

# Sources and Thermo-Chemical Sulfate Reduction for Reduced Sulfur in the Hydrothermal Fluids, Southeastern SYG Pb-Zn Metallogenic Province, SW China

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**ABSTRACT:** Located on the western Yangtze Block, the Sichuan (四川)-Yunnan (云南)-Guizhou (贵州) (SYG) Pb-Zn metallogenic province has been a major source of base metals for China. In the southeastern SYG province, structures are well developed and strictly control about 100 Pb-Zn deposits. Almost all the deposits are hosted in Devonian to Permian carbonate rocks. Lead-zinc ores occur either as veinlets or disseminations in dolomitic rocks with massive and disseminated textures. Ore minerals are composed of pyrite, sphalerite and galena, and gangue minerals are calcite and dolomite. Sulfide minerals from four typical Pb-Zn deposits are analyzed for sulfur isotope compositions to trace the origin and evolution of hydrothermal fluids. The results show that  $\delta^{34}\text{S}$  values of sulfide minerals range from +3.50‰ to +20.26‰, with a broad peak in +10‰ to +16‰, unlike mantle-derived sulfur (0±3‰). However, the mean  $\delta^{34}\text{S}_{\text{sulfide}}$  and  $\delta^{34}\text{S}_{\Sigma\text{S-fluids}}$  values are similar to that of sulfate-bearing evaporites in the host rocks (gypsum: ~+15‰ and barite: +22‰ to +28‰) and Cambrian to Permian seawater sulfate (+15‰ to +35‰). This suggests that reduced sulfur in hydrothermal fluids was likely derived from evaporates in the host rocks by thermo-chemical sulfate reduction (TSR). Calculated  $\delta^{34}\text{S}_{\Sigma\text{S-fluids}}$  values of the Shanshulin (杉树林), Qingshan (青山), Shaojiwan (筲箕湾) and Tianqiao (天桥) Pb-Zn deposits are +21.59‰, +18.33‰, +11.43‰ and +10.62‰, respectively, indicating sulfur-bearing hydrothermal fluids may be evolved from the Shanshulin to Qingshan and then the Shaojiwan to Tianqiao deposition sites along the Yadu (埡都)-Ziyun (紫云) lithospheric fracture in the southeastern SYG province.

**KEY WORDS:** sulfur isotope, hydrothermal fluid, TSR, southeastern SYG province, SW China.

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## INTRODUCTION

In the western Yangtze Block, more than 400 Pb-Zn-(Ag) deposits (including the world-class Huize deposit) have been found in the past several decades (Fig. 1). These deposits form the important Sichuan-Yunnan-Guizhou (SYG) Pb-Zn metallogenic province with total Pb and Zn metal reserves more than 20 million tons (Mt) and have been the major sources of base

metals in China (e.g., Liu and Lin, 1999). However, the origin of these deposits and mechanism of such a giant accumulation of Pb and Zn in the SYG province are under hot debated for long time (e.g., Zhou J X et al., 2013a, b, c; Huang et al., 2010; Han et al., 2007; Li et al., 2007; Zhou C X et al., 2001; Liu and Lin, 1999; Zheng and Wang, 1991; Chen, 1986; Liao, 1984; Tu, 1984; Xie, 1963).

Lead-zinc deposits in the SYG province are

hosted in Sinian (Ediacaran) and Devonian to Permian carbonate rocks. A close association between these deposits and the Emeishan flood basalts is evidenced to classify them as distal magmatic-hydrothermal type (Xie, 1963). Liao (1984) proposed a hypothesis of diverse metals sources and all Zn-Pb-(Ag) deposits in this province are thought to be the same hydrothermal-sedimentary type. In the 1980s, Tu (1984) used the concept of strata-bound deposit to interpret all

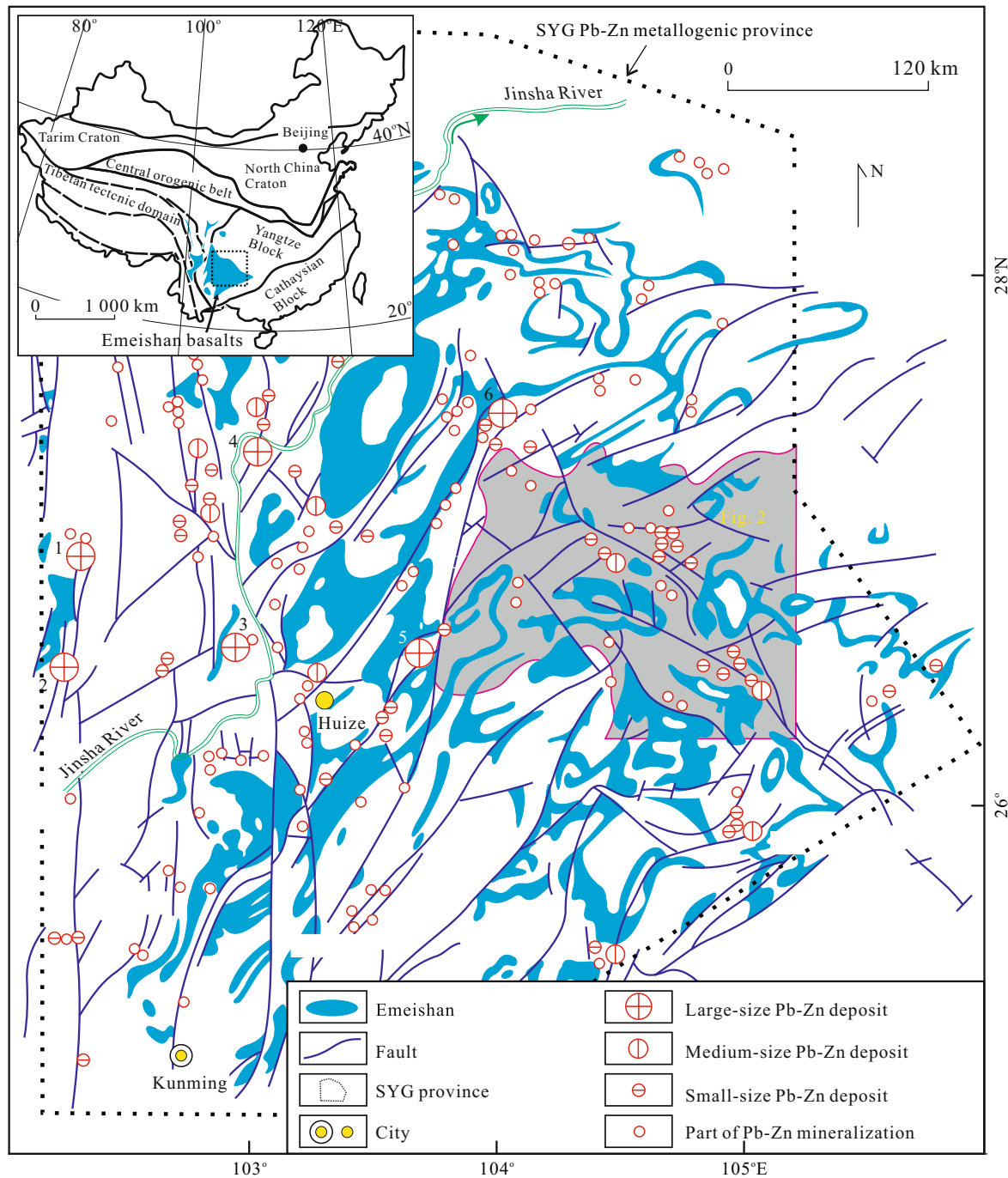


Figure 1. Regional geological map of the SYG Pb-Zn metallogenic province (revised after Huang et al., 2010).

these deposits. This viewpoint was popular in the 1980's and 1990's (e.g., Mao et al., 1998; Chen, 1986). However, it was also believed that the Emeishan flood basalt was one of the important metals sources and heat (e.g., Huang et al., 2010; Han et al., 2007; Liu and Lin, 1999). In addition, some Pb-Zn deposits were reinterpreted to be typical Mississippi valley-type (Zhou et al., 2001; Zheng and Wang, 1991). Despite of these controversies and a large number of publications, it is still unclear how these metals became so highly concentrated in the province.

In the southeastern SYG province, about 100 Pb-Zn deposits are distributed in the Weining-Shuicheng (F-1), Yunguiqiao-Mangdong (F-2) and Yunluhe-Yinchangpo (F-3) faults (Fig. 2). The Shanshulin, Qingshan, Shaojiwan and Tianqiao, four studied deposits in the F-1 and F-2 faults (Fig. 2) have been explored in the past decades. Ore bodies in these deposits are hosted in Devonian to Permian dolostone and dolomitic limestone. Studies of them are available in a few Chinese literatures (e.g., Jin, 2008; Gu, 2007; Mao, 2001, 2000; Gu et al., 1997; Wang, 1994; Zheng, 1994; Chen, 1986), but it is still unclear the sources and evolution of hydrothermal fluids. For example, Chen (1986) and Wang (1994) considered that the ore-forming fluids were derived from the host carbonate

rocks. Zheng (1994) believed that it was originated from Cambrian sedimentary rocks and Precambrian basement rocks (Kunyang and Huili groups). It was also believed that the Emeishan flood basalt was important metals source (e.g., Huang et al., 2010, 2003; Han et al., 2007). Maybe all the Cambrian to Permian sedimentary rocks, Precambrian basement rocks and Permian Emeishan flood basalts have contributions to form these deposits (Zhou et al., 2013a, 2011; Jin, 2008).

Stable isotope is a powerful tool to determining sources of hydrothermal fluids. For example, sulfur isotope is useful in tracing sulfur sources and evolutions of the ore-forming fluids (e.g., Han et al., 2007; Wilkinson et al., 2005; Ohmoto and Goldhaber, 1997). However, systemic sulfur isotope studies are not available, even though it could provide important insight to tracing the origins and evolutions of hydrothermal fluids. Four representative deposits (Shanshulin, Qingshan, Shaojiwan and Tianqiao) are taken as example in this paper, by analyzing new sulfur isotope compositions, as well as a compilation of data from previous studies, to discuss the sources and mechanisms for the reduced sulfur formed in the hydrothermal fluids and its flow pathways.

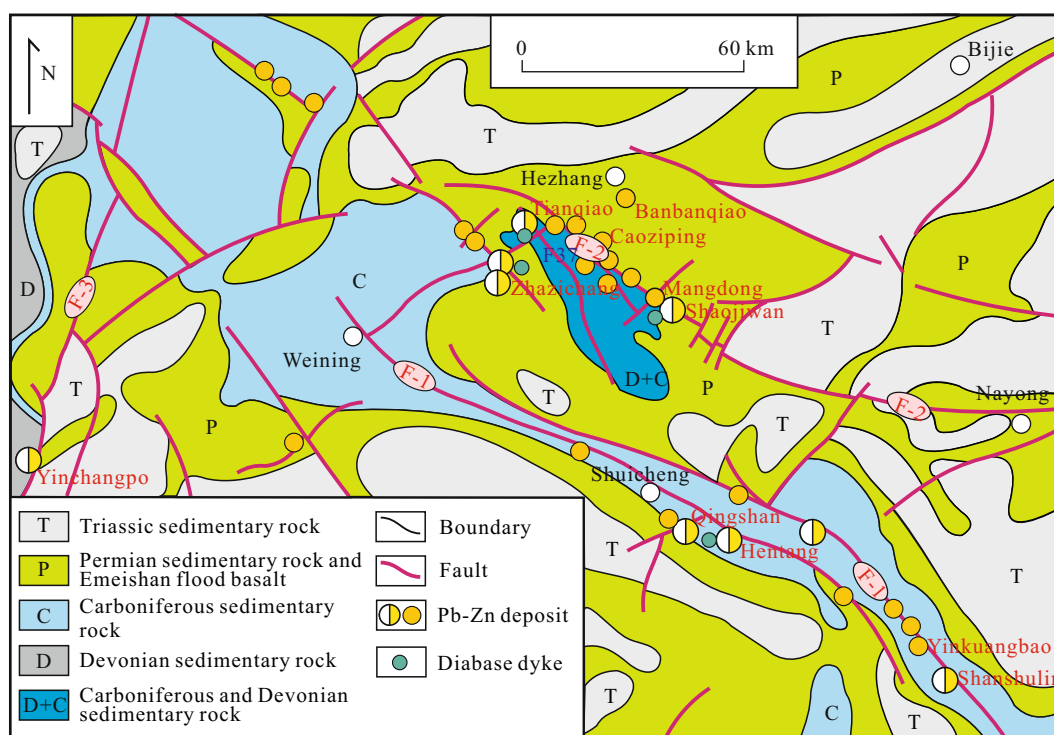


Figure 2. Geological sketch map of southeastern SYG province (revised after Zhou et al., 2011).

## GEOLOGICAL BACKGROUND

Lead-zinc deposits in the western Yangtze Block are distributed in a large triangular area of  $1.7 \times 10^5$  km<sup>2</sup> in NE Yunnan, NW Guizhou and SW Sichuan provinces. This area represents the eastern part of the ~260 Ma Emeishan large igneous province, contains abundant and well-exposed Emeishan flood basalts (Fig. 1). Both Upper Paleozoic and Lower Mesozoic sedimentary rocks are also exposed within the province. Four hundred and eight Pb-Zn deposits have been found in this region (e.g., Liu and Lin, 1999). These are mostly composed of irregular ore bodies with simple mineralogy, weak wall rock alteration and high Pb and Zn grades, usually associated with Ag, Ge, Cd, Ga and In (Zhou et al., 2011). These deposits are mainly hosted in Upper Sinian Dengying Formation, Upper Devonian Rongxian Formation, and Carboniferous Baizuo, Maping and Huanglong formations, of which the country wall rocks are older in the west than that in the east. Notably the host rocks are all overlain by Permian Emeishan flood basalts (Huang et al., 2010). Tectonic within the SYG province are very complex and control the distribution of these Pb-Zn deposits. Most faults in the western part of the province are NS-trending, whereas those in the east trend NE and NW (Fig. 1).

In the southeastern SYG province, the cover sequence includes Devonian, Carboniferous, Permian and Triassic sedimentary rocks, and the Emeishan flood basalts. Diabase dykes, may be part of the Emeishan large igneous province are also locally presented (Fig. 2). The Devonian sedimentary rocks are composed of sandstone, siltstone, limestone and dolostone and the Carboniferous sedimentary rocks consist of shale, limestone and dolostone. The Early Permian sedimentary rocks consist of sandstone, shale, coal layers and limestone, all of which are overlain by the Emeishan flood basalts. The basalts are overlain by Late Permian sandstone, siltstone and coal measures. The Triassic sedimentary rocks are consisted of siltstone, sandstone, dolostone and limestone. NW- and NNE-striking faults are complex, which can be divided into three groups (Zhou et al., 2011; Jin, 2008). The Weining-Shuicheng tectonic belt (F-1), which is composed of NW Weining-Shuicheng and Shuishan anticlines and longitudinal faults, and is formed later

than Early Permian. This belt is characterized by intensive compression deformation and a large amount of cleavages on fault planes, where are formed by pressure solution and structural lens-shaped bodies in the wing of the fold belt. All of the fold belt's longitudinal faults are high-angle thrust faults, whose planes are inclined along the SW or NE direction and have a dip angle ranging from 70° to 80°; (2) The Yunguiqiao-Mangdong tectonic belt (F-2), a regional tectonic system incised into the basement rocks and composed of a series of high dip-angle thrust faults, is extend along the direction of NW 310° and have a dip angle ranging from 70° to 85°, which is formed later than Upper Triassic; (3) The Yinchangpo-Yunluhe tectonic belt (F-3), located in the east of the Zhaotong-Qujing buried fault (Han et al., 2007), is the NNE extension of the Kuangshanchang-Qilingchang fault in the Huize deposit and formed later than Upper Triassic.

The carbonate-hosted Pb-Zn deposits in the southeastern SYG province are mainly located along the NW-trending faults, particularly the F-1 and F-2 faults (Fig. 2), which are belong to the Yadu-Ziyun lithospheric fracture (Jin, 2008), an important fault in the SYG province (Fig. 1). Ore bodies are hosted in Devonian to Permian dolostone and dolomitic limestone. The Shanshulin and Qingshan deposits, controlled by the F-1 fault are hosted in dolostone of Upper Carboniferous Huanglong and Maping formations, respectively (Fig. 2). The Tianqiao and Shaojiwan deposits, controlled by the F-2 fault are hosted in dolostone of Lower Carboniferous Baizuo Formation and limestone of Lower Permian Qixia Formation, respectively (Fig. 2). Because of the common geological and geochemical features, many researchers considered them to be epigenetic deposits (e.g., Zhou et al., 2011; Jin, 2008; Gu, 2007). Recently, we get the Tianqiao sulfides Rb-Sr isotopic age of  $191.9 \pm 6.9$  Ma (Zhou et al., 2013a) and the Maozu hydrothermal calcite Sm-Nd isotopic age of  $196 \pm 13$  Ma (Zhou et al., 2013d), making the ~200 Ma metallogenic age of the Pb-Zn mineralization in the SYG province consistent with its tectonic setting.

Wall-rock alterations of these deposits are mainly dolomitization, pyritization, Fe-Mn carbonation, ferritization, calcitization, and silicification. According to

the ore textures and structures, interpenetration relations and minerals assemblages, the ore-forming periods could be divided into the sedimentary, hydrothermal and weathering periods. The hydrothermal period could be further divided into two stages, including sulfide-carbonate and carbonate stages. There are three minerals assemblages in the sulfide-carbonate stage that are pyrite-brown sphalerite-calcite/dolomite, pyrite-brown yellow sphalerite-galena-pyrite-calcite/dolomite and light-yellow sphalerite-galena-calcite/dolomite assemblages (Zhou et al., 2013a, b).

### SAMPLE PREPARATION AND ANALYTICAL METHODS

About 40 ores samples were collected from the main ore bodies of the studied Pb-Zn deposits. Ore samples were crushed into 40–60 mesh sizes and sulfide minerals were handpicked. Sulfur isotope compositions were analyzed using EA-IRMS method by continuous flow mass spectrometer at the State Key Laboratory of Environment Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang. Samples are wrapped tightly with a tin can and put into the EA reaction furnace, followed by combustion and decomposition to produce  $\text{SO}_2$ , and hydrogen gas was used to blow  $\text{SO}_2$  into the mass spectrometer, followed by the determination of  $\delta^{34}\text{S}$ . In the procedure of analysis the internal standard was added to control the data accuracy. Sample was analyzed at least twice in the parallel manner so as to guarantee the accuracy to reach the index. GBW 04415 and GBW 04414  $\text{Ag}_2\text{S}$  were used as the external standards and CDT as the standard, with the analytical accuracy of  $\pm 0.1\text{‰}$  ( $2\sigma$ ).

### RESULTS

Sulfur isotope compositions of pyrite, sphalerite and galena from the studied Pb-Zn deposits, together with previous results of other deposits (such as Banbanqiao, Yinchangpo, Mangdong, Hentang, Zhazichang, Caoziping and Yinkuangbao) are listed in Tables 1 and 2 is a statistic value. All sulfide minerals have positive  $\delta^{34}\text{S}$  values (Table 1).  $\delta^{34}\text{S}$  values of sulfide minerals from all deposits are between  $+3.50\text{‰}$  and  $+20.26\text{‰}$ , most of them range from  $+8\text{‰}$  to  $+20\text{‰}$ , and a peak in  $+10\text{‰}$  to  $+16\text{‰}$  (Fig. 3). This

indicates that sulfur in the hydrothermal fluids has identical and single source, but different from meteorite sulfur ( $0\text{‰}$ ; Chaussidon et al., 1989).  $\delta^{34}\text{S}$  values of pyrite range from  $+7.60\text{‰}$  to  $+18.30\text{‰}$ , sphalerite has  $\delta^{34}\text{S}$  values ranging from  $+3.90\text{‰}$  to  $+20.26\text{‰}$  and  $\delta^{34}\text{S}$  values of galena range from  $+3.50\text{‰}$  to  $+17.20\text{‰}$  (Table 2). A trend of  $\delta^{34}\text{S}_{\text{pyrite}} > \delta^{34}\text{S}_{\text{sphalerite}} > \delta^{34}\text{S}_{\text{galena}}$  is observed in each studied deposits and becomes more obviously in the same hand specimen (Table 1 and Fig. 4). It indicates that sulfur isotope balance fractionation has been achieved.

### DISCUSSION

#### Possible Sources and Mechanisms of Reduced Sulfur in the Hydrothermal Fluids

Sulfur isotopic compositions can be used to tracing the sources of reduced sulfur in the hydrothermal fluids (e.g., Haest et al., 2010; Basuki et al., 2008; Han et al., 2007; Seal, 2006; Wilkinson et al., 2005). Overall, primary ores from the studied deposits have simple mineralogy, containing galena, sphalerite and pyrite as ore minerals, and calcite and dolomite as gangue minerals, but lack of sulfate. Therefore, the  $\delta^{34}\text{S}_{\text{pyrite}}$  can largely represent the  $\delta^{34}\text{S}_{\Sigma\text{S-fluids}}$  values

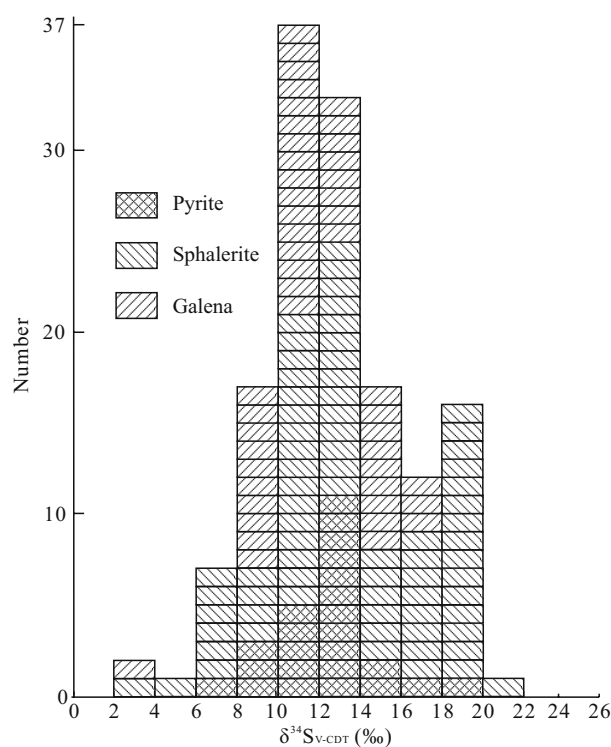


Figure 3. Histogram of the  $\delta^{34}\text{S}$  values of sulfide minerals.

Table 1  $\delta^{34}\text{S}$  values (‰) of sulfides from the southeastern SYG province

Name	No.	Obj.	$\delta^{34}\text{S}_{\text{CDT}}$	Sources	Name	No.	Obj.	$\delta^{34}\text{S}_{\text{CDT}}$	Sources
Shanshulin	SS07	Py	17.60	Fu, 2004	Shaojiwan	SJW-9	Py	11.35	Zhou et al., 2013c; Zhang et al., 2011
	78-59	Sp	16.30	Chen, 1986		SJW-15	Py	11.34	
	78-80	Sp	16.10			SJW-14	Py	11.57	
	3	Sp	17.01			SJW-1	Br Sp	11.06	
	12	Sp	18.26			SJW-11	Br Sp	9.78	
	78-66	Sp	15.90			SJW-7	Br Sp	10.05	
	SSL-6	Br Sp	19.56	This study		SJW-6	Br Sp	11.09	
	SSL-17	Br Sp	19.32			SJW-9	Br Sp	10.27	
	SSL-14	Br Sp	19.03			SJW-15	Br Sp	9.84	
	SSL-13	Br Sp	18.93			SJW-16	Br Sp	10.14	
	SSL-1	Br Sp	20.26		SJW-12	Gl	8.44		
	SSL-12	Br Sp	19.07		Qingshan	QSC-4S	Py	18.30	Gu, 2007
	SSL-11	Br Sp	19.16			1800A4-S2	Sp	17.60	
	SS13	By Sp	18.69	1816B4-S1		Sp	18.50		
	SS14	By Sp	18.68	QSC-3S1		Sp	18.40		
	SS01	By Sp	17.19	1816B4-S2		Gl	17.20		
	SS03	By Sp	17.48	1800A4-S1		Gl	15.90		
	SS14-1	By Sp	18.37	QSC-3S2		Gl	15.80		
	SS16	Br Sp	18.55	QS03		Py	16.90	Fu, 2004	
	78-79	Gl	13.40	QS04		By Sp	18.50		
78-64	Gl	13.40	QS04	Gl		14.00			
11	Gl	13.64	QS02	Gl	13.70				
A1159-4	Gl	13.70	This study	Q-2-1	Sp	15.90	This study; Zhou et al., 2013b; Mao et al., 1998		
SSL-17	Gl	15.81		Q-2-2	Gl	11.40			
SSL-12	Gl	15.67		Q-6	Sp	15.70			
SSL-6	Gl	17.09		QS01SP	Sp	17.50			
SSL-10	Gl	15.60	QS01	Sp	6.78				
SS14-1	Gl	14.21	GQ3-Py	Py	10.70				
SS14	Gl	14.10	F9-Py	Py	12.60				
Hentang	HT-12S2	Sp	16.06	Gu, 2007	GQ11-Cc	Py		13.60	
	HT-12S1	Gl	14.44		Q-Py	Py		14.00	
Tianqiao	HTQ-T7S	Py	13.44	Zhou et al., 2013a	Q-Sph	Sp		19.60	
	TQ-18	Py	13.69		Q-Gal	Gl	16.80		
	TQ-19	Py	14.44		Yinchangpo	YC-C	Py	8.50	Hu, 1999
	TQ-23	Py	12.81			YC-A	Py	7.60	
	TQ-24-1	Py	12.87			YC-B	Py	10.30	
	TQ-60	Py	13.18	YC-5	Sp	13.30			
	HTQ-T1S1	Sp	11.54	YC-1	Sp	12.70			
HTQ-T2S2	Sp	14.23	YC-4	Sp	11.20				
HTQ-T3S1	Sp	12.38	YC-7	Sp	12.40				

## Continued

Name	No.	Obj.	$\delta^{34}\text{S}_{\text{CDT}}$	Sources	Name	No.	Obj.	$\delta^{34}\text{S}_{\text{CDT}}$	Sources
Tianqiao	HTQ-T6S1	Sp	11.58	Gu, 2007	Yinchangpo	YC-6	Sp	12.90	Hu, 1999
	HTQ-T4S1	Sp	11.51			YC-2	Sp	11.90	
	TQ-13	Ly Sp	11.70	Zhou et al., 2013a, 2010		YC-3	Sp	14.20	
	TQ-18	By Sp	13.10			YC6-21	Gl	11.00	
	TQ-60	By Sp	12.40			YC6-19-1	Gl	10.00	
	TQ-10	Br Sp	13.70			YC6-25	Gl	10.10	
	TQ-3	Br Sp	14.00			YC6-A	Gl	10.80	
	TQ-16	By Sp	13.70			YC6-22	Gl	11.50	
	TQ-24-3	Br Sp	12.30			YC3-3	Gl	9.60	
	TQ-54	By Sp	12.20			YCW-4	Gl	10.70	
	TQ-25	Ly Sp	12.10		8-2	Py	12.20	Liu and Lin, 1999	
	TQ-24-4	By Sp	11.90	4	Py	12.00			
	TQ-24-5	Ly Sp	10.90	1	Gl	10.50			
	HTQ-T1S2	Gl	11.05	Gu, 2007	3	Gl	10.20		
	HTQ-T2S1	Gl	12.55		Mar-83	Gl	10.90		
	HTQ-T3S2	Gl	10.74		2	Gl	9.90		
	HTQ-T5S	Gl	10.95		58	Py	13.00		
	HTQ-T6S2	Gl	11.42		Banbanqiao	902	Py	8.80	This study
	HTQ-T4S2	Gl	11.88	906		Py	9.80		
	TQ-13	Gl	9.26	920		Sp	4.80		
TQ-24-2	Gl	8.86	915	Sp		3.90			
TQ-25	Gl	8.51	904	Sp		6.00			
TQ-3	Gl	9.83	908	Sp		8.40			
TQ-52	Gl	8.35	917	Sp		6.10			
TQ-54	Gl	8.40	909	Sp	6.40				
TQ-65	Gl	8.66	921	Sp	9.00				
Mangdong	HMD-S	Py	13.08	Gu, 2007	924	Sp	7.10	Jin, 2008	
	HMD-4S	Sp	13.37		910	Gl	3.50		
	HMD-6S2	Sp	13.74	Zhazichang	Z-1	Py	14.00		
	HMD-7S2	Sp	11.34	Caoziping	CZP-1	Sp	10.10		
	HMD-8S2	Sp	10.90		CZP-2	Gl	9.20		
	HMD-9S	Sp	11.50		CZP-3	GL	7.80		
	HMD-6S1	Gl	11.52	Yinkuangbao	Yk-1	Py	20.00		
	HMD-7S1	Gl	12.84		Yk-2	Sp	18.80		
	HMD-8S1	Gl	12.13		Yk-3	Gl	17.20		

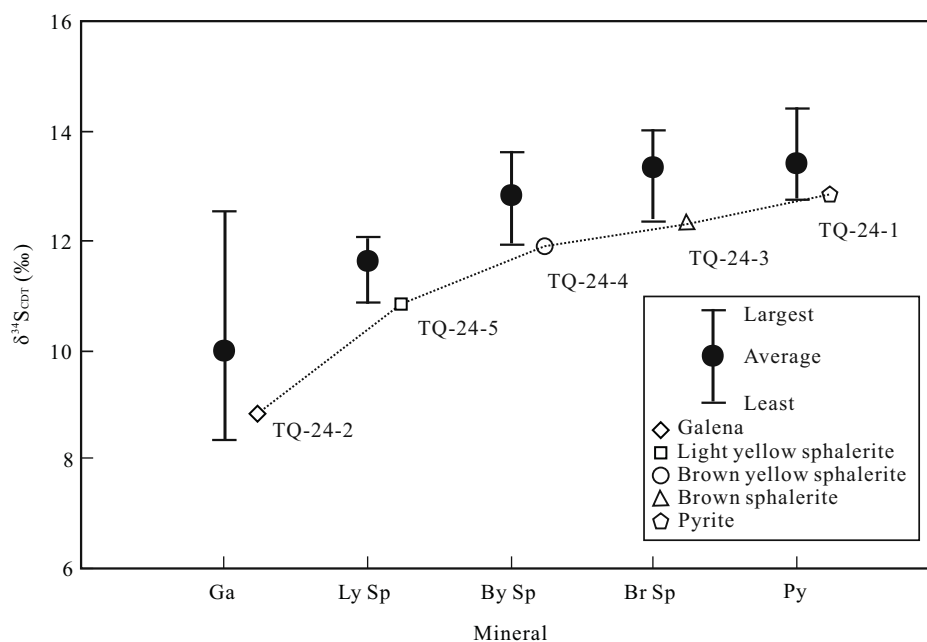
Py. pyrite; Sp. sphalerite; Br Sp. brown sphalerite; By Sp. brown yellow sphalerite; Ly Sp. light yellow sphalerite; Gl. galena.

**Table 2 Statistics of  $\delta^{34}\text{S}$  values (‰) in the studied Pb-Zn deposits**

Name	Host strata	Object	Analysis number	$\delta^{34}\text{S}$	Mean value
Tianqiao	Lower Carboniferous Baizuo Fm.	Py	6	12.81–14.44	13.41
		Sp	5	11.51–14.23	12.25
		Br Sp	3	12.30–14.00	13.30
		By Sp	5	11.90–13.70	12.70
		Ly Sp	3	10.90–12.10	11.60
		G1	13	8.40–12.55	10.04
Shanshulin	Upper Carboniferous Huanglong Fm.	Py	1	17.60	17.60
		Sp	5	15.90–18.26	16.71
		Br Sp	8	18.55–20.26	19.24
		By Sp	5	17.19–18.69	18.08
		G1	10	13.40–17.09	14.66
Qingshan	Upper Carboniferous Maping Fm.	Py	6	10.70–18.30	14.30
		Sp	8	6.78–19.60	16.90
		Br Sp	1	18.50	18.50
		G1	7	11.40–17.20	14.60
Shaojiwan	Lower Permian Qixia Fm.	Py	3	11.34–11.57	11.42
		Br Sp	7	9.84–11.09	10.32
		G1	1	8.44	8.44
Yinchang-po	Lower Carboniferous Baizuo Fm.	Py	6	7.60–13.00	12.30
		Sp	7	11.20–14.20	12.20
		G1	11	9.60–11.50	10.40
Mangdong	Upper Devonian Rongxian Fm.	Py	1	13.08	13.08
		Sp	5	11.50–13.74	12.71
		G1	3	10.90–11.50	11.30
Banban-qiao	Upper Carboniferous Huanglong Fm.	Py	2	8.80–9.80	9.30
		Sp	8	3.90–8.40	6.50
		G1	1	3.50	3.50
Hentang	Upper Carboniferous Maping Fm.	Sp	1	16.10	16.10
		G1	1	14.40	14.40
Zhazi-Caoziping	Lower Carboniferous Datang Fm.	Py	1	14.00	14.00
		Sp	1	10.10	10.10
		G1	2	7.80–9.20	8.50
Yin-kuang-bao	Upper Carboniferous Huanglong Fm.	Py	1	20.00	20.00
		Sp	1	18.20	18.20
		G1	1	17.20	17.20
Region	Cambrian–Permian	Gypsum		15	15
		Barite		22–28	25

Py. pyrite; Sp. sphalerite; Br Sp. brown sphalerite; By Sp. brown yellow sphalerite; Ly Sp. light yellow sphalerite; G1. galena. Fm.. Formation. The primitive data see Table 1.





**Figure 4. Contrastive diagram of  $\delta^{34}\text{S}$  values, take the Tianqiao Pb-Zn deposit as example. Sample Nos. TQ-24-1, TQ-24-2, TQ-24-3, TQ-24-4 and TQ-24-5 are selected from the same hand specimen.**

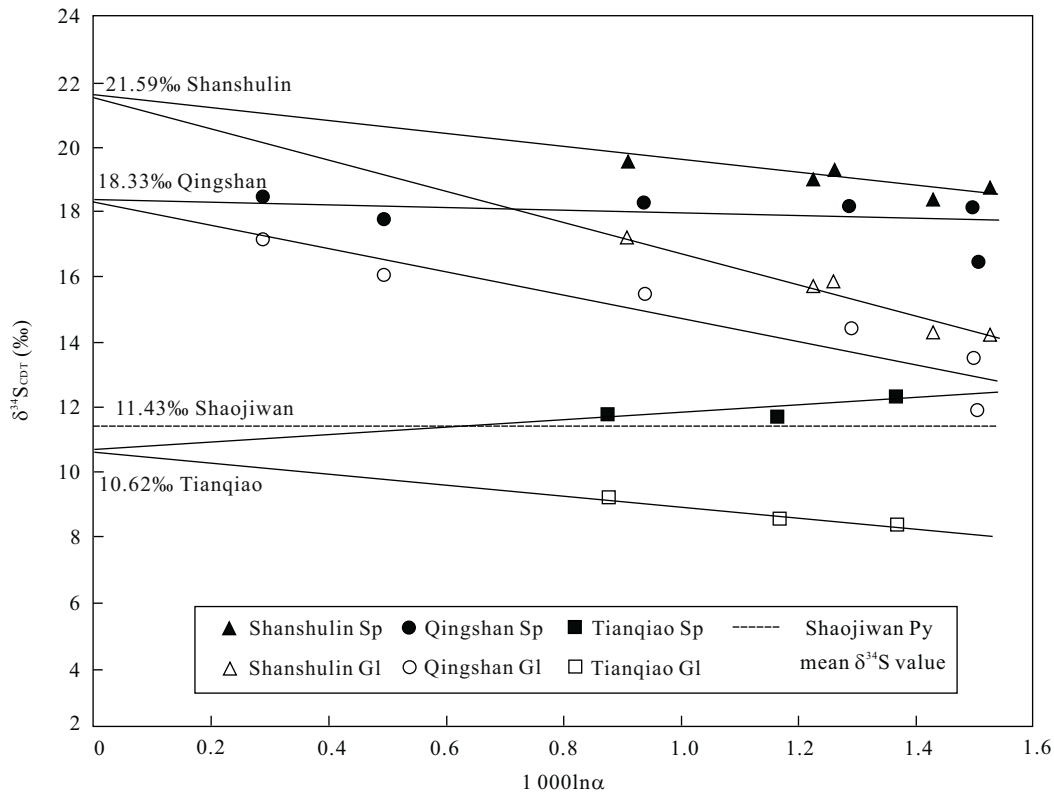
(Basuki et al., 2008; Seal, 2006; Ohmoto, 1972). The  $\delta^{34}\text{S}$  values of pyrite range from +7‰ to +18‰ and its mean value is +12.37‰, so we consider that the  $\delta^{34}\text{S}_{\Sigma\text{S-fluids}}$  value should be near  $\sim +12\%$ . In addition, it is feasible to calculate  $\delta^{34}\text{S}_{\Sigma\text{S-fluids}}$  values using the methods of Pinckney and Rafter (Shen, 1987). The results show that the  $\delta^{34}\text{S}_{\Sigma\text{S-fluids}}$  values of the Tianqiao, Shaojiwan, Qingshan and Shanshulin deposits are +10.62‰, +11.43‰, +18.33‰ and +21.59‰, respectively (Fig. 5). So the  $\delta^{34}\text{S}_{\Sigma\text{S-fluids}}$  values range from +11‰ to +22‰. Gypsum and barite-bearing evaporites have been found in the host rocks, whose  $\delta^{34}\text{S}$  values are  $\sim +15\%$  and +22‰ to +28‰, respectively (Jin, 2008; Han et al., 2007; Liu and Lin, 1999), similar to that of Cambrian to Permian seawater sulfates (+15‰ to +35‰; Claypool et al., 1980). Therefore, reduced sulfur in the hydrothermal fluids might be derived from evaporites in the host rocks.

Two main views, namely bacterial sulfate reduction (BSR) and thermal-chemical sulfate reduction (TSR) are proposed to explain the reduction mechanism (Basuki et al., 2008; Seal, 2006). They are temperature-dependent. BSR occurs under a relatively low temperature (lower than 120 °C, Basuki et al., 2008; Jorgenson et al., 1992). The homogenization temperatures of calcite and quartz fluid inclusions from these Pb-Zn deposits vary from 140 to 270 °C

(Jin, 2008) and the calculated mineralization temperatures range from 170 to 350 °C based on the  $\Delta^{34}\text{S}$  between sulfide minerals ( $\Delta^{34}\text{S} = \delta^{34}\text{S}_a - \delta^{34}\text{S}_b = A \times 10^6 / T^2$ , Czamanske and Rye, 1974). Therefore, the temperature is too high for bacteria to survive. So BSR play a limited role in the formation of reduced sulfur. TSR occurs at a relatively high temperature (higher than 140 °C, Worden et al., 1995) and can produce a large amount of reduced sulfurs, which have relatively stable  $\delta^{34}\text{S}$  values (Ohmoto et al., 1990). There are about 100 Pb-Zn deposits with total Pb and Zn reserves more than 5 Mt, which require huge amounts of reduced sulfur. Thus, we considered the TSR to be the main mechanism. On the other hand, some studies have confirmed the reaction ( $\text{SO}_4^{2-} + \text{CH}_4 = \text{H}_2\text{S} + \text{CO}_3^{2-} + \text{H}_2\text{O}$ ) could be take place at 140 °C (Worden et al., 1995). Although, the contribution of the sulfur-bearing organic matter thermal-degradation is very difficult to evaluate, yet organic matters have played reductive agent in the TSR process (Zhou et al., 2013a; Li et al., 2007; Ottaway et al., 1994), so it is also an important contributor.

#### **Possible Evolution Flow Pathways of Reduced Sulfur-Bearing Hydrothermal Fluids**

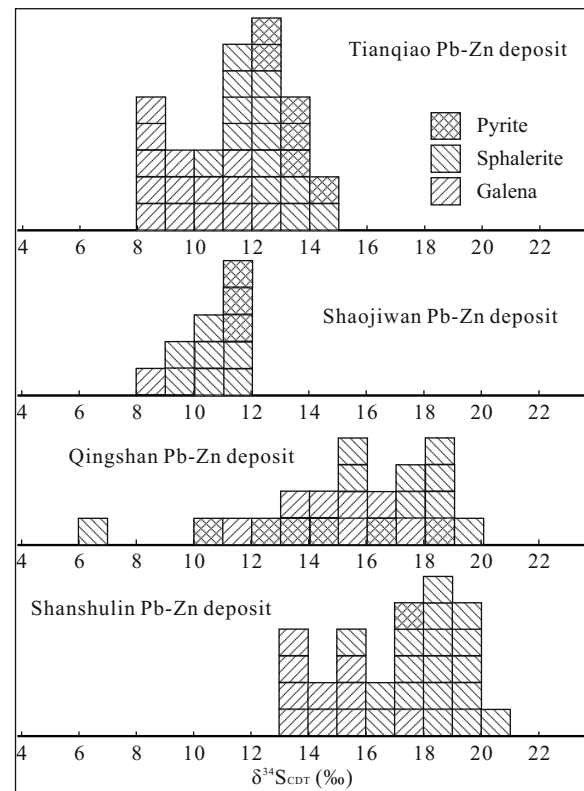
The Pb-Zn deposits in southeastern SYG province have the common geological setting (western



**Figure 5. Total sulfur isotopic compositions of the hydrothermal fluids in the studied deposits.**

Yangtze Block) and conditions (structurally controlled and carbonate-hosted). They also have common sources of ore-forming fluids and metals, of which sulfur in the hydrothermal fluids was derived from sulfate-bearing evaporites in the host rocks by TSR (Zhou et al., 2013a, b; Gu, 2007; this article); CO<sub>2</sub> was sourced mainly from the host carbonate rocks by marine carbonate dissolution (Zhou et al., 2012; Jin, 2008; Mao, 2000); ore lead was originated from mixed sources of Proterozoic basement rocks and the host carbonate rocks (Zhou et al., 2013a, b; Jin, 2008); ore strontium has a mixture sources of Proterozoic basement rocks, Sinian to Permian sedimentary rocks and Permian Emeishan flood basalts (Zhou et al., 2013c; Hu, 1999; Gu et al., 1997); and REE of hydrothermal calcite and sulfide minerals were inherited from the host carbonate rocks (Han et al., 2012; Zhou et al., 2011; Jin, 2008; Mao, 2001). However, the flow pathways of hydrothermal fluids are still unknown.

According to the methods of Pinckney and Rafter (Shen, 1987), we get the  $\delta^{34}\text{S}_{\Sigma\text{S-fluids}}$  values of +10.62‰, +11.43‰, +18.33‰ and +21.59‰ for the Tianqiao, Shaojiwan, Qingshan and Shanshulin deposits, respectively (Figs. 5 and 6), indicating an



**Figure 6. Histogram of the  $\delta^{34}\text{S}$  values of sulfide minerals from the studied deposits.**

increased  $\delta^{34}\text{S}_{\Sigma\text{S-fluids}}$  value from the Tianqiao to Shanshulin deposits. As the common sources of sulfur for these deposits, so we consider that the sulfur-bearing hydrothermal fluids may be flow from the Shanshulin to Qingshan deposit and then Shaojiwan to Tianqiao deposition sites (Fig. 7). The following evidences are also support this conclusion. (1) The NW-trending faults could provide a channel for the

enriched sulfur-bearing hydrothermal fluids; (2) The mean homogenization temperature of fluid inclusions in calcite from the Qingshan and Tianqiao deposits are 186 and 175 °C, respectively (Jin, 2008). Additionally, the calculated sulfur isotope balance fractionation temperatures for the Tianqiao, Shaojiwan, Qingshan and Shanshulin deposits are 210, 235, 250 and 272 °C, respectively.

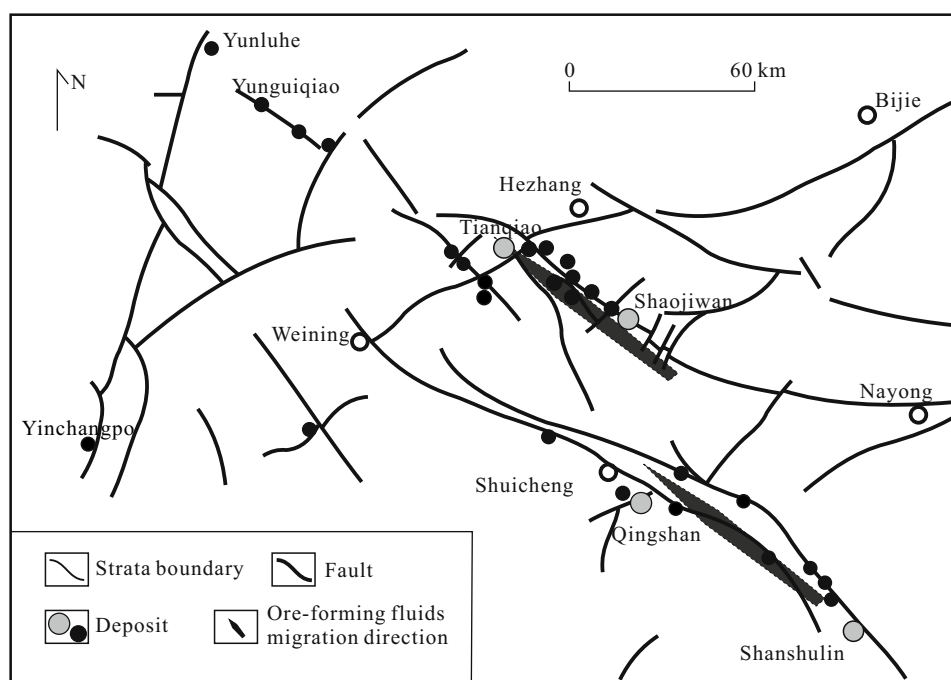


Figure 7. Direction of the hydrothermal fluids evolution.

## CONCLUSION

(1)  $\delta^{34}\text{S}$  values of sulfide minerals range from +3.50‰ to +20.26‰, similar to sulfate-bearing evaporites in the host rocks (gypsum: ~+15‰ and barite: +22‰ to +28‰) and Cambrian to Permian seawater sulfate (+15‰ to +35‰), indicating reduced sulfur was derived from evaporates in the host rocks by TSR.

(2)  $\delta^{34}\text{S}_{\Sigma\text{S-fluids}}$  of the Tianqiao, Shaojiwan, Qingshan and Shanshulin deposits are +10.62‰, +11.43‰, +18.33‰ and +21.59‰, respectively, indicating reduced sulfur-bearing hydrothermal fluids were transported from the Shanshulin to Qingshan and then the Shaojiwan to Tianqiao deposition sites.

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