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Structure of short-range-ordered iron(III)-precipitates formed by iron(II) oxidation in water containing phosphate, silicate, and calcium

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The oxidation of Fe(II) in water leads to the formation of Fe(III)-precipitates that strongly affect the fate of nutrients and contaminants in natural and engineered systems. Examples include the cycling of As in rice fields irrigated with As-rich groundwater or the treatment of drinking water for As removal. Knowledge of the types of Fe(III)-precipitates forming in such systems is essential for the quantitative modeling of nutrient and contaminant dynamics and for the optimization of water purification techniques on the basis of a mechanistic understanding of the relevant biogeochemical processes.

In this study, we investigated the local coordination of Fe, P, and Ca in Fe(III)-precipitates formed by aeration of synthetic Fe(II)-containing groundwater with variable composition (pH 7, 2-30 mg/L Fe(II), 2-20 mg/L phosphate-P, 2-20 mg/L silicate-Si, 8 mM Na-bicarbonate or 2.5 mM Ca-&1.5 mM Mg-bicarbonate). After 4 hours of oxidation, Fe(III)-precipitates were collected on 0.2 μm nylon filters and dried. The precipitates were analyzed by Fe K-edge EXAFS (XAS beamline, ANKA, Germany) and by P and Ca K-edge XANES spectroscopy (LUCIA beamline, SLS, Switzerland).

The Fe K-edge EXAFS spectra indicated that local Fe coordination in the precipitates systematically shifted with water composition. As long as water contained P, mainly short-range-ordered Fe(III)-phosphate formed (with molar P/Fe $\sim$0.5). In the absence of P, Fe(III) precipitated as hydrous ferric oxide at high Si/Fe>0.5, as ferrihydrite at intermediate Si/Fe, and mainly as lepidocrocite at Si/Fe<0.2. Analysis of the EXAFS by shell-fitting indicated that Fe(III)-phosphates mainly contained mono- or oligomeric (edge- or corner-sharing) Fe and that the linkage between neighboring Fe(III)-octahedra changed from predominantly edge-sharing in Si-rich hydrous ferric oxide to edge- and corner-sharing in ferrihydrite. Electron microscopic data showed that changes in local precipitate structure were systematically reflected in particle morphology and SAED patterns. The P K-edge XANES spectra revealed that phosphate was bound to both Fe as well as Ca (if present). The Ca K-edge XANES spectra showed that the mode of Ca uptake by the Fe(III)-precipitates shifted from mainly adsorption at high Fe/P to coprecipitation at low Fe/P ratio. Despite oversaturation, neither calcite nor hydroxyapatite formed to a significant extent.

The results from this study indicated that, depending on water composition, Fe(II) oxidation in natural waters leads to different types of short-range-ordered Fe(III)-phases. Since these phases are expected to differ in their effect on contaminant and nutrient dynamics, their specific physical and chemical properties warrant further research. Methodologically, this work demonstrated the usefulness of investigating the local structure of short-range-ordered precipitates along compositional gradients and by combining the element-selective information from different X-ray absorption edges.