Anoxic conditions in ~2.48 Ga old Transvaal shallow marine habitats

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Stromatolitic carbonates are shallow-marine, biogenic chemical sediments that provide an excellent archive of geochemical proxies for Early Earth's seawater. Here we report rare earths and yttrium (REY) data and Nd and Mo isotope signatures of stromatolitic carbonates from the ~2.48 Ga old Rooinekke Formation, Transvaal Supergroup (South Africa). Underlying the Makganyene diamictite, these limestones formed immediately before the Great Oxidation Event (GOE).

The shale-normalized REY patterns of the biogenic limestones are (except for redox-sensitive Ce) sub-parallel to those of modern seawater and show positive La_{SN} and Gd_{SN} anomalies, Yb_{SN}/Pr_{SN} ratios >3 and super-chondritic Y/Ho ratios, indicating a pristine seawater-derived REY budget. However, the lack of negative Ce_{SN} anomalies indicates anoxic environmental conditions that did not allow Ce(III) oxidation to Ce(IV) during terrestrial weathering and in the shallow marine photic environment in which the Rooinekke stromatolites formed. The lack of positive Eu_{SN} anomalies reveals insignificant REY input from black smoker-style, high-temperature hydrothermal fluids to shallow marine "Transvaal" seawater, which is consistent with Nd isotope data that suggest only minor to negligible input of mantle Nd.

The Mo isotopic composition of the stromatolitic limestones is close to crustal values and ranges from 0.13 to 0.53 ‰ for $\delta^{98/95}$Mo. This relatively small fractionation of Mo isotopes corroborates the absence of Ce_{SN} anomalies and supports low oxygen levels in the atmosphere and in shallow seawater during the deposition of the Rooinekke Fm. This is in marked contrast to significantly stronger Mo isotope fractionation in the older (~2.64-2.50 Ga) Ghaap Group, that suggests the presence of free atmospheric oxygen at the time of carbonate deposition [1]. Our new study, therefore, provides further evidence for significant short-term fluctuations of the redox level of the atmosphere-hydrosphere system immediately before and after the GOE.

[1] Voegelin et al. (2010). *Precam. Res.* 182, 70-82.