

## **Influence of multi-electron excitation on EXAFS spectroscopy of trivalent rare-earth ions and elucidation of change in hydration number through the series**

**ATSUYUKI OHTA,<sup>1,\*</sup> HIROYUKI KAGI,<sup>2</sup> HIROSHI TSUNO,<sup>3</sup> MASAHARU NOMURA,<sup>4</sup> AND IWAO KAWABE<sup>5</sup>**

<sup>1</sup>Geological Survey of Japan, AIST, Tsukuba 305-8567, Japan

<sup>2</sup>Geochemical Laboratory, Graduate School of Science, The University of Tokyo, Tokyo 113-0033, Japan

<sup>3</sup>Faculty of Education and Human Sciences, Yokohama National University, Kanagawa, 240-8501, Japan

<sup>4</sup>Photon Factory, Institute of Materials Structure Science, KEK, Tsukuba 305-0801, Japan

<sup>5</sup>Department of Earth and Planetary Sciences, Graduate School of Environmental Studies, Nagoya University, Nagoya 464-8602, Japan

### **ABSTRACT**

We have made a detailed study of the extended X-ray absorption fine spectra (EXAFS) at the  $K$  edge of aqueous Y ion and at  $L_3$  edges of aqueous lanthanide ions and thereby elucidated the systematic changes in their hydration structures. Anomalous peaks arising from double-electron excitation ( $2p, 4d \rightarrow 5d, 5d$ ) appear in the EXAFS signals of  $\text{La}^{3+}$ - $\text{Tb}^{3+}$  between  $5\text{--}7 \text{ \AA}^{-1}$ . We established a removal process of double-electron excitation from EXAFS spectra. Using that process, we confirmed that the intensity and energy position of the extracted double-electron excitation are comparable to previously reported data. The presence of double-electron excitation engenders a smaller error than the errors estimated in the fitting process. Consequently, double-electron excitation does not seriously affect the determination of the structures of  $\text{REE}^{3+}$  aquo ions in the first coordination sphere. Subsequent EXAFS analyses of hydrated  $\text{REE}^{3+}$  ions suggest that the hydration numbers, the interatomic distances, and the Debye-Waller factors decrease from 9.7, 2.55  $\text{\AA}$ , and  $9.0 \times 10^{-3} \text{ \AA}^2$  for  $\text{La}^{3+}$  to 7.9, 2.31  $\text{\AA}$ , and  $5.7 \times 10^{-3} \text{ \AA}^2$  for  $\text{Lu}^{3+}$ . These parameters change as a sigmoid curve with increasing atomic number. The hydration structures of  $\text{REE}^{3+}$  ions are inferred to change from the nonhydrated structure for  $\text{La}^{3+}$ - $\text{Nd}^{3+}$  to the octahydrated structure for  $\text{Tb}^{3+}$ - $\text{Lu}^{3+}$  through intermediate structures for  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ , and  $\text{Gd}^{3+}$ . In addition, the hydration state of  $\text{Y}^{3+}$  closely resembles that of  $\text{Ho}^{3+}$  because the two have almost identical ionic radii.

**Keywords:** EXAFS, rare-earth elements, multi-electron excitation, hydration structure, structural change