

Vivianite oxidation and dissolution: mechanisms and rates

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Vivianite ($\text{Fe(II)}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) has been increasingly recognized for its importance in phosphorus cycling within natural systems, as well as its potential for phosphorus recovery from agricultural drainage and wastewater. Its subsequent utilization in fertilizer formulations presents opportunities for advancing a circular phosphorus economy. In order to further our understanding of vivianite reactivity and its impact on stabilizing P in sediments or its potential as fertilizer, we elucidated rates and mechanisms of vivianite oxidation and dissolution, including influence of redox conditions, the presence of biogenic ligands, substitutions in the vivianite lattice and other pertinent geochemical parameters.

Fast vivianite dissolution under reducing conditions was described by a rate law. However, partial oxidation of the mineral had a strong influence on dissolution rates even at low degrees of oxidation. Hence, the oxidation process was further investigated. It was observed that the oxidation of vivianite is passivated by the formation of an oxidized shell. A mechanistic rate-law was parameterized based on these observations. Substitution of structural Fe and phosphate by redox active and non-redox active cations and anions, respectively, had only a small effect on solubilities and dissolution rates, suggesting that vivianite may constitute a kinetically stable P sink in sediments even under variable redox conditions. Biogenic ligands promote P and Fe dissolution from partially oxidized vivianite. This effect is modified by competing cations with high affinity for complexation by the ligands and by the presence of humic substance.

With the present study, we hope to provide basic information for the understanding of the potential for vivianite (which is already marketed as a component in fertilizer formulations) in plant nutrition and as a P sink in sediments.