EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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**: ES171
Beamline: ID21	**Date of experiment**: from: 16/04/2014 to: 22/04/2014	**Date of report**: 9.3.2015
Shifts:	**Local contact(s)**: Camille Rivard	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Summary of approach

The goal of project ES171 was to identify the mineral phases responsible for burial of phosphorus (P) in low-oxygen marine sediments, using a combination of micro XRF mapping and micro XANES. We gathered data at the P, Fe and Mn K-edges. ES171 was a continuation of ES45 (carried out at ID21 in April 2013).

Resin-embedded sediment samples from two marine systems (the Baltic Sea and the Bothnian Sea) were prepared in advance of the visit to ID21 by anoxic epoxy-resin embedding. Pre-mapping was performed on a desktop Orbis micro XRF at Utrecht. The samples were also pre-drilled with a grid of holes which were visible under the video microscope at ID21.

Several samples from each location were analysed at ID21, including a series of samples from increasing sediment depth at a site in the Bothnian Sea. Initially, micro XRF maps were made of the samples of interest using a focused beam at 7.2 keV. Co-incident enrichments of Fe, Mn and P were identified for micro XANES and EXAFS analyses. The experiment was started with XRF mapping above the Fe K-edge and Fe and Mn K-edge XAS analyses, before shifting the energy to the P K-edge and returning to the same enrichments to collect P K-edge XANES.

A series of phosphate mineral standards, and additional Fe and Mn-contaning materials, were prepared and analyzed at the relevant edges by XANES. Additionally, a number of P-EXAFS spectra were collected on both samples and standards materials, to test the feasibility of this technique for future work. All XAS analyses were performed in fluorescence mode.

Results

XANES spectra of the standard materials show distinct fingerprints at the P, Fe and Mn K-edges (Fig. 1), which were subsequently used for the linear combination fitting of sample spectra.

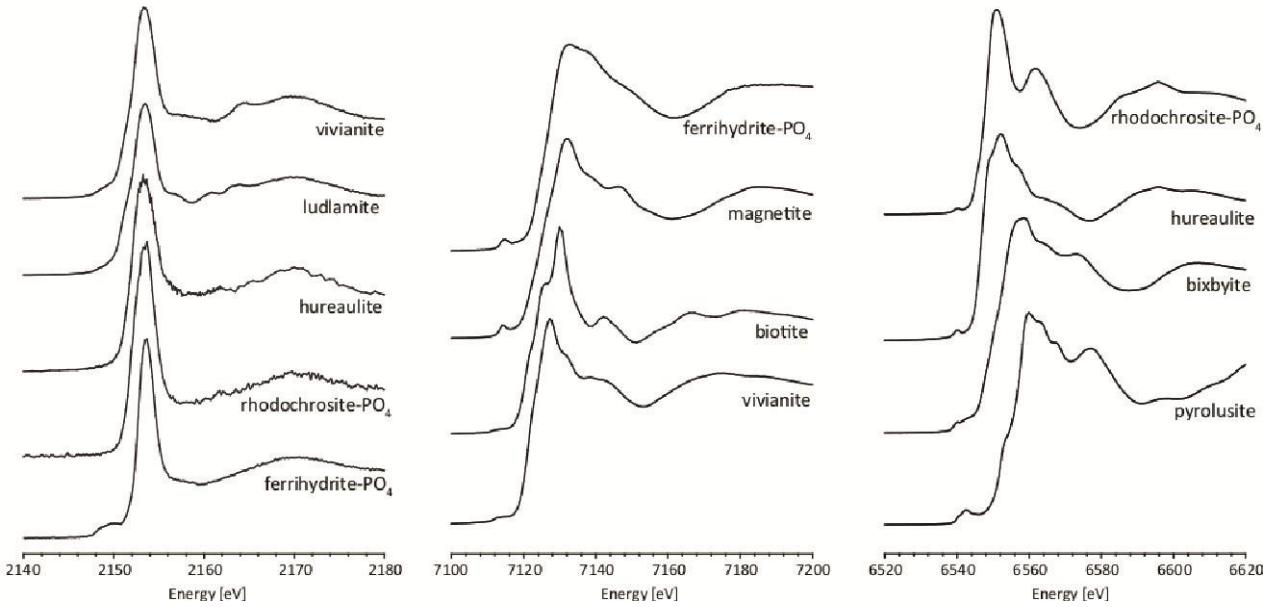

Figure 1. P, Fe and Mn XANES spectra of standard materials (from Egger et al., in preparation for Geochimica et Cosmochimica Acta)

Multiple 100-micron-scale co-enrichments of Fe, Mn and P were found in the samples (Fig. 2), indicating authigenic Fe-Mn phosphate crystals in the sediments. The P, Fe and Mn XANES spectra collected on these crystals (not shown) suggest a combination of Fe(II) and Fe (III) phosphates with variable concentrations of Mn. These results are consistent with bulk sediment extraction data and porewater concentrations of Fe and Mn.

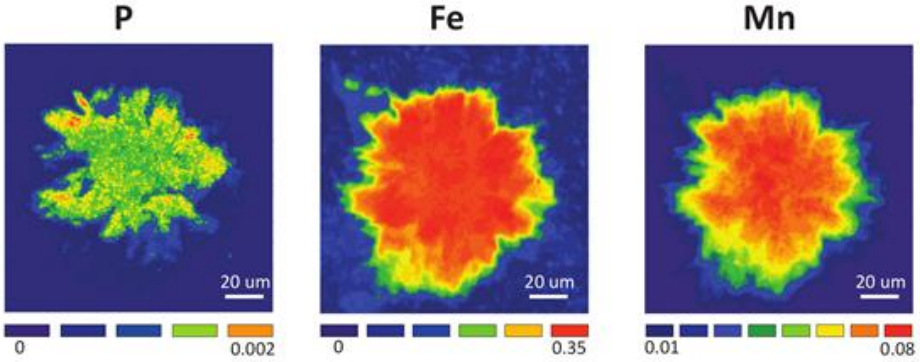

Figure 2. P, Fe and Mn XRF maps made at 7.2 keV, showing coincident enrichments of all theree elements in a resin-embedded sediment sample from the Bothnian Sea (from Egger et al., in preparation for Geochimica et Cosmochimica Acta).

The P-EXAFS test data yielded reasonable results on both standard powders (Fig. 3) and on P enrichments in samples, providing the P XRF counts were sufficiently high to give low-noise spectra.

The experiment proceeded as planned, without technical problems, and was greatly assisted by the expertise of Camille Rivard. This work will contribute to three manucripts for publication in peer-reviewed journals. The first of these is at an advanced stage of preparation as of March 2015.

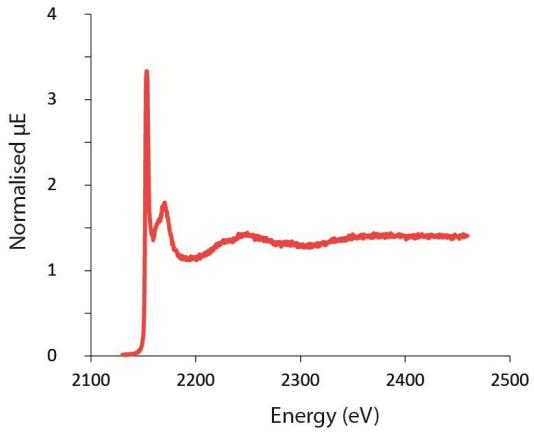

Figure 3. Example P-EXAFS spectrum of Mn(II) phosphate powder pellet analysed at ID21.