Oxidation pathway for iron-rich stromatolites deposited in the lead up to the GOE

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The role of cyanobacteria in building pre-GOE stromatolites has been inferred back to 2.7 Ga [1], and geochemical proxies suggest shallow-marine oxygen oases up to 500 Myr before the GOE [*e.g.* 2-4], but alternative interpretations exist [5], and an O_2 production site for pre-GOE oxygen oases has not yet been geochemically fingerprinted. We present Fe isotopic and elemental data for stromatolitic layers at the top of the 2.43 Ga Griquatown Granular Iron Formation (GIF), Western Kaapvaal craton, South Africa. The stromatolite layer overlies the above-wave-base GIF, and large reworked fragments between intact stromatolitic columns indicate their formation in a high energy environment. An apparent gradual contact with the 2.42 Ga Makganyene diamictite, which has been linked to global glaciation driven by surface oxidation and destruction of methane [6], lies ~7 m above the stromatolitic horizon. These samples thus provide a chance to explore for signatures of pre-GOE O_2 production.

Bulk $\delta^{56}Fe$ values for stromatolites span a narrow range of strongly negative values between -1.45 and -1.55 ‰. Negative $\delta^{56}Fe$ values indicate partial removal of isotopically heavy phases from Fe^{2+} in upwelling waters. The $\delta^{56}Fe$ range is narrower than variations typically seen at centimeter-scale in deep-water BIFs formed by partial Fe^{2+} oxidation, and implies quantitative oxidation of dissolved Fe^{2+} by O_2 produced near stromatolite surfaces. High Mn/Fe ratios and negative $\delta^{56}Fe$ are similar to those for Mn-rich IFs formed in pre- or syn-GOE oxygenated environments [2,3]. Co-enrichment of Fe and Mn within stromatolitic layers, and Ce/Ce*>1, imply that Mn and Ce were oxidized along with Fe in the lead up to the GOE [7].

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