Dissolved species controlling isotope effect for cerium during adsorption and precipitation

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An examination of stable isotopic fractionation of cerium (Ce) during adsorption and precipitation showed that Ce can be used as a (paleo-)redox proxy (Nakada et al., 2013). The experiment was, however, performed under low pH condition which is different from natural seawater. Taking into account the fact that stable chromium isotope showed different fractionation mechanisms between acidic and neutral pH condition (Zink et al., 2010), an examination between Ce stable isotopic fractionation and dissolved Ce species is of great importance for the better understanding of the factors controlling isotopic fractionation of heavy elements.

Cerium chloride solution with various concentrations were added to both synthesized ferrihydrite and δ-MnO_2 suspensions. In addition, the same solution was bubbled by O_2 gas to obtain the spontaneous precipitation of Ce as $Ce(OH)_4$. In all the systems, pH was adjusted to 6.80, 8.20, and 11.00 (± 0.05) with 2.25 mM dissolved carbonate concentration. $CeCl_3$ solution used in the experiments was employed as a standard of stable Ce isotope ratios, which is shown in the equation as follows: $\delta^{142}Ce = (R_{sample}/R_{STD} - 1)\times10^3$, where R was defined as $^{142}Ce/^{140}Ce$. For the solid phase, K-edge EXAFS of filtered samples was measured at BL01B1 in SPring-8 to obtain the information of the coordination environment. DFT calculation was also performed to investigate the cause of isotopic fractionation.

The mean isotopic fractionation of Ce/ferrihydrite system was almost constant irrespective of dissolved Ce species, while that of Ce/δ-MnO_2 system gradually became smaller with increasing pH. Heavier isotope was enriched in the liquid phases for these two systems. However, lighter Ce was enriched in the liquid phase for Ce/precipitation system at pH=8.20 and 11.00, where $Ce(CO_3)_2^-$ species dominates. The EXAFS spectra of Ce precipitates showed $Ce(OH)_4$ for all the pH condition, meaning that dissolved species controll the isotopic fractionation. Indeed, DFT calculation confirmed the lighter isotope enrichment in the liquid phase with increasing carbonate ions.