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 Fe$^{2+}$ to become thermodynamically feasible. In aquatic sediments, 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 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 Fe$^{2+}$ concentrations reflected the dissolution of FeS. With increasing pH level, FeS dissolution proceeded slower. After several days, the trend reversed and dissolved 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 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
