Rare earth elements in the paleo- and present granitic groundwater in the Tono area, Japan

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The chemical properties of rare earth elements 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. We investigated YREE evolution in the paleo- to the present groundwater in order to understand YREE behavior in natural deep groundwater systems.

The groundwater was sampled from boreholes in the bedrock granite (providing groundwater 200, 300, 400, 650 and 1150 meters with depth). Additionally, we collected the fracture filling calcite from the drill cores. The groundwaters were grouped into HREE-rich “shallow” groundwater (-200 – 400m) and MREE-rich “deep” groundwater (-650 and -1150m). For the shallow groundwater, aqueous $REE(CO)_3^+$ complex was predominant in LREE. The HREE-enrichment in the “shallow” groundwater can be accounted for by preferential sorption of the positively charged aqueous complex to negatively charged minerals on fracture flow path in the weak alkaline groundwater [1]. Y/Ho ratio in the “deep” groundwater was lower than that of chondrite. The concentration of Fe in the “deep” groundwater was significantly higher than that in the “shallow” groundwater and Eh showed strongly reducing. The MREE-enrichment and low Y/Ho are well-characterized by distribution of YREE on Fe-oxide [2], and the dissolution of Fe-oxide produce MREE-enrichment in water [3]. Our results suggest the “deep” groundwater was possibly affected by the redistribution of MREE-rich minerals such as Fe-oxide. YREE in the paleogroundwater was estimated from that in the fracture calcite and distribution coefficient of YREE [4]. The YREE pattern of paleogroundwater was enriched in HREE overlapping with the present “shallow” groundwater. Our results suggest YREE in the present “shallow” groundwater was originated from dissolution of the fracture calcite.

[1] Munemoto et al. (2014) *PEPS*, 1:28, [2] Bau (1999) *GCA*, **63**, 67-77, [3] Haley et al. (2004) *GCA*, **68**, 1265-1279, [4] Zhong and Mucci (1995), *GCA*, **59**, 443-453