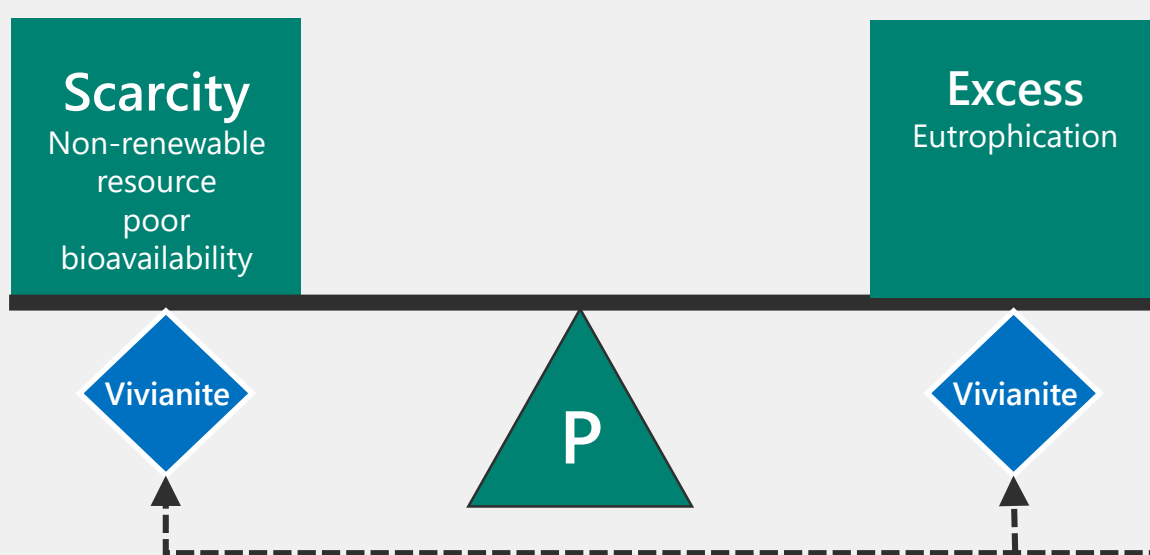
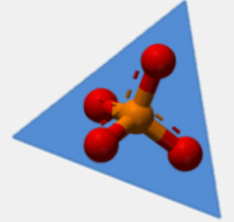


Biogeochemical Mechanisms Influencing the Bioavailability of P and Fe from Vivianite

Rouven Metz¹, Naresh Kumar¹, Walter Schenkeveld² and Stephan Krämer¹

Phosphorus (P) Extremes in the Environment

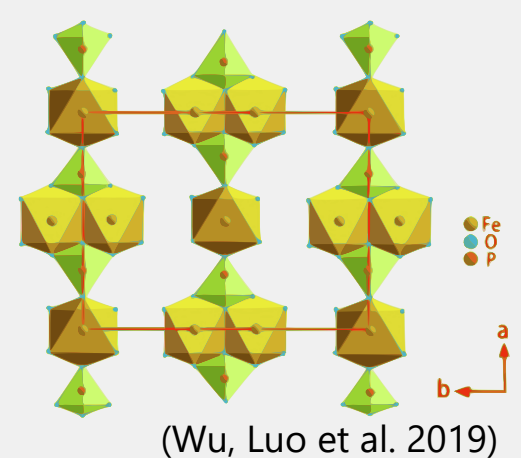


Vivianite - $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$

- Hydrous ferrous iron phosphate
- Forms naturally under reducing conditions with high Fe(II) and PO_4 concentrations:
 - P sink → precipitation and fixation of dissolved P
 - P source → application as slow releasing Fe-P fertilizer

Vivianite may help to stabilize the P balance

- Structure:
 - Single $(\text{FeO}_2(\text{H}_2\text{O})_4)$ octahedral groups and Double $(\text{Fe}_2\text{O}_6(\text{H}_2\text{O})_4)$ octahedral groups, linked by PO_4 tetrahedra groups and $\text{H}_2\text{O}-\text{H}_2\text{O}$ hydroxyl bonds (Rouzies & Millet, 1993).

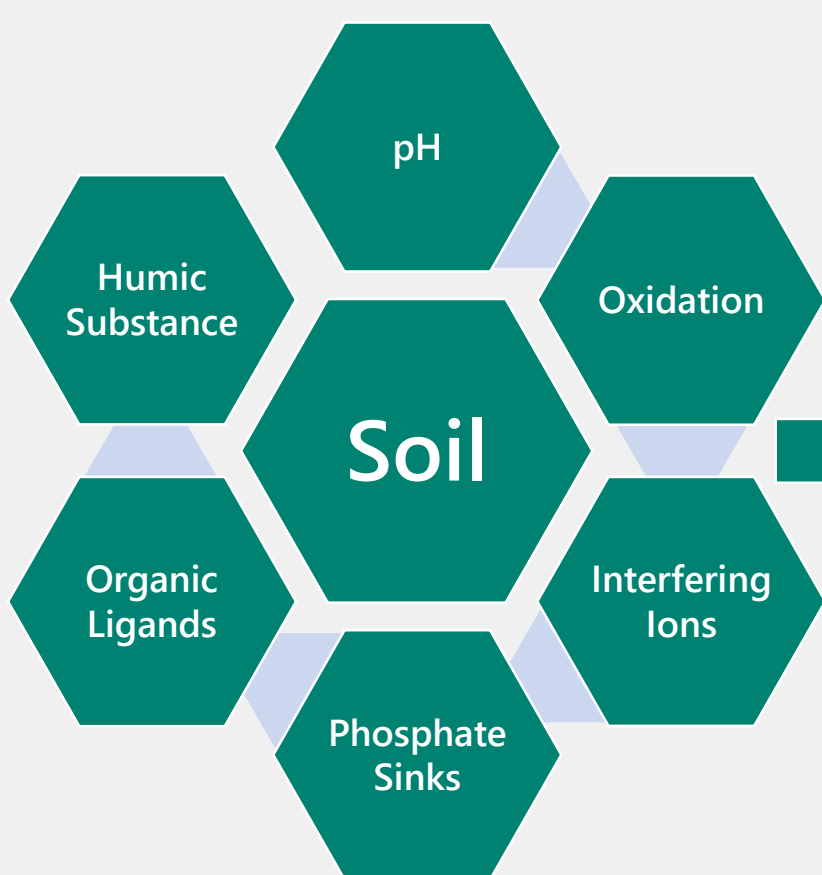


- Metastable under oxic conditions due to Fe-oxidation:

$$2[\text{Fe}^{2+} - \text{H}_2\text{O}] + \frac{1}{2} \text{O}_2 \rightarrow 2[\text{Fe}^{3+} - \text{OH}] + \text{H}_2\text{O}$$

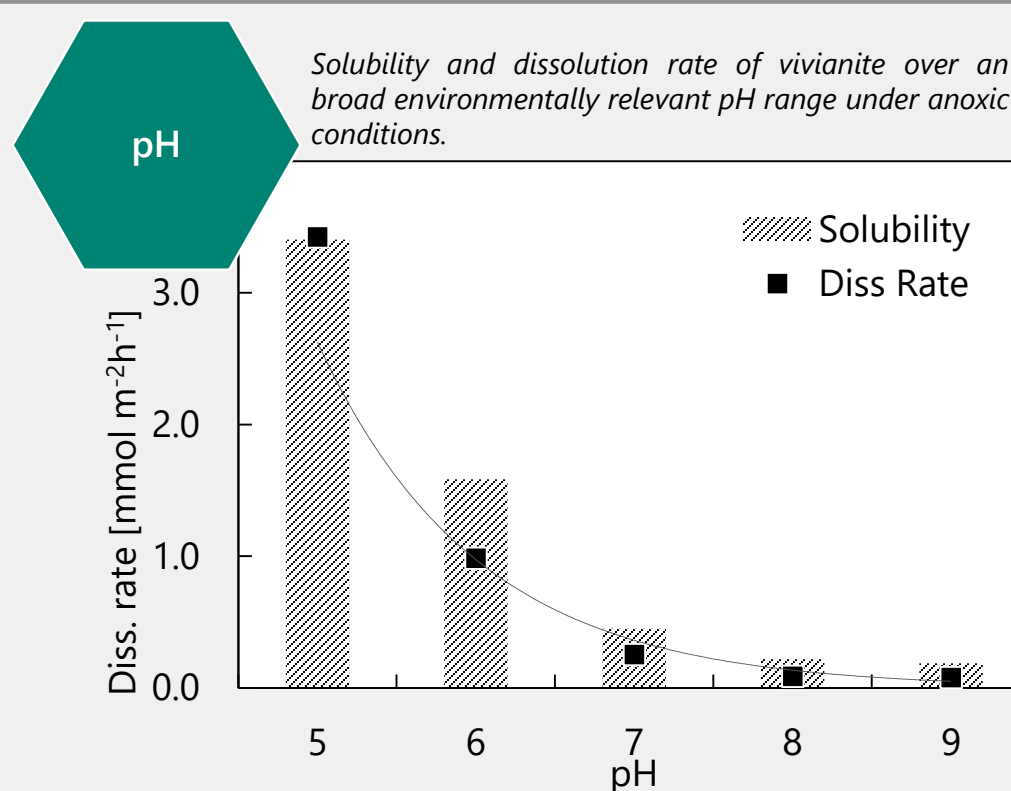
- Proposed transformation sequence with increasing oxidation degree
Vivianite → *Metavivianite* → *amorphous Santabarbaraite*

How does Vivianite behave in Soils?



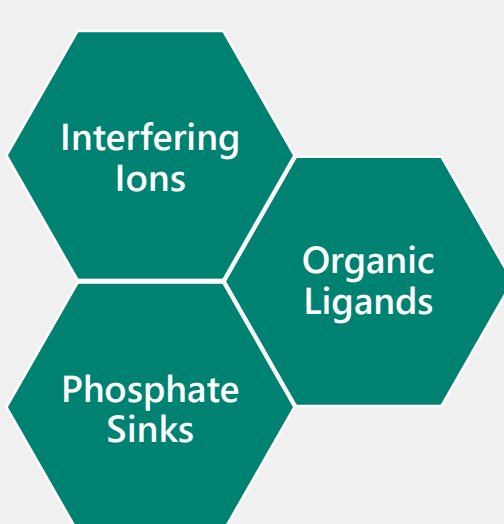
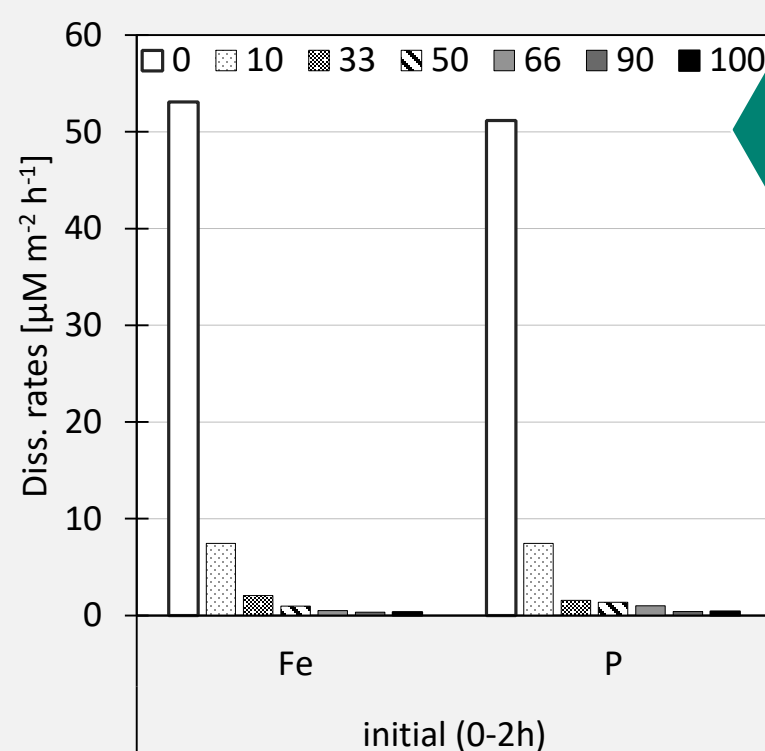
- Formation of secondary phases
- Bioavailability of P and Fe

Mechanistic and Quantitative Understanding



Dissolution rates and solubility were determined under oxic and anoxic conditions over an environmentally relevant pH range. Both, solubility and dissolution rates increase strongly with decreasing pH. While vivianite dissolves under anoxic conditions stoichiometrically, PO_4 is preferentially released under oxic conditions at alkaline pH. The mobilization of PO_4 is hereby a slower process than the initial dissolution, and it is related to the oxidation of Fe and the formation of secondary Fe(III)-phases.

The degree of oxidation of vivianite plays a crucial role on the availability of Fe and P from the mineral. In experiments we could show, that even low degrees of oxidation (%-Fe(III)/Fe(tot) of solid material) decreased the solubility and dissolution rates of vivianite strongly. Moreover, PO_4 was preferentially released at higher oxidation degrees even though at low absolute concentrations. We propose a mechanism where the oxidation leads to the formation of surface amorphous Fe(III)- PO_4 phases with a low solubility, which hinder the further dissolution of the mineral.



Dissolution experiments with interfering ions as Ca and Si showed minor effects contrary to organic ligands (citrate, DFOB) which are exuded by plants and microorganisms to increase the Fe and P availability. Those led to a very fast effective (~1:1) and congruent dissolution of vivianite, independent on its oxidation degree. Our results suggest, that the vivianite dissolution is not kinetically, but thermodynamically hindered due to the low solubility especially of Fe(III)- PO_4 phases which form during the oxidation process under oxic conditions. However, the organic ligand experiments are promising, suggesting that vivianite can be applied as an "intelligent fertilizer" – releasing Fe and PO_4 depending on the root activity.

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This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 813438.



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