A mechanistic and kinetic study of vivianite(Fe₃(PO₄)₂·8H₂0) formation from FeS

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15s-Summary

Question: Can FeS be a source of Fe(II) for vivianite formation?

Experimental study of the possible conversion from **Objective:** FeS to vivianite.

Vivianite formation is confirmed at pH 7, 8 and 9 by **Results:** adding phosphate to FeS in batch exepriments.

Results

Time evolution of dissolved Fe(II) concentration indicates the formation of vivianite after 6 to 29 days



XRD analysis confirms the formation of vivianite in all batch experiments



-Background-

Phosphorus(P) is an important element for both life and the environment. However, the excess abundance of **P often links to eutrophication** and results in **low surface water quality**. A stable and long-term P sink is therefore of preference in aquatic environments, and authigenic phosphate minerals could then be the key for P management. Vivianite $(Fe_3(PO_4)_2 \cdot 8H_2 0)$ is thus of great interest as it has the potential to act as a permanent P sink under reduced conditions in lake and ocean sediments. Vivianite has been reported in various aquatic sediments. It is known that the formation of vivianite requires sufficient dissolved Fe(II) which, however, is often constrained by other Fe(II)-containing solids such as mackinawite(FeS). Although the competition exists, FeS could also be a source of Fe(II), when S(-II) is, for example, oxidized by cable bacterial, or when environmental conditions change and S(-II) concentrations decline. The conversion from FeS to vivianite has not been experimentally confirmed yet, and the rate and mechanism are unknow.

-Hypothesis

We suppose the transformation is a **dissolution-nucleation process** instead of solid-solid phase conversion due to the activation energy limitation.

• Time evolution of dissolved Fe(II) concentration supports the hypothesis that the transformation of FeS into vivianite proceeds via dissolution and precipitation.

The following two reactions could represent the dissolution of FeS and the subsequent nucleation of vivianite formation: 1: dissolution of FeS: $FeS(s) \ll Fe^{2+} + S^{2-}$

2: precipitation of vivianite: $3Fe^{2+} + 2PO_{A}^{3-} + 8H20 <=>Fe_{3}(PO_{A})_{2} \cdot 8H_{2}O$

The rate-limiting step is supposed to be the precipitation of vivianite.

-Methods-



Batch experiments under conditions: FeS: 1.2mM Phosphate: 0-5 mM



Sampling

Daily sampling to monitor the concentration during the transformation

Wet-chemistry analysis

Analysing both dissolved and solid-bound: S(-II): Methylene blue method $PO_{4}(-III)$: Ascorbic acid method Fe(II)(III): Ferrozine method

• Relative extent of vivianite formation from FeS is independent of phosphate concentration at pH 6 & 7 but increases with phopshate concentration at pH 8.

• Combining these conlusions suggests that the rate of vivianite formation is limited by FeS dissolution but not vivianite nucleation or growth.

• FeS dissolution rates at pH 8 are lower compared to pH 6 & 7 explaining the lower relative concentrations of vivianite at this pH.

• At pH 6 & 7, the dissolution rate is not affected by phosphate concentration, while the presence of phosphate increases the dissolution rate at pH 8.

Conclusion.

Can FeS become a source for vivianite formation?

Yes, vivianite is confirmed in our incubation experiment by XRD and XAFS.

How does it happen?

When FeS dissolves, it provides Fe(II) for vivianite precipitation. The pace of the transformation is controlled by the dissolution rates of FeS, which, in turn, depend on pH and phosphate concentrations.

How long does this conversion take?

Base on our observation, this could happen from a few days to few weeks.

What does this mean to us?

Usually FeS is considered as an antagonist for vivianite formation. Here, we show that it can also be a substrate for vivianite formation when the transformation becomes thermodynamically feasible. This can occur at decreasing dissolved sulfide concentrations or increasing phosphate concentration. The transformation of FeS into vivianite is a possible pathway for long-term burial of phosphate in aquatic sediments, which has not received much attention so far.

Solids characterization X-ray diffraction(XRD) X-ray spectroscopy Mössbauer Spectrocopy Transmission electron microscope(TEM)



References ____

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