

Structure of Fe(III)-Precipitates formed by Fe(II) Oxidation at Redox Interfaces and their Impact on Element Cycling

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Introduction

The oxidation of Fe(II) at redox interfaces leads to amorphous or short-range-ordered Fe(III)-precipitates, for instance in mine drainage (Fig. 1), in the rhizosphere of rice (Fig. 2), or in water treatment for P and As removal. Precipitates formed under varied conditions may substantially differ with respect to their role as colloidal carriers or immobilizing sorbents of essential nutrients and toxic contaminants as well as with regard to their biogeochemical reactivity, for instance their reductive dissolution or their stability over time.

Objectives & Approach

This project aims at elucidating the formation, structure and morphology of Fe(III)-precipitates under varying chemical conditions as well as their biogeochemical reactivity and impact on trace element dynamics in laboratory experiments and field systems by combining „macroscopic“ observations with electron microscopy and synchrotron-based X-ray techniques, most importantly X-ray absorptions spectroscopy (XAS, Fig. 4). The work is carried out as a collaboration between Andreas Voegelin (Molecular Environmental Geochemistry), Ralf Kaegi (Particle Laboratory) and Stephan Hug (Chemistry of Water Resources).



Fig. 4: Research in Molecular Environmental Geochemistry heavily relies on the use of synchrotron-based X-ray methods for element speciation and distribution mapping (image of ESRF).

Recent Results

We identified different types of short-range-ordered Fe(III)-precipitates that form in groundwaters with variable composition. For example, we demonstrated that as long as P is present, Fe(II) oxidation leads to the formation of Fe(III)-Ca-phosphates with distinct morphology at the single-particle level and characteristic molecular-level coordination (Fig. 3). Due to their high colloidal stability and potentially high reactivity, Fe(III)-Ca-phosphates may play a key role in the cycling of nutrients and contaminants at aquatic redox interfaces.

Outlook

In continuing work, we plan to further elucidate the mechanisms of Fe(III)-precipitate formation under varying chemical conditions combining laboratory experiments with state-of-the-art analytical tools. Further future research will also address the transfer of laboratory-based results to real systems such as element removal in water and wastewater treatment or trace element sequestration in sediments.

References

- Voegelin, A., Kaegi, R., Frommer, J., Vantelon, D., and Hug, S. J. (2010) *Effect of phosphate, silicate, and Ca on Fe(III)-precipitates formed in aerated Fe(II)- and As(III)-containing water studied by X-ray absorption spectroscopy*. *Geochim. Cosmochim. Acta* 74, 164-186.
- Kaegi, R., Voegelin, A., Folini, D., Hug, S. J. (2010) *Effect of phosphate, silicate, and Ca on the morphology, structure, and elemental composition of Fe(III) precipitates formed in aerated Fe(II) and As(III) containing water*. *Geochim. Cosmochim. Acta* 74, 5798-5816.



Fig. 1: Fe(III)-precipitates in metal-rich mine drainage discharging into a stream.

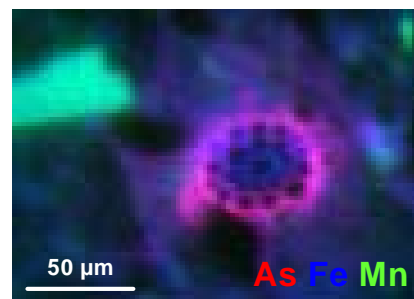


Fig. 2: Fe(III)-precipitates around rice root in As-contaminated soil (element distribution by micro-X-ray fluorescence spectrometry).

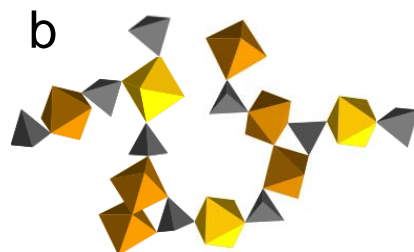
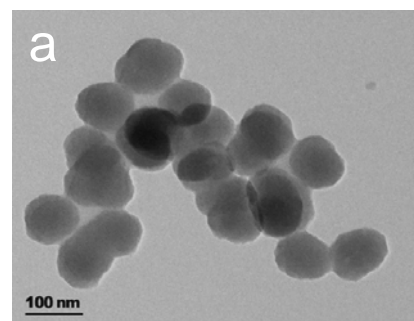


Fig. 3: (a) TEM image of Fe(III)-Ca-phosphate formed in presence of P and Ca in groundwater. (b) Local coordination of Fe (orange), P (gray) and Ca (yellow) derived from X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy at the K-edges of Fe, Ca and P.