

The effect of particle size on stable cerium (Ce) isotope fractionation and isotope exchange kinetics between soluble and sorbed Ce species

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Previous experimental studies have demonstrated significantly larger fractionation of stable Ce isotope ratios ($^{142}\text{Ce}/^{140}\text{Ce}$) during oxidative sorption of Ce onto $\delta\text{-MnO}_2$ surfaces in contrast to non-oxidative adsorption onto ferrihydrite (Nakada et al. 2013, 2017). It also has been observed that $^{142}\text{Ce}/^{140}\text{Ce}$ variations in modern weathering profiles are closely related to the presence of Mn oxides (Li et al., 2023), underscoring the potential of stable Ce isotope as a useful redox proxy for investigating environmental changes related to manganese (Mn) cycles. However, a comprehensive understanding of the factors controlling Ce isotope fractionation across various geological processes remains lacking. Notably, the impact of particle size on Ce isotope fractionation for the same mineral phase has yet to be explored, limiting our ability to fully interpret natural $^{142}\text{Ce}/^{140}\text{Ce}$ variability. Additionally, uncertainty remains regarding whether isotope exchange between soluble and sorbed Ce species continues after the system reaches steady state.

We conducted laboratory experiments to investigate Ce isotope fractionation during sorption onto two types of magnetite that have different particle sizes, namely, micron-sized ($<5\ \mu\text{m}$) and nano-sized magnetite (50-100 nm). Interestingly, we discovered for the first time that nano-sized magnetite can partially oxidize Ce under ambient conditions via synchrotron analyses and is accompanied by a large isotopic fractionation of 0.279‰ with sorbed Ce being isotopically lighter. In contrast, micron-sized magnetite surfaces cannot oxidize Ce and produced a perceptibly smaller isotopic fractionation of 0.118‰. Additionally, we explored the isotopic exchange kinetics between soluble and sorbed Ce species through enriched Ce isotope tracer experiments using several different iron oxide minerals. A small amount of ^{142}Ce -enriched spike solution was introduced into each reactor after the steady state to increase the $^{142}\text{Ce}/^{140}\text{Ce}$ ratio in the liquid phase without significantly disrupting the chemical steady state. The extent of isotope exchange between soluble and sorbed Ce species was determined by monitoring changes in $^{142}\text{Ce}/^{140}\text{Ce}$ ratios of the liquid phase over time. Our study provides an essential framework for understanding the behavior of stable Ce isotope fractionation.

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