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REE geochemical characteristics of the No. 302 uranium deposit in northern Guangdong, South China

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Abstract The No. 302 uranium deposit, located in Guangdong Province, is a typical granite-type uranium ore deposit. REE geochemical characteristics of the wall rocks, pitchblende, altered rocks, calcite and fluorite from this deposit have been systematically studied in this paper. The result showed that the alkali-metasomatic granites and other altered rocks have the same REE distribution patterns as Indosinian granites. It is indicated that the hydrothermal ore-forming solution had altered the Indosinian granites, and ore-forming materials may directly originate from the Indosinian granites. Calcite and fluorite of different stages are the products derived from the same source but different stages. The evolution and degassing of the mineralizing solution might induce LREE enrichment to varying degree. Mantle fluid and a large volume of mineralizer may be the crucial factors controlling uranium mineralization, and the hydrothermal solution with mineralizer played an important role in U transport and concentration. Meanwhile, the degassing of CO_2 might promote U and REE precipitation.

Key words No. 302 uranium deposit; granite-type uranium deposit; REE; ore-forming hydrothermal fluid; South China.

The rare-earth elements (REE) are often transported as a whole in geological processes, because of their different physicochemical properties in some aspects. Like stable isotopes, REE can play a vital role in constraining the origin of ore-forming materials and the evolution of mineralizing fluid. Thus, REE have found wide applications both at home and abroad (Fryer and Taylor, 1987; Bau et al., 2003; Schwinn and Markl, 2005; Xie Qiaoqin et al., 2006; Huang Zhilong et al., 2001; Peng Jiantang et al., 2002 and 2004). Previous authors put their focus on the geological characteristics and genesis of the ore deposit, as well as fluid inclusions and stable isotopes in the No. 302 uranium deposit (Jin Jingfu and Hu Ruizhong, 1987 and 1988; Chen Peirong and Liu Yi, 1990; Chen Peirong et al., 1992), and only a few granites were studied with respect to their REE geochemistry (Jin Jingfu and Hu Ruizhong, 1985). Moreover, these researches were mainly developed from the late 1980's to the early 1990's. Therefore, this paper deals with the REE compositional characteristics of the mineralizing solution, the origin of ore-forming materials and REE geochemical behaviors during mineralization.

1 Geological background

The Changjiang uranium ore field is one of the main U-producing granite-type uranium ore fields in China and is located in the southeastern part of the Zhuguang pluton of the Nanling granite belt. Regionally, together with the neighboring uranium ore districts, it is located in the Caledonian fold belt of South China, and within the South China Uranium Province. The No. 302 uranium deposit is located in the eastern part of the Changjiang uranium ore field and is controlled mainly by both the NE-trending Mianhuakeng fault and NW-trending Youdong fault (Fig. 1.), which is the largest granite-type hydrothermal uranium deposit so far reported in the Changjiang uranium ore field.

The ores occur near the contact of the medium-grained mini-porphyritic two-mica granite (Early Jurassic) with medium- to fine-grained porphyritoid biotite granite (Late Jurassic to Late

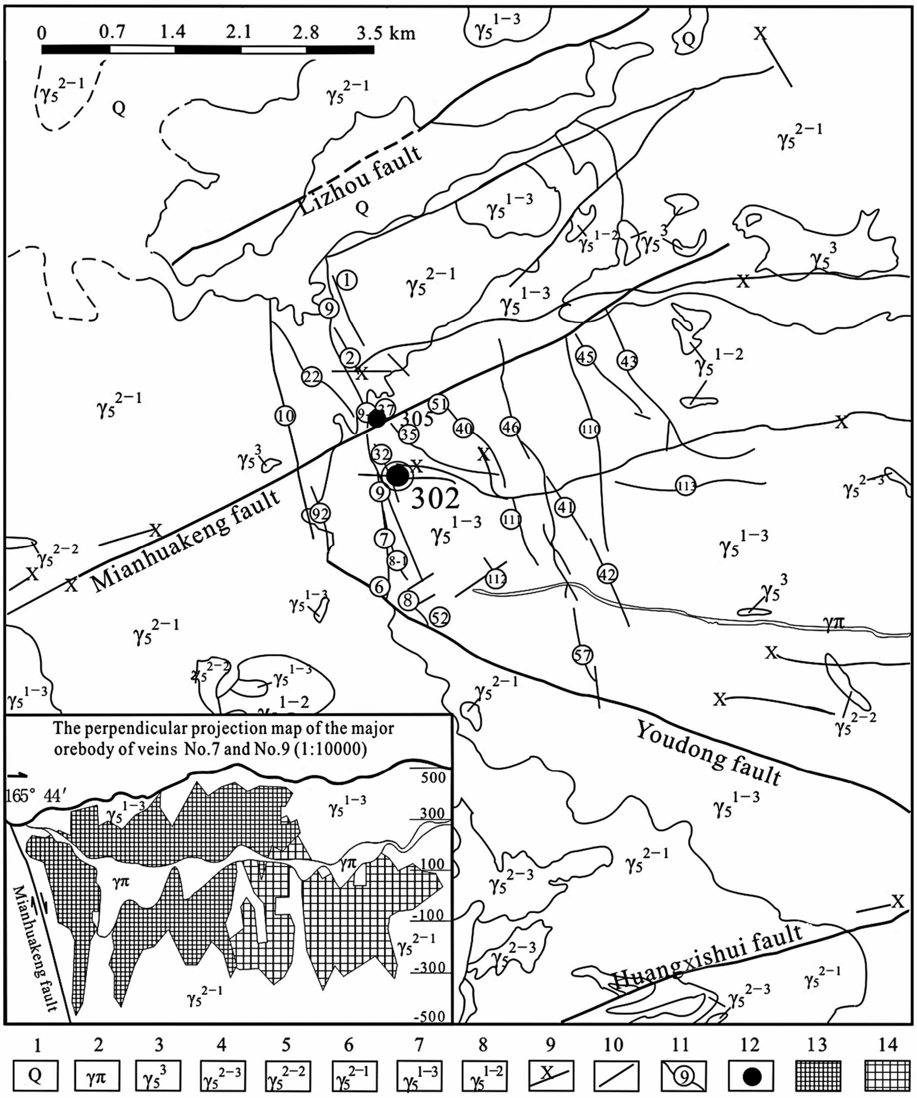

Fig. 1 Geological sketch map of the eastern part of the Changjiang uranium ore field [Rich uranium metallogenic prospect and target area of the No. 211 Uranium Mining District in Renhua, Guangdong. China National Nuclear Shaoguan Jingyuan Uranium Industry Co., Ltd., 2004 (unpublished data)]. 1. Quaternary; 2. granite porphyry dike; 3. fine-grained two-mica granite or garnet two-mica granite; 4. fine- or medium-grained two-mica granite; 5. fine-grained biotite granite or biotite granite; 6. medium- to fine-grained porphyroid biotite granite; 7. medium-grained mini-porphyritic two-mica granite; 8. medium-grained porphyroid two-feldspar granite; 9. diabase dike; 10. fault; 11. ore vein and serial number; 12. uranium deposit; 13. orebody No. 9; 14. orebody No. 7.

Cretaceous) (Fig. 1). The ore bodies, occurring mostly as veins and lenses, are hosted predominantly in a NNW-trending brecciation zone caused by a pivotal tension fault. The main uranium minerals are pitchblende, uranium black and secondary uranium minerals. The common mineral associations are mainly pitchblende-hematite-red microcrystalline quartz, pitchblende-purplish-black fluorite and pitchblende-colloidal pyrite-greyish-black microcrystalline quartz, the former is dominant and hence it is the main target of exploitation, while the latter two are recognized in the locally distributed pitchblende-rich veins only.

Varying-degree alterations such as alkali metasomatism, hydromicatization and chloritization can be found in the deposit. Based on field observations on the cutting relations among hydrothermal veins in combination with the results of laboratory studies, hydrothermal activities in this area can be divided into three stages, i.e., the early-ore stage (alkali metasomatism, hydromicatization and chloritization), the main mineralization stage (hydromicatization, chloritization, carbonatization, fluoritization, etc.) and the late-ore stage (carbonatization, fluoritization). Calcites formed at the early-ore stage are mainly flesh red in color and massive in shape;

those formed at the main stage occur mainly as light flesh red-white fine-grained lumps, distributed in the center of ore veins; those formed at the late-ore stage are mostly white, colorless and veined, distributed in the periphery of the fault silicification belt, somewhat distant from the ore veins. These calcites commonly coexist with late-stage cream-white microcrystalline quartz and light-colored-colorless fluorite, but almost have nothing to do with uranium mineralization. Similar to calcites, fluorites formed at the ore-forming stage are mainly purple-black faveolate, and always associated with uranium minerals.

2 Sample collection and analysis

In this study all samples were collected from different ore fields at the elevation of 250–0 m in uranium deposit 302, including Indosinian (γ_5^{1-3}) and Yanshanian (γ_5^{2-1}) granites, alkali metasomatized, hydromicatized and chloritized rocks, massive or veined pitchblende rich ores and slenderly veined or dispersive pitchblende lean ores, flesh-red calcites, light flesh red-white calcites, white or colorless calcites, purple-black fluorites and light-colored-colorless fluorites.

The contents of REE in the samples were determined by ICP-MS at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. In the analysis process, the domestic sample standard GSR-5 was adopted. The analytical precision is 5% and the analytical error is 10%. The analysis results are listed in Table 1.

3 REE characteristics of the No. 302 uranium deposit

As shown in Fig. 2 and listed in Table 1, the contents of REE in the Yanshanian granites are 91×10^{-6} and 135×10^{-6}, $(La/Yb)_N$=0.66 and 2.1, $(La/Sm)_N$=0.79 and 1.83, $(Gd/Yb)_N$=0.44 and 0.72, δEu=0.07 and 0.20, showing a slight LREE enrichment (ΣLREE/ΣHREE=1.37 and 3.1) but flat

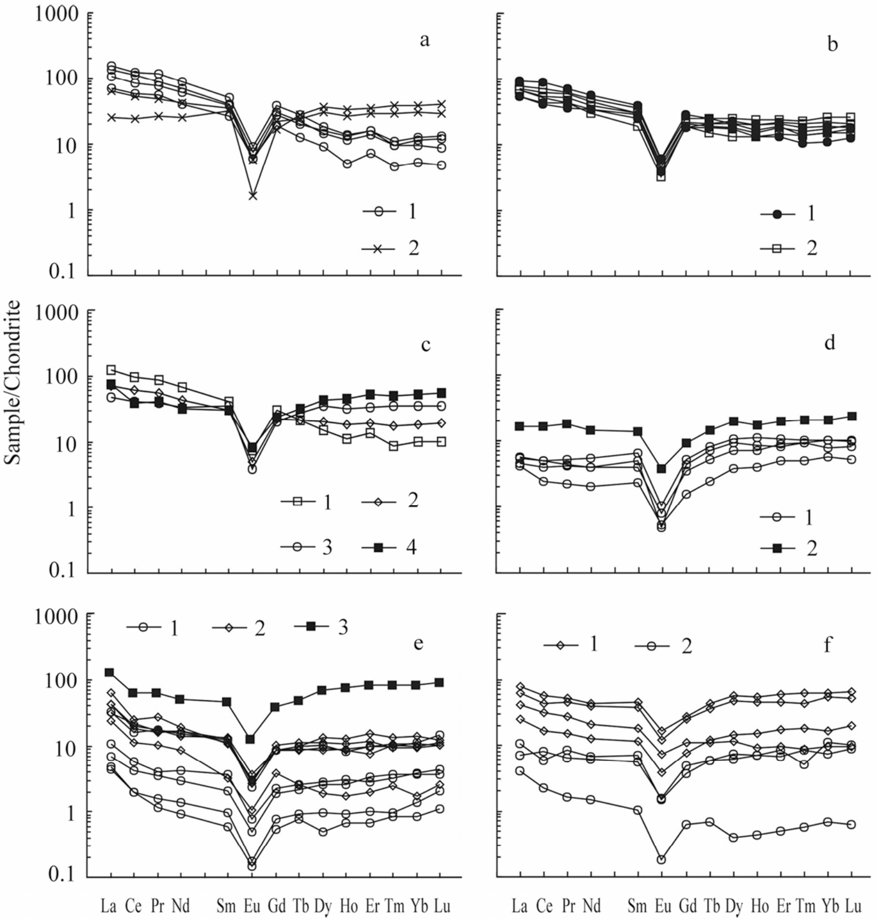

Fig. 2. Chondrite-normalized REE distribution patterns of the granites, altered rocks, ores, fluorites and calcites from the No. 302 uranium deposit. a: 1. Yanshanian (γ_5^{2-1}) granite; 2. Indosinian (γ_5^{1-3}) granite. b: 1. Alkali metasomatized rock; 2. hydromicatized and chloritized rock. c: 1. Indosinian (γ_5^{1-3}) granite (average); 2. altered rock (average); 3. Yanshanian (γ_5^{2-1}) granite(average); 4. pitchblende (average). d: 1. Early-ore stage calcite; 2. pitchblende in lean ore. e: 1. Main mineralization-stage calcite; 2. ore-forming stage fluorite;.3. pitchblende in rich ore. f: 1. Late-ore stage fluorite; 2. late-ore stage calcite (chondrite-normalized REE data from Boynton, 1984).

REE distribution curves (Fig. 2a). On the contrary, most of the REE parameters for the Indosinian granites are higher than those for the Yanshanian granites (the ΣREE values are 119×10^{-6}–254×10^{-6}, $(La/Yb)_N$=8.7–14, $(La/Sm)_N$=2.7–3.3, $(Gd/Yb)_N$=2.2–3.7, and δEu values varying from 0.18 to 0.27) and the former's REE distribution curves are also steeper than the latter's [the REE distribution patterns are of the LREE-enrichment type (ΣLREE/ ΣHREE=7.6–9.7) (Fig. 2a)]. Strong Eu depletion suggests that the magma has experienced feldspar differentiation.

The ΣREE values of the alkali metasomatized rocks are within the range of 99×10^{-6}–178×10^{-6}, with $(La/Yb)_N$=4.7. The ΣREE values of the hydromicatized and chloritized rocks are within the range of 108×10^{-6}–158×10^{-6}, with $(La/Yb)_N$=3.6. All of the altered rocks are characterized by LREE enrichment (Fig. 2b) and the δEu values vary between 0.17 and 0.20. It is indicated that they were formed in similar environments with consistent material sources. According to REE characteristics, the altered rocks are similar to the Indosinian granites and their REE characteristics have mainly inherited from the Indosinian granites.

For pitchblende in U-rich and U-poor ores, the ΣREE values are 213×10^{-6} and 51×10^{-6}, $(La/Yb)_N$ values are 1.57 and 0.81, $(La/Sm)_N$ values are 2.8 and 1.20, and the ΣLREE/ΣHREE values are 1.74 and 1.58, respectively. Both of them are enriched in LREE, but the former is much richer in LREE than the latter (Fig. 2d, e).

The REE characteristic parameters are listed in Table 2. From the table, we can see that most gangue minerals are enriched in LREE, but the gangue minerals crystallized at the main mineralization stage are obviously richer in LREE than those at the late stage; the ore-forming hydrothermal fluid changed from strongly-depleted to relatively strongly depleted in Eu during mineralization, suggesting the ore-forming fluid found its way into a relatively oxidizing

Table 1. REE contents of the granites, altered rocks, ores and hydrothermal calcites and fluorites from the No. 302 uranium deposit ($\times10^{-6}$)

Lithology	Yanshanian granite (γ_5^{2-1})		Indosinian granite (γ_5^{1-3})				Alkali metasomatized rock			Hydromicatized and chloritized rock				Pitchblende		Early-ore stage calcite			
														Rich ore	Lean ore				
Sample No.	2-38	2-24	3-55	3-56	3-57	3-37	3-30	2-32	2-09	3-22	3-23	3-17	3-11	2-70	3-03	3-26'	2-21	2-15	3-15
La	20	7.8	34	42	49	22	17	29	17	21	22	21	24	39	5.0	1.68	1.61	1.34	1.26
Ce	44	20	69	89	101	48	35	72	33	42	51	44	58	49	13	3.8	3.9	3.0	1.85
Pr	5.8	3.3	9.5	11	14	6.7	5.3	8.9	4.4	5.3	7.2	6.3	7.7	7.7	2.2	0.52	0.60	0.48	0.26
Nd	25	15	36	42	55	24	21	35	21	18	27	24	30	30	8.3	2.3	3.1	2.3	1.17
Sm	7.0	6.3	7.5	8.0	9.8	5.2	5.7	7.9	5.0	3.8	6.0	5.9	7.0	8.9	2.6	0.74	1.20	0.95	0.43
Eu	0.42	0.12	0.43	0.55	0.66	0.45	0.29	0.46	0.29	0.24	0.38	0.33	0.44	0.90	0.27	0.06	0.07	0.03	0.04
Gd	5.7	4.4	7.1	7.7	10	5.0	4.7	7.7	4.8	5.0	5.8	5.4	6.7	9.7	2.3	0.86	1.26	1.06	0.39
Tb	1.16	1.31	0.96	1.05	1.29	0.61	0.99	1.19	0.87	0.72	0.98	0.91	1.22	2.2	0.66	0.24	0.38	0.32	0.11
Dy	9.7	12	5.1	4.7	5.8	2.9	7.6	6.8	5.8	4.3	6.9	5.8	8.1	21	6.1	2.2	3.3	2.9	1.18
Ho	2.0	2.4	0.96	0.82	1.00	0.36	1.45	1.19	0.98	0.96	1.48	1.09	1.70	5.2	1.22	0.50	0.76	0.59	0.28
Er	6.1	7.5	3.3	2.9	3.4	1.51	4.4	4.0	2.8	3.1	4.6	3.8	5.2	17	4.0	1.79	2.2	1.67	0.98
Tm	0.97	1.23	0.35	0.31	0.31	0.14	0.59	0.46	0.35	0.45	0.67	0.53	0.76	2.6	0.65	0.29	0.32	0.29	0.15
Yb	6.4	8.0	2.6	2.0	2.4	1.10	4.0	3.2	2.3	3.2	4.6	3.8	5.6	17	4.2	2.1	2.1	1.57	1.12
Lu	0.94	1.31	0.42	0.28	0.39	0.15	0.59	0.57	0.41	0.50	0.67	0.64	0.85	2.8	0.76	0.32	0.31	0.26	0.16
∑REE	135	91	178	213	254	119	109	178	99	108	140	124	158	213	51				
LREE	102	53	156	192	229	106	84	153	80	90	114	101	127	134	31				
HREE	33	38	21	20	25	12	24	25	18	18	26	22	30	78	20				
LREE/HREE	3.1	1.37	7.5	9.7	9.3	9.0	3.4	6.1	4.4	4.9	4.4	4.6	4.2	1.73	1.57				
$(La/Yb)_N$	2.1	0.66	8.7	14	14	14	2.9	6.2	4.9	4.4	3.2	3.8	2.9	1.57	0.81				
$(La/Sm)_N$	1.83	0.79	2.8	3.3	3.2	2.7	1.9	2.3	2.1	3.5	2.3	2.2	2.2	2.8	1.20				
$(Gd/Yb)_N$	0.72	0.44	2.2	3.1	3.4	3.7	0.94	1.94	1.70	1.25	1.01	1.15	0.96	0.47	0.45				
δEu	0.20	0.07	0.18	0.21	0.20	0.27	0.17	0.18	0.18	0.17	0.19	0.18	0.20	0.30	0.34				

Table 1. (to be continued)

Lithology	Main mineralization stage calcite					Late-ore stage calcite			Ore-forming stage fluorite					Late-ore stage fluorite		
Sample No.	3-13	3-18	3-26	3-27	3-33	1-38	1-47	2-40	3-02	3-28	3-21	3-50	1-45	2-43	2-29	1-28
La	3.4	10	2.2	1.50	1.37	2.1	3.2	1.23	7.5	9.5	13	20	13	7.6	24	19
Ce	4.6	13	3.4	1.60	1.61	6.3	4.7	1.76	9.0	17	15	20	16	13	46	35
Pr	0.49	2.2	0.43	0.19	0.14	0.79	1.00	0.20	1.23	2.1	1.9	3.3	2.2	1.9	6.3	5.5
Nd	2.5	9.1	1.77	0.83	0.55	3.7	3.9	0.89	5.2	9.8	9.8	11.2	8.5	7.7	26	23
Sm	0.71	2.4	0.39	0.19	0.12	1.07	1.33	0.20	0.62	2.2	2.5	2.1	2.6	2.2	8.8	7.2
Eu	0.06	0.17	0.04	0.01	0.01	0.11	0.11	0.01	0.08	0.23	0.20	0.21	0.28	0.28	1.23	0.89
Gd	0.57	2.2	0.48	0.20	0.14	1.22	0.96	0.16	0.99	2.2	2.7	2.2	2.3	2.0	7.2	6.3
Tb	0.12	0.46	0.10	0.04	0.04	0.27	0.28	0.03	0.12	0.41	0.53	0.43	0.47	0.56	2.05	1.67
Dy	0.90	3.3	0.82	0.32	0.16	2.0	2.4	0.13	0.61	3.0	3.6	2.8	4.3	4.7	19	15
Ho	0.22	0.59	0.19	0.07	0.05	0.50	0.50	0.03	0.13	0.62	0.76	0.65	0.92	1.09	3.9	3.2
Er	0.59	2.1	0.70	0.21	0.14	1.36	1.78	0.10	0.41	1.57	2.4	2.0	3.2	3.6	13	9.6
Tm	0.11	0.31	0.12	0.03	0.03	0.27	0.17	0.02	0.08	0.34	0.31	0.35	0.42	0.58	2.0	1.40
Yb	0.81	2.4	0.77	0.29	0.18	1.49	2.3	0.15	0.37	2.0	1.9	2.3	2.9	3.4	13	11
Lu	0.14	0.46	0.12	0.07	0.04	0.28	0.33	0.02	0.08	0.36	0.33	0.33	0.39	0.65	2.1	1.68

environment.

4 Discussion

4.1 Source of mineralizing materials

The U contents of the Indosinian and Yanshanian granites in this area are as high as 10×10^{-6}–25×10^{-6}, several times higher than those of the global granites (3.5×10^{-6}), 2–4 times higher than those of metamorphic rocks (U contents are 4×10^{-6}–6×10^{-6}), too (Jin Jingfu, 1984; Du Letian, 2001). It is indicated that the granites have higher regionally geochemical background values of uranium, and provide the material basis for the formation of U orebodies. Most of the granites (which can't produce uranium orebodies) also have similar high U contents. Thus, the high U contents of the granites are not the main factor controlling the intensity of uranium mineralization. Whether the granites are associated with mineralization or not and form lean ores or high-grade ores are decided by the degree of uranium mobilization. Activation is an alteration making the fixed U remobilize and enter into hydrothermal fluids. So, activation intensifies with alteration. Zhang Bangtong et al. (1990) suggested that the early-stage altered hydrothermal fluid is an omen for large-scale mineralization, it can not only change the state of U and cause the mobile U increase, but also provide a partial uranium source; some altered host rocks provided an advantageous geochemical environment for uranium enrichment and precipitation.

Table 2. REE characteristic parameters for the calcites and fluorites

Lithology		LREE	HREE	LREE/HREE	∑REE	$(La/Yb)_N$	$(La/Sm)_N$	$(Gd/Yb)_N$	δEu
Early-ore stage calcite	Scope	5.0—10	4.4—11	0.93—1.14	9.4—21	0.53—0.76	0.84—1.86	0.28—0.54	0.10—0.28
	Average value	8.0	8.0	1.04	16	0.6	1.26	0.41	0.19
Main mineralization stage calcite	Scope	3.8—36	0.76—12	2.5—5.0	4.6—48	1.90—5.3	2.6—7.4	0.50—0.75	0.20—0.27
	Average value	13	4.1	3.5	17	3.3	4.3	0.61	0.25
Late-ore stage calcite	Scope	4.3—14	0.64—8.6	1.65—6.7	4.9—23	0.96—5.7	1.25—3.9	0.34—0.89	0.27—0.30
	Average value	11	5.6	3.4	16	2.6	2.2	0.63	0.29
Ore-forming stage fluorite	Scope	24—57	2.8—15	2.9—8.4	26—68	3.1—14	2.7—7.6	0.63—2.2	0.24—0.35
	Average value	41	10	4.7	52	6.1	4.6	1.13	0.30
Late-ore stage fluorite	Scope	33—111	17—62	1.80—2.0	50—174	1.16—1.50	1.68—2.1	0.44—0.47	0.40—0.48
	Average value	78	43	1.86	122	1.29	1.84	0.46	0.43

Graf (1977) revealed that the REE concentrations and REE distribution in hydrothermal fluids are controlled principally by source rocks. Thus, the ore-forming materials of hydrothermal uranium deposits can be addressed on the basis of the similar principle. The mineralization ages of nodular and brecciated pitchblende ores (at the early-ore stage) are 130 Ma–157 Ma in the No. 302 uranium deposit and most deposits in the Zhuguang-Guidong area (Tan Mutao and Liu Shixian, 1998; Zhang Yanchun, 2002; Wu Lieqin et al., 2003). This is consistent with the age of early-stage crustal extension in South China (Li Xianhua, 2000). Moreover, Wu Junqi et al. (1998) and Zhang Yanchun (2002) discovered that alkali-metasomatzed rocks were also formed during that period of time. The authors suggested that alkalic hydrothermal fluids derived from the mantle at the early stage of crustal extension led to metasomatism of the country rocks, and after that, nodular and brecciated pitchblende ores were formed. Deng Ping et al. (2005) also suggested uranium can be directly enriched and mineralized by alkalic hydrothermal fluids under a certain condition (particularly at the late stage of alkali-metasomatism) in their study of the Shituling uranium deposit. There are numbers of alkali-metasomatized rocks beneath the No. 302 uranium deposit and alterations are mainly alkali-metasomatism, hydromicatization and chloritization, etc. during uranium mineralization. Therefore, studies of these altered rocks can reveal the characteristics of early-stage ore-bearing hydrothermal fluids. As depicted above, early altered hydrothermal fluids are important for uranium mineralization and, therefore, the activation and migration of ore-forming materials should be consistent with those of the altered hydrothermal fluids. If ore-forming materials were derived mainly from the Yanshanian granites, the altered rocks should possess similar or even the same REE characteristics as the Yanshanian granites. However, significant differences have been recognized between them, for example in REE distribution pattern and values of $(La/Yb)_N$, $(La/Sm)_N$ and $(Gd/Yb)_N$. Similar REE characteristics between the altered rocks and the Indosinian granites indicate that the ore-forming materials were derived mainly from the Indosinian granites.

The HREE have stronger complexing ability than the LREE in hydrothermal fluids, and REE (especially HREE) and U would be remobilized at the same time when CO_2-rich mantle-source fluids reacted with crust-derived granites. Thus, they would be leached from crust-derived granites. As shown in Fig. 2c, the HREE in the altered rocks and pitchblende ore obviously increased relative to fresh Indosinian granites, but the HREE in the altered rocks obviously decreased relative to fresh Yanshanian granites. It is indicated that the HREE originated from the Indosinian granites during alteration. Although the REE distribution patterns of the Yanshanian granites are similar to those of pitchblende, just as depicted above, the HREE in the altered rocks which represent the early-ore stage solution, are impossible to have originated from the Yanshanian granites. Therefore, the early-stage hydrothermal fluids played a role mainly in altering the Indosinian granites and leaching U and REE from them. The Yanshanian granites may have provided abundant heat and a part of U source. In addition, more minor fractures were formed in the rocks. Thus, these minor fractures can provide channel ways for mineralizing hydrothermal solutions. And then, tectogenesis and early-stage hydrothermal fluids are easier to destroy U-rich minerals as well as the textures of granites, and laid down a foundation for U-minerals to be oxidized and transported by hydrothermal fluids in later periods (Zhang Guoquan et al., 2007). Moreover, the REE characteristics of gangue minerals formed at the main- and late-ore stages are similar to those of the altered rocks formed at the early- and main-ore stages, suggesting ore-forming materials (U, REE) would originate from the Indosinian granites, too. Chen Peirong (2004) pointed out that no obvious uranium metallogenic specialiality in the Yanshanian granites, close relations between uranium metallogenesis and the Indosinian granites, and they being possible uranium source bodies have also confirmed this conclusion.

4.2 Genetic relations of gangue minerals

Because the colorless gangue minerals (fluorite, calcite) are far away from the orebodies, and there is no obvious relationship between them and mineralization, some people considered that the the hydrothermal fluid responsible for the colorless gangue minerals postdated mineralizing fluid. However, accessory gangue minerals of the same mineralization system may be discussed in the light of LREE/HREE ratios (Lottermoser, 1992). Bau and Dulski (1995) pointed out that the accessory gangue minerals show a horizontal distribution pattern in the Y/Ho-La/Ho diagram in their study of the REE geochemical characteristics of fluorite and calcite in the Tannenboden and Beihilfe ore deposits in Germany. The same gangue minerals of different colors from the No. 302 uranium deposit have different REE contents, characteristic parameters and distribution patterns, but there is a horizontal distribution pattern in the Y/Ho-La/Ho diagram (Fig. 3), too. It is indicated that they originated from the same source. In Fig. 4, there are shown continuous changing tendencies in Tb/La-Sm/Nd and

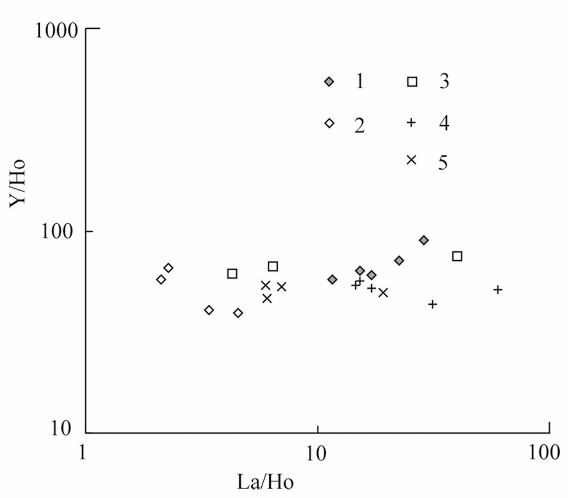

Fig. 3. Y/Ho-La/Ho diagram of the calcites and fluorites. 1. Early-ore stage calcite; 2. late-ore stage calcite; 3. main mineralization stage calcite; 4. ore-forming stage fluorite; 5. late-ore stage fluorite.

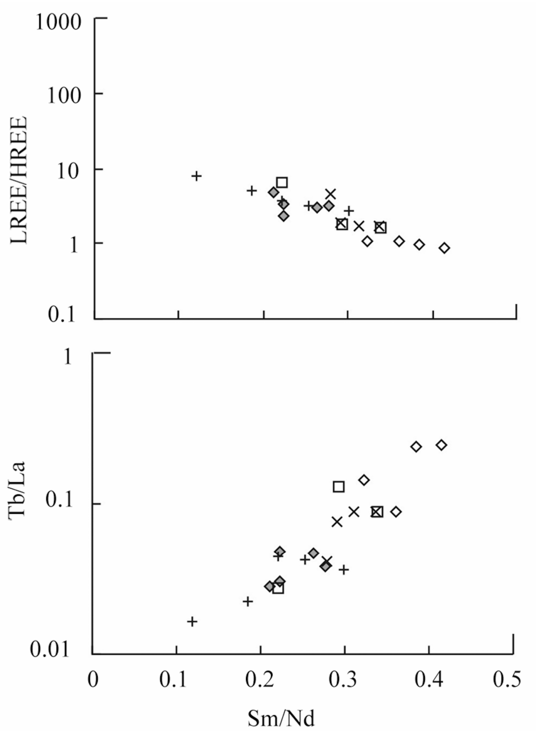

Fig. 4. LREE/HREE vs. Sm/Nd and Tb/La vs. Sm/Nd diagrams of the calcites and fluorites (The legends are the same as in Fig. 3).

LREE/HREE-Sm/Nd, suggesting these gangue minerals are the products derived from the same source but formed from hydrothermal fluids at different stages, too. Furthermore, six samples of early-ore stage calcite showed their $\delta^{13}C$ values varying from -4.3‰ to -4.9‰ and their $\delta^{18}O$ values varying from 7.8‰ to 13.3‰; seven samples of main stage calcite gave their $\delta^{13}C$ values within the range of -6.7‰ to -9.3‰ and their $\delta^{18}O$ values within the range of 10.5‰ to 12.7‰; six samples of late-ore stage calcite gave their $\delta^{13}C$ values of -8.7‰ to -9.7‰ and $\delta^{18}O$ values of 12.3‰ to13.2‰. These data display a negative correlation and obvious mantle magma degassing characteristics, lending a further support to the conclusion that the calcites originated from the same source.

4.3 REE evolution in the process of mineralization

It is found that trivalent REE can replace Ca^{2+} when REE find their way into hydrothermal calcite or fluorite. The ionic radius of $LREE^{3+}$ is bigger than that of $HREE^{3+}$, thus $LREE^{3+}$ is easier to replace Ca^{2+} when entering calcite or fluorite. The REEs are proved to be transported as complexes in hydrothermal fluids, and the stability of the complexes increases with atomic number. Therefore, calcite or fluorite often shows LREE enrichment and HREE depletion as observed in many hydrothermal deposits (Wood, 1990a, b; Lottermoser, 1992; Haas et al., 1995; Rimstidt et al., 1998). McLennan and Taylor (1979) pointed out that the carbonic acid complexes of HREE are easier to dissolve than those of LREE, uranium and REE were transported together as carbonic acid complexes. Furthermore, the REEs can be transported as stable carbonic acid anionic complexex, the HREEs are easier to dissolve and transport than the LREEs in CO_2-rich hydrothermal fluids (Wendlant and Harrison, 1979; Michard et al. 1987; Cantrell and Bryne, 1987). Brecciform pitchblende and much strongly altered rocks (such as alkali-metasomatized rocks) were formed and quite a part of LREE would be precipitated in the early-ore stage. Simultaneously, hydrothermal fluid degassing caused a large volume of CO_2 to lose and uranium and REE complexes to disintegrate. But the HREE would be precipitated much more than the LREE under the same condition. Thus, early-ore stage calcite is relatively enriched in HREE, with the REE distribution pattern being similar to that of pitchblende in lean ores (Fig. 2d). In the process of continuous mineralization, a large amount of HREE would be co-precipitated with minerals formed at the early stage. Therefore, later pitchblende or gangue minerals showed HREE depletion relative to early-ore stage gangue minerals, and the REE distribution patterns are also characterized as being smooth (Fig. 2e and f). That is why calcites show different REE distribution patterns between common hydrothermal ore deposits and the deposit studied (LREE enrichment is not obvious in the early-stage calcites).

Generally speaking, La is the most strongly alkaline element among the REEs. And as for the REEs, their alkalinity decreases and acidity increases with increasing atomic number. The activity of HREE is stronger than that of LREE in alkaline solution, and the solubility of HREE is also higher than that of LREE. Thus, the HREE are not so easy to separate and precipitate. But the HREE are easier to precipitate in acidic solution. McLennan and Taylor (1979) expounded the direct relations between uranium concentrations and REE enrichment. Michard (1989) also pointed out that REE concentrations generally increase with decreasing pH in hydrothermal solutions. REE fractionation degree is not very obvious in the No. 302 uranium deposit, but LREE/HREE, La/Yb and La/Sm, etc. are gradually reduced from rich pitchblende ore to lean pitchblende ore. The REE parameters for altered country rocks and gangue minerals tend to reduce from early stage to late stage, too. These characteristics indicate the reduction of alkalinity of ore-forming fluids during mineralization. This is consistent with the conclusion drawn by Jin Jingfu and Hu Ruizhong (1987) in terms of their fluid inclusion studies.

4.4 Mantle fluids and metallogenesis

Typical mantle fluids have a high $(La/Pr)_N$ value (Huang Zhilong et al., 2001). The average $(La/Pr)_N$ values of calcite and fluorite in the U-mineralization stage are 2.1 and 2.3, respectively; however, the values of calcite and fluorite formed at the late stage are 1.60 and 1.50, respectively. Obviously, $(La/Pr)_N$ values at the U-mineralization stage are similar to those of mantle fluids and the $(La/Pr)_N$ values of calcite and fluorite formed at the late-ore stage are lower than those of mantle fluids (meteoric water plus U-mineralizing solution maybe make the $(La/Pr)_N$ value reduce). Furthermore, carbon isotopic values suggested that CO_2 would originate from the mantle at the stage of uranium mineralization. It is implicated that mantle fluids can provide a large volume of mineralizer and part of early ore-forming fluid, and then make U transport from the country rocks to U-mineralizing hydrothermal fluids.

5 Conclusions

(1) Ore-forming materials were derived mainly from the Indosinian granites. The Yanshanian granites may induce mineralization to carry on and provide a small part of ore-forming materials.

(2) From the early-ore stage to the late-ore stage Eu showed a tendency of strong depletion to moderately strong depletion, indicating that the mineralization environment had turned into a relatively oxidizing one; U-mineralizing solutions tend to become relatively enriched in LREE to relatively enriched in HREE, the alkalinity of U-mineralization solutions was reduced during mineralization.

(3) Calcites and fluorites of the different stages are the products derived from the same source but different stages of hydrothermal fluid. The evolution and degassing of mineralizing solutions might induce LREE enrichment to various degrees and this may be the reason why calcites show different REE distribution patterns between common hydrothermal ore deposits and the deposit studied.

(4) Mantle fluids possibly provided a large volume of mineralizer (CO_2) and part of early ore-forming fluid for the formation of the No.302 uranium deposit.

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References

Bau M. and Dulski P. (1995) Comparative study of yttrium and rare-earth element behaviors in fluorine-rich hydrothermal fluids [J]. *Contrib. Mineral. Petrol.* **119**, 213–223.

Bau M., Romer R.L., LÜders V., and Dulski P. (2003) Tracing element sources of hydrothermal mineral deposits: REE and Y distribution and Sr-Nd-Pb isotopes in fluorite from MVT deposits in the Pennine Orefield, England [J]. *Mineralium Deposita*. **38**, 992–1008.

Boynton W.V. (1984) Cosmochemistry of the rare-earth elements: Meteorite studies. In *Rare-Earth Element Geochemistry* // [A]. pp.63–114. Elsevier, Amsterdam.

Cantrell K.J. and Bryne R.H. (1987) Rare-earth element complexation by carbonate and oxalate ions [J]. *Geochim. et Cosmochim. Acta.* **51**, 597–605.

Chen Peirong and Liu Yi (1990) The physicochemical conditions for metallogenesis of No.302 uranium deposit and the source and migration direction of its hydrothermal solution [J]. *Mineral Deposits*. **9**, 149–157 (in Chinese with English abstract).

Chen Peirong (2004) Geodynamic setting of Mesozoic magmatism and its relationship to uranium metallogenesis in southeastern China [J]. *Uranium Geology*. **20**, 265–270 (in Chinese with English abstract).

Chen Peirong, Zhang Bangtong, and Zhang Zhuhuan (1992) Speciation and precipitation of uranium complexes in hydrothermal solutions related to granite-type uranium deposits [J]. *Chinese Journal of Geochemistry*. **11**, 252–260.

Deng Ping, Ling Hongfei, Shen Weizhou, Gao Jianfeng, Tan Zhengzhong, Zhu Ba, and Huang Guolong (2005) A discussion on alkali metasomatism in Shituling uranium deposit, Northern Guangdong Province [J]. *Geological Review*. **51**, 557–565 (in Chinese with English abstract).

Du Letian (2001) *The Basic Metallogenic Criteria of Hydrothermal Uranium Deposits in China and the General Hydrothermal Metallogeny* [M]. Atomic Energy Press, Beijing (in Chinese).

Fryer B.J. and Taylor R.P. (1987) Rare-earth element distributions in uraninites: implications for ore genesis [J]. *Chem. Geo1.* **63**, 101–108.

Graf J.L. (1977) Rare-earth elements as hydrothermal tracers during the formation of massive sulfide deposits in volcanic rocks [J]. *Econ. Geol.* **72**, 527–548.

Haas J.R., Shock E.L., and Sassani D.C. (1995) Rare-earth elements in hydrothermal systems: Estimates of standard partial molal thermodynamic properties of aqueous complexes of the rare-earth elements at high pressures and temperatures [J]. *Geochim. et Cosmochim. Acta.* **59**, 4329–4350.

Huang Zhilong, Chen Jin, Han Runsheng, Li Wenbo, Gao Derong, Zhao Deshun, and Liu Congqiang (2001) REE geochemistry of calcite—A gangue mineral in the Huize ore deposit, Yunnan [J]. *Acta Mineralogica Sinica*. **21**, 659–666 (in Chinese with English abstract).

Jin Jingfu (1984) The material source and mineralization of the Mesozoic uraniferous granitic rock in southeast of China [J]. *Acta Petrologica Mineralogica et Analytica*. **3**, 112–119 (in Chinese with English abstract).

Jin Jingfu and Hu Ruizhong (1985) The Genesis of uranium deposit No.302 [J]. *Journal of Chengdu College of Geology*. **4**, 1–11 (in Chinese with English abstract).

Jin Jingfu and Hu Ruizhong (1987) Transportation and deposition of uranium in hydrothermalore-forming fluids as exemplified by uranium deposit No.302 [J]. *Geochimica*. **4**, 320–329 (in Chinese with English abstract).

Jin Jingfu and Hu Ruizhong (1988) Transport deposition of uranium in hydrothermal ore fluids as exemplified by uranium deposit 302 [J]. *Chinese Journal of Geochemistry*. **7**, 221–232.

Li Xianhua (2000) Cretaceous magmatism and lithospheric extension in Southeast China [J]. *Journal of Asian Earth Sciences*. **18**, 293–305.

Lottermoser B.G. (1992) Rare-earth elements and hydrothermal ore formation processes [J]. *Ore Geol. Rev.* **7**, 25–41.

McLennan S.M. and Taylor S.R. (1979) Rare-earth element mobility associated with uranium mineralization [J]. *Nature.* **282**, 247–250.

Michard A., Beaucarite C., and Michard G. (1987) Uranium and rare-earth element in CO_2-rich waters from Vals-Les-Basin (France) [J]. *Geochim. et Cosmochim. Acta.* **51**, 901.

Michard A. (1989) Rare-earth element systematics in hydrothermal fluids [J]. *Geochim. et Cosmochim. Acta.* **53**, 745–750.

Peng Jiantang, Hu Ruizhong, Qi Liang, and Jiang Guohao (2002) REE geochemistry of fluorite from the Qinglong antimony deposit and its geological implications [J]. *Chinese Journal of Geology*. **37**, 277–287 (in Chinese with English abstract).

Peng Jiantang, Hu Ruizhong, Qi Liang, Zhao Junhong, and Fu Yazhou (2004) REE distribution pattern for the hydrothermal calcites from the Xikuangshan antimony deposit and its constraining factors [J]. *Geological Review*. **50**, 25–32 (in Chinese with English abstract).

Rimstidt J. D., Balog A., and Webb J. (1998) Distribution of trace elements between carbonate minerals and aqueous solution [J]. *Geochim. et Cosmochim. Acta.* **62**, 1851–1863.

Schwinn G.. and Markl G. (2005) REE systematics in hydrothermal fluorite [J]. *Chem. Geol.* **216**, 225–248.

Tan Mutao and Liu Shixian (1998) *Granite-Type and Volcanic-Type Uranium Deposits in Nanling* [M]. Geology Press, Beijing (in Chinese).

Wendlant R.F. and Harrison W.J. (1979) Rare-earth partitioning between immiscible carbonate and silicate liquids and CO_2 vapor, result and implications for the formation of light earth-enriched rocks [J]. *Contrib. Mineral. Petrol.* **4**, 409.

Wood S.A. (1990a) The aqueous geochemistry of the rare-earth elements and yttrium. 1. Review of available low-temperature data for inorganic complexes and the inorganic REE speciation of natural waters [J]. *Chem. Geol.* **82**, 159–186.

Wood S.A. (1990b) The aqueous geochemistry of the rare-earth elements and yttrium. 2. Theoretical predictions of speciation in hydrothermal solutions to 350℃ at saturation water vapor pressure [J]. *Chem. Geo1.* **88**, 99–125.

Wu Junqi, Min Maozhong, Zhai Jianping, Luo Xianzhang, Lai Yitang, and Wei Xingzhang (1998) Alkali metasomatic alteration of the granite in middle Chuguang mountain,South China [J]. *Acta Petrologica Sinica*. **14**, 90–98 (in Chinese with English abstract).

Wu Lieqin, Tan Zhengzhong, Liu Ruzhou, and Huang Guolong (2003) Discussion on uranium ore-formation age in Xiazhuang ore-field, northern Guangdong [J]. *Uranium Geology*. **19**, 28–33 (in Chinese with English abstract).

Xie Qiaoqin, Xu Xiaochun, Li Xiaoxuan, Chen Tianhu, and Lu Sanming (2006) Rare-earth elements geochemistry of Laowan Gold Deposit in Henan Province: Trace to source of ore-forming materials [J]. *Journal of Rare Earths*. **24**, 115–120.

Zhang Bongtong, Wu Junqi, Qiu Zhili, and Liu Yi (1990) On the relationship between hydrothermal alteration and uranium enrichement [J]. *Geological Review*. **38**, 238–245 (in Chinese with English abstract).

Zhang Guoquan, Hu Ruizhong, Shang Pengqiang, Liu Lei, and Yang Shefeng (2007) An overview of mineralization mechanism of granite-type uranium deposits in South China [J]. *Bulletin of Mineralogy, Petrology and Geochemistry* (in Chinese with English abstract, in press).

Zhang Yanchun (2002) Alkalic mantle fluids and uranium ore-formation in Zhuguang and Guidong granite massifs [J]. *Uranium Geology*. **18**, 210–219 (in Chinese with English abstract).