Isotope geochemistry of the Huize Zn-Pb ore field, Yunnan Province, Southwestern China: Implication for the sources of ore fluid and metals

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The Huize ore field, which is the most famous high-grade Zn-Pb ore field in China, comprises the Kuangshanchang and Qilinchang deposits. The Zn and Pb reserves of these two deposits are more than 5 Mt with ore grades ranging from 25% to 35% in weight. Lead, sulfur, carbon, oxygen, hydrogen and strontium isotope geochemistry is reported to help understand the sources of the ore fluid and metals. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values of the ores range from 18.251–18.530, 15.663–15.855 and 38.487–39.433, respectively. These values are similar to those of the wall rocks. The pyrites disseminated in the wall rocks have indistinguishable Pb isotope composition with the ores. These data indicate that the wall rocks provided metals to the ore fluid. Most $\delta^{34}\text{S}$ values of the ores range from 13 to 17 per mil. The sulfur of the ores originated by *in situ* reduction of sulfate. Three kinds of gangue calcite from the ores have similar isotope compositions, which have $\delta^{13}\text{C}$ values in the range of –2.1 to –3.5 per mil with respect to PDB and $\delta^{18}\text{O}$ values in the range of 16.8 to 18.6 per mil with respect to SMOW. The $\delta\text{D}_{\text{FI}}$ values of fluid inclusions in the three kinds of gangue calcites have a narrow range of –50 to –60 per mil and the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values calculated from $\delta^{18}\text{O}$ values of calcite range from 7.0 to 8.8 per mil at 200°C. These data suggest that the ore fluid was a basinal brine that passed through shale, clastic rocks and mudstone underlying the host rock. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ values of the pyrite, sphalerite and calcite from the ores range from 0.714 to 0.717. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ values of unaltered host rock (0.7083–0.7093) are lower than that of the altered host rock (0.7106). It suggests that the ore fluids have higher initial $^{87}\text{Sr}/^{86}\text{Sr}$ values than the wall rocks. These high initial $^{87}\text{Sr}/^{86}\text{Sr}$ values may be due to the reaction between the ore fluid and the shale, clastic rocks and mudstone underlying the host rock or the fluid might have originated from these rocks.

Keywords: isotope geochemistry, ore fluid, metal sources, MVT deposit, Huize Zn-Pb orefield

INTRODUCTION

The Huize Zn-Pb ore field is located in Huize County, Yunnan Province, Southwestern China (Fig. 1) and comprises the Kuangshanchang (>1 Mt of Zn + Pb metals) and Qilinchang (>3 Mt of Zn + Pb metals) deposits, which are separated by a distance of 3 km and connected by underground workings. The ore grade is generally between 25% and 35% of Pb + Zn, and can reach grades of 65% in weight. The byproducts are Ag, Ge and Ga.

Because of its large size, high grade and many associated byproduct elements (Ag, Ge and Ga), the Huize Zn-Pb ore field has attracted considerable attention from researchers. Previous studies, mainly based on studies in geology, isotope and element geochemistry, proposed four kinds of source rocks: (1) Carbonate wall rocks and the Emeishan flood basalt (Liao, 1984; Chen, 1993; Liu and

Lin, 1999; Han, 2002; Huang *et al.*, 2001; Li *et al.*, 2002; Han *et al.*, 2004), (2) Upper Sinian, Lower Cambrian, Devonian and Carboniferous rocks (Li *et al.*, 1999), (3) Precambrian basement rocks (Hu, 2000) and (4) Lower Sinian volcanic rocks (Zhou *et al.*, 2001). The sources of metal and fluid are still controversial and need to be constrained further.

Isotope geochemistry is a powerful tool in deciphering the genesis of ore deposits (Zheng and Chen, 2000). Hydrogen, oxygen and carbon isotope systems can trace the sources of the ore fluids and lead, sulfur and strontium isotope analyses can constrain the source rocks of the ore metals (Rye and Ohmoto, 1974; Ohmoto, 1986; Hoefs, 1997; Jiang *et al.*, 1999; Ding and Jiang, 2000; Wu *et al.*, 2004; Chen *et al.*, 2004, 2005; Zhang *et al.*, 2005). However, in some cases, results based on a small dataset may lead to premature conclusions. In other cases, conclusions have been drawn without taking into account all the geological constraints or contradictory conclusions were based on detailed isotope studies on several different elements (Dejonghe *et al.*, 1989). This study will fo-

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Fig. 1. Simplified regional geologic map of the Huize ore field, showing major faults and location of major deposits.

cus on sulfur, hydrogen, oxygen, carbon, lead and strontium isotope systematics in an attempt to constrain the sources of the ore fluid and metals of the Huize Zn-Pb ore field.

GEOLOGY

The Huize ore field is located at the fault intersections of the NE-, NS- and NW-trending structural belts between the Xiaojiang and Zhaotong-Qijing buried fault, which are the main deep faults in this region (Fig. 1). The NE-SW-trending subsidiary faults in the Huize ore field, including Kuangshanchang, Qilinchang, Yinchangpo and Niulanjiang faults, control the distribution of the deposits (Fig. 2). The Kuangshanchang deposit occurs in the upper plate of the Kuangshanchang fault while the Qilinchang deposit occurs in the upper plate of the Qilinchang fault (Fig. 2). The igneous rocks in the mine area are represented by the Emeishan flood basalt, which is located about 1 km away from the Kuangshanchang deposit.

We have investigated three profiles in this area. One

is the Sunjiagou profile, which is 3 km on the southwest of the Kuangshanchang deposit and the others are the Ershun profile (20 km on the north of the Kuangshanchang deposit) and the Maojiacun Reservoir profile (60 km on the southwest of the Kuangshanchang deposit). The rock types in these three profiles are similar. The stratigraphic column for the Sunjiagou profile is shown in Fig. 3. Sinian to Permian Carbonate strata outcrop in the mine area (Fig. 3), but the ore bodies are all hosted in dolomite of the Baizuo Formation (Lower Carboniferous, C_{1b}) coarse dolomite and locally in contact with middle Carboniferous (C_2) marine limestone. The alteration of the host rock is dominated by dolomitization and to a lesser extent silicification, pyritization and carbonation.

During the last five decades, More than 30 orebodies have been found in Qilinchang and Kuangshanchang deposits (Fig. 4). This ore field has become the second largest and most economically productive ore field in China. The No. 1, No. 3, No. 6, No. 8 and No. 10 orebodies are the largest orebodies and contain about 90% of the reserves. The Kuangshanchang deposit comprises No. 1 and some other small ore bodies with a Pb + Zn reserve of

Fig. 2. Simplified geological map of the Huize ore field.

more than 1 Mt. The Qilinchang deposit comprises No. 3, No. 6, No. 8, No. 10 and some other small ore bodies with a Pb + Zn reserve of more than 3 Mt. High grades and the contents of many associated byproducts (Ag, Ge and Ga) are the most important features of this ore field. The average grade of Zn + Pb of the No. 1, No. 3, No. 6, No. 8 and No. 10 orebody are 32.6%, 36.5%, 34.6%, 25.8% and 33.5% in weight, respectively. Ag, Ge and Ga occur in notable concentrations. Take the No. 8 orebody as an example, it contains 64t Ag and 200t Ge.

The shapes of the ore bodies are irregular. Pipe-like, lensoid and vein styles predominate. Ores are massive, disseminated, veined and banded with granule, poikilitic, metasomatic, wrinkle, network and interstitial texture. The ores in the upper part of the deposits are oxidized. Un-oxidized, primary ores occur at depth. Mixed sulfide-oxide ores occur in the transition zone. Compositions of the oxidized ores are rather complex, but those of the primary ores are quite simple. The primary ores are mainly composed of galena, sphalerite and pyrite. Minor minerals are chalcopryrite, antimony, boulangerite, acanthite, freibergite, matildite. Gangue minerals are calcite and some dolomite. Mineral assemblages in orebodies change from the footwall to the hanging wall. Mineral assemblage in the lower portion of the ore bodies is marmatite, coarse pyrite and small amounts of calcite. In the transition zone are sphalerite, galena, pyrite, and calcite and in the upper zone is fine-grained pyrite and calcite. The thickness and grade of the orebodies increase with depth. Grades of zinc and lead are very high. The average grade

of Zn + Pb is 30% and the Pb + Zn contents of some ores exceed 60% in weight. Ag, Ge and Ga occur in notable concentrations.

Based on field observations and petrographic studies, the mineralization can be divided into four stages: (1) Galena-marmatite-pyrite-calcite, (2) Galena-sphalerite-pyrite, (3) Chalcopryrite-galena-pyrite-acanthite-sphalerite, (4) Calcite.

Based on the geological background, Zhang *et al.* (1988) considered that there are several mineralization stages and the age of mineralization in this region is thought to be late Hercynian (about 405 ± 5 to 250 Ma) and Yanshanian (about 205 to 66 ± 2 Ma). Yang and Guan (1994) and Liu and Lin (1999) considered the time of mineralization to be Hercynian and Indosinian (about 250 to 205 Ma)-Yanshanian. According to Pb model age determinations, Guan and Li (1999) obtained a Pb mold age of 245 Ma and considered that the Zn-Pb mineralization in this region maybe related to Emeishan Basalt magmatic event that took place about 250 Ma ago (Thompson *et al.*, 2001; Boven *et al.*, 2002; Zhou *et al.*, 2002; Ali *et al.*, 2005). Based on the studies on geological settings, Han (2002) and Zhang (1997) suggested that mineralization occurred in the Permian. Zhou *et al.* (2001) considered the mineralization in the Huize Zn-Pb ore field is related to the closure of the paleo-Tethys ocean, so they supported an Eocene age. Li *et al.* (2007b) reported an age of 225 ± 9.9 Ma for No. 6 and an age of 228 ± 16 Ma for No. 1 orebody, constrained by Sm-Nd system in hydrothermal calcite from the Huize ore field.

Fig. 3. Schematic stratigraphic column for the Huize ore field, showing the main facies and the thickness distribution of the sequences. The orebodies are hosted by the C_{1b} dolomite. Some small ore veins occur in D_{3z} dolomite.

The type of mineralization in this ore field is still a matter of debate. Some researchers consider that the Kuangshanchang and Qilinchang deposits are MVT deposits (Zhou *et al.*, 2001; Li *et al.*, 2007b). Others do not

think that they are MVT deposits because of their high ore grades, large size for single orebody (nearly 1 Mt Pb + Zn reserve) and may have relationship with Emeishan basalt magmatic event (Chen, 1993; Liu and Lin, 1999;

Fig. 4. Cross section of the orebodies in the Qilinchang deposit.

Li *et al.*, 1999; Hu, 2000; Huang *et al.*, 2001; Zhang 2006). Because geological setting, host rocks, mineral assemblages and the features of ore fluid and isotopic compositions are similar to MVT deposits (Anderson, 1975;

Sverjensky, 1981, 1986; Bethke and Marshak, 1990; Leach and Sangster, 1993; Leach *et al.*, 2001), the Huize ore field is here considered to be typical of a MVT ore field.

SAMPLES AND ANALYTICAL PROCEDURE

Calcite, sphalerite, galena and pyrite samples were selected from underground workings or outcrops in the Huize ore field. Samples from No. 8 orebody were collected from two drill holes. Only fresh samples were collected. Individual minerals were extracted from the ores and wall rocks and were lightly crushed to 40-60 mesh, washed and then handpicked to a purity of more than 99% under a binocular microscope.

Sulfide samples were dissolved using 14.0N ultrapure HNO_3 and then dried and transformed into chloride using 12.0N ultrapure HCl . For galena samples, Pb was separated by anion exchange resin. After transformation into chloride, pyrite and sphalerite were dried and dissolved using 0.5N HBr ; lead was separated using anion exchange resin with 6.0N HCl after removing Fe^{3+} ion and other interfering ions, using 0.5N HBr and 2.0N HBr , respectively. Lead isotope ratios were determined on a MAT-262 at the National Museum of Japanese History. The replicate analyses of NBS-981 gave $^{206}\text{Pb}/^{204}\text{Pb} = 16.913 \pm 0.002$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.457 \pm 0.002$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.611 \pm 0.004$. The 2-sigma uncertainty is less than 0.05%.

Sulfur isotope analyses were carried out using 200-mesh pyrite, galena and sphalerite pure samples. They were combusted with CuO in an oven at 1000°C and in vacuum condition. Liberated SO_2 was frozen in a liquid nitrogen trap and after cryogenic separation from other gases the isotopic compositions were determined on a MAT-253 mass spectrometer at the Institute of Geochemistry, Chinese Academy of Sciences. Both Canyon Diablo troilite and pyrrhotite standards were used. Routine analytical precision for standards material was less than 0.2 per mil. For comparison, six pyrite samples selected from carbonate wall rocks and host rock were analyzed.

Pure calcite separates were prepared for carbon and oxygen isotope analysis. Carbonate gas extractions were carried out following the standard procedure of McCrea (1950). The reaction time for calcite is 4h using a thermostated water bath at 25°C (McCrea, 1950). The CO_2 was analyzed on a MAT 251 EM mass spectrometer at the Institute of Geology, Chinese Academy of Geological Sciences. The reproducibility is better than 0.1 per mil and 0.2 per mil for carbon and oxygen, respectively. Carbon and oxygen isotope results are expressed as per mil deviation from the PDB and SMOW, respectively.

40-mesh pure calcite samples were heated at 100°C to 120°C to exclude adsorbed water and secondary fluid inclusions. Then the fluid inclusions were crushed at 350°C under the protection of N_2 flow. Water from the fluid inclusions was separated by cryogenic means and reduced to H_2 using Zn . δD was determined by MAT 251

EM mass spectrometer. $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ was calculated according to oxygen isotope compositions of the calcite using the following equation: $1000\ln\alpha_{\text{calcite-H}_2\text{O}} = 4.01 \times 10^6/T^2 - 4.66 \times 10^3/T + 1.71$ (Zheng and Chen, 2000).

For sphalerite and pyrite samples, separates were digested with 6N HCl + 18N HNO_3 , dried, and dissolved again with 6N HCl + 18N HNO_3 . For galena samples, 500 mg of separate was digested with 6N HCl , dried, and again dissolved with 6N HCl . After centrifuging, the solution for each of the above sulfides was filtered, dried, and dissolved with 2.5N HCl . The resulting solution was passed through an AG50W1 anion exchange resin and Pb, Zn, and other interfering ions were adsorbed in this resin. Then the resultant solution was passed through an AG50W $\times 8$ (H^+) cation exchange resin. Rb and Sr were separated by 0.8N and 2.5N HCl , respectively. For calcite, 100 mg samples were dissolved with 2.5N HCl and the solution passed through an AG50W $\times 8$ (H^+) cation exchange resin. Rb and Sr were separated using 0.8N and 2.0N HCl , respectively. Rb and Sr isotope measurements were carried out at the Modern Analysis Center, Nanjing University, and analyzed on a VG-354 ionization mass spectrometer. The Rb/Sr ratios are accurate to better than 1%. Total procedure blanks for Rb and Sr were 20 pg and 50 pg, respectively, less than 1% of most of the samples. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for NBS987 standard sample was determined to be 0.710223 ± 8 (2 sigma). All isotopic compositions were normalised to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$, using power law fractionation correction.

RESULTS AND DISCUSSION

Lead

Newly reported and published lead isotope data of sulfides, wall rocks and Permian Emeishan basalt are shown in Table 1 and plotted in Fig. 5.

Lead isotope compositions of 88 sulfide samples from different orebodies are isotopically homogeneous. Their $^{206}\text{Pb}/^{204}\text{Pb}$ values range from 18.251–18.530 (mean 18.462), the $^{207}\text{Pb}/^{204}\text{Pb}$ values range from 15.663–15.855 (mean 15.720) and the $^{208}\text{Pb}/^{204}\text{Pb}$ values range from 38.487–39.433 (mean 38.894). The average $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values of 21 ore pyrite samples are 18.473, 15.725 and 38.912, respectively, and the $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values of 6 pyrite samples disseminated in carbonate wall rocks ($\text{C}_{2\text{w}}$ and $\text{C}_{1\text{b}}$) range from 18.480–18.514 (mean 18.495), 17.712–17.733 (mean 15.724) and 38.765–38.934 (mean 38.885).

Lead isotope compositions of sulfide ore samples are remarkably homogeneous. All data cluster in a narrow field above the line of Upper Crust in the $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram (Zartman and Haines, 1988, Fig. 5). Because the

Fig. 5. $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram, showing that Pb isotopic values of the ores are similar to those of the wall rocks, host rock and pyrite from the carbonate wall rocks. The data of the ores define a linear trend.

carbonate wall rocks and Emeishan basalt in this area also have similar Pb isotope compositions to those of the ores (Table 1), we cannot exclude any of them as one of the source rocks.

Six pentagonal dodecahedron pyrite samples from the carbonate wall rocks (C_{1w} and C_{1b}) display similar Pb isotope features as the sulfide ores. Because these pyrite crystals are disseminated in the carbonate wall rocks, the metals in these crystals might derive from the carbonate wall rocks. Moreover, the data of the ores plot in the field near the carbonate wall rocks in the $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 5). These signatures indicate that the carbonate wall rocks might have contributed metals for mineralization. Previous studies revealed that the carbonate rocks in the Huize ore field are hydrothermally al-

tered and recrystallized, and their Pb, Zn, Ge, Ga, Cd and In contents are lower than both the mean contents of the carbonate rocks of East China and the Clarke values (Li *et al.*, 2002). This may be a signature that metals were leached out and transported to structures during metallogenesis. REE geochemistry data also suggest that the carbonate wall rocks in the ore field have contributed ore-forming elements to the fluids (Li *et al.*, 2007a).

The Carboniferous and Devonian carbonate wall rocks have similar Pb isotope compositions. If the metals came from these rocks, the ore samples should have similar model ages to these rocks. The calculated $^{207}\text{Pb}/^{206}\text{Pb}$ two-stage model ages (Stacey and Kramers, 1975) are mainly between 300 and 400 Ma (average 364 Ma), which are close to the ages of the enclosing Carboniferous and Devonian wall rocks. $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values of the ores are slightly lower than the carbonate wall rocks. This may be due to the carbonate wall rocks containing more uranium and thorium than sulfides. Thus the radiogenic ^{206}Pb , ^{207}Pb and ^{208}Pb in the ores are less than the wall rocks after the ores precipitated.

Zhou *et al.* (2001) proposed a single source rock for the lower Sinian igneous rock suite, which consists of an acidic, intermediate-acidic igneous rock suite (volcanic, volcanoclastic, clastic rocks, and granite). But it only occurs in NS-trending Dongchuan rift and cannot be found in the three profiles we have investigated in the Huize area. The oldest strata in this area include the Upper Sinian (Dengying Formation, Z_{2d}). Though many authors mentioned Proterozoic basement rocks as source rocks, such as Kunyang Group, Dahongshan Group and Kangding Group (Li *et al.*, 1999; Hu, 2000), these strata mainly occur along the NS-trending Dongchuan rift (see Zhou *et al.*, 2001), about one hundred kilometers from the Huize ore field. In addition, the deposits related to basement in this area are Cu and Fe deposits, such as the Yimen Cu deposit, Dahongshan and Dongchuan Cu-Fe deposit, but not any Zn-Pb ores. Therefore, we suggest that these basement rocks were not involved during ore formation.

In conclusion, the Pb isotope compositions of the ores are remarkably homogeneous. These data are all plotted in a narrow field above the Upper Crust line in the $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram. The Pb isotope compositions of pyrite in the carbonate wall rocks are indistinguishable from those of the ores. It suggests that the ore metals have multiple sources traceable to the wall rocks.

Sulfur

$\delta^{34}\text{S}_{\text{CDT}}$ values for sphalerite, galena and pyrite from different orebodies and pyrite disseminated in carbonate wall rocks far from ores were determined. These data are presented in Table 2. It can be seen from Table 2 that: (1) the $\delta^{34}\text{S}$ values for pyrite, sphalerite and galena from four

Table. 1. Pb-isotope compositions of ores and rocks from the Huize ore field

Sample	Location	Mineral	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	
44-5	No. 6	Galena	18.436	15.683	38.861	(1)
38-3	No. 6	Galena	18.471	15.702	38.847	(1)
23-4	No. 6	Galena	18.469	15.701	38.85	(1)
13-55	No. 6	Galena	18.461	15.701	38.857	(1)
13-61	No. 6	Galena	18.45	15.692	38.823	(1)
13-34+1	No. 6	Galena	18.474	15.701	38.844	(1)
6-10	No. 6	Galena	18.454	15.691	38.82	(1)
14-1-11	No. 6	Galena	18.469	15.7	38.85	(1)
14-1-12	No. 6	Galena	18.471	15.709	38.839	(1)
14-2-11	No. 6	Galena	18.434	15.672	38.749	(1)
14-3-3	No. 6	Galena	18.47	15.7	38.849	(1)
14-3-17	No. 6	Galena	18.458	15.69	38.817	(1)
S1-20	No. 6	Galena	18.53	15.855	39.433	(1)
S3-11	No. 6	Galena	18.251	15.693	38.487	(1)
HQ84	No. 6	Galena	18.496	15.75	39.001	(2)
1571-8	No. 6	Pyrite	18.393	15.688	38.82	(2)
HQ99-1	No. 6	Pyrite	18.464	15.696	38.828	(2)
14-3-4	No. 6	Pyrite	18.474	15.7	38.845	(1)
F-131	No. 6	Pyrite	18.432	15.664	38.729	(1)
1571-11	No. 6	Sphalerite	18.339	15.676	38.753	(2)
1631-7-1	No. 6	Sphalerite	18.385	15.676	38.771	(2)
1631-7-2	No. 6	Sphalerite	18.441	15.679	38.772	(2)
1631-7-3	No. 6	Sphalerite	18.353	15.663	38.719	(2)
HQ497	No. 8	Pyrite	18.493	15.74	38.963	
HQ478	No. 8	Sphalerite	18.5	15.748	38.977	
HQ488	No. 8	Sphalerite	18.494	15.739	38.947	
HQ491	No. 8	Sphalerite	18.484	15.726	38.927	
HQ493	No. 8	Sphalerite	18.486	15.739	38.946	
HQ494	No. 8	Sphalerite	18.495	15.754	38.995	
HQ495	No. 8	Sphalerite	18.482	15.736	38.936	
HQ497	No. 8	Sphalerite	18.477	15.733	38.925	
HQ524	No. 8	Ore	18.494	15.744	38.975	
HQ537	No. 8	Ore	18.478	15.734	38.929	
HQ538	No. 8	Ore	18.487	15.741	38.957	
HQ542	No. 8	Ore	18.481	15.737	38.941	
10-3-1	No. 10	Galena	18.462	15.713	38.884	
10-11-1	No. 10	Galena	18.478	15.731	38.918	
10-9-1	No. 10	Galena	18.485	15.751	38.941	
10-16-1	No. 10	Galena	18.469	15.724	38.899	
10-18	No. 10	Galena	18.472	15.728	38.909	
10-22-1	No. 10	Galena	18.475	15.737	38.938	
10-3-2	No. 10	Sphalerite	18.47	15.725	38.907	
10-6-1	No. 10	Sphalerite	18.476	15.728	38.915	
10-16-2	No. 10	Sphalerite	18.476	15.738	38.929	
10-19	No. 10	Sphalerite	18.465	15.714	38.893	
10-22-2	No. 10	Sphalerite	18.481	15.748	38.948	
HQ483	C _{1b}	Pyrite	18.514	15.712	38.765	
HQ484	C _{1b}	Pyrite	18.499	15.725	38.909	
HQ503	C _{1b}	Pyrite	18.484	15.732	38.934	
	C _{1b}	Dolomite	18.673	15.963	39.685	(1)
	C _{1b}	Dolomite	18.51	15.791	39.124	(1)
	D _{3z}	Dolomite	18.54	15.899	39.562	(1)
	D _{3z}	Dolomite	18.842	15.681	38.716	(2)
	P _{1q}	Limestone	18.759	15.609	38.542	(2)

Table 1. (continued)

Sample	Location	Mineral	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	
44-5	No. 6	Sphalerite	18.487	15.72	38.867	(1)
14-2-8	No. 6	Sphalerite	18.458	15.694	38.814	(1)
F1	No. 6	Sphalerite	18.455	15.709	38.859	(1)
F126	No. 6	Sphalerite	18.458	15.698	38.863	(1)
F135	No. 6	Sphalerite	18.462	15.713	38.874	(1)
HQLC1b	No. 6	Ore	18.475	15.723	38.9	
HQLC1b	No. 6	Ore	18.464	15.713	38.873	
HQLC9	No. 6	Ore	18.467	15.722	38.888	
HQLC13	No. 6	Ore	18.476	15.733	38.923	
HQLC30a	No. 6	Ore	18.46	15.715	38.868	
HQLC30b	No. 6	Ore	18.467	15.723	38.884	
HQLC34	No. 6	Ore	18.486	15.734	38.946	
HQLC50	No. 6	Ore	18.488	15.735	38.952	
HQLC57	No. 6	Ore	18.483	15.73	38.928	
HQ485	No. 8	Pyrite	18.495	15.742	38.973	
HQ486	No. 8	Pyrite	18.498	15.741	38.968	
HQ487	No. 8	Pyrite	18.506	15.751	39.009	
HQ488	No. 8	Pyrite	18.486	15.731	38.936	
HQ489	No. 8	Pyrite	18.487	15.731	38.942	
HQ490	No. 8	Pyrite	18.493	15.744	38.973	
HQ492	No. 8	Pyrite	18.491	15.738	38.955	
HQ493	No. 8	Pyrite	18.481	15.73	38.925	
HQ495	No. 8	Pyrite	18.491	15.743	38.967	
10-3-3	No. 10	Pyrite	18.468	15.719	38.897	
10-6-2	No. 10	Pyrite	18.468	15.719	38.889	
10-9-2	No. 10	Pyrite	18.479	15.748	38.935	
10-16-3	No. 10	Pyrite	18.471	15.731	38.921	
10-20	No. 10	Pyrite	18.467	15.724	38.91	
10-5	No. 10	Ore	18.471	15.739	38.928	
10-12	No. 10	Ore	18.469	15.725	38.911	
10-21	No. 10	Ore	18.464	15.722	38.898	
1-6-1	No. 1	Galena	18.419	15.678	38.813	
1-11-1	No. 1	Galena	18.439	15.721	38.887	
1-17-1	No. 1	Galena	18.417	15.687	38.879	
1-22	No. 1	Galena	18.425	15.701	38.875	
1-6-2	No. 1	Sphalerite	18.428	15.705	38.867	
1-11-2	No. 1	Sphalerite	18.427	15.709	38.869	
1-17-2	No. 1	Sphalerite	18.423	15.703	38.88	
1-17-3	No. 1	Pyrite	18.431	15.716	38.876	
1-23	No. 1	Pyrite	18.457	15.728	38.899	
1-10	No. 1	Ore	18.466	15.729	38.907	
1-12	No. 1	Ore	18.437	15.718	38.894	
1-17-1	No. 1	Galena	18.417	15.687	38.879	
HQ473	C _{2w}	Pyrite	18.495	15.715	38.844	
HQ480	C _{2w}	Pyrite	18.496	15.731	38.928	
HQ481	C _{2w}	Pyrite	18.48	15.733	38.929	
	Z _{2d}	Dolomite	18.517	15.851	39.271	(1)
	Z _{2d}	Dolomite	18.482	15.784	39.142	(1)
	P _{2β}	Basalt	18.545	15.591	38.882	(3)
	P _{2β}	Basalt	18.436	15.55	38.931	(3)
	P _{2β}	Basalt	18.855	15.5815	39.344	(3)
	P _{2β}	Basalt	18.732	15.5283	38.928	(3)
	P _{2β}	Basalt	18.843	15.602	39.107	(3)
	P _{2β}	Basalt	18.584	15.5545	39.068	(3)

Notes: The data marked (1), (2), (3) are from Zhou et al. (2001), Han (2002) and Zhang and Wang (2003), respectively. The other data are from this study.

Table 2. Sulfur isotope data for sulfides from the Huize ore field

Samples	Ore body	Minerals	$\delta^{34}\text{S}$ (‰)	Samples	Ore body	Minerals	$\delta^{34}\text{S}$ (‰)
HZ911-9	No. 1	Galena	11.1	H10-20-1	No. 10	Sphalerite	13.5
HZ911-17	No. 1	Galena	11.5	H10-20-2	No. 10	Sphalerite	14.2
H1-6-5	No. 1	Galena	13.0	H10-20-3	No. 10	Sphalerite	14.5
H1-11-1	No. 1	Galena	11.0	H10-20-4	No. 10	Sphalerite	14.2
H1-12-2	No. 1	Galena	11.6	H10-22-1	No. 10	Sphalerite	13.6
H1-6-1	No. 1	Sphalerite	17.2	H10-3-2	No. 10	Galena	14.4
H1-6-2	No. 1	Sphalerite	15.5	H10-22-2	No. 10	Galena	13.5
H1-6-3	No. 1	Sphalerite	14.4	HQ485	No. 8	Pyrite	14.4
H1-17-1	No. 1	Sphalerite	14.0	HQ486	No. 8	Pyrite	14.9
H1-17-2	No. 1	Sphalerite	12.5	HQ487	No. 8	Pyrite	15.8
H1-22-1	No. 1	Sphalerite	15.4	HQ488	No. 8	Pyrite	16.2
H1-23	No. 1	Sphalerite	16.0	HQ489	No. 8	Pyrite	16.4
H1-10-1	No. 1	Sphalerite	13.0	HQ490	No. 8	Pyrite	15.6
H1-10-2	No. 1	Sphalerite	15.1	HQ492	No. 8	Pyrite	16.0
H1-10-3	No. 1	Sphalerite	17.7	HQ493	No. 8	Pyrite	15.8
H1-11-2	No. 1	Sphalerite	13.8	HQ495	No. 8	Pyrite	16.2
H1-11-3	No. 1	Sphalerite	14.3	HQ497	No. 8	Pyrite	16.7
H1-12-3	No. 1	Sphalerite	14.1	HQ487	No. 8	Sphalerite	15.8
HZQ21	No. 6	Pyrite	15.8	HQ488	No. 8	Sphalerite	16.0
HZQ38	No. 6	Pyrite	15.1	HQ491	No. 8	Sphalerite	15.3
HZQ81	No. 6	Pyrite	16.7	HQ493	No. 8	Sphalerite	13.5
HZQ38	No. 6	Sphalerite	14.1	HQ494	No. 8	Sphalerite	13.5
HZQ53	No. 6	Sphalerite	14.7	HQ495	No. 8	Sphalerite	13.4
HZQ69	No. 6	Sphalerite	15.9	HQ497	No. 8	Sphalerite	13.6
HZQ81	No. 6	Sphalerite	17.2	8-1	No. 8	Sphalerite	15.5
HZQ21	No. 6	Galena	12.6	8-2	No. 8	Sphalerite	15.8
HZQ38	No. 6	Galena	11.6	15	No. 8	Sphalerite	14.8
HZQ69	No. 6	Galena	13.0	8-1	No. 8	Galena	14.5
HZQ81	No. 6	Galena	14.1	15	No. 8	Galena	11.3
H10-3-3	No. 10	Pyrite	17.4	H10-23	No. 10	Pyrite (C_{1b})	5.2
H10-18	No. 10	Pyrite	15.7	HQ480	No. 8	Pyrite (C_{2w})	6.8
H10-20-5	No. 10	Pyrite	16.5	HQ481	No. 8	Pyrite (C_{2w})	10.6
H10-3-1	No. 10	Sphalerite	15.3	HQ483	No. 8	Pyrite (C_{1b})	4.2
H10-19-1	No. 10	Sphalerite	15.4	HQ484	No. 8	Pyrite (C_{1b})	8.1
H10-19-2	No. 10	Sphalerite	14.9	HQ503	No. 8	Pyrite (C_{1b})	5.3

Note: Pyrite samples H10-23, HQ483, HQ484 and HQ503 were selected from host rock (C_{1b} , Baizuo Formation). Pyrite samples HQ480, HQ481 were selected from wall rock (C_{1w} , Weining Formation). The other samples were all selected from ores.

orebodies (No. 1, 6, 8 and 10 orebodies) range from +10.9 to +17.4 per mil. Most of them range from 13 to 17 per mil (Fig. 6). (2) The $\delta^{34}\text{S}$ values for the same sulfide minerals from different orebody or the same orebody are similar except for the No. 1 orebody. The lower $\delta^{34}\text{S}$ values for the sulfides from the No. 1 orebody may indicate that oxidized ores are depleted in ^{34}S because there are some mixed sulfide-oxide ores occurring in the lower part of the No. 1 orebody. Liu and Lin (1999) analyzed 13 galena samples from the No. 1 orebody and the $\delta^{34}\text{S}$ values range from 4.8 to 7.9 per mil. (3) Comparing the individual sulfides, $\delta^{34}\text{S}$ values of pyrites are higher than sphalerites and sphalerites are higher than galenas, it may indicate that isotopic equilibrium among sulfides was attained (Ohmoto, 1986). (4) $\delta^{34}\text{S}$ values of pyrite from the carbonante wall rocks sampled far from ores are lower

than those for pyrite from the ores.

The source of reduced sulfur for the sulfide phases is important in order to understand the mechanism of MVT deposits. The homogenous sulfur isotope compositions suggest a single source for the different kinds of sulfide from the ores. The sulfur of the ores may come from sulfates in the host rocks. Evaporite sulfates were formed in the Sinian, Cambrian, Devonian and Carboniferous strata in the area adjacent of the Huize ore field and the Zn-Pb polymetallic deposits mainly hosted by these strata in this region. One gypsum sample from C_{1b} dolomite in the Huize ore field has a $\delta^{34}\text{S}$ value of 14.0 per mil (Han, 2002) and one barite from C_{1b} dolomite has a $\delta^{34}\text{S}$ value of 17.6 per mil (Liu and Lin, 1999). The high $\delta^{34}\text{S}$ values of the sulfides from the Huize ore field can be explained by the reduction of sulfur from the sulfates.

Fig. 6. $\delta^{34}\text{S}$ histogram for the sulfide ore minerals from the Huize ore field, note that most of the data range is from 13 per mil to 17 per mil.

The mechanisms for sulfate reduction may be either thermochemical (TSR) or bacterial (BSR) (Ohmoto *et al.*, 1990). The mineralization temperature determined by fluid inclusion studies is 150°C to 250°C (Liu and Lin, 1999; Han, 2002; Zhang, 2006), which exceeds conditions for bacteria to metabolize sulfur (Machel, 1989; Jorgenson *et al.*, 1992). In addition it is difficult to explain ores deposited in opened-system by BSR process. Sulfur isotope compositions generated through BSR are typical about 40 per mil lower than the $\delta^{34}\text{S}$ values of the original sulfate (Ohmoto and Rye, 1979; Ohmoto, 1986). Therefore TSR may be the most likely mechanism. At high temperatures (higher than 175°C), TSR can produce large amount of reduced sulfur rapidly (Ohmoto *et al.*, 1990). TSR is characterized by much smaller (or even no) isotope fractionations between sulfate and sulfide (or elemental sulfur) (Hoefs, 1997). Moreover, organic matter played a key role in thermochemical sulfate reduction in that it acted as reactant and product (Ottaway *et al.*, 1994; Cheilletz and Giuliani, 1996). The presences of organic matter in the black shale underlying the host rocks might have provided organic matter in sulfate reduction.

This view is also supported by carbon and oxygen isotope studies (see below).

Because isotopic equilibrium among sulfides was attained, geothermometric calculations can be carried out by $\Delta^{34}\text{S}$ -values for adjacent sphalerite and galena (Rye and Ohmoto, 1974; Rye, 1974; Czamanske and Rye, 1974). Except for sample 8-1, which corresponds to an unrealistically high temperature of 548°C, the other seven pairs provide temperatures of 173°C to 263°C, which are consistent with homogenisation temperatures in fluid inclusions of calcite and sphalerite (150°C to 250°C, Liu and Lin, 1999; Han *et al.*, 2004; Li *et al.*, 2005; Zhang, 2006). This is a good temperature for TSR.

$\delta^{34}\text{S}$ values for the pyrite from carbonate wall rocks far from ores are lower than those of the ores. These six pyrite samples were selected from drill hole of the No. 8 orebody and they are very fresh samples. They have much lower $\delta^{34}\text{S}$ values than the ores from the orebodies, but they have similar Pb isotope compositions with the ores. It indicates that these two kinds of sulfides have the same metal source but the sulfur reduction mechanism may have been different and/or the sulfur isotope composition of the original sulfate available for reduction had a different isotopic composition.

Sulfur isotope study indicates that the sulfur was provided by sulfate *in situ* reduction in the host rocks. The mechanisms for sulfate reduction may be thermochemical sulfate reduction (TSR) and the organic matter in the black shale underlying the wall rocks had played an important role during the sulfate reduction process.

Carbon and oxygen

The carbon and oxygen isotope compositions of massive (11 samples), disseminated (6 samples) and veined calcite (4 samples) were analyzed. Two calcite samples from NE-trending faults, four host dolomites and two calcite samples from the cavities in the wall rocks, which represent the products of the fluid leached wall rocks, were also analyzed (Table 3). Three kinds of calcite from the ores have very similar isotope compositions with $\delta^{13}\text{C}$ values ranging from -2.1 to -3.5 per mil with respect to PDB and $\delta^{18}\text{O}$ values in the range of 16.8 to 18.6 per mil with respect to SMOW. 2 NE-trending fault calcite samples (one is 540 m from orebody and the other is 150 m from the orebody) have $\delta^{13}\text{C}$ values in the range of -3.0 to -3.4 per mil and $\delta^{18}\text{O}$ values of 16.3 to 16.7 per mil. In contrast, calcite from the cavities has $\delta^{13}\text{C}$ values in the range of 0.5 to 1.1 per mil and $\delta^{18}\text{O}$ values of 22.1 to 23.5 per mil. The range of $\delta^{13}\text{C}$ values for 4 host dolomites is -0.8 to 0.7 per mil and $\delta^{18}\text{O}$ is 22.6 to 23.2 per mil.

Two calcite samples from the cavities in the wall rocks have $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values similar to those of the carbonate wall rocks. These data show that this calcite is derived from the fluid that leached the wall rock. The $\delta^{13}\text{C}$

Table 3. Carbon and oxygen isotope data of the Huize ore field

Samples	Sample descriptions	$\delta^{13}\text{C}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{SMOW}}$
HZ911-3	Disseminated calcite from ore of No. 1 orebody	-2.2	17.5
HZ911-10	Massive calcite from No. 1 orebody	-3.4	18.4
HZ911-15	Massive calcite from No. 1 orebody	-3.5	18.6
HZQ25	Massive calcite from No. 6 orebody	-2.5	17.5
HZQ40	Disseminated calcite from ore of No. 6 orebody	-2.6	17.7
HZQ47	Massive calcite from No. 6 orebody	-3.1	17.5
HZQ55	Veined calcite from ore of No. 6 orebody	-2.7	17.7
HZQ66	Massive calcite from No. 6 orebody	-3.4	18.1
HZQ70	Disseminated calcite from ore of No. 6 orebody	-3.3	18.1
HZQ77	Veined calcite from ore of No. 6 orebody	-2.8	17.8
HZQ85	Disseminated calcite from ore of No. 6 orebody	-2.7	17.3
HZQ90	Disseminated calcite from ore of No. 6 orebody	-2.7	17.2
HZQ96	Massive calcite from No. 6 orebody	-2.1	17.5
HQ10-7	Massive calcite from No. 10 orebody	-2.9	17.0
HQ10-12	Massive calcite from No. 10 orebody	-3.2	18.5
HQ10-18	Massive calcite from No. 10 orebody	-2.3	16.8
HQ10-25	Disseminated calcite from ore of No. 10 orebody	-3.0	17.9
HQ10-5	Veined calcite from ore of No. 10 orebody	-2.8	17.2
HQ8-115	Massive calcite from No. 8 orebody	-2.2	17.0
HQ8-143	Massive calcite from No. 8 orebody	-2.7	17.6
HQ8-98	Veined calcite from ore of No. 8 orebody	-3.0	17.8
HZQ35	Calcite from caves occurred in Permian carbonate rock from Qilinchang deposit, 500 m away from orebody	0.5	22.1
HZK33	Calcite from caves occurred in Permian carbonate rock from Kuangshanchang deposit, 450 m away from orebody	1.1	23.5
HZQ74	Coarse dolomite whole rock from host rock of the No. 10 orebody	-0.8	22.6
HZ2053-29	Coarse dolomite whole rock from host rock of the No. 1 orebody	0.4	23.2
HZS40	Coarse dolomite from Baizuo Formation, 1500 m away from orebody	0.7	22.8
HZX-3	Coarse dolomite from Baizuo Formation, 1000 m away from orebody	-0.2	23.1
HZ911-4	Calcite from NE-trending fault, 540 m away from No. 1 orebody	-3.0	16.7
HZQ28	Calcite from NE-trending fault, 150 m away from orebody	-3.4	16.3

and $\delta^{18}\text{O}$ values of the calcites from NE-trending faults are significantly different from the wall rock but close to the values of the gangue calcite and many researchers concluded that the NE-trending faults are the pathways for ore fluid (Liu and Lin, 1999; Han, 2002; Li *et al.*, 2005). If assuming the ore fluid equilibrated with the wall rocks and gangue calcite, based on fractionation factors for dolomite and water (Matthews and Katz, 1977), the calculated mean $\delta^{18}\text{O}$ value of ore fluid is 12.5 per mil at 200°C and 15.0 per mil at 250°C. According to the mean $\delta^{18}\text{O}$ value for gangue calcite and fractionation factors for calcite and water (O'Neil *et al.*, 1969), the calculated $\delta^{18}\text{O}$ value of ore fluid is 8.2 per mil at 200°C and 10.5 per mil at 250°C. These two results are inconsistent with each other. This may indicate that these different carbonates formed from two or more different types of fluids and that the regional dolomites have not equilibrated completely with the fluids precipitating the calcite related to the ore formation.

The $\delta^{13}\text{C}$ values of 20 gangue calcite samples range from -2.1 to -3.5 per mil and indicates that the ore fluid

has lower $\delta^{13}\text{C}$ values. The mean $\delta^{13}\text{C}$ value of 4 dolomite samples from $\text{C}_{1\text{b}}$ host rock is 0 per mil and nearly all the orebodies are hosted in red coarse-grained dolomite of $\text{C}_{1\text{b}}$. This suggests that the wall rock have high permeability and was strongly bleached by ore fluid, which has negative $\delta^{13}\text{C}$ values. The rocks of Devonian, Cambrian and Sinian underlying the orebodies consist of sedimentary carbonate rocks, black shale and sandstone. They contain some fossils and organic carbon. If the ore fluid originated or passed through the organic material contained in these rocks, it may have negative $\delta^{13}\text{C}$ values (Zheng and Chen, 2000). When this fluid reacted with carbonate wall rocks and moved upward to $\text{C}_{1\text{b}}$, its $\delta^{13}\text{C}$ value became higher and the $\delta^{13}\text{C}$ value of host rock became lower.

Carbon and oxygen isotope studies suggest the ore fluid had passed through strata containing organic matter. This fluid reacted with these rocks when it moved to the site of ore deposition. These reactions produced higher carbon and oxygen isotope composition for the ore fluid and lower values for the wall rocks.

Table 4. Hydrogen and oxygen isotope data for fluid inclusions in calcites from the ores

Samples	Ore body	Minerals and occurrence	$\delta^{18}\text{O}_{\text{SMOW}}$	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$	δD
HZ-911-10	No. 1	Massive calcite	18.4	8.6	-59.8
HZ-911-15	No. 1	Massive calcite	18.6	8.8	-52.4
HZQ-25	No. 6	Massive calcite	17.5	7.7	-50.2
HZQ-40	No. 6	Disseminated calcite	17.7	7.9	-55.6
HZQ-47	No. 6	Massive calcite	17.5	7.7	-57.9
HZQ-55	No. 6	Veined calcite	17.7	7.9	-54.1
HZQ-66	No. 6	Massive calcite	18.1	8.3	-53.9
HZQ-77	No. 6	Veined calcite	17.8	8.0	-58.0
HZQ-85	No. 6	Disseminated calcite	17.3	7.5	-52.7
HQ-10-12	No. 10	Massive calcite	18.5	8.7	-53.2
HQ-10-18	No. 10	Massive calcite	16.8	7.0	-57.3
HQ-10-25	No. 10	Disseminated calcite	17.9	8.1	-53.0
HQ-10-5	No. 10	Veined calcite	17.2	7.4	-52.8
HQ-8-115	No. 8	Massive calcite	17.0	7.2	-55.2
HQ-8-143	No. 8	Massive calcite	17.6	7.8	-54.1
HQ-8-98	No. 8	Veined calcite	17.8	8.0	-54.3

Note: $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ was calculated according to oxygen isotope compositions of the calcite using the following equation: $1000\ln\alpha_{\text{calcite-H}_2\text{O}} = 4.01 \times 10^6/T^2 - 4.66 \times 10^3/T + 1.71$ (Zheng and Chen, 2000), $t = 200^\circ\text{C}$.

Hydrogen and oxygen

The δD values were analyzed directly from inclusion fluids in massive (9 samples), disseminated (3 samples) and veined calcite (4 samples). The $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values were calculated from $\delta^{18}\text{O}$ values of calcite using the formula: $1000\ln\alpha_{\text{calcite-water}} = 4.01 \times 10^6/T^2 - 4.66 \times 10^3/T + 1.71$ (Zheng and Chen, 2000). The inclusion fluids in three kinds of calcites have similar δD and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values with respect to SMOW. The results are listed in Table 4.

In contrast to fluid inclusions of quartz, the $\delta\text{D}_{\text{FI}}$ values obtained from inclusion fluids in calcite can accurately reflect the δD values of the hydrothermal fluid (Faure, 2003). The $\delta\text{D}_{\text{FI}}$ values of gangue calcites are indistinguishable and have a narrow range of -50 to -60 per mil. Using the formula reported by Zheng and Chen (2000), the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values calculated from $\delta^{18}\text{O}$ values of calcite range from 7.0 to 8.8 per mil at 200°C (Median temperature of homogenization temperatures of fluid inclusions in gangue calcite). In the $\delta^{18}\text{O}_{\text{H}_2\text{O}}-\delta\text{D}_{\text{H}_2\text{O}}$ diagram, all the data overlap in the metamorphic and magmatic waters boxes (Fig. 7). Though most of calculated $\delta^{18}\text{O}$ and δD values of the ore fluid do plot in the field of magmatic fluid, the igneous rocks in this field are from the Emeishan basalt, which have low $^{86}\text{Sr}/^{87}\text{Sr}$ (see below). On the other hand, the ore deposits related to the Emeishan basalt in this area are Cu-Ni-PGE deposits and V-Ti-Fe deposits (Song *et al.*, 2003; Tao *et al.*, 2004; Hu *et al.*, 2005). Therefore, the mineralizing fluids cannot be magmatic waters.

Han *et al.* (2004) and Zhang (2006) have studied the fluid inclusions in gangue calcite and dolomite. The homogenization temperatures of fluid inclusions in gangue

Fig. 7. Plot of $\delta^{18}\text{O}$ vs. δD values of fluid inclusion waters in gangue calcites from the Huize ore field.

calcite range from 150°C to 250°C . The salinity ranges from 5 to 21 wt% NaCl (mean 13.2 wt% NaCl). Gases in the fluid inclusions are mainly CO_2 , CO , CH_4 and H_2 . Ions in the inclusion fluids are K^+ , Na^+ , Ca^{2+} , Mg^{2+} , F^- and Cl^- . These natures of the ore fluids are similar to those of MVT deposits except for lower Br- contents (Kesler *et al.*, 1995, 1996, 1997). The calculated $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of fluid inclusions of calcites from the Huize ore field are 7 to 11 per mil and the δD values range from -44 to -56 per mil. These data are plotted in the field of Illinois-Kentucky calcite-barite ore field (Richardson *et al.*, 1988), which is thought to be a MVT ore field. The lower δD

Table 5. Sr isotope data of the Huize ore field

Samples	Location	Minerals	Rb (ppm)	Sr (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$(^{87}\text{Sr}/^{86}\text{Sr})_0$
L1-1	No. 1	Sphalerite	0.5	0.7	0.70	0.719123	0.716847
L1-3	No. 1	Sphalerite	16.0	1.0	47.51	0.869687	0.715362
L1-9	No. 1	Sphalerite	9.7	1.0	28.21	0.807449	0.715815
L1-10	No. 1	Sphalerite	23.2	1.4	50.03	0.877686	0.715175
1-17	No. 1	Sphalerite	0.7	0.5	14.09	0.762086	0.716318
HZQ38	No. 6	Sphalerite	4.7	0.5	25.10	0.797653	0.716122
HZQ81	No. 6	Sphalerite	1.9	0.9	6.22	0.736765	0.716564
28	No. 8	Sphalerite	0.9	0.5	5.31	0.733923	0.716688
15	No. 8	Sphalerite	0.8	0.5	4.34	0.730642	0.716548
10-16-1	No. 10	Sphalerite	13.8	1.0	39.66	0.844739	0.715913
L10-5	No. 10	Sphalerite	0.6	5.1	0.35	0.717833	0.716686
L10-5	No. 10	Sphalerite	1.0	0.9	0.72	0.719104	0.716779
L10-4	No. 10	Sphalerite	0.9	0.9	2.85	0.725816	0.716552
L10-2	No. 10	Sphalerite	6.4	1.2	15.48	0.766775	0.716492
10-20-1	No. 10	Sphalerite	1.6	1.6	1.48	0.721359	0.716565
LC-5	No. 6	Sphalerite	0.7	3.2	0.65	0.719091	0.716989
LC-5	No. 6	Sphalerite	19.9	1.0	61.28	0.913104	0.714050
LC-7	No. 6	Sphalerite	14.0	1.0	42.14	0.851804	0.714922
LC-7	No. 6	Pyrite	16.1	1.0	47.59	0.869129	0.714544
LC-5	No. 6	Pyrite	23.5	1.0	69.71	0.940112	0.713676
LC-5	No. 6	Calcite	1.1	313	0.0106	0.717046	0.717012
LC-7	No. 6	Calcite	0.8	267	0.0088	0.716382	0.716353
1	No. 6	Calcite	0.1	411	0.0007	0.717012	0.717010
3	No. 6	Calcite	3.0	418	0.0218	0.717079	0.717008
5	No. 6	Calcite	1.0	218	0.0149	0.717057	0.717009
HZQ47	No. 6	Calcite	5.0	311	0.0471	0.717154	0.717001
HZQ89-1	No. 6	Calcite	2.2	303	0.0207	0.717076	0.717009
HZQ89-2	No. 6	Calcite	0.8	281	0.0084	0.717025	0.716998
HZQ90	No. 6	Calcite	2.0	232	0.0252	0.717088	0.717006
HZQ100	No. 6	Calcite	2.5	281	0.0094	0.717028	0.716997
HZ911-29	No. 1	Calcite	3.0	400	0.2181	0.717164	0.716456
HZ911-12	No. 1	Calcite	0.2	390	0.0018	0.716472	0.716466
HZ911-10	No. 1	Calcite	3.7	270	0.0405	0.716586	0.716454
HZ911-3	No. 1	Calcite	1.9	180	0.0315	0.716567	0.716465
HZ911-37	No. 1	Calcite	3.1	402	0.0243	0.716554	0.716475
P_{1qm}	1 sample	Carbonate rock				0.7080	
C_{1b} (unaltered)	4 samples	Dolomite				0.7083–0.7093	
C_{1b} (altered)	1 sample	Dolomite				0.7106	
D_{3z}	1 sample	Carbonate rock				0.7105	
$P_{2\beta}$	85 samples	Basalt				0.7039–0.7078	

Note: $(^{87}\text{Sr}/^{86}\text{Sr})_0$ was calculated using $t = 230$ Ma. The data of P_{1qm} , C_{1b} , D_{3z} and $P_{2\beta}$ are from Hu (2000) and Zhou et al. (2001).

values may reflect the fact that the ore fluid could have reacted with D-depleted organic matter (Goldfarb *et al.*, 1989, 2004; McCuaig and Kerrich, 1998) in shale, clastic rocks and mudstone underlying the host rock. It is widely accepted that MVT deposits precipitate from basinal brines (White, 1958; Hanor, 1979). The Emeishan flood basalt widely spreads in southwest China. It is considered the product of mantle plume and covers 250,000 km² area in Southwest China. Though the age of the Emeishan basalt is about 250 Ma (Thompson *et al.*, 2001; Boven *et al.*, 2002; Zhou *et al.*, 2002; Ali *et al.*, 2005), ⁴⁰Ar/³⁹Ar plateau and isochron ages of the native copper

mineralizations related to the Emeishan flood basalts in the Huize area are 226 Ma to 228 Ma (Zhu *et al.*, 2005). The ages of the No. 1 and No. 6 ore bodies constrained from Sm-Nd system in hydrothermal calcite are 228 ± 16 Ma and 225 ± 9.9 Ma (Li *et al.*, 2007b). The center of the Emeishan large igneous province is “Panxi rift” (He *et al.*, 2003), which trends north to south in the west of Xichang to Huili (on the left on Fig. 1). Based on the biostratigraphic and sedimentologic investigations, He *et al.* (2003) concluded that the magnitude of uplift resulted by the Emeishan flood basalt is greater than 1000 m. As many MVT ore field, the crust uplift may result basinal

brine migration and precipitate ores in carbonate rocks several hundred kilometers from the original basins. As a matter of fact, there are many basins in southwest China, such as Kunming basin, Chuxiong basin, which are about two hundred kilometers from the Huize orefield.

Strontium isotopes

The $^{87}\text{Sr}/^{86}\text{Sr}$ values of calcite, sphalerite and pyrite from the ores have been analyzed. The results are listed in Table 5. To determine whether the original $^{87}\text{Sr}/^{86}\text{Sr}$ values changed significantly and not due to ^{87}Rb decay since the ores were formed, the initial strontium isotope compositions of calcite, sphalerite and pyrite are calculated using the formula: $(^{87}\text{Sr}/^{86}\text{Sr})_i = ^{87}\text{Sr}/^{86}\text{Sr} - ^{87}\text{Rb}/^{86}\text{Sr} (e^{\lambda t} - 1)$, $\lambda = 1.42 \times 10^{-11}$ and $t = 230$ Ma (Li *et al.*, 2007b). The results are list in Table 5. The $(^{87}\text{Sr}/^{86}\text{Sr})_i$ values of pyrites range from 0.713676 to 0.714544 with mean value of 0.71411 and the values of sphalerites range from 0.714050 to 0.716989 with a mean value of 0.716133 and the $(^{87}\text{Sr}/^{86}\text{Sr})_i$ values of calcites are 0.716353 to 0.717012 with a mean value of 0.716781.

The initial $^{87}\text{Sr}/^{86}\text{Sr}$ values of the carbonate wall rocks ($P_{1\text{qm}}$ and D_{3z}) are 0.708 and 0.710. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ values of four unaltered host dolomites (C_{1b}) are 0.7083 to 0.7093, while one altered host dolomite is 0.7106. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ value of the altered dolomite host rock in contact with the orebody is higher than that of the unaltered host rock. It seems to suggest that the host rock had reacted with the ore fluid, which must have high $^{87}\text{Sr}/^{86}\text{Sr}$ values. Because the carbonate rocks usually have much lower $^{87}\text{Sr}/^{86}\text{Sr}$ values than shale, clastic rocks and mudstone, the $^{87}\text{Sr}/^{86}\text{Sr}$ values of the shale, clastic rocks and mudstone underlying the host rock should be much higher than the carbonate rocks. When the ore fluid passed through these shale, clastic rocks and mudstone, it might have required much higher $^{87}\text{Sr}/^{86}\text{Sr}$ value.

CONCLUSIONS

1. Lead isotope systematics shows that the metals of the Huize ore field derived from carbonate wall rocks, which have similar Pb isotope compositions.
2. Sulfur isotope study indicates that isotopic equilibrium among sulfides was attained and that the sulfur of the ores may have been obtained from the reduction of sulfate sulfur by thermochemical reduction processes.
3. Carbon and oxygen isotope studies suggest the ore fluid passed through the organic matter-bearing strata and reacted with wall rocks when it moved up to the site of ore deposition.
4. Hydrogen and oxygen isotope data of the fluid inclusions suggest that the ore fluid could have been basinal brines, which had reacted with D-depleted organic matter in shale, clastic rocks and mudstone underlying the

host rock.

5. Strontium isotope study indicates that ore fluid is deep-seated basinal brine, with high $^{87}\text{Sr}/^{86}\text{Sr}$ value. On its pathway to site of ore deposition, it obtained its high Sr-isotope values from the underlying shales, clastic rocks and mudstone.

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REFERENCES

- Ali, J. R., Thompson, G. M., Zhou, M. F. and Song, X. Y. (2005) Emeishan large igneous province, China. *Lithos* **79**, 475–489.
- Anderson, G. M. (1975) Precipitation of Mississippi Valley-type ores. *Econ. Geol.* **70**, 937–942.
- Bethke, C. M. and Marshak, S. (1990) Brine migrations across North America—The plate tectonics of groundwater. *Ann. Rev. Earth Planet. Sci.* **18**, 228–315.
- Boven, A., Pasteels, P., Punzalan, L. E., Liu, J., Luo, X., Zhang, W., Guo, Z. and Hertogen, J. (2002) $^{40}\text{Ar}/^{39}\text{Ar}$ geochronological constraints on the age and evolution of the Permo-Triassic Emeishan Volcanic Province, Southwest China. *J. Asian Earth Sci.* **20**, 157–175.
- Cheilletz, A. and Giuliani, G. (1996) The genesis of Colombian emeralds: A restatement. *Mineralium Deposita* **31**, 359–364.
- Chen, J. (1993) Genesis and metallogenic pattern of the Qilingchang Pb-Zn deposit. *Geological Exploration for Non-ferrous Metals* **2**, 85–89 (in Chinese with English abstract).
- Chen, Y. J., Pirajno, F. and Sui, Y. H. (2004) Isotope geochemistry of the Tieluping silver deposit, Henan, China: A case study of orogenic silver deposits and related tectonic setting. *Mineralium Deposita* **39**, 560–575.
- Chen, Y. J., Pirajno, F. and Sui, Y. H. (2005) Geology and D-O-C isotope systematics of the Tieluping silver deposit, Henan, China: Implications for ore genesis. *Acta Geologica Sinica* **79**, 106–119.
- Czamanske, G. K. and Rye, R. O. (1974) Experimentally determined sulfur isotope fractionations between sphalerite and galena in the temperature range 600°C to 275°C. *Econ. Geol.* **69**, 17–25.
- Dejonghe, J., Boulégue, J., Demaffe, D. and Létolle R. (1989) Isotope geochemistry (S, C, O, Sr, Pb) of the Chaudfontaine mineralization (Belgium). *Mineralium Deposita* **24**, 132–134.

- Ding, T. P. and Jiang, S. Y. (2000) Stable isotope study of the Langshan polymetallic mineral district, Inner Mongolia, China. *Resource Geology* **50**, 25–38.
- Faure, K. (2003) δD values of fluid inclusion water in quartz and calcite ejecta from active geothermal systems: Do values reflect those of original hydrothermal water? *Econ. Geol.* **98**, 657–660.
- Goldfarb, R. J., Leach, D. L., Rose, S. C. and Landis, G. P. (1989) Fluid inclusion geochemistry of gold-bearing quartz veins of the Juneau gold belt, southeastern Alaska: Implications for ore genesis. *Econ. Geol. Monogr.* **6**, 363–375.
- Goldfarb, R. J., Ayuso, R., Miller, M. L., Ebert, S. W., Marsh, E. E., Petsel, S. A., Miller, L. D., Bradley, D., Johnson, C. and McClelland, W. (2004) The Late Cretaceous Donlin Creek Gold Deposit, Southwestern Alaska: Controls on Epizonal Ore Formation. *Econ. Geol.* **99**, 643–671.
- Guan, S. P. and Li, Z. X. (1999) REE geochemistry of rocks and lead-zinc ores at the eastern margin of Kangdian Axis. *Geology-geochemistry* **27**, 5–16 (in Chinese with English abstract).
- Han, R. S. (2002) Characteristics of geology and geochemistry and prognosis of concealed ores in the Huize super-large Zn-Pb-(Ag) district, Yunnan, China. Post-doctorate report of the Institute of Geochemistry, Chinese Academy of Sciences, 99 pp. (unpub.) (in Chinese with English abstract).
- Han, R. S., Liu, C. Q., Huang, Z. L., Ma, D. Y., Li, Y., Hu, B., Ma, G. S. and Lei, L. (2004) Fluid inclusions of calcite and sources of ore-forming fluids in the Huize Zn-Pb-(Ag-Ge) district, Yunnan, China. *Acta Geologica Sinica* **78**, 583–591.
- Hanor, J. S. (1979) The sedimentary genesis of hydrothermal fluids. *Geochemistry of Hydrothermal Ore Deposits* (Barnes, H. L., ed.), 137–142, Wiley-Interscience, New York.
- He, B., Xu, Y. G., Chung, S. L., Xiao, L. and Wang, Y. M. (2003) Sedimentary evidence for a rapid, kilometer-scale crustal doming prior to the eruption of the Emeishan flood basalts. *Earth Planet. Sci. Lett.* **213**, 391–405.
- Hoefs, J. (1997) *Stable Isotope Geochemistry*. 4th ed., Springer-Verlag, Berlin, 201 pp.
- Hu, R. Z., Tao, Y., Zhong, H., Huang, Z. L. and Zhang, Z. W. (2005) Mineralization systems of a mantle plume: A case study from the Emeishan igneous province, southwest China. *Earth Science Frontiers* **12**, 42–54 (in Chinese with English abstract).
- Hu, Y. G. (2000) Preserving State, Source of Ore-forming Substances and Ore-forming Mechanism of Rich Ag Metallic Deposit in Yinchangpo, Guizhou province, China. Ph.D. thesis of the Institute of Geochemistry, Chinese Academy of Sciences, 159 pp. (unpub.) (in Chinese with English abstract).
- Huang, Z. L., Chen, J., Liu, C. Q., Han, R. S., Li, W. B., Zhao, D. S., Gao, D. R. and Feng, Z. H. (2001) A preliminary discussion on the genetic relationship between Emeishan basalt and deposits as exemplified by Huize Pb-Zn deposit, Yunnan Province. *Acta Mineralogica Sinica* **21**, 681–688 (in Chinese with English abstract).
- Jiang, S. Y., Han, F., Shen, J. Z. and Palmer, M. R. (1999) Chemical and Sr-Nd isotopic systematics of tourmaline from the Dachang Sn-polymetallic ore deposit, Guangxi Province, China. *Chem. Geol.* **157**, 49–67.
- Jorgenson, B. B., Isaksen, M. F. and Jannasch, H. W. (1992) Bacterial sulfate reduction above 100°C in deep sea hydrothermal vent sediments. *Science* **258**, 1756–1757.
- Kesler, S. E., Appold, M. S., Martini, A. M., Walter, L. M., Huston, T. J. and Kyle, J. R. (1995) Na-Cl-Br systematics of mineralizing brines in Mississippi Valley-type deposits. *Geology* **23**, 641–644.
- Kesler, S. E., Martini, A. M., Appold, M. S., Walter, L. M., Huston, T. J. and Furman, F. C. (1996) Na-Cl-Br systematics of fluid inclusions from Mississippi Valley-type deposits, Appalachian Basin: Constraints on solute origin and migration paths. *Geochim. Cosmochim. Acta* **60**, 225–233.
- Kesler, S. E., Vennemann, T. W., Frederickson, C., Breithaupt, A., Vazquez, R. and Furman, F. C. (1997) Hydrogen and oxygen isotope evidence for origin of MVT-forming brines, southern Appalachians. *Geochim. Cosmochim. Acta* **61**, 1513–1523.
- Leach, D. L. and Sangster, D. F. (1993) Mississippi Valley-type lead-zinc deposits. *Mineral Deposit Modeling* (Kirkham, R. V., Sinclair, W. D., Thorpe, R. I. and Duke, J. M., eds.), Geol. Assoc. Can. Spec. Pap. 40, 289–314.
- Leach, D. L., Bradley, D., Lewchuk, M. T., Symons, D. T., Marsily, G. and Brannon, J. (2001) Mississippi valley-type lead-zinc deposits through geological time: implications from recent age-dating research. *Mineralium Deposita* **36**, 711–740.
- Li, C. Y., Liu, Y. P., Zhang, Q., Pi, D. H., Zhang, W. L. and Chen, J. (2005) Discovery of antimony and distribution characteristics of associated elements in Huize Pb-Zn deposit. *Mineral Deposits* **24**, 52–60 (in Chinese with English abstract).
- Li, L. J., Liu, H. T. and Liu, J. S. (1999) A discussion on the source bed of Pb-Zn-Ag deposits in Northeast Yunnan. *Geological Exploration for Non-ferrous Metals* **8**, 333–339 (in Chinese with English abstract).
- Li, W. B., Huang, Z. L., Chen, J., Han, R. S., Guan, T., Xu, C., Gao, D. R. and Zhao, D. S. (2002) Sources of ore-forming materials of the giant Huize Zn-Pb deposit, Yunnan Province: Evidence from contents of ore-forming elements in the wall rocks and Emeishan Basalt in this district. *Mineral Deposits* (Suppl.) **21**, 413–416 (in Chinese with English abstract).
- Li, W. B., Qi, L., Huang, Z. L. and Zhang, Z. L. (2007a) REE geochemistry of sulfide from the Huize Zn-Pb ore field, Yunnan Province: Implication for the sources of ore-forming fluid and metal. *Acta Geologica Sinica* (in press).
- Li, W. B., Huang, Z. L. and Yin, M. D. (2007b) Dating of the giant Huize Zn-Pb ore field of Yunnan Province, southwest China: constraints from Sm-Nd system in hydrothermal calcite. *Resource Geology* **57** (in press).
- Liao, W. (1984) Mineralization model and the characters of isotope composition of S and Pb in the Pb-Zn metallic area in the East and West Yunnan Province, China. *Geology and Prospecting* **1**, 1–6 (in Chinese with English abstract).
- Liu, H. C. and Lin, W. D. (1999) *Study on the Law of Pb-Zn-Ag Ore Deposit in Northeast Yunnan, China*. Yunnan University Press, 455 pp. (in Chinese).
- Machel, H. G. (1989) Relationships between sulphate reduction and oxidation of organic compounds to carbonate

- diagenesis, hydrocarbon accumulations, salt domes, and metal sulphide deposits. *Carbonates Evaporites* **4**, 137–151.
- Matthews, A. and Katz, A. (1977) Oxygen isotope fractionation during the dolomitization of calcium carbonate. *Geochim. Cosmochim. Acta* **41**, 1431–1438.
- McCrea, J. M. (1950) On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.* **18**, 849–859.
- McCuaig, T. C. and Kerrich, R. (1998) P-T-t-deformation-fluid characteristics of lode gold Deposits: Evidence from alteration systematics. *Ore Geol. Rev.* **12**, 381–453.
- Ohmoto, H. (1986) Stable isotope geochemistry of ore deposits. *Rev. Mineral.* **6**, 491–559.
- Ohmoto, H. and Rye, R. O. (1979) Isotopes of sulfur and carbon. *Geochemistry of Hydrothermal Ore Deposits* (Barnes, H. L., ed.), 2nd ed., J. Wiley & Sons, Inc., New York, 798 pp.
- Ohmoto, H., Kaiser, C. J. and Geer, K. A. (1990) Systematics of sulphur isotopes in recent marine sediments and ancient sediment-hosted base metal deposits. *Stable Isotopes and Fluid Processes in Mineralisation* (Herbert, H. K. and Ho, S. E., eds.), **23**, 70–120, Geol. Dep. Univ. Extens., Univ. of Western Australia.
- O'Neil, J. R., Clayton, R. N. and Mayada, T. K. (1969) Oxygen isotope fractionation in divalent metal carbonates. *J. Chem. Phys.* **51**, 5547–5558.
- Ottaway, T. L., Wicks, F. J., Bryndzia, L. T., Kyser, T. K. and Spooner, E. T. C. (1994) Formation of the Muzo hydrothermal deposit in Colombia. *Nature* **369**, 552–554.
- Richardson, C. K., Rye, R. O. and Wasserman, M. D. (1988) The chemical and thermal evolution of the fluids in the cave-in-rock district, Illinois: Stable isotope systematics at the Deardorff Mine. *Econ. Geol.* **83**, 765–783.
- Rye, R. O. (1974) A comparison of sphalerite-galena sulfur isotope temperatures with filling temperatures of fluid inclusions. *Econ. Geol.* **69**, 26–32.
- Rye, R. O. and Ohmoto, H. (1974) Sulfur and carbon isotopes and ore genesis: A review. *Econ. Geol.* **69**, 826–842.
- Song, X. Y., Zhou, M. F., Cao, Z. M., Sun, M. and Wang, Y. L. (2003) Ni-Cu-(PGE) magmatic sulfide deposits in the Yangliuping area, Permian Emeishan igneous province, SW China. *Mineralium Deposita* **38**, 831–843.
- Stacey, J. S. and Kramers, J. D. (1975) Approximation of terrestrial lead isotope evolution by two-stage model. *Earth Planet. Sci. Lett.* **26**, 207–221.
- Sverjensky, D. A. (1981) The origin of a Mississippi Valley-type deposit in the Viburnum Trend, southeast Missouri. *Econ. Geol.* **76**, 1848–1872.
- Sverjensky, D. A. (1986) Genesis of Mississippi Valley-type lead-zinc deposits. *Ann. Rev. Earth Planet. Sci.* **14**, 177–199.
- Tao, Y., Luo, T. Y., Gao, Z. M. and Zhu, D. (2004) The relationship between Emeishan continental flood basalt and Cu-Ni-PGE deposits of southwestern China trap—A case study Jinbaoshan mafic-ultramafic intrusion, Yunnan Province. *Geol. Rev.* **50**, 9–15 (in Chinese with English abstract).
- Thompson, G. M., Ali, J. R., Song, X. Y. and Jolley, D. W. (2001) Emeishan basalts, SW China: reappraisal of the formation's type area stratigraphy and a discussion of its significance as a large igneous province. *J. Geol. Soc., London* **158**, 593–599.
- White, D. E. (1958) Liquid inclusions in sulfides from Tri-State (Missouri, Kansas and Oklahoma) are probably connate in origin (abstract). *Geol. Soc. Amer., Bull.* **69**, 1660–1661.
- Wu, N. P., Jiang, S. Y., Liao, Q. L., Pan, J. Y. and Dai, B. Z. (2004) Lead and sulfur isotope geochemistry and the ore sources of the vein-type copper deposits in Lanping-Simao Basin, Yunnan Province. *Acta Petrologica Sinica* **19**, 799–807.
- Yang, Y. X. and Guan, S. P. (1994) *Genesis and Ore-Forming Regularity of the Lead-Zinc Ores at the Eastern Margin of Kangdian Axis*. Sichuan University Science and Technology Press, 195 pp. (in Chinese).
- Zartman, R. E. and Haines, S. M. (1988) The plumbotectonic model for Pb isotopic systematics among major terrestrial reservoirs: A case study for bi-directional transport. *Geochim. Cosmochim. Acta* **52**, 1327–1339.
- Zhang, J., Yan, G. P., Ye, L., Li, G. P., Li, Z. L., and Wang, Z. G. (2005) The C-H-O isotope systematics of the Yindonggou Ag-dominated poly-metals deposit in the Neixiang County, Henan Province. *Acta Petrologica Sinica* **21**, 1359–1364.
- Zhang, L. S. (1997) Hydrothermal karst genesis of stratabound Pb-Zn- (F-Ba) deposits in Northeast Yunnan. *Acta Geoscientia Sinica* **18**, 41–52 (in Chinese with English abstract).
- Zhang, Y. X., Luo, Y. N. and Yang, C. X. (1988) *The Panzhihua-Xichang Rift in China*. Geology Press, 325 pp. (in Chinese with English abstract).
- Zhang, Z. C. and Wang, F. S. (2003) Sr, Nd and Pb isotopic characteristics of Emeishan basalt province and discussion on their source region. *Earth Science-Journal of China University of Geosciences* **28**, 431–439 (in Chinese with English abstract).
- Zhang, Z. L. (2006) Feature and sources of ore-forming fluid in the Huize Zn-Pb ore field, Yunnan Province of China: evidences for fluid inclusions and water-rock reaction experiments. Unpublished Ph.D. thesis of the Institute of Geochemistry, Chinese Academy of Sciences, 128 pp. (in Chinese with English abstract).
- Zheng, Y. F. and Chen, J. F. (2000) *Stable Isotope Geochemistry*. Science Press, 316 pp. (in Chinese).
- Zhou, C. X., Wei, C. S., Guo, J. Y. and Li, C. Y. (2001) The source of metals in the Qilingchang Pb-Zn deposit, Northeastern Yunnan, China: Pb-Sr isotope constraints. *Econ. Geol.* **96**, 583–598.
- Zhou, M. F., Malpas, J., Song, X. Y., Robinson, P. T., Sun, M., Kennedy, A. K., Leshner, A. M. and Keays, R. R. (2002) A temporal link between the Emeishan large igneous province (SW China) and the end-Guadalupian mass extinction. *Earth Planet. Sci. Lett.* **196**, 113–122.
- Zhu, B. Q., Dai, T. M., Hu, Y. G., Zhang, Z. W., Chen, G. H., Peng, J. H., Tu, X. L., Liu, D. H. and Chang, X. Y. (2005) $^{40}\text{Ar}/^{39}\text{Ar}$ and U-Th-Pb dating for native copper mineralization of two stages from the Emeishan flood basalts in Northeastern Yunnan Province, China. *Geochimica* **34**, 235–147 (in Chinese with English abstract).