

The mechanism and effect of Vivianite oxidation on the bioavailability of P and Fe

ROUVEN METZ¹, NARESH KUMAR², WALTER D.C. SCHENKEVELD³ AND STEPHAN M. KRAEMER²

¹Univeristy of Vienna

²University of Vienna

³Wageningen University & Research

Presenting Author: rouven.metz@univie.ac.at

The ferrous iron-phosphate mineral vivianite ($\text{Fe(II)}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) forms naturally in sub-/anoxic environments with high Fe(II) and phosphate (PO_4) concentrations, and is a sink to the dissolved PO_4 . However, vivianite has also been proposed as a phosphorus (P) source through application as a slow-release Fe-P fertilizer prepared from recycled P. Thus, vivianite has potential to mitigate both major problems of the modern P-cycle: (i) P scarcity in crop production, and (ii) eutrophication by P excess in surface waters.

However, vivianite is a metastable mineral and readily oxidizes in oxic environments. While the exact mechanism and kinetics of the oxidation reaction are still elusive, this transformation changes the properties of the mineral (surface), and consequently, the suitability as a potential fertilizer.

In a series of batch and flow-through reactor experiments, we investigated the solubility and dissolution rates of synthesized, unoxidized vivianite under various (pH, temperature, O_2 partial pressure) environmental conditions. Our results show, that the oxidation of vivianite strongly impacts its solubility and dissolution rates. Already a low oxidation ratio ($\text{Fe(III)}/\text{Fe(II)}$) of the mineral leads to a strong decrease in mobilized Fe and P concentrations. Additionally, with an increasing degree of oxidation, PO_4 was preferentially released in the solution. Similar effect of preferential PO_4 mobilization was also observed for alkaline pH values (pH 8-9). With decreasing pH however, the solubility and dissolution rates increased and vivianite dissolved congruently. We ascribe the influence of pH on the dissolution mainly to the Fe redox chemistry, where increase in pH leads to an increase in oxidation rate of Fe(II).

A mechanistic understanding of vivianite dissolution and the quantification of dissolution rates and secondary mineral formation under environmentally relevant conditions provides the fundamental knowledge needed to assess the suitability of vivianite as Fe and P fertilizer and is also paramount to the idea of a circular economy concept: the reduction of P loads of (waste) waters and usage of the byproduct vivianite as P source for fertilization.