Lanthanoid coordination and speciation in rare earth minerals using the L_3-edge XANES

A. OHTA[1], K. TANAKA[2]

[1] Geological Survey of Japan, AIST, Tsukuba 305-8567, Japan; a.ohta@aist.go.jp

[2] Japan Atomic Energy Agency, Tokai, Naka, Ibaraki 319-1195, Japan; tanaka.kazuya@jaea.go.jp

X-ray absorption fine structure (XAFS) spectra are a powerful tool for characterizing local coordination and chemical form. However, the proximity of lanthanoid (Ln) L edges and the overlap of Mn and Fe K edges on Ln L edges make it difficult to conduct structure and speciation analysis of geomaterials. Recently, Asakuras' group reported that a full wide at half maximum (FWHM) of the white line at Ln L_3-edge X-ray absorption near edge structure (XANES) relates to the local coordination structures and distortion of local environment around the Ln site (e.g., Asakura *et al*., 2015). Ohta *et al*. (2018) suggested that FWHM values of Ln compounds are rather sensitive to their chemical forms. Thus, we measure lanthanum L_3-edge XANES spectra of monazite, apatite, carbonatite, and ion-adsorption type deposit to characterize their local coordination and chemical forms. As for references, XANES spectra of Ln oxides, Ln aqueous ions, Ln-doped FeOOH, Ln-doped MnO_2, Ln-doped calcite, and Ln-doped humic acid, and Ln-doped clay were also measured.

The FWHM values of Ln^{3+}(aq) and Ln-doped samples decrease in the following order; 1) Ln_2O_3 (coordination number (CN) = 7 for LREE and 6 for HREE), 2) Ln-doped calcite (CN = 7 for LREE and 6 for HREE), 3) Ln-doped FeOOH, MnO_2, and humic acid (CN = 10–9 for LREE and 8 for HREE), 4) Ln^{3+}(aq) (CN = 9 for LREE and 8 for HREE). FWHM values of La L_3-edge XANES of monazite and apatite (CN = 9) are the largest among geomaterials, but smaller than that of La_2O_3. FWHM value of carbonatite is comparable to that of La-doped calcite. FWHM value of ion-adsorption type deposit is the smallest among samples and similar to that of La^{3+}(aq). These results suggest that FWHM values of La L_3-edge XANES relate not only to coordination numbers but also to chemical forms such as carbonate and phosphate. Unfortunately, we cannot obtain analyzable La L_3-edge XANES spectra of xenotime, some ion-adsorption type deposit, and La-doped clay, which have high V/La concentration ratios because of V K-edge XANES spectra overlapped on their spectra.

[References]

Asakura *et al*., 2015. *J. Phys. Chem. C*. **119**, 8070–8077.

Ohta *et al*., 2018. *J. Phys. Chem. A*. **122**, 8152–8161.