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Ore genesis of the Tianbaoshan carbonate-hosted Pb–Zn deposit, Southwest China: geologic and isotopic (C–H–O–S–Pb) evidence

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Ore genesis of the Tianbaoshan carbonate-hosted Pb–Zn deposit, Southwest China: geologic and isotopic (C–H–O–S–Pb) evidence

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The Tianbaoshan Pb–Zn deposit, part of the Sichuan–Yunnan–Guizhou (SYG) Pb–Zn metallogenic province, is located in the western Yangtze Block and contains 2.6 million tonnes of 10–15 wt.% Pb + Zn metals. Ore bodies occur as vein or tubular types and are hosted in Sinian (late Proterozoic) carbonate rocks and are structurally controlled by the SN-trending Anninghe tectonic belt and NW-trending concealed fractures. The deposits are simple in mineralogy, with sphalerite, galena, pyrite, chalcopyrite, arsenopyrite, freibergite, and pyrargyrite as ore minerals and dolomite, calcite, and quartz as gangue minerals. These phases occur as massive, brecciated, veinlet, and dissemination in dolostone of the upper Sinian Dengying Formation. Hydrogen and oxygen isotope compositions of hydrothermal fluids range from –47.6 to –51.2‰ and –1.7 to +3.7‰, respectively. These data suggest that H_2O in hydrothermal fluids had a mixed origin of metamorphic and meteoric waters. Carbon and oxygen isotope compositions range from –6.5 to –4.9‰ and +19.3 to +20.2‰, respectively. These compositions plot in the field between mantle and marine carbonate rocks with a negative correlation, suggesting that CO_2 in the ore-forming fluids had multiple sources, including the Permian Emeishan flood basalts, Sinian-to-Permian marine carbonate rocks, and organic matters in Cambrian-to-Permian sedimentary rocks. Sulphur isotope compositions range from –0.4 to +9.6‰, significantly lower than Cambrian-to-Permian seawater sulphate (+15 to +35‰) and sulphate (+15 to +28‰) from evaporates in Cambrian-to-Permian strata, implicating that the S was derived from host-strata evaporates by thermal–chemical sulphate reduction. $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios range from 18.110 to 18.596, 15.514 to 15.878, and 38.032 to 39.221, respectively, which plot in field of the upper crust Pb evolution curve, unlike those of Proterozoic basement rocks, Sinian dolostone, Devonian-to-Permian carbonate rocks, and the Permian Emeishan flood basalts, implying complex derivation of Pb metal in the ore-forming fluids. Geological and isotopic studies of the Tianbaoshan Pb–Zn deposit reveal that constituents in the hydrothermal fluids were derived from multiple sources and that fluid mixing was a possible metallogenic mechanism. The studied deposit is not distal magmatic–hydrothermal, sedimentary exhalative (SEDEX), or Mississippi Valley (MVT) types, rather, it represents a unique ore deposit type, named in this article the SYG type.

Keywords: C–H–O–S–Pb isotopes; sources of chemical constituents in hydrothermal fluids; aqueous fluid mixing; Tianbaoshan carbonate-hosted Pb–Zn deposit; Southwest China

Introduction

Over four hundred Pb–Zn–Ag–Ge deposits hosted in late Sinian (Dengying Formation) to early Permian carbonate rocks have been reported in the Sichuan–Yunnan–Guizhou (SYG) Pb–Zn metallogenic province, western margin of the Yangtze Block (Figure 1A), and they contain more than 20 million tonnes (Mt) of lead–zinc metal reserves at grades of 10–35 wt.% Pb and Zn (e.g. Zheng and Wang 1991; Cromie *et al.* 1996; Liu and Lin 1999; Deng *et al.* 2000; Zhou *et al.* 2001, 2013b, 2013c; Han *et al.* 2007a). The Tianbaoshan carbonate-hosted Pb–Zn deposit is located in the western part of the SYG province (Figure 1B), contains 2.6 Mt lead–zinc metals at 10.4 wt.% Zn, 1.4 wt.% Pb, and 93.6 g/t Ag (Zheng and Wang 1991;

Cromie *et al.* 1996; Wang *et al.* 2000, 2010). A close spatial association with Permian Emeishan flood basalts led Xie (1963) to classify it as a distal magmatic–hydrothermal deposit. However, Tu (1984) interpreted it as strata-bound deposit. On the other hand, it has been reinterpreted to be Mississippi Valley type (MVT) (e.g. Cromie *et al.* 1996; Wang *et al.* 2000; Wang *et al.* 2003, 2010). Despite many investigations, the ore genesis of the Tianbaoshan deposit is still unclear.

C–H–O–S–Pb isotopes are powerful tools for determining sources of chemical compositions in ore-forming fluids (e.g. Zheng and Wang 1991; Huston *et al.* 1995; Ohmoto and Goldhaber 1997; Zhou *et al.* 2001, 2010, 2013c; Wilkinson *et al.* 2005; Han *et al.* 2007a; Li *et al.*

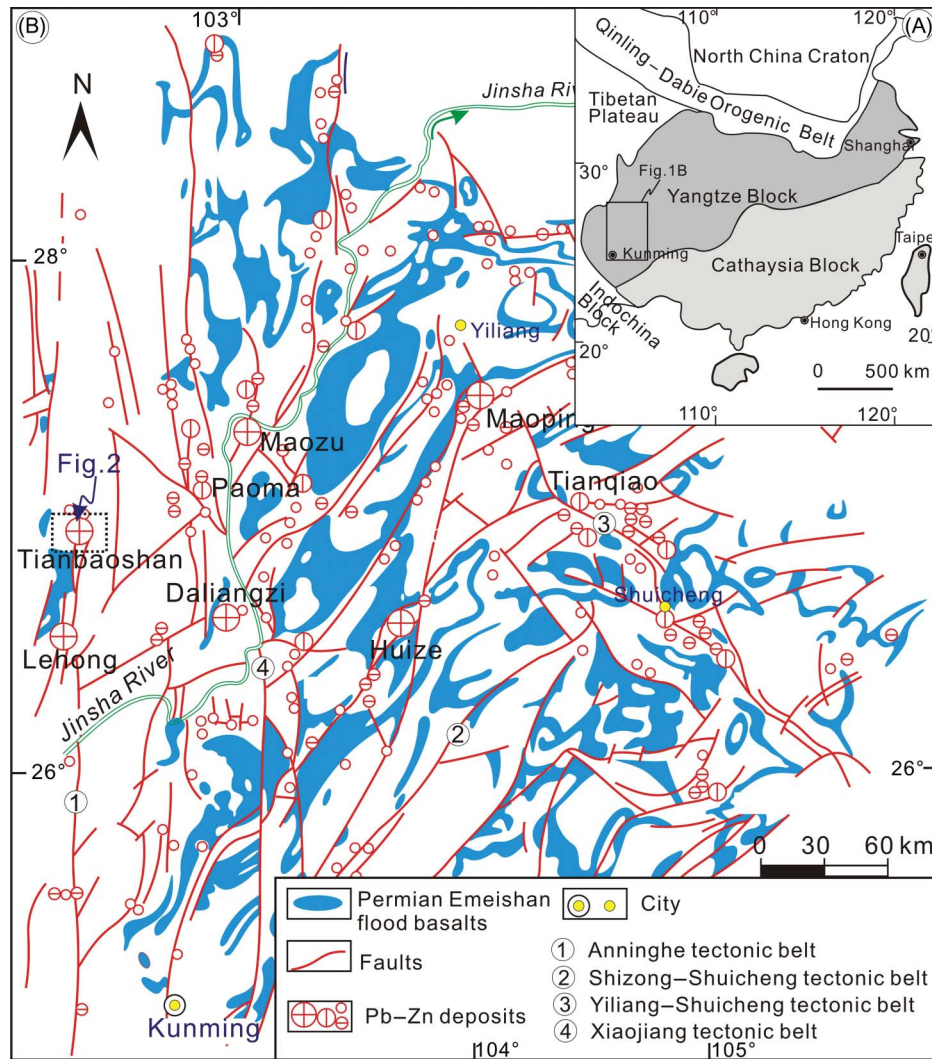*Corresponding author. Email: zhoujiaxi@vip.gyig.ac.cn

Figure 1.   (A) Regional geological setting. (B) Sketch geological map of Sichuan–Yunnan–Guizhou (SYG) Pb–Zn metallogenic province.

2007; Yavuz *et al.* 2011; Dou and Zhou 2013). Multiple isotopic studies of the Tianbaoshan Pb–Zn deposit are not available, but may provide important insights into the ore genesis. In this article, we describe the geology and report new C–H–O–S–Pb isotopes, together with previously published results, and we discuss the metallogenic mechanism of the Tianbaoshan Pb–Zn deposit and implications of our study for the giant Pb–Zn accumulation in the SYG province.

Geological setting

The crystalline basement of the Yangtze Block consists of late Archaean and early Proterozoic metamorphic complexes (Zheng and Wang 1991; Zhou *et al.* 2001). The ca. 1.7 Ga Dongchuan and ca. 1.1 Ga Kunyang groups, and their equivalents represent the folded basement in the western Yangtze Block (Sun *et al.* 2009; Zhao *et al.* 2010),

which were overlain unconformably by Palaeozoic to lower Mesozoic strata of shallow marine origin (Yan *et al.* 2003) and Jurassic to Cenozoic strata of continental facies (Liu and Lin 1999). A significant feature in this region is the mantle plume-derived ca. 260 Ma Emeishan large igneous Province covering an area of about 500,000 km^2, which is dominantly composed of volcanic rocks known as the Emeishan flood basalts (Zhou *et al.* 2002).

About 408 Pb–Zn deposits have been reported in the western Yangtze Block, which distribute in a large triangular area of 170,000 km^2 in northeast Yunnan, northwest Guizhou, and southwest Sichuan provinces (Figure 1B). They are characterized by irregular ore bodies with simple mineralogy, weak wall rock alteration, and high grading of Pb and Zn metals, usually associated with trace Ag, Ge, Cd, Ga, and In and hosted in late Sinian to early Permian dolomitic limestone or dolostone (e.g. Zheng and Wang 1991; Cromie *et al.* 1996; Liu and Lin 1999; Wang

et al. 2000, 2003, 2010; Zhou *et al.* 2001, 2011, 2013a, 2013b, 2013c; Han *et al.* 2007a, 2007b), which are all below the Emeishan flood basalts (e.g. Liu and Lin 1999; Huang *et al.* 2010). In the northwestern SYG province, the cover sequences include Sinian to Palaeozoic sedimentary rocks, Permian Emeishan flood basalts, and Triassic to Jurassic sedimentary rocks (Zheng and Wang 1991; Wang *et al.* 2000). The dolostone of the upper Sinian Dengying Formation is the most important hosted rocks in this region (Zheng and Wang 1991; Cromie *et al.* 1996). The Cambrian strata are characterized by clastic rocks rich in organic matter (black shale), which are the important contributor of organic matter involved in Pb–Zn mineralization (Wang *et al.* 2003; Wu *et al.* 2013). SN-, NW-, and NE-striking structures are well developed and control the Pb–Zn deposits in this region.

Geology of the Tianbaoshan deposit

The Tianbaoshan Pb–Zn deposit is located 50 km north of Huili city, hosted in Sinian carbonate rocks and structurally controlled by the NS-trending Anninghe tectonic belt and its branch structures (Figure 1B). In the Tianbaoshan ore field, the Sinian stratum is the upper Sinian Dengying Formation, and chiefly consists of dolostone. The overlying middle Cambrian Xiwangmiao Formation consists of clastic rocks rich in black shale and the Upper Triassic Baiguowan Formation is composed of continental sand shale. Faults and folds are intensively developed in the ore district. The main faults are the branch faults (F_1) of the Anninghe lithosphere fracture and the NW-trending concealed tensile–shear brecciated fractures (F_2) and other secondary faults (Figure 2). The main folds are the Tianbaoshan syncline and its secondary anticlines

(Figure 2). Zhang *et al.* (2006) studied the metallogenic tectonic stress fields in the Tianbaoshan ore field and divided them into the late Indosinian and Yanshanian groups. The maximum compressive stress direction of the former is 290° or 110° and the latter is 20–30° or 200–210°. The late Indosinian NW-trending compressive stress fields are related to the Yangtze Block colliding with adjacent blocks associated with the closure of the Tethys Ocean (Zhang *et al.* 2006; Zhou *et al.* 2013c). In the ore field, diabase dikes occur in the NS- and NW-trending faults and usually cut the ore bodies, showing chilled borders with thicknesses of 20–30 m.

Major ore bodies occur in dolostone of Dengying Formation and are structurally controlled by the NW-trending concealed fractures (Figures 2 and 3). Underground mining and exploratory drilling provide excellent access to two ore sections (Tianbao and Xinshan) and three ore bodies. The number one ore body of the Tianbao section is the largest, 400 m in depth, 285 m in length, and 2.1 to 50 m in width. Ores in this body contain 1.8 Mt Pb and Zn metals at grades of 1.28 to 2.5 wt.% Pb, 7.76 to 10.1 wt.% Zn, and 96.3 g/t Ag. The mean ratio of $Zn/(Zn + Pb)$ is 0.87 (Wang *et al.* 2000). Ores from the Tianbaoshan deposit contain small amounts of Ge, Ga, Cd, and Ag (Fu 2004). These trace metals are thought to be hosted in sphalerite and galena (Zhou *et al.* 2011). Ore bodies are strata-bound as tabular, lenticular and pipe-like with sharp boundaries against the host rocks (Figure 3).

Primary ores are massive, disseminated, or banded and are composed of sphalerite, galena, pyrite chalcopyrite, arsenopyrite, freibergite, and pyrargyrite, with calcite, dolomite, and quartz as gangue minerals (Wang *et al.* 2000). Ores from the Tianbaoshan deposit have experienced diagenetic, hydrothermal, and oxidized periods.
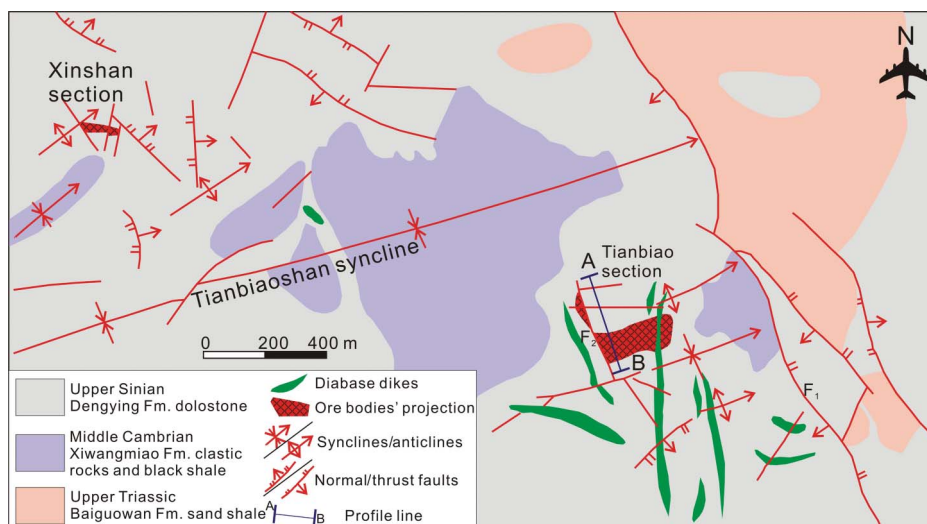

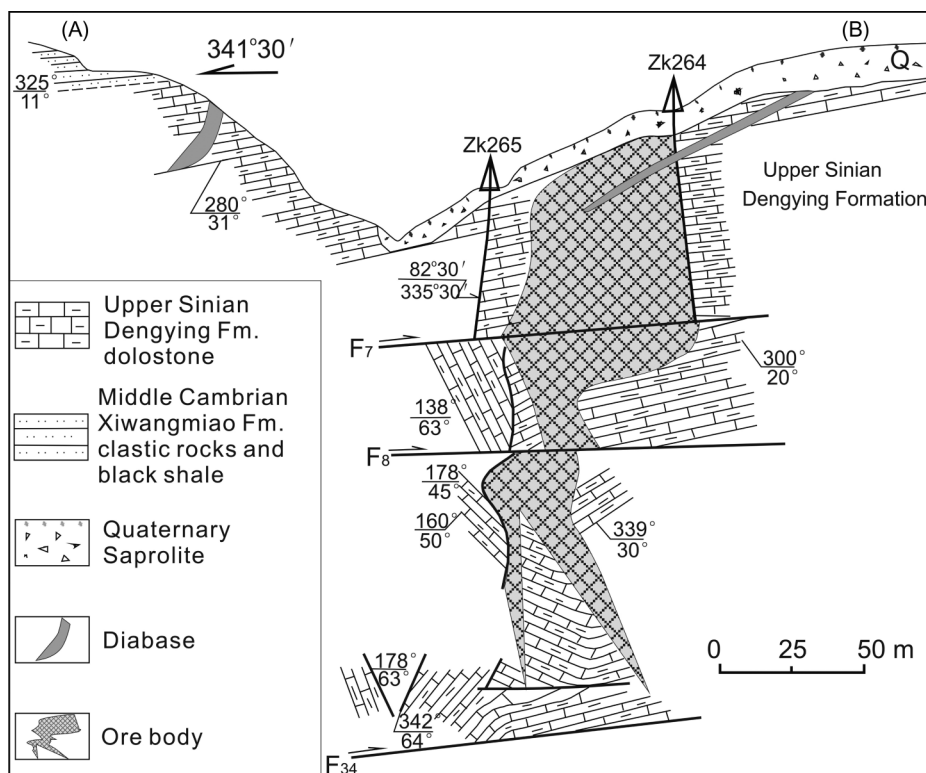Figure 2.   Sketch geological map of the Tianbaoshan Pb–Zn deposit.

Figure 3. A–B geological profile of the Tianbaoshan Pb–Zn deposit.

The hydrothermal period is composed of sulphide–quartz, sulphide–carbonate, and carbonates stages. There are two principal mineral assemblages formed in the sulphide–quartz or carbonate stage. In the pyrite–chalcopyrite–arsenopyrite–quartz assemblage, pyrite is fine-grained (0.1–0.5 mm) with xenomorphic granular textures. In the sphalerite–galena–pyrite–calcite assemblage, sphalerite is fine to coarse-grained (0.06–11 mm) with xenomorphic to automorphic granular textures. It occurs in massive and banded forms or in disseminated aggregates and is brown to yellow in colour. Galena has a granular and corrugated texture. Wall rock alterations include dolomitization, calcitization, silicification, and ferritization, of which the dolomitization, calcitization, and silicification are closely associated with Pb–Zn mineralization.

Analytical methods

Hydrogen and oxygen isotope compositions were obtained using a Finnigan MAT–253 mass spectrometer at the Beijing Institute of Uranium Geology. Results are reported to Standard Mean Ocean Water (SMOW) with an analytical precision of ±1‰ for hydrogen isotopes and ±2‰ for oxygen isotopes. $\delta^{18}O$ values of water in fluids inclusions from quartz were calculated using the quartz–water fractionation equation described by Clayton *et al.* (1972).

Carbon and oxygen isotope compositions were obtained using a Finnigan MAT–253 mass spectrometer at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. Calcite reacts with pure phosphoric acid to produce CO_2. The analytical precisions (2σ) are ±0.2‰ for carbon isotope and ±2‰ for oxygen isotope. $\delta^{13}C$ and $\delta^{18}O$ values 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).

Sulphur isotope analyses were carried out using a Finnigan MAT-251 gas mass spectrometer at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. GBW 04414 and 04415 Ag_2S were used as the external standards and the analytical precision was ±0.1‰. $\delta^{34}S$ values are reported to Canyon Diablo Troilite (CDT).

Lead isotope analyses were carried out using a GV Isoprobe-T thermal ionization mass spectrometer at the Beijing Institute of Uranium Geology. The analytical procedure involved dissolution of samples using HF and $HClO_4$ in crucibles, followed by basic anion exchange resin to purify Pb. Analytical results for the standard NBS 981 are $^{208}Pb/^{204}Pb = 36.611 \pm 0.004$ (2σ), $^{207}Pb/^{204}Pb = 15.457 \pm 0.002$ (2σ) and $^{206}Pb/^{204}Pb = 16.937 \pm 0.002$ (2σ), in agreement with the reference value (Belshaw *et al.* 1998).

Analytical results

Hydrogen and oxygen isotope compositions

H–O isotope compositions of fluid inclusions in sphalerite and quartz from the Tianbaoshan Pb–Zn deposit are listed in Table 1 and shown in Figure 4. The mean mineralization temperature is 200°C based on fluid inclusion microthermometry by Wang *et al.* (2000). $\delta^{18}O_{H_2O} = \delta^{18}O_{quartz} - 3.38 \times 10^6/T^2 + 2.90$ (Clayton *et al.* 1972). Fluid inclusion in sphalerite has a $\delta D_{H_2O\text{-}SMOW}$ value of –47.6‰ (Wang *et al.* 2000), higher than that of fluid inclusions in quartz (–51.2 to –47.9‰) and a $\delta^{18}O_{H_2O\text{-}SMOW}$ value of –1.7‰ (Wang *et al.* 2000), lower than that of fluid inclusions in quartz (–0.5 to +3.7‰).

Carbon and oxygen isotope compositions

C–O isotope compositions of hydrothermal calcite, together with previously published data (Wang *et al.* 2000), are listed in Table 2 and shown in Figure 5. Hydrothermal calcites have $\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$ values ranging from

–6.5 to –4.9‰ and +19.3 to +20.2‰, respectively. These carbon isotope data are similar to that of CO_2 in sphalerite fluid inclusions, but lower than that of calcite in wall rocks (Wang *et al.* 2000).

Sulphur isotope compositions

S isotope compositions of sulphides, together with previously published data (Fu 2004) are listed in Table 3 and shown in Figure 6. Sulphides have $\delta^{34}S_{CDT}$ values ranging from –0.4 to +9.6‰. Pyrite, sphalerite, and galena separates have slightly different $\delta^{34}S$ values of +5.3‰, +3.3 to +9.6‰, and –0.4 to +4.1‰, respectively.

Lead isotopes compositions

Pb isotope compositions of sulphides, together with previously published data (Wang *et al.* 2000; Fu 2004), are listed in Table 4 and shown in Figure 7. Sulphides have homogeneous and low radiogenic Pb isotope compositions with

Table 1. Hydrogen and oxygen isotope compositions of the Tianbaoshan Pb–Zn deposit, Southwest China.

No.	Object	$\delta D_{H_2O\text{-}SMOW}/‰$	$\delta^{18}O_{H_2O\text{-}SMOW}/‰$	Sources
	Fluid inclusions in sphalerite	−47.6	−1.7	Wang *et al.* (2000)
TBS06	Fluid inclusions in quartz	−47.9	−0.5	
TBS11	Fluid inclusions in quartz	−48.4	+0.1	This article
TBS17-7	Fluid inclusions in quartz	−51.2	+3.7	

Notes: The average temperature of hydrothermal fluids is 200°C based on fluid inclusion microthermometry by Wang *et al.* (2000). Isotope fractionation equation for quartz and fluids: $\delta^{18}O_{H_2O} = \delta^{18}O_{quartz} - 3.38 \times 10^6/T^2 + 2.90$ (Clayton *et al.* 1972).
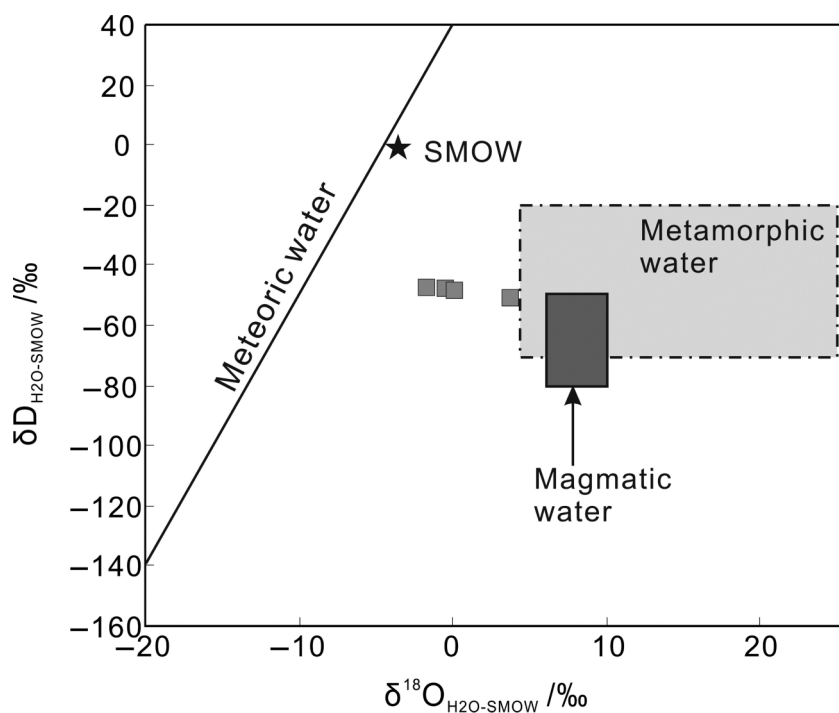

Figure 4.   Plot of $\delta D_{H_2O\text{-}SMOW}$ *versus* $\delta^{18}O_{H_2O\text{-}SMOW}$ for the Tianbaoshan Pb–Zn deposit.

Table 2. Carbon and oxygen isotope compositions of the Tianbaoshan Pb–Zn deposit, Southwest China.

No.	Object	$\delta^{13}C_{PDB}$/‰	$\delta^{18}O_{SMOW}$/‰	Sources
	CO_2 in sphalerite fluid inclusions	−6.1		Wang *et al.* (2000)
	Calcite in wall rocks	+0.02		
TBS03	Hydrothermal calcite	−6.5	+20.2	
TBS07	Hydrothermal calcite	−5.8	+19.6	This article
TBS09	Hydrothermal calcite	−4.9	+19.3	

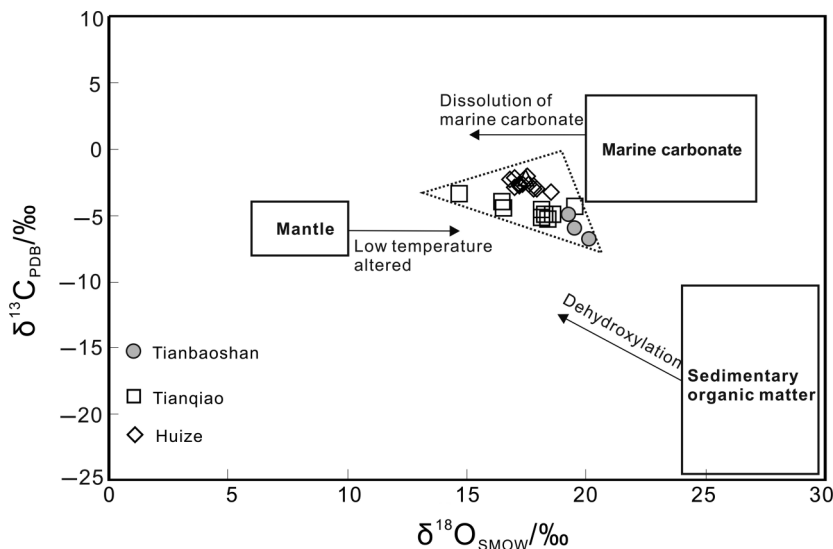Note: $\delta^{18}O_{SMOW} = 1.03086 \times \delta^{18}O_{PDB} + 30.86$ (Friedman and O'Neil 1977).

Figure 5. Plot of $\delta^{13}C_{PDB}$ *versus* $\delta^{18}O_{SMOW}$ for the Tianbaoshan Pb–Zn deposit. $\delta^{13}C_{PDB}$ *versus* $\delta^{18}O_{SMOW}$ values of the Huize and Tianqiao deposits are taken from Huang *et al.* (2010) and Zhou *et al.* (2013c), respectively.

Table 3. Sulphur isotope compositions of the Tianbaoshan Pb–Zn deposit, Southwest China.

No.	Object	$\delta^{34}S_{CDT}$/‰	Sources	No.	Object	$\delta^{34}S_{CDT}$/‰	Sources
TB101	Py	5.3	Fu (2004)	TBS06-2	B Sp	4.5	This article
TB612-01	LY Sp	3.3		TBS12-1	B Sp	5.1	
TB612-02-@1	LY Sp	3.7		TBS09-1	Gl	1.2	
TBP1-13	LY Sp	4.0		TBS11-2	Gl	2.2	
TBP2-09	B Sp	4.6		TBS17-7-@2	Gl	4.1	
TBP1-07	B Sp	5.7		TBS11-1	Gl	1.6	
TBP1-09	B Sp	5.0		TB612-02-@2	Gl	0.2	
TBP1-10-@1	B Sp	4.8		TBP1-10-@2	Gl	1.4	Fu (2004)
TBP1-11-@1	B Sp	4.1		TBP1-11-@2	Gl	−0.4	
TBP1-11-1-@1	B Sp	4.9		TBP1-11-1-@2	Gl	−0.1	
TBP2-06-@1	B Sp	4.3		TBP1-12	Gl	0.7	
TBS17-7-@1	B Sp	9.6	This article	TBP2-04	Gl	0.0	
TBS07-1	B Sp	4.5		TBP2-06-@2	Gl	0.1	
TBS03-1	LY Sp	4.3		TB105	Gl	1.1	

Notes: Py, pyrite; LY Sp, light yellow sphalerite; B Sp, brown sphalerite; Gl, galena. Samples TB612-02-@1 and TB612-02-@2 are taken from sample TB612-02,; TBP1-10-@1 and TBP1-10-@2 are taken from sample TBP1-10; TBP1-11-@1 and TBP1-11-@2 are taken from sample TBP1-11; TBP1-11-1-@1 and TBP1-11-1-@2 are taken from sample TBP1-11-1; TBP2-06-@1 and TBP2-06-@2 are taken from sample TBP2-06; and TBS17-7-@1 and TBS17-7-@2 are taken from sample TBS17-7.
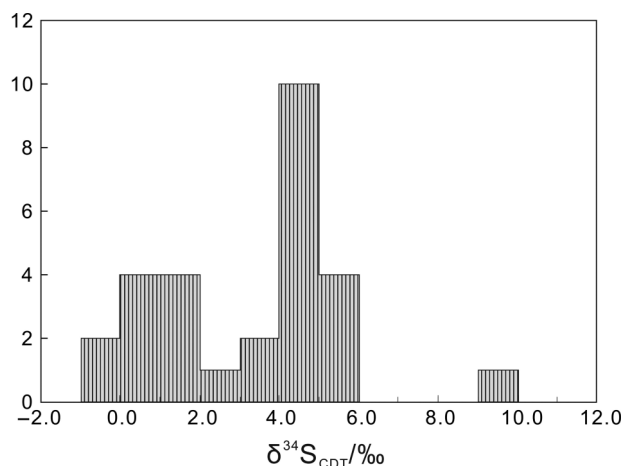
Figure 6. Sulphur isotope composition histogram of the Tianbaoshan Pb–Zn deposit.

$^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios ranging from 18.110 to 18.596, 15.514 to 15.878, and 38.032 to 39.221, respectively

Discussion

Possible origins of chemical constituents in hydrothermal fluids

Water

Previous studies have shown that the water in the ore-forming solutions of the Tianbaoshan deposit was likely to be meteoric in origin (Wang *et al.* 2000). In this study, we find that $\delta D_{H_2O\text{-SMOW}}$ and $\delta^{18}O_{H_2O\text{-SMOW}}$ values of fluid inclusions in quartz are slightly different from that of fluid inclusions in sphalerite, that is, the $\delta D_{H_2O\text{-SMOW}}$ value of the latter is higher than the former, whereas the $\delta^{18}O_{H_2O\text{-SMOW}}$ value of the latter is lower than the former

Table 4. Lead isotope compositions of the Tianbaoshan Pb–Zn deposit, Southwest China.

No.	Object	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	Sources
TBP1-07	B SP	18.365	15.646	38.480	Fu (2004)
TBP1-09	B SP	18.419	15.657	38.568	
TBP1-10-@1	B SP	18.373	15.657	38.549	
TBP1-11-@1	B SP	18.390	15.675	38.603	
TBP1-11-1-@1	B SP	18.364	15.628	38.463	
TBP1-13	LY Sp	18.405	15.738	38.769	
TB612-01	B SP	18.386	15.673	38.578	
TB612-02-@1	B SP	18.458	15.729	38.781	
TB101	Py	18.406	15.677	38.636	
TBP1-10-@2	Gl	18.389	15.740	38.754	
TBP1-11-@2	Gl	18.522	15.878	39.221	
TBP1-11-1-@2	Gl	18.360	15.705	38.641	
TBP2-06	Gl	18.309	15.650	38.465	
TB105	Gl	18.394	15.808	38.947	
TB612-02-@2	Gl	18.434	15.758	38.849	
A-006	Gl	18.389	15.690	38.478	Wang *et al.* (2000)
G	Gl	18.359	15.682	38.493	
P63	Gl	18.288	15.604	38.259	
P831	Gl	18.214	15.576	38.090	
P832	Gl	18.517	15.683	38.598	
P53	Gl	18.402	15.780	38.800	
P47	Gl	18.402	15.678	38.598	
PT1	Gl	18.596	15.803	39.050	
PT2	Gl	18.483	15.691	38.785	
T4	Gl	18.110	15.514	38.032	
TBS11-2	Gl	18.247	15.698	38.531	This article
TBS11-1	Gl	18.222	15.655	38.404	
TBS17-7-@2	Gl	18.416	15.740	38.793	
TBS09-1	Gl	18.336	15.706	38.619	
TBS02-2	B SP	18.349	15.679	38.548	
TBS06-2	B SP	18.369	15.713	38.659	
TBS12-1	B SP	18.407	15.709	38.731	
TBS17-7@1	B SP	18.326	15.673	38.568	

Notes: Py, pyrite; LY Sp, light yellow sphalerite; B Sp, brown sphalerite; Gl, galena. Samples TBP1-10-@1 and TBP1-10-@2 are taken from sample TBP1-10; TBP1-11-@1 and TBP1-11-@2 are taken from sample TBP1-11; TBP1-11-1-@1 and TBP1-11-1-@2 are taken from sample TBP1-11-1; TB612-02-@1 and TB612-02-@2 are taken from sample TB612-02; and TBS17-7-@1 and TBS17-7- @2 are taken from sample TBS17-7.
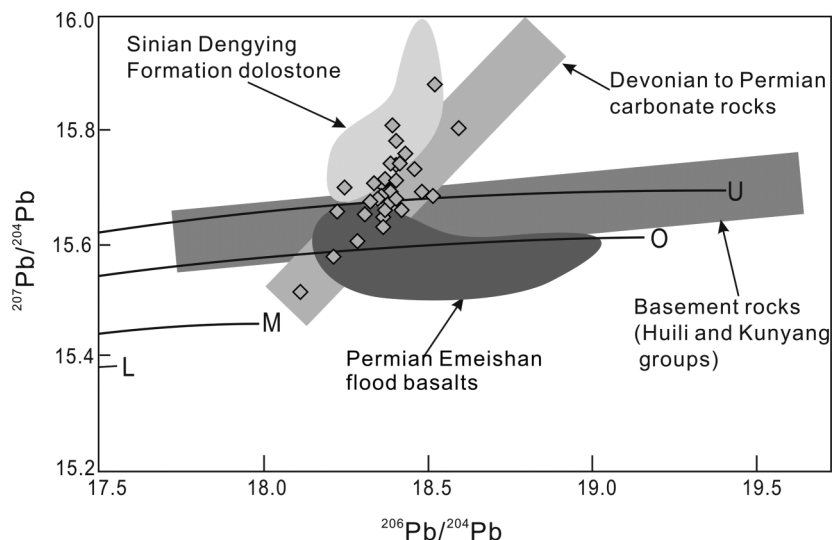
Figure 7. Plot of $^{207}Pb/^{204}Pb$ *versus* $^{206}Pb/^{204}Pb$ for the Tianbaoshan Pb–Zn deposit. Trends for the upper crust (U), orogenic belt (O), mantle (M), and lower crust (L) are taken from Zartman and Doe (1981). Sources of other data are taken from Zheng and Wang (1991), Wang *et al.* (2000), Zhou *et al.* (2001, 2013b, 2013c), Han *et al.* (2007a), and Yan *et al.* (2007).

(Table 1). In addition, all the H–O isotopic data are plotted in field between meteoric and metamorphic waters in the $\delta D_{H_2O\text{-SMOW}}$ *versus* $\delta^{18}O_{H_2O\text{-SMOW}}$ diagram (Figure 4), but near to the metamorphic water. This implies that H_2O in hydrothermal fluids should be originated from a mixed source of meteoric and metamorphic waters.

Carbon

The $\delta^{13}C_{PDB}$ values of calcite in wall rocks and CO_2 in fluid inclusion from sphalerite show that the carbon was derived from marine carbonate and organic matter (Wang *et al.* 2000). Hydrothermal calcite separates are plotted in the field among mantle, marine carbonate rocks, and sedimentary organic matter with a weakly negative correlation in the $\delta^{13}C_{PDB}$ *versus* $\delta^{18}O_{SMOW}$ diagram (Figure 5), similar to the Tianqiao (Zhou *et al.* 2013c) and Huize typical SYG-type deposits (Han *et al.* 2007a; Huang *et al.* 2010). If CO_2 in the hydrothermal fluids was derived from mantle, the precipitated calcite would show constant $\delta^{13}C$ values with increased $\delta^{18}O$ values. Similarly, if CO_2 originated from marine carbonate, the precipitated calcite would display constant $\delta^{13}C_{PDB}$ values with depressed $\delta^{18}O_{SMOW}$ values. The negative correlation between $\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$ values indicates that CO_2 in the hydrothermal fluids was derived neither from mantle and/or marine carbonate, nor from sedimentary organic matters. Because organic matter acts as a reducing agent in the thermal chemical sulphate reduction process (e.g. Ottaway *et al.* 1994; Worden *et al.* 1995), it is also an important contributor of CO_2. Therefore, a mixture of ternary members (^{18}O-depleted Permian Emeishan flood basalts, ^{18}O-enriched to Sinian to

Permian carbonate rocks, and ^{13}C-depleted organic matter in Cambrian strata) is possible origin of CO_2 (Zhou *et al.* 2013b, 2013c).

Sulphur

Geological studies indicate that primary ores from the Tianbaoshan Pb–Zn deposit are chiefly composed of sphalerite, galena, and pyrite, but lack sulphates. This suggests that sulphur isotope compositions of sulphides can basically represent $\delta^{34}S_{\sum S\text{-fluids}}$ values (Ohmoto 1972). Sulphides from the Tianbaoshan deposit have $\delta^{34}S$ values ranging from –0.4 to +9.6‰ (Table 3; Figure 6) and based on the $\delta^{34}S$ values of sphalerite and coexisting galena, the calculated $\delta^{34}S_{\sum S\text{-fluids}}$ value is 4.7‰ (Wang *et al.* 2000); all of them are different from the $\delta^{34}S$ value of mantle-derived sulphur (–3 to +3‰: Chaussidon *et al.* 1989). Sulphates from evaporites in Cambrian-to-Permian strata in the SYG province have $\delta^{34}S$ values ranging from +15 to +28‰ (Liu and Lin 1999; Han *et al.* 2007a), similar to Cambrian-to-Permian seawater sulphates (+20 to +35‰: Claypool *et al.* 1980; Seal 2006). As $\Delta^{34}S_{sulphate–sulphide}$ could be up to +15‰ in the sulphate reduction process in a MVT Zn-Pb hydrothermal system (Ohmoto *et al.* 1990; Machel *et al.* 1995; Ohmoto and Goldhaber 1997), so the sulphur isotope signature of the Tianbaoshan deposit indicates that reduced sulphur in the ores was derived from evaporites in the host strata. Some studies have confirmed that the reaction $SO_4^{2-} + CH_4 = H_2S + CO_3^{2-} + H_2O$ can take place at 140°C (e.g. Worden *et al.* 1995), indicating that the thermal–chemical sulphate reduction could be a way that transferred SO_4^{2-} from sulphate into H_2S in hydrothermal solutions.

Metal

Contents of U and Th for the sulphides are too low to influence their Pb isotope 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). Sulphides from the Tianbaoshan deposit have homogeneous and low radiogenic Pb isotopes (Table 4), unlike age corrected Permian Emeishan flood basalts (e.g. Li *et al.* 2007; Yan *et al.* 2007), Sinian-to-Permian carbonate rocks (e.g. Zheng and Wang 1991; Zhou *et al.* 2001, 2013c; Han *et al.* 2007a), and Proterozoic basement rocks (e.g. Zhou *et al.* 2013c). In the plot of $^{206}Pb/^{204}Pb$ *versus* $^{207}Pb/^{204}Pb$ (Figure 7), most samples from the Tianbaoshan deposit fall close to the upper crust Pb evolution curve of Zartman and Doe (1981) and overlap with the fields of the basement rocks, dolostone, carbonate rocks, and flood basalts. This implies complex derivation of Pb metal in hydrothermal fluids.

Possible ore genesis

Previous studies have yielded a hydrothermal calcite Sm–Nd age (222 ± 14 Ma) of the Huize Pb–Zn deposit (Li *et al.* 2007) and sulphide Rb–Sr ages of the Paoma (200.1 ± 4.0 Ma: Lin *et al.* 2010) and Tianqiao Pb–Zn deposits (191.9 ± 6.9 Ma: Zhou *et al.* 2013c), so ca. 200 Ma is considered to be the main time of Pb–Zn mineralization in the SYG province (Zhou *et al.* 2013c), which is consistent with the results of the metallogenic tectonic stress field studies in the Tianbaoshan ore field (Zhang *et al.* 2006). Pb–Zn deposits in the SYG province are much younger than Permian Emeishan flood basalts (~260 Ma: Zhou *et al.* 2002) and are not thought to be related to the Emeishan magmatism. Therefore, the ore genesis of the Tianbaoshan deposit should not belong to a distal magmatic–hydrothermal- or sedimentary exhalative (SEDEX)-type deposit. Because ore bodies are hosted in carbonate rocks, it is also thought to be a typical MVT (Wang *et al.* 2000, 2003, 2010). However, the Tianbaoshan Pb–Zn deposit was sulphide precipitation resulting from Ca^{2+}–Mg^{2+}–Cl^-–HCO_3^--enriched hydrothermal fluids at moderate temperatures (150–250°C) and low salinities (lower than 4.9 wt.% NaCl) (Wang *et al.* 2000), similar to the Daliangzi (Zheng and Wang 1991), Huize (Zhou *et al.* 2001; Huang *et al.* 2003, 2010; Han *et al.* 2004, 2007a; Li *et al.* 2007), and Tianqiao (Zhou *et al.* 2010, 2011, 2013c) carbonate-hosted Pb–Zn deposits in the SYG province. The salinity and temperature data are slightly different from the intrabasinal brines related to MVT Pb–Zn deposits that have high salinity (usually >10 wt.% NaCl) and low temperature (usually <150°C). In addition, the Tianbaoshan deposit has homogeneous but non-radiogenic Pb isotopes (Table 4) and much higher Pb and Zn grades (10–15 wt.%

Pb+ Zn) than MVT deposits (less than 10 wt.% Pb + Zn). Although there is no direct relationship between flood basalts and deposits, the C–O–Pb isotopes indicate contribution of Emeishan flood basalts to Pb–Zn mineralization, and there is a close association of the basalts and deposits (Figure 1B). Typical MVT deposits are not linked with known igneous activities and are associated with the extensional basin setting. Therefore, the Pb–Zn deposits in the SYG province are considered to be a unique type, namely the SYG type (Zhou *et al.* 2013c).

Evolutions of hydrothermal fluids

At ca. 200 Ma, the Yangtze Block collided with adjacent blocks associated with the closure of the Tethys Ocean (e.g. Zhang *et al.* 2006), which is known as the Indosinian Orogeny. Thermal activity related to this event resulted in hydrothermal fluids and extraction of metals from late Proterozoic-to-Palaeozoic sedimentary rocks. Extensive hydrothermal fluid migration and circulation resulted in reduction of sulphur from evaporites in Cambrian-to-Permian strata. Hydrothermal fluids circulated underneath the Permian Emeishan flood basalts, whereas the basalts acted as an impermeable layer. Driven by Indosinian tectonic movement, the resulting hydrothermal fluids enriched in Pb–Zn–Ag–Ge metals migrated upwards along the Anninghe regional tectonic belt (Figure 1B) and incorporated reduced sulphur-bearing solutions, leading to the sulphides, precipitation.

Conclusions

Different chemical compositions in the hydrothermal fluids had contrasting origins: H_2O had a mixed source of metamorphic and meteoric waters; CO_2 originated from three end-member-mixed sources of basalts, carbonates, and organic matter; the reduced sulphur was derived from evaporites in the host strata; and Pb had a more complex derivation involving basement rocks, dolostone, carbonates, and basalts.

The ore genesis of the Tianbaoshan deposit is unlike the distal magmatic–hydrothermal or SEDEX types, but is also different from the typical MVT; it is of the unique SYG type.

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