu deposit (−0.06 to +0.23‰) could be ascribed to the inheritance of the Zn isotopic variations in the original incoming fluid (+0.10 to +0.34‰). For instance, John et al. (2008) observed that modern seafloor hydrothermal fluids yield Zn isotopic ratios mostly between +0.1‰ and +0.3‰, suggesting an ~0.2‰ Zn isotopic variation in hydrothermal fluid, which was also proposed by Gagnevin et al. (2012). Additionally, it is noted that the Zn isotopic compositions of sphalerite (−0.06 to +0.23‰) in the Maozu deposit are slightly lighter than the Zn isotopic signatures of the original fluids (+0.10 to +0.34‰). This may indicate that minor fractionation (~0.1‰) occurred between the sphalerite and incoming hydrothermal fluid. Alternatively, it could be ascribed to the mixing of minor Zn metals sourced from host rocks that are of widely varying Zn isotopic composition, and the similar mechanism is also proposed on the Pb and Sr isotopic system in the deposit (Zhou et al., 2013; Zheng et al., 2015).

#### 5.4. Possible sources of ore-forming sulfur

In the SYG, the possible sulfur sources have been systemically studied with three alternative interpretations, including mantle-derived sulfur associated with the Emeishan basalts (Guan and Li, 1999), basements-derived sulfur (Zhu et al., 2016) and evaporates-derived sulfur (Zhou et al., 2013, 2014a, b). Due to the absence of sulfates, the δ<sup>34</sup>S values of sulfide could approximately represent the sulfur isotopic compositions of the incoming hydrothermal fluid (Ohmoto et al., 1990; Basuki et al., 2008; Zhou et al., 2014a, b). In the Maozu deposit, the sulfur isotopic compositions of the sphalerite range from +12.9 to +17.3‰, and those of the galena and pyrite have been reported to range from +8.8 to +19.9‰ (Liu and Lin, 1999; Zhou et al., 2013). The much higher sulfur isotopic signals of sphalerite, galena, and pyrite are significantly different from those of mantle-derived magmatic sulfur (~0‰; Chaussidon et al., 1989). Similarly, the sulfur isotopic compositions of the basements have been proposed to range from +0.2 to +5.0‰ (Zhu et al., 2016), which are also much lower than those of sulfides in the Maozu deposit. Therefore, the Emeishan flood basalts and the basements are not expected to provide major ore-forming sulfur for the Maozu deposit.

In the SYG, sulfur-bearing evaporates are widespread in the Dengying Formation (Han et al., 2007; Zhou et al., 2014b), which is another potential sulfur source. Studies have demonstrated that evaporates in the Dengying Formation yield sulfur isotopic variations from



+20.0 to +38.7‰ (Zhang et al., 2004; Han et al., 2007). Bacterial sulfate reduction (BSR) and thermochemical sulfate reduction (TSR) are two possible mechanisms of obtaining reduced sulfur from sulfates, which have been well-studied in previous studies (Machel et al., 1995; Strauss, 1997; Zhou et al., 2014a, b; Leticariu et al., 2017). Generally, BSR requires temperature conditions below 80 °C (Machel, 2001) and yields extremely negative  $\delta^{34}\text{S}$  values in sulfides (e.g., Leticariu et al., 2017). The much higher ore-forming temperature conditions (153–282 °C; Liu and Lin, 1999; He et al., 2006) and all positive  $\delta^{34}\text{S}$  values in sulfides (+8.8 to +19.9‰) indicate that the possibility of BSR could be ruled out. The experimentally determined degrees of sulfur isotopic fractionation between sulfates and sulfides triggered by TSR are 20, 15, and 10‰ at 100 °C, 150 °C, and 200 °C, respectively (Machel et al., 1995). In consideration of the sulfur isotopic fractionation during TSR, in the Maozu deposit, the sulfur isotopic signals in the sulfides (+8.8 to +19.9‰) are very possibly inherited from the evaporates hosted in the country rocks (+20.0 to +38.7‰). Therefore, it is suggested that the ore-forming sulfur in the Maozu deposit has been most likely sourced from the sulfur-bearing evaporates hosted in the Dengying Formation via TSR.

### 5.5. Implications of Zn and S isotopes

The light and homogeneous Zn isotopic compositions of the sphalerite from the Maozu deposit suggest an isotopically light and homogeneous Zn source that has been constrained to the Mesoproterozoic to lower Ediacaran basements. However, the ore-forming sulfur, in the Maozu deposit, is most likely derived from the sulfur-bearing evaporates hosted in the country rocks via TSR. Furthermore, previous studies have demonstrated that the mixing of two-source fluids, Zn-bearing and sulfur-bearing, respectively, would induce decoupled  $\delta^{66}\text{Zn}$  and  $\delta^{34}\text{S}$  values (Kelley et al., 2009; Pašava et al., 2014), which are indeed observed in the Maozu deposit (Fig. 6). Therefore, the mixing model of Zn-bearing fluid from the basement rocks and sulfur-bearing fluid from the host rocks could be constructed. This model is also consistent with the conclusions from previous H-O isotopic research, in which the mixing of metamorphic fluid from the basement rocks and brine from host rocks has been proposed (Liu and Lin, 1999; He et al., 2006). Moreover, the mixing of metamorphic hot fluid and surface cool brine could be responsible for the sharp decline in temperature of the incoming fluid, which further resulted in limited isotopic fractionation of Zn between the sphalerite and original fluid (e.g., Gagnevin et al., 2012).

In the SYG, Zn isotopic studies have been conducted at the Shanshulin (+0.00 to +0.55‰ and +0.25‰ on average; Zhou et al., 2014a), Tianqiao (−0.26 to +0.58‰ and +0.26‰ on average; Zhou et al., 2014b), Banbanqiao (+0.07 to +0.71‰ and +0.42‰ on average; Zhou et al., 2014b), Tianbaoshan (+0.15 to +0.73‰ and +0.38‰ on average; He et al., 2015) and Wusihe deposits (+0.05 to +0.40‰ and +0.30‰ on average; Zhu et al., 2018). Note that all these deposits are geographically located in the SYG margin, whereas the Maozu deposit is very close to the SYG center (Fig. 1B). Wilkinson et al. (2005) and Kelley et al. (2009) suggested that regional migration of hydrothermal fluid could produce Zn isotopic fractionation, with the Zn isotopic compositions in fluid gradually increasing away from the center of the Zn-bearing fluid system. The Zn isotopic compositions of sphalerite from the Maozu deposit (−0.06 to +0.23‰ and +0.08‰ on average) are integrally lower than those of the other deposits along the SYG margin (Fig. 9), which may indicate that the Maozu deposit is closer to the regional Zn-bearing fluid center. In another word, the center of the regional Zn-bearing fluids system could approximately equal to the geographical center of the SYG.

## 6. Conclusion

In this study, the Zn and S isotopes and Fe and Cd contents of sphalerite of the Maozu Zn-Pb deposit from the SYG in Southwestern

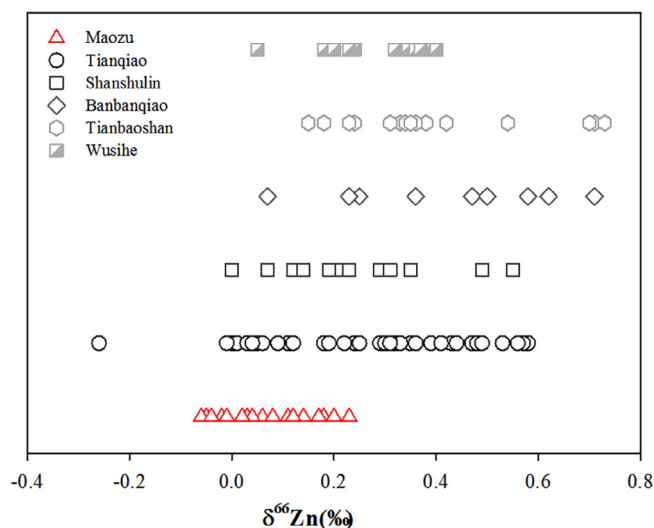


Fig. 9. Comparison of the Zn isotopic compositions of the sphalerites between the center-closed Maozu deposit and the other marginal deposits in the SYG. The integrally lower Zn isotopic compositions of the Maozu deposit suggest that it could be closer to the regional Zn-bearing fluid center. Data sources: Maozu (this study), Tianqiao (Zhou et al., 2014b), Banbanqiao (Zhou et al., 2014b), Shanshulin (Zhou et al., 2014a), Tianbaoshan (He et al., 2015), and Wusihe (Zhu et al., 2018).

China were investigated. The Zn isotopic fractionation between the sphalerite and original fluid during sphalerite precipitation is limited, which could be attributed to the striking decrease in the temperature of the incoming fluid. Therefore, in the Maozu deposit, the Zn isotopic compositions of the sphalerite could approximately represent the Zn isotopic compositions of the original incoming fluid. The Zn isotopic compositions of the original incoming fluid are very similar to those of the basement rocks, which suggests that the ore-forming Zn metals of the Maozu deposit could have been predominantly sourced from the basements. However, the ore-forming sulfur, in the Maozu deposit, has been most likely sourced from the sulfur-bearing evaporates hosted in the country rocks through TSR. The contrasting sources of zinc and sulfur, in the Maozu deposit, suggest the mixing of Zn-bearing fluid from the basement rocks and sulfur-bearing fluid from host rocks. In addition, the mixing of metamorphic hot fluid and surface cool brine could be responsible for the striking decrease in temperature of the incoming fluid, which further resulted in minor isotopic fractionation of Zn between the sphalerite and original fluid. Combined with the results of previous studies, the integrally lower Zn isotopic compositions of sphalerite in the Maozu deposit compared to the other deposits along the SYG margin may indicate that the Maozu deposit is closer to the regional Zn-bearing fluid center. However, this hypothesis may need more evidence to prove it.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.oregeorev.2019.04.004>.

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