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Sulfide induced vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) formation from iron (oxyhydr)oxides in the presence of dissolved phosphate

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Eutrophication caused by excess phosphorus remains a significant concern in aquatic systems. The strong affinity between phosphate (P) and ferric iron (oxyhydr)oxides (FeOx) provides an effective pathway for removing dissolved P from eutrophic waterbodies and transferring it to the sediments. In anaerobic, sulfide-rich sediments, P-loaded FeOx undergo reduction, and, therefore, release the bound-P. However, the released P can combine with reduced Fe(II) from FeOx reduction to form vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$), a key P sink in reducing environments. Based on thermodynamic calculations, we demonstrate that concurrent formation of FeS and vivianite during sulfidation of FeOx is feasible under typical sediment conditions of dissolved P and pH.

To investigate the reaction kinetics and identify potential constraints, we performed flow-through mixed reactor experiments at pH 7.3 using lepidocrocite and ferrihydrite as FeOx sources. After optimizing experimental parameters such as S(-II) and P inflow concentrations, flow rates, and experiment duration, we confirmed the presence of vivianite via transmission electron microscope in experiments with excess ferrihydrite (with final consumption <25%). Under static (no-flow) conditions, XRD analysis confirmed vivianite formation after 5 and 11 days of reaction time.

Our results show that vivianite precipitation can occur within days as a by-product during sulfidation of FeOx. However, effective vivianite formation requires two key conditions: rapid S(-II) consumption and fast release of Fe(II) from the solid phase to achieve sufficient dissolved Fe(II) concentrations for vivianite nucleation and growth at given P concentrations. Meeting these requirements necessitates excess amounts of highly reactive FeOx.

This study reveals a previously unexplored yet viable pathway for vivianite formation in aquatic sediments through partial FeOx reduction by dissolved S(-II). This may be particularly relevant in sediments naturally abundant in or amended with reactive FeOx phases, where sulfide production via sulfate reduction is either temporary or limited by sulfate availability.