Specific sorption processes of REEs and actinides induced by biomolecules

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Manganese(IV) oxide has received considerable attention because of its strong sorption property and ubiquity in the environment. It is widely accepted that the formation of Mn oxide is microbially mediated in the environment. Considering the microbial formation of Mn oxide, sorption behavior of trace elements should be investigated using biogenic Mn oxide. Therefore, we have studied sorption of rare earth elements (REEs) and actinides on Mn oxide produced by Mn(II)-oxidizing fungus.

Sorption experiments of REEs and actinides (Th(IV), Np(V), U(VI) and Pu(IV)) on biogenic Mn oxide were carried out in 10 mmol/L NaCl solution at various pH conditions. We cultured *Acremonium* sp. strain KR21-2, Mn(II)-oxidizing fungus, to prepare biogenic Mn oxide. The harvested biogenic Mn oxides were not separated from fungal cells for sorption experiments.

Sorption experiments of REEs showed a positive Ce anomaly in partition coefficients (defined by solid to solution ratios) under weak acidic condition, which is consistent with the observation in previous works using abiotic Mn oxide. However, the degree of positive Ce anomaly decreased with pH, and negative Ce anomaly was observed under circumneutral conditions irrespective of Ce(III) oxidation to Ce(IV) by Mn oxide. Size-exclusion column HPLC ICP-MS analysis confirmed that Ce was complexed with organic ligands in solution. A line of data indicates that the negative Ce anomaly under circumneutral pH conditions arose from Ce(III) oxidation on biogenic Mn oxide and subsequent complexation of Ce(IV) with biomolecules released from fungal cells.

Thorium(IV) was quickly sorbed on biogenic Mn oxide, but desorbed into solution with time. The desorption of Th(IV) is possibly attributed to organic ligands released from fungal cells as observed in the sorption behavior of Ce. In contrast, sorption of Pu(IV) increased with time, which was similar to that of U(VI). Pultonium(IV) was possible to be oxidized to Pu(VI) by Mn oxide. Sterilized biogenic Mn oxide did not show the desorption behavior of Th(IV), indicating that living cells would release organic ligands strongly complexed with Th(IV).