

Sequential extraction for Palaeoproterozoic BIF and implications

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The rhythmically mesobanded Kuruman banded iron formation (BIF) and the overlying granular Griquatown BIF, form a major part of the lower Transvaal Supergroup in South Africa. As these BIFs were deposited just prior to the Great Oxidation Event (GOE) at ~2.4 Ga, continuous drill-cores thereof potentially provide new insights into the evolution of atmosphere and ocean chemistry during this period.

An apparent stratigraphic relationship between bulk Fe-isotopes and mineralogy is evident in the studied BIFs. Specifically, low $\delta^{57}\text{Fe}$ values (-2.7 to -1.4) correlate with samples rich in bulk modal carbonate, whereas higher $\delta^{57}\text{Fe}$ values (-0.6 to 0.9) correspond to magnetite-rich samples. In order to interrogate this relationship further, a sequential extraction scheme was developed based on the speciation work by Poulton and Canfield [1]. The latter protocol was adapted to the specific mineralogy of BIF which is dominated, in terms of Fe, by three key mineral fractions: Fe-carbonate, magnetite and Fe-silicate assemblages. Since ferric oxides are quantitatively insignificant in the studied rocks, the hydroxylamine and dithionite leaches can be safely omitted. The acetate leach was tested at variable temperatures and reaction times, in order to ensure that all micro-crystalline Fe-carbonates are effectively dissolved. Finally, a HF-HClO₄-HNO₃ leach is added to dissolve the residual silicate fraction which has previously not been considered in any detail.

The tests established a 3-step sequential extraction procedure to quantitatively separate the Fe-mineral fractions. These fractions were then processed further in order to break down the organic solvents and thus avoid interference with the Fe purification process [2]. Iron isotope analyses on the individual fractions can provide important constraints with respect to the Fe isotope composition of Fe_(aq) in the pre-GOE ocean, and specifically whether or not apparent secular trends relate entirely to secular isotopic evolution in $\delta^{57}\text{Fe}_{\text{(aq)}}$ during BIF deposition [3] or are largely a mineralogical artefact.

[1] Poulton & Canfield (2005) *Chem. Geo.*, **214**, 209-221. [2] Staubwasser *et al.* (2013) *Min. Mag.*, **77(5)**, 2253. [3] Rouxel *et al.* (2005) *Science*, **307**, 1088-1091