



Isotope geochemistry of Zn, Pb and S in the Ediacaran strata hosted Zn-Pb deposits in Southwest China

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ABSTRACT

The Sichuan–Yunnan–Guizhou (SYG) area is a world-class Zn–Pb metallogenic zone and contains over four hundred of carbonate-hosted hydrothermal Zn–Pb deposits, six of which are super large-scale deposits with significant sources of Cd, Ge, and Ag, including the Huize, Wusihe, Xiaoshifang, Maozu, Tianbaoshan and Daliangzi deposits. Although previous studies focused fully on these deposits, the ore genesis of which are still in controversial. Interestingly, four of those super large scale deposits are hosted in the Ediacaran Dengying Formation, including the Maozu, Wusihe, Tianbaoshan and Daliangzi deposits. Based upon previous studies, we investigate the extent, causes and consequences of Zn and Pb isotope signatures at hand specimen scale and ore genesis of the Daliangzi and Tianbaoshan deposits, associated with published data for the Wusihe deposit. Lead isotope ratios, coupled with published data, demonstrate that Pb in the studied deposits was predominantly derived from two components: basements and sedimentary rocks. Meanwhile, a strong positive linear correlation between $\delta^{66}\text{Zn}$ and $\delta^{34}\text{S}_{\text{CDT}}$ values was observed in hand specimen D-2084, suggesting the variations may be resulted by fluid mixing. Furthermore, the Zn isotope and Cd/Zn dataset from the Tianbaoshan, Daliangzi and Wusihe deposits defines a logarithmic curve ($R^2 = 0.82$), which, to our knowledge, is firstly reported and lies between two unidentified components: a low Cd/Zn end-member with high $\delta^{66}\text{Zn}$ values and a high Cd/Zn end-member with low $\delta^{66}\text{Zn}$ values. Based upon previous studies, we suggest that Zn and Pb in the Wusihe and Tianbaoshan deposits were predominantly derived from basements and Ediacaran sediments; in contrast, Zn and Pb in the Daliangzi deposit were predominantly derived from Ediacaran sediments and upper sedimentary rocks, but we cannot rule out metal contributions of the basements. Furthermore, we suggest that fluid mixing is more appropriate to better explain Zn isotope signatures in the studied deposits.

In summary, Zn and Pb isotope ratios reflect similar ore genesis and metal sources of the Daliangzi, Tianbaoshan and Wusihe Zn–Pb deposits in the SYG area. The application to the studied deposits with the discovery of Zn, S and Pb isotope compositions for sulfides indicates the potential of Zn isotope, combined with Cd/Zn ratio, as new geochemical tracers, which may be useful for distinguishing the metal sources in large hydrothermal systems as suggested previously.

1. Introduction

The Sichuan–Yunnan–Guizhou (SYG) metallogenic area, a world-class Zn–Pb metallogenic zone in southwestern China, hosts over four hundred of carbonate-hosted hydrothermal Zn–Pb deposits (Zaw et al.,

2007; Zhou et al., 2013a,b; Wang et al., 2014). These deposits contain more than 20 million tons (Mt) of Zn–Pb metal reserves at grades of 10–35 wt%, with associated resources of other metals such as Ag, Cd, Ge, and Ga (Han et al., 2007; Ye et al., 2011; Zhang et al., 2015; Zhu et al., 2016, 2017, 2018a). Among these deposits, six Zn–Pb deposits are

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classified as large or super-large scale deposit with 1 to 3 Mt Pb and Zn metals, including the Huize Zn-Pb-Ge deposit (Yunnan province), the Maozu Zn-Pb deposit (Yunnan province), the Tianbaoshan Zn-Pb-Cd deposit (Sichuan Province), the Daliangzi Zn-Pb-Cd deposit (Sichuan Province), the Wusihe Zn-Pb deposit (Sichuan Province) and the Xiaoshifang Zn-Pb-Cu deposit (Yunnan province) (Zheng and Wang, 1991; Huang et al., 2004; Zhou et al., 2013a,b; Yuan et al., 2014; Wang, 2015; Xiong, 2015; Zhu et al., 2018a), four of which, interestingly, are present in the Ediacaran strata (mainly the Dengying Formation), including Maozu, Tianbaoshan, Daliangzi and Wusihe. Although the ore genesis of these deposit have been studied for years, the metal sources are still in controversial. Due to similar host rocks between the deposits in SYG and in Mississippi valley, most of studies suggested that the Zn-Pb deposits in SYG are MVT deposits (Zhou et al., 2001; Han et al., 2007; Zhang et al., 2015); however, the geochemical characteristics (S and Pb stable isotope signatures) and tectonic setting of these deposits are quite different from typical MVT deposits, arguing for that the deposits own a unique origin that distinctly different from typical MVT deposits (Huang et al., 2004; Zhou et al., 2013a,b; Zhu et al., 2016; Han et al., 2017).

Recently, with the technological advances in the past decades, such as multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS), it is enabled us to obtain high precision analysis of Zn isotope ratios with the long-term reproducibility of less than $\pm 0.06\%$ for $\delta^{66}\text{Zn}$ measurements over a two year period (Moynier et al., 2017), opening a new opportunity for cycling of Zn by detecting minor changes in its isotopic composition in extra-terrestrial and terrestrial samples (e.g., Cloquet et al., 2008; Moynier et al., 2017). These studies have shown that stable isotope geochemistry of Zn could be a powerful tool to better understand various geological processes (Moynier et al., 2017 and references therein). Due to high Zn abundance and well-constrained formation conditions, ore deposits, especially for Zn-Pb deposits, are considered particularly suitable for studies of Zn isotope fractionation. Its high abundance relative to other ore-forming elements makes Zn a good tracer of formation in ore deposits and a major application of its isotopes have been related to better constrain ore-formation processes and Zn sources in those deposits (Kelley et al., 2009; Fujii et al., 2011; Zhou et al., 2014a,b).

In this study, we investigated Zn isotope variations associated with traditional stable isotope systematics (S and Pb) in ores from the Ediacaran strata hosted Zn-Pb deposits, including the Tianbaoshan deposit and the Daliangzi deposit. In order to avoid inhomogeneous distribution of Zn, Pb and S isotope in small scales, micro-drilling system was employed to take tiny sphalerite from ores for stable isotope measurements. Combined with previous studies, the objectives of this study were to: (1) figure out metal sources and ore genesis of the deposits that hosted in Ediacaran strata; (2) track ore formation processes in low-T hydrothermal systems. Utilizing Zn stable isotope, coupled with S and Pb stable isotope, allows us to better understand sources and processing pathways that offer insights in the geochemical behavior of ore-forming fluids in the large-scale hydrothermal systems and constrain mass balance.

2. Geological setting and sampling

2.1. Regional geology

In the SYG area, four large-scale Zn-Pb deposits (as mentioned above), hosted in the Ediacaran strata, are located in the northwestern part of the SYG metallogenic province at the northwestern margin of the Yangtze Craton, where the strata consist of two components, including crystalline basements and sedimentary rocks (Fig. 1). Generally, the crystalline basements consist mainly of (from lower to upper) the Lower Proterozoic Kangding Group (Pt₁^{1k}, migmatite and gneiss; ~2957 Ma, Yuan et al., 1985) and the Dahongshan Group (Pt₁^{2d}, meta-clastic rock and spilite-keratophyre sequence; ~1711 Ma, Yang et al.,

2012), and the Middle-Upper Proterozoic Kunyang Group (Pt_{2-3k}, clastic rock with minor carbonate; 1000 Ma, Li et al., 2013). By contrast, the sedimentary rocks are comprised of (from lower to upper) Ediacaran to Quaternary strata, which are mainly consist of limestone and dolomite. The Ediacaran strata of the Yangtze Craton is composed of two main intervals (the Doushantuo and Dengying Formations), to which marine carbonates and shales assigned. The Doushantuo Formation is 60–180 m in thickness and consists of interbedded black shale and limestone; whereas the Dengying Formation is > 800 m in the shelf to < 150 m in the basin and is comprised of thick dolomite and limestone in the shelf and black shale and silicious carbonate in the basin (Jiang et al., 2007). In addition, the Emeishan flood basalts (Late Permian) are the largest igneous event in the SYG area and cover an area of over 250,000 km² with a total thickness up to several hundred meters to 5 km (Zhou et al., 2001). Interestingly, all large-scale Zn-Pb deposits and most of medium to small scale Zn-Pb deposits in the SYG area are hosted in the rocks underlying the Emeishan flood basalts, and the deposits, hosted in the the Dengying Formation, account for about 46% of the proven Zn + Pb reserves (Liu and Lin, 1999a,b; Chen, 2015; Tan et al., 2013).

2.2. Deposit description

2.2.1. The Daliangzi Zn-Pb deposit

The Daliangzi district is located at east of the Kangdian Axis and west of Ganluo-Xiaojiang tectonic belt (Fig. 1). In the mining area, there are more than thirty regional faults, which are the branches of the Ganluo-Xiaojiang tectonic belt. Geological investigations show that the NW-trending faults (e.g., F₁₅) and their branches (the NWW trending faults (e.g., F₆)) play important roles in controlling the occurrence of orebodies (Fig. 2A and B), which are located between the F₅ and F₁₅ faults and cover an area of ~0.1 km² (Fig. 2A and B). The faults strike (NE) and dip (NW) are reported on the map at an angle of 20–40° (Fu, 2004).

The field outcrops in the Daliangzi ore district are simple and contain the Ediacaran Dengying Formation, the Lower Cambrian Qiongzhusi Formation and the Quaternary eluvium and alluvium. The Ediacaran Dengying Formation is the primary bearing ore strata and mainly consists of dark grey to light grey dolomite, with a total thickness up to 900 m in thickness; the Lower Cambrian Qiongzhusi Formation is parallel unconformity to the underlying Dengying Formation and mainly consists of sandstone and shale, with a thickness of ~143 m (Fu, 2004). Interestingly, the carbonized breccias are developed in the mining area. Due to the temporally close relationship between the breccias and the ores, the carbonized breccias are considered to have close relationships with Zn-Pb mineralization of the Daliangzi deposit (Wu, 2013). However, the formation mechanisms of the breccias are still in controversial.

The Daliangzi deposit has two orebodies, namely, No. I and No. II. The No. I is the primary Zn and Pb ore reserve and contains 99.4% Zn and Pb ores in the deposit, with 630 m long, 326 m deep and 0.81–169.79 m wide (Liu, 2016). By contrast, the the No. II have much smaller ore reserves than No. I, and contains 0.18% Zn and Pb ores in the deposit. Similarly to typical Zn-Pb deposits in the SYG area, primary ores in the Daliangzi deposit are massive, disseminated, and veined ores, in which massive is the dominant type. Detailed field and microscopic investigations show that the mineralogy is relatively simple and mainly includes sphalerite, pyrite, galena, chalcopyrite, arsenopyrite, marcasite, freibergite and pyrrargyrite. The major ore minerals are sphalerite and galena, associated with minor chalcopyrite, arsenopyrite, marcasite, freibergite and pyrrargyrite. Gangue minerals are primarily calcite, quartz and dolomite.

2.2.2. The Tianbaoshan Zn-Pb deposit

The Tianbaoshan Zn-Pb deposit is located in the northwestern part of the SYG area, where is the northwestern margin of the Yangtze

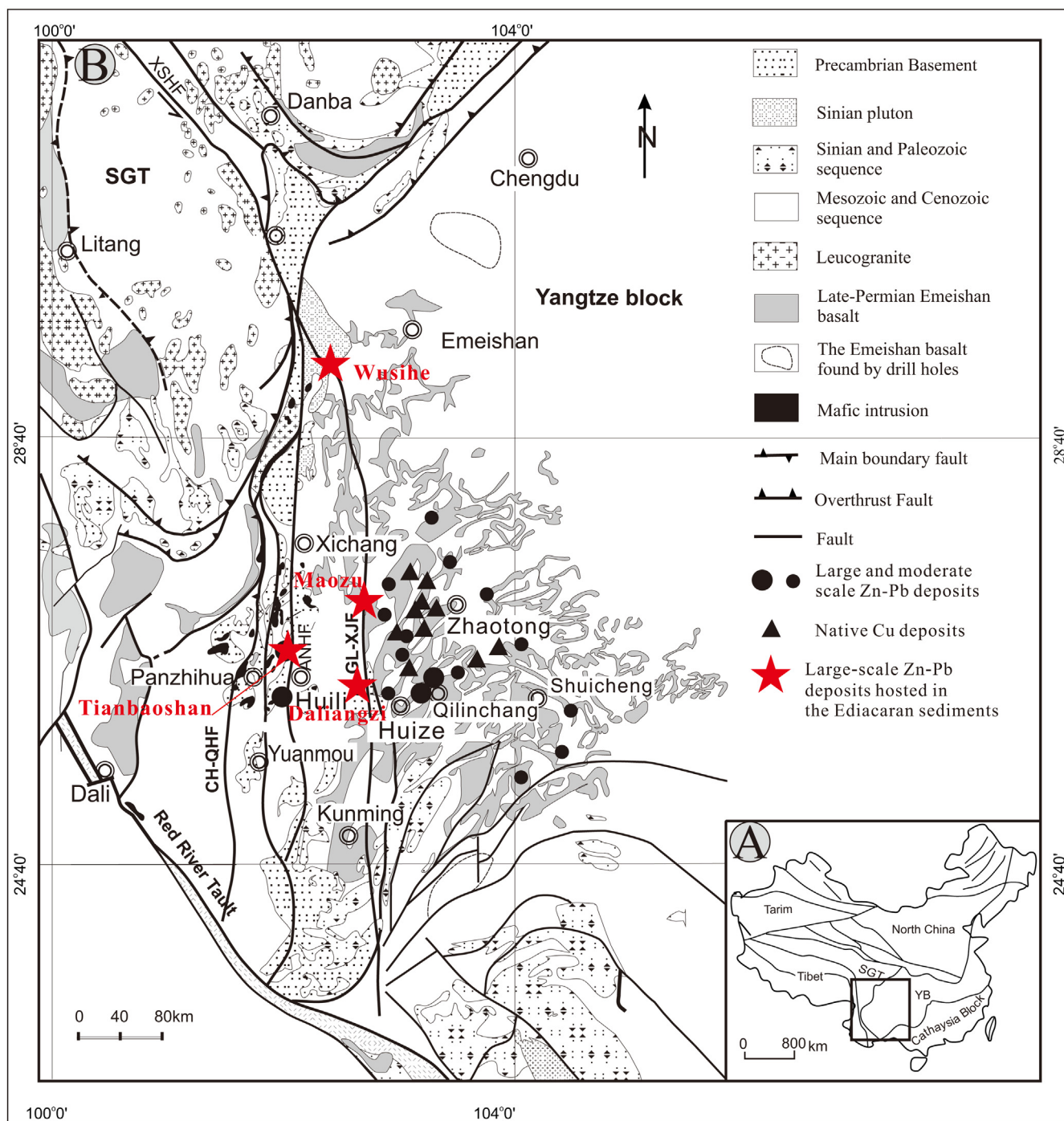


Fig. 1. (A) Sketch of tectonic framework of China; (B) Regional geological map of the SYG district associated with locations of ore deposits (Modified from Zhu et al., 2017). GL-XJF: Ganluo-Xiaojiang fault zone; ANH: Anninghe fault zone; CH-QHF: Chenghai-Qinghe fault zone.

Craton. The deposit contains two ore blocks, namely, the Tianbao and Xinshan, of which previous studies have described the regional geological background and the geological characteristics in detail (Fig. 2C and D) (Wang et al., 2000; Zhou et al., 2013a,b; Zhu et al., 2016). In the mining area, the primary fold is the Tianbaoshan syncline and its secondary anticlines; the main faults are the NW-trending fractures, which are the branches of the Anninghe tectonic belt (Fig. 1). The field outcrops in the Tianbaoshan deposit are simple and contain the Ediacaran Dengying Formation, the Cambrian Xiwangmiao Formation, and the upper Triassic Baiguowan Formation, in which the Ediacaran Dengying Formation is the primary host strata that consist of grey dolostone with a thickness of ~160 m. By contrast, the Xiwangmiao Formation consists

of light green and red argillaceous siltstone with a thickness of ~300 m; the Baiguowan Formation is composed of carbonaceous shale and sandstone with a thickness up to 380 m.

Exploratory drilling and underground mining provide easy access to the two ore blocks that the demonstrated reserves in the Tianbaoshan deposit are 1.8 Mt Zn and Pb metals at grades of 7.76–10.1 wt% Zn and 1.28–2.5 wt% Pb, respectively (Wang et al., 2000; Zhu et al., 2016). In addition, the zinc ores contain proven reserves of approximately 7289 tons of Cd, 258 tons of Ga, 122 tons of Ge and 20 tons of In, respectively. Primary ores are massive, disseminated, brecciated, veined and banded, in which massive ores are dominant; the textures are granular, metasomatite-relict and cataclastic, in which granular texture is

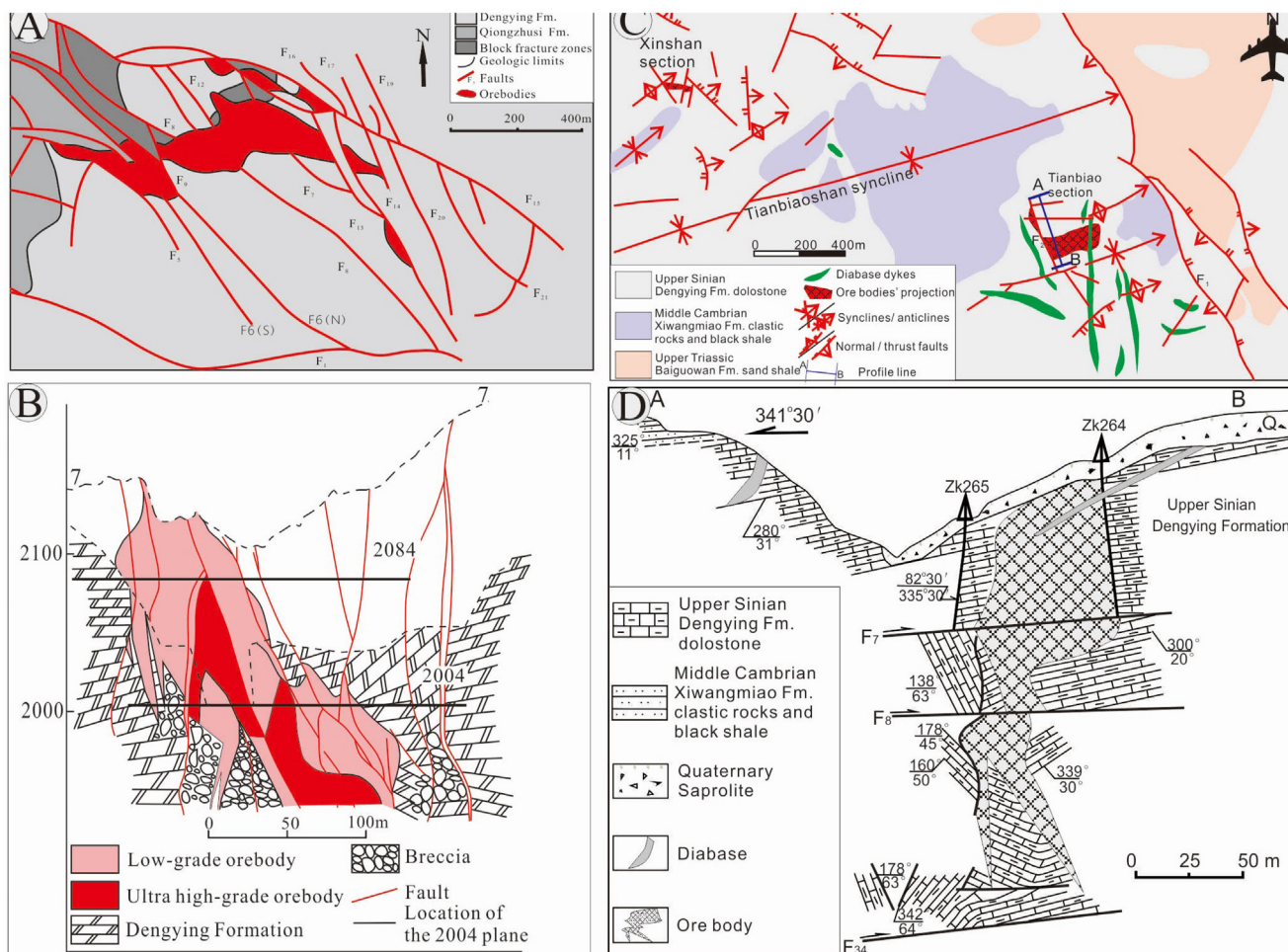


Fig. 2. Regional geological map and cross section of the Daliangzi (A and B; modified from Zhang, 2008) and Tianbaoshan (C and D; modified from Zhu et al., 2016) deposits.

dominant. Previous studies have shown that the mineralogy is simple and metallic minerals primarily include sphalerite, galena, pyrite, and chalcopyrite, with minor arsenopyrite, pyrrargyrite, freibergite; while the gangue minerals are quartz, calcite and dolomite.

3. Samples and methods

3.1. Microsampling

In this study, we collected more than 20 hand specimens at various levels from the Daliangzi and Tianbaoshan deposit. Previous studies have shown that sphalerite color is an indicator that dark ones were precipitated earlier than light ones during the forming of sphalerite in the SYG area (Zhu et al., 2017 and the references therein), thus, it is better to investigate the spatial and temporal variations of Zn, Pb and S isotopes in epigenetic sphalerite with clear color demarcations. In our samples, two representative hand specimens with different color sphalerite, namely D-2004 and D-2084 (Fig. 3), were collected from lower (height, 2004 m) and upper (height, 2084 m) orebody (No. 1) of the Daliangzi deposit, respectively; whereas one representative hand specimen, namely T-8 (Fig. 3), was collected at No.8 mining level (height, 2036 m) from the Tianbaoshan deposit. The economic minerals of microdrilling samples from the Daliangzi deposit mainly comprise sphalerite with minor pyrite and galena; gangue minerals include calcite and dolomite. In contrast, sulfide in hand specimen from the Tianbaoshan deposit is primary consist of sphalerite with minor galena; the dominant gangue mineral is calcite. Microdrilling system was

employed to collect sphalerite samples using a Microdrill sampling system (Relion MSS IV; USA) with the drill diameter of 1 mm. At hand specimen scale, there is a clear boundary between sulfides and the host rocks (or gangue minerals) and between different colored sphalerite as shown in Fig. 3. Samples for microdrilling were constantly collected at sphalerite concentrated area with different colored sphalerite from edge to core of the studied hand specimens. Care was taken to drill sphalerite that was visually free of other minerals. Minute crystals of calcite, pyrite and galena could not be avoided during microsampling; however, these minerals would have negligible impact on Zn, Pb and S isotopic signatures in comparison with that of sphalerite.

3.2. Methods

Zinc and Pb separation were performed at the clean laboratory of State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. A detailed description of the procedures used for Zn and Pb separation is given in Zhu et al. (2018a,b). Prior to Zn and Pb isotopic analysis, sphalerite micro-samples were chemically separated on columns that contain 3 ml of pre-cleaned 100–200 mesh AG MP-1 M anion-exchange resin (BIO-RAD, USA). Major and trace elements were measured in each unprocessed and processed sample to monitor recoveries of Zn and Pb. The results show that full recoveries of Zn and Pb between unprocessed and processed of each sample are found to be complete > 98% and ~100%, respectively.

Isotope ratios of Zn and Pb were measured by a Thermo Scientific

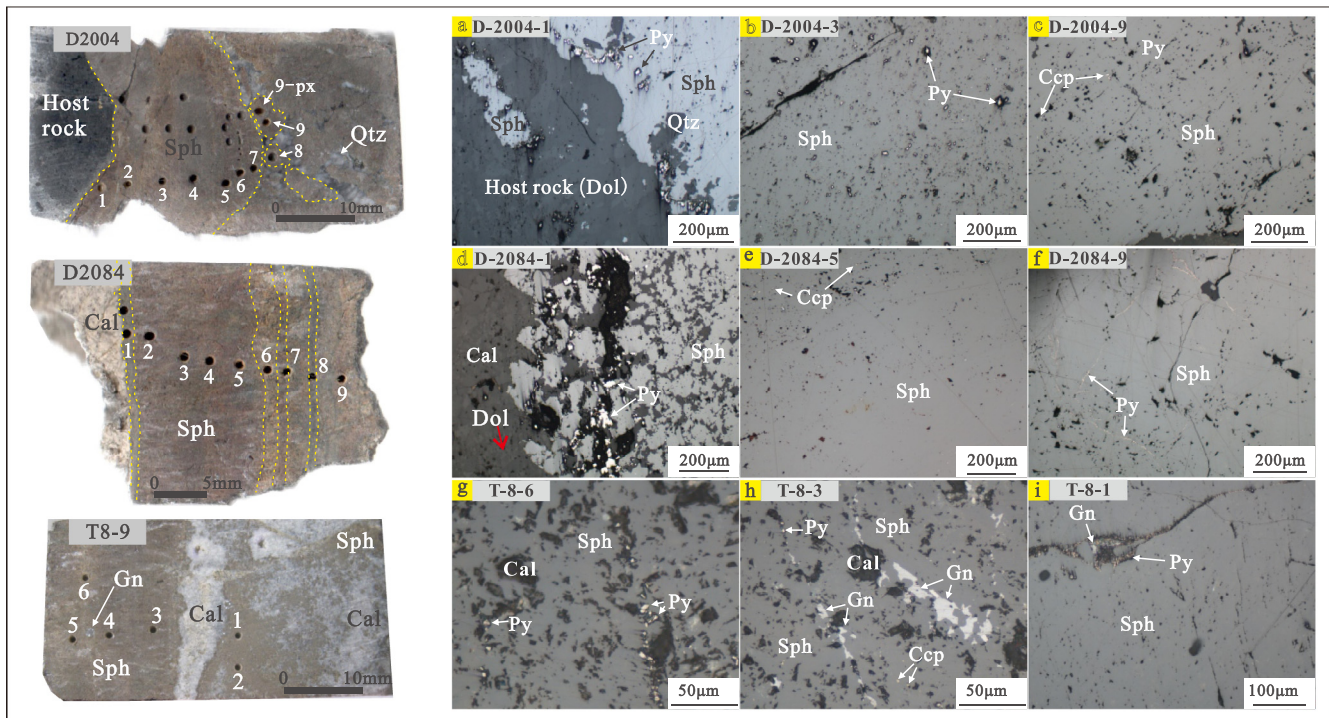


Fig. 3. Specimen photograph of three studied samples with the textural and structural features of sulfide minerals under an electron microscope. The BSE images of a to i are obtained near the sampling locations as marked on the images. (a) Sphalerite (Sph), associated with minor pyrite (Py), coexists with gangue minerals of dolomite (Dol) and quartz (Qtz); (b) Pure sphalerite with pyrite micro-inclusions; (c) Pure sphalerite with pyrite and chalcopryrite (Ccp) micro-inclusions; (d) Sphalerite coexists with pyrite, calcite (Cal) and dolomite, and the contents of dolomite and calcite were constantly decreased from left to right; (e) Chalcopryrite occurs as micro-inclusions in pure sphalerite; (f) Pyrite occurs as veins in pure sphalerite; (g) Sphalerite coexists with calcite associated with veined pyrite; (h) pyrite and galena (Gn) occur as veined in sphalerite with grained chalcopryrite and calcite; (i) pyrite and galena (Gn) occur as veined in sphalerite.

Neptune Plus MC-ICP-MS instrument at the State Key Laboratory of Crust–Mantle Evolution and Mineralization at Nanjing University, following the procedure detailed described in our previous studies (Zhu et al., 2018a). Total procedural blanks for Zn and Pb were less than 100 ng and 10 ng, respectively, which are insignificant relative to the amount of Zn (> 500 µg) and Pb (> 1 µg) put through chemical purification. Repeated analyses of mineral grains show excellent consistency of Zn and Pb isotope data.

Up to date, the Johnson Matthey (JMC) Zn “Lyon solution” is an accepted international Zn isotope standard and most of Zn isotopic data are reported relative to JMC; however, the solution of this standard are limited and an alternative Zn isotope standard (IRMM 3702) is commonly used as a “zero” standard during Zn isotope analyzing. Thus, IRMM 3702 was used to Zn isotope measurement in this study. Recalculations relative to the IRMM 3702 Zn standard were performed for normalization purpose using the formula:

$$\delta^{x/64}\text{Zn}(\text{‰}) = \left[\left(\frac{{}^x\text{Zn}/{}^{64}\text{Zn}}{\text{sample}} / \frac{{}^x\text{Zn}/{}^{64}\text{Zn}}{\text{IRMM 3702}} - 1 \right) \times 1000 \right]$$

where ${}^x\text{Zn}$ represents the ${}^{66}\text{Zn}$, ${}^{67}\text{Zn}$, ${}^{68}\text{Zn}$ and ${}^{70}\text{Zn}$ isotopes.

The CAGS-1 Zn standard solution was employed to use as a secondary reference material, of which the analysis yields an average value of $\delta^{66}\text{Zn}_{\text{IRMM 3702}} = -0.83 \pm 0.06\text{‰}$ ($n = 5$) that shows excellent agreement with literature values ($\delta^{66}\text{Zn}_{\text{IRMM 3702}} = -0.84 \pm 0.03\text{‰}$, Zhu et al., 2018a). In order to comparing the measured and literature values in this study, Zn isotopic data that reported relative to the JMC Zn isotope standard is also listed in Table 1 using the equation expressed as $\delta^{66}\text{Zn}_{\text{JMC}} = \delta^{66}\text{Zn}_{\text{IRMM 3702}} + 0.27$ (Wang et al., 2017), and the data are discussed relative to the JMC below.

Isotopic ratios of ${}^{206}\text{Pb}/{}^{204}\text{Pb}$, ${}^{207}\text{Pb}/{}^{204}\text{Pb}$ and ${}^{208}\text{Pb}/{}^{204}\text{Pb}$ were analyzed using a method of standard bracketing that coupled with Tl (NIST-997)-doping (mixed at a ratio of ~1) for correction of isobaric interference. The standard NIST NBS-981 was used as the external

reference. Repeated analyses ($N = 6$) of Pb standard (NIST NBS-981) yielded a ${}^{206}\text{Pb}/{}^{204}\text{Pb}$ ratio of 16.9330 ± 0.0003 (1SD), a ${}^{207}\text{Pb}/{}^{204}\text{Pb}$ ratio of 15.4869 ± 0.0005 (1SD) and a ${}^{208}\text{Pb}/{}^{204}\text{Pb}$ ratio of 36.6834 ± 0.007 (1SD), which show excellent agreement with the reference values reported by Yuan et al. (2016) for NIST NBS-981 (${}^{206}\text{Pb}/{}^{204}\text{Pb} = 16.9405$, ${}^{207}\text{Pb}/{}^{204}\text{Pb} = 15.4963$ and ${}^{208}\text{Pb}/{}^{204}\text{Pb} = 36.7219$).

Sulfur isotope ratio measurements were performed using a Thermo Finnigan MAT 253 isotope ratio mass spectrometer (Thermo Scientific, Bremen, Germany) at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. Three international S isotope standard materials (Ag_2S) were used to control data quality during S isotope analyzing, including IAEA-S-1 (reference material 8554; $\delta^{34}\text{S}_{\text{CDT}} = 0.3\text{‰}$), IAEA-S-2 (reference material 8555; $\delta^{34}\text{S}_{\text{CDT}} = 22.62 \pm 0.17\text{‰}$), and IAEA-S-3 (reference material 8529; $\delta^{34}\text{S}_{\text{CDT}} = -32.49 \pm 0.17\text{‰}$). The analysis yielded a relative error of < 0.2‰ (all errors are 2 sigma of the standard error). The S isotopic data reported in this study are relative to the Canyon Diablo Troilite (CDT).

In addition, Zn and Cd concentrations were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES; Varian Vista MPX) at the clean laboratory of State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences.

4. Results

The powdered microdrilling samples are tiny and it is a big challenge to obtain the weights of each sample with high precision. Thus, we measured Zn, Pb and Cd concentrations in both the unprocessed and processed solution to monitor the recoveries of Zn and Pb during chemical separation. In this study, we report the Zn, Pb and S isotope

Table 1

Zinc, sulfur and lead isotopic compositions coupled with Zn/Cd ratio in samples from the Daliangzi and Tianbaoshan deposits.

Name	Sample No.	$^{206}/^{204}\text{Pb}$	$^{207}/^{204}\text{Pb}$	$^{208}/^{204}\text{Pb}$	$\delta^{66}/^{64}\text{Zn}_{\text{IRM3702}}$	2SD	$\delta^{66}/^{64}\text{Zn}_{\text{JMC}}$	$\delta^{34}\text{S}_{\text{CDT}}$	Cd/Zn
Daliangzi	D2084-1	18.3069	15.6912	38.5510	-0.22	0.03	0.05	14.5	0.0169
	D2084-2	18.5967	15.7210	38.9106	-0.34	0.02	-0.07	14.7	0.0425
	D2084-3	18.5941	15.7217	38.9252	-0.38	0.00	-0.11	14.3	0.0536
	D2084-4	18.6163	15.7232	38.9694	-0.37	0.02	-0.10	14.4	0.0191
	D2084-5	18.7095	15.7353	39.1118	-0.33	0.01	-0.06	14.9	0.0174
	D2084-6	18.6847	15.7322	39.0974	-0.30	0.03	-0.03	15.3	0.0200
	D2084-7	18.4275	15.7020	38.7182	-0.24	0.03	0.03	15.5	0.0259
	D2084-8	18.3504	15.6929	38.6088	-0.34	0.01	-0.07	15.0	0.0468
	D2084-9	18.4125	15.6996	38.7020	-0.37	0.00	-0.10	15.6	0.0410
	D2004-1	18.6692	15.7236	39.0256	-0.18	0.01	0.09	13.6	0.0136
	D2004-2	18.5938	15.7139	38.9093	-0.25	0.00	0.02	14.0	0.0157
	D2004-3	18.6352	15.7207	38.9773	-0.17	0.03	0.10	13.9	0.0103
	D2004-4	18.6552	15.7235	39.0065	-0.25	0.00	0.02	13.8	0.0191
	D2004-5	18.5356	15.7088	38.8162	-0.16	0.02	0.11	13.5	0.0121
	D2004-6	18.5217	15.7082	38.7991	-0.14	0.02	0.13	13.4	0.0121
	D2004-7	18.5146	15.7081	38.7886	-0.14	0.01	0.13	14.1	0.0039
	D2004-8	18.4594	15.7013	38.7038	-0.14	0.06	0.13	13.8	0.0044
	D2004-9*	18.5045	15.7075	38.7784	-0.12	0.06	0.15	13.8	0.0057
	D2004-9*	18.4973	15.7032	38.7490	-0.12	0.04	0.15	/	0.0064
	Tianbaoshan	T8-1	18.4408	15.7247	38.7373	-0.03	0.03	0.24	/
T8-2		18.4391	15.7248	38.7343	-0.01	0.05	0.26	/	0.0078
T8-3		18.4258	15.7276	38.7265	-0.10	0.01	0.17	/	0.0064
T8-4		18.4197	15.7259	38.7189	-0.13	0.03	0.14	/	0.0075
T8-5		18.4184	15.7224	38.7101	-0.02	0.04	0.25	/	0.0062
T8-6		18.4374	15.7227	38.7102	0.02	0.02	0.29	/	0.0055

Note: “*” parallel samples were randomly targeted within a small area where the color of sphalerite is visually homogenous; “/” not analyzed.

compositions as well as Zn/Cd ratios of the studied samples and the results are listed in Table 1.

Microdrilled sphalerite from the Daliangzi deposit has $\delta^{34}\text{S}_{\text{CDT}}$ values ranging from +13.4‰ to +15.6‰ (mean = +14.3‰), which are consistent with previous reported values with $\delta^{34}\text{S}_{\text{CDT}}$ values varying from 10.5 to 15.0‰ (Zhu et al., 1995a,b). In contrast, sphalerite has a narrow $\delta^{66}\text{Zn}_{\text{JMC}}$ values changing from -0.11 to 0.15‰ (mean = 0.03‰), with a total fractionation of 0.26‰ ($\Delta^{66}\text{Zn}_{\text{JMC}}$), which is small in comparison with the reported fractionation in Zn-Pb deposits in the SYG area, such as the Banbanqiao ($\Delta^{66}\text{Zn}_{\text{JMC}} = 0.64\%$), Tianqiao ($\Delta^{66}\text{Zn}_{\text{JMC}} = 0.84\%$) and Shanshulin ($\Delta^{66}\text{Zn}_{\text{JMC}} = 0.55\%$) deposit (Zhou et al., 2014a,b). Interestingly, sphalerite sampled at higher height has higher $\delta^{34}\text{S}_{\text{CDT}}$ values (mean = 14.9‰) than the one collected at lower height (mean = 13.8‰). On the contrary, sphalerite sampled at upper orebody has lower $\delta^{66}\text{Zn}_{\text{JMC}}$ values (mean = 0.01‰) than the one collected at lower orebody (mean = 0.19‰). The variations in Pb isotopic compositions of the D-2004 are small, with $^{206}/^{204}\text{Pb}$, $^{207}/^{204}\text{Pb}$, and $^{208}/^{204}\text{Pb}$ ranging from 18.4594 to 18.6692, 15.7013 to 15.7236, and 38.7038 to 39.0256, respectively. Pb isotopic compositions of the D-2084 have relatively large variations in comparison with that of D-2004, with $^{206}/^{204}\text{Pb}$, $^{207}/^{204}\text{Pb}$, and $^{208}/^{204}\text{Pb}$ ranging from 18.3069 to 18.7095, 15.6912 to 15.7353, and 38.5510 to 39.1118, respectively (Table 1).

By contrast, sphalerite from the Tianbaoshan deposit has relatively homogenous Zn and Pb isotope compositions, as shown in Table 1. The $\delta^{66}\text{Zn}_{\text{JMC}}$ values are varying from 0.20 to 0.35‰, with a mean value of 0.29‰. Sphalerite from the Tianbaoshan deposit has relatively homogenous S isotope ratios, with $\delta^{34}\text{S}_{\text{CDT}}$ values varying from 4‰ to 5‰ (Zhu et al., 2016). Thus, S isotope compositions of samples from the Tianbaoshan deposit are not measured in this study.

Interestingly, we collected two samples (D-2004-9; Table 1) at a same color zone and the geochemical signatures of these two samples are strongly similar, including Zn and Pb isotope compositions, indicating that metal isotopes in a same color zone are homogenous.

5. Discussion

5.1. Lead isotope ratios

Galena is the predominant Pb-bearing mineral in Zn-Pb deposits, and it is proposed that the occurrence of galena makes its isotope ratios close to the initial isotopic signatures of ore-forming fluid during the formation of galena (Bao et al., 2017). Although we measured the Pb isotope ratios in sphalerite, back-scatter electron (BSE) images show that Pb is likely present as galena micro-inclusions in sphalerite (Fig. 3), indicating that the Pb isotope ratios in sphalerite are represent that of galena micro-inclusions. Due to low U and Th contents of sulfide minerals in Zn-Pb deposits, it is commonly that Pb isotope ratios of sulfides, especially for galena, do not have to be corrected basing on their formation ages.

In the SYG area, Pb isotope signatures of different geological end-members have been well established geochemically in the past decades, including the basements and sedimentary rocks, and the Pb isotope ratios of which are plotted at various areas with only a small area of overlap as shown in Fig. 4 (e.g., Zheng and Wang, 1991; Huang et al., 2004; Zhou et al., 2013a,b; Bao et al., 2017). The Pb isotopic compositions of the sphalerite in this study, coupled with published Pb isotopic data, are mostly plotted closely to the upper crust Pb evolution curve (Zartman and Doe, 1981) in the plots of $^{206}/^{204}\text{Pb}$ verse $^{207}/^{204}\text{Pb}$. By comparing Pb isotope ratios between Zn-Pb deposits and end-members, we could figure out the Pb sources of those deposits. Fig. 4 shows that the Wusihe deposit has relatively homogenous Pb isotopic compositions and most of samples are located at the areas of basements and Dengying Formation, suggesting that Pb in the Wusihe deposit is more likely derived from the basements and the Ediacaran Dengying Formation, as also suggested by the Sr isotopic data (Xiong et al., 2018). Similarly, most of samples from the Tianbaoshan deposit are located at the areas of basements and Dengying Formation, indicating that the Tianbaoshan and the Wusihe deposits share similar metal sources as suggested previously by Zn and Cd isotope studies (He et al., 2016; Zhu et al., 2016). By contrast, most of samples from the Daliangzi deposit seem to have more variable Pb isotopic compositions and Pb in the this deposit has more complicated sources and different end-members in the

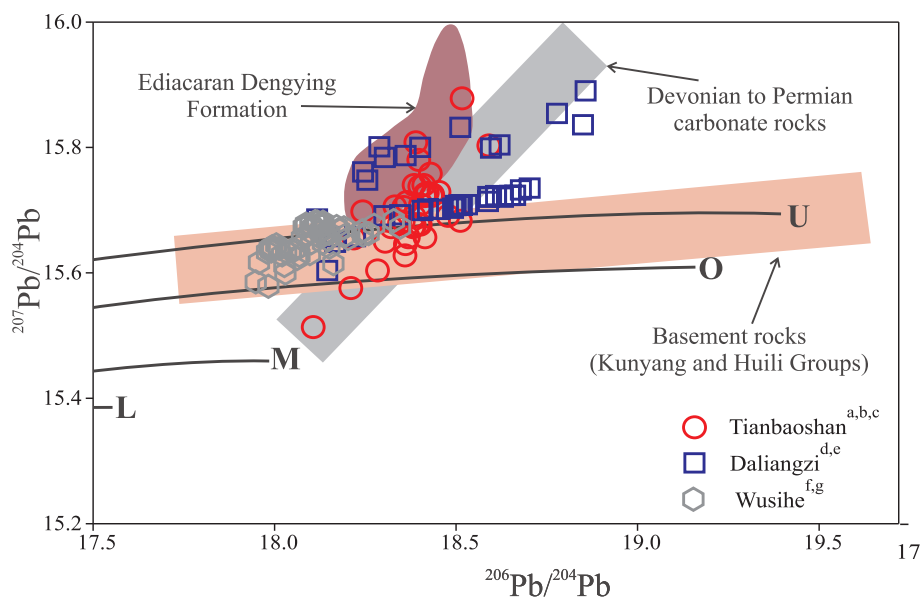


Fig. 4. Plots of $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ for three Zn-Pb deposits that are hosted in the Ediacaran Dengying Formation. Curves for the upper crust (U), orogenic belt (O), mantle (M), and lower crust (L) are taken from Zartman and Doe (1981). Data sources: this study and ^aWang et al., (2000); ^bFu (2004); ^cZhou et al. (2013); ^dZhu et al. (1995a,b); ^eLiu (2016); ^fZhu et al. (2018a); ^gXiong et al. (2018).

SYG area seem to be potential Pb sources as suggested previously (Zheng and Wang, 1991; Yuan et al., 2014; Zhou et al., 2013a,b; Liu, 2016).

5.2. Zn and S isotope variations in Zn-Pb deposits

Where the reduced S comes from is one of the key questions to better understand the formation mechanisms of Zn-Pb deposits. With S isotopic signatures in well-defined sources, researchers may evaluate and track the relative sources of S through the comparison of S isotope compositions in different geological end-members (e.g., Rye and Ohmoto, 1974; Zhou et al., 2014a,b; Zhu et al., 2016). It is thus the S isotope signatures of ore deposits are considered as a power tool to track S sources. In the SYG area, S isotope compositions of sulfides, sulfate and sedimentary rocks in Zn-Pb deposits have been well studied for dozens of years (e.g., Zheng and Wang, 1991; Liu and Lin, 1999a,b; Huang et al., 2004; Zhang, 2005; Wu, 2013; Zhu et al., 2016, 2017, 2018a,b). These studies have shown that the Zn-Pb deposits in this area could generally be divided into two groups basing their S isotope signatures on sulfide minerals (Zhang, 2008): (1) $\delta^{34}\text{S}_{\text{CDT}}$ values ranging from 11‰ to 19‰, such as the Daliangzi and Huize deposits (Huang et al., 2004; Han et al., 2007); (2) $\delta^{34}\text{S}_{\text{CDT}}$ values ranging from 4‰ to 7‰, such as the Tianbaoshan and Jinshachang deposits (Zhou et al., 2015; Zhu et al., 2016). Previous studies have shown that microbial sulfate reduction (MSR) and thermochemical sulfate reduction (TSR) could result in extremely large S isotope fractionations with $\Delta^{34}\text{S}_{\text{SO}_4\text{-H}_2\text{S}}$ values up to 20‰ (Machel et al., 1995) and 72‰ (Lefticariu et al., 2017, and references therein), respectively. In these deposits, there are few biogenic sulfides and mineral textures have been reported previously; meanwhile, by comparing $\delta^{34}\text{S}_{\text{CDT}}$ values between sulfides in Zn-Pb deposits and marine sulfates in the host rocks, researchers all agreed that reduced S in Zn-Pb deposits was mainly derived from sedimentary rocks through TSR in the SYG area (e.g., Han et al., 2007; Zhou et al., 2013a,b; Hu et al., 2017).

At hand specimen scale, two parallel samples (D-2004-9; Table 1) collected at a same color zone have strongly similar Pb and Zn isotope signatures. Zhu et al. (2017) also demonstrated that same color sphalerites that collected from a hand specimen have homogenous Cd isotope compositions. It is thus that metal isotopes are likely homogenous within a same color zone in hand specimens. Fig. 3 show that samples D-2084 has clear color boundaries between different colored sphalerites, which exhibit banded texture; on the contrary, samples D-2004 and T-8 have unclear color boundaries. Previous studies have shown

that two processes are considered to result in Zn isotope fractionations in hydrothermal fluids, including: (1) kinetic fractionation; and (2) mixing between fluids (Wilkinson et al., 2005; Gagnevin et al., 2012; Zhou et al., 2014a,b; Deng et al., 2016). Commonly, dark sphalerite was crossed or surrounded by light sphalerite and these textures were reported in the Huize, Fule and Tianbaoshan deposits, thus, dark sphalerite was considered to precipitate earlier than light one in these Zn-Pb deposits (Huang et al., 2004; Han et al., 2007; Zhu et al., 2016, 2017). In the Daliangzi deposit, dark sphalerites seem to have lower $\delta^{66}\text{Zn}$ values than light ones. For example, D-2084-2, D-2084-3, D-2084-4 and D-2084-5, collected at dark color zones, have lower $\delta^{66}\text{Zn}$ values than D-2084-6 and D-2084-7 that collected at light color zones. Similarly, sphalerite sampled at light color zone (T-8-6) has the highest $\delta^{66}\text{Zn}$ value in sample T-8 from the Tianbaoshan deposit. Thus, it is possible that Zn isotope fractionation in the studied deposits is likely controlled by kinetic fractionation that earlier precipitated sphalerite has lower $\delta^{66}\text{Zn}$ values, consisting with previous studies by Zhou et al. (2014a,b). However, we cannot rule out the possibility that fluid mixing could also result in such Zn isotope signatures by two Zn-bearing fluids with isotopically distinct sources. In this study, we observed a strong positive linear correlation between $\delta^{66}\text{Zn}$ and $\delta^{34}\text{S}_{\text{CDT}}$ values in D-2084, excluding the D-2084-1 and D-2084-9 samples (Fig. 5). Spatially, D-2084-1 and D-2084-9 were close to gangue minerals and seem to have different mineral assemblages (Fig. 3), which may result in these two samples plotted offset from the regression line. Thus, mixture between two Zn sources is also a potential explanation for some of the observed variation in $\delta^{66}\text{Zn}$ values as suggested previously (Wilkinson et al., 2005).

In the SYG area, Zn-Pb deposits were thought to share a common genetic origin with Mississippi Valley Type (MVT) ore deposits (Zhang et al., 2015, and reference therein) and Zn isotope compositions of sphalerite in several Zn-Pb deposits have been well-defined, including the Tianbaoshan (+0.15–+0.73‰, mean = 0.41‰; He et al., 2016), Shanshulin (0.00‰–+0.55‰, mean = 0.25‰; Zhou et al., 2014a), Tianqiao (−0.26 to +0.58‰, mean = 0.26‰; Zhou et al., 2014b), Banbanqiao (+0.07–+0.71‰, mean = 0.42‰; Zhou et al., 2014b) and Wusihe (+0.11–+0.46‰, mean = 0.36‰; Zhu et al., 2018a) deposits (Fig. 6). Comparing Zn isotope signatures in different types of Zn-Pb deposits, there is a large overlap between these deposits (Fig. 6). Thus, it is proposed that Zn isotope signatures should combine with other geochemical tracers to figure out the ore genesis of Zn-Pb deposits in this area.

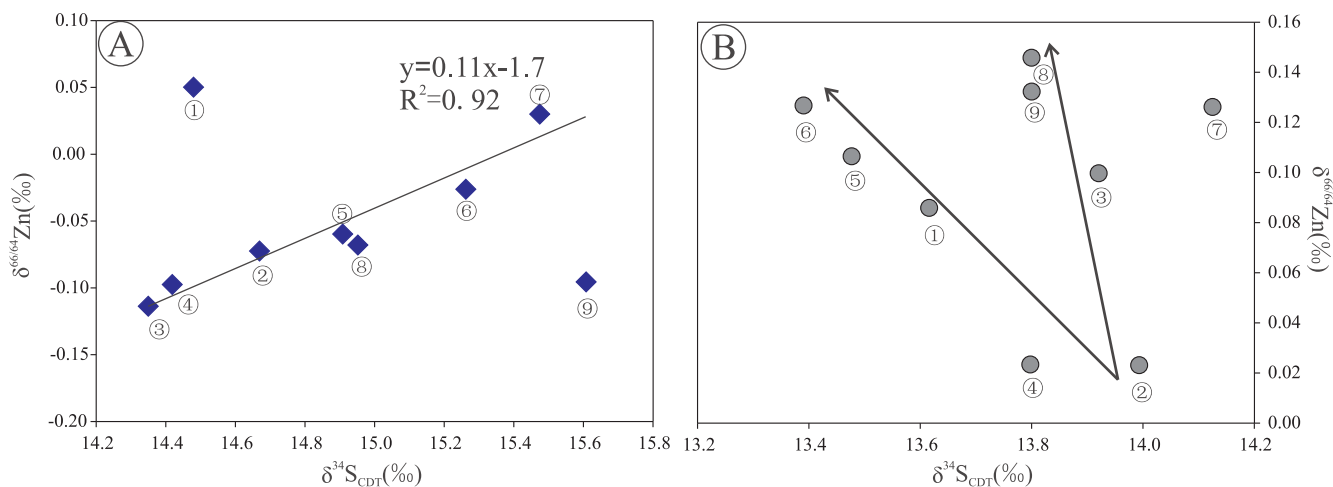


Fig. 5. Plots of Zn versus S isotope compositions of sphalerite from the Daliangzi deposit. A strong positive correlation for sphalerite in the hand specimen D-2084 was observed, excluding D-2084-1 and D-2084-9. By contrast, Zn versus S isotope compositions seem to have a weak relationship for sphalerite in the hand specimen D-2004.

5.3. Relationships between Cd/Zn ratios and Zn isotopic compositions

As a transition metal, Zn is a member of Group IIB of the periodic table, which also includes cadmium (Cd) and mercury (Hg). Its geochemical property is close to Cd because of their similarities in electron structures and ionization potentials. Indeed, leaching experiments demonstrated that Cd/Zn ratios have minor variations between sulfide (0.016) and leaching solutions (0.009–0.012), and more recent studies also show that there are minor fractionations during sulfide weathering, suggesting minor fractionations between Zn and Cd during leaching processes (Zhang et al., 2016; Zhu et al., 2018b). It is thus that Zn and Cd exhibit very similar behavior in terms of extraction efficiencies from basalt, transport, mixing, sulfide precipitation and remobilization in hydrothermal systems, and Cd/Zn ratio was considered as a geochemical indicator to track metal sources and/or to classify the types of Zn-Pb deposits in various hydrothermal systems (Jonasson and Sangster, 1978; Viets et al., 1992; Metz and Trefry, 2000; Gottesmann

and Kampe, 2007; Demir et al., 2013; Zhu et al., 2016, 2018b; Wen et al., 2016). In this study, we found that a logarithmic regression between $\delta^{66}\text{Zn}$ values and Cd/Zn ratios can be fitted through sphalerite samples from the Tianbaoshan, Daliangzi and Wushihe deposits, and the Zn isotope dataset seem to lie between two components: a low Cd/Zn end-member with high $\delta^{66}\text{Zn}$ values and a high Cd/Zn end-member with low $\delta^{66}\text{Zn}$ values. It is thus that Zn isotope signatures can be explained by binary mixing model which results in such variations of $\delta^{66}\text{Zn}$ values and Cd/Zn ratios. Previous studies have investigated the Zn isotope compositions of the basements and Ediacaran to Permian sedimentary rocks from the SYG area (Zhou et al., 2014a; He et al., 2016). Due to limited Zn isotopic data of end-members from the SYG area, it is hard to figure out the components whose geochemical features match the two end-members well. However, the results clearly show that basements have low Cd/Zn ratios and high $\delta^{66}\text{Zn}$ values; on the contrary, sedimentary rocks seem to have high Cd/Zn ratios and low $\delta^{66}\text{Zn}$ values (Fig. 7). Meanwhile, a logarithmic

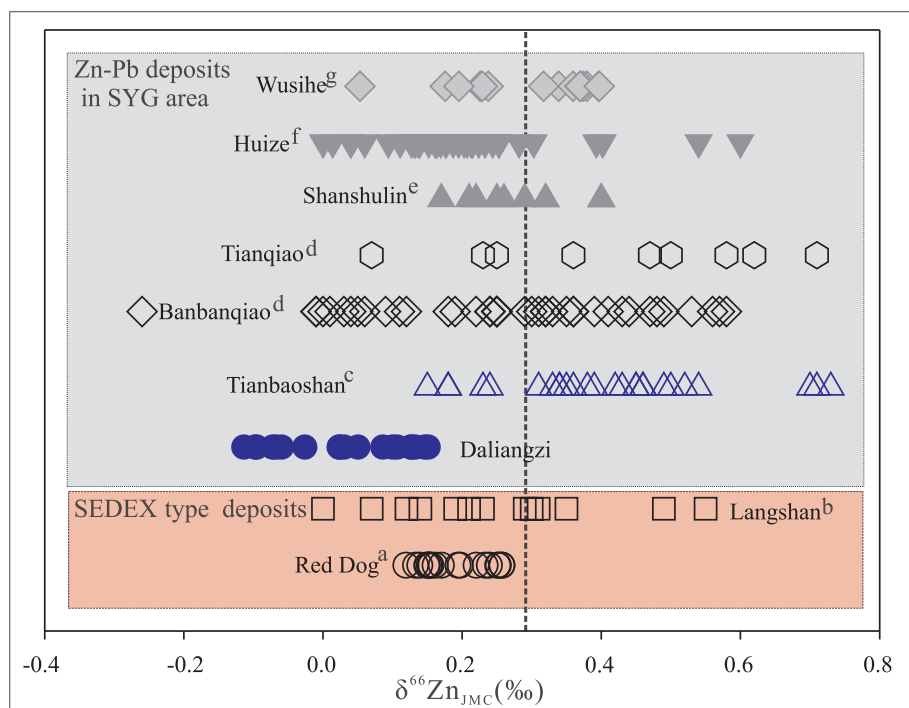


Fig. 6. Zn isotope compositions of sphalerite from this study and previously reported Zn-Pb deposits. The black dash line is the estimated $\delta^{66}\text{Zn}$ value of Bulk Silicate Earth ($0.28 \pm 0.03\text{‰}$; Chen et al., 2013). Data sources: ^aKelley et al. (2009); ^bGao et al. (2018); ^cHe et al. (2016); ^dZhou et al. (2014a); ^eZhou et al. (2014b); ^fWu (2013); ^gZhu et al. (2018a,b).

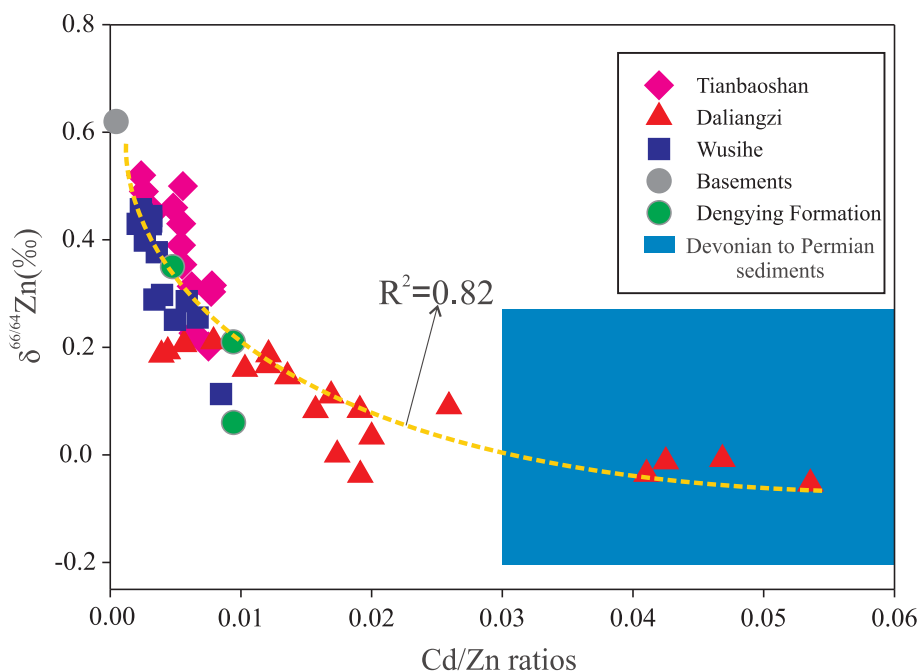


Fig. 7. Relationship between $\delta^{66}\text{Zn}$ and Cd/Zn ratios in the basements, the Ediacaran Dengying Formation and the upper sedimentary rock, associated with sphalerite from the studied deposits. The yellow dash curve is logarithmic fit through the sphalerite from the studied deposits. Data sources: $\delta^{66}\text{Zn}$ and Cd/Zn ratios in basements and Dengying Formation are cited from He et al. (2016); the range of $\delta^{66}\text{Zn}$ (-0.22‰ to $+0.32\text{‰}$) in Devonian to Permian sediments is cited from Zhou et al. (2014b); the range of Cd/Zn ratios (0.03 to 0.07) is cited from Zhu (2014). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

regression can also be fitted through a subset of the Wusihe and Tianbaoshan deposits which are plotted between the basements and the Ediacaran Dengying Formation, suggesting that the variations may be reconciled with mixing as well. Altogether, we propose that Zn in the Wusihe and Tianbaoshan deposits was predominantly derived from the basements and the Ediacaran Dengying Formation, consisting with previous studies (He et al., 2016; Xiong et al., 2018); in contrast, Zn in the Daliangzi deposit was mainly derived from the Ediacaran Dengying Formation and the upper sedimentary rocks, but we cannot rule out the possible metal contributions of basements. The conclusions are consistent with the explanation of Pb isotope ratios. Taken together, we suggest that Zn isotope fractionations in the studied deposits were likely resulted by fluid mixing but not a kinetic controlled fractionation.

6. Conclusions

Combined with published Pb isotopic data of the Daliangzi, Tianbaoshan and Wusihe deposits, we figure out the Pb sources of the studied deposits by comparing Pb isotope signatures between end-members and Zn-Pb deposits in the SYG area. The results clearly show that the basements, host rocks and sedimentary rocks are potential Pb sources.

Interestingly, $\delta^{66}\text{Zn}$ values and Cd/Zn ratios of sphalerite from the studied deposits show a logarithmic regression, which, to our knowledge, has not been reported previously. In the studying area, by comparing with published $\delta^{66}\text{Zn}$ values and Cd/Zn ratios in identified end-members, we found that Zn in the Tianbaoshan and Wusihe deposits was derived from basements and Ediacaran sediments; in contrast, Zn in the Daliangzi deposit was derived from Ediacaran sediments and upper sedimentary rocks, but we cannot rule out the contribution of basements. These conclusions are consistent with the explanation by Pb isotope ratios. Thus, the kinetic fractionation was not likely to control the Zn fractionations in the studied deposits. We suggest that fluid mixing is a better explanation for the Zn isotope signatures in those deposits.

In summary, the application to the Zn-Pb deposits with the discovery of Zn and Pb isotopic ratios for sphalerite and potential source rocks indicates the potential of Zn isotope as a new geochemical tracer. This study also presents a mass balance model of Zn isotope and gives new insights into the ore genesis of the Zn-Pb deposits in the SYG area.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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