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

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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 L3 edges of aqueous lanthanide ions and thereby elucidated the systematic changes in their hydration structures. Anomalous peaks arising from double-electron excitation (2p, 4d → 5d, 5d) appear in the EXAFS signals of La3+-Tb3+ between 5–7 Å−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 REE3+ aquo ions in the first coordination sphere. Subsequent EXAFS analyses of hydrated REE3+ ions suggest that the hydration numbers, the interatomic distances, and the Debye-Waller factors decrease from 9.7, 2.55 Å, and 9.0 × 10−3 Å2 for La3+ to 7.9, 2.31 Å, and 5.7 × 10−3 Å2 for Lu3+. These parameters change as a sigmoid curve with increasing atomic number. The hydration structures of REE3+ ions are inferred to change from the nonahydrated structure for La3+-Nd3+ to the octahydrated structure for Tb3+-Lu3+ through intermediate structures for Sm3+, Eu3+, and Gd3+. In addition, the hydration state of Y3+ closely resembles that of Ho3+ because the two have almost identical ionic radii.

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

INTRODUCTION

Rare-earth element (REE) complexes are not isomorphous across the entire series because their ionic radii are influenced strongly by the lanthanide effect. For example, the hydration numbers of REE3+ ions change from nine in the first coordination sphere for light REEs (La to Nd) to eight for heavy REEs (Tb-Lu), with intermediate ions (Sm to Gd) having eight or nine waters (Habenschuss and Spedding 1979a, 1979b, 1980). Change in the hydration structure causes anomalous behavior (“S-shape”) in thermodynamic and transport properties (Habenschuss and Spedding 1979a). However, little attention has been devoted to the effect of hydration change of REE aquo ions on thermodynamic properties in geochemistry. Kawabe (1999a, 1999b) and Kawabe et al. (1999) pointed out that the hydration change in the REE series strongly affects REE complexation by carbonate ions and REE partitioning between ferromanganese deposits and seawater. Moreover, Kawabe et al. (1999) and Ohta and Kawabe (2001) showed that the changes of REE coordination in solid phases (Fe oxyhydroxides and Mn dioxide) also affect REE partitioning coefficient patterns. Therefore, investigation of REE coordination both in solid phases and liquid phases is an important study for geochemistry.

The REEs coprecipitated with or adsorbed on Fe-Mn oxides (or oxyhydroxides) both in nature and in the laboratory probably lack long-range order; their coordination states are unknown. Extended X-ray absorption fine structure (EXAFS) spectroscopy is applicable to structural analyses of such materials because it is highly selective to the central elements. In addition, the fluorescent mode is extremely sensitive to minor elements in samples. A disadvantage of the EXAFS method is its larger error for determination of coordination numbers because the coordination number strongly correlates to the Debye-Waller factor (Ohtaki and Radnai 1993). In addition, a small irregular feature caused by a multi-electron excitation is superimposed on the EXAFS oscillation of light REEs (Chaboy and Tyson 1994; Chaboy et al. 1994). Chaboy et al. (1994) and Solera et al. (1995) suggested that multi-electron excitation affects the determination of coordination number and interatomic distance. Different procedures to remove multi-electron excitation from EXAFS spectra have been introduced by researchers (e.g., Chaboy et al. 1994; Kodre et al. 1994; Solera et al. 1995; Allen et al. 2000). It is desirable that we establish an isolation process for the multi-electron excitation and systematically elucidate.