EUROPEAN SYNCHROTRON RADIATION FACILITY
INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: **Phosphorus burial mechanisms in deep Black Sea sediments**	**Experiment number**: ES-288
Beamline: ID21	**Date of experiment**: from: 22 April 2015 to: 25 April 2015	**Date of report**: 26-02-2016
Shifts: 9	**Local contact(s)**: Camille Rivard, Murielle Salome	*Received at ESRF:*

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Report:

Summary of approach

The goal of project ES288 was to identify P burial phases in the strongly reducing deep Black Sea, where chemical data suggested the (highly unlikely) abundant presence of Fe-bound P. We took resin-embedded blocks of surface sediment from the deep Black Sea to ESRF (beamline ID21) to collect micro-XRF maps of Ca, Fe, Mn and P distributions and spot Fe K-edge and P K-edge X-ray absorption spectra to determine Fe and P speciation. The sediment blocks were already analyzed by µXRF (Orbis µXRF, 30x30 µm resolution) at our home institute. Using a micro-drill, we drilled a 2-D grid with 2 mm spacing into the resin blocks before our ESRF trip for easy spatial navigation at ID21. In addition, we took powdered bulk samples from anoxic sediment intervals from the Black Sea and of the Baltic Sea to collect bulk P K-edge XANES spectra and determine P speciation in these anoxic sediments. Linear combination fitting (Athena) of the spectra with a P and Fe reference library collected at ESRF and other synchrotrons was used to quantify Fe and P speciation.

The experiment was performed in the following order:

1. (*Unfocused mode*) Collection of Fe EXAFS at 7.0 – 7.65 keV from several Fe standards
2. (*Focused mode*) Collection of µXRF maps at 7.2 keV (above Fe edge) from various areas of the resin-embedded surface sediment block, and collection on Fe EXAFS from selected observed Fe enrichments
3. (*Unfocused mode*) Collection of P XANES at 2.1 – 2.4 keV from several powdered samples to obtain bulk P speciation
4. (*Focused mode*) Collection of µXRF maps at 2.3 keV (above P edge) from various areas of the resin-embedded sediment, and collection on P XANES from selected observed P enrichments and also from the background in places where it showed slight P enrichment
5. (*Unfocused mode*) Switched back to unfocused mode at the end of the experiment to collect more bulk P XANES spectra from powdered samples

Results

The resin-embedded surface sediment showed numerous Fe enrichments that consisted of clay-Fe, pyrite (FeS_2) or a combination of the two (**Fig. 1**). The sediment also showed small P enrichments that had remained undetected by analysis with our in-house Orbis Orbis µXRF. The P enrichments consisted of calcium phosphate and, in one case, iron phosphate (**Fig. 2**). The presence of iron phosphate in these sediments is a remarkable finding, but it is quantitatively insignificant. The P-enriched background showed an indistict P XANES spectrum that suggests organic P or adsorbed P.

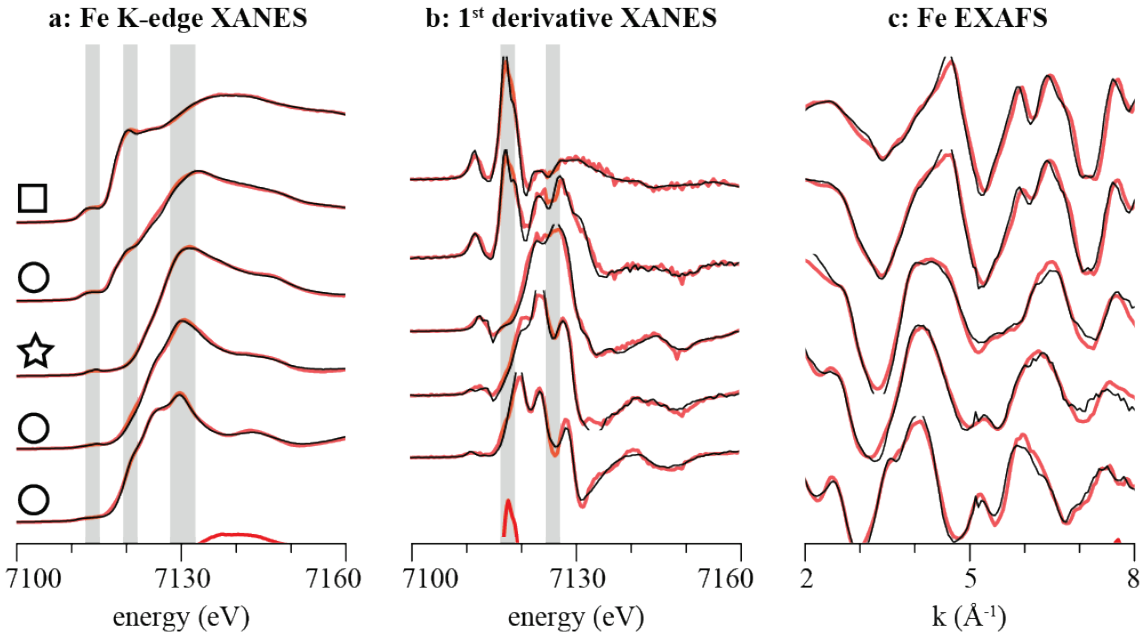

Fig. 1*. Fe K-edge EXAFS from various Fe enrichments in the surface sediment from the deep Black Sea. Symbol indicates pyrite (square), clay-Fe (star) and mixed clay-Fe/pyrite (circle).*

The spectra from powdered bulk samples mostly showed indistinct P XANES spectra that suggest that the majority of P in the deep Black Sea is buried as organic P or adsorbed P.

The data collected at the ESRF feature prominently in a manuscript about Black Sea P cycling that will be submitted to Biogeosciences in the next two weeks.

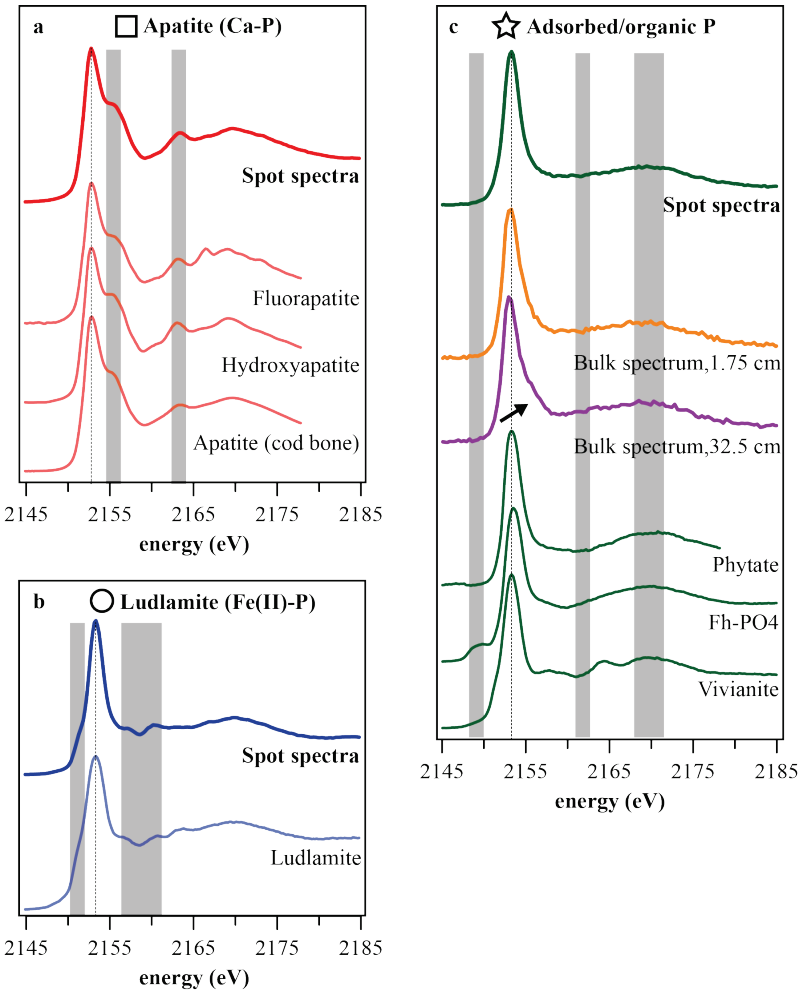

***Fig. 2**. Phosphorus K-edge XANES results for several P enrichments showing the presence of calcium phsophate (a) and iron(II) phosphate (b). The spectra from P-enriched bakcground, as well as the bulk P K-edge XANES from powdered samples from the sediment surface (1.75 cm) and deep sediment (32.5 cm), show predominantly organic or adsorbed P (c). Arrow indicates formation of post-edge shoulder indicative of calcium phosphate. Reference spectra from our library built up during previous visits to ESRF and other synchrotrons.*