



The origin of the Maozu carbonate-hosted Pb–Zn deposit, southwest China: Constrained by C–O–S–Pb isotopic compositions and Sm–Nd isotopic age



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ABSTRACT

The Maozu Pb–Zn deposit, located on the western margin of the Yangtze Block, southwest China, is a typical carbonate-hosted deposit in the Sichuan–Yunnan–Guizhou Pb–Zn metallogenic province with Pb + Zn reserves of about 2.0 million tonnes grading 4.15 wt.% Pb and 7.25 wt.% Zn. Its ore bodies are hosted in Sinian (635–541 Ma) Dengying Formation dolostone and show stratiform, vein and irregular textures. Ores are composed of sphalerite, galena, pyrite, calcite, dolomite, quartz and fluorite with massive, banded, disseminated and veined structures. The C–O–Sm–Nd isotopic compositions of hydrothermal calcites and S–Pb isotopic compositions of sulfides were analyzed to constrain the origin of the Maozu deposit. $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{SMOW}}$ values of hydrothermal calcites range from -3.7‰ to -2.0‰ and $+13.8\text{‰}$ to $+17.5\text{‰}$, respectively, and plot near the marine carbonate rocks field in a plot of $\delta^{13}\text{C}_{\text{PDB}}$ vs. $\delta^{18}\text{O}_{\text{SMOW}}$, with a negative correlation. It suggests that CO_2 in the hydrothermal fluids was mainly originated from marine carbonate rocks, with limited influence from sedimentary organic matter. $\delta^{34}\text{S}_{\text{CDT}}$ values of sulfides range from $+9.9\text{‰}$ to $+19.2\text{‰}$, similar to that of Cambrian to Triassic seawater sulfate ($+15\text{‰}$ to $+35\text{‰}$) and evaporate ($+15\text{‰}$ to $+30\text{‰}$) in the Cambrian to Triassic sedimentary strata. It suggests that reduced sulfur was derived from evaporate in sedimentary strata by thermo chemical sulfate reduction. Sulfides have low radiogenic Pb isotope compositions ($^{206}\text{Pb}/^{204}\text{Pb} = 18.129\text{--}18.375$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.640\text{--}15.686$ and $^{208}\text{Pb}/^{204}\text{Pb} = 38.220\text{--}38.577$) that plot in the field between upper crust and the orogenic belt evolution curve in the plot of $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$, and similar to that of age corrected Proterozoic basement rocks (Dongchuan and Kunyang Groups). This indicates that ore-forming metals were mainly derived from basement rocks. Hydrothermal calcite yields a Sm–Nd isotopic age of 196 ± 13 Ma, possibly reflecting the timing of Pb–Zn mineralization in the SYG province, younger than the Permian Emeishan mantle plume (~ 260 Ma). All data combined suggests that hydrothermal fluids circulated through basement rocks where they picked up metals and migrated to surface, mixed with reduced sulfur-bearing fluids and precipitated metals. Ore genesis of the Maozu deposit is different from known magmatic–hydrothermal, Sedimentary Exhalative or Mississippi Valley-types, which maybe represent a unique ore deposit type, named as the SYG-type.

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1. Introduction

About 408 Pb–Zn–(Ag) ore deposits occur in the western Yangtze Block, southwest China (Fig. 1; Liu and Lin, 1999). These deposits form the famous Sichuan–Yunnan–Guizhou (SYG) Pb–Zn metallogenic province, contain total Pb + Zn reserves of about 26 million tonnes (Mt) grading >10 wt.% Pb and Zn metals, and have been the major source of base metals in China (Liu and Lin, 1999). All the Pb–Zn deposits in this province are hosted in Sinian (635–541 Ma) to Permian carbonate rocks and are spatially coexist with the Permian Emeishan flood basalts (Zheng and Wang, 1991;

Liu and Lin, 1999; Zhou et al., 2001, 2013a; Han et al., 2007a, 2007b). This fact leads some scholars to consider them as distal magmatic–hydrothermal deposits (Xie, 1963; Liu and Lin, 1999). On the other hand, based on the restriction of the Pb–Zn deposits to carbonate rocks, Liao (1984) and Tu (1984) interpreted them as strata-bound sedimentary-reworked deposits. Some Pb–Zn deposits in this province were interpreted to be typical Mississippi Valley-type (MVT) (e.g., Zheng and Wang, 1991; Zhou et al., 2001; Liu, 2009), whereas other deposits were considered to be Sedimentary Exhalative-type (SEDEX) (e.g., Chen, 2002; He et al., 2006). Therefore, despite many investigations, a widely accepted genetic model for the regional Pb–Zn mineralization is still not available, due to lack of precise ages of Pb–Zn mineralization in this province.

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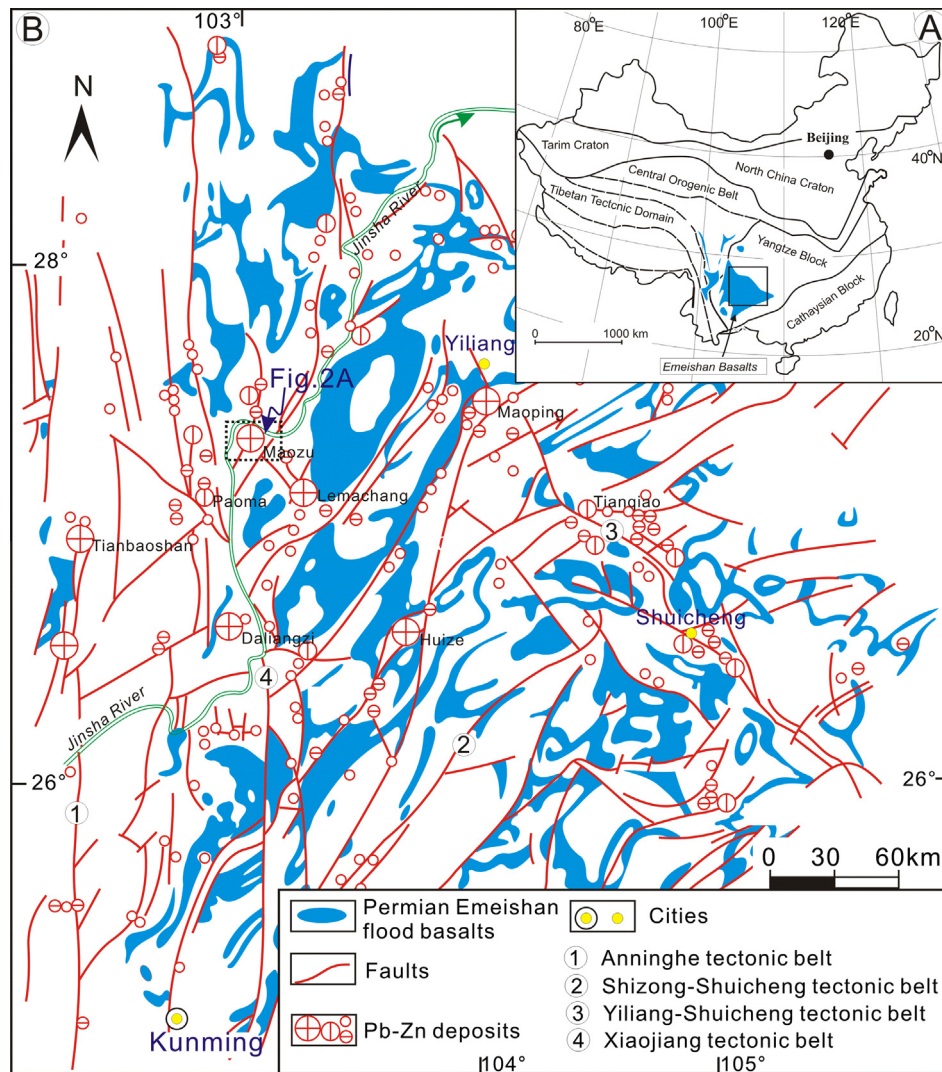


Fig. 1. (A) Tectonic map of South China; (B) Regional geological map of the Sichuan–Yunnan–Guizhou Pb–Zn metallogenic province (modified from Liu and Lin, 1999).

In the southwestern SYG province, there are about 160 Pb–Zn deposits distributed along NS- and NE-trending faults. Among these deposits, there are three large Pb–Zn–Ag deposits (1–3 Mt Pb + Zn metals reserves), namely the Maozu Zn–Pb deposit (Liu and Lin, 1999; Liu, 2009), Maoping Zn–Pb–Ge deposit (Han et al., 2007a) and Lemachang Ag–Pb–Zn deposit (Deng et al., 2000), and one world-class deposit (7 Mt Pb + Zn reserves) named the Huize Zn–Pb–Ge–Ag deposit (e.g., Zhou et al., 2001; Han et al., 2007b). Previous studies were mainly focused on the Huize deposit (e.g., Zhou et al., 2001; Huang et al., 2003, 2010; Han et al., 2007b, 2012; Zhang et al., 2005a, 2005b; Li et al., 2006, 2007a, 2007b, 2007c; Yin et al., 2009). The Maozu Pb–Zn deposit which was controlled by the Maozu thrust–fold tectonic system (Fig. 2A and B) has been mined for several decades (He et al., 2006). Due to a lack of precise mineralization ages, researchers considered it to be a distal magmatic–hydrothermal (Liu and Lin, 1999), MVT (Liu, 2009) or SEDEX (Chen, 2002; He et al., 2006) deposit.

C–O–S–Pb isotopes have been widely used to trace the source of hydrothermal fluids (e.g., Zheng and Wang, 1991; Ohmoto and Goldhaber, 1997; Zhou et al., 2001, 2010, 2013a, 2013b; Huang et al., 2003; Wilkinson et al., 2005; Seal, 2006). Several studies have explored the application of the Sm–Nd isotopic system to determine the age of hydrothermal mineral deposition (e.g., Peng et al., 2003; Li et al., 2007b; Barker et al., 2009; Su et al., 2009).

In this paper, we describe the geology of the Maozu Pb–Zn deposit and report new C–O isotopic data and a Sm–Nd isotopic age of hydrothermal calcite and additional S–Pb isotopic compositions of sulfides. These new data, together with previously published results are utilized to constrain the source of ore-forming fluids and timing of the Maozu Pb–Zn mineralization.

2. Geological setting

2.1. Regional geology

South China is made up of the Yangtze Block to the northwest and the Cathaysian Block to the southeast (Fig. 1A). The Yangtze Block is composed of ~2.9 to ~3.3-Ga crystalline basement complexes (e.g., Qiu et al., 2000; Gao et al., 2011), Meso- to Neo-proterozoic folded basement and a Paleozoic to Mesozoic cover sequence (e.g., Yan et al., 2003; Sun et al., 2009; Zhao et al., 2010; Wang et al., 2010, 2012). In the western Yangtze Block, the folded basement rocks include the ~1.7-Ga Dongchuan and ~1.1-Ga Kunyang Groups and equivalents (e.g., Sun et al., 2009; Zhao et al., 2010). They are well-bedded greywackes, slates and carbonaceous to siliceous sedimentary rocks that are tightly folded but only weakly metamorphosed. The widely distributed, shallow marine Paleozoic and Lower Mesozoic cover rocks include Cambrian

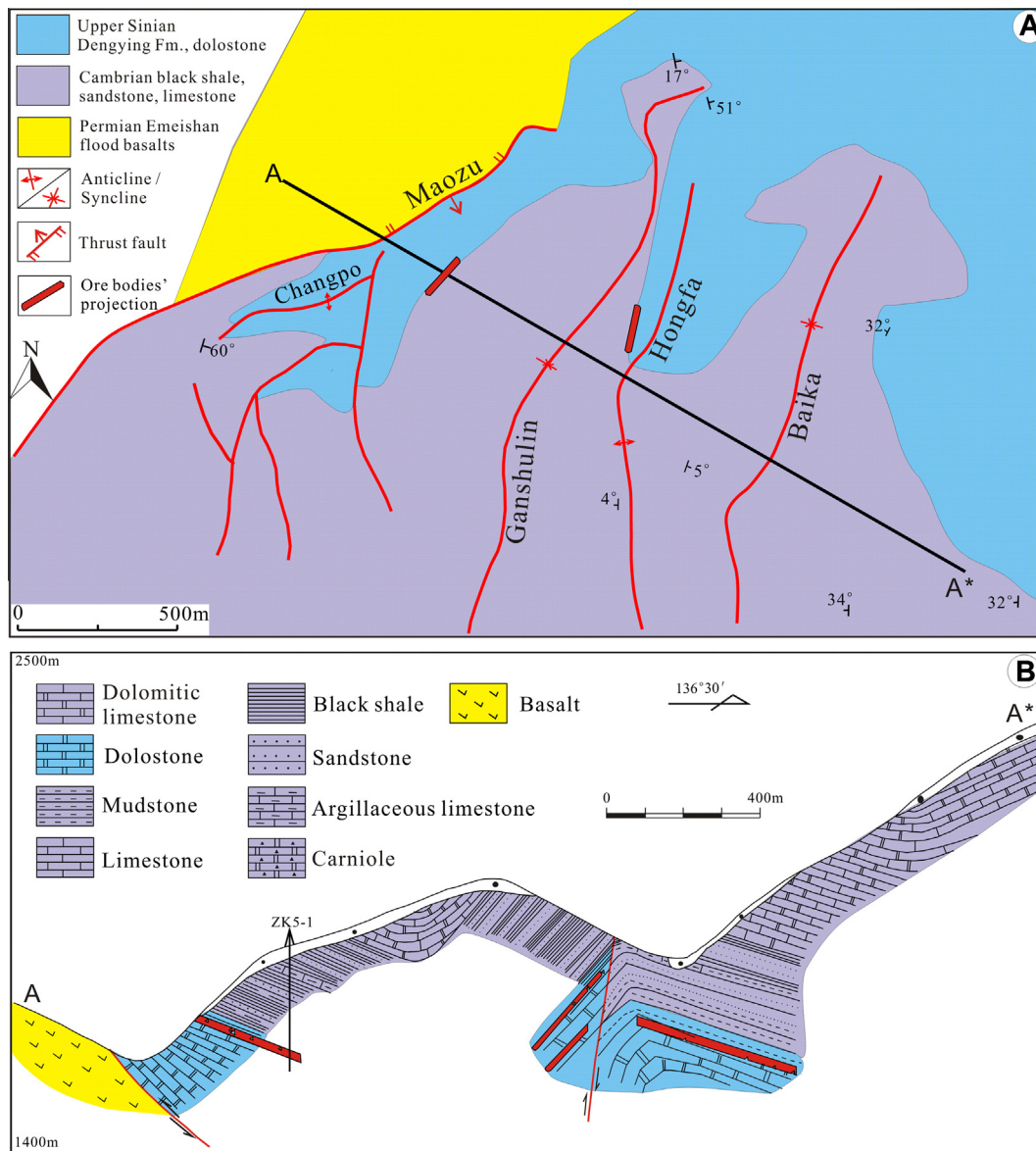


Fig. 2. (A) Geological map of the Maozu deposit (modified from Liu, 2009); (B) A–A* cross section of the Maozu deposit.

sedimentary strata of black shale, sandstone and limestone interbedded with dolostone, Ordovician sequences of thick-bedded limestone inter-layered with dolostone and argillaceous siltstone, Lower–Middle Silurian shale, fine-grained sandstone, and Devonian to Triassic sedimentary rocks. Evaporite rocks were widely distributed in the Cambrian to Triassic sedimentary rocks. Jurassic, Cretaceous and Cenozoic strata are entirely continental in character (Liu and Lin, 1999). In addition, a major feature of the western Yangtze Block is the mantle plume-derived Emeishan Large Igneous Province (ELIP) that is dated at about 260 Ma, covering an area of more than 250,000 km² (Zhou et al., 2002). The ELIP is dominantly composed of volcanic rocks known as the Emeishan flood basalts. Tectonically, after the eruption of the Emeishan flood basalts, the Yangtze Block was collided with adjacent Yidun arc associated the closure of the Tethys Ocean (e.g., Zhang et al., 2006; Reid et al., 2007; Han et al., 2012; Zhou et al., 2013a, 2013b). This event is known as the Indosinian Orogeny and it result in deformation of the strata through thrust fault–fold structures (e.g., Han et al., 2012; Zhou et al., 2013a).

The Pb–Zn deposits in the western Yangtze Block are distributed in a large triangular area of 170,000 km² in NE Yunnan, NW

Guizhou and SW Sichuan (Fig. 1B; Zheng and Wang, 1991; Zhou et al., 2001, 2011, 2013a, 2013b; Han et al., 2007b). This area is within the region covered by Emeishan flood basalts of the ELIP (Liu and Lin, 1999). Both Paleozoic and Lower Mesozoic sedimentary rocks are also exposed within the SYG province (Liu and Lin, 1999; Zhou et al., 2001). All of the 408 Pb–Zn deposits in this province are hosted in Sinian (635–541 Ma) to Permian carbonate rocks that are spatially coexist with the Emeishan flood basalts (e.g., Zheng and Wang, 1991; Zhou et al., 2001, 2013a; Han et al., 2007b). Pb–Zn deposits are controlled by thrust-fold tectonic fractures (Han et al., 2007b, 2012; Zhou et al., 2013a, 2013b). Faults in the western part of the province trend NS and NE (Han et al., 2007b), whereas those in the east trend NE and NW (Zhou et al., 2013a).

In the southwestern part of the SYG province, the cover sequences above Upper Proterozoic acidic, intermediate–acidic igneous rocks include the Upper Sinian Dengying Formation dolostone and Paleozoic sedimentary sequences and Emeishan flood basalts (Zhou et al., 2001). The NS- and NE-striking faults and anticlines in this district control the distribution of 160 Pb–Zn deposits (Liu and Lin, 1999). These deposits are hosted in the Upper Sinian

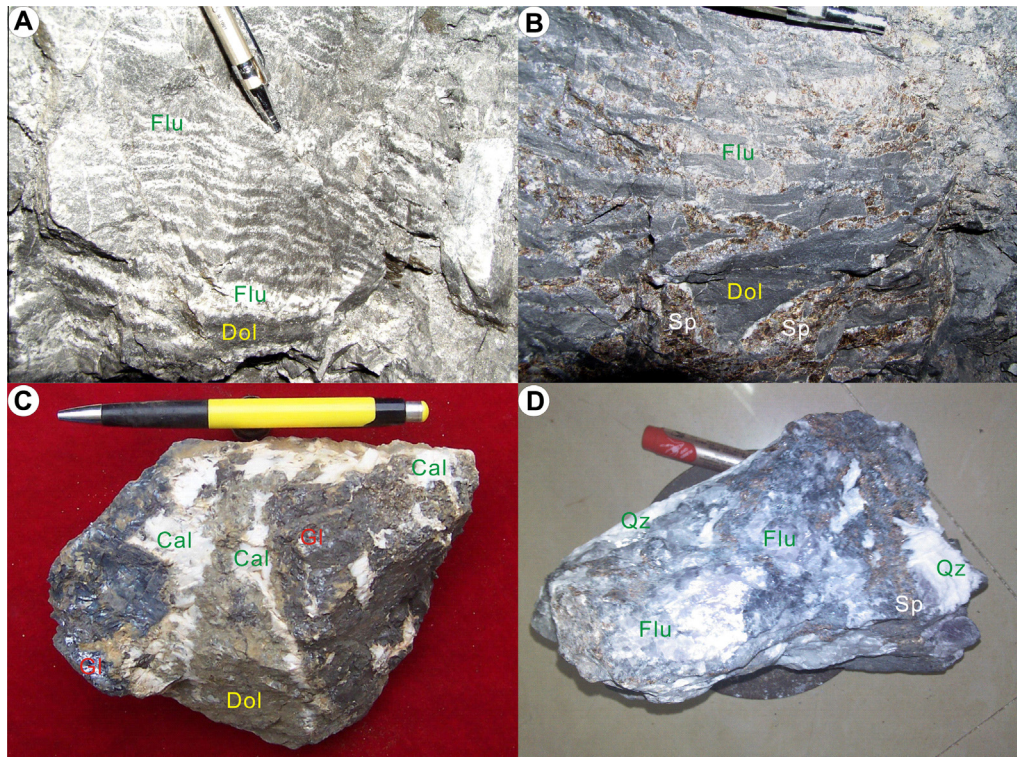


Fig. 3. Mineral assemblages and textures of ores from the Maozu deposit. (A) Banded (wave) fluorite vein; (B) Fluorite and sphalerite vein; (C) Porphyritic and veinlet calcite; (D) Veinlet sphalerite and porphyritic fluorite and quartz Flu-fluorite; Dol-dolostone; Sp-sphalerite; Gl-galena; Qz-quartz.

Dengying Formation, Middle–Upper Devonian, Lower Carboniferous and Lower Permian carbonate rocks (e.g., Liu and Lin, 1999; Han et al., 2007b).

2.2. Geology of the Maozu deposit

Ore bodies of the Maozu deposit are hosted in the Upper Sinian Dengying Formation dolostone and are structurally controlled by the Maozu thrust-fold tectonic fractures (Fig. 2A). In the Maozu ore fields, Upper Sinian carbonates and Cambrian sediments (sandstone, limestone and black shale) formed the Ganshulin and Baika syncline, and Hongfadong and Changpo anticline. The axial trend of the Ganshulin, Baika and Hongfadong structures is NE 20° and NNE-trending, whereas the Changpo anticline trends NE 40°. Four ore bodies are delineated in the upper part of the Dengying Formation, of which single ore body is 440–850 m long, 221–725 m wide and 2.63–5.09 m thick, with 0.77–6.11 wt.% Pb and 3.85–11.48 wt.% Zn. The Zn/Pb ratios range from 5 to 9. Ore bodies are strata-bounded and are located clearly within the boundaries of the wall rocks units (Fig. 2B). Five ore bodies are recognized in the lower part of the Dengying Formation, one of which is 240–930 m long, 45–346 m wide and 1.73–8.29 m thick, with 1.13–7.20 wt.% Pb and 3.61–12.27 wt.% Zn. The Zn/Pb ratios are 3–5. There are also some vein ore bodies with 60–94 m in length, 47–80 m in width and 4.04–5.96 m thick, with 1.36–4.40 wt.% Pb and 5.24–8.36 wt.% Zn. Ore bodies of this type trend dominantly 20–43°NW with some NE-striking veins. The Pb + Zn metals reserves of all the ore bodies are about 2.0 Mt, grading 4.15 wt.% Pb, 7.25 wt.% Zn, 33.6 g/t Ag and 180 ppm Ga (Liu, 2009).

Ores from the Maozu Pb–Zn deposit can be classified as oxidized, transitional and sulfide ores. According to the mineral textures, the sulfide ores can be divided into massive, veinlets and disseminated ores (Fig. 3). Sulfide ores are predominated by massive textures and composed of sphalerite, galena, pyrite, calcite, dolomite, quartz and fluorite. Ore textures and structures include

granular, porphyritic and eutectic, and metasomatic, massive, banded, disseminated and veined (Fig. 3). The mineralization can be divided into diagenesis, hydrothermal and oxidized periods, of which the hydrothermal period can further divided into two stages, i.e., the sulfide–carbonate–quartz–fluorite and carbonate stages. For the prior stage, the minerals assemblages are pyrite–sphalerite–calcite, quartz–sphalerite–pyrite–galena–calcite, and sphalerite galena–calcite–quartz–fluorite (Fig. 3). Wall rock alterations are mainly dolomitization, calcitization, Fe–Mn carbonatization and ferritization, of which dolomitization and calcitization are closely associated with Pb–Zn mineralization, and Fe–Mn carbonatization and ferritization are the important indicators of ore prospecting on the earth's surface.

3. Analytical methods

C and O isotope analysis was completed at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, by using a Finnigan MAT-253 mass spectrometer. Calcite reacts with 100% phosphoric acid (H_3PO_4) to produce CO_2 . The analytical precision (2σ) is $\pm 0.2\text{‰}$ for $\delta^{13}C$ value and $\pm 2\text{‰}$ for $\delta^{18}O$ value. Carbon and oxygen isotope compositions are reported relative to Pee Dee Belemnite (PDB). $\delta^{18}O_{SMOW} = 1.03086 \times \delta^{18}O_{PDB} + 30.86$ (Friedman and O'Neil, 1977).

S isotopic compositions were obtained by using Elemental Analyzer (EA) method on a Continuous Flow Isotope Ratio Mass Spectrometer at State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. Samples are wrapped tightly with a tin can and put into the EA reaction furnace, followed by combustion and decomposition to produce SO_2 . GBW 04415 and GBW 04414 Ag_2S are used as the external standards and Canyon Diablo Troilite (CDT) as the reference standard, with the analytical accuracy of $\pm 0.1\text{‰}$ (2σ).

Table 1

Carbon and oxygen isotopic compositions of hydrothermal calcite separates from the Maozu Pb–Zn deposit, SW China.

Nos.	Mineral	$\delta^{13}\text{C}_{\text{PDB}}/\text{‰}$ (2σ)	$\delta^{18}\text{O}_{\text{SMOW}}/\text{‰}$ (2σ)	Source
MZ-17	Hydrothermal calcite	-3.2 ± 0.2	$+13.8 \pm 0.5$	This paper
MZ-26	Hydrothermal calcite	-2.7 ± 0.1	$+15.8 \pm 0.8$	
MZ-36	Hydrothermal calcite	-2.1 ± 0.1	$+17.5 \pm 1.1$	
MZ-38	Hydrothermal calcite	-2.0 ± 0.1	$+14.1 \pm 0.6$	
MZ-39	Hydrothermal calcite	-3.7 ± 0.2	$+15.0 \pm 0.9$	

Pb isotopes analyses were carried out using the GV IsoProbe-T Thermal Ionization Mass Spectrometer at the Beijing Institute of Uranium Geology. The analytical procedure involves dissolution of samples using HF and HClO₄ in crucibles, followed by addition of a basic anion exchange resin to purify Pb. Analytical results for the standard NBS 981 are $^{208}\text{Pb}/^{204}\text{Pb} = 36.611 \pm 0.004$ (2σ), $^{207}\text{Pb}/^{204}\text{Pb} = 15.457 \pm 0.002$ (2σ) and $^{206}\text{Pb}/^{204}\text{Pb} = 16.937 \pm 0.002$ (2σ), in agreement with the referenced value (Belshaw et al., 1998).

Sm and Nd concentrations and isotopic compositions in hydrothermal calcite were determined using the procedure described by Peng et al. (2003). The samples were dissolved in Teflon vessels at 150 °C for at least 12 h, until complete decomposition was achieved. Sm and Nd concentrations were determined by isotope dilution using ^{149}Sm – ^{146}Nd spike solution. Isotopic ratio measurements were carried out with an IsoProbe-T TIMS at the Institute of Geology and Geophysics, Chinese Academy of Sciences. Nd ratios were normalized to a $^{146}\text{Nd}/^{144}\text{Nd}$ ratio of 0.7219. Analytical uncertainty for Sm and Nd concentrations is less than 0.5% (2σ). Replicate analyses of the Johnson and Matthey® Nd standard (JMC) yielded the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.511132 ± 5 (2σ , $n = 6$). Blanks during this study averaged 0.03 ng for Sm and 0.05 ng for Nd. The decay constant used in the age calculation is $\lambda^{147}\text{Sm} = 6.54 \times 10^{-12} \text{ t}^{-1}$.

4. Analytical results

C and O isotopic compositions of hydrothermal calcite are listed in Table 1. $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{SMOW}}$ values range from -3.7‰ to -2.0‰ (mean -2.7‰) and $+13.8$ to $+17.5\text{‰}$ (mean $+15.2\text{‰}$), respectively.

New and previously published (Liu and Lin, 1999; Liu, 2009) sulfur isotopic compositions are listed in Table 2 and shown in Fig. 4A. $\delta^{34}\text{S}_{\text{CDT}}$ values of 8 sulfides analyzed in this study range from $+9.9\text{‰}$ to $+19.2\text{‰}$ (mean $+14.0\text{‰}$).

Pb isotopic compositions of sphalerite and galena, together with previously published data (Liu and Lin, 1999; Liu, 2009) are listed in Table 3. Sulfides analyzed in this study have $^{206}\text{Pb}/^{204}\text{Pb}$,

$^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios ranging from 18.129 to 18.375, 15.640 to 15.686 and 38.220 to 38.577, respectively.

Hydrothermal calcites have $^{147}\text{Sm}/^{144}\text{Nd}$ ratios ranging from 0.1279 to 0.4024, $^{143}\text{Nd}/^{144}\text{Nd}$ ratios ranging from 0.512097 to 0.512449 (Table 4), and yields a Sm–Nd isotopic age of $196 \pm 13 \text{ Ma}$, with epsilon Nd = -8.8 , MSWD = 0.89 (Fig. 5A).

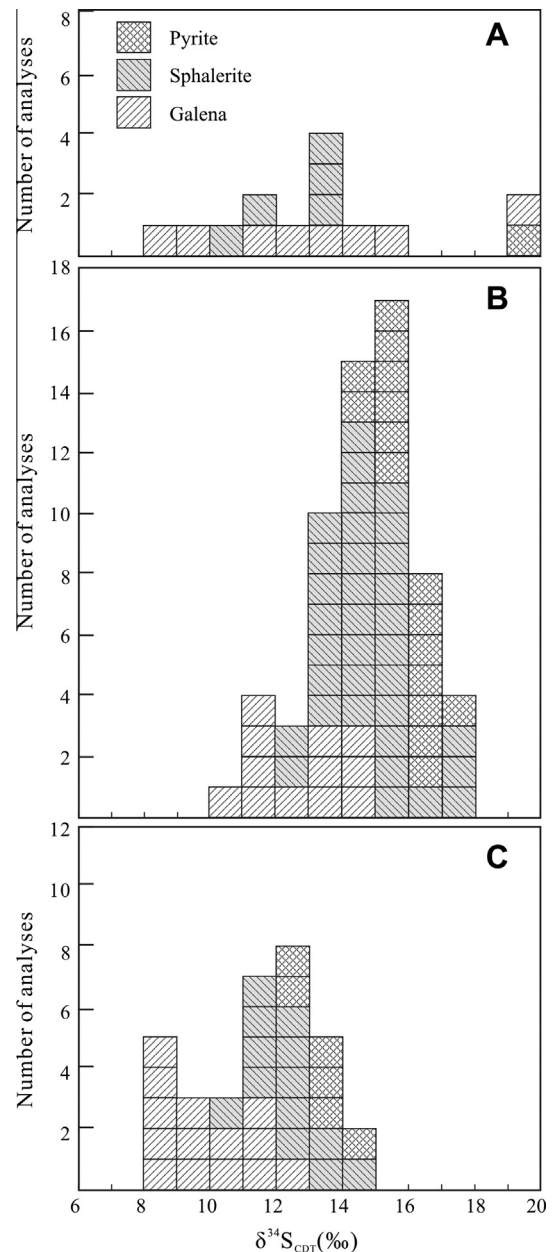


Fig. 4. (A) Histogram of sulfur isotopic compositions of sulfides from the Maozu deposit; (B) Histogram of sulfur isotopic compositions of sulfides from the Huize deposit (Han et al., 2007b); (C) Histogram of sulfur isotopic compositions of sulfides from the Tianqiao deposit (Zhou et al., 2013a).

Table 2

Sulfur isotopic compositions of sulfide separates from the Maozu Pb–Zn deposit, SW China.

Nos.	Mineral	$\delta^{34}\text{S}_{\text{CDT}}/\text{‰}$ (2σ)	Sources
MZ-5	Sphalerite	$+13.4 \pm 0.1$	This paper
MZ-11	Sphalerite	$+13.5 \pm 0.1$	
MZ-40	Galena	$+9.9 \pm 0.1$	
MZ-21	Galena	$+15.4 \pm 0.1$	
MZ-36	Galena	$+13.9 \pm 0.1$	
MZ-38	Galena	$+19.2 \pm 0.1$	
MZ-34	Galena	$+12.1 \pm 0.1$	
MZ-37	Galena	$+14.2 \pm 0.1$	
Mao-11	Sphalerite	$+13.9 \pm 0.2$	Liu and Lin (1999)
Mao-8-2	Sphalerite	$+11.5 \pm 0.2$	
Mao-8-1	Galena	$+8.8 \pm 0.2$	
Mao-3	Pyrite	$+19.9 \pm 0.2$	Liu (2009)
Mao-2	Sediment barite	$+30.4 \pm 0.2$	
M-1	Sphalerite	$+10.7 \pm 0.2$	
M-2	Galena	$+11.9 \pm 0.2$	

Table 3
Lead isotopic compositions of sulfide separates from the Maozu Pb–Zn deposit, SW China.

Nos.	Mineral	$^{206}\text{Pb}/^{204}\text{Pb}$ (2σ)	$^{207}\text{Pb}/^{204}\text{Pb}$ (2σ)	$^{208}\text{Pb}/^{204}\text{Pb}$ (2σ)	Sources	
MZ-11	Sphalerite	18.375 ± 0.003	15.686 ± 0.003	38.577 ± 0.006	This paper	
MZ-5	Sphalerite	18.260 ± 0.001	15.655 ± 0.001	38.396 ± 0.002		
MZ-21	Sphalerite	18.161 ± 0.002	15.640 ± 0.002	38.246 ± 0.004		
MZ-34	Galena	18.162 ± 0.005	15.644 ± 0.004	38.272 ± 0.009		
MZ-40	Galena	18.194 ± 0.004	15.676 ± 0.002	38.362 ± 0.006		
MZ-36	Galena	18.129 ± 0.002	15.658 ± 0.001	38.220 ± 0.003		
MZ-21	Galena	18.170 ± 0.002	15.660 ± 0.002	38.313 ± 0.004		
I-104	Galena	17.980 ± 0.004	15.470 ± 0.003	38.010 ± 0.003		Liu and Lin (1999)
MT-Pb2	Galena	18.109 ± 0.003	15.629 ± 0.002	38.161 ± 0.004		
MT-Pb1	Galena	18.220 ± 0.003	16.626 ± 0.005	38.377 ± 0.005		
Mao-6	Galena	18.128 ± 0.004	15.587 ± 0.003	38.068 ± 0.003		
Mao-9	Galena	18.147 ± 0.002	15.621 ± 0.002	38.171 ± 0.006	Liu (2009)	
Mao-13	Galena	18.305 ± 0.001	15.641 ± 0.003	38.434 ± 0.005		
Mao-3	Galena	18.191 ± 0.003	15.643 ± 0.002	38.306 ± 0.005		
Mao-11	Galena	18.444 ± 0.003	15.746 ± 0.003	38.858 ± 0.008		
M-1	Galena	18.154 ± 0.003	15.632 ± 0.002	38.216 ± 0.003		
M-2	Galena	18.124 ± 0.002	15.628 ± 0.003	38.176 ± 0.003		

Table 4
Sm–Nd isotopic compositions and parameters of hydrothermal calcite separates from the Maozu Pb–Zn deposit, SW China.

Nos.	Sm/ 10^{-6}	Nd/ 10^{-6}	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	2σ	$\epsilon_{\text{Nd}}(t)$	Source
MZ-17	0.53	2.53	0.1279	0.512097	0.000011	–8.8	This paper
MZ-26	0.86	4.04	0.1287	0.512110	0.000012	–8.6	
MZ-36	0.80	2.55	0.1900	0.512171	0.000017	–8.9	
MZ-38	3.16	4.75	0.4024	0.512449	0.000014	–8.9	
MZ-39	2.07	4.61	0.2952	0.512325	0.000011	–8.6	

$\epsilon_{\text{Nd}}(t)$ calculated at 200 Ma.

5. Discussion

5.1. Possible sources of CO_2 in the hydrothermal fluids

In the diagram of $\delta^{13}\text{C}_{\text{PDB}}$ vs. $\delta^{18}\text{O}_{\text{SMOW}}$ (Fig. 6), all the samples plot in the field between marine carbonate rocks ($\delta^{13}\text{C}_{\text{PDB}} = 0 \pm 4\text{‰}$, $\delta^{18}\text{O}_{\text{SMOW}} = +20\text{‰}$ to $+24\text{‰}$; Veizer and Hoefs, 1976) and mantle-derived carbonatite ($\delta^{13}\text{C}_{\text{PDB}} = -4\text{‰}$ to -8‰ , $\delta^{18}\text{O}_{\text{SMOW}} = +6\text{‰}$ to $+10\text{‰}$; Taylor et al., 1967) with a negative correlation. These values are similar to the Huize (Huang et al., 2003, 2010; Han et al., 2007b) and Tianqiao (Zhou et al., 2013a) deposits in the SYG province. Previous investigations have proposed that if CO_2 in the hydrothermal fluids was derived from the mantle-derived carbonatite by crystallization differentiation, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of which should be higher than these of carbonatite (Fig. 6; Demény et al., 1998). Similarly, if CO_2 in the hydrothermal fluids was a product of marine carbonate rocks' dissolution, it should be characterized by ^{18}O -depleted (Fig. 6; Liu and Liu, 1997). Organic matter can act as a reducing agent in thermo chemical sulfate reduction processes (e.g., Ottaway et al., 1994) and produce CO_2 for the hydrothermal fluids, and so if CO_2 was mainly originated from sedimentary organic matter, it should be showing ^{13}C -enriched and ^{18}O -depleted (Fig. 6; Liu and Liu, 1997). Therefore, the carbon and oxygen isotopic data in this study plot near the marine carbonate rocks with a negative relationship, indicating that CO_2 in the hydrothermal fluids was mainly originated from marine carbonate rocks, with limited influence from sedimentary organic matter.

5.2. Origin of reduced sulfur in the hydrothermal fluids

Ores from the Maozu deposit are composed chiefly of galena, sphalerite, pyrite, calcite, quartz and fluorite (Fig. 3). The lack of sulfate minerals in the ores suggests that $\delta^{34}\text{S}$ values of sulfides could basically represent the $\delta^{34}\text{S}_{\Sigma\text{S-fluids}}$ value (Ohmoto, 1972).

Sulfides have $\delta^{34}\text{S}_{\text{CDT}}$ values ranging from $+8.8\text{‰}$ to $+19.9\text{‰}$ (Table 2 and Fig. 4A), similar to the Huize (Fig. 4B; Zhou et al., 2001; Li et al., 2006, 2007a; Han et al., 2007b) and Tianqiao deposits (Fig. 4C; Zhou et al., 2013a) in the SYG province, significantly different from that of mantle-derived magmatic sulfur ($\sim 0\text{‰}$; Chaussidon et al., 1989). In addition, the evaporite rocks in Cambrian to Triassic sedimentary strata in the SYG province, such as gypsum and barite, have $\delta^{34}\text{S}_{\text{CDT}}$ values ranging from $+15\text{‰}$ to $+30\text{‰}$ (Table 2; Liu and Lin, 1999; Han et al., 2007b), and similar to Cambrian to Triassic seawater sulfate ($+15\text{‰}$ to $+35\text{‰}$; Claypool et al., 1980). Owing to the fact that the $\Delta^{34}\text{S}_{\text{sulfate-sulfide}}$ in sulfate reduction processes can be up to $+10\text{‰}$ to $+15\text{‰}$ (Ohmoto et al., 1990; Ohmoto and Goldhaber, 1997; Basuki et al., 2008), the sulfur isotope signature of sulfides in the deposit suggests that reduced sulfur in the hydrothermal fluid may have been derived predominantly from evaporates in the Cambrian sedimentary strata (Fig. 2A).

5.3. Possible sources of metals constrained by Pb isotopes

Previous studies suggested that metals in the hydrothermal fluids that formed Pb–Zn deposits in the SYG province were sourced from Sinian to Permian carbonate rocks (e.g., Li et al., 1999; Li et al., 2007a). Zhou et al. (2001) suggested that metals were dominantly derived from Precambrian basement volcanic rocks. However, most scholars considered that Proterozoic basement rocks (Dongchuan and Kunyang Groups), Sinian to Permian sedimentary rocks and Permian Emeishan flood basalts all contributed metals (e.g., Liu and Lin, 1999; Huang et al., 2004, 2010; Zhang et al., 2005a; Han et al., 2007b). Contents of U and Th for the sulfides are too low to influence the Pb isotopic compositions, whereas contrasted whole rocks of basalts, sedimentary and basement rocks need to be age-adjusted (e.g., Carr et al., 1995; Zhang et al., 2002). The $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios of sulfides from the Maozu deposit plot in the field between upper crust and the

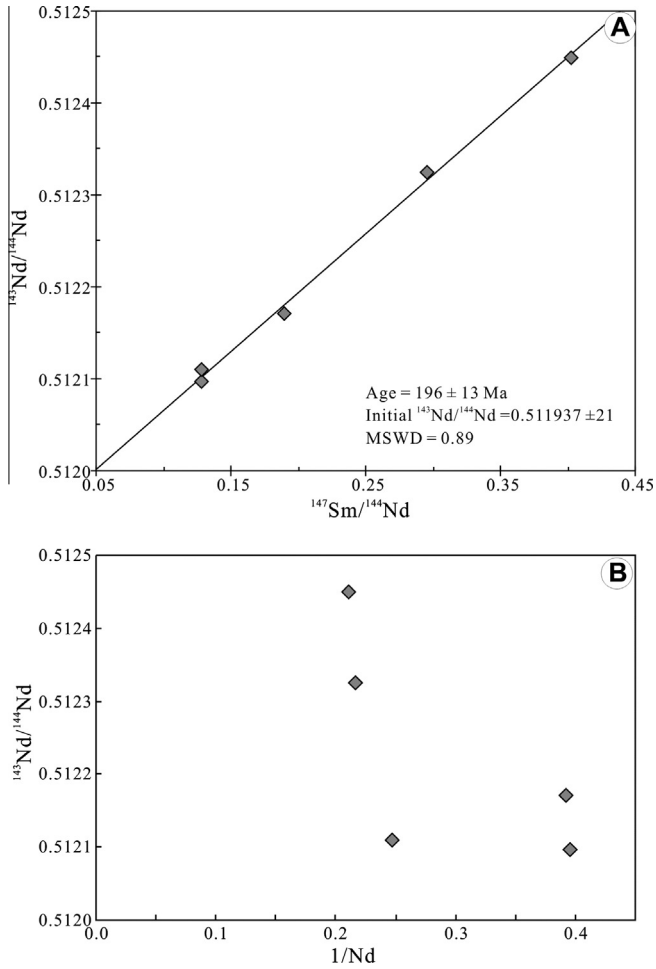


Fig. 5. (A) Sm–Nd isochron for hydrothermal calcites from the Maozu deposit; (B) Plot of $1/Nd - {}^{143}Nd/{}^{144}Nd$ for the hydrothermal calcites.

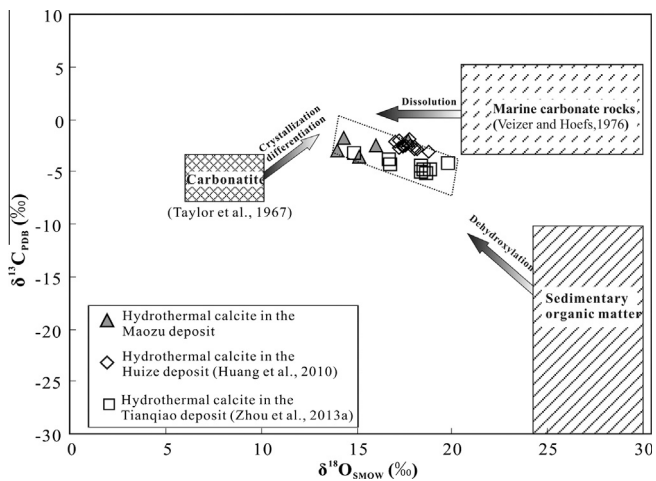


Fig. 6. Diagram of $\delta^{13}C_{PDB}$ vs. $\delta^{18}O_{SMOV}$ for hydrothermal calcites from the Maozu deposit (modified from Liu and Liu, 1997). Data from the Tianqiao deposit are taken from Zhou et al. (2013a); Data from the Huize deposit are taken from Huang et al. (2010).

orogenic evolution curve (Fig. 7; Zartman and Doe, 1981), and similar to that of age-corrected Proterozoic basement rocks. Only a few samples plot in the field of the age-corrected Devonian to Permian carbonate rocks, Permian Emeishan flood basalts and the Upper

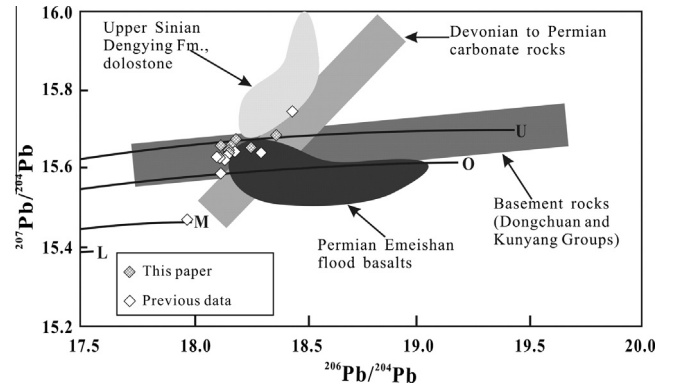


Fig. 7. Diagram of ${}^{207}Pb/{}^{204}Pb$ vs. ${}^{206}Pb/{}^{204}Pb$ for sulfides from the Maozu deposit U – upper crust; O – orogenic belt; M – mantle; L – lower crust. Data for the Upper Sinian Dengying Formation dolostone, Devonian to Permian carbonate rocks, Permian Emeishan flood basalts and Proterozoic basement rocks are taken from Zheng and Wang (1991), Zhou et al. (2001, 2013a, 2013b), Huang et al. (2004), Han et al. (2007b) and Li et al. (2007a) and age-corrected at 200 Ma.

Sinian Dengying Formation dolostone (Fig. 7). Therefore, we suggest that although lead metal was partly supplied by the basalts and carbonate rocks, most was sourced from the basement rocks.

5.4. Timing of the Pb–Zn mineralization

Isotope dilution measurements on five hydrothermal calcite separates from the Maozu deposit show Sm and Nd concentrations of 0.53–3.16 ppm and 2.53–4.75 ppm, respectively, and yield a Sm–Nd isochron age of 196 ± 13 Ma (Fig. 5A), with an initial ${}^{143}Nd/{}^{144}Nd$ ratio of 0.511937 ± 21 . The absence of covariance between $1/Nd$ and ${}^{143}Nd/{}^{144}Nd$ (Fig. 5B) for these calcites indicates that the isochron age is not a pseudoisochron and has isochronal meaning (Peng et al., 2003; Li et al., 2007b; Barker et al., 2009; Su et al., 2009). Previous studies reported that hydrothermal calcite from the Huize Pb–Zn deposit yields a Sm–Nd isotopic age of 222 ± 14 Ma (Li et al., 2007b), sphalerite from the Paoma Pb–Zn deposit yields a Rb–Sr isotopic age of 200.1 ± 4.0 Ma (Lin et al., 2010) and sulfides from the Tianqiao Pb–Zn deposit yield a Rb–Sr isotopic age of 191.9 ± 6.9 Ma (Zhou et al., 2013a). Our Sm–Nd isotopic age is broadly similar to these early reported ages. Hence, we consider that these deposits formed simultaneously and the predominant Pb–Zn mineralization event in the SYG province occurred at ~ 200 Ma.

5.5. Possible ore genesis and mineralization process

5.5.1. Ore genesis

If the assumption is true that Pb–Zn mineralization event in the SYG province occurred at ~ 200 Ma, it suggests that mineralization was much younger than the Permian Emeishan mantle plume (~ 260 Ma; Zhou et al., 2002) and the host late Sinian to early Permian sedimentary strata. This suggests that Pb–Zn deposits in the SYG province are not related to the Emeishan mantle plume and their ore genesis is not belonging to SEDEX or distal magmatic–hydrothermal type. Because ore bodies are hosted in the late Sinian to early Permian carbonate rocks, their ore genesis is also thought to be a typical MVT-type (Zheng and Wang, 1991; Zhou et al., 2001; Wang et al., 2010). However, sulfides in the Maozu Pb–Zn deposit were precipitated from Ca^{2+} – Mg^{2+} – Cl^- rich fluids at moderate temperatures (153 – 248 °C; Liu, 2009) with low salinities (2.8 – 5.3 wt.% NaCl; He et al., 2006). The salinity and temperature data are similar to the Huize (Han et al., 2004, 2007b) and Tianqiao (Zhou et al., 2013a) deposits in the SYG province, but different from

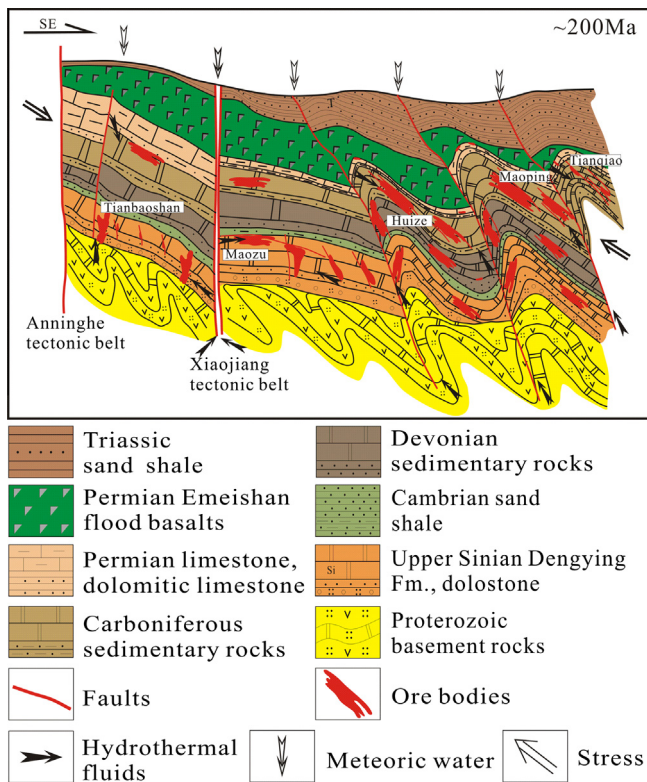


Fig. 8. Metallogenic model of the SYG-type Pb–Zn deposits (modified after Han et al., 2012). At ~200 Ma, the closure of the Palaeo-Tethys Ocean resulted in deformation of the strata through thrust fault–fold structures, which is known as the Indosinian Orogeny. Thermal activity related to this event resulted in circulation of hydrothermal fluids within basement rocks where they picked up metals, and then migrated upward along regional faults to surface, and precipitated metals along fracture and contact zones.

the basin brines related to MVT-type deposits (Leach et al., 2005, 2010) that have high salinities (usually higher than 10 wt.% NaCl) and low temperatures (usually lower than 150 °C). In addition, the Maozu deposit has non-radiogenic Pb isotope (Table 3) and much higher Pb + Zn grades (10–15 wt.%) than MVT deposits (less than 10 wt.%). Most important, typical MVT deposits are not linked with known igneous activities and associated with the extensional basin setting (Leach et al., 2005, 2010). However, the Maozu deposit is spatially coexisting with the Emeishan flood basalts and structurally controlled by the thrust–fold tectonic fractures (Figs. 1B and 2A). Therefore, the Maozu Pb–Zn deposit is similar to the Huize (Han et al., 2007b) and Tianqiao (Zhou et al., 2013a) deposits in the SYG province is considered to be a unique type, named as the SYG-type.

5.5.2. Ore-forming process

The ages of Pb–Zn mineralization in the SYG province have been available constrained (Li et al., 2007b; Lin et al., 2010; Zhou et al., 2013a; this paper), which suggests that the predominant Pb–Zn mineralization event in this province occurred at ~200 Ma in response to the closure of the Palaeo-Tethys Ocean (Hu and Zhou, 2012). This event is known as the Indosinian Orogeny and it result in deformation of the strata through thrust fault–fold structures (e.g., Han et al., 2012; Zhou et al., 2013a). Thermal activity related to the Indosinian Orogeny resulted in circulation of hydrothermal fluids within basement rocks where they picked up metals, and then the compressional tectonics drove the large scale hydrothermal fluids migrated upward along regional faults to surface, mixed

with reduced sulfur-bearing fluids and precipitated metals along fracture and contact zones (Fig. 8).

6. Conclusions

1. Different components of the hydrothermal fluids have different sources. For example, CO₂ may have been derived from a mixture of marine carbonate rocks and sedimentary organic matter, reduced sulfur was originated from evaporate in the Cambrian to Triassic sedimentary rocks and lead metal was derived predominantly from the Proterozoic basement rocks.
2. Hydrothermal calcite yields a Sm–Nd isotopic age of 196 ± 13 Ma, possibly reflecting the timing of Pb–Zn mineralization in the SYG province. This age is younger than the Permian Emeishan mantle plume (~260 Ma), suggesting that the eruption of the Emeishan flood basalts associated with the mantle plume had no direct relationship with the Pb–Zn mineralization event in the SYG province.
3. Ore genesis of the Maozu Pb–Zn deposit is not belong to SEDEX or distal magmatic–hydrothermal types, but it is also different from typical MVT deposit, rather, it represents a unique ore deposit type, named in this article as the SYG-type.

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