EXAFS Study on the Cause of Enrichment of Heavy Rare Earth Elements on Bacterial Cell Surfaces

Extended X-ray absorption fine structure (EXAFS) spectra of rare earth elements (REE) adsorbed on bacteria showed that multiple phosphate complexation causes enrichment of heavy REE (HREE) at bacterial cell surfaces. The difference of the affinities among REE for bacteria, the mechanism of which was suggested by the structural information obtained by EXAFS in this study, enables us to use the adsorption of REE on bacteria as (a) a biomarker of the REE pattern in natural waters and (b) a method of separating mutual REE in the recycling of REE as industrial resources.

Bacteria can affect the environmental behavior of various metal ions in natural waters. On the other hand, the relative abundances of rare earth elements (REE), known as the REE pattern, are important for understanding the migration of REE and other elements in natural waters and for clarifying the chemical reactions of REE in natural systems. Thus, the interaction of REE and bacteria is a unique topic in aqueous environmental geochemistry. In particular, we found that bacteria cause anomalous enrichment of heavy REE (HREE) (Fig. 1), which suggests that (a) the REE pattern can be a signature of bacteria-related materials in natural samples and (b) bacteria can be used for mutual separation of REE by the adsorption reaction on cell walls. In this study, the REE binding site on the cell surface of a Gram-positive bacterium (*Bacillus subtilis*) responsible for the HREE enrichment has been identified by EXAFS, thus paving the way for applications of the adsorption reaction such as (a) and (b).

EXAFS of various REE adsorbed on bacteria were measured at BL-12C (Fig. 2). The results showed that (i) HREE is bound to multiple phosphate sites at lower REE-bacteria ratio (= [REE]/[bac]), but the fraction coordinated to carboxylate increased as the ratio increased, and (ii) the binding sites of light and middle REE (LREE and MREE, respectively) changed from phosphate with lower coordination number to carboxylate sites as the [REE]/[bac] ratio increased. As the [REE]/[bac] ratio increased, the enrichment of HREE in the REE distribution patterns of bacteria was less marked. This trend is consistent with the EXAFS results, since (i) the REE pattern of multiple phosphate sites exhibits a monotonous increase for heavier REE and (ii) phosphates with lower coordination number and fewer carboxylate sites have maxima around Sm. Based on these results, it was shown that phosphate sites are more stable than carboxylate sites as the binding sites for REE. Similar EXAFS results and REE patterns obtained for *B. subtilis*

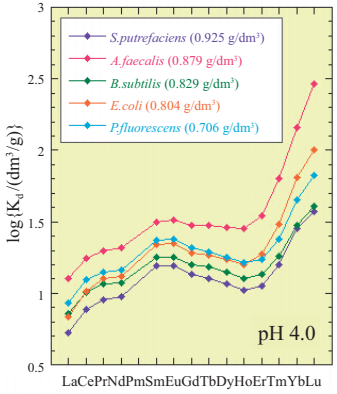

Figure 1
Adsorption coefficient K_d of REE on *Alcaligenes faecalis*, *Bacillus subtilis*, *Escherichia coli*, *Alcaligenes faecalis*, *Shewanella putrefaciens*, and *Pseudomonas fluorescens* at pH 4.0.

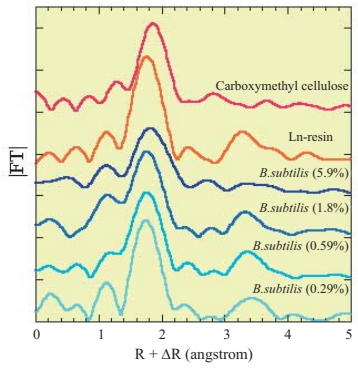

Figure 2
Radial structural function (RSF) at Lu L_{III}-edge for Lu sorbed on the reference materials (carboxymethyl cellulose and Ln resin) at pH 3.5 and *B. subtilis*.

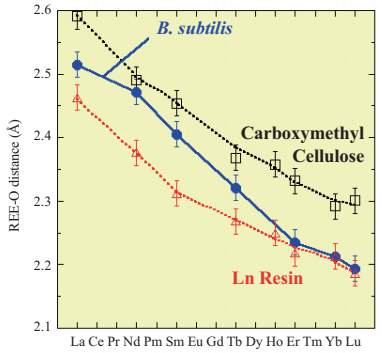

Figure 3
Average REE-O bond lengths of REE adsorbed on reference materials (carboxymethyl cellulose and Ln resin) and *B. subtilis*.

were also found for Gram-negative bacterium such as *E. coli, S. putrefaciens*, *A. faecalis*, and *P. fluorescens* (Fig. 1), showing that similar phosphate and carboxylate sites are available also in the cell wall of Gram negative bacteria. In all the results above, the variation of REE pattern was correlated with that of the binding site indicated by EXAFS, showing that the REE pattern itself reflects the binding site of REE at bacterial surfaces. Thus, the REE pattern can be used to estimate the binding site even at low REE concentration where spectroscopic techniques cannot be applied.

The average bond lengths between REE and oxygen were compared among various REE adsorbed on bacteria (Fig. 3), showing that the bond length was much shorter for HREE (Er to Lu) than those extrapolated from the trend between La and Dy due to the selective binding of HREE to the multiple phosphate sites. The results are reasonably consistent with the selective enrichment of HREE at bacterial cell surfaces, considering that chemical species with shorter bond length are more stable. Thus, it is clear that the HREE enrichment to bacterial cell surfaces is caused by their binding to the multiple phosphate sites. The results suggest that materials having such phosphate sites can induce anomalous HREE enrichment in natural systems. Since multiple phosphate sites are unique to bacteria and bacteria-related materials in nature, the results imply that the REE pattern is a potential biomarker in natural samples. In addition, the difference in adsorption affinities of REE and bacteria (Fig. 1), the mechanism of which was supported by EXAFS in this study, suggests that adsorption on bacteria can be used for the mutual separation of REEs.

REFERENCE

[1] Y. Takahashi, M. Yamamoto, Y. Yamamoto and K. Tanaka, *Geochim. Cosmochim. Acta.* **74** (2010) 5443.

BEAMLINES

12C and 9A

Y. Takahashi (Hiroshima Univ.)