Characteristics of Cd isotopic compositions and their genetic significance in the lead-zinc deposits of SW China

ZHU ChuanWei[1,2], WEN HanJie[1]*, ZHANG YuXu[1], FAN HaiFeng[1], FU ShaoHong[1],
XU Juan[3] & QIN TingRong[4]

[1] *State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China;*
[2] *University of Chinese Academy of Sciences, Beijing 100049, China;*
[3] *State Key Laboratory of Marine Environment Science (Xiamen University), Xiamen 361005, China;*
[4] *Non-Ferrous Metals and Nuclear Industry Geological Exploration Bureau of Guizhou, Liupanshui 553004, China*

Up to now, the evaporation and condensation, as well as the biological absorption and inorganic absorptions, have been proved to be major factors in Cd isotope fractionation. And Cd isotopes have been widely applied in studies on the universal evolution and marine environment and so on. However, only a few researches have been conducted in applying Cd isotopes to trace the source of metallogenic material and the evolution of the ore-forming fluid in a complex mineralization environment, especially in a hydrothermal ore-formation system. We measured the Cd isotopic compositions of sphalerite, galena, and ores from five lead-zinc deposits in SW China, and found that the $\delta^{114/110}$Cd values varied from −1.53‰ to 0.34‰, with a total range of 1.87‰, which is greater than most of measured geological samples. Meanwhile, through contrasting the Cd content with Cd isotopic compositions of different deposits, it may be concluded that different genetic lead-zinc deposits have different Cd content and isotopic compositions, which could be a tool for the studies on the origin of ore deposits. Also, the biomineralization and crystal fractionation may also result in Cd isotope fractionation. In a word, although the research of Cd isotopes is presently at the preliminary stage (especially in hydrothermal ore-formation system), this study demonstrated that Cd isotopes can give a clue in tracing the evolution of ore-forming fluid and metallogenic environment.

dispersed elements, Cd isotopes, isotope fractionation, lead-zinc deposits, isotopic tracer

Cadmium (Cd) is a typical dispersed element, but not an extremely rare element in the Earth's crust (about 0.2 ppm) (Tu et al., 2004). Accordingly, for Cd to form independent mineral is difficult. There are twelve Cd minerals which were proved by the International Mineralogical Association (IMA). Due to the low concentration and the difficulty to form independent minerals, Cd does not form specific ore deposits. However, Cd is a thiophile element, which can be hosted in other minerals as isomorphic impurities (e.g., Cd can substitute extensively for Zn in sphalerite) and even reach the pay grade. Cd always occurs as an associated element in the ore deposits of other elements, and there is a tendency for Cd to be enriched in metallic deposits, especially in low-medium lead-zinc deposits. However, the accumulation characteristics for Cd are different in various lead-zinc deposits. For example, the content of Cd in sphalerite (Cd_{sp}) is greatly changed in different types of lead-zinc deposits, and the highest concentrations of Cd are sphalerite ores in Mississippi Valley-type (MVT) deposits (the mean

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content of Cd was 4850 ppm from 106 MVT deposits), the lowest are volcanic-associated exhalative (VOLCEX) and the sediment-hosted exhalative (SEDEX) (the mean value for 87 VOLCEX deposits is 2360 ppm Cd_{sp} and for 19 SEDEX 2560 ppm Cd_{sp}), and 54 Skarn deposits (3540 ppm Cd_{sp}) have intermediate concentrations (Schwartz, 2000). Obviously, these differences are resulted from several factors during mineralization process, such as inhomogeneity of primary chemical compounds, Cd/Zn ratio, fluid property, the quantity and species of ligand in mineralizing fluid (Cl^-, HS^-, S^{2-}).

With the development of analytical instrumentation such as thermal ionization mass spectrometer (TIMS) and multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), a new isotopic system (non-traditional stable isotopes) has an explosive advances (e.g., Fe, Cu, Zn, Se, Mo, Cr, Hg, Ca). Meanwhile, these new isotopic systems are widely applied to mineral deposits, environmental science and etc., and become an important geochemical proxy for scientists. As a dispersed element, Cd has its own special isotope fractionation effect and its isotopic study is becoming more and more important, playing a unique role in tracing field (Fan et al., 2009).

In nature, Cd has eight isotopes, they are ^{106}Cd (1.25%), ^{108}Cd (0.89%), ^{110}Cd (12.5%), ^{111}Cd (12.8%), ^{112}Cd (24.1%), ^{113}Cd (12.2%), ^{114}Cd (28.7%), and ^{116}Cd (7.49%) (Christophe et al., 2005). Currently, the mechanism of isotope fractionation of Cd is not well understood; however, preliminary studies indicated that evaporation, condensation, and absorption mechanisms can result in Cd isotope fractionation. In addition, uptake of dissolved seawater Cd by phytoplankton can generate kinetic isotope effects, and phytoplankton preferentially takes up lighter isotopes of Cd such that light isotopes are enriched in organic matrix (Ripperger et al., 2007; Lacan, et al., 2006). Also, Cd isotope fractionation has been observed in inorganic adsorption process. Studies by Schmitt et al. (2009) have proved that the range of $\delta^{114/110}$Cd values in Fe-Mn hydrogenic nodules was from −0.16‰ to 0.35‰. The above-mentioned processes of Cd isotope fractionation may be the main reasons that resulted in the enrichment of heavier isotopes of Cd in the seawater. Cadmium is a highly volatile element which displays obviously stable isotopic effects when evaporation and condensation processes happened during the formation of the universe (Wombacher et al., 2003, 2004, 2008). As a result, Cadmium isotopic compositions could be used to trace the source of meteorites, lunar samples and etc., and also trace the evolution of the universe (Sands et al., 2001; Schediwy et al., 2006). As interpreted by Wombacher et al. (2003), ordinary chondrite and some enstatite chondrites have large isotopic effects, and the analyses displayed that the range of $\delta^{114/110}$Cd values was from −8‰ to 16‰. Moreover, the Cd isotopic compositions of type I, II, EH4 enstatite chondrites, eucrites, and the bulk silicate Earth

(BSE) are identical at $\delta^{114/110}$Cd $\approx 0\pm0.4$‰. This result indicated that the portion of the solar nebula from which the inner solar system bodies were accreted was homogeneous with respect to its Cd isotope composition.

Up to now, most of studies of Cd isotopes focus on meteorite and lunar samples to trace the evolution of nebula; Cd isotopes also have been used to trace the cycling and evolution of marine nutrients (Sands et al., 2001; Wombacher et al., 2003; Wombacher et al., 2004; Schediwy et al., 2006; Lacan et al., 2006; Ripperger et al., 2007; Wombacher et al., 2008; Schmitt et al., 2009). As an important toxic element, Cd isotope also has been used to trace the pollution sources in recent years (Christophe et al., 2006). The lead-zinc deposits are one of the most important reservoirs of Cd element in the Earth, and there are few studies focused on whether the Cd isotopes can be used to trace the ore-forming metals or the evolution processes of mineralization in lead-zinc deposits. So, exploring the Cd isotope composition and fractionation mechanisms in the ore-forming fluids may provide some important information pertaining to the formation mechanism of hydrothermal deposits. As a result, the purpose of this study is to use Cd isotopes to trace the ore-forming fluids and mineralization environments in lead-zinc deposits, and we expect that Cd isotope can be a new tool for the studies of the genesis for lead-zinc deposits.

1   Samples and methods

The southwestern margin of the Yangtze Craton is an important domain of epithermal mineralization, and also a significant Au, Hg, Sb, As, Pb, Zn, and Ag metallogenic belt in China. This area is also one of the most important dispersed elements concentration areas in the world (Tu et al., 2004). There are abundant lead-zinc deposits located in Chuan-Dian-Qian (Sichuan-Yunan-Guizhou, CDQ) area (southwestern margin of the Yangtze Craton), for example, the Daliangzi, Tianbaoshan, Huize, Fule, Shanshulin, Niujiaotang, Qingshan lead-zinc deposits and so on. These deposits not only have very significant reserves of Pb and Zn but also have abundant reserves of dispersed elements (for example, Cd, Ge, In, Ga, Se). All samples for this study were collected from above-mentioned deposits. The Jinding deposit, the largest lead-zinc deposit in China, is also included in this study, and its reserves of associated elements (Cd, Ag and Tl) are considerable.

In the 1970s, a double spike method was used to measure the Cd isotopic composition in meteorite by Rosman et al. (1976). However, the samples from the Earth have only small scale of Cd isotope fractionation; so, it is difficult for the mass spectrograph instrument to measure the Cd isotopic composition accurately and precisely. This resulted in that the study on Cd isotopes had been in a standstill. During the past ten years, with the development of high-

precision mass spectrograph, the precision of the instrument is up to ±0.10‰ ($\delta^{114/110}$ Cd) (Ripperger et al., 2007) and this is adequate to measure the Cd isotopic compositions in the earth samples.

Samples have to be pre-treated by chemical separation and purification to avoid interferences and matrix effects. And isotopes of Sn, Pd and In are potentially important isobaric interference on Cd (^{106}Pd to^{106}Cd, ^{108}Pd to^{108}Cd, ^{110}Pd to ^{110}Cd, ^{112}Sn to ^{112}Cd, ^{113}In to ^{113}Cd, ^{114}Sn to ^{114}Cd, and ^{116}Sn to ^{116}Cd). Up to now, there are mainly two chemical separation methods: (1) two-stage column chemical procedure (Wombacher et al., 2003), the processes of this method are too complicated; (2) one-stage column chemistry procedure (Christophe et al., 2005; Gao et al., 2008), this method is relatively simple and it is used by most of laboratories. One stage column chemical procedure improved by Zhang et al. (2010) (Table 1) was adopted in this study for chemical separation.

For sphalerite and galena samples, typically 150 mg of powder were weighed into 10 mL Teflon digestion vessels. Samples were first reacted with 6 mL of sub-boiling HNO_3 at 110°C for about 24 h and then taken to dry on an electric platen at 110°C. Adding 5 mL 2 mol/L HCl and then centrifugation, 2 mL of supernatant were transferred to measure the Cd content, and 2 mL of supernatant were transferred to Teflon digestion vessels to do chemical separation. The processes of chemical purification are listed in Table 1.

Cadmium isotopic ratios were measured using MC-ICP-MS. Matrix effects, concentration effects, and medium effects had been studied carefully in detail by Wombacher et al. (2003, 2004) and Christophe et al. (2005), and these are solid bases for us to measure the Cd isotopic compositions accurately and precisely. Samples were measured using a Nu Plasma HR coupled with membrane desolvation (DSN-100), and a Teflon nebulizer with an uptake rate of 100 μL min^{-1} was used for sample introduction and the content of Cd in the samples were 0.2 μg mL^{-1} with 1% nitric acid medium. These parameters can result in about 52 V ppm^{-1} signal intensity.

Signal sampling models were similar to that of Wombacher et al. (2003, 2004) and Christophe et al. (2005). All the eight Cd isotopes were measured and ^{105}Pd, ^{115}In, and ^{117}Sn were also monitored to assess isobaric interference on Cd. All samples and bracketing reference solutions were run in 2 blocks of 30 cycles of measurements on each amu. Twenty seconds were designed to measure the background value of the instrument before the sample measured, and this value was taken off by the computer automatically.

During the measuring process, sample-standard-bracketing (SSB) involves the use of matrix matched isotopic standard, which is run before and after the sample to controlling the mass fractionation of the instrument (relative deviation of Cd concentration is less than 10%). While in the process of measuring, we only adopted the data that were collected in the case that both the instrument working conditions and the signals were stable. In order to control data quality, two methods had been used during the chemical purification: (1) after digestion, all the samples had been collected a few liquid which is run before and after chemical purification to monitor the potential interferences on Cd isotopes (including Sn, In, Zn, Pd and other interfering matrix elements) and recovery. We only measured the Cd isotopic compositions of the sample in which the recovery of Cd was up to 95% and the potential interferences were present at negligible levels. The study by Christophe et al. (2005) demonstrated that when the recovery of Cd can get to 95%, the mass fractionation (resulted by resin) of Cd isotopes were negligible during the chemical purification process. When the samples were qualified, the matrix effects and the mass fractionation of Cd isotopes had been eliminated during the chemical separation. (2) We had added couples of parallel samples and standard samples (Münster) to monitor the pre-treatment and instrument measuring. Table 2 indicated that the data of Cd isotopic compositions were reliable.

So far, there is no international standard for Cd isotopic analysis. In this study, SPEX had been introduced as the Cd isotopic standard, which was suggested by Christophe et al. (2005). The long-term external reproducibility of SPEX was evaluated at 0.12‰ (2SD) for the ^{114}Cd/^{110}Cd. All the results were reported as the deviation relative to the Cd SPEX reference solution, which are given in per mil (delta) notation following the equation:

$$\delta^{114/110}\text{Cd} (‰) = (^{114/110}\text{Cd}_{\text{sample}}/^{114/110}\text{Cd}_{\text{standard}} - 1) \times 1000.$$

2 Results

The analytical results (including duplicate analysis) of Cd contents and isotopic compositions of samples from five representative lead-zinc deposits are presented in Table 2. On the basis of the Cd content of sphalerite, these deposits can be divided into two groups. The first group was represented by the Huize deposit and the Shanshulin deposit, which had a low Cd content. The mean content of Cd in the Huize deposit and the Shanshulin deposit is 862 and 683 ppm, respectively. The second group was represented by the Fule deposit, the Niujiaotang deposit, and the Jinding deposit, which had a high Cd content. The mean content of Cd

Table 1 Improved ion-exchange elution method

Eluent	Volume (mL)	Eluted
AG-MP-1M	3	
2 mol/L HCl	20	Resin conditioning
Sample	2	Sample solution
2 mol/L HCl	10	Matrix
0.3 mol/L HCl	30	Pd
0.06 mol/L HCl	20	Sn
0.012 mol/L HCl	5	Zn, Sn
0.0012mol/L HCl	20	Cd

Table 2 Cadmium content and isotopic compositions of samples from different lead-zinc deposits and Münster Cd standard solution used during MC-ICPMS analysis[a]

Name	Sample No.	Sample type	Color	Cd (ppm)	$\delta^{114/110}$Cd (‰)
Huize	HZP5-11-2	sphalerite	black	913	0.12 ± 0.08
Huize	HZP5-11-2	sphalerite	black	923	0.07 ± 0.04
Huize	HZP9-2-1-①	sphalerite	reddish-brown	770	0.16 ± 0.23
Huize	HZP9-2-1-②	sphalerite	reddish-brown	1410	0.31 ± 0.28
Huize	HZP9-6-1	sphalerite	black	623	0.24 ± 0.21
Huize	HZP9-7-1	sphalerite	black	673	0.15 ± 0.11
Huize	HZP10-7	sphalerite	black	725	-0.08 ± 0.20
Huize	HZP5-11-2	galena		8	-1.53 ± 0.18
Huize	HZP9-2-2	galena		24	-0.60 ± 0.10
Huize	HZP9-8-2	galena		21	-0.63 ± 0.12
Huize	HZP9-8-2	galena		15	-0.58 ± 0.08
Shanshulin	SS01	sphalerite	black	590	-0.13 ± 0.24
Shanshulin	SS13	sphalerite	black	571	0.12 ± 0.03
Shanshulin	SS14-1	sphalerite	black	930	-0.07 ± 0.21
Shanshulin	SS14-3	sphalerite	reddish-brown	884	0.02 ± 0.34
Shanshulin	SS16	sphalerite	black	608	-0.34 ± 0.24
Shanshulin	SS16	sphalerite	black	510	-0.28 ± 0.28
Fule	FL128-①	sphalerite	reddish-brown	5430	0.32 ± 0.16
Fule	FL128-②	sphalerite	buff	11477	0.32 ± 0.13
Fule	FL43-①	sphalerite	reddish-brown	9263	0.34 ± 0.21
Fule	FL43-②	sphalerite	black	19714	0.03 ± 0.07
Fule	FL48	sphalerite	black	6953	-0.20 ± 0.13
Fule	FL46	sphalerite	black	10799	-0.30 ± 0.11
Fule	FL86	sphalerite	reddish-brown	7116	0.02 ± 0.03
Niujiaotang	LJP3-3	sphalerite	buff	5330	-0.48 ± 0.01
Niujiaotang	LJP4-3	sphalerite	buff	7128	-0.34 ± 0.16
Niujiaotang	LJP2-2	sphalerite	buff	2177	0.18 ± 0.07
Niujiaotang	LJP2-8	sphalerite	buff	5207	-0.59 ± 0.01
Niujiaotang	LJP 3-1	sphalerite	buff	2075	-0.41 ± 0.07
Jinding	Z-3	oxide		3240 (13697)	-0.58 ± 0.09
Jinding	Z-4	oxide		4440 (15290)	-0.74 ± 0.09
Jinding	Z-5	primary ores		541 (7490)	-0.35 ± 0.13
Jinding	Z-6	primary ores		1930 (13685)	-0.39 ± 0.07
Jinding	Z-7	primary ores		344 (30941)	-0.50 ± 0.10
Münster		standard			4.47 ± 0.08

a) The reference Cd isotopic composition value of Münster is 4.48‰ (Christophe et al, 2005). There are three parallel samples, namely HZP5-11-2, HZP9-8-2 and SS16. We assumed that Cd was only hosted in sphalerite and smithsonite in primary ores and oxides, respectively. Data of Cd content in brackets were those of sphalerite and smithsonite converted according to the Zn content in the sample.

in these three deposits is 10107, 4383 and 16221 ppm, respectively.

The range of Cd isotopic compositions in the sphalerite is wide from −0.59‰ to 0.34‰, with a total range of 0.93‰. The average of Cd isotopic compositions was 0.14‰ in the sphalerite from the Huize deposit, ranging from −0.08‰ to 0.31‰; −0.11‰ in the sphalerite from the Shanshulin deposit, ranging from −0.34‰ to 0.12‰; 0.07‰ in the sphalerite from the Fule deposit, ranging from −0.30‰ to 0.34‰; and −0.33‰ in the sphalerite from the Niujiaotang deposit, ranging from −0.59‰ to 0.18‰. Meanwhile, the mean content of Cd isotopic compositions in primary ores and oxides from the Jinding deposit was −0.41‰ and −0.66‰, respectively. These results indicated that the samples from

the Jinding deposit were rich in lighter isotopes of Cd. Especially, we found that the range of the Cd isotopic compositions in three galena ores from the Huize deposit was wide, from −1.53‰ to −0.60‰, and the mean value was −0.92‰. It is notable that besides meteorite samples, these three samples were the richest in lighter isotopes of Cd in the geological samples thus far.

3 Discussions

3.1 Cd isotopic compositions in different geological samples

For a new isotopic system of Cd, it is necessary to compare

the Cd isotopic compositions of our samples with other geological samples to investigate the differences and possible reasons. This is the most appropriate and effective way to study the fractionation mechanisms of Cd isotopic system. Compared to other non-traditional isotopic systems (for example, Fe, Cu, Zn, Se and Mo), the study of Cd isotopic composition is not well developed and the data of Cd isotopic compositions are relatively few. So, comparative studies of Cd isotopic data are necessary.

Except for meteorite samples, the Cd isotopic data ($\delta^{114/110}$Cd) of other earth samples have been plotted in Figure 1. The Cd isotopic compositions in two MORB and two OIB samples were well-distributed with a mean value of $-0.24‰ \pm 0.11‰$. Schmitt et al. (2009) pointed out that this value can represent the Cd isotopic compositions of the bulk silicate Earth (BSE). However, the distribution of Cd isotopes is inhomogeneous in the modern marine waters. Ripperger et al. (2007) reported that the Cd isotopic compositions varied in different Oceans. For example, the range of Cd isotopic compositions in north Pacific water, north Atlantic deep water, and Arctic Ocean water samples vary from $-0.65‰$ to $3.75‰$, $0.26‰$ to $1.08‰$, and $0.34‰$ to $0.65‰$, respectively. It was discovered that the most Cd-depleted water samples were found to be most enriched in the heavy isotopes of Cd, and this demonstrated that the fractionations are probably due to kinetic isotope effects that occurred during the absorption of dissolved seawater Cd by phytoplankton (Ripperger et al., 2007). So, the differences of Cd isotopic compositions in different ocean samples may be controlled by temperature and salinity of sea waters and other factors, which resulted in different populations of phytoplankton. Meanwhile, thirty-two Fe-Mn hydrogenic nodules measured for Cd isotopes have a range from $-0.17‰$ to $0.35‰$. There are few fractionations of Cd isotopes among Fe-Mn nodules with different depths and corresponding surrounding sea waters; this indicated that inorganic absorption may result in small Cd isotope fractionation.

Nine sphalerite samples from different VMS type lead-zinc deposits and seven oceanic hydrothermal sulphides from the EPR at 9°–10°N had been measured for Cd isotope by Schmitt et al. (2009). The results showed that the range of $\delta^{114/110}$Cd values from VMS type deposits and oceanic hydrothermal sulphides was $-0.24‰$ to $-0.04‰$ and $-0.65‰$ to $0.19‰$, respectively. Meanwhile, Wombacher et al. (2003) measured a sphalerite sample for Cd isotopic composition and the $\delta^{114/110}$Cd value was $0.19‰$. These data indicated that the total range of Cd isotopic compositions in hydrothermal systems can be $0.84‰$, and the sphalerite samples from different hydrothermal systems have different total ranges of Cd isotopic compositions.

In this paper, there are 33 samples measured for Cd isotopic compositions from five lead-zinc deposits, and they displayed several characteristics: (1) the Cd isotopic com-

position varied widely ranging from $-1.53‰$ to $0.34‰$, with a total range of $1.87‰$, which is similar to that of modern seawater samples; (2) the total Cd isotopic compositions of sphalerite samples was $0.93‰$ which is wider than that of VMS type sphalerite ($0.25‰$) (Schmitt et al., 2009), and is similar to (the changes) that of oceanic hydrothermal sulphides; (3) three galena samples from the Huize deposit were strongly rich in lighter isotopes of Cd ranging from $-1.53‰$ to $-0.60‰$, with a mean value of $-0.92‰$. Although this result should be proved by more analyses, it is still demonstrated that the Cd isotope fractionation existed in different minerals in a hydrothermal system from which these minerals were crystallized.

3.2 The relationships between the genesis of lead-zinc deposit and the Cd isotopic compositions

Five deposits selected for this study have been investigated in detail, so they are valuable for Cd isotope studies. The main geological and geochemical characters of these deposits were listed in Table 3. Excepting the Jinding deposit, others are similar to the MVT type deposits (e.g., wall rocks, orebody shape, mineralization temperature, sulfur isotope
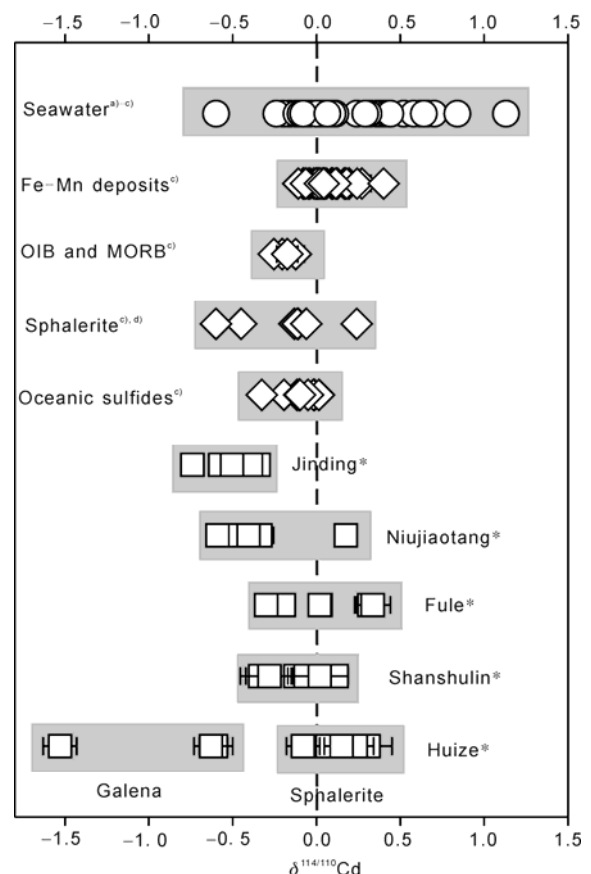

Figure 1 Summary of Cd isotopic composition of various samples from different deposits, as well as other Earth materials. Data sources: * this study, a) Ripperger et al. (2007); b) Lacan et al. (2006); c) Schmitt et al. (2009); d) Wombacher et al. (2003).

composition), and it was generally acknowledged that they were MVT type deposits (Li et al., 2002; Khin Zaw et al., 2007; Zhang et al., 2008; Ye et al., 2011). However, there is a hot debate on the genesis of these deposits. Khin Zaw et al. (2007) provided a detailed description of the types and the origins of lead-zinc deposits located in South China, and they held that Huize was a MVT type deposit. Also, Ye et al. (2011) showed that Huize and Niujiaotang were MVT type deposits. Xu et al. (2009) pointed out that Huize was related to an MVT type deposit, but the grade of lead and zinc, mineral assemblage, single orebody scale, wall rock alteration, and physicochemical conditions of mineralization were different from those of typical MVT type deposits; so, the Huize deposit was named as "Qilingchang type" deposit. Generally, the origins of lead-zinc deposits in CDQ area are divided into two groups: (1) these deposits are related to the Emeishan basalt thermal activity and the main viewpoints are magmatic hydrothermal complex mineralization type (Xue et al., 2006; Xie et al., 2009), sedimentary-transform type (Liu et al., 1999), "passing through ore-forming deep source fluid in deep fountainhead-extraction of vaporizing rocks evaporate layer-structure controlling of structure" (Han et al., 2006), passing through homogenized ore-forming fluid (Huang et al., 2004); (2) these deposits are MVT type deposits (Zhang et al., 2005, 2008; Liu et al., 1996; Zhou et al., 1998; Wang et al., 2001, 2002) or "Yangtze type" deposits (Hou et al., 2007) and had no relationship with the Emeishan basalt thermal activity.

Comparing the Cd isotopic compositions and Cd content

in the different sphalerite from CDQ area, we can easily distinguish two groups (I and II) (Figure 2): (1) Rich in Cd, type (I), Fule and Niujiaotang were the representatives which had a wide changes of Cd content from 2075 ppm to 19714 ppm, and the $\delta^{114/110}$Cd values were -0.59‰ to 0.34‰, with no correlation between Cd content and isotopic compositions. (2) Poor in Cd, type (II), Huize and Shanshulin were the representatives which had a low concentrations from 510 ppm to 1410 ppm and the $\delta^{114/110}$Cd values were −0.34‰ to 0.31‰, and 1/Cd is inversely correlated with $\delta^{114/110}$Cd values.

According to the Cd isotopic compositions of these four deposits (Fule, Niujiaotang, Huize, and Shanshulin), it is hard to discriminate the genesis of these deposits. However, compared to typical MVT type deposits (Fule and Niujiaotang), Huize and Shanshulin had different metallogenic evolution mechanisms. Although these two groups had similar Cd isotopic compositions, the difference of Cd concentration was remarkable among these two groups, which were located in different fields (Figure 2).

So far, the data of Cd isotopic composition in SEDEX type deposits have never been published. Schmitt et al. (2009) measured Cd isotopic compositions in seven oceanic hydrothermal sulphides from three different seafloor chimneys located in the East Pacific Rise (EPR), and the studies demonstrated that compared to high temperature settings, low temperature settings can result in large Cd isotope fractionation during the precipitation of sphalerite. These seven samples consist mainly of sphalerite and pyrite. We can
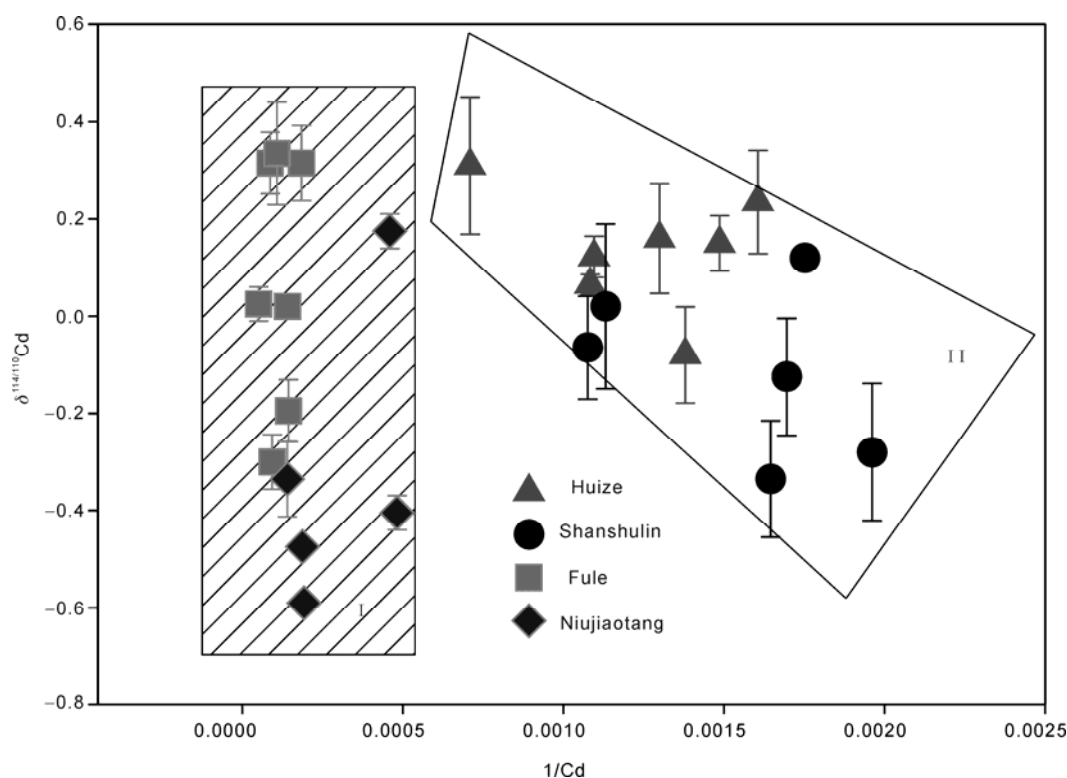

Figure 2 The Cd content and isotopic compositions in lead-zinc deposits from Chuan-Dian-Qian area.

reasonably assume that the Cd isotopic compositions in these samples can represent the Cd isotopic compositions in Sedimentary Exhalative Deposit (SEDEX). It is obvious that different origins of lead-zinc deposits had different field in 1/Cd-$\delta^{114/110}$Cd diagram (Figure 3). Meanwhile, Figure 3 shows that MVT type deposits had great variances of Cd content and $\delta^{114/110}$Cd values in sphalerite, these variances in VMS type were the least, and the "SEDEX-like" type was in the middle. The VMS type deposits had a small Cd isotope fractionation, which may result from the ore-forming fluid that was derived from the evolution of magma ($\delta^{114/110}$Cd $\approx$ 0.0‰) (Wang et al., 2009). And the ore-forming

fluid of MVT type deposits was derived from basin brine, which was reacted with wall rocks, and it may be the likely potential explanation for obvious fractionation of Cd isotope in MVT type deposits. All above suggested that different types of lead-zinc deposits had different Cd content and isotopic compositions, and so it is likely to be true that Cd isotopes can be a tracer for the studies on the origin of ore-deposits.

The Jinding deposit has attracted great attention because of its unique properties since its discovery in the 1960s. And there is a debate on the genesis of this deposit. The major view-points are: syngenetic sedimentary and late re-

Table 3   Geological and geochemical characters of the Huize, Shanshulin, Fule, Niujiaotang and Jinding deposits

	Huize [a),b)]	Shanshulin [b),c)]	Fule [d),e)]	Niujiaotang [f)]	Jinding [g),h)]
Main ore-forming elements	Pb, Zn	Pb, Zn	Pb, Zn	Zn, Pb	Pb, Zn
By-product commodities	Ge, Cd	Cd, Ge	Cd, Ge, Tl, Se	Cd	Cd, Sr
Orebody morphology	stratiform, lens-shaped	stratiform, stockwork	vein-stockwork, stratiform	lens-shaped, stratiform	stratiform, stockwork
Host lithology	Baizuo Fm. dolomite	Baizuo Fm. dolomite and limestone	Maokou Fm. limestone	Qingxudong Fm. dolomite	Jingxing Fm., Yunlong Fm. sandstone and breccia
Mineralization age	Early Carboniferous	Hercynian-Yanshanian	Yanshanian	Middle-Late Caledonian	Late Eocene to Oligocene
Mineralization temperature (°C)	175–276	175–276	140–280	110–170	50–240
Salinity (wt%)	−10	15–22	5–10	±12	±7.5
δ^{34}S (‰)	11–17	11–17	8–15	22–30	−4.5—19
^{206}Pb/^{204}Pb	17.980–18.830	18.276–19.030	18.470–18.821	18.148–18.226	18.168–18.402
^{207}Pb/^{204}Pb	15.010–16.180	15.448–15.990	15.542–15.592	15.674–15.802	15.345–15.607
^{208}Pb/^{204}Pb	36.930–40.620	38.299–39.190	38.283–38.638	38.214–38.651	37.803–38.329

a) Huang et al.,(2004); b) Zhou (2011); c) Bai et al., (2010); d) Si (2005); e) Zhang et al., (2005); f) Ye L et al., (2005); g) Xue et al., (2002); h) Xiu et al., (2007).
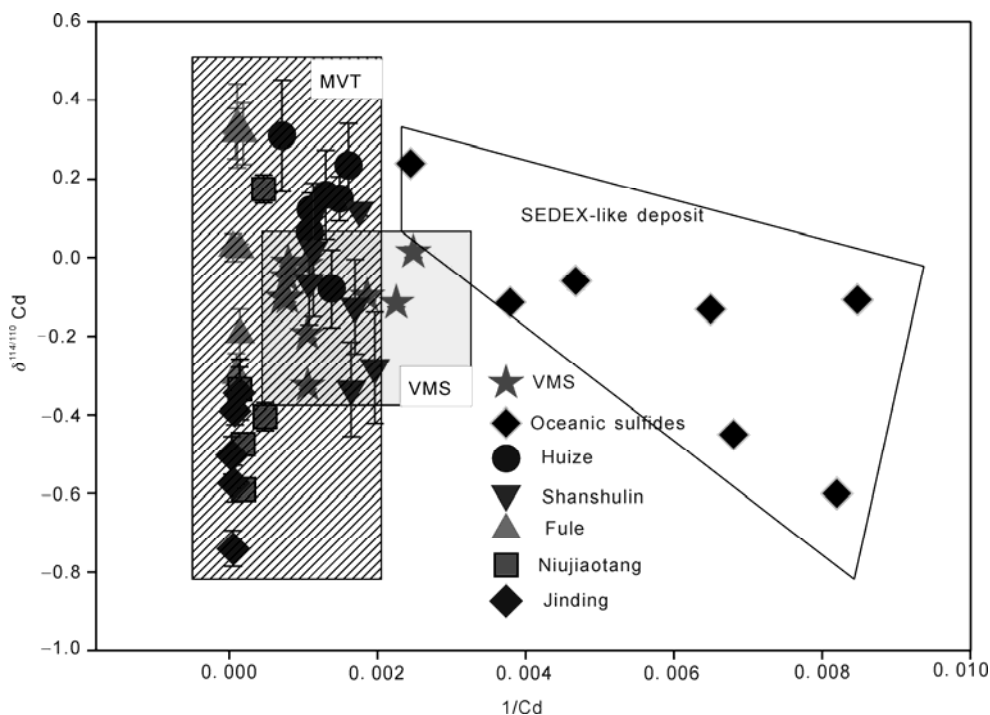

Figure 3   The Cd content and isotopic compositions in different types of lead-zinc deposits.

worked type (Bai et al., 1985), non-magmatic hydrothermal mineralization at low-medium temperatures (Gao, 1989), syngenetic sedimentary-deformation-superimposition deposit (Wu et al., 1989), exhalation-sedimentation type (Zhao et al., 1989), karst mineralization (Hu et al., 1989), crust-mantle fluid mixing model (Yi et al., 1990) and so on. Wang et al. (2009) pointed out that Jinding was a new type of lead-zinc deposit which was very different from MVT, SST, and SEDEX type deposits, and it was named "JinDing Type (JDT)" deposit which was formed during the process of continental collision in Cenozoic, and fluids with abundant oil gas, salt and metals were deposited in the structure trap. From the data of Cd isotopic compositions, the mean values of primary ores and oxides are −0.41‰ and −0.66‰, which displayed an enrichment of lighter isotopes of Cd. Meanwhile, the range of Cd content and isotopic compositions in the Jinding deposit was different from MVT and VMS type deposits. It indicated that the genesis of the Jinding deposit was different from MVT, SEDEX, and VMS type deposits and it should be a special type of lead-zinc deposits.

Liu et al. (2000) found that the Niujiaotang deposit had abundant nodular and framboidal sphalerite and pyrite ores, which were considered to be an indicator of biological mineralization. Meanwhile, the studies by Xue et al. (2009) and Wang et al. (2009) found lots of organic inclusions and rich organic matters with different maturity (such as kerogen, light crude oil, hydrocarbon gas), which displayed that organic matter possibly played a role in the forming process of the Jinding deposit and the parent material of biogenesis was mainly I-type. Because Cd is understood to be very close to the nutrient element—phosphor, biological absorption of Cd results in the lighter isotopes enrichment in or-

ganisms. So, the deposits in which organisms were involved during the mineralization are rich in Cd lighter isotopes. It is the likely potential explanation that Cd isotopic composition in Jinding and Niujiaotang is −0.50‰ and −0.59‰, respectively, which were richer in lighter isotopes of Cd than those of other three deposits (Huize, Shanshulin, Fule).

3.3 The relationship between the colors and Cd isotopic compositions of sphalerite

Color is the typomorphic characteristic of sphalerite. Pure sphalerite is colorless, but most sphalerite ores are rich in Fe, which can result in buff, tawny, reddish-brown, and even black colors, with the increase of Fe content. Generally, light and dark sphalerite ores are crystalized in the same mineralization period, but dark sphalerite crystalized earlier than the light one. The ranges of Cd content and isotopic compositions in 25 sphalerite samples with different colors from five deposits are the same (Figure 4). This result indicated that the Cd content and isotopic compositions are not controlled by the color of sphalerite. However, the samples from the Fule deposit show that $\delta^{114/110}$Cd values increased from −0.30‰ to 0.30‰ when the color of sphalerite changes from black to buff (Figure 5). This result demonstrated that dark sphalerite was rich in Cd lighter isotope whereas light sphalerite was rich in heavier isotopes of Cd. We can reasonably infer that the process of crystal fractionation is a potential mechanism of Cd isotope fractionation; it resulted in that early-stage crystallized black sphalerite is rich in lighter isotopes of Cd and later crystallized buff sphalerite is rich in heavier isotopes of Cd in the Fule deposit. This shows that Cd isotope kinetic fractionation exists in a small space, and it may be controlled by the temperature, the
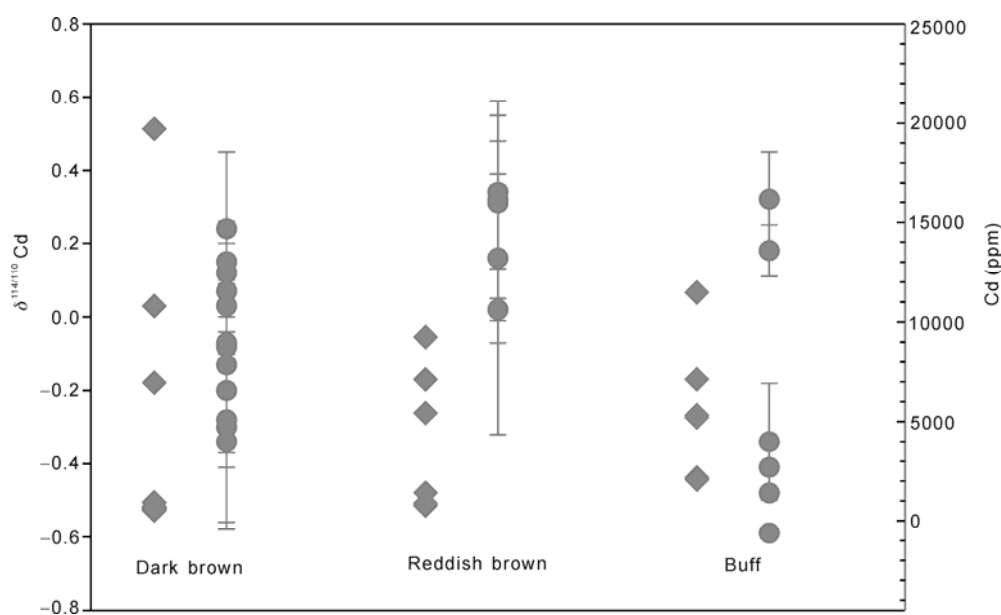

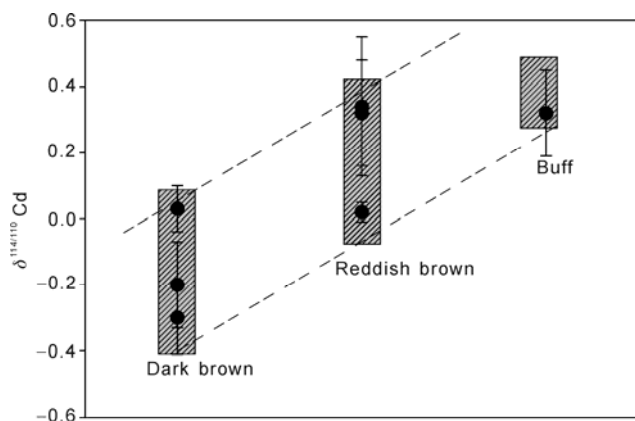**Figure 4**   Cd content and isotopic compositions in different colors of sphalerite.

Figure 5　Cd isotopic compositions in different colors of sphalerite from the Fule deposit.

number and kinds of ligands, Eh condition, and pH condition of the ore-forming fluid.

Cadmium and zinc have similar geochemical behavior and similar evolutionary characteristics in hydrothermal systems (Tu et al., 2004). So, we infer that the isotopes of Cd and Zn have similar evolutionary laws. Marchal et al. (2002) proved that Zn carbonate sedimentation assay showed that lighter isotopes of Zn were rich in deposited minerals. John et al. (2008) measured the Zn isotopic compositions in the fluids and minerals in submarine hydrothermal system, and the results showed that whether the samples were collected from high or low temperature hydrothermal chimney, minerals were rich in lighter isotopes while fluids were rich in heavier isotopes. Wang et al. (2010) summarized the evolutionary characteristics of Zn in the ore-forming fluids, and pointed out that the process of crystal fractionation can result in Zn isotope fractionation and crystallized minerals were rich in lighter isotopes. This demonstrated that the isotopes of Zn and Cd have similar fractionation mechanisms, and they may provide some important information about the evolutionary of ore-forming fluid. Meanwhile, based on these conclusions, active probe into the differences between Zn and Cd isotopes may be important to tracing and exploring the ore-forming fluid (e.g., lead-zinc deposits).

4　Conclusions

Based on the researches of Cd isotopes in five lead-zinc deposits, we have reached the following conclusions.

(1) Cd isotopic compositions vary in a wide range, from $-1.53‰$ to $0.34‰$, in sphalerite and galena, with a total range of $1.87‰$. This total range is larger than that of most geological samples and just smaller than that of seawater samples.

(2) By comparing the Cd content and isotopic compositions from different deposits, it is seen that different types of lead-zinc deposits have different Cd content and isotopic

compositions, which may be an important indicator to distinguish the origins of lead-zinc deposits.

(3) Biomineralization and crystal fractionation may result in Cd isotope fractionation. Up to now, the studies on Cd isotopes are in a preliminary stage, especially in the field of mineralization. However, this study proved that Cd isotope can be a tracer in tracing sources and evolution of ore-forming fluid.

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