

Characteristics of rare-earth elements (REE), strontium and neodymium isotopes in hydrothermal fluorites from the Bailashui tin deposit in the Furong ore field, southern Hunan Province, China

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Abstract In this paper the authors present the REE concentrations and Sr and Nd isotopic compositions of fluorites from the Bailashui tin deposit of the Furong ore field, southern Hunan Province. The results showed that the total amount of REE in fluorites is usually low, ranging from 0.705 to 8.785 $\mu\text{g/g}$ with the chondrite-normalized REE distribution patterns similar to those of the Qitianling granites in the study area, characterized by LREE-enrichment patterns with pronounced negative Eu anomalies. The fluorites vary in Sr isotopic composition within the range of 0.7083–0.7091, the values are lower than those of the granites and higher than those of the host carbonate rocks in this area. The $\epsilon_{\text{Nd}}(t)$ values of fluorites vary between -9.4 and +10.3, revealing that both the crust- and mantle-source materials were involved in the ore-forming hydrothermal fluids. Combined with previous studies on this ore deposit, the Bailashui tin deposit is temporally and spatially closely related with granitic magmatism in this area. The hydrothermal fluorites are the product of fluid/rock interactions between granitic magmatic hydrothermal fluid and marine carbonate rocks. The REE and F in the ore-forming fluid were derived from the granites, whereas Sr in the ore-forming fluid came mainly from the granitic magmatic hydrothermal fluid and marine carbonate rocks, although variations in Sr isotopic composition cannot be explained by a simple mixture of these two end-members. Evidence demonstrated that the ore-forming fluids are of crustal-mantle mixing origin, but that the fluids were probably incompletely homogenized and this may be caused by inhomogeneous mixing of the fluids of different sources.

Key words Bailashui tin deposit; fluorite; REE; Sr and Nd isotopes

1 Introduction

The newly discovered world-class tin-polymetallic (W, Pb, Zn) Furong ore field is located in the southern part of the Qitianling pluton emplaced in southern Hunan Province, China (Huang Gefei et al., 2001, 2003). The ore field has attracted considerable attention because of its huge reserves and prospecting potential. Up to now, studies on this ore field are focused on its geological characteristics, ore-controlling factors, metallogeny, timing of rock and ore formation, and geodynamic setting (Huang Gefei et al., 2001, 2003; Cai Jinhui et al., 2002; Hu Zhike et al., 2003; Mao Jingwen et al., 2004a, b; Peng Jiantang et al., 2007). However, little work has been

done on the source of ore-forming fluid and associated fluids. Helium isotope studies by Li Zhaoli et al. (2006, 2007) have shown that the ore-forming fluids have a mixed mantle-crustal source. However, it is debated that the dominant crustal end-member is either provided by granite, or mainly derived from the host carbonate rocks, or is a mixture of the two.

Numerous studies have indicated that the REE and Sr isotopic composition of fluorites can be effectively used in tracing the sources of ore-forming materials and the evolution of ore-forming fluid in various hydrothermal deposits (Halliday et al., 1990; Galindo and Tornos, 1994; Galindo et al., 1997; Simonetti and Bell, 1995; Menuge and Feely, 1997; Peng Jiantang et al., 2002, 2003a; Zhang Guoquan et al., 2007). In recent years, the Sm-Nd isotope system

of fluorites has successfully been applied to dating the mineralization event and to tracing the source of ore-forming materials in hydrothermal deposits (Halliday et al., 1990; Chesley et al., 1991; Peng Jiantang et al., 2003b; Xu Cheng et al., 2003). Zhao Kuidong et al. (2005) studied the Sr-Nd isotopic composition of the Furong tin-polymetallic ore field, and found that the fluorites from different ore veins show significant

differences in Sr isotopic composition. However, the genesis of the Furong tin ore system is still controversial because of the lack of absolute age data of tin mineralization. In this study, we attempt to constrain the source of ore-forming materials and fluids as well as the genesis of the ore system based on the studies of REE and Sr-Nd isotopic compositions of fluorites from the No. 19 ore vein in the Bailashui tin deposit.

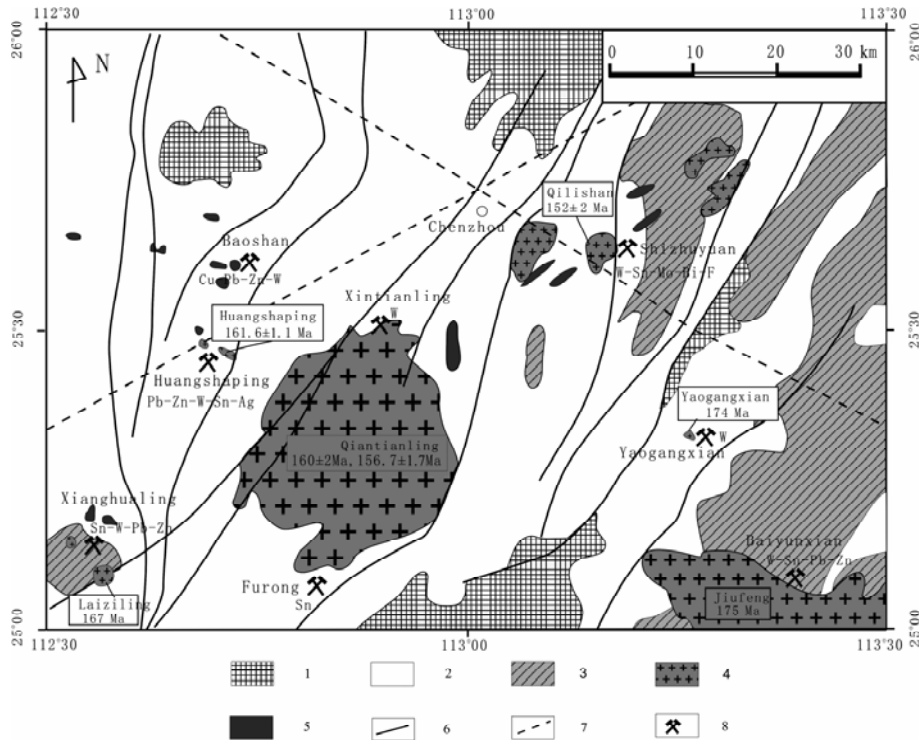


Fig. 1. Sketch map of tin and tungsten deposits in the central Nanling region, South China (Modified after Peng Jiantang et al., 2006a, b). 1. Upper Triassic to Tertiary sandstone, siltstone; 2. Devonian to Lower Triassic limestone, shale; 3. Sinian to Cambrian slate, meta-sandstone; 4. granite; 5. granodiorite; 6. fault; 7. concealed fault; 8. metal deposit.

2 Geological characteristics of the tin-polymetallic ore field

The Bailashui tin deposit is located in the southwestern part of the Furong ore field, and is tectonically situated at the intersection between the Hercynian-Indosinian belt between the Yangtze craton and the Cathaysian block and the transition zone between the Luoxiao-Wuyi uplift and the northern Guangdong Province-Dongjiang depression (Shi Mingkui et al., 1993). The exposed sedimentary rocks consist predominantly of Permian carbonate, sandstone and shale. The dominant structures are NNE-trending (locally SN-trending), which controls the spatial distribution of the tin ore belt, where the medium-grained porphyritic hornblende- and biotite-bearing monzonitic granites are associated with tin mineralization. Ore bodies are mainly hosted in fracture zones within the granite or in the contact zone between the granite and Permian carbonate and sandstone rocks (Fig. 2). Up to

now, more than 40 ore veins have been discovered in this area, including the skarn type, the structurally-controlled altered granite type, the greisens type and the porphyry type. About 72.4% of the tin resources in the Furong ore field are concentrated in the Bailashui district (Huang Gefei et al., 2001, 2003). The orebodies tend to increase in size and tin grade (from 0.2%–0.8% to 0.5%–1.2%) gradually from north to south. The No. 19 ore vein is located in the Tiepokeng-Wuchangping tin belt of the Bailashui deposit, which is regarded as a typical skarn-type deposit in this area, which is developed in the inner contract zone between the carbonate rocks of the Permian Qixia Formation and the southern part of the Qitianling pluton and is controlled by a series of nearly SN-trending faults. It has a strike length of 1650 m, a thickness of 150 m and a width of 150 m, with an average grade of 0.79% Sn. Proven tin reserves are about 270000 tons, accounting for approximately 70% of the total tin resources in the

Bailashui tin deposit (Cai Jinhui et al., 2004a). Main ore types include the cassiterite-magnetite, cassiterite-pyrite, galena-sphalerite and pyrite-chalcopyrite. Disseminated, banded and massive ores are predominated. Cassiterite is most abundant in the No. 19 ore

vein, together with minor amounts of magnetite, chalcopyrite, galena, sphalerite, scheelite and bismuthinite. Gangue minerals are predominately tremolite, diopside and quartz.

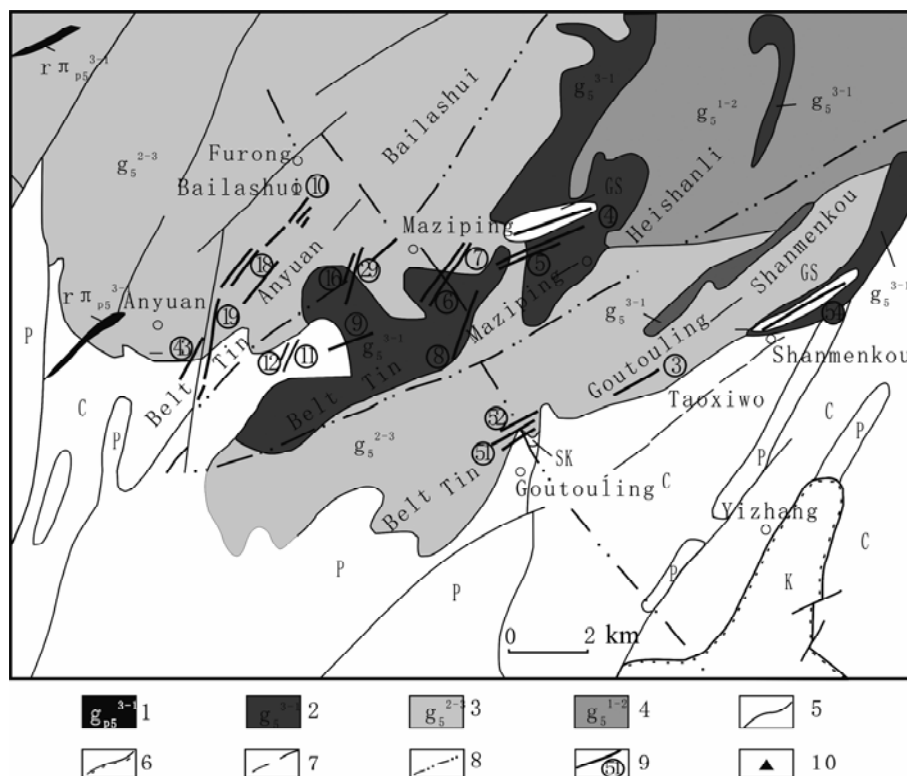


Fig. 2. Geological sketch map of the Furong tin orefield, southern Hunan Province. 1. Cretaceous; 2. Permian; 3. Carboniferous; 4. granite; 5. granite porphyry; 6. geological boundary; 7. unconformable interface; 8. measured fault; 9. inferred fault; 10. ore vein and its serial number.

3 Sampling and analytical methods

All the samples analyzed in this study were collected from the No. 19 ore vein of the Bailashui tin deposit. Fluorites of different colors such as purple, light purple, light blue, dark red and white, disseminated and massive, occurred in skarn ores. Based on field investigations and microscopic observations, the selected samples were crushed as fine as 40–60 meshes, and fluorites were handpicked to a purity of >99% under a binocular microscope, and finally milled to 200 meshes in a clean agate mortar for the following treatment.

The REE concentrations of fluorites were determined by inductively coupled plasma mass spectrometry (ICP-MS) at Hongkong University. Procedures are described as follows: Approximately 50 mg of fluorite powder (<200 meshes) were put into an acid-cleaned Teflon beaker and 1 mL HF (38%) and 0.5 mL HNO₃ (68%) were added and the beaker was subsequently evaporated to dryness on a hot plate to remove Si. Then, 1 mL HF (38%) and 0.5 mL HNO₃ (68%) were added in the residue and the beaker tightly

locked with stainless sleeves was put into a temperature-controlled oven (190°C) for 12 hours. 1 mL 1×10⁻⁶ (µg/mL) Rh was added as a spike after it cooled down and then the beaker was left on the hot plate before evaporation to dryness. Another 1 mL HNO₃ was added and let it evaporate to dryness and the procedure was repeated with a little HNO₃. At last 8 mL HNO₃ was added in the residue and the beaker was again put into a temperature-controlled oven (150 °C) for 3 hours. After cooling down, the final volume of the solution was completed to 100 mL with some deionized water for ICP-MS analysis. Details are described in Qi Liang et al. (2000).

Sr and Nd isotope measurements were carried out at the Isotopic Laboratory of the Tianjin Institute of Geology and Mineral Resources, the Chinese Geological Survey Bureau. Sm, Nd, Rb and Sr concentrations were determined by the isotopic dilution method. Samples were dissolved using a mixture of HF and HClO₄ in closed beakers. Sm and Nd were separated by a reversed phase extraction technique with HDEHP to avoid interference of ¹⁴⁴Sm with ¹⁴⁴Nd. The Sm and Nd abundances and ¹⁴³Nd/¹⁴⁴Nd ratios were measured

on a thermal ionization mass spectrometer (TIMS). Nd isotopic ratios were normalized to $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$, using power law fractionation correction. The abundances of Sm and Nb in the BCR-1 standard determined in this study are 6.5919 and 28.8203 $\mu\text{g/g}$, respectively and the Rb and Sr concentrations measured in the NBS607 standard are 521.955 and 65.304 $\mu\text{g/g}$, respectively.

4 Results and discussion

The REE compositions of fluorites are given in Table 1 and the chondrite-normalized REE distribution patterns are shown in Fig. 2. REE chondrite-normalization factors are adopted in this study from Boynton et al. (1984).

As can be seen in Table 1, fluorites from the No. 19 ore vein of the Bailashui tin deposit have low total REE amount within the range of 0.705–8.785 $\mu\text{g/g}$.

Nearly all the fluorite samples are characterized by LREE-enrichment patterns ($\Sigma\text{LREE}/\Sigma\text{HREE}=5.2\text{--}7.1$) with negative Eu anomalies ($\delta\text{Eu}=0.16\text{--}0.61$) (Fig. 3).

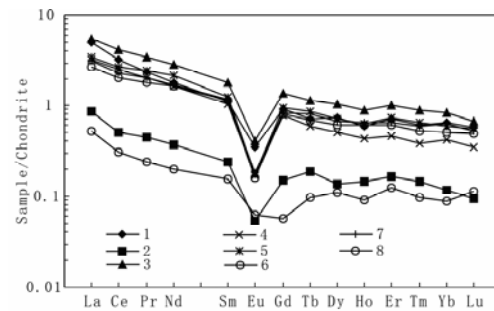


Fig. 3. Chondrite-normalized REE distribution patterns of fluorites from the No. 19 ore vein in the Bailashui tin deposit. 1. FRB-7; 2. FRB-8; 3. FRB-9; 4. FRB-10; 5. FRB-10-1; 6. FRB-11; 7. FRB-12-1; 8. FRB-12-2.

Table 1. REE concentrations of and parameters for fluorites from the No. 19 ore vein in the Bailashui tin deposit

Sample No.	FRB-7	FRB-8	FRB-9	FRB-10	FRB-10-1	FRB-11	FRB-12-1	FRB-12-2
La	1.58	0.265	1.7	1	1.08	0.163	0.984	0.827
Ce	2.64	0.411	3.35	2.04	2.21	0.245	1.85	1.64
Pr	0.289	0.055	0.42	0.252	0.302	0.03	0.247	0.224
Nd	1.09	0.222	1.71	0.991	1.29	0.119	1.01	0.973
Sm	0.212	0.046	0.348	0.199	0.244	0.03	0.228	0.222
Eu	0.025	0.004	0.03	0.012	0.013	0.005	0.013	0.012
Gd	0.233	0.038	0.348	0.204	0.24	0.015	0.215	0.211
Tb	0.034	0.009	0.054	0.028	0.04	0.005	0.038	0.032
Dy	0.236	0.044	0.328	0.163	0.229	0.035	0.212	0.198
Ho	0.043	0.01	0.063	0.031	0.045	0.006	0.046	0.043
Er	0.149	0.035	0.207	0.098	0.152	0.026	0.135	0.127
Tm	0.02	0.005	0.029	0.013	0.021	0.003	0.019	0.017
Yb	0.135	0.025	0.176	0.088	0.121	0.019	0.13	0.104
Lu	0.019	0.003	0.022	0.012	0.018	0.004	0.017	0.016
Y	2.67	1.3	3.58	1.58	2.85	0.66	2.83	2.45
ΣREE	6.705	1.172	8.785	5.131	6.005	0.705	5.144	4.646
LREE/HREE	6.7	5.9	6.2	7.1	5.9	5.2	5.3	5.2
δCe	0.87	0.78	0.93	0.95	0.92	0.79	0.88	0.9
δEu	0.35	0.28	0.26	0.19	0.16	0.609	0.18	0.16
$(\text{La}/\text{Yb})_{\text{N}}$	7.9	7.2	6.57	7.7	6	5.9	5.1	5.4
$(\text{La}/\text{Sm})_{\text{N}}$	4.7	3.61	3.1	3.2	2.8	3.4	2.7	2.3
$(\text{Gd}/\text{Yb})_{\text{N}}$	1.4	1.2	1.6	1.9	1.6	0.64	1.3	1.6
Sm/Nd	0.19	0.21	0.2	0.21	0.19	0.25	0.23	0.23
Y/Ho	62.3	124.7	56.5	51.5	62.8	102.5	60.9	56.6
La/Ho	36.9	25.5	26.8	32.6	23.8	25.4	21.2	19.1

The Rb, Sr, Sm and Nd concentrations of fluorites and their isotopic compositions are summarized in Table 2. The concentrations of these elements in the fluorites range from 0.10 to 1.93 $\mu\text{g/g}$ for Rb, 46.18 to 253.27 $\mu\text{g/g}$ for Sr, 0.042 to 0.336 $\mu\text{g/g}$ for Sm and 0.209 to 1.697 $\mu\text{g/g}$ for Nd. The Rb concentrations of some samples were below the limit of detection (<0.1 $\mu\text{g/g}$). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of fluorites determined in this study are within the range of 0.7083–0.7094, whereas $^{143}\text{Nd}/^{144}\text{Nd}$ ratios show considerable variations within the range of 0.51202–0.51309 (Table 2).

4.1 Characteristics of REE composition

REE^{3+} can be incorporated into fluorites as Ca^{2+}

replacement because of the similarity in ionic radius between REE^{3+} and Ca^{2+} (Elzinga et al., 2002). Fluorites may enrich REE from a fluid in which it is precipitated, thus the REE composition of fluorites can be used effectively in tracing the source of REE in ore-forming fluids. Moreover, fluorine is always enriched in the fluid where fluorite is precipitated and it is usual to observe REE-F complexation in various hydrothermal environments (Wood, 1990a, b; Hass et al., 1995). So, the REE composition of fluorites can also be used to trace the source of fluorine in ore-forming fluid.

The chondrite-normalized REE distribution patterns of the fluorites in this study are similar to those of the Qitianling granite in the Bailashui deposit (Fig.

4), suggesting that both REE and F in the ore-forming fluid were derived from the granite in this area. In addition, the REE data of calcite in the Furong tin ore-

field reported by Shuang Yan et al. (2006) lend a support to this conclusion.

Table 2. The Sm, Nd and Rb, Sr isotopic compositions of fluorites from the No. 19 ore vein in the Bailashui tin deposit

Sample No.	Rb ($\mu\text{g/g}$)	Sr ($\mu\text{g/g}$)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$(^{87}\text{Sr}/^{86}\text{Sr})_0$	Sm ($\mu\text{g/g}$)	Nd ($\mu\text{g/g}$)	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	ϵ_{Nd}
FRB-7	1.871	47.734	0.1134	0.708952±24	0.7087	0.2124	1.1031	0.1164	0.512216±18	-6.6
FRB-8	0.275	48.885	0.0163	0.708332±25	0.7083	0.0424	0.4411	0.0581	0.512018±19	-9.4
FRB-9	1.932	46.820	0.1194	0.708622±24	0.7084	0.336	1.6969	0.1197	0.512302±17	-5.0
FRB-10	0.929	51.675	0.052	0.709123±18	0.7090	0.2266	1.1712	0.117	0.512350±27	-4.0
FRB-10-1	0.954	48.939	0.0564	0.709028±24	0.7089	0.2845	1.4271	0.1205	0.512525±20	-0.7
FRB-11	1.340	48.581	0.0798	0.708824±28	0.7086	0.2447	1.212	0.1241	0.512467±25	-1.9
FRB-12-1	1.186	46.184	0.0743	0.709404±27	0.7092	0.2142	1.0268	0.1261	0.513093±24	10.3
FRB-12-2	1.076	48.692	0.0639	0.708783±28	0.7086	0.2232	1.0642	0.1268	0.512435±26	-2.6
FR-9	<0.1	124.49		0.707868±11	0.7079	0.068	0.178	0.231	0.51221±22	-9.1
FR-17	<0.1	202.87		0.707721±8	0.7077	0.079	0.209	0.227	0.51228±37	-7.5
FR-18	<0.1	253.27		0.707697±14	0.7077	0.09	0.253	0.215	0.51222±33	-8.5

Note: The data of sample Nos. FR-9, FR-17 and FR-18 after Zhao Kuidong et al. (2005).

Bau and Dulski (1995) studied the fluorite and calcite from the Tannenboden and Beihilfe deposits and concluded that variations in Y/Ho ratio in co-genetic hydrothermal fluorites are usually almost negligible compared with those of La/Ho ratios. The fluorites analyzed in this study showed the same distribution characteristics in the Y/Ho-La/Ho diagram (Fig. 5), indicating that all fluorites from this mine are from the same source. Besides, the Y/Ho ratios of all samples range from 51.5 to 124.7 with an average value of 72.2, obviously higher than those of chondrites (Y/Ho ratios=28, Anders and Grevesse, 1989), confirming that these fluorites are of hydrothermal origin. In the Tb/Ca-Tb/La diagram of Möller et al. (1976), all fluorite samples are distributed in the hydrothermal field and along the boundary with the sedimentary field (Fig. 6). All samples display a trend marked by uniform Ta/Ca ratios but present a large variation range of Tb/La ratios (Fig. 6). This vertical arrangement of fluorites in this variogram is usually considered the result of interaction of hydrothermal fluids with the carbonate rocks (Subias and Fernandez-Nieto, 1995).

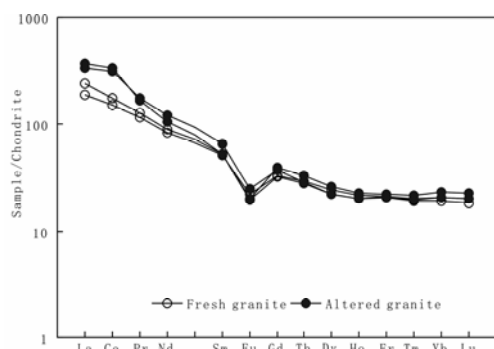


Fig. 4. Chondrite-normalized REE distribution patterns of granite from the Bailashui mining district (after Shuang Yan et al., 2006).

Constantopoulos (1988) suggested that the fluorites with low Tb/La ratios were precipitated from hydrothermal fluids in the early stage. Therefore, the

low Tb/La ratios (0.02–0.03) of fluorites here may indicate that they are the products of early-stage crystallization.

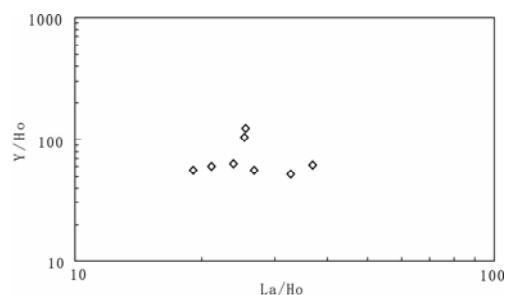


Fig. 5. Y/Ho-La/Ho diagram of fluorite from the No. 19 ore vein in the Bailashui tin deposit.

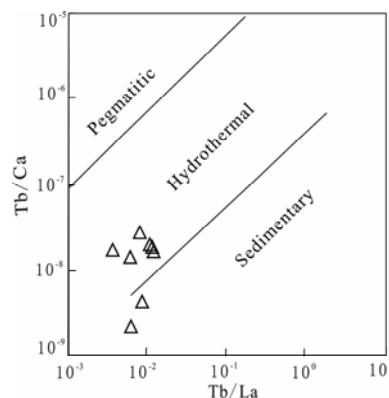


Fig. 6. Logarithmic plot of Tb/Ca vs. Tb/La for fluorite from the No. 19 ore vein in the Bailashui tin deposit.

4.2 Sr, Nd isotopic compositions and their implications

Due to their similarities in ionic radius between Sr^{2+} and Ca^{2+} , Sr is more easily incorporated into fluorite as Ca^{2+} replacement than Rb, which will cause the fluorites to possess very low Rb/Sr ratios (Deer et al., 1966). Thus, we can define $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the fluid in which fluorite was precipitated by determining

the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of fluorites. It is confirmed by the fact that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of fluorites determined in this study are very close to the corrected values.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of fluorites (0.7083–0.7094) are high relative to those of ancient seawater of the Permian Qixia Formation (0.7068–0.7079, Burke et al., 1982; Popp et al., 1986; Yan Jiaxin and Wu Ming, 2004), and are lower than those of the Qitianling granites (0.7085–0.7128, Zhu Jinchu et al., 2003; Bai Daoyuan et al., 2005). Therefore, Sr in the ore-forming fluid was unlikely to have originated from one of the above two end-members, instead, it was probably a mixture of the two. However, there is no obvious linear relationship in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vs. $1/\text{Sr}$ ($\times 10^{-6}$) diagram (not shown), suggesting that the ore-forming fluid is not a simple mixture of these two end-members.

The REE in fluorite diffuse considerably slowly because REE including Sm, Nd are easily incorporated into the fluorite as Ca^{2+} replacement, and the Sm-Nd isotopic system is easily kept closed in common geochemical processes. Therefore, the Nd isotopic composition of fluorite is efficient in tracing the source of REE in ore-forming fluid (Peng Jiantang et al., 2003a, b). Fluorites in this study have a relatively narrow range of Sm/Nd ratios (0.19–0.25), and a reliable isochron can not be obtained. Except for sample FRB-12-1 with an outlier at +10.3, ϵ_{Nd} values are low relative to the chondritic values. Its average value (-5.5) is close to that of the Qitianling granite (-5.05–-7.57, Zhu Jinchu et al., 2003; Zhao Kuidong et al., 2005; Bai Daoyuan et al., 2005). This result is in good agreement with the REE data, suggesting that the REE of fluorites were derived mainly from the Qitianling granite. Previous Sr and Nd isotope studies suggested that there is an obvious involvement of mantle materials during granite emplacement, and that mantle-crust interaction is important in the petrogenetic processes of the Qitianling granite (Zhu Jinchu et al., 2003). The Nd isotopic composition of fluorite in this study revealed that the ore-forming fluids represent a mixture of crust and mantle sources, which is in good agreement with the He isotope results obtained by Li Zhaoli et al. (2006, 2007). Due to the lack of mafic magmatism in the area, the ore-forming fluids are likely to have been derived from granitic magma that originated from a mixed crust/ mantle source.

Usually, the REE concentrations of ore-forming fluids are very low (Michard and Albarede, 1986; Michard, 1989), so it is possible that the Nd isotopic composition of the ore-forming fluids will change significantly as the Nd supplied from the local wall rocks will change slightly. Fluorites from different ore veins, or fluorites in the same ore vein, even in the same sample, will have different initial Nd isotopic compositions (Halliday et al., 1990; Chesley et al.,

1991; Menuge and Feely, 1997). Differences in initial Nd isotopic composition may be due to the mixing of different sources (Peng Jiantang et al., 2003b). The initial Nd isotopic composition of fluorites from the same ore vein in this study are obviously inhomogeneous with a larger range than those of granite, which may be caused by inhomogeneous mixing of the fluids from different sources. The REE and He isotopic compositions of the ores studied by Li Zhaoli et al. (2006) also revealed that the ore-forming fluids are inhomogeneous. Recently, a study of fluid inclusions has shown that the ore-forming fluid is a mixture of high-temperature magmatic hydrothermal fluid and low-temperature meteoric water (Li Taoye and Liu Jiaqi, 2005). The fluid immiscibility and boiling usually occurred during the ascent of the fluid.

4.3 Discussion of the ore deposit genesis

In recent years, many researchers have attempted to determine the timing of mineralization in the Bailashui tin deposit with different methods, with the results showing a large range of models. Wang Denghong et al. (2003) dated the samples of porphyritic granite characterized by a strong chlorinization from the No. 10 ore vein by the whole-rock Rb-Sr isochron method and obtained an isochron age of 136 Ma; Li Huaqin et al. (2006) studied samples collected from the Nos. 10, 19 and 42 ore veins using the Sm-Nd, Rb-Sr, and U-Pb methods and constrained that the timing of mineralization from the different ore types lies between 133 and 146 Ma. These ages are all younger than the age of granite emplacement (155–160 Ma). Based on the above dates, some researchers considered that the Furong tin orefield has no direct genetic connection with the emplacement of the Qitianling granite pluton. In addition, Cai Jinhui et al. (2004b) dated fluid inclusions from a cassiterite-sulfide-quartz vein using the Rb-Sr isotopic method, and obtained an isochron age of 177 Ma, which is even older than the age of the granites in the area. Therefore, there are two contrasting viewpoints on ore genesis. One holds that the Furong tin orefield is a high-temperature hydrothermal deposit, which was formed along the fracture zone during the late stage of granite magma fractionation. The other considers that the mineralization resulted from water-rock interactions post-dating the granite emplacement (Zhao Kuidong et al., 2005, 2006; Jiang Shaoyong et al., 2006).

Most of the age data in previous studies were obtained by different methods, such as whole-rock Rb-Sr, zircon U-Pb ages from granite, or Sm-Nd ages from ores. Therefore, those ages obtained cannot effectively represent the timing of mineralization. Recently, Peng Jiantang et al. (2007) performed

^{40}Ar - ^{39}Ar dating on phlogopite and hornblende in association with the tin ore from the Bailashui tin deposit, and constrained the timing of mineralization at 151–157 Ma, which is in good agreement with the ^{40}Ar - ^{39}Ar dates of muscovites from other two Sn deposits of the Furong ore field, namely the Sanmengkou (156.1 Ma) and Taoxiwo (160.1 Ma). The ages of mineralization from the Shizhuyuan super-large W deposit to the NE of Furong ore field (Fig. 1), determined by various methods, are within the range of 149–161 Ma (Li Hongyan et al., 1996; Liu Yimao et al., 1997; Mao Jinwen et al., 1998, 2004a; Li Xianhua et al., 2004; Peng Jiantang et al. (2006a, b) obtained a well-defined ^{187}Re - ^{187}Os isochron for molybdenite from the Yaogangxian W deposit to the E of the Furong ore field (Fig. 1) and the age obtained is 154.9 Ma, which is in good agreement with the ^{40}Ar - ^{39}Ar dates of phlogopite and muscovite (153.0 Ma and 155.1 Ma, respectively) from quartz veins in the same mining district (Peng Jiantang et al., 2006a, b). Besides, we determined the ^{40}Ar - ^{39}Ar ages of muscovites and the U-Pb age of cassiterite from the Xianghualing tin orefield to the W of the Furong ore field (Fig. 1), and the results suggested that the timing of mineralization is at 154–161 Ma (Yuan Shunda et al., 2006, 2007, in press). Therefore, the ^{40}Ar - ^{39}Ar ages of the Bailashui tin deposit recently reported by Peng Jiantang et al. (2007) are reliable, and are well consistent with the age of the Qitianling pluton emplacement (155–161 Ma) (Zhu Jinchu et al., 2003, 2005; Fu Jianming et al., 2004; Mao Jingwen et al., 2004b; Bai Daoyuan et al., 2005), suggesting that the Bailashui tin deposit is temporally related to the Qitianling pluton. Fluid inclusion studies indicated that the ore-forming fluid is a mixture of high-temperature magmatic hydrothermal fluid and low-temperature meteoric water (Li Taoye and Liu Jiaqi, 2005). The REE concentrations, Sr and Nd isotopic compositions in this study have confirmed that the Bailashui tin mineralization has a close genetic relationship with the Qitianling granite. In combination with previous studies on deposit geology, and petrogenetic and mineralization ages, the Bailashui mineralization is temporally and spatially related to granitic magmatism in this area.

5 Conclusions

(1) Fluorites from the Bailashui tin deposit are the products of interactions between hydrothermal fluids associated with granitic magmatism and marine carbonate rocks; the REE and F in the ore-forming fluid are derived mainly from the Qitianling granite pluton.

(2) Strontium in the ore-forming fluid mainly originated from magmatic hydrothermal fluids and

marine carbonate rocks in the area, but is not a simple mixture of these two end-members.

(3) The ore-forming fluids are a mixture of crust and mantle sources, but these fluids are homogenized incompletely.

(4) The Bailashui tin deposit is temporally and spatially related with granitic magmatism in this area, and magmatic hydrothermal fluids rather than meteoric waters played an important role in the tin mineralization.

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