Isotopic fractionation and trace element partitioning of green rust

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Iron formations (IFs) provide a potential window into the Precambrian chemical evolution of Earth's oceans and overlying atmosphere [1]. However, use of this information to infer the conditions in Earth's early oceans and atmosphere has been hindered by an incomplete understanding of the genesis of IF, the controls over the dominant Fe-bearing mineralogy and the processes governing their isotopic composition. Previous studies of IF genesis have suggested post-depositional transformation of a ferric hydroxide precursor [2, 3], but have not considered that the near-surface oxidation of an Fe-rich ocean would cause saturation of the ferrous-ferric hydroxysalt, green rust (GR), often at lower Fe levels than required for precipitation of ferric hydroxides. Preliminary experiments in our laboratory have demonstrated the formation of carbonate green rust from Precambrian-analog seawater solutions [4], which then transformed into the pre-metamorphic minerologies in IFs and displayed similar microtextures. We suggest that formation and settling of green rust may have played a role in the genesis of IFs.

In order to provide tests for our hypothesis of IF genesis via a green rust precursor, we explored the isotopic and trace element fingerprints of this process. Equilibrium synthesis of GR was effected by slow oxidation of a buffered solution of Fe(II) in the presence of bicarbonate, at a range of temperatures (20-60°C). The isotopic composition of the Fe and O in the resulting mineral were measured (by MC-ICPMS and laser fluorination gas-source IRMS, respectively) to give temperature-dependent equilibrium fractionation factors between GR and its parent solution. To determine kinetic isotope fractionations, rapid precipitation was effected by co-precipitation of Fe(II) and Fe(III) in an unbuffered solution, whereby the pH was rapidly raised to the range conducive to GR formation (>8). Partition coefficients of trace elements (Ni, Zn, Cu, etc.) and PO_4^{3-} between GR and solution were examined by synthesis of GR from a mother liquor containing the specified elements.

Results from this study have implications on our understanding of Fe mineralogy and cycling in the Precambrian.

[1] Bekker *et al* (2010) *Econ. Geol.*, **105**, 467-508. [2] Kappler *et al* (2005) *Geology* **33**, 865–868. [3] Fischer and Knoll (2008) *GSA Bull.* **121**, 222–235. [4] Halevy *et al* (2014) *Min. Mag.* this volume.