

# Effect of biogenic ligands and NOM on the mobility of Fe and P from vivianite under changing redox conditions

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The natural mineral vivianite ( $\text{Fe(II)}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) is currently examined for recycling P; it can be recovered from wastewater and applied as sustainable fertilizer. In previous studies we demonstrated that it strongly depends on redox conditions whether vivianite can act as an efficient P source. Structural Fe(II) readily oxidizes to Fe(III) in the presence of oxygen, leading to a long-term decrease of P and Fe mobility, thus compromising the suitability of vivianite as a fertilizer. To increase P and Fe bioavailability, organisms can exude organic ligands including low molecular weight organic acids (LMWOA, *e.g.* citrate) or high-affinity Fe-binding ligands (siderophores, *e.g.* DFOB). To examine whether such biogenic ligands can preserve vivianite as an efficient P-source under oxic conditions a series of highly controlled batch experiments were performed. The redox state, pH, presence of humic acid (HA) and background electrolyte cation (Ca or Na) were varied to develop a quantitative and mechanistic understanding of the efficacy and constraints of organic ligands in mobilizing Fe and P from vivianite.

Our results demonstrate that citrate and DFOB are efficient in mobilizing both P and Fe from vivianite. However, the rate and degree of mobilization are highly dependent on environmental conditions and the nature of the ligand. The initial oxidation state of vivianite and the prevailing redox conditions during the experiments influenced both the mobilization of P and Fe by citrate and DFOB. While the efficacy of citrate was strongly dependent on the solution composition (pH, electrolyte cation), the efficacy of DFOB remained relatively constant due to its much higher affinity and specificity for Fe(III). Although HA had little direct effect on vivianite dissolution, in combination with DFOB it strongly enhanced the kinetics of ligand-promoted dissolution. By conducting experiments with pre-oxidized vivianite under anoxic conditions we were able to disentangle vivianite dissolution from the progressive oxidation reaction, and hence to develop a mechanistic understanding of the underlying process of ligand-promoted dissolution.

Within this study we demonstrate the potential importance of biogenic ligands for enhancing the bioavailability of P and Fe from vivianite under (oxic) environmental conditions.