

## Distribution of rare earth elements between deep granitic groundwater and fracture filling carbonate

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The chemical properties of rare earth elements (REEs) and yttrium (YREE) have been widely studied as geochemical tracer in aqueous environments. The YREE abundances in groundwater are mainly regulated by mineral-water interaction. The YREE variability in natural groundwater system is very complex and dependent upon geologies, water flow-path, mixing and chemical condition of groundwater. We investigated distribution of rare earth elements (YREE) between deep granitic groundwater with diverse geochemical character and fracture filling calcite in order to understand YREE behavior in natural groundwater systems.

In Tono area, central Japan, the chemical types of groundwater varied with depth; Na-HCO<sub>3</sub> type of groundwater in sedimentary rock, Na-Cl type in upper part of base rock granite and Ca-Cl type in deeper granite. The Na-Cl type groundwater was collected using boreholes from 200, 300 and 400 m, the Ca-Cl type from 650 and 1150 m below ground surface. The concentrations of YREE were measured by ICP-MS. The fracture filling calcite was obtained from drill core of boreholes similar to the groundwater sampling. The collected samples were dissolved into 1M NH<sub>4</sub>-acetate buffer solution (pH = 4.8) and the concentrations of YREE in the leached solutions were measured by ICP-MS. Furthermore, in order to assess the precipitation condition, we measured isotopic composition of O and C for calcite.

Chondrite-normalized YREE patterns of Na-Cl type groundwater exhibited enrichment in heavy REEs relative to light REE, which was well explained by the predominance of YREE carbonate aqueous complex in the groundwater. On the other hand, YREE patterns of Ca-Cl type groundwater were enriched in middle REEs (MREEs). In addition, Y/Ho of the Ca-Cl type groundwater was significantly lower than that of chondrite. MREE-enrichment in natural water occurs from dissolution of MREE-enriched Fe-oxyhydroxide [1], and lower Y/Ho than chondrite is common in distribution patterns of Fe-oxyhydroxide [2]. The concentration of Fe in the groundwater increased with depth and the Eh measurement of the groundwater showed strongly reducing condition. Consequently, YREE in the Ca-Cl type groundwater can be explained by dissolution of MREE-rich Fe-oxyhydroxide with sub-chondritic Y/Ho.

Oxygen isotopic composition of fracture filling calcite varied regardless of depth. The correlation between precipitation temperature and depth was not observed. On the other hand, carbon isotopic composition became heavier with depth. This result indicates the fracture filling calcite precipitated from mixture of seawater and freshwater. For YREE patterns of fracture filling calcite collected from 200~400 m depth exhibited negative Eu anomaly, while the samples from 670~1294 m along borehole showed positive Eu anomaly when the YREE contents were normalized by granite. For the fracture filling calcite from 200~400 m depth were precipitated from groundwater with YREE eluted from granite, because the negative Eu anomaly has been observed in mother rock granite [3]. Therefore, the positive Eu anomaly in calcite indicates that the groundwater precipitated calcite was enriched in Eu.

[1] Johannesson and Zhou, 1999, *Geochim. Cosmochim. Acta* 63, 153-165.

[2] Bau, 1999, *Geochim. Cosmochim. Acta* 63, 67-77.

[3] Takahashi et al., 2002, *Chem. Geol.* 184, 311-335.

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