

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



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| | Experiment title: Structure of amorphous to poorly crystalline Fe(III) nanoparticles | Experiment number: 01-01-930 |
| Beamline: BM01B | Date of experiment: from: 13.12.2013 to: 17.12.2013 | Date of report: 8.7.2014 |
| Shifts: 12 | Local contact(s): Hermann Emerich | <i>Received at ESRF:</i> |
| Names and affiliations of applicants (* indicates experimentalists): *Andreas Voegelin, Eawag, Switzerland *Anna-Caterina Senn, Eawag, Switzerland *Bas Vriens, Eawag, Switzerland Stephan Hug, Eawag, Switzerland Ralf Kaegi, Eawag, Switzerland | | |

Structure of amorphous to poorly crystalline Fe(III) nanoparticles

Introduction

Amorphous to poorly-crystalline Fe(III)-precipitates formed by Fe(II) oxidation or rapid Fe(III) hydrolysis in near-neutral water control the fate of co-transformed major and trace elements in a wide range of natural environments and technical systems. The main goal of our continuing research on such precipitates¹⁻³ is to gain detailed understanding of their structure and reactivity as a function of solution chemistry as a basis for improved quantitative models to describe their formation and impact on co-transformed elements, for example in the context of drinking water treatment for the removal of toxic arsenic.^{4, 5}

Use of beamtime allocated for experiment 01-01-930

In experiment 01-01-930, we proposed to use Fe K-edge EXAFS spectroscopy to investigate the effects of Si and humic acid on the structure of Fe(III)-precipitates over a range of phosphate/Fe ratios. The experiments with silicate allowed us to complete an extensive dataset of macroscopic and spectroscopic data on the interdependent effects of phosphate, silicate and Ca on Fe(III)-precipitate structure and composition. These results have been presented at several international conferences (e.g.,^{6, 7}). They will be published in two articles (one in preparation; one planned) and serve as a basis for ongoing experiments on the reactivity of different types of precipitates (e.g., oxyanion uptake, dissolution kinetics, heterogeneous oxidation kinetics). Because samples synthesized in the presence of humic acid could be measured during previous beamtime at another synchrotron facility, we instead analyzed a set of nearly 100 samples from an experiment addressing the effect of increasing Al fractions on Fe coordination in fresh and aged precipitates formed from Fe(II) and Al containing solutions. The results for fresh precipitates have recently been presented at an international conference⁸ and are briefly described in the following section. Overall, the experimental setup at the SNBL proved highly effective for these experiments, which rely on the characterization of large number of samples formed over multifactorial parameter spaces by Fe K-edge EXAFS spectroscopy.

Structure and arsenate uptake of Fe(III)-Al-precipitates

Introduction. Mixing of acidic Fe(II)- and Al-containing acidic mine drainage with near-neutral surface water results in rapid Fe(II) oxidation and formation of Fe(III)-Al-precipitates that may incorporate trace elements including toxic As.⁹ The structure of these precipitates and the extent of As(V) uptake are expected to depend on the dissolved Fe/Al ratio and the concentrations of ions such as phosphate. Our objective was to examine how the molar Fe(II)/Al ratio in acidic drainage water and dissolved phosphate in near-neutral surface water affect the structure and arsenate uptake of Fe(III)-Al-precipitates formed upon mixing. Macroscopic data on phosphate and As(V) uptake were combined with results on precipitate structure from Fe K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy.

Experimental. Four mM CaCO₃ were dissolved in CO₂-purged water, 500 µg/L As(V) (Na₂HAsO₄×7H₂O) added, the pH raised to 7.0 by purging with air, and the solutions spiked with 0-1 mM phosphate (NaH₂PO₄×H₂O). Precipitate formation was initiated by adding 0.5 mM (Al+Fe(II)) using a 50 mM (Al+Fe(II)) (in 1 mM HCl) stock solution prepared from FeSO₄×7H₂O and Al₂(SO₄)₃×H₂O. Samples were synthesized at 6 molar Al/(Al+Fe) ratios (0.00, 0.05, 0.10, 0.20, 0.50, 1.00) and ten P/(Al+Fe) ratios from 0.00 to 1.5. After 4 h, the solution and precipitates were collected and the precipitates dried for analysis.

Fe K-edge EXAFS spectra were recorded in transmission mode on dried precipitates prepared as pellets (with cellulose). All Al-containing samples were analyzed during experiment 01-01-930 (50 fresh samples). For each sample, two EXAFS scans over a k-range up to 13 Å⁻¹ were recorded in continuous-scan mode (~25 min per sample). Spectra of precipitates without Al and of most references were measured previously at ANKA (Karlsruhe, Germany). The averaged spectra were treated and evaluated by linear combination fitting (LCF) using the software code Athena.¹⁰

Results. Fe K-edge EXAFS spectra of references and selected samples are shown in Fig. 1. The LCF analysis of the Fe K-edge EXAFS spectra of 50 sample spectra (Fig. 2) revealed that increasing Al (i) reduced lepidocrocite and increased ferrihydrite-like Fe in phosphate-free precipitates and (ii) moved the transition to exclusive Fe(III)-phosphate-like Fe coordination to lower initial dissolved P/(Al+Fe) ratios. At

low P/(Al+Fe) ratios, Al induced schwertmannite-like Fe coordination and at high P/(Al+Fe) ratios, Ca induced mitridatite-like Fe coordination. To date, additional insight into the effect of Al in the absence of phosphate was gained from X-ray diffraction (XRD) and transmission electron microscopy (TEM) images, and further complementary precipitate characterization is planned. The structural variations as a function of Al/(Al+Fe) ratio resulted in up to two orders of magnitude differences in residual dissolved arsenate (not shown). The direction of this effect depended on the initial dissolved P/(Al+Fe) ratio: Increasing Al fractions (i) increased As(V) uptake by Fe(III)-Al-precipitates at low P/(Al+Fe) ratios by decreasing the crystallinity of the Fe-rich precipitate but (ii) reduced As(V) uptake at elevated P/(Al+Fe) ratios by reducing the oxyanion sorption capacity of the Fe(III)-Al-precipitates and by increasing their preference for phosphate over arsenate.

Conclusions. The results from this experiment on the effect of Al on precipitate formation over ranges in Al/(Al+Fe) and P/(Al+Fe) ratios document the highly interdependent effects of different solutes – here Al and phosphate – that can interfere with Fe(III)-polymerization in different ways. A detailed understanding of these interdependent effects is essential to reliably quantify the uptake of co-transformed trace elements such as As, and requires the characterization of large sets of samples over multifactorial parameter spaces. Ultimately, this approach enables to develop quantitative models for the structure of Fe(III)-precipitates and their ion uptake behavior as a function of variations in solution chemistry relevant for natural aquatic and terrestrial as well as technical systems.

References

(proposers in **bold**; papers/presentations including data recorded at SNBL marked with *)

1. **Voegelin, A.; Senn, A.-C.; Kaegi, R.; Hug, S. J.**; Mangold, S., Dynamic Fe-precipitate formation induced by Fe(II) oxidation in aerated phosphate-containing water. *Geochim. Cosmochim. Acta* **2013**, *117*, 216-231.
2. **Voegelin, A.; Kaegi, R.**; Frommer, J.; Vantelon, D.; **Hug, S. J.**, 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* **2010**, *74*, 164-186.
3. **Kaegi, R.; Voegelin, A.**; Folini, D.; **Hug, S. J.**, 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* **2010**, *74*, 5798-5816.
- *4. **Voegelin, A.; Kaegi, R.**; Berg, M.; Nitzsche, K. S.; Kappler, A.; Lan, V. M.; Trang, P. T. K.; Göttlicher, J.; Steininger, R., Solid-phase characterization of an effective household sand filter for As, Fe and Mn removal from groundwater in Vietnam. *Environmental Chemistry* **in press**.
5. Neumann, A.; **Kaegi, R.; Voegelin, A.**; Hussam, A.; Munir, A. K. M.; **Hug, S. J.**, Arsenic removal with composite iron matrix filters in Bangladesh: a field and laboratory study. *Environ. Sci. Technol.* **2013**, *47*, 4544-4554.
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- *7. **Voegelin, A.**, Formation of Fe precipitates at dynamic redox interfaces and their impact on trace elements. *International Seminar "Dynamic Processes in Capillary Fringes"*, Karlsruhe, Germany, 24-25 February **2014**.
- *8. **Voegelin, A.; Senn, A.-C.**, Structure and arsenate uptake of Fe(III)-Al-precipitates. In *Goldschmidt Conference*, Sacramento, CA, USA, 8-13 June **2014**.
9. Adra, A.; Morin, G.; Ona-Nguema, G.; Menguy, N.; Maillot, F.; Casiot, C.; Bruneel, O.; Lebrun, S.; Juillot, F.; Brest, J., Arsenic scavenging by aluminum-substituted ferrihydrites in a circumneutral pH river impacted by acid mine drainage. *Environ. Sci. Technol.* **2013**, *47*, 12784-12792.
10. Ravel, B.; Newville, M., ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Rad.* **2005**, *12*, 537-541.

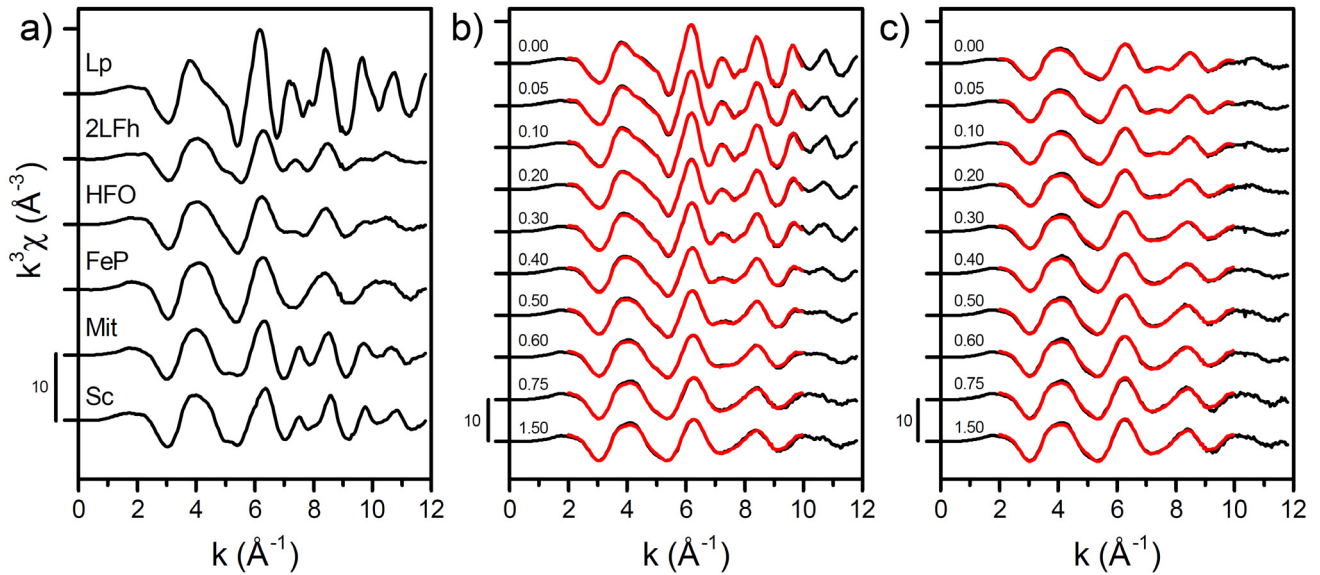


Fig. 1: Fe K-edge EXAFS spectra. **(a)** References used for LCF analysis (Lp= lepidocrocite, 2LFh= ferrihydrite, HFO= hydrous ferric oxide, FeP= amorph. Fe(III)-phosphate., Mit= mitridatite; Sc= schwertmannite). **(b/c)** Experimental (black) and LCF spectra (red) of precipitates formed at Al/(Al+Fe) ratios of 0.05 and 0.50 and P/(Fe+Al) ratios from 0.00 to 1.50.

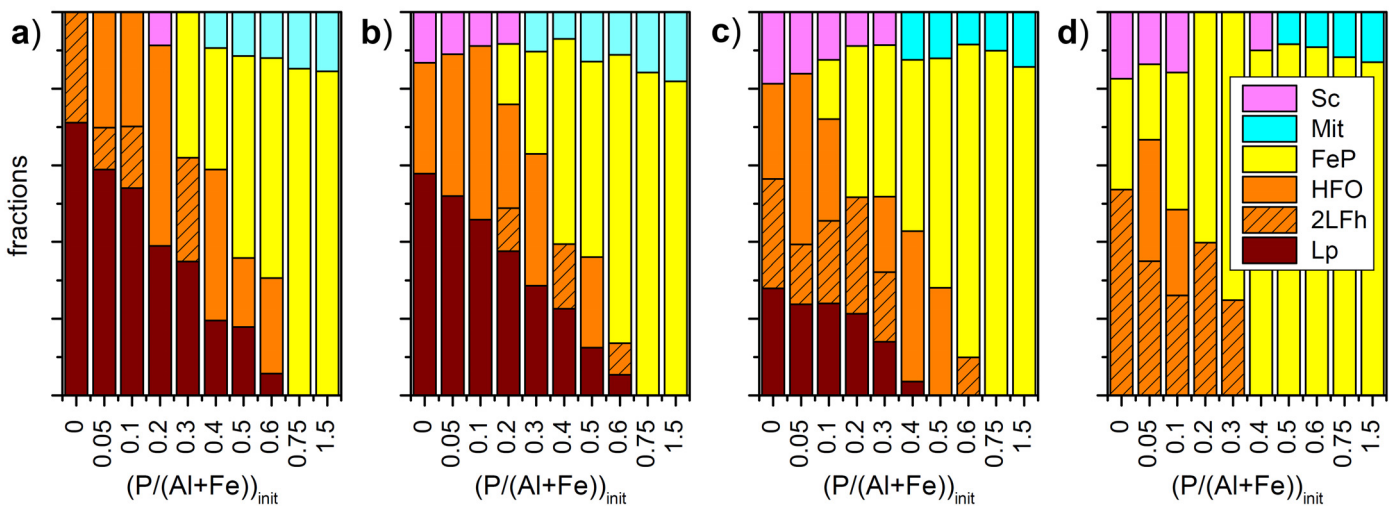


Fig. 2: LCF fractions (i.e., fraction of reference spectra needed to reproduce sample spectra) for precipitates formed at Al/(Al+Fe) ratios of **(a)** 0.00, **(b)** 0.05, **(c)** 0.20 and **(d)** 0.50. Results for an Al/(Al+Fe) ratio of 0.10 (not shown) fell in between those for ratios 0.05 and 0.20. $(P/(Al+Fe))_{init}$ denotes the initial molar P/(Al+Fe) ratio in solution.