

## Limiting factor for weathered granitic rocks to be ion adsorption ore

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Main rock of ion adsorption type deposit which is important as rare earth element (REE) resource is weathered granite, from which we can extract REE readily using aqueous solution such as ammonium chloride or ammonium sulfate solution, because REE can be extracted from weathered granite by ion exchange reaction. Previous studies of the ion adsorption type REE deposit has been carried out mainly using weathered granite found in the Southeast Asia, but there are few studies on the weathered granite present in Japan in terms of the REE deposit. In addition, there are no studies which clarify the relationship between REE chemical state and extraction properties in the weathered granite at molecular level. Therefore, the aim of this study is (i) to clarify the relationship between the extraction characteristic of REE in the weathered granite and its chemical state at the molecular level using XAFS method and molecular orbital calculation and (ii) to study the dependence of extraction rate of REE on the degree of weathering of the granitic rocks. In this study, we analyzed granite or weathered granite samples collected in Hiroshima, Shimane, and Tottori in Japan, Sri-Lanka, and Myanmar. The collection of the samples from various sites are strongly needed to cover granitic rocks having various degrees of weathering. Initially, the mineral and major element compositions were examined by XRD and X-ray fluorescence (XRF) analyses. After the analysis, local chemical state of Y, one of REE, was determined using bulk XAFS and  $\mu$ -XRF-XAFS method at SPring-8 and KEK-PF, scanning electron microscopy (SEM), and molecular orbital calculation. As a result, it was suggested that REE in the samples with high CIA can be readily extracted and the REE chemical state suggested by Y K-edge EXAFS is outer-sphere complex adsorbed weakly in the weathered granite. The  $\mu$ -XRF-XAFS and SEM analyses showed that REE was mainly adsorbed on phyllosilicates such as halloysite and weathered biotite. On the other hand, the extraction ratio of REE in the samples with low CIA are low and its REE chemical state is inner-sphere complex, or REE incorporated possibly into primary minerals or phosphate. The ratio of outer-sphere complex among total REE determined by the fitting of EXAFS spectra in k space is positively correlated with that of REE extraction ratio. In addition, weathered granite with higher REE extraction ratio exhibits larger negative Ce anomaly, suggesting that REE with negative anomaly in aqueous phase was adsorbed to the granitic rocks, which finally induces the correlation between the degree of negative Ce anomaly and REE extraction ratio. Thus, it is suggested that the degree of negative Ce anomaly is one of the characteristics of ion adsorption type REE deposit. However, strongly weathered granite samples with CIA values higher than 85 do not show high REE extraction ratio. Mineralogy of the samples is dominated by kaolinite and gibbsite, which suggests that the fraction of REE adsorbed on clay minerals is minimal for the strongly weathered granites compared with intermediately weathered granitic rocks with CIA value around 70. Thus, we can conclude that medium weathering characterized by the presence of vermiculate/smectite with CIA value around 70 is an important limiting factor to establish the sample as an REE ion adsorption ore.