Structure, composition and arsenate uptake of Fe oxidation products

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The oxidation of dissolved Fe(II) in oxygenated water leads to the formation of amorphous to poorly-crystalline Fe(III)-precipitates that profoundly impact the fate of nutrients and contaminants in natural and engineered aquatic systems. In previous work, we found that dissolved phosphate (P), silicate (Si) and Ca strongly influence the structure of Fe(III)-precipitates [1]. In this continuing study, we quantified the interdependent effects of P, Si and Ca on the structure, composition and arsenate (As(V)) uptake of Fe(III)-precipitates following a multifactorial approach with 72 treatments. The precipitates were formed by oxidation of 0.5 mM Fe(II) at 12 P/Fe ratios from 0 to 2 in aerated 8 mM bicarbonate-buffered (pH 7.0) electrolyte containing 7 μM As(V), with 8 mM Na, 4 mM Ca, 4 mM Mg or 7 mM Na + 0.5 mM Ca as electrolyte cations. Additional experiments in Na and Ca electrolyte were performed in the presence of 0.5 mM Si. After complete Fe oxidation and precipitation (4 h), unfiltered and filtered solutions were collected for ICP-MS and dried precipitates for Fe K-edge XAS analysis.

The evaluation of the 72 Fe XAS spectra by linear combination fitting (LCF) revealed gradual variations in precipitate structure between the endmembers lepidocrocite, hydrous ferric oxide (HFO) and amorphous Fe(III)-phosphate as a function of P/Fe ratio, electrolyte cation and presence of Si. Enhanced co-precipitation of P in Ca-containing electrolytes could be attributed to electrostatic effects as well as formation of mixed Ca-Fe(III)-phosphate in which the Fe(III)-octahedra exhibited enhanced mitridatite-like corner- and edge-sharing linkage. By combining ICP-MS and LCF results, the characteristic P/Fe ratios of HFO and Fe(III)-phosphate formed in different electrolytes were derived. Depending on initial P/Fe ratios and type of electrolyte cation and thus precipitate type, dissolved As(V) concentrations varied by up to 3 orders of magnitude. These results provide insight into the link between water chemistry and the structure and reactivity of Fe(III)-precipitates that is essential to assess the dynamics of As and other trace elements in natural aquatic systems and water treatment.

[1] Voegelin *et al Geochim. Cosmochim. Acta* **74**, 164, 2010.