

Linking atmospheric oxygenation to marine deoxygenation during Earth's Great Oxidation

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The ~2.35 to 2.32 Ga [1, 2] correlative Duitschland and Rooihogte formations (Transvaal Supergroup, South Africa) archive a singular shift from mass-independent (MIF-S) to mass-dependent fractionation of sulfur isotopes MDF-S [3, 4], indicating oxygenation of the atmosphere above 10⁻⁶ of its present level [5]. While multiple sulfur isotope systematics from the Duitschland/Rooihogte formations have fundamentally shaped our understanding of atmospheric oxygenation during the time of their deposition, the contemporaneous redox evolution of shallow to deep water masses of the Transvaal basin has so far received comparatively little attention.

Here we present geochemical transects focusing on marine redox proxies ($\delta^{98}\text{Mo}$, $\delta^{34}\text{S}$, $\delta^{13}\text{C}$, total S, TOC, Mo, U, V) from four drill cores of the *CIMERA-Agouron GOE and Biomarker Drilling Project* intersecting the Duitschland/Rooihogte formations and the overlying lowermost Timeball Hill Formation. Our new geochemical data disclose an interesting, however, somewhat counterintuitive marine response to increasing atmospheric oxygen levels. In stratigraphic intervals predating MIF-S loss, $\delta^{98}\text{Mo}_{\text{NIST}+0.25}$ compositions display strongly negative values along with sedimentary MnO concentrations accompanied by two-fold MnO enrichments relative to the Post Archean Average Shale (PAAS), indicating a marine redox landscape with suboxic-oxic conditions. Remarkably, just succeeding the loss of MIF-S, Mo-isotope data document an approximately +1 ‰ shift in $\delta^{98}\text{Mo}_{\text{NIST}+0.25}$ accompanied by increasing Fe/Mn ratios, TOC and sulfur contents, and a negative trend in $\delta^{34}\text{S}$ from approximately +10 to -25 ‰, indicative of bacterial sulfate reduction at the sediment-water interface. The combined observations in the mentioned parameters expose a geobiological feedback-driven causality between the earliest oxygenation of the atmosphere and decreased redox potentials of deeper marine environments, at least within the Transvaal Basin.

[1] Zeh et al. (2020), *Precambrian Research* 345, p. 105760

[2] Hannah et al. (2004), *Earth and Planetary Science Letters* 225, p. 43-52

[3] Luo et al. (2016), *Science Adv.* 2(5), p. e1600134

[4] Guo et al. (2009), *Geology* 37(5), p. 399-402

[5] A. Pavlov, J. Kasting (2016), *Science* 289, p. 756-758