

Stable cerium (Ce) isotope fractionation during sorption by different iron oxides: a combined isotope and XAFS study

WEIMING DING¹, WEI REN², YANYI YANG², TINGYING XU² AND XINYUAN ZHENG¹

¹University of Minnesota - Twin Cities

²Oklahoma State University

Presenting Author: ding0304@umn.edu

Recent analytical advances have made it possible to resolve natural stable isotopic variations of several rare earth elements. Stable Ce isotope ratios ($^{142}\text{Ce}/^{140}\text{Ce}$) are of particular interest due to unique redox properties of Ce. Previous studies have shown that Ce can be oxidized by $\delta\text{-MnO}_2$, and this oxidative adsorption is associated with larger Ce isotope fractionation relative to non-oxidative adsorption of Ce on ferrihydrite (Nakada et al. 2013, 2017). These results highlighted the great potential of stable Ce isotopes as a novel tracer to infer suboxic redox cycling of manganese in the geological past. Cerium speciation during adsorption by other common iron oxides (e.g., hematite, goethite), however, remain ambiguous. For example, contradicting results were previously reported with regard to whether or not Ce could be oxidized by goethite minerals (Li et al. 2023; Yu et al. 2017). Stable Ce isotope fractionation during (ad)sorption by common Fe oxides is unknown.

Here, we report results from a series of laboratory experiments intended to quantify stable Ce isotope fractionation during Ce (ad)sorption by various Fe (hydro-)oxides widespread in nature, including two-line ferrihydrite, goethite, and hematite. Cerium speciation on minerals was characterized by synchrotron-based X-ray absorption near edge spectroscopy (XANES) analyses. Our results confirmed that ferrihydrite cannot oxidize Ce^{3+} even in the presence of ambient atmospheric O_2 . Intriguingly, we discovered for the first time that hematite could easily oxidize Ce under ambient environments, regardless the morphological variations of the mineral. Goethite could oxidize Ce only when the initial Ce loading was low. Meanwhile, our stable Ce isotope data quantified different Ce isotope fractionation during (ad)sorption by ferrihydrite, hematite, and goethite. Combined with previous studies on Ce isotope fractionation during oxidative adsorption by Mn oxides, our results provide an essential framework to interpret stable Ce isotope data in natural Fe- and/or Mn-rich samples, such as Precambrian banded iron formations, marine Fe-Mn crusts, and Fe-Mn oxides in marine sediments.

Nakata et al. 2013, *GCA*, 103, 49-62. Nakada et al. 2017, *GCA*, 218, 273-290. Li et al. 2023, *EPSL*, 602, 117962. Yu et al. 2017, *GCA*, 199, 370-389.