



Kinetics and mechanism of phosphate release upon sulfidation of phosphate-containing lepidocrocite

Mingkai Ma¹, Andreas Voegelin², and Thilo Behrends¹

¹Department of Earth Sciences-Geochemistry, Utrecht University, Utrecht, The Netherlands (m.ma@uu.nl)

²Eawag, Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, Switzerland

Sulfidation of Fe(III) (hydr)oxides plays an important role in the phosphate(P) cycle in oceans and lakes. P has a strong affinity to Fe(III) (hydr)oxides and can either become incorporated via coprecipitation or adsorb onto the solid's surface. Consequently, P enters aquatic sediments often associated with Fe(III) (hydr)oxides. In the sediments, when sulfidic conditions are prevalent, the reaction of Fe(III) (hydr)oxides with sulfide can lead to the formation of Fe(II) sulfides and P release. The released P can, in turn, diffuse upwards into the overlying water and thus aggravate eutrophication in water bodies. Although it is generally expected that P is released during the sulfidation of P containing Fe(III) (hydr)oxides, questions remain whether part of the P could be re-adsorbed onto the products of the sulfidation reaction, or trigger the formation of vivianite^[1] (Fe₃(PO₄)₂ · 8H₂O). Furthermore, it is still unclear how the rates of P release are related to the progress of the sulfidation reaction.

In order to study the P dynamics during sulfidation, we performed experiments in flow-through reactors with P-bearing lepidocrocite (γ -FeOOH). The inflow solution contained sulfide and we monitored P, dissolved S(-II) and Fe(II) in the outflow to follow the progress of sulfide consumption and P release. Sulfide concentrations in the outflow of reactors containing lepidocrocite with adsorbed P tended to be lower than in the outflow of reactors with lepidocrocite but no P. Consequently, the preliminary results indicate that consumption rates of sulfide by the reaction with lepidocrocite were lower when P was present, implying that adsorbed P reduced the rates of sulfidation. At the beginning of the experiment, P concentrations in the outflow remained low, then started to increase and reached a steady state after passing several reactor volumes. This indicates that P was not instantaneously released upon sulfide adsorption but only as lepidocrocite sulfidation progressed. At the end of the experiment, the fraction of P released from the reactor was significantly lower than the fraction of lepidocrocite that had reacted with sulfide(calculated from cumulative sulfide consumption and solid phase characterization). This implies that part of the P has been retained in the solid phase despite the reductive transformation of lepidocrocite. The underlying mechanisms of P retention and the complex relationship between the rates of sulfide consumption and P release will be discussed.

References

[1] Jilbert and Slomp, 2013. *Geochimica et Cosmochimica Acta* 107, 155-169.

