

Cadmium and sulfur isotopic compositions of the Tianbaoshan Zn–Pb–Cd deposit, Sichuan Province, China



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ABSTRACT

Although Zn–Pb deposits are one of the most important Cd reservoirs in the earth, few studies have focused on the Cd isotopic fractionation in Zn–Pb hydrothermal systems. This study investigates the causes and consequences of cadmium and sulfur isotope fractionation in a large hydrothermal system at the Tianbaoshan Zn–Pb–Cd deposit from the Sichuan–Yunnan–Guizhou (SYG) metallogenic province, SW China. Moderate variations in Cd and S isotope compositions have been measured in sphalerite cover a distance of about 78 m. Sphalerite has $\delta^{114/110}\text{Cd}$ values ranging from 0.01 to 0.57‰, and sulfides (sphalerite, galena and chalcopyrite) have $\delta^{34}\text{S}_{\text{CDT}}$ values ranging from 0.2 to 5.0‰. Although $\delta^{34}\text{S}_{\text{CDT}}$ and $\delta^{114/110}\text{Cd}$ values in sphalerites have no regular spatial variations, the $\delta^{34}\text{S}_{\text{CDT}}$ values in galena and calculated ore-forming fluid temperatures decreased from 2.1 to 0.2‰ and from about 290 to 130 °C, respectively, from the bottom to the top of the deposit. Heavy Cd isotopes are enriched in early precipitated sphalerite in contrast to previous studies. We suggest that Cd isotopic compositions in ore-forming fluids are heterogeneous, which result in heavy Cd isotope enrichment in early precipitated sphalerite. In comparison with other Zn–Pb deposits in the SYG area, the Tianbaoshan deposit has moderate Cd contents and small isotope fractionation, suggesting differences in origin to other Zn–Pb deposits in the SYG province.

In the Tianbaoshan deposit, the calculated $\delta^{34}\text{S}_{\Sigma\text{S-fluids}}$ value is 4.2‰, which is not only higher than the mantle-derived magmatic sulfur ($0 \pm 3\text{‰}$), but also quite lower than those of Ediacaran marine sulfates (about 30 to 35‰). Thus, we suggest that reduced sulfur of ore-forming fluids in the deposit was mainly derived from the leaching of the basement, which contains large amount of volcanic or intrusive rocks. Based upon a combination of Cd and S isotopic systems, the Tianbaoshan deposit has different geochemical characteristics from typical Zn–Pb deposits (e.g., the Huize deposit) in SYG area, indicating the unique origin of this deposit.

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1. Introduction

Although it is important to determine the ore-forming fluid pathways and the environment, and to quantify of sulfide crystallization, these factors are often poorly known. The extent and causes of isotope fractionation of transition metals (e.g., Zn and Cd) have shown potential for ore exploration (Kelley et al., 2009; Gagnevin et al., 2012; Zhou et al., 2014; Zhu et al., 2015). Studies of Cd isotopes in hydrothermal systems suggest the incorporation of light isotopes in sphalerite in deeper parts of the hydrothermal environments, with Raleigh isotope fractionation accounting for the evolution from light to heavy Cd isotopic composition (Schmitt et al., 2009; Zhu et al., 2013). In published studies, the Cd isotope databases are limited in terms of their sample coverage, mass balance and their ability to quantify relative fractionations.

In the western Yangtze Block, SW China, more than 400 Zn–Pb deposits with about 200 Mt. of Zn–Pb ores are located in the Sichuan–Yunnan–Guizhou (SYG) metallogenic province, which contains

deposits known for super-enrichment of trace elements, such as the Huize Ge-rich Zn–Pb deposit (Fu, 2004; Han et al., 2012; Ye et al., 2011; Wu, 2013; Zhu, 2014), the Fule Cd-rich Zn–Pb deposit (Si, 2005; Zhu et al., 2013; Zhu, 2014) and the Tianbaoshan Cd-rich Zn–Pb deposit (Fu, 2004; Zhu, 2014). These deposits are hosted in Ediacaran to Permian carbonate rocks and structurally controlled by thrust fault-fold, and are spatially associated with the Emeishan flood basalts (~260 Ma). Previous studies focused on the geology and origin of these deposits (e.g., Xie, 1963; Huang et al., 2003, 2004; Li, 2003; Li et al., 2007; Zhang et al., 2015), and proposed many models to determine the enrichment of Zn and Pb in this region. More detailed information on the arguments concerning the enrichment mechanisms have been described in Huang et al. (2003), Zhu et al. (2013) and Zhang et al. (2015).

This study examines the Tianbaoshan Zn–Pb–Cd deposit, located in the SYG metallogenic province (Fig. 1), to elucidate temporal variations of Cd isotopes within a large hydrothermal system. These data are coupled with new data on S isotopes, whose behavior in the Tianbaoshan Zn–Pb deposit is already well established (e.g., Wang et al., 2000; Zhou et al., 2013). By taking samples of sphalerites from

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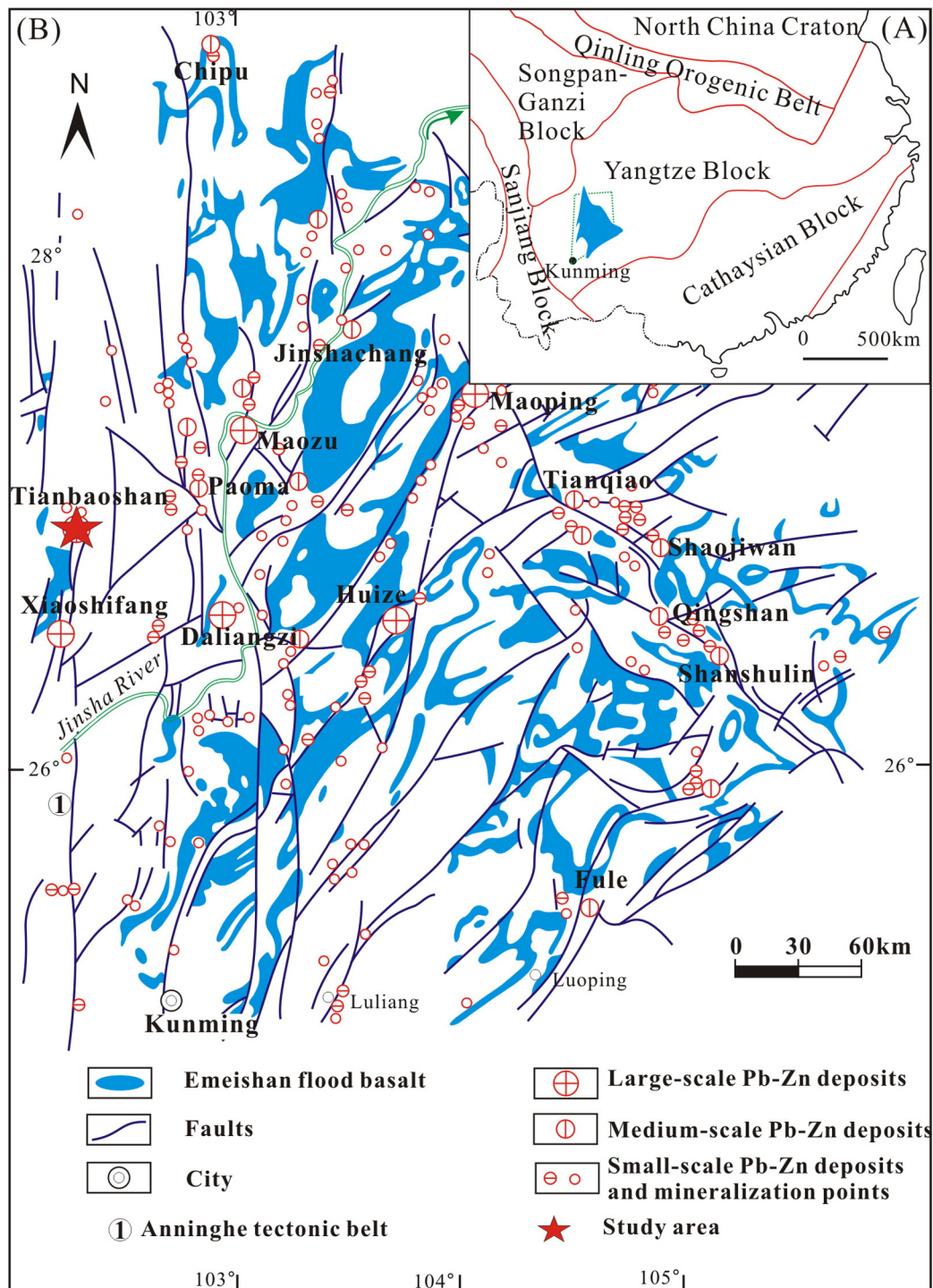


Fig. 1. (A) Tectonic sketch; (B) regional geological map of the Sichuan–Yunnan–Guizhou Zn–Pb metallogenic province, SW China. Modified from Liu and Lin (1999).

the deposit, we are able to examine the processes of Cd isotopic fractionation and to gain insights into the behavior of Cd isotopes during the formation of the Zn–Pb deposits. The Cd isotopic compositions in sphalerite of different stages were measured to understand temporal Cd isotopic variations during hydrothermal fluid precipitation.

2. Geological setting and sampling

The Tianbaoshan Zn–Pb–Cd deposit, including the Tianbao and Xinshan ore blocks, is located in the northwestern part of the SYG

metallogenic province at the northwestern margin of the Yangtze Craton. The Yangtze Craton is composed of ~2.9 to ~3.3 Ga crystalline basement complexes (mainly consisting of metamorphic series), Meso- to Neo-Proterozoic folded basements (mainly magmatic rocks) and Paleozoic to Mesozoic cover sequences (mainly carbonate rocks) (Liu and Lin, 1999; Fu, 2004). Wang et al. (2000) and Zhou et al. (2013) have described the regional geological background and the geological characteristics of this deposit in detail. The deposit is hosted in Ediacaran carbonate rocks and structurally controlled by the NS-trending Anninghe tectonic belt and its branch structures (Figs. 1

and 2A). In the Tianbaoshan ore blocks, the Upper Ediacaran Dengying Formation (Zbd) is the most important ore-hosting formation and mainly consists of dolostone. The main folds present are the Tianbaoshan syncline and its secondary anticlines; the main faults are the branch faults (F_1) of the Anninghe tectonic belt and the NW-trending fractures (F_2) (Fig. 2).

Exploratory drilling and underground mining provide excellent access to two ore blocks (Fig. 2) that contain 1.8 Mt. Zn and Pb metals at grades of 7.76–10.1 wt.% Zn and 1.28–2.5 wt.% Pb (Wang et al., 2000; Zhou et al., 2013). Geochemically, the Tianbaoshan deposit is rich in dispersed elements, with more than 7289 tons of Cd, 258 tons of Ga, 122 tons of Ge and 20 tons of In, respectively. These metals are hosted in sphalerite (Fu, 2004; Tu et al., 2004; Zhu, 2014).

At Tianbaoshan, ores are predominately sulfide, with small amounts of oxidized ores (Fig. 3). The ore mineralogy includes sphalerite, galena, pyrite, chalcopyrite, arsenopyrite, pyrrargyrite, freibergite, quartz, calcite and dolomite (Fig. 3). Sulfide ores have granular, metasomatite-relict and cataclastic textures, and the massive, disseminated, brecciated, veined and banded structures. Three types of sphalerite are observed

in hand specimens: dark brown sphalerite, light brown sphalerite and light yellow sphalerite (Fu, 2004) (Fig. 3B and C). The paragenetically earliest sphalerite is dark brown, subhedral to xenomorphic, and 0.03–0.05 mm in size (Fig. 3B and C). Light brown sphalerite is xenomorphic and granular in form (0.05–0.1 mm), and present as veins in dark brown sphalerite (Fig. 3C). Dark brown sphalerite is cross-cut by light yellow sphalerite, which is xenomorphic, and 0.5–2.2 mm in size. These observations indicated that early precipitated sphalerites are darker than late ones (Fig. 3B and C; Fu, 2004), as observed in other Zn–Pb deposits in the SYG area (Han et al., 2007; Zhou et al., 2014). Galena is fine-grained, euhedral to subhedral, subhedral to xenomorphic, and 0.03–5 mm in size. Chalcopyrite occurs as massive patches and veins in primary ores, subhedral to xenomorphic, and 0.1–2 mm in size (Fig. 3D and E).

Nineteen Zn–Pb ore samples were collected at varies levels in the Tianbao ore block. Six, ten, and three samples were collected from No. 8 (height, 2036 m), No. 7 (height, 2074 m), and No. 6 (height, 2114 m) adits, respectively. Three massive chalcopyrite ore samples were collected at No. 8 adits. Twenty-five sphalerite, thirteen galena

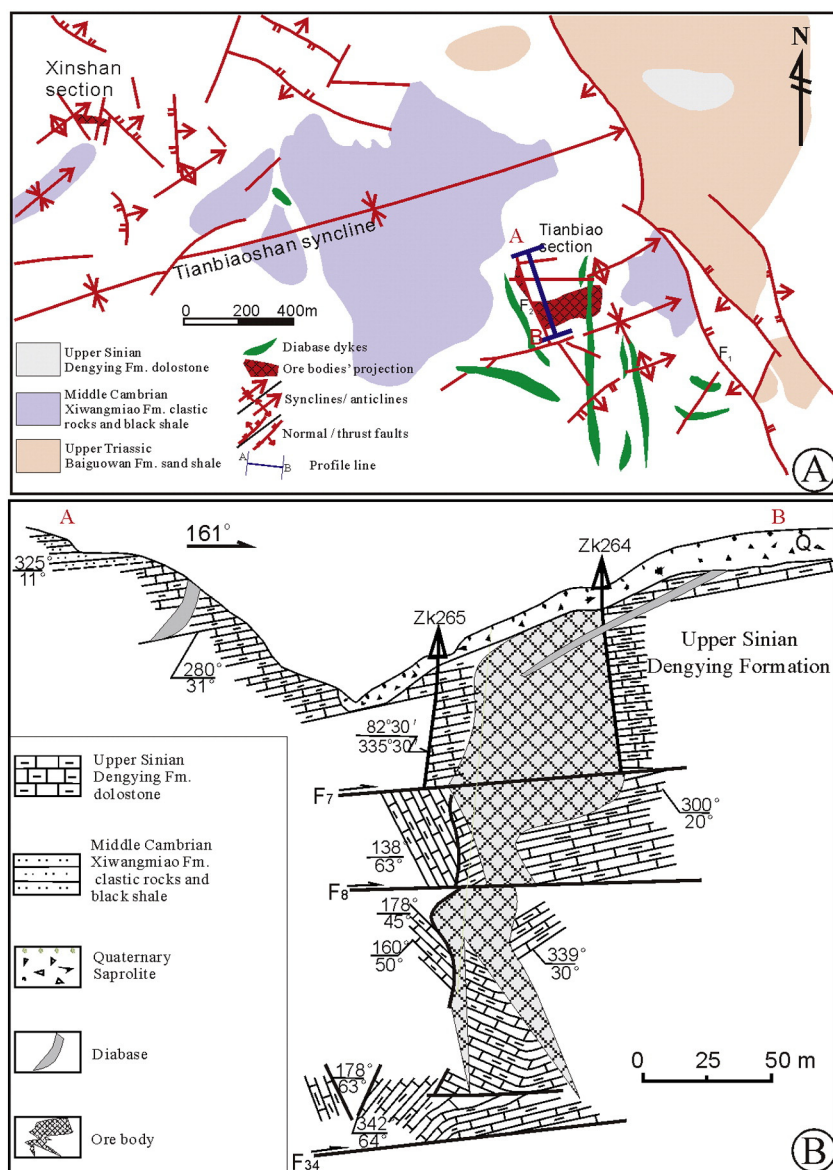


Fig. 2. Geological map (A) and the typical cross section (B) for the Tianbaoshan Zn–Pb–Cd deposit. Modified from Zhou et al. (2013).

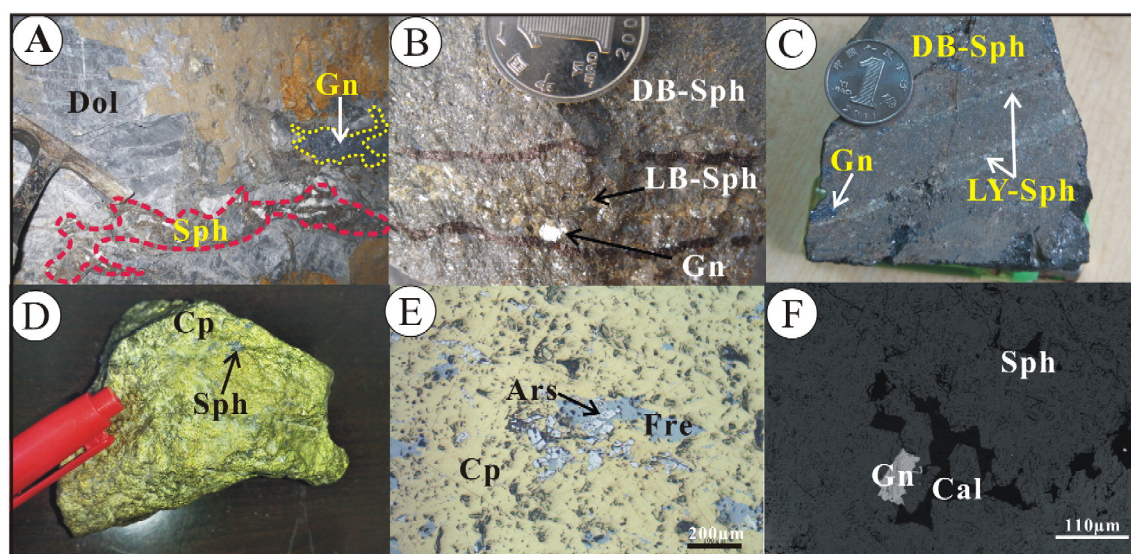


Fig. 3. (A) Field photograph of ore-body (Dol, dolostone; Gn, galena; Sph, sphalerite); (B) specimen photograph showing banded light-brown sphalerite (LB-Sph) and massive dark-brown sphalerite (DB-Sph); (C) specimen photograph showing banded light-yellow sphalerite (LY-Sph) and massive dark-brown sphalerite (DB-Sph); (D) specimen photograph showing massive chalcopyrite (Cp); (E) photo micrograph showing massive chalcopyrite (Cp) and spotted freibergite (Fre) and arsenopyrite (Ars); and (F) back-scatter electron (BSE) image showing galena (Gn) and calcite (Cal) micro-inclusions in sphalerite.

and three chalcopyrite grains (425 to 850 μm) separated from these ore samples are handpicked under a binocular microscope. Panels C and F in Fig. 3 show that galenas are present as micro-veins and/or micro-inclusions in sphalerites. Thus, it is hard to separate pure sphalerites from ores without galenas and calcites in the Tianbaoshan deposit.

3. Analytical techniques

As sphalerite is the main Cd-bearing mineral (Palero-Fernández and Martín-Izard, 2005; Zhu, 2014), galena and chalcopyrite are not measured for Cd isotopes. Less than 150 mg of sphalerite was accurately weighed into PTFE digestion vessels. Samples were first reacted with 3 ml of concentrated HNO_3 at 110 $^\circ\text{C}$ for more than 24 h and taken to dryness on a hot plate at 110 $^\circ\text{C}$. A final digestion of the dried residue obtained after HNO_3 dissolution was then performed by using 1 ml of concentrated HF and 1 ml of milli-Q water. After wards, the solution was heated at 110 $^\circ\text{C}$ to dryness. Finally 5 ml of 1% HNO_3 was added and the solution was transferred into a 15 ml polypropylene centrifuge tube. After centrifugation, 2 ml supernatant was transferred for trace element measurements, while another 2 ml supernatant was transferred for chemical purification. Before chemical purification, the 2 ml supernatant was evaporated to dryness at 110 $^\circ\text{C}$ followed by adding 2 ml of 2 N HCl. Cadmium was separated from matrix elements using anion exchange chromatography (Christophe et al., 2005; Gao et al., 2008), a modified procedure was selected, as described in Zhu et al. (2013) and Wen et al. (2015), with the Cd recovery of 99.82%. The potential interferences on Cd isotopes, including Sn, In, Zn, and other interfering matrix elements were presented at negligible levels relative to Cd.

After the adsorption of Cd onto the column, 10 ml of 2 N HCl, 30 ml of 0.3 N HCl, 20 ml of 0.06 N HCl, and 5 ml of 0.012 N HCl was passed one by one through the column, respectively (Zhu et al., 2013). The Cd was then eluted by using 20 ml of 0.0012 N HCl and the solution was evaporated to dryness at 110 $^\circ\text{C}$. After evaporation, the residue was dissolved in 3 ml of 1% HNO_3 , and 1 ml of the final solution was used for Cd measurement to monitor the Cd recovery, while the residue was then used for Cd isotope analysis.

Major and trace element of sphalerite were determined by inductively coupled plasma optical emission (ICP-OES) at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese

Academy of Sciences. Two standards have been selected for the measurement of major and trace element (ALSWAT01 and ALSWAT10, Inorganic Ventures, USA), and the relative deviation and the relative error are less than 10%.

The Cd isotope measurements were performed at the State Key Laboratory of Crust–Mantle Evolution and Mineralization at Nanjing University, using a Thermo-Scientific Neptune plus MC-ICP-MS coupled with membrane desolvation system (CETAC Aridus II). Samples and bracketing reference solutions were run in 2 blocks with 30 cycles per block. This system typically generated a total Cd signal of about 87 V/ppm at an uptake rate of $\sim 100 \mu\text{l}/\text{min}$, which corresponds to ca. 200 ng of analyzed Cd. After each run, the membrane desolvation system was rinsed with 5% (1 min) and 1% HNO_3 (1 min) until the signal intensity reached the original background level (generally after 2 min). The standard-sample bracketing (SSB) method was chose to calculate delta values. $\delta^{*110}\text{Cd} (\text{‰}) = [({}^{*110}\text{Cd}/{}^{110}\text{Cd})_{\text{sample}} / ({}^{*110}\text{Cd}/{}^{110}\text{Cd})_{\text{std}} - 1] \times 1000$, where * is the ${}^{114}\text{Cd}$, ${}^{113}\text{Cd}$, ${}^{112}\text{Cd}$ and ${}^{111}\text{Cd}$ isotope, and std. is the Nancy Spex Cd standard. Cd concentrations in samples and the Cd standard reference (Nancy Spex Cd standard) were matched within 10% (Christophe et al., 2005). A fractionated Cd metal sample (Münster Cd standard) has also been used as a second reference material, and the analyses of Münster Cd relative to Nancy Spex Cd yielded $\delta^{114/110}\text{Cd} = 4.48 \pm 0.04$. This result was identical to that of a previous study (Christophe et al., 2005), when accounting for the uncertainty. Accuracy and reproducibility were assessed by replicated analyses of the Münster Cd, which yielded an average $\delta^{114/110}\text{Cd} = 4.50 \pm 0.08$ (2σ , $n = 18$), within error in agreement with the previously published values by Christophe et al. (2005) and Zhu et al. (2013). The $\delta^{112/110}\text{Cd}_{\text{spex}}$ vs $\delta^{114/110}\text{Cd}_{\text{spex}}$ diagram (Fig. 4) shows that the Cd isotopic compositions of all sphalerite samples fall within the error for the equilibrium and kinetic theoretical mass fractionation lines, as is the case for both Nancy Spex and Münster Cd standards, indicating that isobaric interference has been efficiently removed by the chemical purification (matrix interference) and by the isobaric interference correction (e.g., Sn interference) during the measurements.

The sulfur isotope measurements were performed using a Thermo-Scientific MAT-253 at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. Samples were calibrated to $\delta^{34}\text{S}$ values relative to CDT of IAEA-S-1

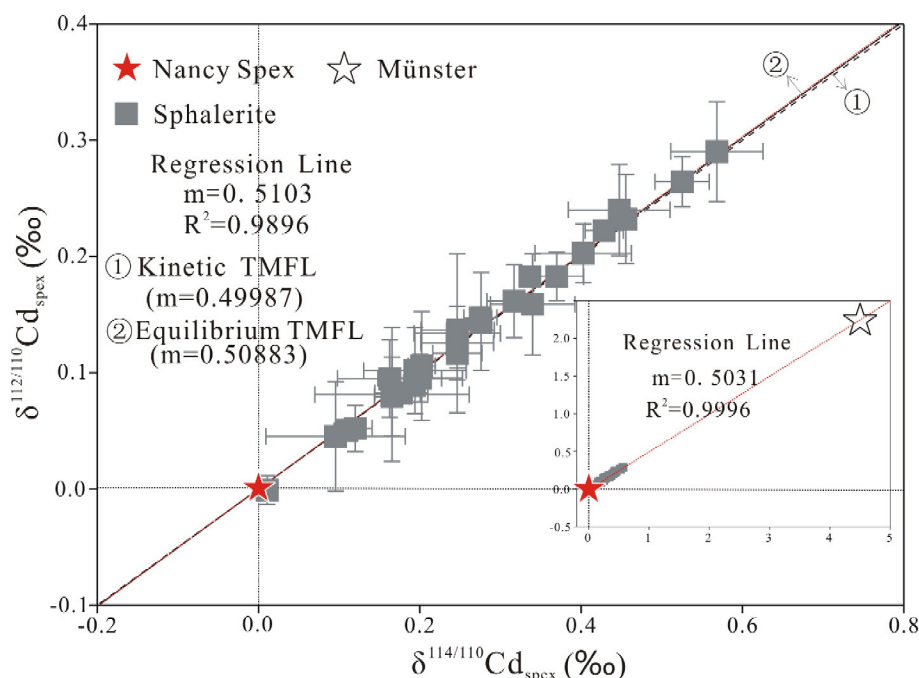


Fig. 4. A $\delta^{114/110}\text{Cd}_{\text{spex}}$ vs $\delta^{112/110}\text{Cd}_{\text{spex}}$ diagram for the samples from the Tianbaoshan deposit. All samples are within the error of the theoretical mass fractionation line (TMFL), on which a Cd standard (Münster Cd standard) of distinct compositions was also plotted.

($\delta^{34}\text{S} = -0.30\text{‰}$), IAEA-S-2 ($\delta^{34}\text{S} = 22.62\text{‰}$) and IAEA-S-3 ($\delta^{34}\text{S} = -32.49\text{‰}$). The analytical precision is less than 0.1‰ (2SD).

4. Results

Sulfur isotope compositions of sphalerite, chalcopyrite and galena separates are listed in Table 1. The $\delta^{34}\text{S}_{\text{CDT}}$ values of twenty-five sphalerite samples are within a narrow range from 4.0 to 5.0‰ , with a mean value of 4.7‰ (Fig. 5A); thirteen galena samples have $\delta^{34}\text{S}_{\text{CDT}}$ values ranging from 0.2 to 2.1‰ , with a mean value of 1.2‰ ; three chalcopyrite samples have a narrow range of $\delta^{34}\text{S}_{\text{CDT}}$ values between 4.3 and 4.9‰ . From bottom to top of the Tianbaoshan deposit, $\delta^{34}\text{S}_{\text{CDT}}$ values in sphalerites have no regular changes, but, $\delta^{34}\text{S}_{\text{CDT}}$ values in galena decreased from 2.1 to 0.2‰ (Table 1).

Sphalerite has $\delta^{114/110}\text{Cd}$ values ranging from 0.01 to 0.57‰ (Table 1; Fig. 5A), yielding an overall variation range of 0.56‰ , which is smaller than that reported by Zhu et al. (2013) (0.93‰ for sphalerites from five Zn–Pb deposits), but larger than that reported for continental sphalerite ores (0.34‰ ; Schmitt et al., 2009). The $\delta^{114/110}\text{Cd}$ values paragenetically do not vary spatially, but, decrease from early stage to late stage (Fig. 5B). This observation is contrasts to previous studies that earlier precipitated sphalerite has lower $\delta^{114/110}\text{Cd}$ values (Schmitt et al., 2009; Zhu et al., 2013; Yang et al., 2015).

Major and trace element concentrations of sphalerite are listed in Table 1. The Tianbaoshan sphalerites contain 44.8 ± 6.0 wt.% Zn and 1.0 ± 0.5 wt.% Fe in average; the Cd, Ca, Cu, Mg, Mn and Sb are consistently detected at mean concentrations of 3427 ± 1530 ppm, 2787 ± 3776 ppm, 532 ± 620 ppm, 1376 ± 1953 ppm, 18 ± 21 ppm, and 277 ± 363 ppm, respectively. In a large scale, the contents of major and trace element in sphalerite have no obviously changes from bottom to top of the Tianbaoshan deposit. However, in a small scale, our data show that early precipitated sphalerite has slightly higher Cd and Fe contents than late ones in a hand specimen (Table 1).

Obviously, the Zn levels in sphalerite are lower than that of pure sphalerite (ideal composition 67.1%). This may result from the presence of impurities in sphalerite, possibly in the form of small amounts of other minerals such as galena and calcite (Fig. 3C and F). Previous studies have also shown that the reported Zn + Fe concentrations are

as low as ~46% in sphalerites from the Tianbaoshan deposit (chemical analyses; Wang, 1992). Considering that sphalerite is the primary Cd-bearing mineral in ores, thus, there are no differences of Cd concentrations and its isotopic compositions between pure and impure sphalerite.

5. Discussion

5.1. Major and trace element in sphalerites

Geological studies showed that primary ores from the Tianbaoshan deposit mainly consist of dark brown sphalerites, which were cut by light brown and light yellow sphalerites (Fig. 3B and C). This can also be observed in other Zn–Pb deposits (McLimans et al., 1980; Han et al., 2007; Zhou et al., 2014). In this study, there is a trend that Cd and Fe concentrations in early precipitated sphalerites are basically higher than those of late precipitated ones as shown by five pairs of different stage sphalerites (e.g., HL-8-4; Table 1), indicating that trace elements were preferentially enriched in early precipitated sphalerite. Belissont et al. (2014) also confirmed that dark brown bands sphalerite from Saint-Salvy deposit (France) have higher Fe and Cd contents than light brown zones in a small scale ($n \times 100 \mu\text{m}$). Previous studies have shown that trace elemental fractionation and the overall concentrations are influenced by the crystallization temperature, metal source and the amount of sphalerite in the ore (Bethke and Borton, 1971; Belissont et al., 2014). Further study for trace element in different stage sphalerites needs to be conducted in the future.

The differences of trace element contents in sphalerite are caused by the source of the ore components, the fluid evolution and the mechanisms of precipitation, thus, the bulk trace element concentrations in sphalerite are intimately related to the type of the ore deposit (Cook et al., 2009; Ye et al., 2011; Belissont et al., 2014). Schwartz (2000) had summarized the Cd contents in sphalerites from about 300 Zn–Pb deposits, and the results showed that different types of lead–zinc deposits have different Cd contents in sphalerites. Based on Cd contents in sphalerites, the Zn–Pb deposits from the SYG area can be classified into three types: (I) low Cd concentrations Zn–Pb deposits (e.g., the Huize deposit), with a mean value of about 1000 ppm; (II) high Cd concentrations Zn–Pb deposits (e.g., the Fule deposit), with a mean

Table 1

Major and trace element concentrations coupled with Cadmium and sulfur isotopic compositions in the samples from the Tianbaoshan deposit.

Sample no.	Sample type	Stages	$\delta^{34}\text{S}_{\text{CDT}}$ ‰	$\delta^{112/110}\text{Cd}$ ‰	2σ ‰	$\delta^{114/110}\text{Cd}$ ‰	2σ ‰	Zn %	Fe %	Cd ppm	Ca ppm	Cu ppm	Mg ppm	Mn ppm	Sb ppm
HL-6-2	Sph(DB)	Early	4.9	0.29	0.04	0.57	0.06	42.46	1.35	4524	3953	334	947	17	354
HL-6-2	Gn		0.2												
HL-6-3	Sph(DB)	Early	4.6	0.12	0.01	0.25	0.03	45.63	1.32	2798	2165	213	605	8	119
HL-6-4	Sph(DB)	Early	4.5	0.23	0.04	0.46	0.01	42.84	1.25	2745	2077	438	1873	6	143
HL-7-1	Sph(DB)	Early	4.8	0.16	0.04	0.34	0.05	44.89	0.85	4296	4825	408	2528	21	286
HL-7-1	Sph(LB)	Middle	4.8	0.13	0.03	0.25	0.05	48.41	0.80	4111	1614	316	597	9	166
HL-7-1	Gn		1.0												
HL-7-2	Sph(DB)	Early	4.7	0.08	0.03	0.17	0.02	44.82	0.94	3488	4942	419	2859	24	196
HL-7-2	Sph(LB)	Middle	4.9	0.05	0.02	0.12	0.02	48.46	0.86	4113	1225	322	319	8	152
HL-7-2	Gn		0.8												
HL-7-3	Sph(DB)	Early	4.9	0.15	0.01	0.28	0.02	44.71	0.90	4402	6250	525	3422	23	372
HL-7-3	Sph(LB)	Middle	4.8	0.09	0.03	0.16	0.06	49.49	0.81	4270	1657	334	622	9	129
HL-7-3	Gn		0.8												
HL-7-6	Sph(DB)	Early	4.5	0.08	0.01	0.18	0.03	46.64	1.24	3445	4181	809	2269	32	246
HL-7-8	Sph(DB)	Early	4.6	0.14	0.00	0.25	0.05	45.35	0.97	3591	1013	617	760	28	269
HL-7-8	Gn		0.9												
HL-7-10	Sph(DB)	Early	4.6	0.13	0.07	0.25	0.05	46.93	1.06	3320	3549	733	2060	27	201
HL-7-10	Gn		0.8												
HL-7-22	Sph(DB)	Early	4.7	0.14	0.04	0.28	0.00	42.67	1.04	2474	1122	323	1903	12	174
HL-7-23	Sph(DB)	Early	4.9	0.18	0.02	0.37	0.03	45.91	1.25	3354	666	992	309	7	354
HL-7-23	Gn		1.8												
HL-7-25	Sph(DB)	Early	5.0	0.05	0.01	0.11	0.02	46.25	1.22	3273	783	1162	308	14	263
HL-7-25	Gn		1.1												
HL-7-26	Sph(DB)	Early	4.8	0.00	0.01	0.01	0.01	40.23	0.86	3273	781	526	1101	10	470
HL-7-26	Gn		1.4												
HL-8-3	Sph(DB)	Early	4.5	0.24	0.04	0.45	0.06	44.14	1.23	2534	4279	423	1937	25	162
HL-8-3	Gn		2.1												
HL-8-4	Sph(DB)	Early	4.6	0.26	0.02	0.53	0.03	46.64	1.14	2608	3714	780	1348	15	150
HL-8-4	Sph (LY)	Late	4.3	0.22	0.01	0.43	0.02	48.47	0.36	2415	3582	63	726	8	13
HL-8-4	Gn		1.3												
HL-8-5	Sph(DB)	Early	4.8	0.09	0.01	0.19	0.00	45.58	1.10	1998	5462	546	2510	30	78
HL-8-10	Sph(DB)	Early	4.7	0.05	0.05	0.10	0.09	43.48	1.35	4266	6747	1317	2994	27	886
HL-8-10	Gn		1.4												
HL-8-13	Sph(DB)	Early	4.7	0.10	0.04	0.19	0.06	41.85	1.33	3348	1362	871	1183	22	413
HL-8-13	Gn		1.6												
HL-8-16	Sph(DB)	Early	4.0	0.20	0.03	0.40	0.06	46.66	1.27	4887	1916	798	663	15	494
HL-8-16	Sph(LB)	Middle	4.8	0.11	0.05	0.2	0.02	36.90	0.79	3058	989	265	318	7	438
HL-8-16	Sph (LY)	Late	4.3	0.08	0.06	0.17	0.10	39.25	0.84	3100	825	274	245	47	393
TB-1	Ccp		4.9												
TB-2	Ccp		4.7												
TB-3	Ccp		4.3												

Note: Sph, sphalerite; Gn, galena; (DB), dark brown; (LB), light brown; (LY), light yellow; Ccp, Chalcopryrite; HL-6-*, HL-7-* and HL-8-* were sampled from Nos. 6, 7, 8 adit, respectively.

value of about 15,000 ppm; and (III) moderate Cd concentrations Zn–Pb deposits (e.g., the Tianbaoshan deposit), with a mean value of about 4000 ppm (Fig. 6A). Zhu et al. (2013) suggested that different genetic Zn–Pb deposits have different Cd content and isotope compositions in sphalerite. Fig. 7 shows that low and high Cd concentrations Zn–Pb deposits (e.g., the Huize deposit and the Fule deposit) show larger Cd isotope fractionation than moderate Cd Zn–Pb deposits (e.g., the Tianbaoshan deposit).

5.2. Possible sources of sulfur

Primary ores in the Tianbaoshan deposit have very simple S-bearing mineralogy that lacks sulfates, indicating that sulfur isotope compositions of sulfides reflect $\delta^{34}\text{S}_{\text{S-fluids}}$ values (Ohmoto, 1972). Based on the $\delta^{34}\text{S}_{\text{CDT}}$ values of sphalerite and coexisting galena, the calculated $\delta^{34}\text{S}_{\text{S-fluids}}$ value is 4.2‰ (Fig. 7), which is consistent with previous study (4.7‰; Wang et al., 2000). Meanwhile, $\Delta^{34}\text{S}_{\text{sulphate-galena}}$ of

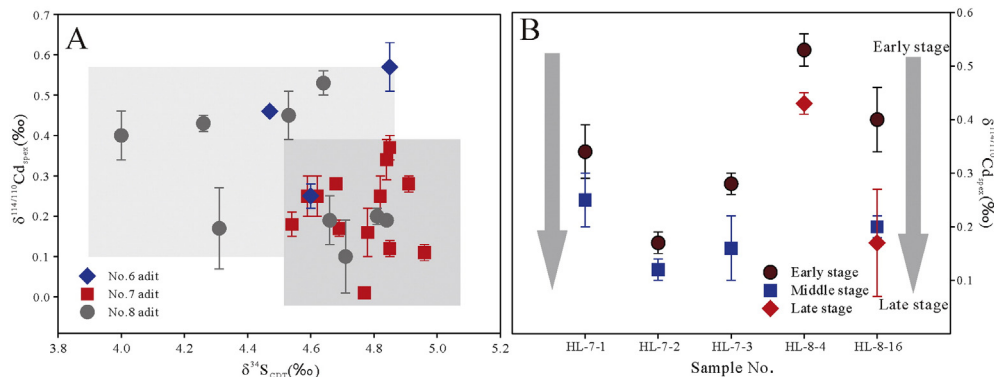


Fig. 5. A: Scatter diagrams of $\delta^{34}\text{S}_{\text{CDT}}$ values and $\delta^{114/110}\text{Cd}$ values for sphalerites; B: Cd isotope compositions in different stages sphalerite in five primary ores.

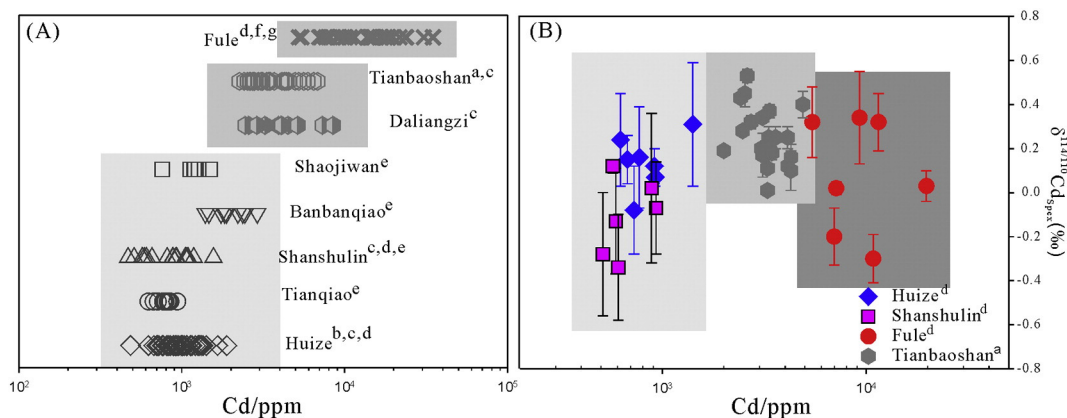


Fig. 6. The Cd concentrations (A) and $\delta^{114/110}\text{Cd}_{\text{spex}}$ values (B) in sphalerite from different Zn–Pb deposits in SYG area. Data resources: ^athis study; ^bHan et al., 2007; ^cFu, 2004; ^dZhu et al., 2013; ^eZhou et al., 2011; ^fZhu, 2014; ^gSi, 2005.

thirteen sphalerite–galena pairs range from +2.4 to +4.7‰ (Fig. 7; Table 2). Assuming sulfides precipitation under thermal equilibrium conditions, the sphalerite–galena pairs correspond to ore-forming temperatures of 130 to 290 °C (Table 2; Clayton, 1981), with a mean value of 190 °C. These calculated temperatures are consistent with the homogenization temperatures derived from previous fluid inclusion studies (80 to 275 °C; Yu, 2014), indicating that the precipitation of sulfide minerals occur under sulfur isotope equilibrium.

In the SYG metallogenic province, $\delta^{34}\text{S}_{\text{CDT}}$ values of sphalerites and galenas can be classified into two groups: (I) $\delta^{34}\text{S}_{\text{CDT}}$ values between 11‰ to 19‰, such as the Huize deposit, the Shanshulin deposit and the Qingshan deposit (Fig. 1) (Zhang, 2008; Zhou, 2011; Zhou et al., 2014; Han et al., 2007); and (II) $\delta^{34}\text{S}_{\text{CDT}}$ values between 1‰ to 8‰, such as the Jinshachang deposit and the Chipu deposit (Fig. 1) (Zhang, 2008; Bai et al., 2013; Wu, 2013). Sulfur isotope geochemistry in the Tianbaoshan deposit has also been systemically studied to assess alternative interpretations: (1) sulfur was derived from evaporates in the host strata, and the thermo-chemical sulfate reduction (TSR) resulted in lower $\delta^{34}\text{S}_{\text{CDT}}$ values than other Zn–Pb deposits in the SYG metallogenic province (Shao and Li, 1997; Li, 2003; Fu, 2004; Zhang, 2008; Wu, 2013; Zhou et al., 2013); (2) Guan and Li (1999) and Kou et al. (2015) pointed out that sulfur could be derived from a mixture of mantle and sedimentary rock sources.

Some amount of massive chalcopyrite ores have been revealed in the No. 8 adit in the Tianbaoshan deposit (Fig. 3D and E) with the $\delta^{34}\text{S}_{\text{CDT}}$ values between 4.3 to 4.9‰, indicating that the Tianbaoshan deposit has very different minerals and ore genesis from other Zn–Pb deposit in the SYG metallogenic province. Our data show that sphalerites and galenas have $\delta^{34}\text{S}_{\text{CDT}}$ values ranging from 0.2 to 5.0‰ and the calculated $\delta^{34}\text{S}_{\Sigma\text{S-fluids}}$ value is 4.2‰. Previous studies demonstrated that sulphates in the host strata have high $\delta^{34}\text{S}_{\text{CDT}}$ values ranging from 30.5 to 34.8‰ (Liu and Lin, 1999; Bai et al., 2013; Zhou et al., 2013). Thus, even if $\Delta^{34}\text{S}_{\text{sulphate-sulfide}}$ could be up to +20‰ in the sulfide reduction process (Machel et al., 1995), the $\delta^{34}\text{S}_{\text{CDT}}$ value of reduced sulfur in the Tianbaoshan deposit is about 10 to 15‰, higher than those of the reduced sulfur in sulfides from evaporates in the host strata. In addition, the calculated $\delta^{34}\text{S}_{\Sigma\text{S-fluids}}$ value is also higher than that of mantle-derived sulfur ($0 \pm 3\%$; Chaussidon et al., 1989) and depleted mantle sulfur (-1.3% ; Labidi et al., 2013), suggesting that the source of S is not the mantle. We conclude that sulfur could be derived from leaching of volcanic or intrusive rocks, which is just as likely a source of S. Geological investigation also shows that there is a large amount of volcanic or intrusive rocks (Meso- to Neo-Proterozoic folded basements) underneath the Dengying Formation (Liu and Lin, 1999; Fu, 2004). Thus, we suggest that reduced sulfur of the Tianbaoshan deposit was derived from the basement.

5.3. Possible causes of cadmium isotope variations

The $\delta^{114/110}\text{Cd}$ values in sphalerites from the Tianbaoshan deposit is varying from 0.01 to 0.57‰. The $\delta^{114/110}\text{Cd}$ values in sphalerites from the No. 8, No. 7 and No. 6 adits varying from 0.10 to 0.45‰, 0.01 to 0.37‰, and 0.25 to 0.57‰, respectively. These results indicate no systematic vertical changes in $\delta^{114/110}\text{Cd}$. Meanwhile, we infer that most of Cd in ore-forming fluids might be precipitated in sulfides. Thus, as the main Cd-bearing mineral in Zn–Pb deposits, the average of $\delta^{114/110}\text{Cd}$ values in sphalerites ($\delta^{114/110}\text{Cd} = 0.27\%$) could represent that of ore-forming fluids.

Significant variations were reported in the $\delta^{114/110}\text{Cd}$ values of sphalerite separates from the Zn–Pb deposits in SYG area (Zhu et al., 2013; Zhu, 2014), including the Huize deposit (-0.08 to 0.32%), the Shanshulin deposit (-0.34 to 0.12%) and the Fule deposit (-0.30 to 0.32%). These studies indicate that the earliest sphalerite precipitated from the hydrothermal systems was enriched in lighter Cd isotopes, followed by the precipitation of sphalerite with progressively heavier Cd isotopic compositions. Meanwhile, Schmitt et al. (2009) suggested that the sulfides are isotopically lighter in Cd isotopes than associated vent fluids. Previous studies by Yang et al. (2015) and Horner et al. (2011) also showed that light isotopes fractionate into solid phase rather than solutions. However, Cd isotope compositions of five pairs of color-different sphalerites from the Tianbaoshan deposit showed that earlier precipitated sphalerite has higher $\delta^{114/110}\text{Cd}$ value. Compared with the Huize, the Shanshulin and the Fule Zn–Pb deposits in SYG area, sphalerites from the Tianbaoshan deposit have moderate Cd contents and Cd isotope fractionation (Fig. 6B), indicating that characteristics of Cd isotopic compositions in the Tianbaoshan Zn–Pb deposit are different from previous studied Zn–Pb deposits, and the ore genesis of this deposit may be of special. In addition, we suggest that Cd and its isotopes can be a potential proxy to trace the ore-forming process and distinguish the origin of Zn–Pb deposits.

At present, the behavior of Cd isotopes in Zn–Pb deposits is still unclear. Recent work (Yang et al., 2015; Zhang et al., 2013) showed that two interpretations may be proposed to explain the variations of $\delta^{114/110}\text{Cd}$ values in the Tianbaoshan deposit: (I) temperature decreasing of ore-forming fluids; or (II) varying of Cd isotopic compositions in the ore-forming fluids. Yang et al. (2015) demonstrated that Cd isotopes show a smaller fractionation at high temperature, indicating that temperature variation of ore-forming fluids could result in heavier Cd isotopes enriched in earlier precipitated sphalerite. Sulfur isotope geothermometry for paragenetic sphalerite and galena confirmed that fluid temperature is decreased from bottom (300 °C) to the top (150 °C) of the Tianbaoshan deposit (Table 2). Thus, if the Cd isotopic fractionation between ore-forming fluids and sphalerites is smaller at

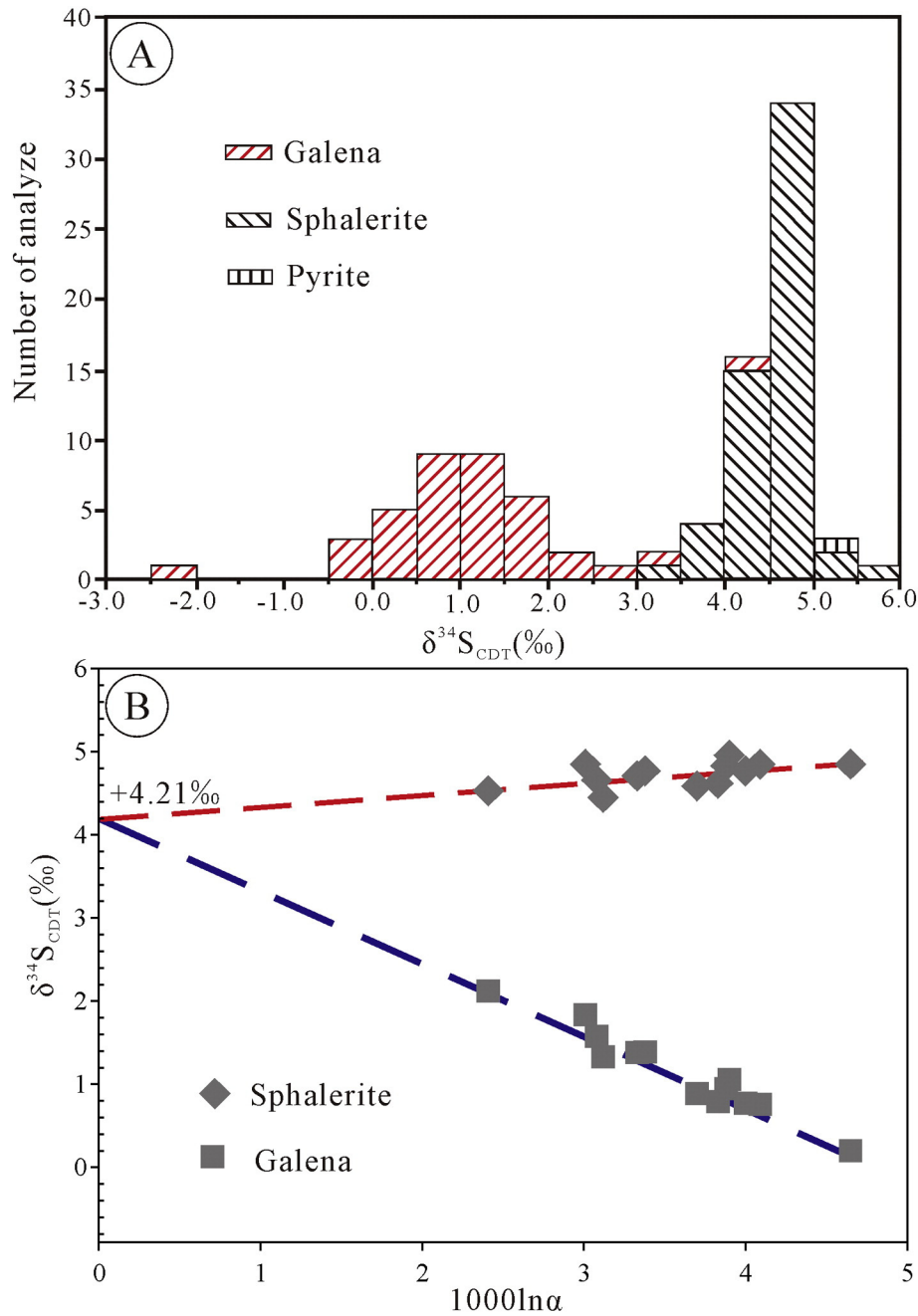


Fig. 7. A: Sulfur isotopic composition histogram of the Tianbaoshan Zn–Pb–Cd deposit; B: plot of $\delta^{34}\text{S}_{\text{CDT}}$ vs $1000\ln\alpha$ for sphalerite–galena mineral pairs.

Table 2

Sulfur isotope geothermometry for coexisting sphalerite and galena crystallized of the Tianbaoshan deposit.

Sample no.	Sample type	$\delta^{34}\text{S}_{\text{CDT}}$	Mean (‰)	$\Delta^{34}\text{S}_{\text{Sph-Gn}}$ (‰)	T (°C)	Sample no.	Sample type	$\delta^{34}\text{S}_{\text{CDT}}$	Mean (‰)	$\Delta^{34}\text{S}_{\text{Sph-Gn}}$ (‰)	T (°C)
HL-6-2	Sph(DB)	4.9	4.9	4.7	129	HL-7-23	Sph(DB)	4.9	4.9	3.1	222
HL-6-2	Gn	0.2	0.2			HL-7-23	Gn	1.8	1.8		
HL-7-1	Sph(DB)	4.8	4.8	3.8	174	HL-7-25	Sph(DB)	5.0	5.0	3.9	168
HL-7-1	Sph(LB)	4.8				HL-7-25	Gn	1.1	1.1		
HL-7-1	Gn	1.0	1.0			HL-7-26	Sph(DB)	4.8	4.8	3.4	200
HL-7-2	Sph(DB)	4.7	4.8	4.0	163	HL-7-26	Gn	1.4	1.4		
HL-7-2	Sph(LB)	4.9				HL-8-3	Sph(DB)	4.5	4.5	2.4	290
HL-7-2	Gn	0.8	0.8			HL-8-3	Gn	2.1	2.1		
HL-7-3	Sph(DB)	4.9	4.9	4.0	163	HL-8-4	Sph(DB)	4.6	4.4	3.1	222
HL-7-3	Sph(LB)	4.8				HL-8-4	Sph(LY)	4.2			
HL-7-3	Gn	0.8	0.9			HL-8-4	Gn	1.3	1.3		
HL-7-8	Sph(DB)	4.6	4.6	3.7	180	HL-8-10	Sph(DB)	4.7	4.7	3.3	207
HL-7-8	Gn	0.9	0.9			HL-8-10	Gn	1.4	1.4		
HL-7-10	Sph(DB)	4.6	4.6	3.8	174	HL-8-13	Sph(DB)	4.7	4.7	3.1	222
HL-7-10	Gn	0.8	0.8			HL-8-13	Gn	1.6	1.6		

high temperature than at low temperature, earlier precipitated sphalerite could be enriched in heavier Cd isotopes. However, heavy Cd isotopes were not only enriched in high temperature sphalerite (e.g., HL-8-3), but also in low temperature sphalerite (e.g., HL-6-2), indicating that temperature was not the major factor to control the distribution of Cd isotopes. The experiments of Zhang et al. (2013) showed that large isotopic fractionation was found during leaching process between leached liquids and residuum from sulfides, tailings and oxidized ores (up to 0.53‰, 0.49‰ and 0.31‰, respectively), suggesting that heavy Cd isotopes are easier to be leached from solid. Thus, it's reasonable to assume that Cd isotope compositions of the ore-forming fluids are heterogeneous and heavy Cd isotopes were enriched in original ore-forming fluids, which resulted in early stage sphalerite (precipitated from original ore-forming fluids) being rich in heavy Cd isotopes.

In addition, Gagnevin et al. (2012) suggested that sphalerite dominated by the bacteriogenic S isotope signature is exclusively related to heavy Zn isotopes from the world-class Navan Zn–Pb deposit. However, no evidence has been proved that bacteriogenic S had been involved in the formation of the Tianbaoshan deposit. Thus, we suggest that the mineral precipitation and the variations of Cd isotope compositions in the ore-forming fluids could result in heavy Cd isotopes enrichment in early precipitated sphalerite.

5.4. Possible ore genesis

The ore genesis of the Tianbaoshan deposit is still debated (Wang et al., 2000; Zhang, 2008; Zhou et al., 2013; Zhang et al., 2015). Based on the data obtained in this study, we conclude that the origin of the Tianbaoshan deposit is different from typical Zn–Pb deposits (e.g., the Huize deposit and the Fule deposit) in SYG area. The principal evidences concerning the origin of the deposit are as follows: (I) Geological studies showed that the Tianbaoshan deposit is hosted in older strata than typical Zn–Pb deposits (e.g., the Huize deposit; detailed information see Khin Zaw et al., 2007); (II) Some amount of chalcopyrite has been revealed, indicating that the Tianbaoshan deposit has different mineral and metallogenic elements assemblage from other typical Zn–Pb deposits (e.g., the Huize deposit); (III) The $\delta^{34}\text{S}_{\text{CDT}}$ values of sulfides are small ($\delta^{34}\text{S}_{\text{CDT}} = 4.2\text{‰}$), and with a narrow range, indicating that reduced sulfur in the Tianbaoshan deposit was derived from the Meso- to Neo-Proterozoic basements; (IV) Characteristics of Cd isotopic compositions in the Tianbaoshan Zn–Pb deposit are quite different from previous Zn–Pb deposit (e.g., the Fule deposit; Zhu et al., 2013) and heavy Cd isotopes were enriched in early precipitated sphalerite.

Previous studies have showed that the basement, located in the SYG area, could be a potential source for the formation of the Tianbaoshan deposit (Wang et al., 2000; Zhou et al., 2013). The S isotopic data in this study also showed that sulfur was derived from Meso- to Neo-Proterozoic folded basements. Thus, we conclude that the basement was an important potential source, which may result in unique geochemical characteristics (e.g., S and Cd isotopes) of the studied deposit.

6. Conclusion

In the Tianbaoshan deposit, major and trace element in sphalerite showed that early precipitated (dark brown) sphalerite seems to have higher concentrations of trace elements (e.g., Fe, Cd, Mg and Ca) than late precipitated ones (light color) in a hand specimen, but factors that controlled the distribution of trace element in sphalerites from different hand specimens are still unclear.

In this study, we have conducted a combined research of cadmium and sulfur isotopic compositions in sulfides. The calculated ore-forming temperatures are regularly decreased from bottom (290 °C) to top (130 °C) and the calculated $\delta^{34}\text{S}_{\text{CDT}}$ value is 4.2‰, which

are consistent with previous studies (Wang et al., 2000; Yu, 2014; Zhou et al., 2013). The $\delta^{34}\text{S}_{\text{CDT}}$ values of sulfides (0.2–5.0‰) from the Tianbaoshan deposit are not only much lower than that of evaporates (30.5–34.8‰) in the host strata, but also higher than mantle-derived sulfur ($0 \pm 3\text{‰}$). Thus, we suggest that reduced sulfur was derived from leaching of the basement. Meanwhile, our data show that the $\delta^{114/110}\text{Cd}$ values in sphalerites have no spatial variations, and the variations of $\delta^{114/110}\text{Cd}$ value in sphalerite have no correlations with fluid temperature. However, early stage sphalerite was enriched in heavy Cd isotopes, and this is contrary to previous study (Schmitt et al., 2009; Zhu et al., 2013; Yang et al., 2015). Based on previous work by Zhang et al. (2013), we proposed that the decreasing of $\delta^{114/110}\text{Cd}$ values in ore-forming fluid could be the potential mechanism that resulted in early precipitated sphalerite enriched in heavy Cd isotopes.

This study firstly reported the S and Cd isotopic compositions of sphalerite from the Tianbaoshan deposit. The results show that characteristics of S and Cd isotopic compositions are different from other Zn–Pb deposit (e.g., the Huize and Fule deposit), and these differences could give us a new insight into the origin of the Tianbaoshan deposit. However, more work should be done to enhance the conclusions of this study in the future, including the S and Cd isotopic compositions of the potential source rocks.

Conflict of interest

We have no conflicts of interest to declare.

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Appendix A

Appendix Table

Sulfur isotopic composition of sphalerite and galena of the Tianbaoshan deposit

Sample no.	Sample type	Stages	Instrumental data	Average $\delta^{34}\text{S}_{\text{CDT}}$	2SD	Cited $\delta^{34}\text{S}_{\text{CDT}}$ in the study
HL-6-2	Sph(DB)	Early	4.86 4.83	4.85	0.05	4.9
HL-6-2	Gn		0.19 0.21	0.20	0.03	0.2
HL-6-3	Sph(DB)	Early	4.56 4.63	4.59	0.10	4.6
HL-6-4	Sph(DB)	Early	4.51 4.43	4.47	0.12	4.5
HL-7-1	Sph(DB)	Early	4.88 4.81	4.84	0.09	4.8
HL-7-1	Sph(LB)	Middle	4.83 4.81	4.82	0.04	4.8
HL-7-1	Gn		0.95 0.95	0.95	0.01	1.0
HL-7-2	Sph(DB)	Early	4.72 4.66	4.69	0.09	4.7
HL-7-2	Sph(LB)	Middle	4.84 4.86	4.85	0.03	4.9
HL-7-2	Gn		0.79 0.74	0.77	0.07	0.8
HL-7-3	Sph(DB)	Early	4.92 4.91	4.91	0.01	4.9
HL-7-3	Sph(LB)	Middle	4.81 4.75	4.78	0.09	4.8
HL-7-3	Gn		0.77 0.75	0.76	0.02	0.8

Appendix Table (continued)

Sample no.	Sample type	Stages	Instrumental data	Average $\delta^{34}\text{S}_{\text{CDT}}$	2SD	Cited $\delta^{34}\text{S}_{\text{CDT}}$ in the study
HL-7-6	Sph(DB)	Early	4.58 4.50	4.54	0.12	4.5
HL-7-8	Sph(DB)	Early	4.60 4.58	4.59	0.03	4.6
HL-7-8	Gn		0.86 0.93	0.89	0.10	0.9
HL-7-10	Sph(DB)	Early	4.63 4.62	4.62	0.01	4.6
HL-7-10	Gn		0.80 0.79	0.79	0.02	0.8
HL-7-22	Sph(DB)	Early	4.64 4.71	4.68	0.10	4.7
HL-7-23	Sph(DB)	Early	4.88 4.83	4.85	0.06	4.9
HL-7-23	Gn		1.82	1.84	0.04	1.8
HL-7-25	Sph(DB)	Early	4.98 4.93	4.96	0.08	5.0
HL-7-25	Gn		1.06 1.07	1.06	0.02	1.1
HL-7-26	Sph(DB)	Early	4.81 4.74	4.77	0.10	4.8
HL-7-26	Gn		1.40 1.38	1.39	0.02	1.4
HL-8-3	Sph(DB)	Early	4.53 4.53	4.53	0.01	4.5
HL-8-3	Gn		2.15 2.10	2.12	0.06	2.1
HL-8-4	Sph(DB)	Early	4.67 4.62	4.64	0.07	4.6
HL-8-4	Sph(LY)	Late	4.27 4.25	4.26	0.03	4.3
HL-8-4	Gn		1.32 1.33	1.33	0.02	1.3
HL-8-5	Sph(DB)	Early	4.86 4.81	4.84	0.07	4.8
HL-8-10	Sph(DB)	Early	4.74 4.68	4.71	0.08	4.7
HL-8-10	Gn		1.37 1.39	1.38	0.04	1.4
HL-8-13	Sph(DB)	Early	4.68 4.65	4.66	0.06	4.7
HL-8-13	Gn		1.54 1.62	1.58	0.12	1.6
HL-8-16	Sph(DB)	Early	3.99 4.02	4.00	0.04	4.0
HL-8-16	Sph(LB)	Middle	4.79 4.83	4.81	0.06	4.8
HL-8-16	Sph(LY)	Late	4.32 4.29	4.31	0.05	4.3
TB-1	Chalcopyrite		4.90 4.86	4.88	0.05	4.9
TB-2	Chalcopyrite		4.69 4.66	4.68	0.05	4.7
TB-3	Chalcopyrite		4.31 4.33	4.32	0.02	4.3

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