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Experimental study on cerium isotopic fractionation

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Cerium (Ce) anomaly that appears in rare earth element (REE) pattern is a tool to estimate paleoredox condition and has been used for many studies. Discussion in previous studies, however, has been limited to qualitative based on a REE pattern. In addition, the formation process of Ce anomaly is not fully understood. This study, therefore, aims to provide fundamental information on the redox condition in paleoenvironment by Ce stable isotope ratio related to the redox-sensitive property of Ce. If fractionations of Ce stable isotope respond differently to various geochemical processes such as (i) oxidative scavenging on Mn oxide, (ii) precipitation as CeO₂ or Ce(OH)₄, and (iii) adsorption of Ce³⁺ without oxidation, it is possible that Ce stable isotope ratio can give much information on redox condition in paleoenvironment. It is expected that the coupling of the Ce stable isotope ratio and Ce anomaly can be a unique paleoredox tracer.

In this study, a laboratory experiment under equilibrium condition was conducted. Cerium(III) chloride solution was added to manganese oxide and iron hydroxide, respectively, with various Ce concentration. In both systems, pH was adjusted to 5.00 (± 0.05) and shaken for 6 hours before the filtration using 0.2 micrometer membrane filter. In addition, precipitation of Ce was obtained by bubbling of O₂ gas in the same CeCl₃ solution. Stable isotope ratios of Ce in both liquid and solid phases were determined using a MC-ICP-MS at Kochi Institute for Core Sample Research. The isotope ratios are expressed in standard epsilon notation relative to the average standards, which is shown in an equation as follows; $\epsilon^{142}\text{Ce} = [({}^{142}\text{Ce}/{}^{140}\text{Ce})_{\text{sample}}/({}^{142}\text{Ce}/{}^{140}\text{Ce})_{\text{CeCl}_3} - 1] \times 10000$. For solid phase sample, Ce L_{III}-edge XANES was measured at BL-12C in Photon Factory, and Ce K-edge EXAFS was measured at BL01B1 in SPring-8.

Mean isotopic fractionation factors between liquid and solid phases (a_{Lq-So}) of the systems of (i) adsorption on manganese oxide (ii) adsorption on iron hydroxide, and (iii) spontaneous precipitation of Ce were 1.000411 (± 0.000079), 1.000145 (± 0.000022), and 1.000196 (± 0.000031), respectively. In this case, Ce adsorbed onto Mn oxides was oxidized to tetravalent, while that on Fe hydroxide remains trivalent. In addition, XANES spectrum of the spontaneous precipitation of Ce clearly showed that Ce was tetravalent. These facts indicate that isotopic fractionation of Ce between liquid and solid phases becomes larger as the redox condition becomes oxic in the order of adsorption without oxidation, Ce(IV) precipitation, and oxidative adsorption. Thus, it is suggested that the combination of Ce stable isotope ratio and Ce anomaly which respond differently to various redox conditions can be a useful tracer to discuss the change of redox condition of paleocean.

Keywords: Cerium, Stable isotope, XAFS