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Cerium stable isotopic fractionation as a potential paleo-redox proxy

NAKADA, Ryoichi[1]* ; TANAKA, Masato[1] ; TANIMIZU, Masaharu[2] ; TAKAHASHI, Yoshio[1]

[1]Department of Earth and Planetary Systems Science, Graduate School of Science, Hiroshima University, [2]Kochi Institute for Core Sample Research, JAMSTEC

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 one based on the REE pattern. This study, therefore, aims to provide more quantitative 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 responds differently to various geochemical processes such as (i) oxidative scavenging on Mn oxide, (ii) precipitation as $Ce(OH)_4$, and (iii) adsorption of Ce^{3+} without oxidation, it is possible that Ce stable isotope ratio can give more information on redox condition in paleoenvironment.

Cerium(III) chloride solution was added to manganese oxide and iron hydroxide, respectively, with the concentration of Ce systematically changed. In both systems, pH was adjusted to 5.00, 6.80, 8.20, and 11.0 (± 0.05) and shaken for 6 hours before the filtration using 0.2 μm membrane filter. In addition, precipitation of Ce was obtained by bubbling of O_2 gas in the same $CeCl_3$ solution. Stable isotope ratios of Ce in both liquid and solid phases were determined using MC-ICP-MS at Kochi Institute for Core Sample Research. The $CeCl_3$ solution used in the adsorption experiment was employed as standard solutions and the isotope ratio of each element was expressed in delta notation relative to the average standards, which is shown in the equation as follows: $\delta^{142}Ce = [(142Ce/140Ce)_{sample} / (142Ce/140Ce)_{CeCl3} — 1] \times 10^3$.

Assuming equilibrium isotopic fractionation, the mean isotopic fractionation factor between the liquid and solid phases $\alpha_{Lq?So}$ of Ce adsorbed on ferrihydrite was within the analytical uncertainty for all the pH conditions. Meanwhile, the $\alpha_{Lq?So}$ of Ce adsorbed on δ-MnO_2 was gradually decreased with increasing pH. Most surprisingly, the $\alpha_{Lq?So}$ of spontaneous precipitation of Ce showed that, with increasing pH, the direction of the isotopic fractionation was in contrast to those in the adsorbed systems. These results suggests that the degree of mass-dependent fractionation of Ce can be used to clearly distinguish spontaneous precipitation from oxidative adsorption on δ-MnO_2, that occurs under more oxic conditions than the Ce(III)/Ce(IV) boundary. Our results suggest that the combination of the degrees of mass-dependent fractionation and chemical state of Ce can be used to classify the redox condition into the three stages based on Ce geochemistry, thereby offering a powerful tool for exploring redox conditions in paleo-ocean environments.

Keywords: cerium, stable isotope, redox