Fe(II)-phosphate nucleation and limits on the mid Proterozoic biological pump

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After its initial accumulation 2.3 billion years ago, atmospheric oxygen is thought to have remained consistently low for much of the mid-Proterozoic (1.8 − 1.0Ga)[1]. C_{org} burial under anoxic conditions, however, would have driven significant atmospheric O_2 accumulation. To resolve the low-O_2 conditions indicated by the rock record, one group of hypotheses suggests that marine export production may have been suppressed during the mid-Proterozoic[2,3].

Derry (2015) pointed out that anoxic ferruginous sewater may have favored the authigenic precipitation of Fe(II)-phosphate (e.g., vivianite, $Fe^{2+}_3(PO4)_2 \cdot 8H_2O$), which, in turn would have limited primary productivity. Although this predicts solubility equilibrium control on PO_4 by vivianite, the Fe(II)-PO_4 system in seawater is not well understood from a kinetic point of view. Specifically, the initial Fe(II)-phases that precipitate from seawater, the supersaturation required to nucleate Fe(II)-phosphates, and their growth rates under marine conditions are not well quantified.

Here, we explore the Fe(II)-phosphate nucleation in synthetic seawater systems using both both fixed and pH-free drift methods. Laboratory experiments were carried out under strict anoxic conditions using synthetic seawater matrix at varying [Fe^{2+}] and [PO_4] Solution analysis indicates significant reduction in dissolved phosphate and iron concentrations as reactions progress. Powder X-ray diffraction and FT-IR show that vivianite commonly precipitates and also minor amounts of the Mg-bearing isomorph baricite.

However, experiments conducted to date indicate that significant supersaturation is required to nucleate vivianite, which then exhibits slow growth rates. Estimations of growth rates and critical supersaturation required for nucleation should allow quantitative dynamical modeling of the Fe(II)-PO_4 system in Proterozoic environments, and, in turn, provide a robust test of P-limitation under ferruginous conditions.

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