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Marine iron and calcium isotope stratification at the dawn of the Great Oxidation Event

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The iron isotope composition of Precambrian Iron Formations (IFs) records a broadly declining secular trend across the Neoarchaean and Paleoproterozoic, in response to increasingly oxidative conditions driving isotopically heavy, primary ferric iron precipitation, combined with Rayleigh fractionation effects on the residual oceanic $Fe(II)_{aq}$ inventory [1]. Recent studies couple this iron isotope trend with a correspondingly increasing Mn/Fe ratio of IF [2]. In this light, the *ca*. 2.4Ga manganiferous Hotazel IF represents a terminal sedimentary sequence of isotopically lightest Fe isotope signature and highest Mn/Fe ratio at the dawn of the Great Oxidation Event (GOE).

Iron isotope results from the Hotazel strata indicate that the Mn-rich, hematitic fraction of the rocks constitutes the isotopically lightest subfacies, with $\delta^{56}Fe$ values generally ranging between -2 and -3 per mil. By comparison, IF samples *sensu stricto* are essentially hematite- and Mn-free and record $\delta^{56}Fe$ values approximately one per mil heavier on average. Such isotopic relationship is at apparent odds with a common Fe(III) precursor for hematite and magnetite, if it is assumed that the latter represents the product of partial dissimilatory iron reduction during organic matter diagenesis. A more plausible interpretation for the Hotazel iron isotope data would suggest that the two oxides originate from mineral nucleation processes reflecting isotopically distinct parcels of the ambient water column. Iron isotope stratification is envisaged to have resulted from the operation of a Mn shuttle, with Mn(III) acting as key electron acceptor for $Fe(II)_{aq}$ oxidation.

Ongoing work indicates that isotopic stratification in the Hotazel paleobasin also extends to Ca isotopes, as registered in the IF and Mn-rich rocks. The $\delta^{44}Ca$ data for the IF range between -1,5 and -0,5 per mil, and compare well with similar data from Neoarchean carbonates [3]. Manganiferous samples, by contrast, are distinctly heavier, ranging between -0,5 and 0,5 per mil. We favor an interpretation for water-column stratification with respect to Ca isotopes and against a common primary origin of $CaCO_3$ across the various Hotazel subfacies.

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[3] Blättler, C.L., et al., (2017). *Nature Geoscience* 10, 41-45.