Research Group for Bioactinide

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The research objectives of Bioactinides Chemistry Research group are elucidate chemical states change of actinides and lanthanides including nano-particles formation in the biological reaction environments. In the year of 2011, chemical states change of lanthanides by the transfer of phosphorous ions and electron from the cells to lanthanides has been studied.

Formation of phosphate nano-particles in the biological reaction environments

Phosphate minerals containing heavy elements of lanthanides and U are known to be hardly soluble in the aqueous solution in the environments. Phosphorous is an essential element of microorganisms. The microorganisms store P in their cells. We have found that yeast, *Saccharomyces cerevisiae* releases P in solution containing Ce(III), followed by the formation of cerium phosphate mineral of monazite [1]. However, not only mechanism of the formation of REE phosphate mineral, but role of microorganisms for the formation have not been elucidated.

When the yeast cells are exposed to the solution containing 1.44×10^{-4} mol/L Yb(III) (heavy REE) for 2-120 h, and two months at 25 ± 1 °C at an initial pH of 3, 4, or 5, Yb concentrations in solutions decreased as a function of exposure time [2]. Field-emission scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy (FESEM), and transmission electron microscopy (TEM) analyses revealed that nano-sized blocky Yb phosphate with an amorphous phase formed on the yeast cells surfaces in the solutions with Yb. These nano-sized precipitates that formed on the cell surfaces remained stable without changing their size even after two months of exposure at 25 ± 1 °C around neutral pHs.

The synchrotron-based extended X-ray absorption fine structure (EXAFS) analysis revealed that the chemical state of the accumulated Yb on the cell surfaces changed from the adsorption on both phosphate and carboxyl sites at 30 min to Yb phosphate precipitates at 5 days, indicating the Yb-phosphate precipitation as a major post-adsorption process. In addition, the precipitation of Yb phosphate occurred on cell surfaces during 7 days of exposure in Yb-free solution after 2 h of exposure (short-term Yb adsorption) in Yb solution. These results suggest the transformation of the adsorbed Yb to Yb phosphate precipitates on cell surfaces, even though no P was added to the exposure solution. In an abiotic system, the EXAFS data showed that the speciation of sorbed Yb on the reference materials, carboxymethyl cellulose and Ln resin, did not change even when the Yb was exposed to P solution, without forming Yb phosphate species. This result strongly suggests that the cell surface of the yeast plays an important role in the Yb-phosphate precipitation process, not only as a carrier of the functional groups but also as a substrate inducing the nucleation of phosphate nanoparticles.

These results indicate that light and heavy REEs behave different manner at the biological reaction environments. This fact stimulates us to investigate the behaviour of series of REEs at the biological reaction environment. We have a plan to study on the behavior of series of REEs by yeast.

Chemical states change of REEs - desferrioxamine B complexes by *Pseudomonas fluorescens* and γ-Al_2O_3

Biological materials possess functional groups able to complex with metal cations. Siderophores are microbial chelating agents produced to solubilize Fe(III). Desferrioxamine (DFO) B is a trihydroxamate siderophore ubiquitously found in the environment and its interaction with various metal cations has been studied. We found that at pH 7 negative adsorption anomaly of Ce on *P. fluorescens* cells and γ-Al_2O_3 compared to the neighbouring REEs(III), La(III) and Pr(III); this was because the oxidization of Ce(III) to Ce(IV) during complexiation with DFO and the higher stability of the Ce(IV)-DFO complex than that of the Ce(III)-DFO complex and the La(III)- and Pr(III)-DFO complexes [3].

In this study, we have studied the interactions of REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er) - DFO complexes with *P. fluorescens* cells and with γ-Al_2O_3, at pH 4 – 9. The higher percent adsorption of REEs was obtained at lower pHs on *P. fluorescens* cells and at higher pHs on γ-Al_2O_3. Degree of negative anomaly of Ce compared to its neighbouring REEs, La(III) and Pr(III) decreased with increasing pH. XAFS analysis showed that Ce exists as the Ce(IV)-DFO complex in higher pH than 6. Thus, the pH dependence of Ce anomaly is predominantly dependent on the stability of Ce(IV)-DFO complex.

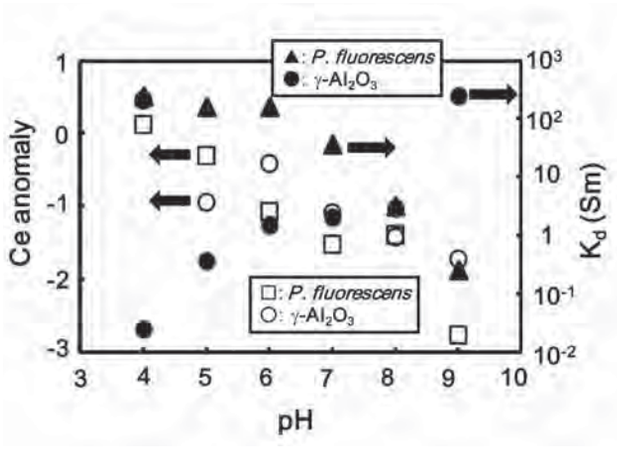

Fig. 1 Degrees of Ce anomaly and K_d(Sm) on *P. fluorescens* cells and γ-Al_2O_3 as a function of pH.The degree of Ce anomaly for the K_d(REE) patterns was expressed by: $DA = \log K_d(Ce) - [\log K_d(La) + \log K_d(Pr)]/2$.

References

[1] M. Jiang *et al*., Chemical Geology, **277**, 61(2010).
[2] M. Jiang, Thesis Kyushu Univ. (2012).
[3] T. Ohnuki, T. Yoshida, Chemistry Letters, **41**, 98(2011) .