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Abstract

Carbon and oxygen isotope constraints on mantle fluid involvement in the mineralization of the Huize super-large Pb-Zn deposits, Yunnan Province, China

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Abstract

The Huize super-large Pb–Zn deposits of Yunnan Province, China are characterized by high Pb–Zn grade (Pb+Zn mostly higher than 25-35%) and the abundance of associated useful elements (Ag, Ge, Cd, In, and Ga, etc.). Calcite is the only vein mineral in primary ores in the orefield. This paper analyzes the carbon and oxygen isotopic compositions of 21 calcites and 4 ore-hosting strata (C₁b). The $\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$ of calcites are -2.1-3.5% and 16.7-18.6%, respectively and fall within a narrow range between primary carbonatite and marine carbonate (or C₁b) in the diagram of $\delta^{13}C_{PDB}$ vs. $\delta^{18}O_{SMOW}$. In combination with other geological and geochemical data, we suggest that the ore-forming fluids represent crustal–mantle fluid mixing. We believe that fluids formed from degassing of magma, accompanying magmatism of the Permian Emeishan basalts, were involved in the mineralization of the Huize super-large Pb–Zn deposits. © 2003 Elsevier Science B.V. All rights reserved.

Keywords: The Huize Pb-Zn deposits; C and O isotope; Ore-forming fluids; Permian Emeishan basalts

1. Introduction

More than 400 Pb–Zn–(Ag) ore deposits and ore spots have been found in the Sichuan–Yunnan– Guizhou Pb–Zn–Ag multimetal mineralization area (SYG Pb–Zn MMA) in China (Fig. 1). Most of them are distributed in the region of the Permian Emeishan basalts which are about 250 Ma old (Boven et al.,

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2002; Zhou et al., 2002) and are controlled by a fault zone (Fig. 1). There is still much controversy on the relationship between the Emeishan basalts and Pb–Zn mineralization in this area (Liu and Lin, 1999; Huang et al., 2001a; Zhou et al., 2001). The Huize Pb–Zn deposits of Yunnan Province are located in the center of SYG Pb–Zn MMA (Fig. 1), which is representative of the super-large deposits in this area. This deposit, which is characterized by high Pb–Zn grade (Pb+Zn mostly higher than 25-35%, the Pb–Zn contents of some ores exceed 60%) and the abundance of associated useful elements (Ag, Ge, Cd, In, and Ga, etc.), has aroused great attention to geologists. Research work has been done by many researchers

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Fig. 1. The geological map of the Huize super-large Pb-Zn deposits.

on this deposit, and different genetic models have been proposed (Liu and Lin, 1999; Han et al., 2001a; Zhou et al., 2001). Because views on the source of ore-forming fluids of this deposit are quite different (Liu and Lin, 1999; Huang et al., 2001b; Li et al., in press), the various genetic models cannot explain the mechanism of formation of the deposits in a consistent way.

This paper analyzes the carbon and oxygen isotope of the Huize Pb–Zn deposits, in combination with other geological and geochemical data in the orefield, discusses the source of ore-forming fluids, and the relationship between Emeishan basalts and Pb–Zn mineralization.

2. Geology and analytical methods

Huang et al. (2001a) and Zhou et al. (2001) described the geological setting of the Huize Pb–Zn deposits. The strata exposed in the orefield are composed of Permian limestone, Carboniferous limestone and dolomite, Devonian limestone and silica dolomite, Cambrian argillite, and Sinian silica dolomite (Fig. 1). The Lower Carboniferous Baizuo Formation (C_1b) is the most important ore-hosting formation in the orefield. The local structure is dominated by NE-extending faults represented by the Kuangshanchang, Qilinchang, Yinchangpo, and Niulanjiang faults (Fig. 1). These faults are characterized by multi-episodic activities and are related to the Pb–Zn mineralization (Han et al., 2001b). Magmatic rocks in the orefield are the Permian Emeishan basalts, which are exposed in the northern and southwestern parts of the orefield (Fig. 1).

The Huize Pb–Zn deposits are composed of Kuangshanchang and Qilinchang ore deposits (Fig. 1). The upper, middle, and lower parts of both ore deposits are oxide ores, mixed ores, and primary ores, respectively. The oxide ores are very complicated in composition while primary ores are relatively simple in composition. The ore minerals of primary ores include galena, sphalerite, and pyrite.

Calcite, the only vein mineral in the primary ores in the Huize Pb–Zn deposit, can be classified in three types in accordance to its occurrence, i.e. massive, porphyritic, and vein. Huang et al. (2001b) described the geological characteristics of three types of calcite and suggested they are products from the same source at different stages.

The carbon and oxygen isotopic compositions were analyzed at the Institute of Mineral Resources, Chinese Academy of Geological Sciences by the 100% Phosphorate Method. The analytical procedures are as described by Xu et al. (in press). The Mass Spectrometer is MAT 251 EM and the analytical precision is $\pm 0.2 \%$.

3. Results

Listed in Table 1 are the results of carbon and oxygen isotope analyses for 21 calcites in primary ores, 4 C₁b, and 2 miarolitic calcites from C₁b in the orefield. The carbon and oxygen isotopic compositions of calcites are relatively stable, and their $\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$ are -2.1-3.5% (average -2.8%) and 16.7-18.6% (average 17.7%), respectively. Moreover, the carbon and oxygen isotopic compositions of calcites from different occurrences and from different orebodies (level) do not show

Table 1

The carbon and oxygen isotopic data

obvious differences. In Fig. 2, all calcites fall within a narrow range between primary carbonatite and marine carbonate. These characteristics show that all calcites from primary ores in the orefield come from the same source. The result is consistent with Huang et al. (2001b).

As can be seen from Table 1, the carbon and oxygen isotopic compositions of C_1b are different from those of calcites from primary ores, and their $\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$ are -0.80% to +0.74% (average +0.01%) and 22.6\% to 23.2\% (average 22.9\%), respectively. In Fig. 2, all of C_1b fall within the range of marine carbonate. The carbon and oxygen isotopic compositions of miarolitic calcites, which are considered as the products of leaching of C_1b at low-temperature conditions ($\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$ are +0.50% to +1.1% and 22.1\% to 23.5\%), are similar to those of C_1b , but are different from those of calcites from primary ores. So, the calcites from

Sample	Ore body (level)	Mineral	Occurrence ^a	$\delta^{13}C_{PDB}$	$\delta^{18}O_{SMOW}$
HZ-911-3	Kuangshanchang No. 1 ore body (1751 m)	Calcite	Porphyritic	- 2.2	17.5
HZ-911-10		Calcite	Massive	- 3.4	18.4
HZ-911-15		Calcite	Massive	- 3.5	18.6
HZQ-25	Qilingchang No. 6 ore body (1631 m)	Calcite	Massive	-2.5	17.5
HZQ-40		Calcite	Porphyritic	-2.6	17.7
HZQ-47		Calcite	Massive	- 3.1	17.5
HZQ-55		Calcite	Vein	-2.7	17.7
HZQ-66		Calcite	Massive	- 3.4	18.1
HZQ-70		Calcite	Porphyritic	- 3.3	18.1
HZQ-77		Calcite	Vein	-2.8	17.8
HZQ-85		Calcite	Porphyritic	-2.7	17.3
HZQ-90		Calcite	Porphyritic	-2.7	17.2
HZQ-96		Calcite	Massive	-2.1	17.5
HQ-10-7	Qilingchang No. 10 ore body (1571 m)	Calcite	Massive	-2.9	17.0
HQ-10-12		Calcite	Massive	-3.2	18.5
HQ-10-18		Calcite	Massive	- 2.3	16.8
HQ-10-25		Calcite	Porphyritic	- 3.0	17.9
HQ-10-5		Calcite	Vein	-2.8	17.2
HQ-8-115	Qilingchang No. 8 ore body (<1431 m)	Calcite	Massive	-2.2	17.0
HQ-8-143		Calcite	Massive	-2.7	17.6
HQ-8-98		Calcite	Vein	- 3.0	17.8
HZQ-35	Miarolitic calcite			0.50	22.1
HZK-33				1.1	23.5
HZQ-74	Clb	Whole rock		-0.80	22.6
HZ-2053-29		Whole rock		0.35	23.2
HZS-40		Whole rock		0.74	22.8
HZ-X-3		Whole rock		-0.24	23.1

^a After Huang et al. (2001b).

Fig. 2. The $\delta^{13}C_{PDB}$ vs. $\delta^{18}O_{SMOW}$ diagram. Trend *A* is sedimentary contamination or high T fractionation (Demény et al., 1998) and Trend *B* is degassing of magma and/or magmatic fluids (Demény and Harangi, 1996). O, calcite; \bullet , miarolitic calcite; Δ , C_1b formation. The dotted rectangle shows the model results calculated for simple binary mixing estimation. In the processes of calculating, the C_1b formation in the orefield (average $\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$ are -6.7% and 8 %, respectively; Demény et al., 1998) are taken as end-members, and the degree of contamination is from 50% to 70%.

primary ores in the orefield are not the products of leaching of $C_1 b$.

4. Discussion and conclusions

Carbon and oxygen isotope signatures are amongst the important discriminatory criteria for recognizing involvement of mantle fluids. However, a lot of analytical data have showed that $\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$ of many of mantle-derived carbonatites are outside the range of primary carbonatite of Taylor et al. (1967) (Reid and Cooper, 1992; Pearce and Leng, 1996; Horstmann and Verwoerd, 1997; Demény et al., 1998; Andrade et al., 1999; Ray and Ramesh, 1999). Previous investigations have used sedimentary contamination and high temperature fractionation to explain the origin of carbonatites with Trend A in Fig. 2 (Reid and Cooper, 1992; Pearce and Leng, 1996: Horstmann and Verwoerd, 1997; Demény et al., 1998; Andrade et al., 1999; Ray and Ramesh, 1999).

In Fig. 2, the carbon and oxygen isotopic compositions of calcites in the Huize Pb-Zn deposits fall within a narrow range between primary carbonatite and marine carbonate and/or C_1b . This isotopic characteristics could be explained by sedimentary contamination or high temperature fractionation of primary carbonatite. Because we determined that the homogenization temperatures of fluid inclusions in calcites from primary ores are relatively low (mostly less than 250 °C) (unpublished), the high temperature fractionation of primary carbonatite can be excluded. So, the carbon and oxygen isotopic features of calcites may be the results of C_1b of the orefield contaminating of the primary carbonatite signature. That is to say, mantle fluids were probably involved in the mineralization of the Huize Pb-Zn deposits. This conclusion can be supported by the following pieces of evidence.

- 1. As can be seen from Fig. 2, most calcites from primary ores in the orefield fall within the dotted rectangle, which corresponds to the model results calculated for simple binary mixing with a degree of contamination from 50% to 70%. It confirms that calcites may be the result of C_1b in the orefield contaminating the primary carbonatite.
- 2. Li et al. (in press) reported that the δ^{34} S of 69 galenas, sphalerites, and pyrites in the orefield is 13–17‰ and confirmed that sulfur in the oreforming fluids came from the S-bearing carbonate strata. Liu and Lin (1999) reported that the δD_{H2O} and $\delta^{18}O_{H2O}$ of five fluid inclusion in calcites from primary ores in the orefield are -55% to 75% and 6.44% to 8.04%, which are within the range of δD_{H2O} and $\delta^{18}O_{H2O}$ for magmatic waters (-50% to 90% and 6% to 10%, respectively). These features show that the ore-forming fluids of the Huize Pb–Zn deposits represent a mixture of mantle and crustal fluids.
- Huang et al. (2001b) suggested that the oreforming fluids of the Huize Pb-Zn deposits are relatively LREE-rich and also proposed that the fluids are a mixture of mantle and crustal fluids.

Because many carbonate strata outcrop in the orefield (Fig. 1), it is not difficult to understand that the crustal compositions in the ore-forming fluids come from these strata. We suggest that the mantle compo-



sitions seen in the ore-forming fluids in the Huize Pb– Zn deposits may be related to magmatism of Permian Emeishan basalt. This is based on the following points:

- (a) The only magmatic rocks in the orefield are the Permian Emeishan basalts (Fig. 1). We obtained the ore-forming age of the Huize Pb-Zn deposits at about 230 Ma (unpublished). It is close to the age of Permian Emeishan basalt (about 250 Ma; Boven et al., 2002; Zhou et al., 2002).
- (b) Previous investigations have shown that the Emeishan basalt is the product of mantle plume activity (Chung and Jahn, 1995; Xu et al., 2001; Song et al., 2001). Pirajno (2000) and Liu et al. (2001) listed a great wealth of geological evidence to indicate that the fluids formed from degassing which accompany magmatism associated with a mantle plume and were involved in the mineralization. Demény and Harangi (1996) suggest that the carbonatites with Trend B in Fig. 2 are the products of degassing of magma and/or magmatic fluids. In Fig. 2, the carbon and oxygen isotopes of calcites in the orefield as well as the feature of Trend B (i.e. negative correlation between $\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$) show that calcites were influenced by degassing of magma and/or magmatic fluids. So, this paper suggests that the fluids formed from degassing of magma and/or magmatic fluids, which accompanied with magmatism of Permian Emeishan basalts, were involved in the mineralization of the Huize Pb-Zn deposits (including SYG Pb-Zn MMA).

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