Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.16508

Stable Ce isotopic composition of the ca. 2.4 Ga Hotazel Formation, South Africa: A deep-water oxygenation in the marine basin at the early stage of the Great Oxidation Episode

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Oxidation of Earth's atmosphere and oceans through the Great Oxidation Episode (GOE) is a turning point in the geological history of our planet and one of the driving factors for the evolution of complex life. The timing, magnitude, trajectory, and origin of this event have been investigated in ancient sedimentary rocks using multiple redox proxies. With its double redox state, Ce is a Rare Earth Element (REE) sensitive to redox conditions. Presence of negative Ce anomalies in REE patterns of sediments have been widely used as evidence for oxic water-column condition. We report stable Ce isotopic composition of modern and ancient lithologies to provide a new perspective on the redox state of the oceans during early stage of the GOE.

We developed a protocol to separate Ce from its rock matrix and measured stable Ce isotope compositions as $\varepsilon^{142}Ce$ ($[(^{142}Ce/^{140}Ce)_{sample}/(^{142}Ce/^{140}Ce)_{AMES\ standard})-1]*10^4$) using MC-ICP-MS (Neptune Plus). Natural samples and synthetic standard solutions were doped with Sm to correct for instrumental mass fractionation using the exponential law. Multiple measurements of Ce AMES standards yielded an average $\varepsilon^{142}Ce = 0.03 \pm 0.78$ (2SD; n=204). Igneous and terrigenous sedimentary rock standards analyzed so far produced $\varepsilon^{142}Ce$ values indistinguishable within uncertainty from the AMES standard. We found strongly fractionated Ce isotopic composition in iron formations (IFs) and Mn deposits of the ca. 2.4 Ga Hotazel Formation, South Africa. The Hotazel Formation deposited in the aftermath of the oldest Paleoproterozoic glacial event records the onset of the GOE. It contains cycles of Fe and Mn deposits linked to sea-level changes in a redox-stratified basin. Both IFs and Mn deposits have seawater-like REE patterns suggesting deposition under open-marine condition. All Hotazel Formation samples have positive $\varepsilon^{142}Ce$ values, up to +3.3, similar to those measured in modern hydrogenous Fe-Mn nodules[1]. Positive $\varepsilon^{142}Ce$ are also present in samples with no Ce anomalies, suggesting that Ce isotopic composition might be more sensitive to redox conditions than Ce anomalies. Stable Ce isotope fractionation in the ca. 2.4 Ga Hotazel Formation require deep-water oxygenation in the basin at the early stage of the GOE.

[1] Nakada et al., (2016), GCA 181, 89-100.