

The role of phosphorus in the formation of vivianite versus green rust under anoxic conditions

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In ancient anoxic and Fe-rich (ferruginous) oceans, green rust (GR; a mixed ferric/ferrous hydroxide) and vivianite (ferrous phosphate) likely played a key role in controlling phosphorus (P) cycling. However, the factors that affect the formation of these minerals under various chemical conditions are not well understood, which limits our understanding of processes that led to the drawdown and retention of P in ancient anoxic environments. In this project, we have investigated how variable concentrations of dissolved P affect the formation of sulfate GR ($\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}_4(\text{OH})_{12}\text{SO}_4$) as opposed to vivianite ($\text{Fe}^{\text{II}}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) under anoxic conditions. Our findings indicate that when the concentration of dissolved P is at a low level (P:Fe(II) molar ratios <1:30), anion exchange and adsorption to the surface of GR dominate the drawdown of P, which forms via amorphous Fe-P precursors. These amorphous Fe-P precursors appear to delay the formation of crystalline GR, however, vivianite is not observed under these conditions. When the concentration of dissolved P is higher, GR is also observed. However, the GR formed under these conditions is unstable, and transforms into amorphous ferric hydroxides and the more stable vivianite. These findings are consistent with previous research on the formation of GR in modern oligotrophic, ferruginous settings, providing support for the control that GR exerts on P cycling in ancient oligotrophic ferruginous oceans. Conversely, in ancient anoxic environments with higher productivity, dissolved P in both the water column and sediments increased via recycling from redox processes. Under these conditions, vivianite formation is promoted and plays a key role in trapping P in the sediments, hence nuancing its recycling back to the water column.