EXAFS study on the cause of enrichment of heavy rare earth elements on bacterial cell surfaces

In our previous studies [1,2], we investigated the adsorption of rare earth elements (REEs) on a bacterial cell surfaces in bacterial suspension system in water. As a result, we found that REEs consisting of lanthanides and yttrium have high affinities to bacterial cell surfaces. In particular, peculiar enrichment to the cell surfaces was found for heavy REEs such as Dy, Tm, Yb, and Lu in the REE distribution patterns between bacteria and water (Fig. 1(a)). These findings are noteworthy from various viewpoints. In the cycle of rare metal resources, the results suggested that bacteria and bacteria-related materials can be used to recover REEs from a solution containing REEs in refining and recycling systems. The high selectivity of HREEs may enable us to use the bacteria for the mutual separation of REEs, since REEs are usually recovered as a mixture from mineral ores. From the biogeochemical point of view, the HREE-enriched REE pattern can be unique, which can be used as a biomarker in natural samples, since other adsorbents of REEs in nature do not exhibit such HREE enrichment signature. To develop applications of our previous results to the engineering field of REE resources using bacteria and also to the biogeochemical field using REE distribution pattern as a biomarker, it is essential to understand the interaction of REE and bacteria from the atomic scale, which must be linked to the high affinity of REEs and the high selectivity of HREEs to bacteria. Thus, we employed extended X-ray absorption fine structure (EXAFS) spectroscopy to reveal the binding site of REE on bacterial cell surfaces.

EXAFS spectra at L_{III}-edge of various REEs were measured at beamline **BL01B1** for REEs adsorbed on a Gram-positive bacterium (*Bacillus subtilis*). The EXAFS data showed that the HREE form complexes with multiple phosphate sites (including phosphoester sites) with a larger coordination number (CN) at lower REE-bacteria ratios ([REE]/[bac]), whereas light and middle REEs form complexes to the phosphate site with a lower CN. The fraction coordinated to carboxylate increased for all REEs with increasing [REE]/[bac] ratio (Fig. 2). On the other hand, the enrichment of HREEs in the REE distribution patterns of the bacteria was less marked with increasing [REE]/[bac] ratio. This result is consistent with the EXAFS data, because the REE pattern of the surface complex with multiple phosphate sites in a reference material (Ln-resin) exhibits a monotonic increase for heavier REEs, whereas the phosphate surface complex with a low CN (cellulose phosphate) and a carboxylate site (carboxylmethyl cellulose) reach a maximum around Sm and Eu. On the basis of

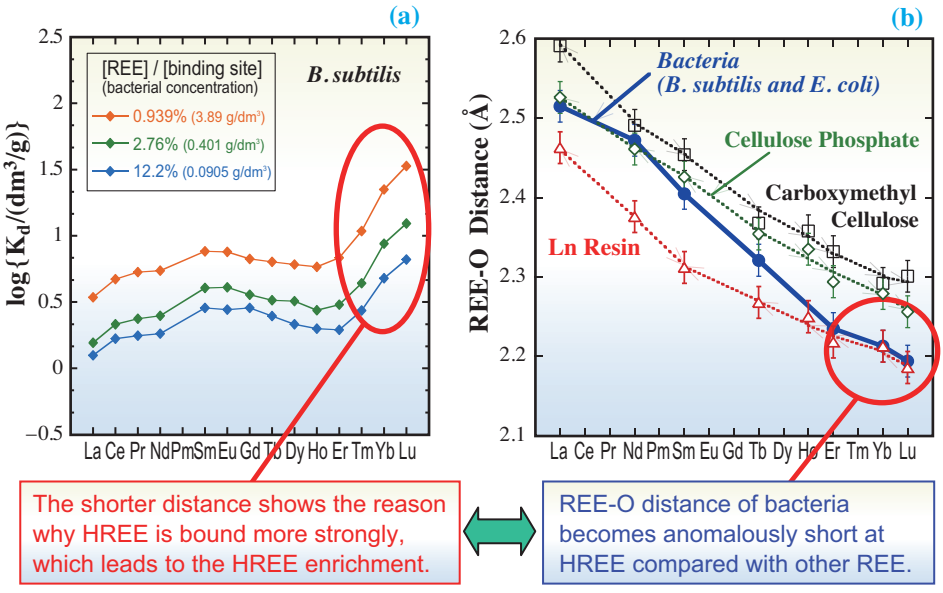

Fig. 1. **(a)** REE distribution pattern of adsorption coefficient (= Kd) at various [REE]/[bac] ratios. **(b)** Average REE-O bond length of REEs sorbed on reference materials, *B. subtilis*, and *E. coli* determined by EXAFS.

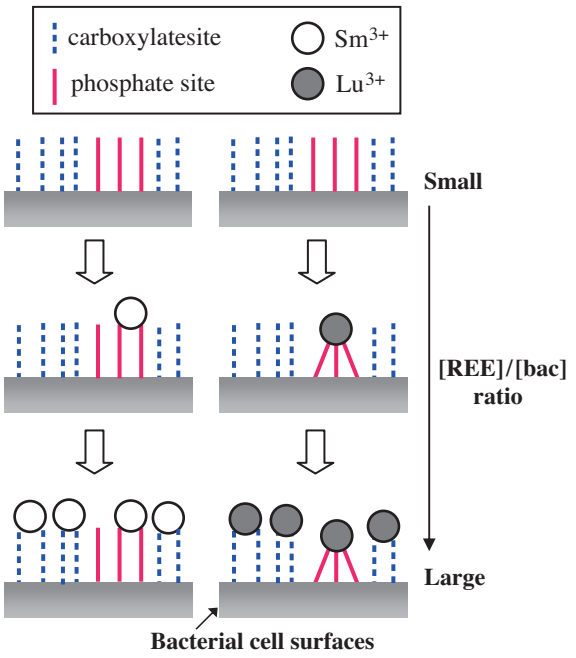

Fig. 2. Schematic of the variation of binding site with increasing in the [REE]/[bac] ratio for Sm^{3+} and Lu^{3+} ions representing middle REEs and HREEs, respectively.

these results, it is clear that the REEs are primarily bound to the phosphate site and subsequently to the carboxylate site on the bacterial cell surface. The variation of the binding sites described above is depicted in Fig. 2.

The results obtained for *B. subtilis* were also valid for *Escherichia coli*, a Gram-negative bacterium, showing that similar phosphate and carboxylate sites are also available in the cell walls of *E. coli*, or other Gram-negative bacteria. The fact that similar adsorption behaviors of REEs were obtained for both Gram-positive and Gram-negative bacteria showed that the high affinity of REEs and enrichment of HREEs are common features for REE adsorption on any bacteria in nature.

In all of our results, the variation in the shape of REE distribution pattern correlated with the binding site indicated by EXAFS, which showed that the REE distribution pattern itself reflects the binding site of REEs on the bacterial surface. Thus, the REE distribution pattern can be used to estimate the binding sites for lower [REE]/[bac] ratios, where spectroscopic techniques such as EXAFS cannot be applied.

The average bond length between the REEs and oxygen was compared for various REEs sorbed on bacteria, showing that the bond length for HREEs (Er to Lu) was much shorter than those extrapolated from the trend between La and Dy, because of the selective binding of the HREEs as multiple phosphate surface complexes. Our results are consistent with the selective enrichment of the HREEs on the bacterial cell surfaces, considering that chemical species with a shorter bond length are more stable. Thus, it is clear that the HREE enrichment on the bacterial cell surfaces is caused by the formation of multiple phosphate surface complexes (Fig. 1). On the basis of these results, it is suggested that materials having such phosphate sites such as bacteria and bacteria-related materials can induce anomalous HREE enrichment in natural systems.

The finding that REEs are associated with phosphate sites on bacterial cell surfaces has various implications both on the technology of REE recovery and separation by bacteria and also on the possibility of the REE distribution pattern as a biomarker. The results showed that bacteria-related materials that have phosphate sites can be used as adsorbents and separation agents of REEs. On the other hand, the fact that the anomalous HREE enrichment is caused by the formation of multiple phosphate sites, which are not usually found in other important REE host phases such as Fe and Mn oxides and humic substances in nature, makes REE patterns a potential tool as a biomarker.

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References

[1] Y. Takahashi *et al.*: Chem. Geol. **219** (2005) 53.
[2] Y. Takahashi *et al.*: Chem. Geol. **244** (2007) 569.
[3] *Y. Takahashi, M. Yamamoto, Y. Yamamoto and K. Tanaka: Geochim. Cosmochim. Acta* ***74*** *(2010) 5443.*