EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

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 via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can 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.

ESRF	**Experiment title:** Phosphorus burial in hypoxic marine sediments	**Experiment number**: ES45
Beamline: ID21	**Date of experiment**: from: 19/04/2013 to: 22/04/2013	**Date of report**:
Shifts: 9	**Local contact(s)**: Camille Rivard, Marine Cotte	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Summary of approach

The goal of project ES45 was to identify the mineral phases responsible for burial of phosphorus (P) in low-oxygen marine sediments, using a combination of micro XRF mapping, P K-edge micro XANES. In particular, we are interested to determine the presence of Fe (II) and Mn (II) phosphates in these sediments. Sediment samples from three low-oxygen systems (the Baltic Sea, the Bothnian Sea and the saline Grevelingen Lake, Netherlands) were prepared by anoxic epoxy-resin embedding. In order to quickly navigate at ID21 to P-rich zones on the samples, pre-mapping at 30 µm resolution was performed on a desktop Orbis micro XRF at Utrecht. One sample from each of the three locations was analysed in turn at ID21. From each sample, a small number of pre-identified P-rich zones was targeted. Initially, micro XRF maps were made of the regions of interest using a focused beam (0.35 x 0.7 µm) at 2.4 keV. XANES spectra across the P K-edge (2.13-2.22 keV) were then collected in fluorescence mode from regions of high P counts in the micro XRF maps. A series of phosphate mineral standards, included freshly synthesized vivianite (stored permanently in an argon-filled jar), were prepared in pellets. XANES spectra were collected in fluorescence mode using an unfocused beam.

Results

Regions of high P concentrations were easily located in the epoxy-embedded sediment samples. In the sample from the central Baltic Sea, P was enriched in biogenic structures of 100-200 µm diameter, and in smaller globular structures elsewhere in the sediment matrix (Fig. 1). The XANES grabs from these samples varied regarding the white line intensity but were similar in view of the lack of pre- and post-edge features. This indicates that P is likely bound in Fe (II) and/or Mn (II) phases in these sediments. Similar XANES spectra were observed in P enrichments in the sample from the Bothnian Sea.

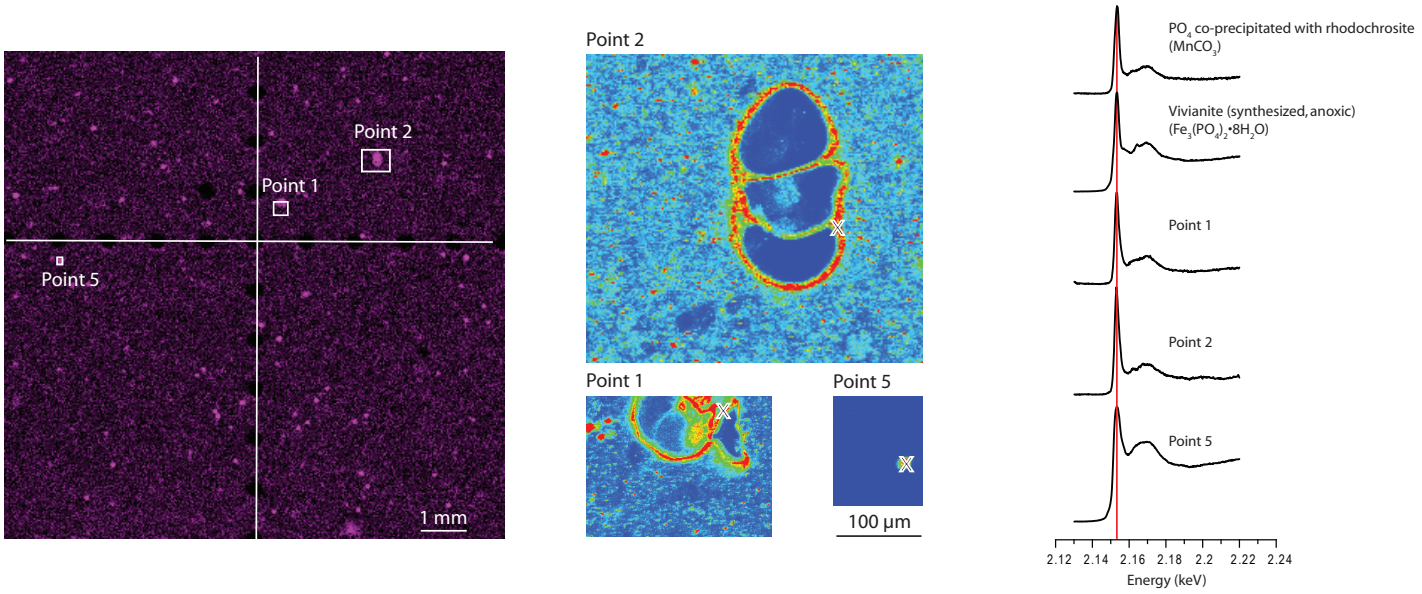

Figure 1. (left) Desktop 30 µm-resolution XRF mapping of P in an epoxy-embedded sediment sample from the central Baltic Sea, performed in Utrecht prior to the visit to ID21. Bright color = higher P counts. Note the grid of 1 mm-separated drilled holes along the x and y axes, which was used for navigation. Rectangles indicate the areas targeted for higher-resolution XRF mapping. (middle) 1 to 2 µm-resolution XRF mapping of P in the targeted areas. Crosses indicate locations selected for XANES grabs. Red = high P counts, blue = low P counts. (right) XANES spectra of the selected locations and of Fe (II) and Mn (II) phosphate standards. Vertical red line indicates the P K-edge white line of variscite.

In contrast, all the prominent P enrichments in the sample from the Grevelingen Lake showed XANES spectra indicative of Ca-phosphates. These spectra are characterized by a P K-edge white line shifted slightly to lower energies with respect to the variscite standard, and by a pronounced post-edge shoulder as observed in the Ca-phosphate standards. The larger P enrichments in this sample also appear to be associated with biogenic structures.

In order to deconvolve potential Fe (II) and Mn (II) phosphate enrichments in the samples from the Baltic and Bothnian Seas, we extracted the distributions of multiple elements from the high resolution XRF maps. In the case of the sample from the Baltic Sea, these results show that the mineral phase present at Point 1 is likely a Mn (II) phosphate in the rim of the biogenic particle, where both P and Mn are enriched while Fe is depleted (Fig. 2). This level of spatial detail is unprecedented in these studies and will greatly assist our efforts to understand the processes by which P is sequestered in low-oxygen sediments.

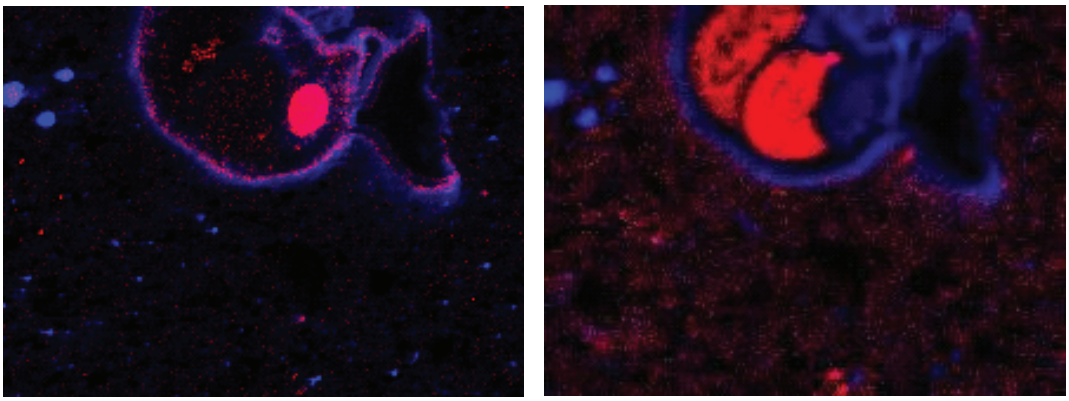

Figure 2. Spatial distribution of the intensity of P K-lines fluoresence (blue) in comparison to those of Mn L-lines (red, left) and Fe L-lines (red, right) at Point 1 of the Baltic Sea sediment sample. Purple zones indicate co-occurrence of the two elements in each map.