Inhibition effect of transformation of ferrihydrite in granitic groundwater from the Mizunami Unederground Research Laboratory

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Fe(III)-(oxyhydr)oxides are ubiquitous in soil and groundwater systems and due to the large surface area and high sorption capacity, they play important roles in the biogeochemical cycles of trace elements. Ferrihydrite is a metastable with respect to stable Fe-oxides such as hematite and goethite. The transformation experiments of ferrihydrite have been conducted in the laboratory, but little in the natural groundwater. In order to understand the transformation behavior of ferrihydrite in natural groundwater systems, we conducted transformation experiments of ferrihydrite in granitic groundwater.

The granitic groundwater was sampled from -300 m research gallery at the Mizunami Underground Research Laboratory. Synthesized ferrihydrite was added to serum vials and sealed with gas-tight stopper in an anaerobic Ar atmosphere. The groundwater was added to the vials without contacting air by using syringe. The suspention was aged up to 96 days. The groundwater had a slightly alkaline pH and reducing condition. Thermodynamic calculation revealed that the groundwater was almost equilibrium with respect to quartz and calcite, and saturated with respect to hematite. X-ray diffraction (XRD) showed that ferrihydrite did not transform to more stable phases. Although the groundwater saturated with respect to hematite, the XRD peaks of hematite were not observed. Scanning transmission electron microscopy showed that approximately ~100 nm of aggregates consist of ~20 nm diameter particles. The d-value of the electron diffraction ring were 0.25 and 0.15 nm, which indicated the ferrihydrite did not transformed to more stable phases in the groundwater. Consequently, our results suggest the transformation of ferrihydrite was probably inhibited by the aqueous components contained in the groundwater.