

## Vivianite precipitation induced by dissolution of FeS in the presence of dissolved phosphate

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Increasing phosphate(P) levels due to anthropogenic inputs are a source for eutrophication of surface waters. Under reducing conditions, formation of vivianite ( $\text{Fe}_3(\text{PO}_4)_2 \cdot (\text{H}_2\text{O})_8$ ) can be a sink for P in the underlying aquatic sediments. Besides dissolved P, vivianite formation requires sufficiently high dissolved  $\text{Fe}^{2+}$  to become thermodynamically feasible. In aquatic sediments,  $\text{Fe}^{2+}$  concentrations are often constrained by other Fe(II)-containing solids such as FeS, which can impede vivianite precipitation. However, FeS can also be a source for dissolved  $\text{Fe}^{2+}$ . For example, cable bacteria (*Desulfobulbaceae*) can induce FeS dissolution by consuming sulphide and producing acidity due to sulphide oxidation [1]. However, to our knowledge, the transformation of FeS into vivianite has not been experimentally demonstrated so far.

We investigated the possibility of FeS transformation into vivianite in batch experiments at different dissolved P concentrations and pH values 6.0, 7.0 and 8.0. In the initial stage of the experiments, increase in dissolved  $\text{Fe}^{2+}$  concentrations reflected the dissolution of FeS. With increasing pH level, FeS dissolution proceeded slower. After several days, the trend reversed and dissolved  $\text{Fe}^{2+}$  concentrations started to drop. This happened when the saturation index(SI) of vivianite had exceeded a value of four. Formation of vivianite has been confirmed by X-ray diffraction. According to Liu et al. [2], vivianite nucleation rates become significant when the corresponding SI is above four, which is in line with our findings.

Our results demonstrate that the transformation of FeS into vivianite is a possible pathway for P immobilization in aquatic sediments. The transformation can occur in the time-scale of days or weeks and appears to proceed faster at low pH, which can be explained by faster FeS dissolution rates. However, at given dissolved P concentrations, the dissolved  $\text{Fe}^{2+}$  concentrations have to be higher at lower pH before vivianite formation is initiated. In this respect, the pH has an opposing effect on the FeS to vivianite transformation in sediments.

### References

[1] Sulu-Gambari et al., 2016. *Geochimica et Cosmochimica Acta* 192 (2016) 49-69

[2] Liu et al., 2018. *Chemical Engineering Journal* 349 (2018) 37-46