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Geochemical Characteristics of Rare-Earth Elements of Guidong Granitic Complex and Relationship with Uranium Mineralization

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ABSTRACT

Some of the granite-type uranium deposits just located nearby the low temperature geothermal system, hot spring system in China. So the study of the mineralization system would be helpful for the understanding of the geothermal system. Granites rich in uranium and other lithophile elements are a potential source of shallow heat energy through enhanced geothermal development. Guidong granitic complex is consists of the Luxi intrusion, Xiazhuang intrusion, Maofeng intrusion, Sundong intrusion, Aizi intrusion and Siqian intrusion, which were emplaced in the Indosinian and early Yanshanian Periods. These intrusions varied from each other not only in major element content, aluminium saturation index, but also in values of ∑ REE, δ_{Eu}, and LREE/HREE, $(La/Yb)_N$, $(La/Sm)_N$ and $(Gd/Yb)_N$. The Maofeng intrusion, which has the closest relationship with uranium mineralization, belongs to peraluminous granite family. Having undergone much intense fluid-rock interaction, it is characterised by typical M-type tetrad effects and lowest values of ∑ REE, δ_{Eu}, LREE/HREE, $(La/Yb)_N$, $(La/Sm)_N$ and $(Gd/Yb)_N$ ratios than other studied intrusions.

1. INTRODUCTION

Some of the granite-type uranium deposits just located nearby the low temperature geothermal system, hot spring system in China. The current studied granitic complex, Guidong granitic complex, not only hosted Xiazhuang uranium ore fields, one of the most important uranium mineralization fields in China, but also had a closed relationship with an active low temperature geothermal system, Xinqiao hot spring system. Xinqiao hot spring system developed along Xinqiao fault, the current temperature of the artesian spring water varied between 38 to 43℃, the fixed-Al calculation by WATCH97 program reveal that the subsurface equilibrium temperature might reached at 100 to 120℃(Zhang, et al, 2004). Therefore the study of the mineralization system would be helpful for the understanding of the geothermal system. Granites rich in uranium might be a potential source of shallow heat energy through enhanced geothermal development.

The Guidong granitic complex is one of the important components of the Dadongshan-Guidong-Wuliting E-W direction magmatite zone in the Nanling area. It consists of many intrusions, such as Luxi, Xiazhuang, Maofeng, Sundong, Aizi and Siqian, and covers an area of 1500 km^2. The Xiazhuang uranium ore-field is one of the most important granite type uranium ore-fields in China. Its major mineralization distributed in the eastern part of Guidong granitic complex and especially manifested in the Maofeng intrusion, Xiazhuang intrusion and Sundong intrusion; while the intrusions located in the western part of Guidong granitic complex, such as Siqian and Aizi didn't developed uranium mineralization at all. Previous studies were focused on the petrological characteristics of the Eastern and Western Guidong granitic complex (Lin, 1992), and geochemistry and petrogenesis of the Xiazhuang intrusion, Sundong intrusion and Maofeng intrusion (Ling et al., 2004; 2005; Wu, 2004). However, this is the first study to characterize the rare earth element geochemistry. In fact, the distribution patterns and the relative parameters of REE are important evidences to trace the source of the mineralization material and the degree of the water-rock interaction. Recently advancements have been made in understanding the genesis of the lanthanide deposits and tetrad effects (Zhao et al., 1992; 1999; Irber, 1999; Zhang and Liu, 2001; Liu and Zhang, 2005).

Most of the uranium deposits in the Xiazhuang ore-field occur in or around Maofeng intrusion. This paper systematically studied the characteristics of the REE in different intrusions of Guidong complex, especially for Maofeng intrusion so that to find out the difference between Maofeng intrusion and the others, to help understanding the mechanism of uranium mineralization.

2. ANALYSIS METHODS AND THE RESULTS

Rare earth element contents were measured by ICP-MS of Finnigan ElementⅡ in State Key Laboratory for Mineral Deposit Research of Nanjing University. GSR-1 granite sample was used as the reference sample. The measured value, recommend values, RSD% and the results are shown in Table 1 and Table 2 respectively. The RSD values for all elements are less than 5％ and corresponding well for multi-measurement.

3. REE PATTERNS

REE contents and some related parameters of different intrusions in Guidong granitic complex are shown in Table 2. The results indicate following aspects of the studied intrusions:

1) Maofeng intrusion has the lowest values of ∑ REE ,δ Eu, $(La/Yb)_N$, $(La/Sm)_N$ and $(Gd/Yb)_N$. Its ∑ REE values vary between 41.03~86.75, (average 71.44), δ Eu value 0.01~0.20 (average 0.11) and $(La/Yb)_N$ value 0.92~7.94 (average 3.26) which means no obvious fractionation between heavy and light REE. $(La/Sm)_N$ and $(Gd/Yb)_N$ vary in 0.72~3.23 and 0.58~2.15 respectively, the average 2.0 and 1.12 respectively, that also means no obviously

fractionation within HREE or LREE.

Table 1. ICP-MS measured results for the GSR-1 reference sample (μ g.g-1) and the RSD%.

Element	Measured	Recommend	RSD%
La	55.09	54	2.02
Ce	106.48	108	1.4
Pr	12.59	12.7	0.83
Nd	47.46	47	0.97
Sm	9.69	9.7	0.09
Eu	0.83	0.85	2.26
Gd	9.09	9.3	2.28
Tb	1.63	1.65	0.94
Dy	10.23	10.2	0.34
Ho	2.07	2.05	0.87
Er	6.68	6.5	2.77
Tm	1.07	1.06	1.31
Yb	7.19	7.4	2.82
Lu	1.15	1.15	0.06

2) Luxi granite has the highest ∑ REE, δ_{Eu}, LREE/HREE, $(La/Yb)_N$, $(La/Sm)_N$ and $(Gd/Yb)_N$ values, which indicated obvious fractionation between HREE and LHEE and also within HREE and LREE. The fractionation within LREE is stronger than that within HREE. Siqian intrusion has a moderate characteristic value of REE and has good coherence between 6 studied samples.

3) Sundong and Xiazhuang intrusion have similar characteristics of REE, they have large variation on ∑ REE, δ_{Eu}, LREE/HREE, $(La/Yb)_N$, $(La/Sm)_N$ and $(Gd/Yb)_N$ values. Samples close to the uranium deposit (such as XZ-2) have characteristic values similar to Maofeng intrusion, while those far from uranium deposit have characteristic values similar to Luxi intrusion.

Figure 1 shows the REE distribution patterns of studied intrusions. Uranium mineralized Maofeng intrusion displays typical M-type tetrad effect, while Xiazhuang, Sundong, Luxi and Siqian intrusions do not, which might indicate that Maofeng intrusion underwent much stronger fluid-rock interaction than other studied intrusions during or after the crystallization. $TE_{1,3}$, the parameter used to characterize the intensity of the tetrad effect, varies greatly in different intrusions. All samples from Maofeng intrusion have $TE_{1,3}$ value >1.1, samples from Luxi intrusion <1.1, samples from Xiazhuang and Sundong intrusions have $TE_{1,3}$ value varied near 1.1, most of them in Siqian intrusion smaller than 1.1 except one sample. Since Maofeng is the most important intrusion for U-mineralization, the interpretation on the REE content and REE distribution patterns should help understand the mechanism of uranium mineralization.

4. DISCUSSION AND CONCLUSIONS

Compared with other intrusions, only Maofeng intrusion shows typical M-type REE tetrad effect. It was the result of the deuterogenic interaction between CO_2-rich mantle derived fluid and granitic rock.

Deuterogenic muscovite yielded the age of 141 Ma (K-Ar method), corresponding with the mineralization age of 138 Ma of No 337 deposit (Wu et al., 2003) and the intrusion age of the Huangpi-Zhangguangyin group diabase (Wu et al., 2005). Isotopic study showed that the average $(^{87}Sr/^{86}Sr)_i$ value of Maofeng intrusion is 0.719, lower than the average $(^{87}Sr/^{86}Sr)_i$ value (varied between 0.729 ~ 0.749) of the regional granites (Wu et al., 2005). The authors attribute this to the stacking remediation of the mantle-derived fluid on Maofeng intrusion was stronger than other studied intrusions.

The major species of the uranium migration in Xiazhuang ore-field were $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ (Hu and Jin, 1990), melt inclusion studies made by Qi et al. had attested that Guidong granitic complex formed at high temperature and high pressure, low CO_2 and HCO^-_3 condition (Qi and Hu, 2000). In U-mineralized intrusions it was quite easy to find conglomeration of carbonate which had the $\delta^{13}C$ value varied in -4～-8‰ (Wu et al., 2005), indicating that the mantle fluid took part in the U-mineralization. Cantrell and Bryne (1987) pointed out that the complex ion $(REE(CO_3)_3)^{3-}$ and $(REE(CO_3)_4)^{5-}$ have high stability in carbonic acid enriched fluid. Wendlant and Harrison (1979) proved that rare earth elements could be mobilized in CO_2-rich thermal fluid through experiment study. Furthermore, Michard proved that CO_2-rich fluid was favorable for the migration of HREE (Michard, 1987). Comparing to continent originated granite, mantle fluid has relatively lower REE content, but stronger dissolution and migration ability, so when CO_2-rich mantle fluid interacted with granite, it reactivated the REE (especially LREE) as well as the uranium, which reduced the total content of REE and LREE/HREE ratio and hence revised the REE distribution pattern of the Maofeng intrusion.

Some difference in the intrusion age, characteristics of chemistry and mineralogy, as well as the distinct crust contamination on the latest group of the mafic dyke (Li, 1997), which might indicate that some difference exists on the characteristics of the mantle derived fluid and mineralization intensity and manner at different stages, this might suggest that chemically speaking, Maofeng, Xiazhuang and Sundong granite intrusions are of peraluminous affinity, but there are some difference in the related parameters of REE and different distribution patterns.

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Table 2. REE contents (10^{-6}) and related parameters of different intrusions in Guidong granitic complex.

Serial No	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Σ REE	δ_{Eu}	δ_{Ce}	$TE_{1,3}$	$(La/Yb)_N$	$(La/Sm)_N$	$(Gd/Yb)_N$
LX-1	67.20	120.20	14.80	53.20	9.95	1.26	6.39	1.11	4.89	0.90	2.21	0.37	2.06	0.28	284.82	0.45	0.86	1.02	22.04	4.25	2.51
LX-2	68.55	131.30	14.90	53.28	9.69	1.26	6.46	1.10	4.68	0.87	2.26	0.36	1.93	0.26	296.90	0.46	0.93	1.04	24.00	4.45	2.71
LX-3	82.24	150.68	19.28	56.56	9.88	1.54	6.23	0.92	3.94	0.82	1.71	0.26	1.53	0.25	335.84	0.56	0.86	1.01	36.32	5.24	3.30
XZ-1	81.50	156.00	21.70	78.10	16.40	0.90	11.20	2.06	11.00	1.81	4.33	0.62	3.37	0.48	389.47	0.19	0.86	1.09	16.34	3.13	2.69
XZ-2	29.00	55.20	7.43	26.65	6.41	0.51	5.66	1.22	7.44	1.49	4.12	0.78	4.91	0.71	151.53	0.25	0.87	1.08	3.99	2.85	0.93
XZ-3	36.90	85.20	10.30	38.30	9.99	0.49	8.04	1.93	12.30	2.57	8.10	1.14	7.74	1.20	224.20	0.16	1.01	1.14	3.22	2.32	0.84
XZ-4	53.91	112.54	13.23	50.24	11.81	0.70	9.82	1.78	9.81	2.03	5.83	0.87	5.36	0.69	278.62	0.19	0.97	1.03	6.80	2.87	1.48
XZ-5	54.03	101.80	10.86	38.42	7.50	0.65	6.35	0.88	5.79	1.17	3.35	0.50	3.17	0.46	234.92	0.28	0.94	0.96	11.51	4.53	1.62
XZ-6	64.65	126.00	13.51	48.14	9.95	0.91	8.35	1.05	6.27	1.17	3.131	0.432	2.725	0.42	286.70	0.30	0.96	0.96	16.03	4.09	2.48
XZ-7	51.91	93.33	10.02	36.80	6.99	0.73	6.45	0.91	6.15	1.25	3.46	0.49	3.02	0.43	221.93	0.33	0.91	0.94	11.62	4.68	1.73
XZ-8	33.36	72.05	7.08	25.00	5.64	0.42	5.06	0.76	5.13	1.04	3.06	0.46	3.06	0.45	162.56	0.24	1.06	1.01	7.36	3.72	1.34
MF-1	9.84	23.57	3.09	11.51	4.34	0.06	5.44	1.25	8.33	1.53	4.73	0.75	4.58	0.69	79.71	0.04	1.00	1.17	1.45	1.43	0.96
MF-2	5.91	13.38	1.79	6.24	2.44	0.12	2.46	0.53	3.30	0.56	1.75	0.29	1.94	0.32	41.03	0.15	0.96	1.18	2.06	1.52	1.03
MF-3	15.04	30.51	3.68	13.12	3.06	0.21	3.40	0.58	3.21	0.52	1.49	0.21	1.28	0.21	76.52	0.20	0.94	1.09	7.94	3.09	2.15
MF-4	14.18	30.27	3.34	11.89	2.76	0.15	3.00	0.53	3.13	0.52	1.50	0.21	1.37	0.21	73.06	0.16	1.00	1.11	6.99	3.23	1.77
MF-5	11.10	28.30	2.57	9.97	2.75	0.15	2.45	0.57	3.91	0.89	2.99	0.49	3.11	0.46	69.71	0.17	1.21	1.12	2.41	2.54	0.64
MF-6	9.30	20.50	2.92	10.44	3.94	0.10	4.21	1.10	7.00	1.33	4.77	0.83	5.93	0.90	73.27	0.07	0.92	1.19	1.06	1.49	0.58
MF-7	8.13	24.60	3.88	15.10	7.09	0.03	5.25	1.40	8.18	1.32	4.24	0.73	5.96	0.84	86.75	0.01	1.02	1.32	0.92	0.72	0.71
SD-1	39.88	71.13	10.15	37.10	7.62	0.54	7.45	1.10	6.27	1.10	3.13	0.44	2.76	0.41	189.08	0.21	0.81	0.99	9.76	3.29	2.19
SD-2	36.44	65.00	9.41	33.35	7.11	0.45	7.34	0.98	5.87	1.07	2.81	0.40	2.29	0.37	172.89	0.19	0.81	0.96	10.74	3.23	2.59
SD-3	32.13	69.14	8.41	30.50	6.63	0.30	6.72	0.83	6.07	1.08	3.36	0.51	2.90	0.45	169.03	0.14	0.97	0.99	7.49	3.05	1.88
SD-4	47.88	92.51	11.46	40.85	7.77	0.77	7.26	1.00	5.91	1.19	3.40	0.49	3.24	0.49	224.21	0.31	0.90	0.97	9.99	3.88	1.82
SD-5	46.71	105.50	11.13	39.29	7.75	0.60	7.97	1.12	7.92	1.65	5.17	0.68	3.98	0.58	240.04	0.23	1.06	1.00	7.94	3.80	1.63
SD-6	52.68	113.40	12.79	44.05	9.33	0.63	9.09	1.34	9.36	1.91	6.20	0.87	5.51	0.80	267.97	0.21	1.00	1.02	6.46	3.56	1.34

SQ-1	28.77	54.87	7.06	25.63	6.24	0.48	5.32	1.05	5.51	0.97	2.78	0.44	2.66	0.39	142.17	0.25	0.88	1.08	7.31	2.90	1.62
SQ-2	27.00	59.80	6.32	28.30	5.89	0.39	4.86	0.84	5.46	1.14	3.47	0.45	2.74	0.37	147.03	0.22	1.04	0.99	6.66	2.89	1.44
SQ-3	29.70	60.40	5.79	25.50	6.29	0.38	5.53	1.01	6.62	1.33	3.80	0.48	2.89	0.45	150.17	0.19	1.02	1.00	6.94	2.97	1.55
SQ-4	36.66	56.37	7.67	30.63	6.56	0.48	5.23	0.93	6.00	1.16		0.45	2.71	0.40	155.25	0.24	0.76	0.95	9.14	3.52	1.56
SQ-5	25.48	53.52	6.03	21.23	4.61	0.36	5.20	0.86	5.43	0.94	2.70	0.37	2.19	0.35	129.27	0.22	0.99	1.08	7.86	3.48	1.92
SQ-6	27.60	61.30	6.95	26.80	5.89	0.56	5.37	1.00	6.64	1.00	3.24	0.42	2.81	0.41	149.99	0.30	1.02	1.14	6.64	2.95	1.55
AIZI	56.50	91.00	12.17	43.77	8.70	1.13	6.58	1.16	6.04	1.17	2.57	0.52	3.06	0.44	234.81	0.44	0.78	0.99	12.48	4.09	1.74

Same serial number as Table 1.

$TE_{1,3} = (t_1 \times t_3)^{0.5}$, $t_1=(Ce/Ce^t \times Pr/Pr^t)^{0.5}$, $t_3=(Tb/Tb^t \times Dy/Dy^t)^{0.5}$, $Ce/Ce^t=Ce_{CN}/(La_{CN}^{2/3} \times Nd_{CN}^{1/3})$, $Pr/Pr^t=Pr_{CN}/(La_{CN}^{1/3} \times Nd_{CN}^{2/3})$, $Tb/Tb^t=Tb_{CN}/(Gd_{CN}^{2/3} \times Ho_{CN}^{1/3})$, $Dy/Dy^t=Dy_{CN}/(Dy_{CN}^{1/3} \times Ho_{CN}^{2/3})$, subscript CN means chondrite normalization (Ref. 12).

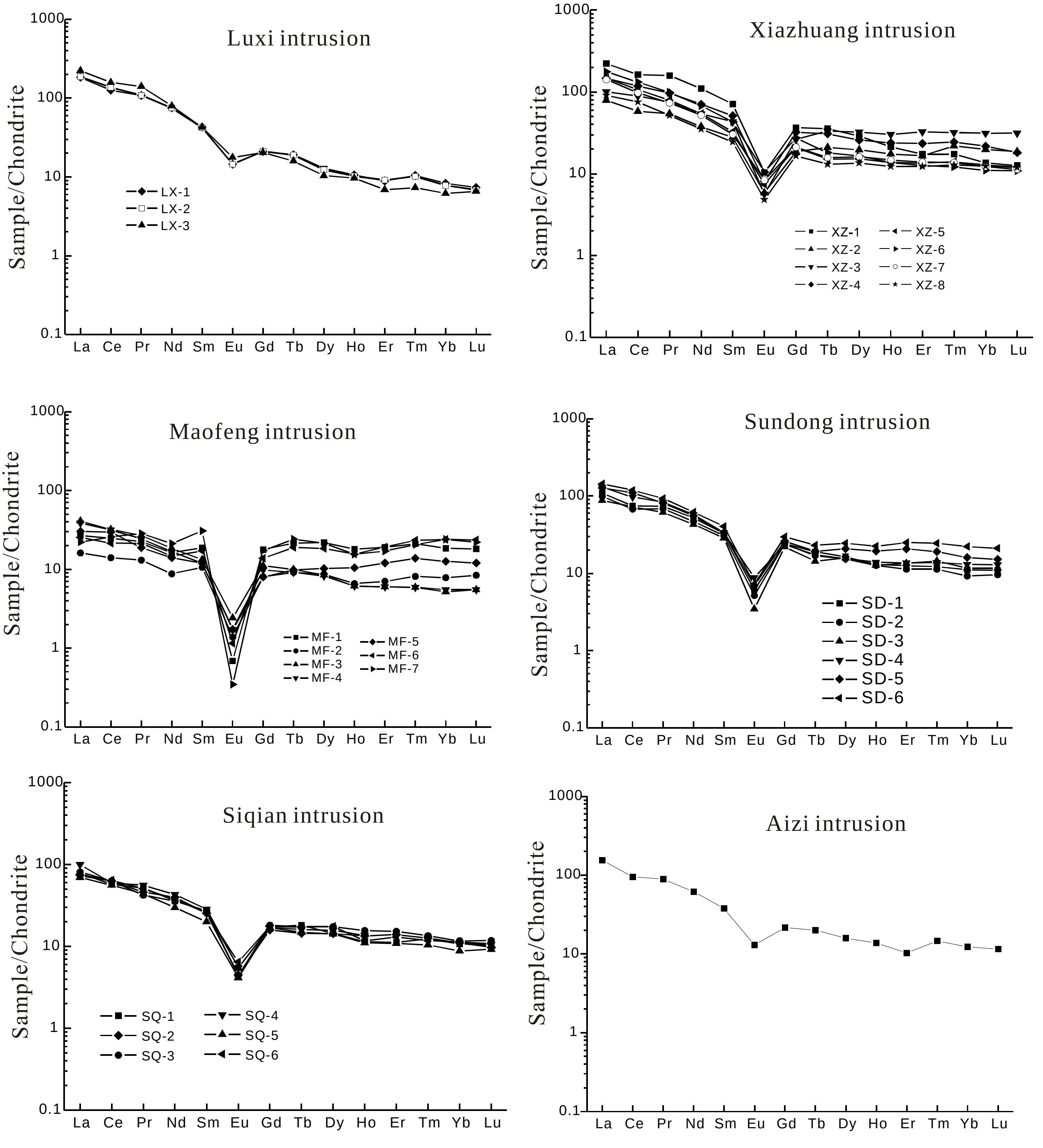

Figure 1. REE distribution patterns of studied intrusions.