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:** What is driving the iron shuttle from coastal shelves to deep basins?	**Experiment number:** ES 591
Beamline: ID21	**Date of experiment:** from: 03/05/2017 to: 09/05/2017	**Date of report:** 28/08/2017
Shifts: 18	**Local contact(s):** Wout de Nolf and Ana Pradas del Real	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The experiment has been very successful and was executed, in most respects, as planned. The extra allocated beamtime and the very favourable course of the experiment allowed us to extend the experimental programme and the set of analysed samples. That is, in addition to Fe also XAFS spectra were collected at the Mn K-edge. Furthermore, suspended material from the Baltic Sea, cable bacteria retrieved from different sediments, and resin-embedded sediments were analysed. The latter were collected at the corresponding sites at which also suspended material had been sampled. First results from μ-XRD measurements of some representative samples demonstrated that the signal from thin sections of resin-imbedded sediments is sufficient to perform μ-XRD analyses.

In total 11 filters were analysed. The suspended material had been collected by different methods. Filters contained only small amounts of suspended material when they were obtained by filtration of bottles with water from distinct depths intervals. μ-XRF results showed the diversity of materials but concentrations of Fe and Mn were usually too low to obtain XAFS spectra of sufficient quality. Filters, which were collected in situ by pumping large quantities of water through a filtration unit, contained sufficient material and were suitable for XAFS analyses. However, the thickness of the material on the filter undermined the advantage of working with a focussed beam. It was possible to distinguish and to identify different Mn containing phases on the filters including different Mn oxides, Mn in silicates, and, at one location in the Black Sea, a Mn sulphide. Most of the analysed Fe-rich spots contained silicate-bound Fe, predominately Fe containing clay minerals (see Fig.1). The omnipresence of clay minerals, however, impeded the unequivocal identification of Fe oxides based on XANES and EXAFS analyses as the quality of the spectra was usually insufficient to separate a small signal from Fe oxides from the overwhelming contribution of silicate-bound Fe.

The ubiquitous presence of Fe containing silicates also presented a challenge in characterizing small quantities of reactive Fe phases in sediment samples. Presence of Fe sulphides and their identification as pyrite could be established in samples from sulphidic sediments but substantiating the presence of Fe oxides and their detailed characterization remained problematic. However, very interesting results were obtained regarding the characterization of Mn phases in Baltic Sea sediments. The results demonstrate that Mn-oxides, which form in the water column and are buried in the sediment, transform into Mn carbonates. The investigated sediments showed layers of Mn carbonate which witness oxidation events in the Baltic. An unexpected and relevant finding is that these carbonates can react further to form Mn phosphates. This mechanism counteracts the release of phosphate, which is formed in deeper sediment layers, into the overlying waters. The combination of μ-XRF and μ-XAS allowed us to demonstrate that, over a depth interval of a few millimetres, several Mn-rich layers are present and differ regarding the presence of Mn phosphates. Presence of Mn carbonates (rhodochrosite) was further confirmed by μ-XRD. It still needs to be investigated whether the relative abundance of Mn phosphates can be obtained from μ-XRD mapping.

Part of the results were presented at the Goldschmidt conference 13-18 August 2017 in Paris, France: 1) Hermans et al: Impact of natural reoxygenation on the sediment geochemistry in a euxinic Baltic Sea basin and 2) Lenstra et al.: The shelf-to-basin iron shuttle in the Black Sea revisited. Manuscripts on these subjects are in preparation.

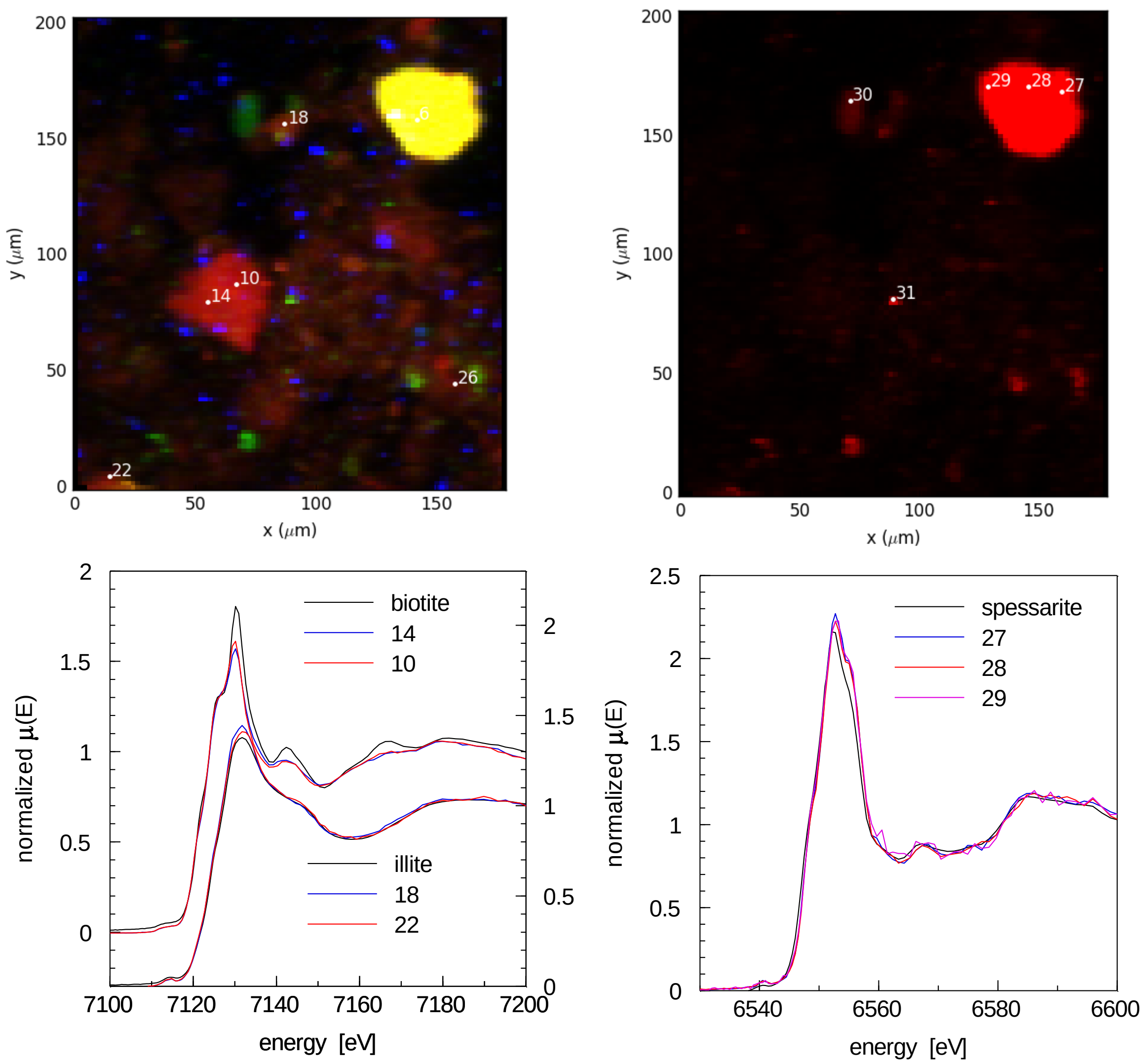

Fig 1. Example of results obtained from filters containing suspended material from the Black Sea. Top: elemental maps obtained by μ-XRF analyses; left panel: blue=P, red=Fe, green=Mn, numbered dots= spots of Fe XAS analysis; right panel: red=Mn, numbered dots= spots of Mn XAS. Bottom: examples of Fe(left) and Mn(right) XANES spectra in comparison with those of reference materials.