

XAFS characterization of La and Nd coprecipitated with Mn dioxide and Fe oxyhydroxide

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Introduction

Ohta et al. (2000a, b) and Ohta and Kawabe (2001) have experimentally and theoretically studied the partitioning reaction of rare earth element (REE) between Fe-Mn deposit and seawater. When analysing 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 (2001) pointed out that preferential adsorption of light Ln onto δ -MnO₂ is obvious compared with their adsorption onto FeOOH. We have tried to characterize the local structure of Ln coprecipitated with δ -MnO₂ and FeOOH with XAFS spectroscopy, which is recently used to examine structural information of the trace amount of element in poorly crystallized material.

Results and discussion

The δ -MnO₂ and FeOOH adsorbing La or Nd were prepared according to Ohta and Kawabe (2001). We express them as Ln/ δ -MnO₂ and Ln/FeOOH (Ln = La and Nd). The La-L_{III} and Nd-L_{III} XAFS spectra were recorded in the fluorescence mode at the BL12C of KEK-PF at under atmosphere and room temperature (Tsuno et al., 2000).

XANES spectra for Ln/ δ -MnO₂ are quite similar to those for Ln/FeOOH. This result indicates that a La and/or Nd form with δ -MnO₂ (Ln(OH)_n·mH₂O) is almost the same as those with FeOOH: the number of hydroxyl ions ligating Ln³⁺ ions does not change between Ln/ δ -MnO₂ and Ln/FeOOH (Ohta and Kawabe, 2001).

The EXAFS spectra of Ln/ δ -MnO₂ do not particularly different from those for Ln/FeOOH. Fourier transfers spectra of Nd/ δ -MnO₂ and Nd/FeOOH have one large peak, but those of Ln/ δ -MnO₂ and La/FeOOH have the multiple shells. The fitting results of first shell (La-O and Nd-O) suggested that the coordination number of La coprecipitated with δ -MnO₂ is possibly different from those with FeOOH. This result will be explained by the hydration change of La.

References

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Geochemical behavior of minor elements and REE in loam and andosol

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Purpose

We studied the geochemical behavior of natural analogue elements, particularly rare earth elements (REE), U and Th in soil environment.

Samples and analytical methods

The samples were collected from outcrop along the mountain path in Yanagawa Hadano city, Kanagawa Pref., Japan. Point A is the cross section of only andosol and point B is the cross section of soil changing from andosol to loam. These samples were analyzed for major elements, minor elements and REE by using ICP-MS and XRF. Minerals in the samples were identified by X-ray diffraction method (XRD).

Results and Discussion

The minerals consisting of the soil for the primary minerals are feldspar, volcanic glass, olivine, pyroxene, magnetite, zircon etc and the secondary minerals are kaolinite, halloysite, allophane, smectite, maghemite, goethite etc. It is possible that the solubility of these minerals is causing a great effect to the soil elemental mobility. To see the behavior in soil, all the concentration is normalized by Al concentration by using its stability, because it is generally accepted that Al migration is very small due to very small solubility of Al-bearing minerals (halloysite etc). From the result, it is apparent that the concentration of minor elements and REE with depth, and the variation is different from element to element. These difference depends on the solubility of minerals and rock facies. Namely it was found that the behaviors are considerably different in andosol and loam. From the relation between loam and the elements in minerals, it is considered that physical parameters(ionic radius, ionpotential etc) are greatly affecting.

Conclusion

Variation of minor elements during weathering is affected by variety of primary minerals consisting of soil and solubility of minerals. There is significant relation between physical parameter, and concentration change in REE. As to the elemental mobility, REE removed from the soil due to the long-term(about 6,000 years) weathering, but the degree of elemental mobility of REE is less than that of alkali and alkali earth elements but more than that of immobile elements such as Fe, Al, and Mn. U and Th mobilities are very small.