Biogeochemical consequences of ferruginous oceans

Louis A. Derry

Cornell University Dept. of Earth & Atmospheric Sciences, Ithaca NY [derry@cornell.edu].

The hyothesis that the global oceans had high dissolved ferrous iron contents during parts or most of the Precambrian^{1,2} poses a number of interesting questions. There are limited analog environments on Earth today with which to test some of the biogeochemical consequences of a ferruginous ocean. Here I explore three hypotheses that derived from the idea of a ferruginous ocean.

Redox interactions between the oceanic crust and seawater today occur withing the upper 500 m of the OC. In the absence of dissolved $\rm O_2$ and $\rm SO_4^=$ this redox interface moves out of the OC and into the water column. Fluid-rock interaction models for low T alteration of the OC indicate that dissolved $\rm Fe^{2+}$ fluxes from the OC to SW are on the order of 10^{12} mol yr¹, in the same range as modern river fluxes of base cations. [Fe] in SW under these conditions is not known with precision but values from 0.1 to >1 mM are plausible. The presence of $\rm Fe^{2+}$ in deep water imposes a constraint on oxygenation.

High ferrous iron levels in deep water can interact directty with phosphate throug the formation of vivianite, Fe₃(PO₄)₂. Previous work indicates that vivianite is both thermodynamically stable and kinetically allowable under ferruginous conditions, and that it can act to buffer deep water P levels to low values³. Upwelling of Fe²⁺ bearing deep water into a more oxidizing mixed layer can rapidly produce Feoxide precipitation. The strong interaction of Pi with Feoxyhydroxides produces a version of the "iron trap", potentially further limiting the deep supply of P to the photic zone. The combination of phosphate buffering by P-bearing mineral precipitation and by surface absorption on Feoxyhydroxides implies strong P limitation for marine export production and a potentially critical feedback for stabilizing low atmospheric pO₂ for geologically long time scales. [1] Poulton and Canfield (2010) Elements 7, 107-112. [2]

[1] Poulton and Canfield (2010) *Elements* 7, 107-112. [2] Planavksy et al. 2011 *Nature* 477, 448-451. [3] Derry (2015) *Geophys. Res. Lett.* 42, 8538–8546.