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Reassessing processes of primary deposition and diagenesis of iron and manganese, using cm-scale variations in iron and carbon isotope ratios of the Palaeoproterozoic Hotazel Formation,

South Africa.

Mhlanga, X.R.¹, Tsikos, H. ¹, Rouxel, O.², Harris, C.³ and Lyons, T.W.⁴



¹ Geology Department, Rhodes University, Grahamstown, South Africa. Mhlangaxr@live.com

² Universite Europe ene de Bretagne, Institut Universitaire Europe en de la Mer, Plouzane 29280, France

³ Department of Geological Sciences, University of Cape Town, South Africa

⁴ Department of Earth Sciences, University of California at Riverside, USA

The Palaeoproterozoic Hotazel Formation in the Transvaal Supergroup of South Africa represents an unusual sequence of banded iron formation (BIF) interbedded with Mn-rich layers, in the form of three sedimentary cycles. The sequence has been interpreted as the product of cyclic Fe and Mn deposition in a marine environment that post-dated the first major event of atmosphere oxygenation at ~2.3Ga, known as the Great Oxidation Event (GOE), despite the fact that geochronological constrains for the Hotazel rocks remain conjectural. The Hotazel deposits are thought to represent the products of anaerobic redox processes involving coupled organic carbon oxidation and reduction of precursor high-valence Fe/Mn oxy-hydroxides in the diagenetic environment. Here we re-assess diagenetic models postulated for the formation of the Fe- and Mn-rich assemblages of the Hotazel Formation, using cm-scale variations in bulk carbonate carbon and iron isotope results combined with major element ratios and modal mineralogy, from three mineralogically and geochemically contrasting rock types: magnetite/Fe-carbonate-rich BIF; Mn carbonate/braunite-rich manganese ore; and transitional hematite/Mn-carbonate lutite.

Low $\delta^{13}\text{C}$ and $\delta^{56}\text{Fe}$ values are recorded in all three rock types examined. Fourteen consecutive sub-samples collected across a continuous 32 cm-long BIF section, have a mean $\delta^{13}\text{C}_{\text{carb}}$ value of $-10.4 \pm 0.7\%$ and a mean $\delta^{56}\text{Fe}_{\text{bulk}}$ value of $-1.9 \pm 0.05\%$. Ten sub-samples from a 24cm-long hematite lutite section show comparatively lower mean δ values for both isotopes ($\delta^{13}\text{C}$ $-12.3 \pm 0.2\%$; $\delta^{56}\text{Fe}$ $-2.1 \pm 0.04\%$), whereas eight sub-samples taken across a 20cm-long section of manganese ore, record a mean $\delta^{13}\text{C}$ value of $-10.5 \pm 0.4\%$ and a mean $\delta^{56}\text{Fe}$ value of $-1.7 \pm 0.1\%$. In terms of major element ratio

geochemistry, the BIF sample set has a Fe/Ca ratio ranging from 2.60 to 16.45, the hematite lutite set has a Fe/Ca ratio of 5.40 to 9.62, and the manganese ore set have has a Mn/Ca ratio ranging between 2.45 and 3.81. These ratios directly reflect the variable proportions of magnetite *versus* ankerite; hematite *versus* kutnahorite; and braunite *versus* Mn calcite respectively, all of whom are the key species controlling relative abundance, distribution and speciation of Fe, Mn and C in the examined samples.

The surprisingly invariant and low carbon and iron isotopic signals, coupled with the small-scale variations in bulk modal mineralogy, carbonate mineral chemistry and bulk oxidation state of the examined rocks in terms of both Fe and Mn, appear to be at odds with classic diagenetic models involving organic carbon oxidation and Fe/Mn reduction. In theory, large isotopic variations on a small-scale are expected to be commonplace in diagenetically modified sedimentary rocks forming under oxygen-deficient conditions. Such variations would reflect fluctuations in the relatively availability and abundance of electron acceptors in the initial sediment (high valence Fe- and/or Mn-oxyhydroxides in this case); variations in pore-water chemistry and organic carbon supply; and open- *versus* closed-system behaviour of aqueous species in the pore-fluids (such as Fe(II), Mn(II) or HCO_3^-), whether these are primary components or are generated diagenetically. We propose that at least part of the initial precipitation of Fe and Mn in the Hotazel strata was in the form of reduced species (e.g. carbonates) and that redox cycling for both metals was active already within the water column overlying the primary sediments. Consequently, isotopic gradients with respect to both C and Fe are likely to have existed in the palaeoenvironment of deposition, and possibly in the Palaeoproterozoic ocean by extension.

