



Potential of recycled vivianite as P and Fe fertilizer - a mechanistic point of view -

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Vivianite - $Fe_3(PO_4)_2 \cdot 8H_2O$

- Hydrous ferrous Fe Phosphate
- Fe-rich end-member of the Vivianite Mineral Group
- Mineral's structure:
 - $\circ~$ Single (FeO_2(H_2O)_4) octahedral groups and
 - $\circ~$ Double (Fe_2O_6(H_2O)_4) octahedral groups,
 - $\circ~$ linked by PO_4 tetrahedra groups and
 - \circ H₂O-H₂O hydroxyl bonds
- Metastable under oxic conditions due to Fe-oxidation:

 $2[Fe^{2+} - H_2O] + \frac{1}{2}O_2 \rightarrow 2[Fe^{3+} - OH] + H_2O$











Phosphorus (P) Extremes in the Environment













Vivianite Dissolution







Anoxic Vivianite Dissolution



- High dissolution rate:
 - Not kinetically constrained
 - Rate determining step: break of hydrogen bonds
- Fast approach of solution saturation
 Thermodynamic controlled dissolution
- pH effect:
 - $\,\circ\,$ Strong ${\color{black} {\color{black} \Lambda}}$ of solubility with ${\color{black} {\color{black} \nu}}$ pH





Vivianite Oxidation







Influence of Oxidation on Vivianite Dissolution







Oxidized Vivianite dissolution under anoxic conditions







STXM – Measurement and Results

Oxidation of vivianite



Spatial resolved acquisition of XANES Definition of OD-masks (particle thickness)

Extraction of averaged XANES spectra and LC-fitting







Contaminant incorporation







Structural incorporation of contaminants or separate phases?







Summary

Potential of recycled vivianite as P and Fe fertilizer - a mechanistic point of view -

- Vivianite dissolution is not kinetically hindered
- Solubility provides adequate dissolved P levels
- Strong pH dependence of vivianite solubility
- Oxidation of vivianite results in much lower solubility and dissolution kinetics
- Oxidation is a surface reaction (surface passivation likely)
- Ready contaminant incorporation into vivianite structure (Co, As)
- No preferential release of contaminants







Questions and Remarks?



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