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Strontium isotopic geochemistry of Tianqiao Pb-Zn deposit, Southwest China

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Abstract Tianqiao carbonate-hosted Pb-Zn deposit, controlled by NW-trending F_{37} thrust fault and NW-trending Tianqiao anticline, is located in the eastern part of Sichuan-Yunnan-Guizhou (SYG) Pb-Zn metallogenic province, southwestern Yangtze Block, southwest China. Ore bodies in this deposit are hosted in the Devonian-Carboniferous carbonate rocks, and ore minerals include sphalerite, galena and pyrite, while the gangue minerals are dominated by calcite and dolomite. Using high–precision solid thermal ionization mass spectrometry (TIMS), this paper reports the strontium isotopic compositions (0.7119 to 0.7167) of sulfide samples from the Tianqiao deposit in order to trace the origin of hydrothermal fluids. Compared with the country rocks, the calculated $^{87}Sr/^{86}Sr_{200\ Ma}$ values of sulfide range from 0.7118 to 0.7130, higher than those of the age-corrected Devonian to Permian sedimentary rocks (0.7073 to 0.7101) and the Middle Permian Emeishan flood basalts (0.7078 to 0.7039), but lower than those of the age-corrected Proterozoic basement rocks (such as the Kunyang and Huili Groups, $^{87}Sr/^{86}Sr_{200\ Ma}$=0.7243 to 0.7288). This implies a mixed strontium source between the older basement rocks and the younger cover sequences. Together with geologic and previous isotopic evidences, we considered that the fluids' mixing is a possible mechanism for sulfide precipitation in the Tianqiao deposit.

Key words Strontium isotope; fluids mixing; Tianqiao Pb-Zn deposit; southwest China

1 Introduction

Located in the southwestern Yangtze Block, the Sichuan-Yunnan-Guizhou (SYG) Pb-Zn metallogenic province (Zhou et al., 2013a), a major producer of base metals in China, has more than four hundreds carbonate-hosted Pb-Zn deposits and contains 260 million tonnes Pb-Zn ores at grades of >10% Pb+Zn (Liu and Lin, 1999; Jin, 2008; Zhou et al., 2013b; Dou and Zhou, 2013). Ore minerals in these deposits include sphalerite, galena and pyrite, with minor chalcopyrite, while the gangue minerals are dominated by calcite and dolomite with subordinate quartz, fluorite and barite. Ore bodies are hosted in dolostone and dolomitic limestone of the Late Sinian to Early Permian (e.g. Zheng and Wang, 1991; Deng et al., 2000; Wang et al., 2000; Zhou et al., 2001; Wang et al., 2003; Han et al., 2007; Yin et al., 2009; Zhou et al., 2010).

Although these deposits show a lot of similarities and belong to epigenetic deposit, however, the origin of them and the mechanism for such giant accumulations of Pb-Zn have long been controversial (e.g. Xie, 1964; Tu, 1984; Liu and Lin, 1999; Han et al., 2007; Zhou et al., 2013a). For example, some researchers considered that the hydrothermal fluids were derived from the host strata (e.g. Chen, 1986; Zheng, 1994; Wang et al., 2000; Wang et al., 2010) or the Precambrian igneous rocks were the main source (Zhou et al., 2001), but other scholars proposed that they have a mixed source of the Middle Permian Emeishan flood basalts, the Proterozoic host carbonate rocks and the underlying Precambrian basement rocks (e.g. Liu and Lin, 1999; Huang et al. 2003; Han et al., 2007; Zhou et al., 2013b, c). In addition, a close spatial association with the Emeishan basalts has been used to classify them as the distal magmatic hydrothermal deposits (Xie, 1964). On the other hand, based on the restriction of the Pb-Zn deposits to carbonate rocks, Tu (1984) interpreted them as strata-bound deposits. However, these deposits were also considered to be typical Mississippi Valley-type (e.g. Zheng and Wang, 1991; Wang et al., 2000; Zhou et al., 2001), or a new type (e.g. Han et al., 2007, 2012; Huang et al., 2010; Zhou et al., 2013a, b, d).

In the southeastern SYG province, there are more than 120 carbonate-hosted Pb-Zn deposits, which are distributed along the NW-trending faults (Fig. 1). Previous studies have shown that these deposits are hosted in dolostone and/or dolomitic limestone of Devonian to Permian (e.g. Zheng, 1994; Mao, 2000, 2001; Jin, 2008; Zhou et al., 2010, 2013e; Dou and Zhou, 2013). The Tianqiao Pb-Zn deposit is one of the largest deposits in this region. Although many studies on ore deposit geology, geochemistry, isotopes and fluid inclusions are available for this deposit (e.g. Mao, 2000, 2001; Gu, 2006, 2007; Jin, 2008; Zhou et al., 2010, 2011, 2013a, 2014), but the origin of hydrothermal fluid is still under debate (e.g. Zhou et al., 2013a).

Strontium isotope is a powerful tool for fingerprinting ore-forming fluids (e.g. Zheng and Wang, 1991; Zhou et al., 2001; Zhou et al., 2013a, b, d). In this paper, we report new strontium isotope data of sulfide from the Tianqiao Pb-Zn deposit. This dataset, combined with our previously results are utilized to constrain the source of the ore-forming fluids. This work can also provide implications for the giant Pb-Zn mineralization in the SYG province.

2 Regional and deposit geology

2.1 Geology of the SYG metallogenic province

The Pb-Zn deposits in the western Yangtze Block, Southwest China are distributed in a large triangular area of 170000 km^2 covering NE Yunnan, NW Guizhou and SW Sichuan provinces (Liu and Lin, 1999). In this area are exposed abundant Emeishan flood basalts, which is the part of the Emeishan Large Igneous Province (Zhou et al., 2002). Both the Upper Paleozoic and Lower Mesozoic sedimentary rocks are also exposed within the SYG province. More than 400 carbonate-hosted Pb-Zn deposits have been found in the SYG province (Liu and Lin, 1999), which are characterized by irregular ore bodies with simple mineral assemblages, weak wall rock alterations, but high Pb+Zn grades of ores (e.g. Zheng and Wang, 1991; Deng et al., 2000; Wang et al., 2000; Zhou et al., 2001; Wang et al., 2003; Han et al., 2007; Zhou et al., 2013c, d, f). They are mainly hosted in carbonate rocks of the Upper Sinian (Ediacaran) Dengying Formation, the Upper Devonian Rongxian Formation and the Carboniferous Baizuo, Maping, and Huanglong formations, which are all overlain by the Middle Permian Emeishan flood basalts (Liu and Lin, 1999). Fault systems within the SYG province are very complex and control the distribution of the Pb-Zn deposits. Most faults in the western part of the province are NS-trending (Han et al., 2007), whereas those in the east are trending NE and NW (Fig. 1).

2.2 Geology of the southeastern SYG province

In the southeastern SYG province, there are more than 120 Pb-Zn deposits (Jin, 2008). In this area, the cover sequence includes the Devonian, Carboniferous, Permian and Triassic sedimentary rocks (Fig. 1), and the Permian Emeishan flood basalts. The Devonian strata include sandstone, siltstone, limestone and dolostone. The Carboniferous strata consist of shale, limestone and dolostone. The Early Permian sequence consists of sandstone, shale, coal layers and limestone, overlain by the Middle Permian Emeishan flood basalts. The basalts are overlain by the Late Permian sandstone, siltstone and coal measures. The Triassic strata consist of siltstone, sandstone, dolostone and limestone. There are NW- and NE-striking faults occurring in this area, and the Pb-Zn deposits are mainly controlled by the NW-trending faults (Fig. 1). The Pb-Zn ore bodies are mainly hosted in dolostone and dolomitic limestone of the Devonian and Carboniferous (Dou and Zhou, 2013).

2.3 Geology of Tianqiao Pb–Zn deposit

In Tianqiao deposit, including the Devonian, Carboniferous and Permian form the Tianqiao anticline, is crosscut by N-, NE- and E-trending faults (Fig. 2A). The Devonian sequence includes the Middle Devonian Dushan and Bangzai Formations and the Upper Devonian Rongxian Formation. The Bangzai Formation consists of siltstone and quartz sandstone with lens and lumps of oolitic hematite, while the Dushan Formation is made up of thick-layered fine to coarsely crystalline dolostone, banded dolomitic limestone and thin-bedded claystone. The Rongxian Formation is composed of thick-layered, micritic limestone, clayey limestone, pebble limestone and medium to coarsely crystalline dolostone. The Carboniferous strata are divided into the Lower Carboniferous Dapu and Baizuo Formations, and the Upper Carboniferous Huanglong and Maping Formations, all of which consist chiefly of limestone with minor claystone. The overlying Lower Permian strata include limestone from the Qixia and Maokou Formations, and quartz sandstone and argillaceous sandstone from the Liangshan

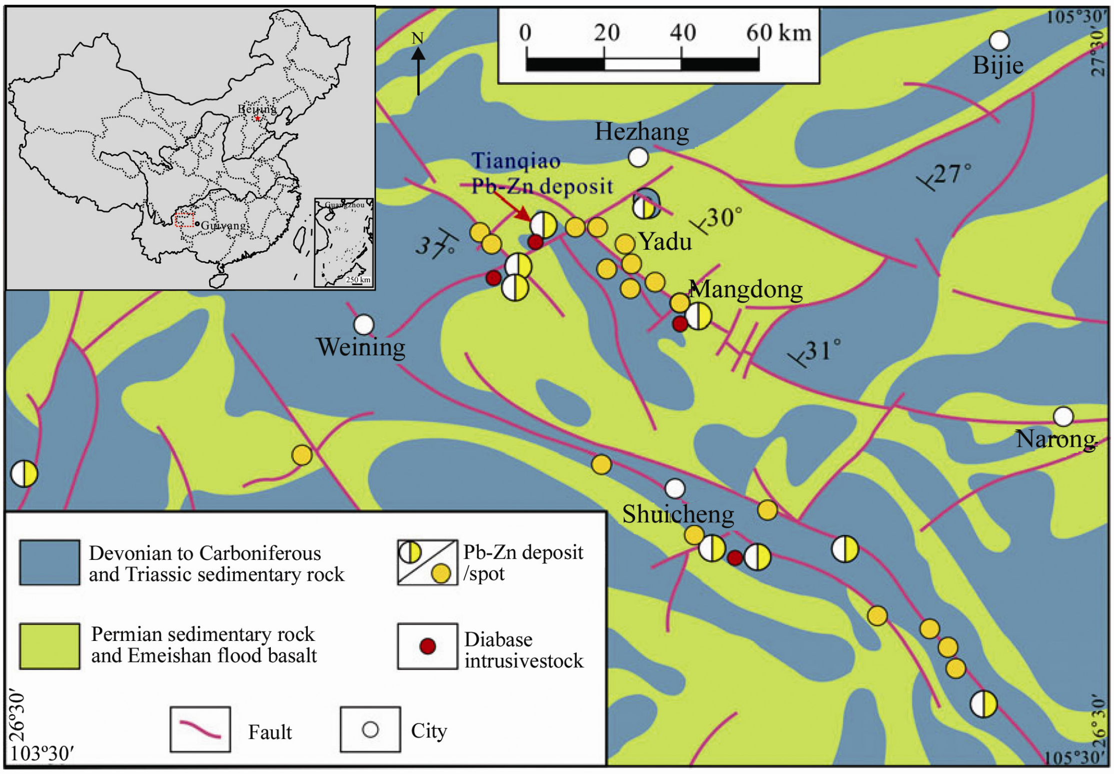

Fig. 1. Geological map of the southeastern SYG province (modified from Zhou et al., 2013a).

Formation. The axial plane of the Tianqiao anticline strikes 45°–60° NW. The Lower Devonian Danlin Formation limestone is located in the core of the Tianqiao anticline, while the limbs are the Middle-Upper Devonian, Carboniferous and Permian carbonates. Being the largest fault in the mining district, F_{37} cuts across the Tianqiao anticline. This fault is 14 km long and is marked by a 1 to 6 m wide shear zone. It strikes 50°–90° NE and dips 50°–70° to NE. Movement along the fault is oblique with 20 to 60 m of vertical displacement and 80 to 240 m of horizontal displacement.

Ore bodies occur in dolostone and dolomitic limestone from the Lower Carboniferous Dapu and Baizuo Formations, which form the NW-trending nose of the plunging anticline, and are distributed along F_{37} fault. Thirty-two ore bodies occur in the limbs from the Tianqiao anticline as the Yingpanshang and Shazidi ore clusters, which are near the axis in the northeastern and southern limbs, respectively (Fig. 2A). Fifteen ore bodies are found from the Yingpanshang cluster, the largest of which is 200 m long, 100 m wide and 1.3 to 1.8 m thick. Ores in this body have an average grade of 1.23 wt% Pb and 5.69 wt% Zn. The Shazidi cluster comprises 17 ore bodies. Two relatively large bodies are 250 m long, 120 m wide and 1.4 to 1.9 m thick, and 320 m long, 220 m wide and 1.7 to 5.2 m thick, respectively. Ore bodies are strata-bound as tabular and lenticular bodies showing sharp boundaries with the wall rocks (Fig. 2B). Ores from these two clusters have Pb and Zn contents significantly variable from 0.04 wt.% to 7.32 wt.% and 0.49 wt.% to 26.7 wt.%, respectively (Jin, 2008).

3 Samples and analytical methods

Ore samples are collected from the main ore bodies in the Tianqiao deposit and are crushed by ore dressing to 40–60 mesh sizes, and then sulfides are handpicked under binocular microscope in the Institute of Geochemistry, Chinese Academy of Sciences. Chemical separation of Rb from Sr and mass spectrometric measurement (Li et al., 2005) are conducted in the Laboratory of Solid Isotope Geochemistry, Institute of Geology and Geophysics, Chinese Academy of Sciences. High-pressure airtight sample fusion is adopted. Spec-Sr exchange resin of special efficiency and HNO_3 are used for the separation and purification of Rb and Sr. In the whole procedure, the background values of Rb and Sr are within the range of 5 to 6 pg (Li et al., 2005). Sr and Rb are loaded on the single W and Ta filaments and the purified TaF_5 is used as the emission agent. Isotopic ratio measurement is carried out on the Isoprobe-T type high-accuracy solid thermal ionization mass spectrometer (Li et al., 2005), and the index rate is adopted to make mass fractionation corrections (the correction parameter $^{88}Sr/^{86}Sr$= 8.37521) for $^{87}Sr/^{86}Sr$ ratios. The Sr isotopic standard NBS 987 is used to monitor the operating status of the instrument. The acquired mean $^{87}Sr/^{86}Sr$ value is 0.710242 ±5 (2σ, *n*=12). A 2% uncertainty is adopted for $^{87}Rb/^{86}Sr$ ratios and 0.005% uncertainty was adopted for Sr isotopic compositions.

4 Analytical results

The Rb-Sr isotopic compositions computed by background and diluents superimposing deducted are listed in Table 1, in which the errors of $^{87}Sr/^{86}Sr$ (2σ) are instrument measurement error. The $^{87}Rb/^{86}Sr$ values of sulfide range from 0.0296 to 1.564, whereas their $^{87}Sr/^{86}Sr$ values are relatively homogeneous, ranging from 0.7119 to 0.7167. Both pyrite and sphalerite have a similar range of $^{87}Sr/^{86}Sr$ values (Table 1), indicating that they are derived from the same source, consistent with the result of sulfur-lead isotopes (Zhou et al., 2013a). Sulfide has low Rb contents ranging from 0.01×10^{-6} to 0.60×10^{-6}, and some of them have Rb contents lower than 0.01×10^{-6}. Sr contents of sulfide range from 0.50×10^{-6} to 2.4×10^{-6} higher than that of Rb (Table 1).

5 Discussion

Studies in the Sichuan-Yunnan-Guizhou Pb-Zn metallogenic province have showed that hydrothermal calcite Sm-Nd ages of the Huize and Maozu Pb-Zn deposits are 222±14 Ma (Li et al., 2007) and 196±13 Ma (Zhou et al., 2013c), respectively, and fluorite Sm-Nd age of the Jinshachang Pb-Zn deposit is 201.1 ±2.9 Ma (Mao et al., 2012) and sulfides Rb-Sr ages of the Paoma, Tianqiao, Jinshachang and Lehong Pb-Zn deposits are 200.1±4.0 Ma (Lin et al., 2010), 191.9± 6.9 Ma (Zhou et al., 2013a), 199.5±4.5 Ma and 200.9 ±2.3 Ma (Mao et al., 2012), respectively. Therefore, we consider that these deposits formed simultaneously and that the main mineralization of the SYG province occurred at ~200 Ma (Zhou et al., 2013a).

Based on the ~200 Ma, the $^{87}Sr/^{86}Sr_{200\ Ma}$ values of sulfide range from 0.7118 to 0.7130, higher than that of the Upper Mantle (0.704±0.002; Faure, 1977) and the Permian Emeishan flood basalts (0.7039 to 0.7078; Huang et al., 2004) indicate that the sulfide is enriched with radioactive genesis Sr isotope, and the ore-forming fluids may be derived from and/or flow through the geological body that is enriched with radioactive genesis Sr isotope. This feature rejects the possibility of the Upper Mantle and Emeishan flood basalts, who individual supplied large number of fluids and metals for ore forming in the SYG province. The $^{87}Sr/^{86}Sr_{200\ Ma}$ values of dolostone rocks from the Lower Carboniferous Baizuo Formation and the Middle Devonian Qujing Formation are 0.7087 to 0.7101 (Hu, 1999; Zhou et al., 2013a) and 0.7101 (Deng et al., 2000), respectively, also lower than that of sulfides. Therefore, this feature also rejects the possibility of the hosting rocks, who individual supplied large number of ore-forming fluids and metals. Basement rocks (Kunyang and Huili Groups) are widely distributed in the SW Yangtze Block, with huge thickness (about 10000 m) in some place (Cong, 1988; Zhang et al., 1988). The $^{87}Sr/^{86}Sr_{200\ Ma}$ values of dolostone and slate samples from the Kunyang Group Yinming Formation are 0.7288 and 0.7249, respectively, and the $^{87}Sr/^{86}Sr_{200\ Ma}$ value of carbonaceous slate from the Hekou-Chahe Formation is 0.7283 (Li and Qin, 1988). The $^{87}Sr/^{86}Sr_{200\ Ma}$ value of sodium volcanic rocks from the Huili Group Hekou Formation is 0.7243 (Cong, 1988), and the $^{87}Sr/^{86}Sr_{200\ Ma}$ value of the Dahongshan Group is 0.7275 (Chen and Ran, 1992). Because the $^{87}Sr/^{86}Sr_{200\ Ma}$ values of sulfide samples from the Tianqiao Pb–Zn deposit (0.7118 to 0.7130) is obviously lower than that of basement rocks (0.7243 to 0.7288), it is difficult to understand that the ore-forming fluids and metals were individual supplied by basement rocks.

Table 1 Sulfide Rb–Sr isotopic compositions of the Tianqiao Pb–Zn deposit

No.	Object	$Rb/10^{-6}$	$Sr/10^{-6}$	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	$(^{87}Sr/^{86}Sr)_i$	2σ	Source
TQ-60	Sphalerite	0.03	2.40	0.0406	0.7126	0.7124	0.0001	Zhou et al., 2013a
TQ-19-1	Pyrite	0.02	2.20	0.0296	0.7125	0.7124	0.0001	
TQ-19-2	Sphalerite	0.01	0.80	0.0324	0.7126	0.7125	0.0001	
TQ-26-0	Sphalerite	0.60	1.10	1.5640	0.7167	0.7123	0.0001	
TQ-26-1	Sphalerite	0.47	0.90	1.0101	0.7152	0.7123	0.0001	
TQ-60	Pyrite	0.01	0.50	0.0625	0.7132	0.7130	0.0002	This paper
TQ-13	Sphalerite	0.01	1.10	0.0330	0.7119	0.7118	0.0001	
TQ-18	Sphalerite	0.02	1.85	0.0755	0.7123	0.7121	0.0001	

Note: $(^{87}Sr/^{86}Sr)_i = {}^{87}Sr/^{86}Sr - {}^{87}Sr/^{87}Rb\ (e^{\lambda t} - 1)$, $\lambda_{Rb} = 1.41 \times 10^{-11}\ t^{-1}$, t = 200 Ma.

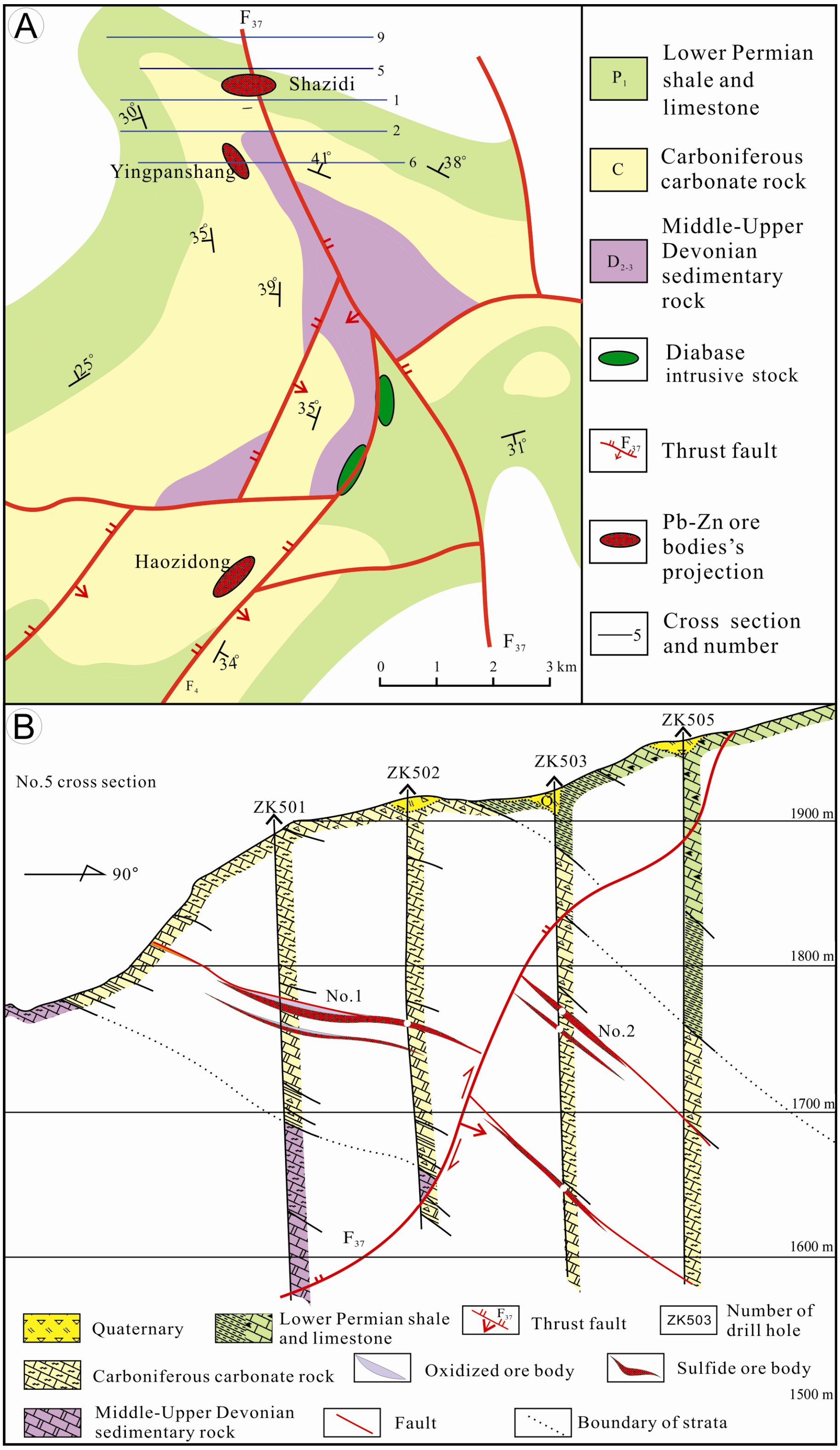

Fig. 2. A. Geological map of the Tianqiao Pb-Zn deposit; B. Geological section of the Tianqiao Pb-Zn deposit (modified after Zhou et al., 2014).

Therefore, it is reasonable that higher $^{87}Sr/^{86}Sr_{200\ Ma}$ components (basement rocks) and lower $^{87}Sr/^{86}Sr_{200\ Ma}$ components (basalts and sedimentary rocks) together supply the ore-forming fluids and metals (Fig. 3). As the metallogenic age (~200 Ma, Mao et al., 2012; Zhou et al., 2013a) of these Pb-Zn deposits is posterior to Emeishan flood basalts (~260 Ma, Zhou et al., 2002), the contribution of basalts is difficult to be estimated, but we couldn't get rid of the ore-forming fluids leaching part of metals from it.

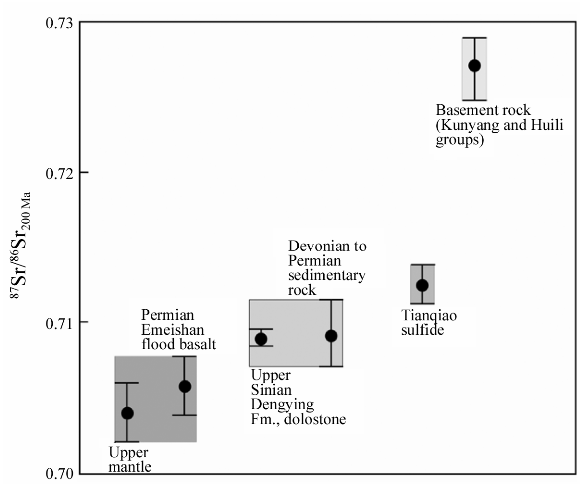

Fig. 3. $^{87}Sr/^{86}Sr_{200\ Ma}$ ratios vs. sulfides from the Tianqiao Pb-Zn deposit, the Sinian to Permian sedimentary rocks, the Proterozoic basement rocks, the Permian Emeishan basalts and the Upper Mantle (modified from Zhou et al., 2013a).

6 Conclusions

The $^{87}Sr/^{86}Sr_{200\ Ma}$ values of sulfides from the Tianqiao deposit range from 0.7118 to 0.7130 and are higher than those of hosting sedimentary rocks (0.7073 to 0.7101) and Emeishan basalts (0.7078 to 0.7039), but lower than those of underlying basement rocks (0.7243 to 0.7288), implying a mixed strontium source between the older basement rocks and the younger cover sequences.

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