

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:

Cable bacteria affect the P cycle in lakes by dissolving Fe-sulfides and Mn-carbonates and forming Mn and Fe oxides in lake sediments

Experiment number:

26-01-1002

Beamline:

BM26

Date of experiment:

from: 23/04/14 to: 26/06/14

Date of report:

24/06/2014

Shifts:

12

Local contact(s):

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Technical aspects

The project was devoted to characterizing the seasonal changes in Fe and Mn speciation in sediments from the Lake Grevelingen, the Netherlands. Resin embedded sediments were investigated by collecting XAFS spectra at the K α -edges of Mn and Fe. X-ray absorption was measured in reference materials in transmission mode while fluorescence mode was used for the sediment samples.

The experiment was performed as planned without any significant problems or amendments. It was fortunate, that the optics were already optimized for the Fe K α edge so that the collection of data was started without any delay. The support by the DUBBLE staff was excellent and ensured optimal use of the beamtime. In addition to several reference materials, Fe and Mn XAS spectra were collected at various depths of 4 resin embedded core sections. The technical facilities at the DUBBLE beamline were perfectly suitable for the experiment. However, for collecting spectra on samples with vertical dimension of several centimeters, a faster z-stage with a larger range than 1.4 cm would be helpful.

Results

Against expectation, all Fe XANES and EXAFS spectra collected from the cores were very similar and showed no pronounced systematic variation with depth or difference between cores collected at different months (exemplarily shown for spectra from cores collected in March and May 2012 in Fig. 1 and 2.). When comparing the spectra with those of reference materials, greatest similarity is found with spectra from clay minerals such as nontronite and glauconite. Preliminary results from linear combination fitting indicate, that the XANES and EXAFS spectra can be satisfactorily reproduced by a combination of spectra from glauconite and biotite. Including the spectra of reactive Fe phases such as ferrihydrite, hematite, pyrite, or siderite into the combinatory fitting improves the quality of the reproduction but the relative contribution of these spectra to the combined fit is less than 10%. The Fe spectra of biotite and glauconite might be representative for, respectively, Fe(II) and Fe(III) bound in silicates in octahedral coordination. This suggests, that the Fe spectra collected from the cores might be dominated by the contribution of silicate-bound Fe while the contribution of oxides, carbonates, and sulfides might be only minor.

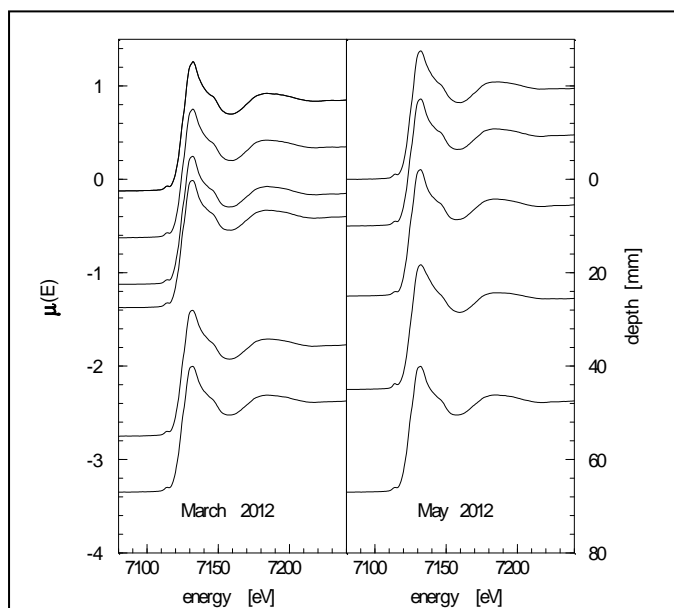


Fig. 1 Fe-XANES spectra from cores retrieved in March and May 2012, respectively. The spectra are stacked so that the position of the pre-edge line corresponds to the vertical position in the core section.

This is in contrast to the results from the chemical extractions which indicate that reactive Fe phases can account for up to about 50% of total Fe in these cores and that total Fe concentrations can vary significantly with depths. The latter trend was also not reflected by the XAS measurements as the fluorescence intensities, for one core section at constant detector distance, did not show pronounced decrease with depth. The reason for the discrepancy between XAS results and chemical extractions is enigmatic but two possible explanations can be given: 1) During the various chemical extractions steps, a significant proportion of silicate-bound Fe is leached in addition to oxides, sulfides, and carbonates. 2) A part of the reactive Fe, in particular Fe oxides, are lost or altered during the resin embedding. The suitability of the method to preserve reduced Fe phases, such as pyrite, has been tested but it might be possible that freshly precipitated Fe oxides might react with sulfide during the preparation procedure. A possible source for sulfide could be FeS occurring in deeper parts of the core. In any case, elucidating the reason for the observed inconsistency between the results from chemical extractions and XAS analyses is of high importance. This is because unraveling the underlying reason for the discrepancy has either direct consequences for the interpretation of results from chemical extractions or might induce adaptations of the embedding method in order to preserve highly reactive, oxidized Fe phases.

Mn concentrations in the cores were, in general, much lower than Fe concentrations. As a consequence, collection of good quality EXAFS spectra was not feasible. On the other hand, enrichment of reactive Mn phases was expected to leave a stronger signature in the XAS spectra compared to Fe phases due to the lower signal from detrital Mn phases. Mn XANES spectra collected for cores during March 2012 (Fig. 3) systematically changed with depth over the upper 4 mm. Within the group of analyzed reference materials, the spectrum of the Mn containing silicate babingtonite bore resemblance to the spectra from deeper parts of the cores. This suggests, that the contribution of detrital Mn silicates dominates the spectra in deeper parts of the sediment. The XANES spectrum at the top of the sediment from March 2012 can be reproduced by a combination of the spectrum collected at 10mm depth plus the spectra of Mn(III) oxides, such as manganite or bixbyite, suggesting that the top part of the sediment contained Mn oxides. However, this trend was not observed in cores from other months for which chemical extractions also indicate enrichment of Mn oxides in the upper part.

Conclusions

Analyses of Fe and Mn XAS spectra from the resin embedded cores do not provide strong support for the seasonal accumulation of Fe and Mn oxides in the sediments due to the activity of cable bacteria. The interpretation of the XAS spectra is in disagreement with the results from the chemical extractions. In order to resolve this contradiction, XAS spectra should be collected from sediment material, which has not been embedded, and compared to those after embedding. These results will reveal the effect of the embedding procedure on reactive Fe and Mn oxides.

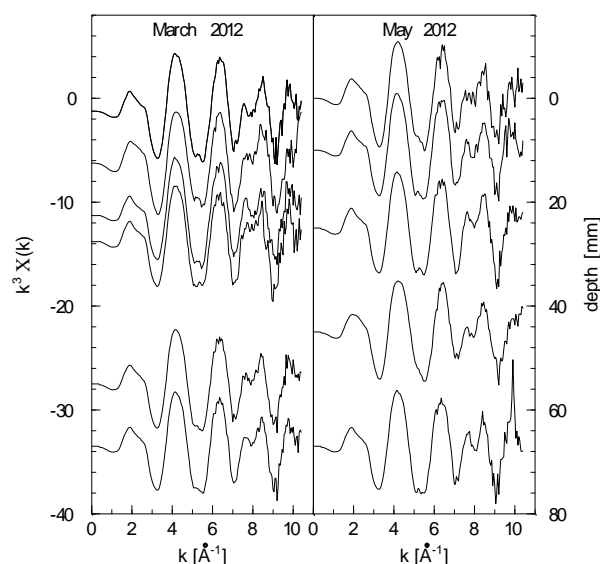


Fig. 2 Fe-EXAFS spectra from cores retrieved in March and May 2012, respectively. The spectra are stacked so that the position of the background line corresponds to the vertical position in the core section.

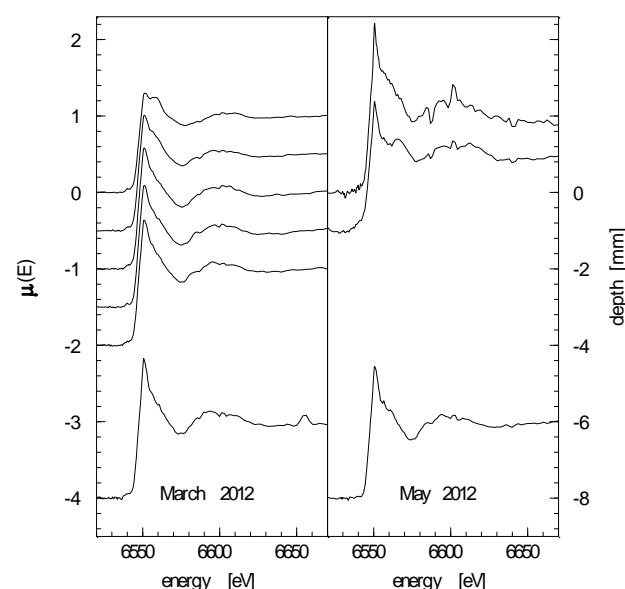


Fig. 3 Mn-XANES spectra from cores retrieved in March and May 2012, respectively. The spectra are stacked so that the position of the pre-edge line corresponds to the vertical position in the core section.