



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://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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:**

Identifying the iron phase and the binding mechanism responsible for phosphate binding in materials applied to reduce the phosphate loading of surface waters

Experiment**number:**

ES1169

Beamline: ID21	Date of experiment: from: 15 July 2022 to: 25 July 2022	Date of report: 01/10/2022
Shifts: 15 (24)	Local contact(s): Luis Colocho Huarte	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The experiment has been very successful and we reached our objectives. We analyzed two types of materials, quartz sand particles coated with Fe and Mn oxides (ICS) and sediment samples. Prior to the experiment, we investigated the suitability of several sample preparation methods together with Luis Colocho Huarte, including cryogenic sectioning of wet, frozen sediment using the cryomicrotome at ID21. For sediment samples, we eventually decided to mount freeze-dried and ground sediment on sulfur-free tape in one of the Al holders with 5 mm holes inside the glove box at ID21 under nitrogen atmosphere. The sample was then covered with ultralene film and only removed from the glove box directly before installing the holder in the loading system. This strategy turned out to be very beneficial for multiple reasons: it increased the efficiency of the experiment as we did not have to use the cryo stage; working with freeze dried powder with very short exposure to the atmosphere minimizes oxidation artefacts, grinding separated particles with different composition and morphology so that we could optimally benefit from the possibility to work with a focussed beam, the size of the particles was in a range allowing to collect XAS spectra occasionally in transmission mode, which are typically of higher quality compared to those collected in FD mode and are not affected by self absorption. For the ICS we used thin sections, which allowed us to investigate coatings in detail, which have been previously analyzed with SEM and selected for this experiment. As we noticed photo-induced changes in the spectra, in particular for Mn, we moved the position of the beam within one area of interest in between XAS scans. In the following some findings are exemplarily presented.

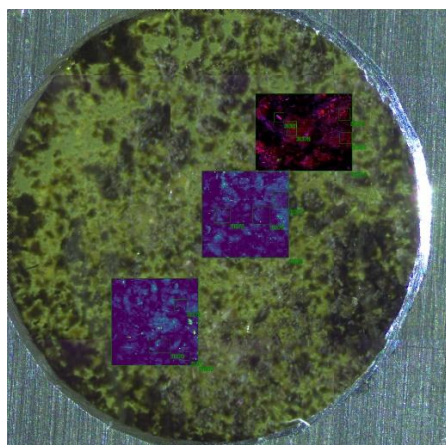


Fig 1

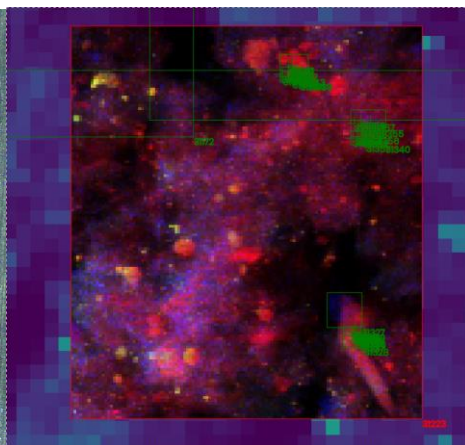


Fig. 2

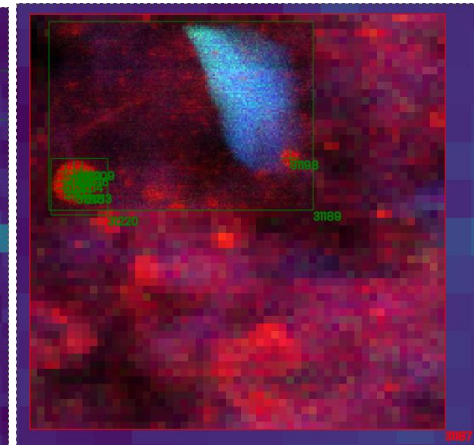


Fig.3

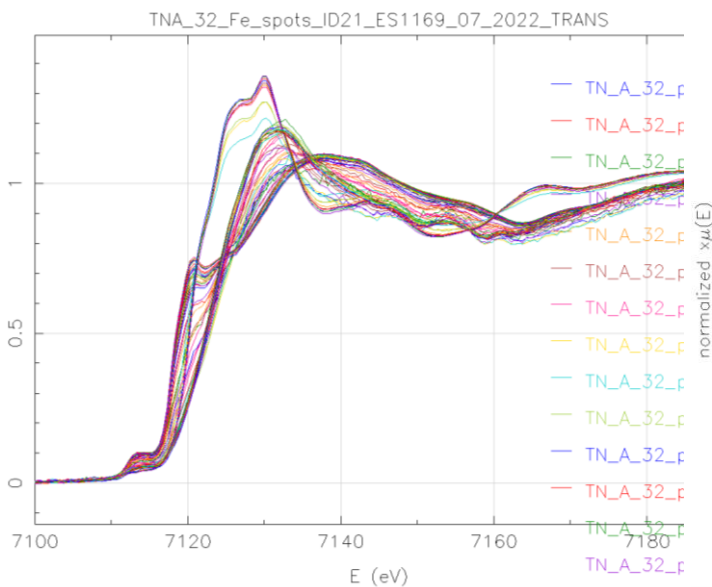


Fig. 4

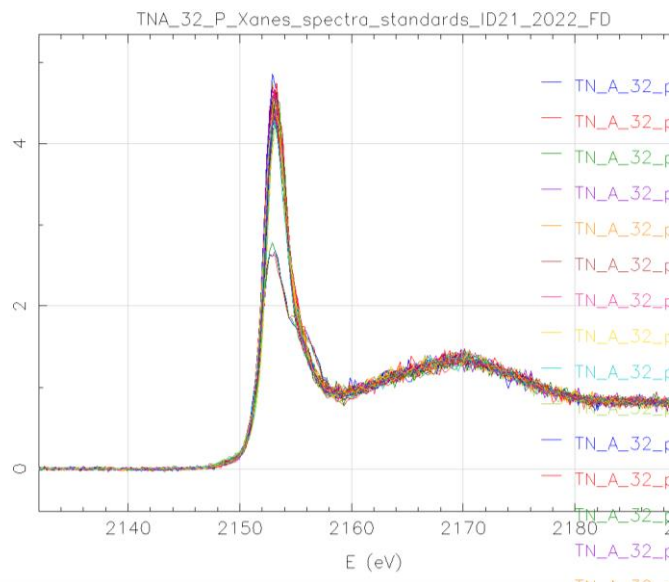


Fig. 5

Sediment Samples

The sample TN-A-32 originates from the top of the sediment in a lake, which has been treated with Fe salts 10 years ago. The material was well dispersed on the tape (Fig. 1) and several low resolution maps (about 1 mm²) were collected with a resolution of 10 μm at an energy of 7.2 keV. Fe was enriched in individual particles with a size between a few and tenths of micrometres, but also diffusively distributed over the organic material, indicating association of Fe with organic matter (Fig. 2, resolution 2 μm, RGB Fe-S-P). The relative P contents turned out to be higher in the zones with diffuse Fe distribution. Some of the Fe-rich particles also showed enrichment in S, indicating the formation of Fe-sulphides. This is in line with the hypothesis that sulfidation of Fe-(hydr-)oxides occurs in micro environments even close to the sediment-water interface and not only in the zone where sulphate reduction is reflected in pore water composition. The hypothesis was based on sequential chemical extractions in combination with pore water profiles. Additionally, particles enriched with P and Ca were identified and based on their shape identified as teeth or bones from higher organisms, likely fish (Fig. 3, resolution 2 μm, RGB Fe-Ca-P). X-ray absorption spectra were collected at spots identified in high resolution maps (resolution 0.5 μm) and provided further insight. Fe XANES spectra reflect the diversity of Fe speciation in the sample (Fig. 4, compilation of all normalized Fe-XANES spectra collected for sample TN-A-32 in transmission mode). Besides the spectra, which could be attributed to Fe bound in silicates, all other Fe XANES spectra could be described as a combination of Fe-sulphides (FeS and FeS₂) and a phase with variable Fe(II)/Fe(III) ratios. The latter could include amorphous Fe(III) hydroxides plus Fe bound to organic matter, possibly in different oxidation states. The detailed analysis of the Fe spectra is still ongoing. The latter will also include the analysis of the EXAFS spectra (until k=10 Å⁻¹), which were of sufficient quality at some spots. For P, all collected spectra fall essentially into two categories: P in apatite and those typical for reference materials with adsorbed phosphate. The responsible sorbent is difficult to identify and requires careful analysis of the pre-edge features. It is noticeable that a pronounced pre-edge peak, found for various Fe-bound P (see also spectra from ICS below), is not clearly visible. This might suggest that a major fraction of the P in the sediment is not directly bound to Fe. The latter would be in disagreement with the expectations and warrants further analysis. Detailed analysis of the pre-edge features is still ongoing.

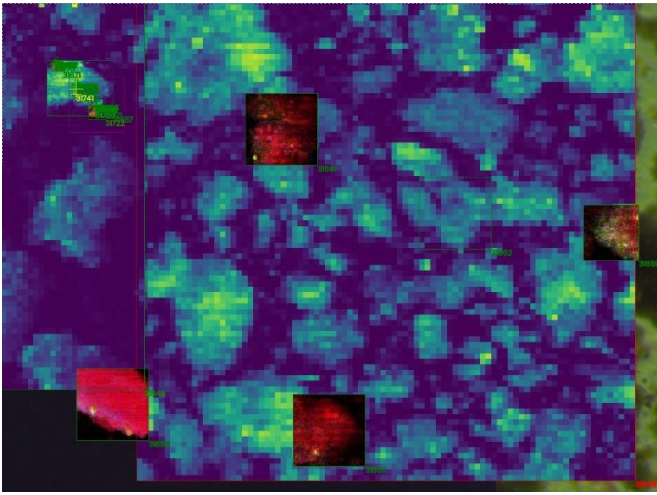


Fig. 6

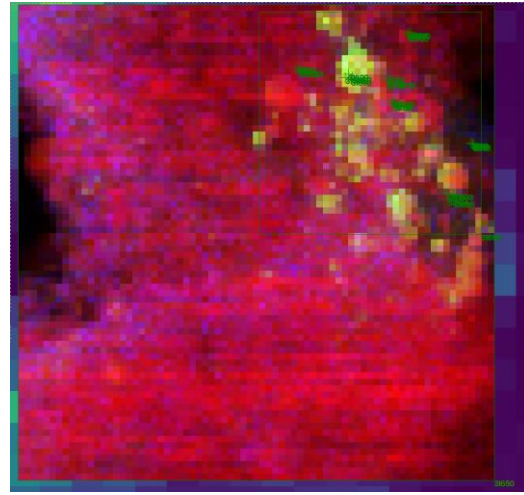


Fig. 7

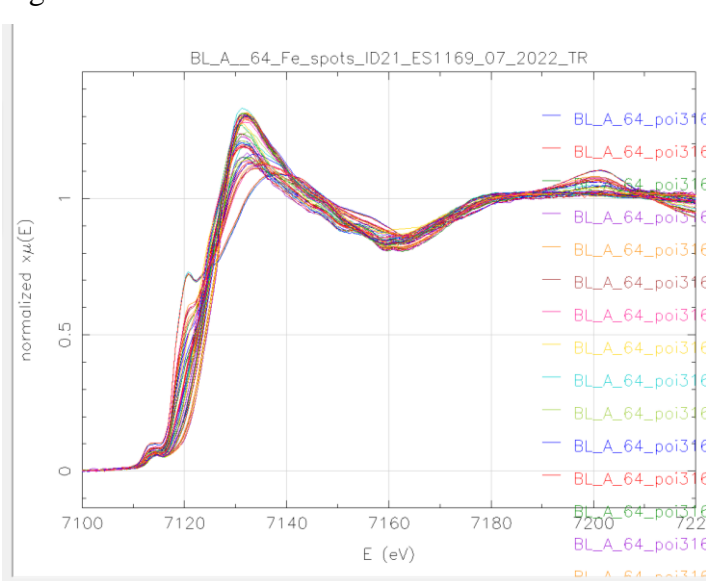


Fig. 8

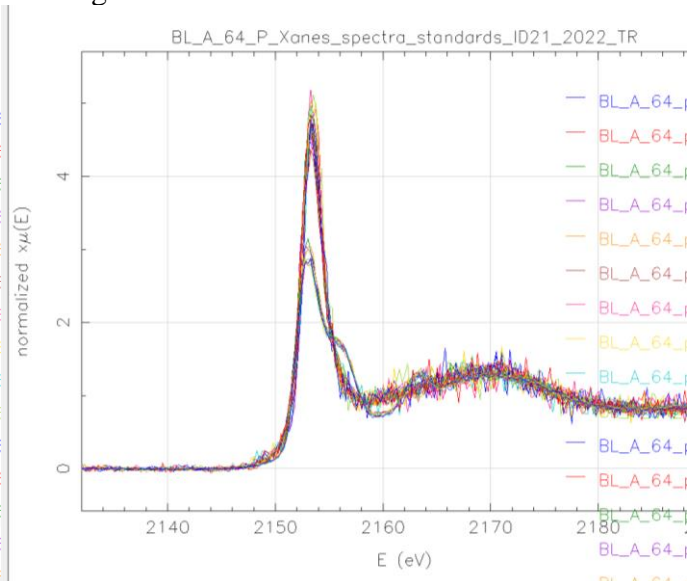


Fig. 9

The observations obtained for the sediment sample BL-A-64, taken from an Fe-treated wetland system, are comparable to those we found for the Fe-treated lake (Fig. 6, one of the 10 μm resolution maps – showing Fe signal, with 2 μm resolution RGB Fe-S-P maps; Fig. 7, 2 μm resolution RGB Fe-S-P maps, Fig. 8 all Fe XANES spectra collected for sample BL-A-64 in transmission mode, Fig. 9 all P XANES spectra collected for sample BL-A-64 in fluorescence mode). In the investigated wetland, the ditches have been amended with water treatment residuals, predominately consisting of Fe (hydr)oxides. The sample has been taken from a depth, showing maximum Fe concentrations above the zone of pronounced sulphate reduction. In contrast to sample TN-A-32, Fe is massively present and no individual Fe-rich particles could be identified. That is, the whole organic matter, is incrustated by Fe-rich material. In these sediments, organic matter represents more than 90 % of the sediment material as the wetland has been formed as a consequence of peat cutting. The objective was to find evidence for the onset of sulfidation of Fe (hydr)oxides in this sediment layer and to investigate the consequences on P distribution at a microscopic level. Figure 7 distinctively illustrates this process, showing the formation of framboidal pyrite at the surface of the Fe-encrusted organic matter. It appears, that P is relatively enriched in the region not affected by sulfidation suggesting P redistribution due to the progressive reaction with sulphide. In contrast to sample TN-A-32, amorphous Fe hydroxides could be identified as one of the end-members in the Fe XANES spectra (Fig. 8) and the collected XANES spectra can be reproduced by a combination of spectra of amorphous Fe hydroxide and pyrite. Similar to TN-A-32, the P spectra do not exhibit a strong pre-edge peak, typical for Fe-bound P. This is in contrast to the correlation between the abundance of Fe and P in the sample and needs further investigation.

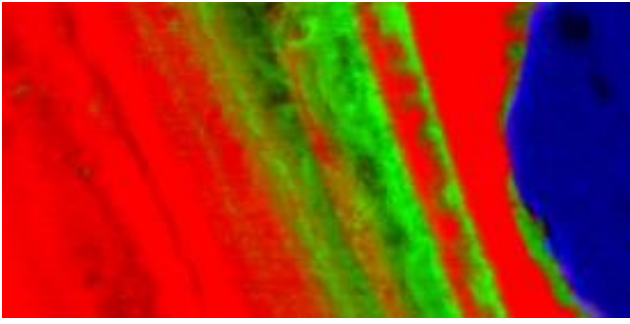


Fig. 10

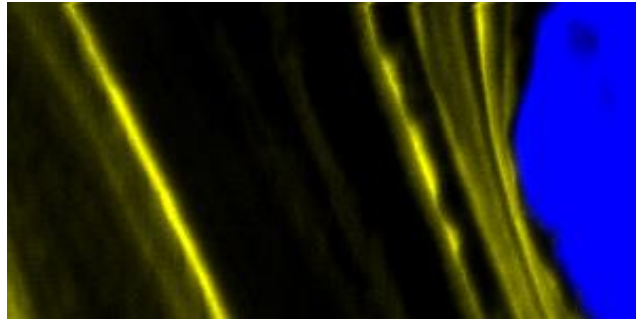


Fig.11

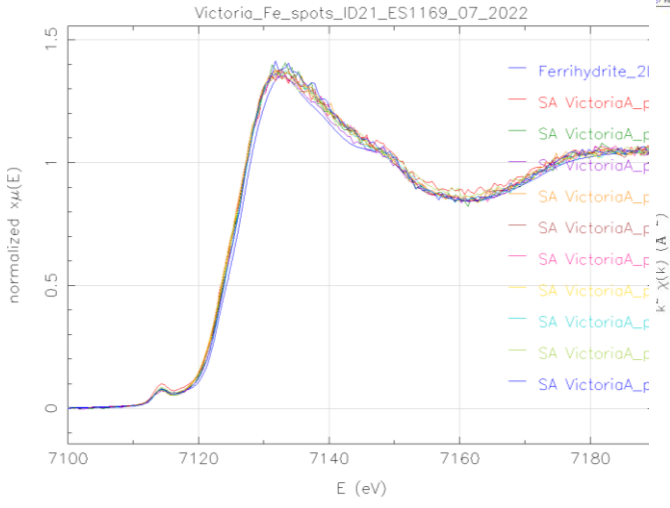


Fig. 13

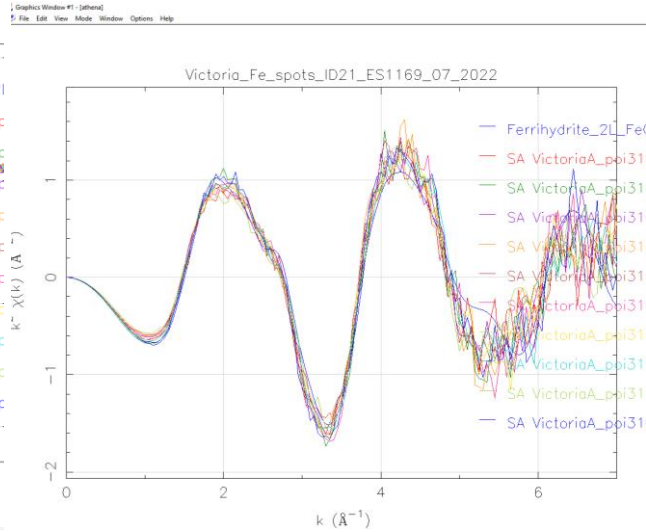


Fig. 14

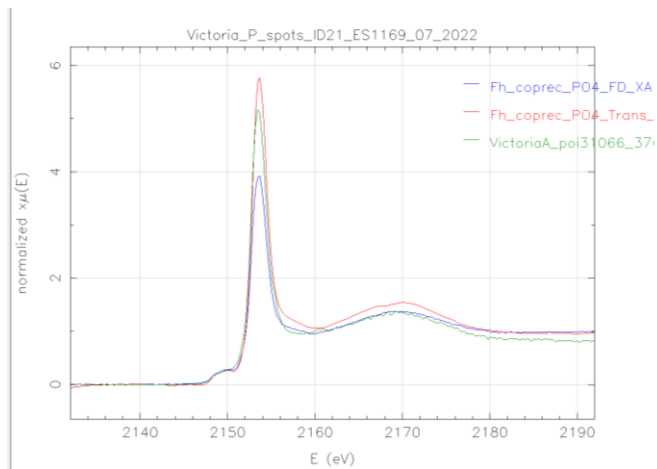


Fig. 15

The goal of the analysis of the ICS samples was to constrain the reasons for inhomogeneous P distribution in the coating, previously detected by SEM analysis. The ICS samples originate from column experiments to investigate the long-term performance of ICS for P removal from water streams. For logistic reasons (minimize the number of transitions between P energy and Fe/Mn energies and required re-optimization of the beam size), elemental maps have been collected twice at 2.4 keV using either the Si-coated or Pt-coated mirrors. With the latter, it was also possible to collect Fe and Mn maps making use of the third harmonic, which is not suppressed by the Pt-coated mirror. The advantage of this approach was that the sensitivity for light elements has been much higher when using the Si-coated mirror as when using the Pt-coated mirror as attenuators were required to optimize the dead time of the detector. This approach allowed us to map the distribution of P in the coating very detailed (Fig.11, 2 μm resolution RGB P-P-Si map, showing distinct P-enriched layers in the coating of the quartz grain) together with the Fe and Mn distribution (Fig.12, 2 μm resolution RGB Fe-Mn-Si map, showing Fe and Mn-rich layers in the coating around the quartz grain). The collection of XANES spectra has only been possible in fluorescence mode due to the thickness of the glass slide sustaining the thin sections. The latter implies that most spectra are affected by self-absorption. When

correcting for the self-absorption, virtually similar Fe-XANES (Fig. 13) and k^3 -weighted EXAFS (Fig. 14) spectra were obtained for the investigated spots along a transect through the coating. When correcting for self-absorption the spectra resemble that of 2-line ferrihydrite. However, the shoulder at around $k=5.2 \text{ \AA}^{-1}$ in the EXAFS spectra is less developed than in ferrihydrite implying that the Fe-Fe scattering path is even more variable than in ferrihydrite. P enrichment was only detected in the Fe-rich zones of the coating and the P-XANES spectra show a similar pre-edge peak as P co-precipitated with Fe hydroxides (Fig. 15, comparing a representative P-XANES spectra with those of ferrihydrite containing co-precipitated Fe determined in fluorescence and transmission mode. The difference in the latter spectra can be attributed to self-absorption. The position of the spectra collected for the sample in between the two of the reference material indicates that the effect of self-absorption was less for the sample, implying that P is more diluted in the sample). These results clearly indicate that the P-rich zones cannot be explained by differences in Fe mineralogy but are likely inherited in the material from the formation process and not caused by P sorption during the column experiments.

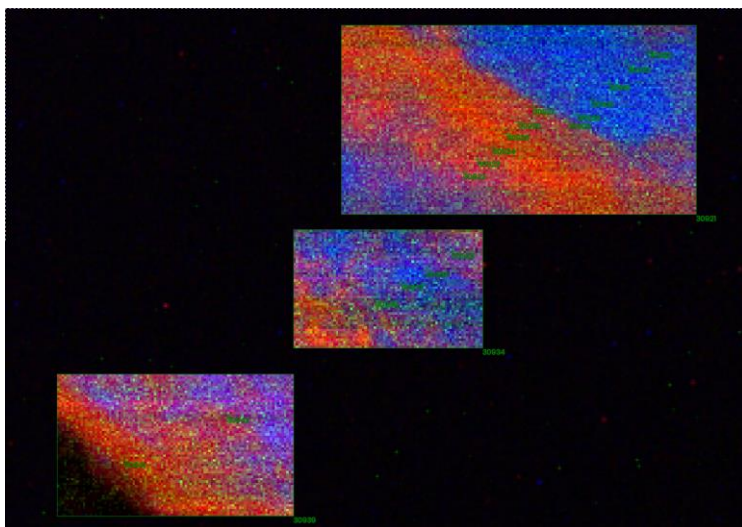


Fig. 16

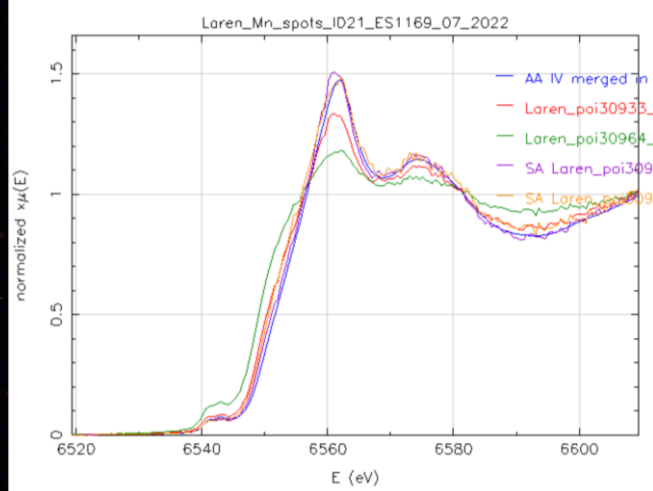


Fig. 17

Finally, we analysed an ICS sample, which has been collected from a rapid sand filter in a drinking water treatment facility. These filters are used to remove Fe, Mn and ammonium after the aeration of ground water. Incomplete Mn removal can cause technical problems in the purification process and understanding the reason for the alternating Fe and Mn layers might help to understand the interplay between Fe and Mn oxidation in the filters. Most interesting are the Mn-rich layers as the Mn speciation can be indicative for the formation process and reduction of Mn-oxides by reduced Fe (Fe(II)) should be reflected in the Mn speciation, too. For this, a transect of spectra has been collected throughout the whole coating (Fig. 16, several $2 \mu\text{m}$ resolution RGB Fe-Mn-P maps of an coating showing alternating Fe and Mn rich layers and including the spots selected for collecting Fe and Mn spectra, respectively). The Mn XANES spectra were affected by self-absorption. After correction, they all resemble that of microbially produced birnessite (nominally $\text{Mn(IV)O}_2 \cdot n\text{H}_2\text{O}$) (Fig. 17, Mn-XANES spectra from two representative spots. The figure also illustrates the effect of correcting for self-absorption, SA spectra are corrected spectra and resemble that of microbially produced birnessite, AA IV merged). The predominance of birnessite at all investigated spots provides a strong indication that Mn oxidation in the filter requires microbial catalysis and that deposited layers of Mn oxides are not being reduced by ferrous iron (Fe(II)) as this reaction should lead to the formation of Mn(III)-containing solids. These results demonstrate the potency of the scanning X-ray microscopy to provide crucial complimentary information to investigate the retention mechanism of Fe and Mn in rapid sand filters, which we aim to investigate in a follow up experiment.