PRELIMINARY INVESTIGATIONS ON THE BEHAVIOR OF REE IN CRUSTS OF WEATHERING OF SOME ROCKS

SONG YUNHUA (宋云华),
(*Institute of Geochemistry, Academia Sinica, Guiyang*)

SHEN LIPU (沈丽璞)
(*Institute of Geology, Academia Sinica, Beijing*)

AND WANG XIANJUE (王贤觉)
(*Institute of Geochemistry, Academia Sinica, Guiyang*)

Received February 8, 1987.

Key words: granitoid, weathered crust, REE, clay mineral, adsorption.

Ion-adsorption type REE ore deposits in crusts of weathering is one of the most significant types of REE ore deposits. Reported in this paper are the experimental and theoretical research results on REE distribution in crusts of weathering of volcanic and granitic rocks in South China and of basic and ultrabasic volcanic rocks in Guizhou Province, and on the fractionation of REE during the weathering processes, as well as on the adsorption of REE by clay minerals.

I. CHARACTERISTICS OF DISTRIBUTION OF REE IN CRUSTS OF WEATHERING OF SOME ROCKS

1. *Distribution of REE in Crusts of Weathering*

REE in crusts of weathering stem mainly from the parental rocks and their concentrations are dependent basically on the types of the parental rocks. For example, REE contents are remarkable in the acidic volcanic and granitic rocks in South China, usually 1—4 times higher than their abundances in acidic rocks (290 ppm)[1]. As a result, the concentrations of REE in corresponding crusts of weathering are also high, generally within the range of 520—1860 ppm for acidic volcanic rocks and 240—1400 ppm for granitic rocks. Another example that can be cited is the crystalline rocks in Ukraine, USSR. A coincidence was found for those crystalline rocks between the tendency of increasing REE contents in the sequence amphibolite—pyroxenite—granite—gabbro—labradoritite—foyaite and the similar tendency in the same sequence of corresponding crusts of weathering[2].

Differences have been observed among the crusts of weathering derived from different facies of a single type of rocks. Typically in South China for crusts of weathering of acidic volcanic rocks, for example, the REE contents (600—1210 ppm) in rhyolite tuff lava (briefly in the following as lava) are lower than those (520—1860 ppm) in granite-porphyry which is classified as metavolcanic facies. Another example refers to granitic rocks. The REE contents in crusts of weathering are slightly higher in muscovite granite (310—1400 ppm) than in biotite granite (240—1250 ppm). The REE contents show also the difference even for the crusts of weathering of the same type of rocks occurring in different areas. Taking basalt and granite as examples, the REE contents in crusts of weathering of the basalt in Shuicheng, Guizhou Province are 1.5 times higher than those in crusts of weathering of basalt in a certain place of Guangdong Province (206 ppm and 125 ppm, respectively). High REE contents feature the crusts of weathering of granitic rocks in South China (sometimes up to 1400 ppm in the crusts of weathering of some rock bodies). On the contrary, however, REE contents in crusts of weathering of granitic rocks in Ukraine, USSR are as less as 60—180 ppm (on the basis of an incomplete statistics)[2].

In comparison with the parental rocks, in crusts of weathering of various rocks the enrichment of REE may reach up to 1—4 times of the value in the parental rocks, but for some acidic rocks the REE contents may be 6—7 times higher than in their parental rocks. Even for the underdeveloped crusts of weathering of the basalt in certain place of Guangdong Province, the REE contents are slightly higher than those in the parental rock.

2. *REE Distribution Within Weathering Profiles*

A complete crust of weathering can be divided, from top to bottom, into three layers: the surface soil layer, the completely weathered layer and the partially weathered layer. The most important characteristic of REE distribution within weathering profiles is the clear vertical zonation, namely, the REE contents in the top layer are lower, often lower than the parental rocks, while the REE contents in the middle part of the completely weathered layer reach their climax. In the partially weathered layer the contents of REE drop down to the values which are close to or only slightly higher than the contents in the parental rocks. Briefly, the REE content curves through the profiles, from top to bottom, show generally in the shape of an asymmetric parabolas.

Several typical examples that are featured by the above-mentioned characteristics of vertical zonation of REE in the crusts of weathering can be enumerated. They include the crusts of weathering of acidic volcanic rocks and granitic rocks in South China and the basic and ultrabasic volcanic rocks in Guizhou Province[3]. Similar rule can also be seen for the crusts of weathering of some other types of rocks. For instance, the crusts of weathering of granodiorite in Australia[4] and the crusts of weathering of sandstone in Victoria, Australia[5], so on and so forth.

II. Fractionation of REE During the Weathering of Rocks

1. *Fractionation of REE*

Generally speaking, the REE distribution patterns in crusts of weathering are mainly controlled by the patterns of their parental rocks, or rather by the patterns of the REE minerals which are apt to be weathered in the parental rocks. That is to say, the crusts of weathering inherit the features of REE composition in the parental rocks. However, some factors, say, the wet weather, the hilly landform

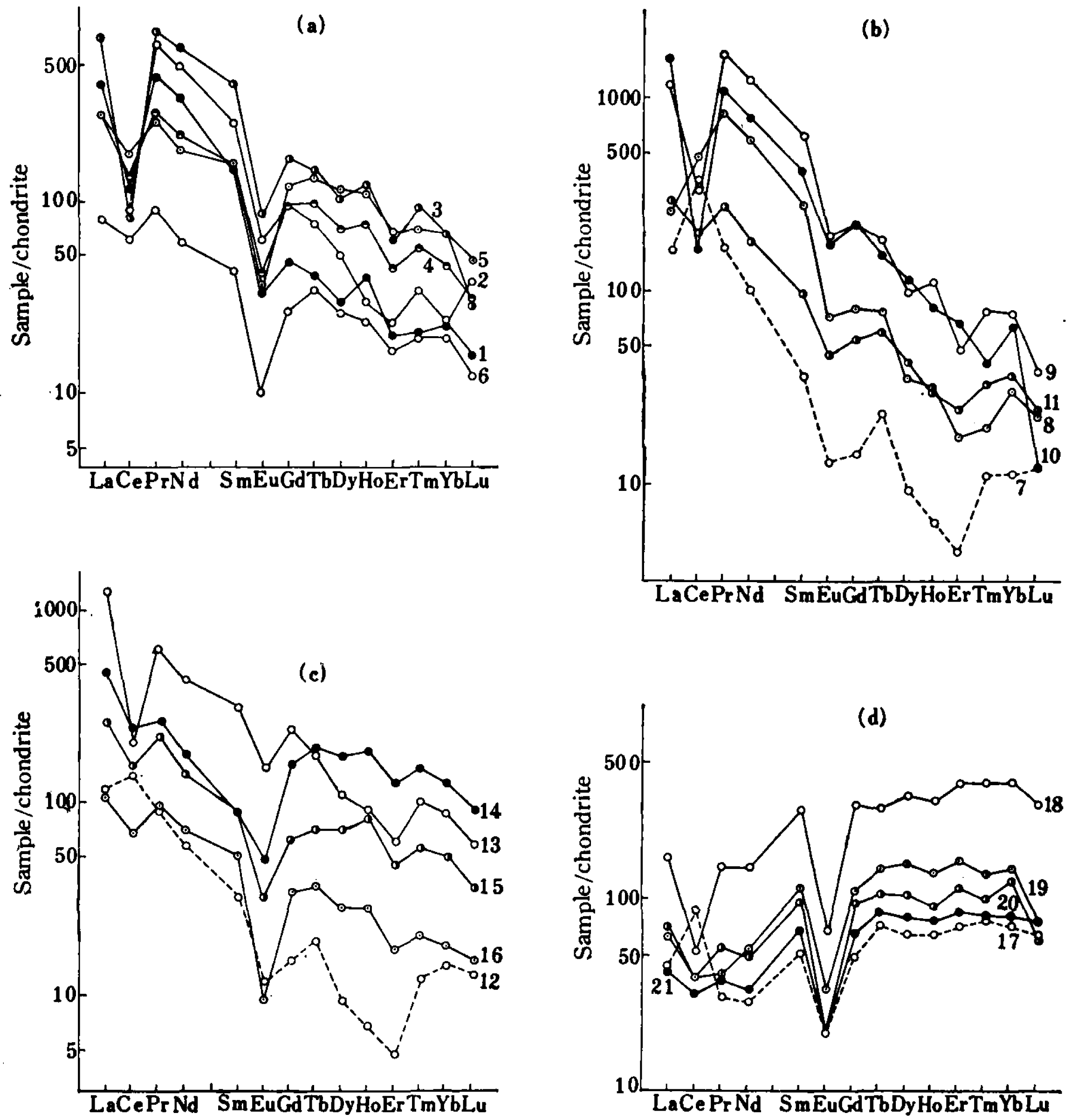

Fig.1. Chondrite-normalized REE distribution patterns for crusts of weathering of some rocks.

(a) Crusts of weathering of lava. 1, completely weathered layer (6 m thick); 2, completely weathered layer (9 m); 3, completely weathered layer (12 m); 4, completely weathered layer (15 m); 5, partially weathered layer (19 m); 6, lava.

(b) Crusts of weathering of granite-porphyry. 7, completely weathered layer (3 m); 8, completely weathered layer (6 m); 9, completely weathered layer (9 m); 10, completely weathered layer (12 m); 11, partially weathered layer (16.5 m).

(c) Crusts of weathering of biotite granite. 12, completely weathered layer (1 m); 13, completely weathered layer (10 m); 14, completely weathered layer (15 m); 15, partially weathered layer (20 m); 16, biotite granite.

(d) Crusts of weathering of muscovite granite. 17, completely weathered layer (the upper part); 18, completely weathered layer (the portion of the middle part); 19, completely weathered layer (the lower part); 20, partially weathered layer; 21, muscovite granite.

and the secondary densely-packing structures, may also influence, to various extent, the REE compositions in the crusts of weathering so as to bestow on them some characteristics other than the parental rocks. Taking the acidic volcanic rocks with the patterns of HREE depletion as an example, their crusts of weathering are enriched in LREE even more than their parental rocks. Hence, it is precise that the crusts of weathering not only inherited the features of their parental rocks but also developed some of their own exclusive characteristics.

Samples were collected at different locations within the weathering profiles of the acidic volcanic rocks and the granitic rocks in South China, and were analyzed to determine the contents of individual REE. The data obtained were normalized against chondrite and the chondrite-normalized REE patterns are shown in Fig. 1.

It can be seen from Fig. 1 that all the weathering profiles studied share a common feature, that is, the similarity in respective REE distribution patterns of the weathering crust and parental rock. This similarity indicates the prominent effect imposed by the parental rocks on the REE distribution patterns. The slopes of the chondrite-normalized patterns (curves) of the crusts of weathering which are featured by the depletion of HREE are even steeper with the $(La/Yb)_N$ becoming greater in comparison with the parental rocks, implying that some changes in REE composition occurred in the crusts of weathering, resulting in the enrichment of LREE. These characteristics in fractionation of REE may also be reflected by the variation of LREE/(HREE + Y) ratio. From top to bottom, the ratio becomes greater and greater in some of the crusts of weathering (for instance, the ratio for the crusts of weathering of granite-porphyry varies from 3.97—3.83—7.09—11.46—18.84), suggesting a tendency of enrichment of LREE with the developing weathering. Both the three-component diagrams and the variation of the concentration enrichment coefficient ρ provide strong supports to the above viewpoint[6].

The REE patterns of the weathering profiles of the basic and ultrabasic volcanic rocks in Guizhou Province show also similar characteristics.

2. *Unusual Geochemical Behavior of* Ce

Usually, on the surface of weathering crusts, the total amount of REE decreases but the Ce content increases. This is embodied in the REE distribution patterns, which exhibit sometimes strong positive Ce anomaly. In completely weathered layers, the highest REE contents are found in the middle part accompanying a strong depletion of Ce, and the REE distribution patterns often show an extremely clear Ce negative anomaly(see Fig. 1). According to Oddo-Harkin's rule, La/Ce ratio in the parental rocks is usually smaller than unity. From the upper parts of the crusts of weathering down to the parental rocks, the change of La/Ce ratio from < 1 to > 1 and to < 1 again has revealed the unusual geochemical behavior of Ce during the weathering processes. Such an unusual behavior of Ce in fractionation of REE on the earth's surface constitutes one of the prominent features of the ion-adsorption type REE ore deposits.

It ought to be pointed out that the above fractionation may be seen in all the REE crusts of weathering which are developed and preserved well. However, the anomaly of Ce in the (HREE + Y) type crusts of weathering sometimes is not as remarkable as in the LREE type crusts of weathering.

The reason why the Ce anomaly occurs on the surface of weathering crusts may be assigned to the susceptibility of Ce^{3+} to oxidation in open systems on the earth's surface and to the susceptibility of Ce^{4+} to hydrolysis in acid-weak-acid environments. This has been verified through our experiments: the abrasion pH of the samples (in pure water) collected from the sites close to the surface of the crusts of weathering of acidic volcanic rocks was determined to be within the range of 4.7—4.9, i.e. it was acidic to weakly acidic[7]. In addition, there is no hydrolysis of RE^{3+} occurring when $pH \leqslant 5$. However, there is hydrolysis of Ce^{4+} when $pH = 3$.

References

[1] Wedepohl, K. H., *Handbook of Geochemistry*, Springer-Verlag, II/2(1970), 57—71, E—11.

[2] Балашов, Ю.А., *Геохимия редкоземельных элементов, изд. наука* Москова, 1976, 128—233.

[3] 宋云华、沈丽璞，贵州水城二迭纪玄武岩风化壳中稀土元素的初步研究，中国科学院地球化学研究所成立二十周年纪念学术报告会专集，贵州人民出版社，贵阳，1 986，115—116.

[4] Nesbitt, H.W., Mobility and fractionation of rare earth elements during weathering of a granodiorite, *Nature*, 1979, 5710:206—210.

[5] Duddy, L.R., Redistribution and fractionation of rare earth and other elements in a weathering profile, *Chemical Geology*, 1980, 3:363—381.

[6] 宋云华、沈丽璞，酸性火山岩类风化壳中稀土元素的地球化学实验研究，地球化学，1986，3：225—234.

[7] ————，江西某酸性火山岩风化壳中粘土矿物及其形成条件的讨论，矿物学报，1982，3：207—213.