Amorphous Ca-Fe(III)-phosphates formed by Fe(II) oxidation in water

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Iron precipitates formed by Fe(II) oxidation at aquatic anoxic-oxic boundaries profoundly influence the fate of Fe and other major and trace elements. We found that Fe(II) oxidation at high phosphate concentrations induces the precipitation of amorphous (Ca-)Fe(III)-phosphate, and that other Fe(III)-precipitates only form in phosphate-free (or depleted) solution [1-3]. Here we report recent results on the composition and structure of amorphous (Ca-)Fe(III)-phosphate formed in the absence and presence of Ca under environmentally relevant conditions [4]. Fe(III)-precipitates were synthesized by oxidation of 0.5 mM Fe(II) at initial molar P/Fe(II) [$(P/Fe)_{init}$] ratios from 0 to 2 in aerated 8 mM $NaHCO_3$ or 4 mM $CaCO_3$ electrolyte adjusted to pH 7.0 with CO_2 gas. After 4 h, unfiltered and filtered solutions and precipitates were collected for analysis.

Above a $(P/Fe)_{init}$ of ~0.5 in Na and ~0.8 in Ca electrolyte, Fe(II) oxidation led to exclusive formation of (Ca-)Fe(III)-phosphate with maximum precipitate P/Fe ratios of ~0.7 in Na and ~1.1 in Ca electrolyte. Fe K-edge XAS revealed that Ca not only enhanced phosphate uptake per Fe, but also induced partial formation of Ca-Fe(III)-phosphate polymers with enhanced edge- and corner-sharing Fe-Fe linkage relative to Fe(III)-phosphate polymers that also form in Ca-free electrolyte. Trends in precipitate composition, Ca K-edge XAS and FT-IR data also indicated formation of Ca-phosphate polymers at high phosphate concentrations in the Ca electrolyte. Overall, our results show that amorphous basic (Ca-)Fe(III)-phosphate formed by oxidation of dissolved Fe(II) can be described as mixtures of different polymer types whose fractions vary with solution chemistry. This conceptual model serves as a basis for a more detailed understanding of variations in Ca-Fe(III)-phosphate composition and structure as a function of solution chemistry and of major and trace element uptake by amorphous (Ca-)Fe(III)-phosphate in environmental systems.

[1] Voegelin et al., *Geochim. Cosmochim. Acta* **74**: 164, 2010. [2] Kaegi et al., *Geochim. Cosmochim. Acta* **74**: 5798, 2010. [3] Voegelin et al., *Geochim. Cosmochim. Acta* **117**: 216, 2013. [4] Senn et al., in review.