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Reductive dissolution of As(V)-containing Fe oxidation products

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Amorphous to poorly-crystalline Fe(III)-precipitates formed by oxidation of dissolved Fe(II) are important sorbents for major and trace elements in environmental systems. Under reducing conditons, however, their reductive dissolution may result in the release of associated elements.

We examined the reductive dissolution kinetics of a range of different As(V)-containing Fe(III)-precipitates formed by oxidation of dissolved Fe(II) in synthetic groundwaters with different compositions. As function of the resulting phosphate (P) and silicate (Si) contents of the precipitates, their structure varied between poorly-crystalline lepidocrocite, amorphous Fe(III)-phosphate, and Si-containing ferrihydrite [1]. The reductive dissolution experiments were performed with 0.2-0.5 mM precipitate-Fe(III), 10 mM ascorbate as reductant, 5 mM bipyridine as Fe(II)-complexing ligand, and 10 mM MOPS / 5 mM NaOH as pH 7.0 buffer.

The times required for the dissolution of half of the precipitate ($t_{50\%}$) ranged from 1.5 to 39 h; i.e., varied by factor 25. Phosphate loadings up to ~0.2 P/Fe (molar ratio) decreased the $t_{50\%}$ of Si-free precipitates by factors ~5, probably by reducing the crystallinity of lepidocrocite. Fe(III)-phosphates with higher P/Fe ratios again dissolved more slowly, possibly because of inhibited ascorbate binding to solid-phase Fe(III). Phosphate-free Si-ferrihydrite with ~0.1 Si/Fe dissolved most slowly, suggesting that Si binding and polymerization may inhibit surface access of ascorbate. The inhibiting effect of Si was reduced by P. Dried precipitates dissolved 1.0 to 1.8-times more slowly than precipitates that were kept wet beore resuspension, pointing to drying-induced nanoparticle aggregation.

Our results emphasize that variations in the structure and composition of amorphous to poorly-crystalline Fe(III)-precipitates are linked to specific formation conditions and lead to substantial variations in their reductive dissolution kinetics. This should be taken into account when assessing the impacts of Fe(III)-precipitates on the fate of co-cycled nutrients and contaminants.

[1] Voegelin, A. et al. (2019) Reductive dissolution of As(V)-bearing Fe(III)-precipitates formed by Fe(II) oxidation in aqueous solutions. Geochem. Trans. 20:2.