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Dynamic marine redox evolution and transient oxygenation at 1.64 Ga: Constraints from a thallium isotope spatial transect

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The mid-Proterozoic (1.7–0.7 Ga) ocean has long been regarded as persistently anoxic[1], whereas emerging evidence suggests the occurrence of transient oxygenation[2]. Thallium (Tl) isotopes (ε^{205}Tl) serve as a robust paleo-redox proxy, primarily tracking the burial of manganese oxides (Mn oxides), providing constraints on global marine redox conditions. Tl isotope records from the early Mesoproterozoic remain sparse, limiting constraints on the global redox architecture. Here, we target the ~1.64 Ga Barney Creek Formation (McArthur Basin, Australia), utilizing three stratigraphically equivalent sections from drill cores (H6, BC3 and BMR2). These cores span a proximal to distal gradient relative to the seafloor hydrothermal system associated with the supergiant McArthur River (HYC) Zn-Pb-Ag deposit.

Tl isotope records exhibit pronounced spatial heterogeneity. The proximal H6 section (~2 km from the hydrothermal center) and intermediate BC3 section (~15km) exhibit significant negative Tl isotope excursions, reaching −5.44 in H6, which is likely more restricted in the basin. In contrast, the distal and more connected BMR2 core (~23 km) records consistent values closer to typical input values (–2.60 ± 1.84, 2SD). These patterns indicate that the global ocean was not pervasively burying Mn oxides at 1.64 Ga, while more restricted McArthur Basin samples record localized Mn oxide deposition.

The negative ε^{205}Tl excursions are confined to H6 and BC3 despite the BMR2 being most favorable for capturing open ocean signals. We therefore propose a “Hydrothermal Mn Pump” hypothesis, in which hydrothermal fluids supplied dissolved Mn that mixed with upper oxygenated seawater, triggering basin burial of Mn oxide (likely hexagonal birnessite) and oxidative Tl uptake. The absence of negative shift in BMR2 reflects limited open ocean Mn oxide burial. Collectively, the Barney Creek record implies appreciable oxidative capacity at ~1.64 Ga sufficient to sustain Mn cycling at least in local regions during the early Mesoproterozoic redox dynamics.

[1] Planavsky, N. J. *et al.* Low Mid-Proterozoic atmospheric oxygen levels and the delayed rise of animals. *Science* **346**, 635–638 (2014).

[2] Zhang, S. *et al.* Sufficient oxygen for animal respiration 1,400 million years ago. *Proc. Natl. Acad. Sci.* **113**, 1731–1736 (2016).