

Speciation of rare earth elements (REEs) in ion-adsorption-type REE mineralization in Japan by X-ray absorption fine structure spectroscopy

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Typical vertical profiles of ion-adsorption-type rare earth element (REE) mineralization discovered in southwest Japan were studied by X-ray absorption fine structure (XAFS) combined with transmission electron microscopy (TEM) and adsorption/desorption experiments.

XAFS analysis revealed that the peak energy of the spectra was slightly shifted depending on the depth (i.e., the difference of soil pH and REE concentration) of hand-augered weathered granite samples, which is thought to reflect the difference of REE species. As a result of adsorption/desorption experiments of REEs onto kaolinite (the host phase of REEs determined by TEM), it was found that outer- and inner-sphere complexation was promoted at relatively low and high pH environment, respectively.

These results suggested that REE speciation, migration, and enrichment in weathered granite is largely controlled by soil pH, which in turn controls the variable charges of kaolinite. More specifically, dissolution and migration of REEs occur in the near-surface acidic environment of the regolith, where hydroxyls of kaolinite basal surfaces and edges are deprotonated to a lesser degree. Meanwhile, REEs accumulate in the relatively high-pH environment below the surface, where hydroxyls of kaolinite basal surfaces and edges are deprotonated to a larger degree, producing REE adsorption sites with variable charges.

An increase of soil pH to greater than 6 in deeper layers promotes inner-sphere complexation of REEs. Although inner-sphere complexation inhibits the ion-exchange extraction of REEs, it was found the inner-sphere complexes can be still extracted by lowering the pH of the extraction solvent. This fact, which indicates that the adsorption of both inner- and outer-sphere complexes is reversible, is important in terms of the efficient recovery of REEs from all depths in the regolith [1].

[1] Nagasawa, Shimizu, Yamaguchi, Tokunaga, Mukai, Aoyagi, Mei & Takahashi (2024). *Chemical Geology*, 670, 122431.