Iron speciation and iron isotopes of Neoarchean Ca-Mg carbonates

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While the deep Archean oceans were predominantly anoxic and rich in dissolved Fe(II), a redox interface with oxygen produced in shallow marine settings has been inferred from sedimentary records. Negative excursions in the δ^{56}Fe record of Neoarchean marine sediments point to an incomplete oxidation of dissolved Fe(II) [1] and/or microbial reduction of Fe(III) oxyhydroxides [2]. Both processes would produce an isotopically light Fe(II) pool. It has been proposed that Ca-Mg carbonates incorporate Fe from seawater without any fractionation, and would therefore be proxies for the Fe isotope composition of seawater Fe(II) [3,4]. However, remobilization during early diagenesis and dolomitization challenge the determination of Fe concentrations and isotope signatures of ancient seawater from sediments [5].

Here, we present new δ^{56}Fe data of stromatolites and mudstones from the 2.58 - 2.50 Ga Campbellrand-Malmani (South Africa). Synchrotron-based X-ray absorption spectroscopy (XAS) indicates that Fe is incorporated into the carbonates as Fe(II), with minor local distribution into Fe-S phases. Fe concentration and isotope data show a dependence on water depth, Fe fluxes from open ocean and riverine sources, as well as a remobilization from adjacent mudstones. Despite isolated Fe mobility during early diagenesis in some samples, the majority of samples seem to record primary seawater Fe signatures.

Replication of depth-dependent Fe concentration and Fe isotope trends observed in our samples in a steady-state, advective-diffusive transport model help to constrain the possible Fe transformation pathways occuring in shallow water. We will discuss the implications for oxygen in shallow Archean seawater. Our dataset illustrates the potential of Fe in Ca-Mg carbonates as a paleo seawater redox proxy.

[1] Rouxel et al. (2005), *Science* **307**, 1088-1091. [2] Johnson et al. (2008), *GCA* **72**, 151-169. [3] Blanckenburg et al. (2008), *Chem. Geol.* **249**, 113-128. [4] Czaja et al. (2012), *GCA* **86**, 118-137. [5] Heimann et al. (2013), *EPSL* **294**, 8-18.