A silica & arsenic controlled early Proterozoic P cycle

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The Fe(III)(oxyhydr)oxide mineral, ferrihydrite, is thought to be of considerable importance in the control of Early Proterozoic dissolved trace element concentrations through adsorption and coprecipitation processes. Ferrihydrite is therefore often modeled in the reconstruction of early ocean chemistry linked to primary productivity, carbon burial and the oxygenation of the ocean-atmosphere system. This has gained particular significance in calculations of marine phosphate (P) concentrations through time, since sedimentary P levels in Fe(III)(oxyhydr)oxides scale positively with dissolved seawater levels [1]. However, as seen previously, P sorption to ferrihydrite decreases with the high Si concentrations that characterized the early oceans [2] with a recent study increasing the complexity with Ca and Mg cations negating the effect of Si on P sorption [3]. To further these models, using a simple empirical model with rapid hydrolysis, this study shows the effect of arsenic, a strong phosphate competitor, on P adsorption onto preformed ferrihydrite & lepidocrocite and coprecipitation with ferrihydrite in a NaCl solution containing As and P. The experiments were carried out at Si concentrations of 0.67 and 2.2 mM, to represent the Si saturation of cristobalite and amorphous Si, respectively. The results iterate that in the presence of As, Si has a negligible effect on the sorption of P on Fe(III)(oxyhydr)oxides. This would have been very important in the Early Proterozoic oceans exposed to at least 3-4 times greater hydrothermal activity and ultra-fast mid-ocean spreading than today [4]. Our results are more in support of the fact that the Early Proterozoic oceans likely had lower dissolved P concentrations than at present.

[1] Feely *et al*. 1998 *Geophys res lett* **25** (3) 2253-2256 [2] Konhauser *et al*. 2007 *Science* **315** 1234 [3] Jones *et al*. 2015 *Geology* **43** (2) 135-138 [4] Baross & Hoffman 1985 *Orig life* **15** 327-345