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Correlation analysis on partition of rare earth in ion-exchangeable phase from weathered crust ores

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Abstract: The rare earth(RE) in weathered crust ores mainly exists as ion-exchangeable phase, approximately 80%. The correlation analysis on partition of 376 samples in ion-exchangeable phase from weathered crust ores was conducted. The results show that partition both among heavy RE elements and light RE elements with high partition appears positive correlation, but partition sums between the heavy RE elements and the light RE elements appear close negative correlation obviously. Clear negative correlations exist between the light RE elements (except Ce) and yttrium(Y). Matrix of correlation analysis on this partition can be divided into three zones. The correlated coefficient variation from negative to positive in zones B and C occurs at Gd, so does that in zones B and A (except Ce, Eu, and Sm), suggesting that RE elements can be divided into two groups with Gd as border. This phenomenon is called Gadolinium-broken effect.

Key words: weathered crust; ore; rare earth partition; correlation analysis

1 Introduction

Weathered crust ores which are widely deposited in Jiangxi, Fujian, Guangdong, Hunan, Yunnan and Guangxi provinces in the south of China[1−3] are the main resources of mid-heavy RE. Their development and utilization have solved the shortage problem of mid-heavy RE for a long time[4]. NESBIT et al[5], PRICE et al[6] and BRAUN et al[7] have researched systematically the theory of RE elements in weathered crust ores since 1960, concluding that RE adsorbed on clay minerals mobilized, fractionated and enriched during adsorption and desorption process. After RE minerals formed by mobilization and fractionation process of clay minerals were found in 1970s, an extraction technique was then explored to recover mid-heavy RE. It is well known that weathered crust rare earth ores, existing as RE aqueous or RE hydroxyl aqueous ions, come from the weathered rock such as bastnasite and ytterbite. The clay minerals are formed by the action of physics, chemistry and biology from lava and granite under warm and humid climate[8−14]. Therefore, exchangeable RE ions adsorbed on clay minerals can be dissolved by cation exchange with ammonium salt, such as ammonium sulfate, and then RE is recovered with oxalic acid[15]. In order to further investigate the rule on partition of exchangeable RE ions adsorbed on clay minerals, the mathematic regression method is applied to describe the partition of RE products extracted from weathered RE ores. In this work, the regular pattern of mobility and fractionation of RE in weathered crust ores is explained and the theory of inorganic chemistry and geochemistry on RE elements is focused.

2 Existing state of RE in weathered ores

RE elements in the weathered crust ores mainly exist as the following four states: water soluble phase, ion-exchangeable phase, colloidal sediment and mineral phase[16−19]. The content of RE in four phases is in the order of ion-exchangeable phase (aqueous or hydroxyl aqueous)＞mineral phase＞colloid sediment　water

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soluble phase, in which RE mainly exists as ion-exchangeable phase in the ores up to 80%.

Since kaolinite and halloysite are the main clay minerals in the weathered crust rare earth ores (more than 80%), it can be conceived that the rare earth primarily exists as RE aqueous or RE hydroxyl ions adsorbed in clay minerals.

The chemical adsorption model can be expressed as follows[18−21]:

Type of halloysite:

$[RE(mH_2O, nOH\cdots)]^{(3-n)+}[Al_4Si_4O_{10}(OH)_{(5-n)}]\cdot 4H_2O$

Type of kaolinite:

$[RE(mH_2O, nOH\cdots)]^{(3-n)+}[Al_4Si_4O_{10}(OH)_{(5-n)}]$

For heavy rare earth:

$m+n$= 6, 7; n=0, 1, 2

For light rare earth:

$m+n$=6, 7, 8; n=0,1,2

As can be seen from the model, hydroxyl or hydroxyl aqueous rare earth ions can take part in the ion-exchange reaction. This is the reason for recovering RE adsorbed on clay minerals with ammonium salt in industry, which demonstrates that RE product from weathered crust ores is ion-exchangeable RE.

3 Mathematics model on partition of RE

3.1 Correlation analysis of partition among 15 RE elements

Linear correlation analysis can be used to find out the dependency relationship between two random variables. Correlation coefficient is an important index that explains both intensity and direction of the dependency relationship[21,22].

Let x and y are random variables which are assumed values in $\{x_1,\cdots,x_n\}$ and $\{y_1,\cdots,y_n\}$, respectively. The Pearson correlation coefficient of x and y is defined as follows[22]:

$$r_{xy}=\frac{\sum_{i=1}^{n}(x_i-\bar{x})(y_i-\bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i-\bar{x})^2}\sqrt{\sum_{i=1}^{n}(y_i-\bar{y})^2}} \tag{1}$$

where $\bar{x}=\frac{1}{n}\sum_{i=1}^{n}x_i$, $\bar{y}=\frac{1}{n}\sum_{i=1}^{n}y_i$. Generally, the closer $|r_{xy}|$ is to 1, the stronger linear correlation between x and y is.

The t-examination is usually used to test significance of the correlation coefficient, and the formula is

$$t=\frac{r_{xy}}{\sqrt{1-r_{xy}^2}}\sqrt{n-2} \tag{2}$$

where n, $n-2$ denote specimen capacity and degree of freedom, respectively. When the confidence level α is given, the critical value $t_{(n-2,\alpha)}$ can be obtained from t-table according to degree of freedom ($n-2$) and α at the same time. If $t\geqslant t_{(n-2,\alpha)}$, r_{xy} is significant, and the linear correlation is thus closed between x and y.

3.2 Regression equation of RE partition

Once linear dependency relationship of random variables is known, a quantitative relationship of variables will be obtained. Regression analysis is a helpful tool for us to establish an equation of variables. The model is[22]

$$\hat{y}=b_0+b_1x_1+\cdots+b_nx_n \tag{3}$$

where $\hat{y}$ is the estimated value of y determined by x_1, $\cdots$, x_n, b_0 is a constant, and $b_1,\cdots,b_n$ are partial regression coefficients corresponding to x_1, $\cdots$, x_n. Partial regression coefficient is the ratio of change of dependent variable due to the change of one independent variable with other variables fixed.

R, R^2 and R_{adj}^2 are the three primary statistic indexes of multiple linear regression, multiple correlation denoting coefficient of determination, and adjusted coefficient of determination, respectively. The definitions are given as follows[22]:

$$R^2=\frac{\sum(\hat{y}-\bar{y})^2}{\sum(y-\bar{y})^2} \tag{4}$$

$$R=+\sqrt{R^2} \tag{5}$$

$$R_{adj}^2=1-\frac{m-1}{m-n-1}(1-R^2) \tag{6}$$

where m and n are specimen capacity and the number of variables, respectively.

The closer R^2 is to 1, the more capable the variable interpreting y is. Usually, the percentage of change of y can be illustrated with R^2 multiplied by 100%. With the increase of the number of independent variables, the fitting accuracy of regression equation is always overestimated by R^2, although the linear correlation between some variables and dependent variable is insignificant.

4 Results and discussion

4.1 Correlation coefficients of RE partition

The Pearson correlation analysis on partitions of 15 RE elements from 376 weathered crust RE samples was conducted by adopting soft ware "SPSS"(statistical package for social science) (version11.0). The results are listed in Table 1.

As can be seen from Table 1, the matrix of correlation analysis on partition of RE in ion-exchangeable phase is divided into three zones. The correlated coefficient variation from negative to positive in zones B and C occurs at Gd, so does that in zones B and A (except Ce, Eu, and Sm). Therefore, RE elements can be divided into two groups by Gd as border. The elements before Gd are called light RE elements and the elements from Gd to Lu, including Y, are called heavy RE elements. This phenomenon is called gadolinium-broken effect, which results from the electron structure of RE ion.

RE elements in the nature exist as third valence in ion compounds (Ln^{3+}) and aqueous or hydroxyl ions adsorbed on clay minerals (except Ce). Consequently, the RE elements mainly manifest the properties of the ions of third valence, which are shown in Table 2.

As shown in Table 2, from La to Gd, the number of the 4f orbit electron is from 1 to 7; while from Gd to Lu, it is from 7 to 14. The non-paired electrons, spectral basic term and colors of RE ions are symmetrical with Gd as border. It also can be seen from Table 1 that the correlation variation between negative and positive appears at Gd. Based on the electron structure of RE, the correlated relationship of RE elements takes symmetrization bounding on Gd as well. That is to say, RE elements can be divided into two groups by Gd, which is called gadolinium-broken effect.

Y without 4f electron is a special element which does not belong to lanthanide series. However, its ion radium, 0.88×10^{-10}m, is interposed between erbium

Table 1 Pearson correlated coefficient matrix among 15 kinds of RE partition

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
La	1.000	−0.060	0.731	0.541	−0.064	0.262	−0.728	−0.624	−0.749	−0.673	−0.707	−0.506	−0.695	−0.470	−0.825
Ce		1.000	0.098	0.157	0.050	−0.033	−0.053	−0.072	−0.068	−0.059	−0.040	−0.101	−0.102	−0.069	−0.150
Pr			1.000	0.834	0.309	0.197	−0.649	−0.661	−0.823	−0.670	−0.721	−0.580	−0.692	−0.541	−0.873
Nd				1.000	0.420	−0.268	−0.547	−0.646	−0.761	−0.577	−0.671	−0.586	−0.641	−0.529	−0.846
Sm					1.000	−0.047	0.189	0.031	−0.130	−0.056	−0.160	−0.044	−0.134	−0.066	−0.314
Eu						1.000	−0.194	−0.307	−0.280	−0.172	−0.303	−0.225	−0.343	−0.168	−0.265
Gd							1.000	0.714	0.799	0.605	0.566	0.556	0.553	0.479	0.607
Tb								1.000	0.820	0.711	0.673	0.638	0.656	0.508	0.593
Dy									1.000	0.773	0.802	0.694	0.785	0.591	0.739
Ho										1.000	0.686	0.671	0.674	0.449	0.600
Er											1.000	0.614	0.856	0.561	0.661
Tm												1.000	0.651	0.672	0.502
Yb													1.000	0.569	0.645
Lu														1.000	0.493
Y															1.000

A zone

B zone

C zone

Table 2 Properties of RE ions

Ion(Ln^{3+})	Non-paired f-electron	Spectral basic term	Color	Spectral basic term	Non-paired f-electron	Ion(Ln^{3+})
La^{3+}	0 ($4f^0$)	$^1S_0$	None	$^1S_0$	0 ($4f^0$)	Lu^{3+}
Ce^{3+}	1 ($4f^1$)	$^2F_{5/2}$	None	$^2F_{5/2}$	1 ($4f^1$)	Yb^{3+}
Pr^{3+}	2 ($4f^2$)	$^3H_4$	Green yellow	$^3H_4$	2 ($4f^2$)	Tm^{3+}
Nd^{3+}	3 ($4f^3$)	$^4I_{9/2}$	Red	$^4I_{9/2}$	3 ($4f^3$)	Er^{3+}
Pm^{3+}	4 ($4f^4$)	$^5I_4$	Pink/canary	$^5I_4$	4 ($4f^4$)	Ho^{3+}
Sm^{3+}	5 ($4f^5$)	$^6H_{5/2}$	Pale red	$^6H_{5/2}$	5 ($4f^5$)	Dy^{3+}
Eu^{3+}	6 ($4f^6$)	$^7F_0$	Pale yellow	$^7F_0$	6 ($4f^6$)	Tb^{3+}
Gd^{3+}	7 ($4f^7$)	$^8S_{7/2}$	None	$^8S_{7/2}$	7 ($4f^7$)	Gd^{3+}

(0.881×10^{-10}m) and thulium (0.869×10^{-10}m), and it usually coexists with lanthanide series in the nature. Therefore, Y, together with scandium, is also called rare earth element. In general, the partition of yttrium is above 10%, even up to 50% in some weathered crust ores such as Longnan ore. Y is regarded a heavy rare earth element because its properties and radium are similar to those of heavy ones, which is also supported by correlated relationship of rare earth partition.

4.2 Correlation analysis of light and heavy RE groups

Separated by Gd, the elements from La to Eu belong to light RE group, and those from Gd to Y belong to heavy RE group. The statistic vectors of light RE group and heavy RE group are obtained by summing the partition of every sample in the same group, and the scatter graph (Fig.1) and regression equation are as follows.

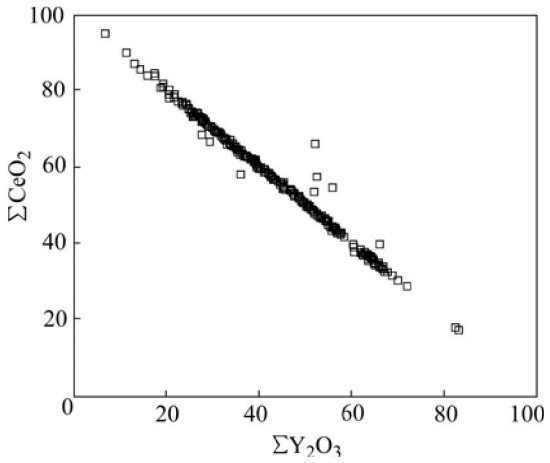

Fig.1 Scatter graph of light RE and heavy RE

The regression equation is

$$\Sigma CeO_2=-0.996\Sigma Y_2O_3+99.954 \quad (7)$$

The R, R^2 and R^2_{adj} values of the equation are 0.993, 0.986 and 0.986, respectively, which implies the close linear correlation between light RE elements and heavy ones.

4.3 Regression equations of RE element partition

To further clarify quantitative correlation among RE partitions, the regression analysis was done based on the mathematic model in 3.2. Given the partitions of 15 RE elements as dependant variables and the others as independent variables, a multiple linear regression equation can be established using stepwise regression in platform of SPSS (version 11.0), which are as follows:

$$Y_2O_3=63.063-0.701Pr_6O_{11}-0.597La_2O_3-0.840Nd_2O_3 \quad (8)$$

$R=0.953$, $R^2=0.909$, $R^2_{adj}=0.908$

$$La_2O_3=83.339-0.873Y_2O_3-1.596Sm_2O_3-0.900Nd_2O_3-2.288Dy_2O_3 \quad (9)$$

$R=0.954$, $R^2=0.911$, $R^2_{adj}=0.910$

$$Pr_6O_{11}=10.184-9.902\times10^{-2}Y_2O_3-0.415Dy_2O_3 \quad (10)$$

$R=0.912$, $R^2=0.832$, $R^2_{adj}=0.831$

$$Nd_2O_3=59.732-0.614Y_2O_3-0.563La_2O_3-1.454Dy_2O_3-1.018Er_2O_3 \quad (11)$$

$R=0.954$, $R^2=0.910$, $R^2_{adj}=0.909$

$$Er_2O_3=6.904+0.472Yb_2O_3+0.158Dy_2O_3-7.556\times10^{-2}La_2O_3-0.213Gd_2O_3-8.640\times10^{-2}Nd_2O_3-5.604\times10^{-2}Y_2O_3 \quad (12)$$

$R=0.897$, $R^2=0.805$, $R^2_{adj}=0.802$

$$Dy_2O_3=1.775-0.262Pr_6O_{11}+1.477Tb_4O_7+0.340Yb_2O_3+0.372Gd_2O_3+0.610Ho_2O_3 \quad (13)$$

$R=0.936$, $R^2=0.875$, $R^2_{adj}=0.874$

$$Yb_2O_3=1.083+0.499Er_2O_3+0.144Dy_2O_3+1.226Tm_2O_3-0.257Eu_2O_3-2.090\times10^{-2}La_2O_3-0.137Gd_2O_3 \quad (14)$$

$R=0.886$, $R^2=0.784$, $R^2_{adj}=0.780$

Analyzing the above correlations, the relationship of RE partition is obtained. The positive correlation emerges among the heavy RE elements and so does the light ones with high partition.

The RE elements containing high oxide, that is to say, with high partition, appear marked correlation among them, and the RE elements with low partition appear relatively bad correlation, as well as the correlation between heavy RE elements and other RE elements. Especially, the negative correlation is distinguishable between Y and light RE elements except Ce.

5 Conclusions

1) The correlation analysis on partition of RE in weathered crust ores indicates that the partition of heavy RE elements and light ones with high partition appears positive correlation. On the contrary, the apparent negative correlation can be found between the total partition value of light RE elements and heavy ones.

2) The matrix of correlation analysis about partition of RE in ion-exchangeable phase is divided into three zones. The correlation variation from negative to positive in both zone B and C occurs at Gd, so does that in zone B and A (except Ce, Eu, and Sm). Therefore, the RE elements are divided into two groups with Gd as border. The elements before Gd are called light RE elements and the elements from Gd to Lu including Y are called heavy RE elements. This phenomenon is called gadolinium-broken effect.

3) The positive correlation between Y and the heavy RE elements of lanthanides is very close, so is the negative correlation between Y and the light RE elements, which further confirms that Y should be classified into the heavy RE elements group.

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