Bio-mineralization of rare earth elements

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Geochemical behaviors of rare earth elements (REEs) are important to understand the migration of trivalent actinides and fission genic REEs from nuclear power plants and high level radioactive waste. When REEs migrates in environemnts, their chemical states may change by the interaction with inorganic and organic materials. Many researchers have studied the interaction of REEs with inorganic materials. However, the biotransformation of REEs have not fully understood. We have conducted the research on the effects of microorganisms on chemical states change of REEs.

We found that Sm(III) phosphate minerals were formed on the cells surface of gram negative bacterium *Pseudomonas fluorescens* after exposure of Sm(III) solution with the resting cells, even though no phosphate is added. TEM-SAED analysis showed that Sm-monazite was developed directly from the surface of cells. Sm(III) ions were first adsorbed by the functional groups of cells surface, followed by the chemical states change by the reaction with phosphate ions released from inside the yeast cells.

When phosphate is provided in the solution as glycerol phosphate-Ca, Yb concentration decreased abruptly with time after *P. fluorescens* exposed to the solution containing Yb(III) and lactic acid. TEM and XAFS analyses showed the nanoprecipitates containing Yb and P were formed directly from the cells surface. Interestingly, precipitates containing Ca and P, but no Yb were observed on the cells. On the contary, without glycerol phosphate, Yb concentration in the solution slightly decreased with time by the formation of Yb-lactate complex in the solution.

These findings strongly indicate that Yb phosphate mineralization was occurred on the cells surface, even when P was provided from inside and outside cells. Thus, cell surface of microorganisms functions as specific reaction environment for biotransportation of REEs.

Speciation study of copper in stream sediments and soils

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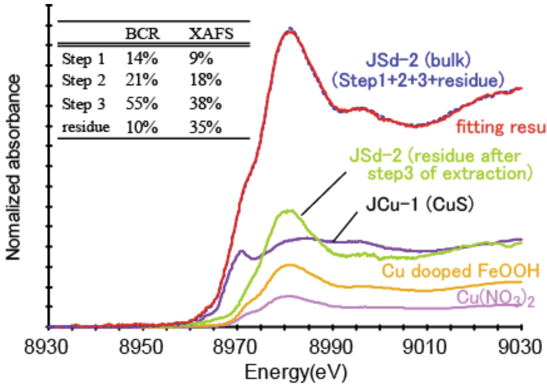
A sequential extraction method has been used widely to elucidate its chemical binding forms in sediments including soil. However, the method might give misleading results due to alteration of the samples during the individual steps of the extraction [1]. We applied a X-ray absorption fine structure (XAFS) spectroscopy to identify the Cu species in the residues after each step of the sequential extraction. The Cu in 7 geo-standard materials (JSd-1~5: stream sediments, JSO-1 and 3: soils) was extracted using a modified three-step extraction developed by the Community Bureau of Reference (BCR) [2]. The steps and extractants are as follows;

(1) Step1: CH_3COOH (0.11 mol/L).
(2) Step 2: $NH_2OH{\cdot}HCl$ (0.5 mol/L).
(3) Step 3: H_2O_2 (8.8 mol/L) and CH_3COONH_4 (1 mol/L).

The residues after each step of extraction were filtrated by a membrane filter. The $Cu^{3+}_{(aq)}$, $Cu(NO_3)_2$, Cu doped FeOOH (or MnO_2), Cu doped humic materials, and JCu-1 (a geochemical reference material of CuS ores) were prepared As a reference compounds. The Cu K-edge XANES spectra were recorded in a fluoresce mode at the BL-12C of KEK-PF. The fluorescence X-ray was measured by a 19 element pure-Ge SSD.

Figure 1 shows the Cu K-edge XANES spectra of JSd-2 and reference materials and its fitting results. The JSd-2 is a stream sediment reference material collected from the drainage basin having Cu mine. The speciation of Cu in JSd-2 is expected to be a mixture of Cu weakly adsorbed on materials (step 1), Cu bound to Fe-Mn hydroxides (step 2), chalcopyrite (step 3) and silicate materials (residue). The linear fitting result was roughly comparable to the results from the BCR scheme, although the relative amount of Cu extracted at step 3 is underestimated. Thus, the method using XAFS spectroscopy combined with BCR scheme is effective to accurately identify and quantify Cu species in sediment samples.



	BCR	XAFS
Step 1	14%	9%
Step 2	21%	18%
Step 3	55%	38%
residue	10%	35%

Figure 1. The Cu K-edge XANES spectra of JSd-2 and the residue of JSd-2 after third step in the BCR scheme, and reference materials.

[1] Calmano *et al.* (2001) *Anal. Chem.* **371**, 823-830.
[2] Rauret *et al.* (1999), *J. Environ. Monit.* **1**, 57-61.