

An experimental study on stable isotopic fractionation of rare earth elements (REE) during the adsorption on iron and ma

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Regarding the isotopic fractionation during the adsorption, it has been clarified that heavier isotopes adsorb onto a solid phase for elements existing as cations in a solution, while elements existing as oxyanions in a solution adsorb lighter isotope fractionation onto a solid phase. However, our study on the stable isotope fractionation of Ce during adsorption on ferrihydrite and d-MnO₂ showed that the heavier isotopes remained in the liquid phase, though Ce should be dissolved as free cation under the experimental condition. This study, therefore, exhibits the results of stable isotopic fractionation of rare earth element (REE) during the adsorption experiment to discuss the cause of the isotopic fractionation among REE.

Lanthanum, Ce, Nd, and Sm chloride solutions were respectively added to both synthesized ferrihydrite and d-MnO₂, with the concentration of REE systematically changed. In all the systems, pH was adjusted to 5.00 (± 0.05) and shaken for 6 hours before the filtration. Stable isotope ratios in both liquid and solid phases were determined using MC-ICP-MS. REE-Cl₃ solutions used in the adsorption experiment were employed as standard solutions and the isotope ratio of each element was expressed in epsilon notation relative to the average standards, which is shown in the equation as follows: $\epsilon = (R_{sample}/R_{STD} - 1) \times 10^4$, where $R = {}^{139}\text{La}/{}^{138}\text{La}$, ${}^{142}\text{Ce}/{}^{140}\text{Ce}$, ${}^{145}\text{Nd}/{}^{143}\text{Nd}$, and ${}^{149}\text{Sm}/{}^{147}\text{Sm}$, respectively. For solid phase, K-edge EXAFS was measured at BL01B1 in SPring-8 to obtain the information of the coordination environment.

Though accurate determination of La isotope ratio was difficult due to the large difference in the isotopic abundance between ${}^{138}\text{La}$ and ${}^{139}\text{La}$, a broad trend obtained here suggested that the lighter isotope was partitioned into the solid phase. On the other hand, in Nd and Sm systems, results clearly show that lighter isotopes remain in the liquid phase, suggesting that physicochemical factors have been changed between Ce and Nd. According to the EXAFS analysis, split first shell (La-O bond) was observed for La-adsorption system, which suggests that the first coordination sphere is distorted in the system. Such distortion is also expected for Ce-adsorption system. On the other hand, split first shell was not observed for Nd and Sm systems. Thus, it is expected that the coordination environment, which can also cause the difference in their hydration numbers, affect the different isotope fractionations among REE.

Keywords: rare earth element, stable isotopic fractionation, XAFS