

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.



	Experiment title: Temporal evolution of Fe(III) precipitates during Fe(II) oxygenation in water and subsequent aging: Effect of phosphate and calcium	Experiment number: 01-01-888	
	Beamline: BM01B	Date of experiment: from: 28.11.2012 to: 3.12.2012	Date of report: 8.3.2013
Shifts: 18	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 Stephan Hug, Eawag, Switzerland Ralf Kaegi, Eawag, Switzerland			

Report

We used Fe K-edge EXAFS spectroscopy to characterize the structure of synthetic Fe(III)-precipitates formed by the oxidation of 0.5 mM Fe(II) in aerated aqueous solutions buffered to pH 7.0 (8 mM $\text{HCO}_3^-/\text{CO}_2$) in the absence and presence of Ca at molar phosphate/Fe ratios from 0 to 2. The analysis included both fresh precipitates collected after complete Fe oxidation (4 h reaction time) as well as precipitates that were aged for 30 d at 40°C in their synthesis solution.

The Fe K-edge EXAFS spectra were recorded at room temperature in transmission mode. Spectra suitable for analysis by linear combination fitting and structural shell fitting could typically be obtained within 30-60 min. In combination with the 10-fold sample changer available at the beamline, this allowed to make very effective use of the available beamtime, despite the reduced ring current in 16-bunch mode. Examples for spectra collected during this experiment are shown in Fig. 1. Note: Because the measurement time per sample was lower than anticipated, we were able to analyze additional samples from other Fe-related projects (Fe speciation in loess from the Chinese loess plateau; characterization of Fe colloids mobilized from different types of soils; redox-state and coordination of Fe(II) and Fe(III) reacted with reduced and oxidized humic acid). Some of these analyses served as feasibility tests. Other results have already been included in a scheduled conference contribution (see references) and form part of a manuscript in preparation.

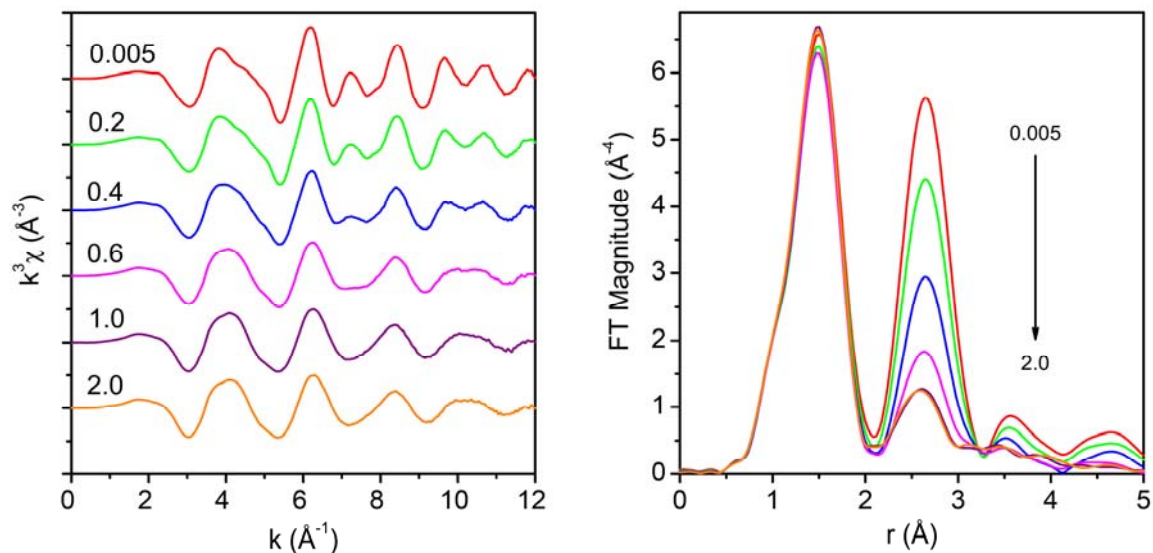


Fig. 1: Fe K-edge EXAFS spectra of fresh precipitates formed in 4 mM CaCO_3 background electrolyte at pH 7.0 at initial dissolved phosphate/Fe(II) ratios from 0.005 to 2.0 (indicated by numbers assigned with spectra in k-space; arrow shows trend in second-shell FT amplitude with increasing P/Fe).

Spectra as shown in Fig. 1 were also collected from fresh precipitates formed in NaHCO_3 background electrolyte, as well as from aged Fe(III)-precipitates. The spectral changes observed in Fig. 1 reflect the transition from predominantly poorly crystalline lepidocrocite in the absence or at very low P/Fe ratios to increasing fractions of amorphous Fe(III)-phosphate as P/Fe ratio in the starting solution increases. For the analysis of these spectra by linear combination fitting (LCF), we relied on spectra for crystalline lepidocrocite and goethite as well as amorphous hydrous ferric oxide and Fe(III)-phosphate measured in previous work (Voegelin et al., 2010). Amorphous Fe(III)-phosphate fractions derived by LCF analysis as a function of initial dissolved phosphate/Fe ratio are shown in Fig. 2.

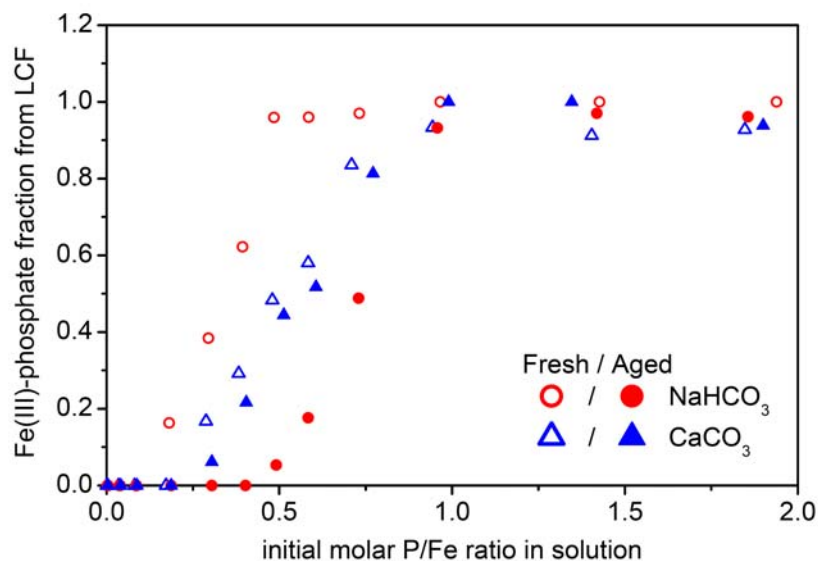


Fig. 2: LCF-derived fractions of amorphous Fe(III)-phosphate in fresh and aged precipitates formed in NaHCO_3 and CaCO_3 background electrolyte as a function of the initial molar phosphate/Fe(II) ratio in solution. Note: part of the LCF results were obtained on spectra previously measured at ANKA.

For fresh precipitates, LCF results showed that exclusive Fe(III)-phosphate formation in the absence of Ca occurred at lower P/Fe ratio than in the presence of Ca. Based on wet-chemical analysis, this could be attributed to a higher molar P/Fe ratio of amorphous Fe(III)-phosphate formed in Ca- than Na-electrolyte. Closer inspection of the EXAFS spectra of precipitates formed at high P/Fe ratios points to the formation of mixed Ca-Fe(III)-phosphates in the presence of Ca. The absence of Fe(III)-phosphate in precipitates formed at low P/Fe ratios (<0.2) can be attributed to the transformation of initially formed Fe(III)-phosphate during continuing oxidation (Voegelin et al., 2013).

Upon aging, substantially lower Fe(III)-phosphate fractions were observed in precipitates in NaHCO₃ background electrolyte, due to continuing Fe(III) polymerisation. This resulted in substantial resolubilisation of phosphate as well as of arsenate (which was present at trace levels in all experiments). In contrast, only a minor decrease of the Fe(III)-phosphate fractions was observed in the presence of Ca, in line with wet-chemical data showing a much lower resolubilisation of P and As. We attribute this difference to inhibited Fe(III)-polymerization as a result of Ca incorporation into mixed Ca-Fe(III)-phosphates.

The results from this experiment provide valuable new insight into the formation and aging of Fe(III)-precipitates formed by Fe(II) oxidation in aqueous solutions and allow to relate changes in dissolved element concentrations to variations in precipitate structure. For publication, EXAFS results are complemented with precipitate characterisation by XRD, FTIR, TEM as well as by wet-chemical data on dissolved element concentrations. The findings from this study have important implications with respect to the fate of Fe and co-transformed major and trace elements in natural and technical systems (surface- and groundwater resources, soils and sediments, drinking water purification and wastewater treatment). In continuing work, we aim to further explore how silicate and humic acid affect Fe(III)-polymerization and phosphate-Fe interactions.

Recent and forthcoming presentations including results from experiment 01-01-888:

Senn, A. C., Kaegi, R., Hug, S., Hering, J. G., Voegelin, A., *Effects of P, Si and Ca on composition, structure and As uptake of fresh and aged precipitates*. International Monte Verità Conference “Iron Biogeochemistry - From Molecular Processes to Global Cycles”, 3-8 March 2013, Ascona, Switzerland.

Regelink, I. C., Weng, L., Voegelin, A., Koopans, G. F., Comans, R., *Characterisation of iron-(hydr)oxides in bulk soils and colloidal fractions using state-of-the-art techniques*. European Geosciences Union General Assembly, 7-12 April 2013, Vienna, Austria.

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.
- Voegelin, A., Senn, A.-C., Kaegi, R., Hug, S. J., and Mangold, S., 2013. Dynamic Fe-precipitate formation induced by Fe(II) oxidation in aerated phosphate-containing water. **in review**.