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Stable Ce isotopic composition of chemical sedimentary rocks from the Transvaal Supergroup, South Africa confirms oscillatory oceanic redox during the early stage of the Great Oxidation Event

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Stable Ce isotope composition of chemical sedimentary rocks is an emerging proxy to estimate redox state of marine environments[1,2]. In the modern oxygenated ocean, Ce(III) is oxidised to Ce(IV) and precipitates from the water column. Cerium isotopic fractionation occurs during redox reactions and precipitation/adsorption[1,2]. We explored stable Ce isotope composition of chemical sedimentary rocks as a paleo-redox proxy. Stable Ce isotope composition (defined as $\varepsilon^{142}Ce = [(^{142}Ce/^{140}Ce_{Sample})/(^{142}Ce/^{140}Ce_{Standard})-1] *10^4$) was measured using a MC-ICP-MS (Neptune Plus). Multiple measurements of Ce AMES standard over two years yielded $\varepsilon^{142}Ce = 0.01 \pm 0.60$ (n=550). The Transvaal Supergroup records deposition of chemical sedimentary rocks during the early stage of the Great Oxidation Event (GOE). A total of 50 samples including Kuruman and Koegas iron formations (IFs) leading to the GOE, syn-GOE Hotazel IFs-Mn formations (MnFs), Beaumont jaspillites, and Mooidraai carbonates were analysed for their chemical composition (major and trace elements) and $\varepsilon^{142}Ce$ composition. Detritus-free chemical sedimentary rocks show modern seawater-like non-redox driven REY anomalies and superchondritic Y/Ho ratio, indicating well-preserved marine signal. Trace element analyses by LA-ICP-MS indicate that Ce is closely associated with Mn. The $\varepsilon^{142}Ce$ composition of the chemical sedimentary rocks strongly depends on Al and Zr contents, with terrigenous detritus significantly lowering the $\varepsilon^{142}Ce$ values towards zero *i.e.* the modern upper continental crust (UCC)[3] composition. The detritus-free Kuruman and Koegas Group IFs show fractionated $\varepsilon^{142}Ce$ composition up to +2.6, substantially higher than the UCC. The IFs and MnFs of the syn-GOE Hotazel Formation, deposited on the upper continental slope during an oxygenation event, also show highly fractionated $\varepsilon^{142}Ce$ up to +3.5. Syn-GOE, deep-water Beaumont jaspillites with lower Fe and Mn contents than that of IFs-MnFs have near-to-zero $\varepsilon^{142}Ce$ values. The magnitude of Ce isotopic fractionation further decreases in syn-GOE, shallow-marine Mooidrai carbonates deposited during a deoxygenation event[4]. The Ce isotope proxy further confirms the previously inferred oscillatory nature of atmospheric and shallow-ocean oxygenation at the early stage of the GOE.

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

[2] Bonnand et al., (2023) Geochem Persp Let (28) 27-30

[3]Li et al., (2023) GCA (359) 20-29

[4]Gumsley et al. (2017) PNAS (114) 1811-1816