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Congruent oxygen fluctuations in Earth's atmosphere and oceans across the GOE

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Our understanding of Earth's Great Oxidation Event (GOE) continues to sharpen, thanks in large measure to an expanding record of sulfur mass-independent fractionation (S-MIF). One recent breakthrough was the discovery of multiple S-MIF reappearances in sulfides from the Rooihoogte and Timeball Hill formations from South Africa [1]. These new S-MIF data require brief returns to a broadly anoxic atmospheric state, and thus a dynamic and protracted initial rise of molecular oxygen (O_2) in Earth's atmosphere during the GOE.

While S-MIF is a very useful tool for tracking the history of O_2 in Earth's atmosphere, it provides no direct information about the history of O_2 in contemporaneous seawater. To help fill this knowledge gap, we applied the thallium (Tl) isotope paleoredox proxy to shales from the Rooihoogte and Timeball Hill formations. Most of the samples we targeted are independently confirmed as having formed beneath an anoxic water column (the same samples targeted in [1]). By analogy with modern equivalents, these shales should be reliable archives of past seawater Tl isotope compositions (ϵ^{205}Tl). The seawater ϵ^{205}Tl value today is, and was probably also in Earth's past, extremely sensitive to sedimentary Mn oxide burial, a phenomenon that takes place exclusively when O_2 is present in marine bottom waters. Generally speaking, lower seawater ϵ^{205}Tl values equate to more Mn oxide burial, and hence a better oxygenated ocean (cf., today).

Shales lacking a S-MIF signal reveal coherent trends toward lower ϵ^{205}Tl values, whereas shales bearing a S-MIF signal reveal shifts to invariant and near-crustal ϵ^{205}Tl values. Interpreted straightforwardly, these paired trends track congruent redox changes to Earth's atmosphere and oceans across the GOE. At times when O_2 briefly accumulated in Earth's atmosphere, congruent O_2 accumulation in the ocean, on an at least regional scale, stimulated widespread Mn oxide burial on the seafloor. And when Earth's atmosphere returned to a broadly anoxic state, congruent oceanic anoxia prevented Mn oxide burial. Our new Tl isotope data confirm the recently identified O_2 dynamics of Earth's atmosphere across the GOE and extend their impact to the marine realm.

[1] Poulton. S.W., et al., *Nature* 592, 232-236 (2021).