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Suitability of vivianite as a long-term phosphate sink in terrestrial and aquatic systems and the effect of metal incorporation

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To remove dissolved phosphate (PO_4) from eutrophic water bodies, iron (Fe) based materials are applied. The main mechanisms underlying such remediation strategies are adsorption of PO_4 to Fe (hydr-)oxides in oxic zones, and the authigenic formation of the ferrous Fe-PO_4 mineral vivianite ($Fe(II)_3(PO_4)_2$âˆ™$8H_2O$) in anoxic zones. However, the persistence of the resulting P-bearing phases under changing environmental conditions is uncertain. We examined the influence of vivianite phase transformations on the mobilization of PO_4 and Fe during redox-fluctuations, common for natural terrestrial and aquatic systems. Anthropogenically influenced waters often contain elevated levels of various (toxic) metal(loids) as well. Therefore, we additionally investigated the effect of metal(loid) incorporation on the suitability of vivianite as long-term PO_4 sink in aquatic systems.

Vivianite is a redox-active phase and structural Fe(II) oxidizes readily in the presence of oxygen. Oxidation is accompanied by phase transformations to amorphous Fe(III)-PO_4 phases resulting in a strongly decreased solubility and dissolution rate, even at low oxidation ratios (Fe(III)/Fe(II)). Using scanning transmission X-ray microscopy (STXM) we demonstrated that vivianite oxidation is a surface reaction leading to the formation of an oxidized shell that inhibits oxidation of the unoxidized core. Consequently, short oxidation events decrease the availability of vivianite-bound PO_4. First experiments suggest that the phase transformations are not per se reversible, supporting the suitability of (surface-oxidized) vivianite as a long-term PO_4 sink.

The vivianite crystal lattice accommodates isomorphic substitution; structural Fe(II) can easily be replaced by various (toxic) divalent metal cations such as Co, Cu, Mg, Mn, Ni and Zn, while structural PO_4 can be replaced by anions such as AsO_4. We substituted up to 25% of structural Fe by Co and PO_4 by AsO_4. Despite the high degree of substitution, vivianite reactivity, regarding solubility and oxidation, changed only slightly. An increase in solubility of substituted vivianites was observed under anoxic conditions, while under oxic conditions this was only true for Co substitutions, due to the higher oxidation potential of Co(II) compared to Fe(II).

Our study provides a mechanistic understanding of vivianite oxidation and demonstrates the importance of phase transformations under fluctuating redox conditions, for the PO_4 and Fe mobility.