

Structural change of REE coprecipitated with Fe-Mn oxyhydroxides

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Introduction

Ohta et al. [1,2] and Ohta and Kawabe [3] have experimentally and theoretically studied the partitioning reaction of rare earth element (REE) between Fe-Mn deposit and seawater. When analyzing their distribution coefficients theoretically, we need to correct the structural changes, because lanthanide (Ln) complexes are not usually isomorphous in the entire Ln series. Ohta and Kawabe [3] pointed out 1) the proportion of hydroxyl ions to the others ligating REE ions scavenged by δ -MnO₂ increases with solution pH, 2) the preferential adsorption of light Ln onto δ -MnO₂ is obvious compared with their adsorption onto FeOOH. We focus the latter case and have tried to characterize the local structure of Ln adsorbed with δ -MnO₂ and FeOOH with XAFS spectroscopy.

Method

The experimental method was based on the report of [1,3]. Iron(III) oxyhydroxide (FeOOH) and manganese dioxide (δ -MnO₂) were formed and react with La(III) or Nd(III) in 0.5 M NaCl solutions with 1.3 mM NaHCO₃. These precipitates were gently stirred with magnetic stirrers in glass flasks placed in a water bath with 25 °C. After 4 or 5 days, the precipitates were filtrated with polycarbonate membrane filters. The precipitates were dried at 40-50 °C and preserved in plastic bags.

The La-L_{III} and Nd-L_{III} XAFS spectra were recorded in the fluorescence mode at the BL12C of KEK-PF [4] under the atmosphere and at room temperature. The fluorescence X-ray was measured by a 19 element pure-Ge SSD [5]. Analysis of the XAFS spectra was performed with a PC program, REX2000 (Rigaku co.).

Result and Discussion

The δ -MnO₂ and FeOOH adsorbing La or Nd are expressed as Ln/ δ -MnO₂ and Ln/FeOOH (Ln = La and Nd). The Ln/ δ -MnO₂ has a quite similar XANES spectra to Ln/FeOOH. This result indicates that the chemical compound of Ln adsorbed onto δ -MnO₂ is almost as same as those with FeOOH: Ln(OH)₃·nH₂O.

The EXAFS spectra of Ln/ δ -MnO₂ also are not particularly different from those for Ln/FeOOH. Fig. 1 shows the Fourier transform of $k^3\chi(k)$ of Ln/ δ -MnO₂ and Ln/FeOOH. The curve-fitting results were summarized in

Table 1. Fourier transformed spectra of Ln/ δ -MnO₂ and Ln/FeOOH have one large peak at 2 Å (no phase-shift correction). The fitting results of first shell (La-O and Nd-O) suggested that the coordination number of Ln coprecipitated with δ -MnO₂ is possibly different from those with FeOOH (Table 1). This result indicates that the preferential adsorption of light Ln onto δ -MnO₂ is caused by the increase of their hydration numbers.

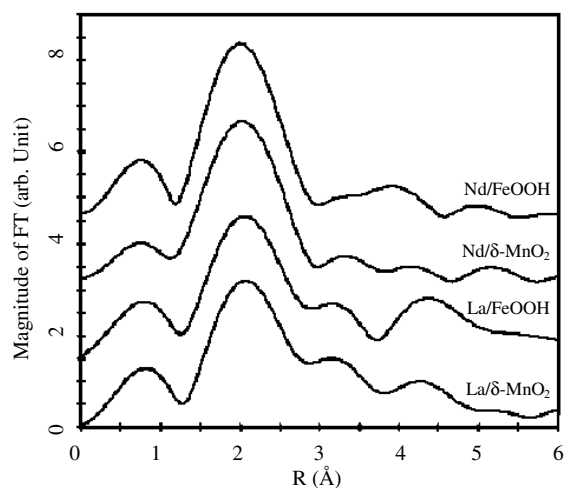


Fig. 1 Fourier transform of k^3 weighted La and Nd L_{III} EXAFS of FeOOH and δ -MnO₂ adsorbing La and Nd. The phase shift is uncorrected.

Table 1: Curve-fitting results for Ln incorporated with FeOOH or δ -MnO₂.

Samples	CN	$R_{Ln-O}/\text{\AA}$	DW/ \AA
La / FeOOH	7.35	2.57	0.117
Nd / FeOOH	7.37	2.51	0.101
La / δ -MnO ₂	7.82	2.58	0.120
Nd / δ -MnO ₂	7.87	2.51	0.108

References

- [1] Ohta A. et al. (2000a), *Geochem. J.* 34, 439-454.
 - [2] Ohta A. et al. (2000b), *Geochem. J.* 34, 455-473.
 - [3] Ohta A. and Kawabe I. (2001), *Geochim. Cosmochimi. Acta* 65, 695-703.
 - [4] Nomura, M. and Koyama, A., KEK Report, 95-15, 1 (1996)
 - [5] Nomura, M., KEK Report, 98-4, 1 (1998).
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