Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.28191

Evolution of Cerium (Ce) redox state in chemical sedimentary rocks: Inferences from Synchrotron-based X-ray absorption near-edge-structure (XANES) and stable Ce isotope geochemistry

DR. PALLABI BASU[1], MARION GARÇON[2], MAUD BOYET[3], TAHAR HAMMOUDA[4], ANDREY BEKKER[5], OLIVIER PROUX[6] AND JEAN-LOUIS HAZEMANN[7]

[1]CNRS-LMV Clermont-Ferrand
[2]Université Clermont Auvergne, CNRS, IRD, OPGC, Laboratoire Magmas et Volcans, F-63000 Clermont-Ferrand, France
[3]Université Clermont Auvergne
[4]Université Clermont Auvergne, LMV
[5]University of California, Riverside
[6]OSUG, CNRS-Univ. Grenoble Alpes, Saint Martin d'Hères
[7]Univ. Grenoble Alpes, Inst NEEL, F-38000 Grenoble, France

The accumulation of free oxygen in the Earth's ocean-atmosphere system during the Great Oxidation Event (GOE) exerted primary control on the emergence and evolution of complex life on Earth [1]. Cerium (Ce) is among few widely used redox-sensitive elements to constrain this transition. The redox couple Ce(III)/Ce(IV) has a standard potential close to manganese redox couple Mn(II)/Mn(IV). In the modern oxic environment, oxidation of Ce (III) to Ce (IV) is driven by O_2 and adsorption on Mn-oxyhydroxides.

We report combined measurement of Ce L_3-edge HERFD-XANES spectra and stable Ce isotope composition (δ^{142}Ce) of fourteen chemical sedimentary rocks to reconstruct the redox potential of Earth's early oceans. The XANES measurements were performed at BM16 FAME UHD beamline at the ESRF. The relative proportion of Ce (III) and Ce (IV) in the samples was calculated by linear combination fitting (LCF) with reference spectra of Ce standards [2]. The pre-GOE Isua (ca. 3.7 Ga) and Abitibi (ca. 2.7 Ga) iron formations (IFs) contain Ce entirely in Ce (III) state. These IFs also show limited variability in δ^{142}Ce composition (<0.2‰) but the variation is resolved considering our analytical precision (0.05‰, 2SD). In contrast, the syn-GOE (ca. 2.4 Ga) Hotazel Fe and Mn-rich sedimentary rocks record a large range in Ce oxidation state (Ce^{4+}/Ce_{Total}) and δ^{142}Ce up to 0.3‰. The oxidation state of Ce in the Hotazel Fe and Mn-rich rocks is linked to the Mn/Fe ratio and Mn-mineralogy of the sediments, indicating that adsorption on Mn-bearing minerals played a key role in the oxidation of Ce(III) to Ce(IV). The abundance of Ce (IV) and fractionated δ^{142}Ce measured in these samples mirror the results obtained for modern ferromanganese nodules [3,4]. Our study indicates active Ce redox cycle operating in the early oceans during the onset of the GOE before the appearance of significant negative Ce anomalies in the global sedimentary rock record [5].

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