RARE EARTH PARTITIONING OF GRANITOID WEATHERING CRUST IN SOUTHERN CHINA ①

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ABSTRACT The rare earth partitionings in parent rock, weathering crust ore and exchangeable state of granitoid weathering crust of Southern China have been studied. Their partitionings have a certain inheritance from interrelated analysis of 338 exchangeable rare earth partitionings. It can be seen that the rare earth elements prior to Gd are positively interrelated, so are those later Gd. But the rare earth elements prior to Gd are negative interrelated to the elements later Gd, which is called the Gd break effect. The order of rare earth partitionings in exchangeable phase is $La_2O_3 > Nd_2O_3 > CeO_2$, possessing cerium lose effect. The light rare earth partitioning as main partitioning type occupies 71.0% and rich Eu light rare earth partitioning type ($Eu_2O_3 \geqslant 0.8\%$) occupies 40.5%. The rich cerium and rich Eu heavy rare earth partitioning types are very few, and only occupy 1.8% and 2.4% respectively.

Key words granite weathering crust rare earth partitioning

1 INTRODUCTION

The weathering crust of Southern China is a loose poly-mineral aggregate, which is mainly composed of clay minerals of kaolinite, halloysite and small amount of montmorillonite, gangue mineral microplagioclase and quartz, etc, in which rare earth as independent mineral and exchangeable phase absorbed by clay mineral. Nearly no Pm and Sc coexist in granitoid weathering crust of Southern China. Therefore, the rare earth partitioning here is the percentage content of 15 kinds of mixing rare earth oxide except Sc and Pm.

The granitoid weathering crust contained rare earth is composed of rich rare earth minerals and granite of rare earth rich mineral which is formed by biological and chemical weathering, in which rare earth elements as hydrated or hydroxyl hydrated ions are absorbed by clay minerals[1, 2]. The rare earth in granitoid crust can be extracted by chemical processing method[3], rare earth chloride and mixed rare earth oxide[4] can be obtained. The enrichment of each rare earth element in earth crust is greatly affected by geochemical environment, especially in the water medium for the clay mineral loaded rare earth of granitoid weathering crust in Southern China. Therefore the study of rare earth partitioning, mobility and enrichments of rare earth elements in clay mineral is helpful to evaluate the industrial utilization of rare earth in granitoid weathering crust rare earth ore.

Summarizing the condition of forming heavy rare earth partitioning type would be helpful to set up a theoretical basis for exploration of new heavy rare earth resources.

2 CHANGING RULE OF RARE EARTH PARTITIONING

2.1 Rare earth partitioning of parent rock, weathering crust ore and exchangeable phase[5]

(1) Rare earth partitioning of parent rock

That is the average value of rare earth ele-

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ments in all minerals of granite which derive from weathering crust. These minerals include independent mineral such as monazite, gadolinite and aeschynite-(Y), accessory rare earth minerals such as allanite, titanite and epidote, and rock making minerals such as mica, muscovite and plagioclase.

(2) Rare earth partitioning of weathering crust ore

It includes difficultly weathered independent rare earth minerals in parent rock such as xenotime and monazite, and the newly weathered secondary rare earth minerals such as cerianite, rhabophane and exchangeable phase absorbed on clay minerals.

(3) Rare earth partitioning of exchangeable phase

That is the average value of rare earth which is absorbed by clay minerals as exchangeable phase and can be recovered with extraction method. In fact only this part of rare earth in granitoid weathering crust of Southern China can be recovered in industry.

2.2 Relationship of rare earth partitioning among parent rock, weathering crust ore and exchangeable phase

2.2.1 Parent rock and weathering crust ore

The alumni-silicate mineral is weathered to mixed clay minerals in weathering parent rock. The rare earth in easy weathering minerals is dissociated to hydrated ion, and in difficult weathering minerals exists as particle form. In weathering process, alkaline metal and alkaline earth metal are prior to mobilizing due to their activities[6]. In other words, the rare earth partitioning of weathering crust has inherited the partitioning of parent rock. But actually there are difference between activities of rare earth elements and weathering crust minerals at its profile, which makes a certain differentiation during the downward mobilizing of rare earth ions from weathered parent rock[7, 8]. A part of cerium at upper layer transfers to CeO_2 and can not mobilize downward, which remains at surface layer[9]. This makes the weathering crust ore partitioning different from the rare earth partitioning of parent rock, but they still have a certain inheritance.

2.2.2 Weathering crust ore and exchangeable state

Because the extraction method can only recover the rare earth in exchangeable phase, and can not recover rare earth in the difficultly weathered minerals and difficultly extracted rare earth minerals. This makes a great difference between the rare earth partitioning of weathering crust ore and the partitioning of extracted rare earth product. The cerium partitioning in the product is low (see Table 1), the cause is that the trivalent cerium from weathering crust is unstable and easily transfers to tetravalent cerium, e. g. secondary rare earth mineral cerianite which is difficult to be extracted.

2.2.3 Changing rule of three kinds of rare earth partitioning

Exchangeable state partitioning is mainly composed of La_2O_3, Nd_2O_3 and Y_2O_3, which are generally high above 70% and determine the change of whole rare earth partitioning. The rare earth partitioning of parent rock, weathering crust ore and exchangeable state is also shown in Table 1. Their changing law can be summarized as follows:

(1) The partitioning value of La_2O_3 has little change from parent rock to weathering crust ore, and increases from weathering crust ore to exchangeable phase.

(2) The partitioning value of CeO_2 has small change from parent rock to weathering crust ore, and obviously decreases from weathering crust to exchangeable state, which has the serious cerium lose phenomenon.

(3) The partitioning value of Nd_2O_3 is similar to La_2O_3, and the partitioning of other rare earth elements are very slightly changed.

(4) The partitioning value of Y_2O_3 increases from parent rock to weathering crust ore, and obviously increases from weathering crust to exchangeable state.

(5) The partitioning value of heavy rare earth type ΣY_2O_3 increases and the partitioning of light rare earth type ΣCeO_2 decreases from parent rock to weathering crust ore and further to exchangeable state.

(6) Atomic ordinal "odd and even effect"

still exists in the rare earth partitioning of parent rock, weathering crust ore and exchangeable state besides cerium. But their partitioning change of "odd and even effect" is that the partitioning values of odd atomic ordinal number rare earth elements are larger than those of even atomic ordinal number rare earth elements.

3 FORMATION OF RICH YTTRIUM RARE EARTH PARTITIONING TYPE WEATHERING CRUST ORE

3.1 Rich yttrium heavy rare earth partitioning type weathering crust

From the statistics of exchangeable state of 338 samples of weathering crust ores, there are 72 samples belong to rich yttrium heavy rare earth partitioning type, and occupy 21.3%. Compared with light rare earth, rich yttrium heavy rare earth mostly exists in easy weathering rich yttrium rare earth minerals yttropariste or gadolinite etc. Few granitoid weathering crust ores in Southern China belong to rich yttrium heavy rare earth partitioning type.

3.2 Main process of enrichment of rich yttrium heavy rare earth elements

There are three main processes of enrichment of heavy rare earth from parent rock to extracted rare earth product.

(1) Differentiation and evolution of magma make heavy rare earth elements enriched in later period intrusive body, and become heavy rare earth mineral of parent rock. The rare earth minerals of parent rock are the weatherable silicate and fluocarbonate, but their extracted rare earth products are heavy rare earth as main partitioning.

(2) Rare earth element fractionation is due to surface weathering effect[10, 11]. Heavy rare earth elements are enriched at middle and low parts of full weathering layer and become heavy rare earth enriching section. For example, the parent rock containing high heavy rare earth exists in weatherable minerals, the deep full weathering crust ore can form heavy rare earth partitioning type if the rock is weathered completely (see Table 2).

Table 1 Rare earth partitioning of parent rock, weathering crust ore and exchangeable state

Rare earth oxide	Parent rock	WO	IV	ES	IV	TIV	TIR /%	Parent rock	WO	IV	ES	IV	TIV	TIR /%
La_2O_3	15.46	16.58	1.12	19.28	2.70	38.2	24.71	19.28	21.32	2.04	23.86	2.54	4.58	23.37
CeO_2	23.68	19.77	−3.91	1.00	−18.77	−22.68	−59.78	21.28	13.86	−7.42	1.54	−12.32	−20.09	−92.80
Pr_6O_{11}	5.24	5.34	0.10	5.30	−0.04	0.06	1.16	6.23	5.74	−0.49	5.56	−0.18	−0.67	−10.75
Nd_2O_3	22.00	21.13	−0.87	26.96	5.83	4.96	22.55	16.46	17.52	1.06	20.23	2.71	3.77	22.90
Sm_2O_3	3.40	3.29	−0.11	4.03	0.74	0.62	18.18	5.85	5.58	−0.29	4.48	−1.12	−1.40	−23.85
Eu_2O_3	0.59	0.73	0.14	0.92	0.19	0.34	57.63	0.30	0.48	0.18	0.5	0.06	0.24	76.67
ΣCeO_2	70.37	66.84	−3.53	57.49	−9.35	−12.88	−18.30	69.75	64.50	−5.25	56.21	−8.29	−13.54	−19.41
Gd_2O_3	4.82	4.85	0.03	5.32	0.47	0.50	10.37	3.92	3.96	0.04	4.02	0.06	0.10	2.55
Tb_4O_7	0.54	0.54	0.00	0.57	0.03	0.03	5.56	0.46	0.47	0.01	0.58	0.13	0.14	30.43
Dy_2O_3	2.73	2.93	0.20	3.42	0.48	0.68	25.66	3.96	4.13	0.17	4.16	0.03	0.20	5.05
Ho_2O_3	0.49	0.58	0.09	0.76	0.18	0.27	56.25	0.84	0.88	0.04	0.93	0.05	0.09	10.71
Er_2O_3	1.15	1.28	0.03	1.66	0.38	0.40	34.18	2.02	2.17	0.15	2.26	0.09	0.24	11.88
Tm_2O_3	0.30	0.30	0.00	0.30	0.00	0.00	0.00	0.30	0.30	0.00	0.30	0.00	0.00	0.00
Yb_2O_3	1.02	1.22	0.20	1.45	0.25	0.54	53.46	1.98	2.07	0.09	2.28	0.21	0.29	14.65
Lu_2O_3	0.30	0.30	0.00	0.30	0.00	0.00	0.00	0.30	0.30	0.00	0.30	0.00	0.00	0.00
Y_2O_3	18.40	21.23	2.83	28.60	7.37	10.20	55.43	16.94	21.35	4.41	28.92	7.47	11.88	70.13
ΣY_2O_3	29.25	33.23	3.48	42.48	9.25	12.73	42.79	30.72	35.63	4.91	43.75	8.14	13.05	42.80
Total	100.12	100.1		99.97				100.02	100.13		99.96			

WO —Weathering ore; IV —Increasing value; ES —Exchangeable state; TIV —Total increasing value; TIR —Total increasing ratio

It is known that rare earth partitioning changes with the variation of ore body depth. The light rare earth content is high at upper layer and heavy rare earth content is high at low layer. This is because some coordinators, such as HCO_3^-, CH_3OO^-, F^- and CO_3^{2-}, exist in earth surface water. They can combine with rare earth ion to form complex. Heavy rare earth elements prior to other rare earth elements form complex with these coordinators[13, 14], and separate from upper clay mineral and enrich at deep layer with downward mobilizing filtering water[15]. This is in accordance with the calculating results of quantum chemistry of rare earth ion absorbed on clay minerals[16].

(3) Chemical extraction method can only recover the exchangeable rare earth, which makes the heavy rare earth further enriched. The part extracted product of yttrium light rare earth partitioning type ore become heavy rare earth partitioning type. From Table 3, it can be seen that ΣY_2O_3 and Y_2O_3 increase from ore to product and their average values are 14.4% and 9.48% respectively. In addition, to transfer light rare earth partitioning type ore to heavy rare earth partitioning type product, ΣY_2O_3 should be larger than 30% and Y_2O_3 should be 20% at least, generally ΣY_2O_3 is larger than 35% and Y_2O_3 is larger than 25%.

Table 2 Rare earth partitioning with change of depth in weathering crust ore

Ore sample	Collecting depth /m	Rare earth partitioning/%					
		La_2O_3	CeO_2	Nd_2O_3	Eu_2O_3	Y_2O_3	ΣY_2O_3
Depth of weathering layer of A mine is 10.5 m	1~ 1.5	30.61	17.45	26.31	0.82	6.80	13.43
	3~ 4.5	33.29	8.63	26.08	1.03	9.95	13.89
	4.5~ 7.5	16.07	5.91	11.01	0.98	39.74	59.91
	7.7	26.90	32.88	21.21	0.70	5.02	9.58
Depth of weathering layer of B mine is 21.3 m	10.6	10.6	29.83	13.03	26.64	1.04	10.95
	13.5	25.78	10.83	19.04	1.10	22.75	34.63
	16.1	17.23	8.12	12.65	0.90	40.49	53.82
	17.0	21.62	29.83	17.88	0.76	13.90	22.10

Table 3 Transferring light rare earth partitioning type to extracted heavy rare earth partitioning type

Sample	Y_2O_3 partitioning/%			Eu_2O_3 partitioning/%			ΣY_2O_3 partitioning/%		
	Ore	Exchangeable state	Increased value	Ore	Exchangeable state	Increased value	Ore	Exchangeable state	Increased value
GXS	30.22	41.48	11.26	0.73	0.76	0.03	45.23	60.70	15.47
XGD	26.73	36.12	9.39	0.51	0.61	0.11	40.89	54.08	13.19
FCY	21.37	35.23	13.86	0.21	0.86	0.65	33.90	51.81	17.91
YHZ	23.86	34.92	11.06	0.33	0.24	- 0.09	39.04	57.39	18.35
YDY	26.72	31.53	4.81	0.53	0.62	0.09	42.42	50.48	8.06
YHG	30.91	39.56	8.65	0.56	0.75	0.19	49.07	59.87	10.80
YLD	31.65	10.83	0.36	0.36	0.26	- 0.10	36.33	50.48	13.15
YYD	33.12	5.96	0.52	0.52	0.61	0.11	44.83	53.35	8.52
Average			9.48			0.12			14.43

4 THE INTERRELATION AND APPLICATION OF RARE EARTH PARTITIONING OF EXCHANGEABLE STATE

4.1 The interrelation of rare earth partitioning of exchangeable state

Because the properties of rare earth elements are very similar, so the rare earth partitioning of product has interrelation. From the interrelated analysis of rare earth partitioning of 338 samples, an interrelated matrix is obtained as shown in Table 4. It can be seen that there exists Gd broken effect, half positive interrelation and the interrelation between rare earth elements from the data in Table 4.

(1) In the matrix of Table 4, the border of positive and negative numerical value appears at Gd element. This shows that Gd element is the border of light and heavy elements. The elements prior to Gd are light rare earth and the elements later to Gd are heavy rare earth. Gd can be heavy rare earth and also be light rare earth, but usually is attributed to heavy rare earth element. The phenomenon can be explained by the electronic structure of Gd element $4f^7 5d^1 6s^2$, in which the electrons in f orbit is half full state, and this phenomenon is called the Gd broken effect.

(2) Divided into two half by Gd as border, light rare earth elements except cerium are positive interrelated and heavy rare earth elements are also positive interrelated, so called it half positive interrelation.

(3) There is a negative interrelation between light rare earth elements and heavy rare earth elements.

(4) In rare earth partitioning, the interrelated absolute value between rare earth elements containing high content of oxide is large, which indicates that their interrelation is good, but contrary to the component of lower partitioning type.

(5) The absolute values of interrelated coefficient between the middle rare earth elements (Sm_2O_3, Eu_2O_3 and Gd_2O_3) are very small, most of which are below 0.5, so their interrelation is poor and has arbitrarity.

(6) The partitioning value of exchangeable phase rare earth is very low, most below 3% and has obvious cerium lose by comparison of the rare earth partitioning of parent rock with weathering crust, which is called cerium lose effect.

(7) A linear regression is applied to the better interrelated rare earth elements with absolute value of interrelated coefficient above 0.86, following regression equations can be obtained:

$$\Sigma CeO_2 = 86.7 - 1.42\ Y_2O_3$$

Table 4 The interrelated matrix of exchangeable state rare earth

Oxide	La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_4O_7	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	Y_2O_3
La_2O_3	1	0.18	0.86	0.75	0.35	0.23	-0.73	-0.77	-0.86	-0.72	-0.80	-0.69	-0.78	-0.64	-0.88
CeO_2		1	0.16	0.11	0.26	0.28	-0.28	-0.20	-0.24	-0.19	-0.19	-0.20	-0.24	-0.15	-0.34
Pr_6O_{11}			1	0.96	0.69	0.40	-0.65	-0.80	-0.89	-0.68	-0.83	-0.77	-0.82	-0.65	-0.93
Nd_2O_3				1	0.80	0.43	-0.55	-0.75	-0.83	-0.62	-0.80	-0.74	-0.79	-0.63	-0.90
Sm_2O_3					1	0.51	-0.28	-0.31	-0.47	-0.34	-0.51	-0.52	-0.52	-0.49	-0.63
Eu_2O_3						1	-0.32	-0.26	-0.31	-0.23	-0.43	-0.39	-0.43	-0.27	-0.29
Gd_2O_3							1	0.81	0.80	0.62	0.70	0.60	0.65	0.42	0.58
Tb_4O_7								1	0.88	0.68	0.85	0.67	0.78	0.54	0.71
Dy_2O_3									1	0.78	0.95	0.84	0.89	0.75	0.82
Ho_2O_3										1	0.76	0.70	0.73	0.68	0.60
Er_2O_3											1	0.85	0.94	0.73	0.74
Tm_2O_3												1	0.84	0.71	0.68
Yb_2O_3													1	0.74	0.76
Lu_2O_3														1	0.62
Y_2O_3															1

$La_2O_3 = 45.8 - 0.64\ Y_2O_3$

$Pr_6O_{11} = 9.84 - 0.14\ Y_2O_3$

$La_2O_3 = -0.94 + 4.35\ Pr_6O_{11}$

$Dy_2O_3 = 1.13 + 1.33\ Er_2O_3$

The above regression equations indicate that the rare earth existing in earth crust has some regularity, and can use them to calculate the oxide content from another oxide content.

4.2 Classifying rare earth mineral of product rare earth partitioning

The recovering method used in industry can only extract the exchangeable phase rare earth, so that the industrial meaning of rare earth of granitoid weathering crust in Southern China can only be evaluated by product rare earth partitioning. Therefore according to the rare earth partitioning types of granitoid weathering crust rare earth mineral in Southern China, it is usually divided into two categories: heavy rare earth partitioning type and light rare earth partitioning type. Heavy rare earth partitioning type has three sub-categories: rich Eu heavy rare earth partitioning type, middle yttrium heavy rare earth partitioning type and rich yttrium heavy rare earth partitioning type. Light rare earth partitioning type also has three sub-categories: rich cerium light rare earth partitioning type, rich Eu light rare earth partitioning type and common light rare earth partitioning type. According to the partitioning of 338 samples of rare earth products, they are classified into different characteristic partitioning types as shown in Table 5.

It can be found that rare earth partitioning in most weathering crust ore shows light rare earth partitioning type as main type, which is about 71.0%. The rich cerium and rich Eu heavy rare earth partitioning types are very little, which are only 1.8% and 2.4% respectively. Partitionings of rich Eu partitioning type occupy 42.9%, mainly belong to light rare earth partitioning type and few belong to heavy rare earth partitioning type, which are 40.5% and 2.4% respectively.

5 CONCLUSIONS

(1) The rare earth partitioning exists a certain inheritance with parent rock, weathering crust ore and exchangeable phase. The variety of rare earth partitioning in most weathering crust rare earth ore and exchangeable phase is that Y_2O_3 partitioning value increases, CeO_2 partitioning value decreases, usually merge serious cerium lose, but no great change of partitioning value occurs from Sm_2O_3 to Lu_2O_3.

(2) Heavy rare earth partitioning type is determined by rare earth partitioning and the mineral bearing heavy rare earth in parent rock, particularly the yttrium existing mineral. Only easily weathered yttroparisite and gadohinite etc can form heavy rare earth partitioning type. The present extraction method used in industry is of advantageous to enrich heavy rare earth.

(3) There are Gd broken effect and half positive interrelation from the interrelated analysis of rare earth partitioning of 338 samples. The rare earth elements prior to Gd are positive interrelated and so are the elements later Gd. There is a negative interrelated between the rare earth elements prior to Gd and the elements later Gd.

(4) From the rare earth partitioning of 338 samples collected from weathering crust rare

Table 5 Different categories of the partitioning of 338 rare earth samples

Type of partitioning	Light rare earth ($\Sigma CeO_2 \geqslant 50\%$)			Heavy rare earth ($\Sigma Y_2O_3 > 50\%$)		
	Common	Rich Eu	Rich Ce	Middle Y	Rich Eu	Rich Y
Characteristics of partitioning/%	$Eu_2O_3 < 0.8$	$Eu_2O_3 \geqslant 0.8$	$CeO_2 > 25$	$20 \leqslant Y_2O_3 \leqslant 35$	$Eu_2O_3 \geqslant 0.8$	$Y_2O_3 > 35$
Numbers	97	137	6	18	8	72
Occupied amount/%	28.7	40.5	1.8	5.3	2.4	21.3
Total/%		71.0			29.0	

earth ores, it can be seen that light, middle and heavy rare earth elements are complete and so are their rare earth element partitionings. The light rare earth partitioning type is the main type occupying 71. 0%. The rich Ce and rich Eu heavy rare earth partitioning types are very little, which are only 1. 8% and 2. 4% respectively. The rich Eu partitioning type occupies as large as 42. 9%, in which the light rare earth partitioning type and heavy rare earth partitioning types are 40. 5% and 2. 4% respectively.

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