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Marine Mn(IV) micronodules at the dawn of the Great Oxidation Event

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Manganese-rich sedimentary rocks from the record pre-dating the Great Oxidation Event (GOE) are scarce. Archean and Paleoproterozoic Iron Formations (IF) are occasionally enriched in bulk-rock Mn by a few wt% and have thus been the focus of intensive research in the context of the coevolution of oxygen and life in deep time [1,2]. Popular interpretations invoke transiently fully oxic marine conditions across the ambient water column during IF deposition, capable of oxidising aqueous Mn(II) to insoluble Mn(IV) oxides in the presence of photosynthetic O_2. Molybdenum isotope ratios combined with low-$\delta^{13}C$ carbonates have been used as records of such processes through anaerobic diagenesis. Positive Ce anomalies offering additional support of aerobic Mn(II) oxidation to Mn(IV), however, are lacking. This applies even to the giant IF-hosted Mn deposits of the ~2.4Ga Hotazel Formation which are the largest accumulation of sedimentary Mn in pre-GOE oceans [3]. Here, aerobic oxidation of Mn(II) to Mn(III) is thought to be the main driver for primary Mn deposition, implying little to no concomitant oxidation of Ce(III) to Ce(IV).

Unequivocal evidence for oxidation of Mn and Ce to their tetravalent states is preserved in a thin (~3m) Mn-rich horizon at the base of the ca. 2.3Ga Lephala black shale sequence of Botswana, a lateral equivalent to the syn-GOE Timeball Hill Formation in adjacent South Africa. The Mn-rich bed contains well-preserved, mm-scale micronodules with spectacular concentric rings, akin to Mn nodules at the modern ocean floor. The Lephala nodules are pseudomorphically preserved through replacement by various Mn-rich, low-$\delta^{13}C$ carbonate phases (mainly kutnahorite). Bulk-rock geochemistry records spectacular positive Ce anomalies (Ce/Ce^*=1.5-3) in all samples, which support a Ce(IV)-bearing, Mn(IV) precursor. These signatures appear to be preserved thereafter in various sedimentary Mn deposits across the entire Rhyacian period. We contend that the Lephala Mn nodules may record the development of Mn oxidizing bacteria capable of driving complete oxidation of Mn(II) to Mn(IV) for the first time at the dawn of the GOE.

[1] Planavsky et al., 2014. Nat. Geosci. 7, 283-286
[2] Kurzweil et al., 2016. Earth Planet. Sci. Lett. 452, 69-78
[3] Mhlanga et al., 2023. Earth-Sci Rev. 104759