

Cerium stable isotope fractionation as a potential paleo-redox proxy

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Cerium (Ce) has anomalously high or low concentrations relative to its neighboring elements, lanthanum (La) and praseodymium (Pr), because of its chemical properties; this phenomenon is known as the Ce anomaly. This redox-sensitive property of Ce allows the estimation of the redox state of paleo-ocean environments and the evolution of the atmosphere. However, a consideration of only the relative abundance of Ce may lead to an incomplete understanding of its oxidation process. In the current study, three important geochemical parameters, namely, abundance, stable isotope ratio, and chemical speciation, were obtained for Ce to derive more information from the Ce anomaly. Assuming equilibrium isotopic fractionation, the mean isotopic fractionation factors between the liquid and solid phases (α_{Lq-Sol}) of (i) Ce adsorbed on ferrihydrite, (ii) spontaneous precipitation of Ce, and (iii) Ce adsorbed on δ -MnO₂ were 1.000145 (± 0.000022), 1.000196 (± 0.000031), and 1.000411 (± 0.000079), respectively. These results indicate that the degree of isotopic fractionation of Ce between the liquid and solid phases becomes larger as the redox condition becomes more oxic in the following order: adsorption without oxidation < spontaneous precipitation < oxidative adsorption. Previously, the appearance of the Ce anomaly and/or XANES analysis constituted the only tool available for exploring the redox state. This study, however, suggests that the degree of mass-dependent fractionation of Ce can be used to clearly distinguish spontaneous precipitation from oxidative adsorption on δ -MnO₂, that occurs under more oxic conditions than the Ce(III)/Ce(IV) boundary. Our results suggest that the combination of the stable isotope ratio 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.

[1] R. Nakada, Y. Takahashi, and M. Tanimizu, Isotopic and speciation study on cerium during its solid-water distribution with implication for Ce stable isotope as a paleo-redox proxy. *Geochim. Cosmochim. Acta* 103 (2013) 49-62.

Stable isotopes of heavy elements in the modern ocean

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Stable isotopes of heavy elements are now emerging as powerful tracers in the modern ocean and proxies in the paleocean (Tanimizu *et al.*, 2013). Mass fractionation of heavy elements in marine environments is expected to provide unique information on a number of processes. The isotopic compositions of dissolved heavy metals in seawater are fundamental data for stable isotope marine chemistry. However, the precise analysis of seawater is highly challenging (Boyle *et al.*, 2012). The target elements occur at nmol/kg to pmol/kg in seawater. For the precise isotopic ratio determination using MC-ICPMS or TIMS, we have to preconcentrate the analytes quantitatively with a 50-1000-fold enrichment factor from a kg scale sample. It is also important to chemically separate the analytes from interfering major and minor constituents. In addition, it is critical to avoid contamination of the analytes through the sampling, pretreatment, chemical separation, and measurement. Preconcentration using chelating resins seems promising for this purpose.

We have developed a new method for the precise determination of Mo isotope ratios in seawater on the basis of preconcentration using the TSK-8HQ chelating resin and measurement by MC-ICPMS (Nakagawa *et al.*, 2008). Using this method, we have analyzed 172 seawater samples obtained from the Pacific, Atlantic, and Southern Oceans, with an oxygen concentration of 16–373 $\mu\text{mol/kg}$ (Nakagawa *et al.*, 2012). The average isotope composition in δMo (relative to a Johnson Matthey Mo standard solution) was as follows: $\delta^{92/95}\text{Mo} = -2.54 \pm 0.16\text{‰}$ (2SD), $\delta^{94/95}\text{Mo} = -0.73 \pm 0.19\text{‰}$, $\delta^{96/95}\text{Mo} = 0.85 \pm 0.07\text{‰}$, $\delta^{97/95}\text{Mo} = 1.68 \pm 0.08\text{‰}$, $\delta^{98/95}\text{Mo} = 2.48 \pm 0.10\text{‰}$, and $\delta^{100/95}\text{Mo} = 4.07 \pm 0.18\text{‰}$. These results demonstrate that Mo isotopes are uniformly distributed in the modern oxic ocean, strongly supporting the possibility of seawater as an international reference material for Mo isotopic composition.

Recently we have developed a new method for the isotopic analysis of dissolved Cu in seawater (Takano *et al.*). We are now studying the isotopic composition of Cu of the modern ocean. Our data suggest that the combination of concentration and isotopic composition of Cu would be useful to evaluate relative significance of biogeochemical processes.