

# Cause of Establishment of Ion Adsorption Ore for Rare Earth Resources

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## Introduction

Rare earth element (REE) is a set of chemical elements essential for high technology industries. Ion-adsorption deposits of REE are appropriate for industries, since REE in the deposits can be easily extracted without treatment of radioactive elements, uranium and thorium. Ion-adsorption deposits are formed by adsorption of REE on weathered granite. However, it is not clear the relationship between the degree of weathering and potential of the weathered granite as REE ion-adsorption deposit. In this study, abundances and extraction ratios of REE were systematically examined for weathered granite samples with different degrees of weathering, which should be related to the variation of secondary minerals formed in the granite. In addition, the interaction of REE with potential secondary minerals was also studied to clarify the characteristics of ion-adsorption deposit, which is likely unique as a resource of REE.

## Methods

Weathered granite samples were collected from Hiroshima, Shimane, and Tottori Prefectures in Japan and also from various climate zones in Sri Lanka. Mineral and major element compositions were examined by X-ray Diffraction (XRD) and X-ray fluorescence (XRF), respectively. CIA, which represents the degree of weathering, is calculated using the results of XRF. To reveal extraction ratio of REE, decomposed solutions of REE were prepared by two methods and their REE were measured by ICP-MS. One was prepared by acid digestion, which gives total REE concentration. The other was obtained by extraction by ammonium chloride solution, which corresponds to extractable concentration. To reveal the relationship between REE and other cations, adsorption experiment was performed, by which  $K_d$  was calculated. REE was adsorbed to vermiculite and ferrihydrite in three solutions; 0.10 M NaNO<sub>3</sub> aq., 1.0 M NaNO<sub>3</sub> aq., and 1.0 M NH<sub>4</sub>Cl aq. To reveal the comparison between REE and other elements, K-edge EXAFS of lanthanum (La), strontium (Sr), barium (Ba), potassium (K), rubidium (Rb), and cesium (Cs) were also performed after their adsorption on the adsorbents to identify their adsorption species.

## Results & Discussion

The result of XRF analysis revealed that the ability of adsorption depends on the degree of weathering and can be highest in mildly weathered granite, or in granite of which CIA (Chemical Index of Alteration) is 65~75. Coupled with the XRD results, it was found that the relationship of REE and clay minerals is very important for ion-adsorption deposit. These results suggest that the potential of ion-adsorption deposit depends on the climate controlling the degree of weathering.

$K_d$ , which is calculated using the results of adsorption experiment, revealed that extraction ratio of REE adsorbed to ferrihydrite is low and extraction ratio of REE adsorbed to clay minerals is high. In the REE pattern of  $K_d$ , REE adsorbed to ferrihydrite shows tetrad effect, which shows the formation of REE inner-sphere complex. REE adsorbed to vermiculite, on the other hand, do not show tetrad effect, or REE outer-sphere complex. Thus, when REE form outer-sphere complex, the extraction ratio of REE becomes high. Furthermore,  $K_d$  of REE and Sc are high. This is because they are trivalent and attracted electrostatically to a larger degree, which suggests that high charges of cations are important for ion-adsorption deposit. XAFS spectrum of the adsorbed mineral species similar to that of solution sample shows that the ion adsorbed to the mineral forms outer-sphere complex. The results revealed that the

types of surface complex depend on the ionic size. Ions which are smaller than  $Ba^{2+}$  form outer-sphere complex, while ions larger than  $Ba^{2+}$  form inner-sphere complex. Thus, ions which can form ion-adsorption deposit are smaller than  $Ba^{2+}$  and have high charges. Among the many hard ions, only REE meet the requirement to form the ion-adsorption deposit.

Keywords: Rare Earth Elements, Ion Adsorption Deposit, Surface complex, Ionic size, Valence