EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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

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 form 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.

ESRF	**Experiment title:** **Understanding the lead pigments darkening on wall paintings induced by cold plasma exposure and their reconversion by chemical and physical treatments**	**Experiment number**: HG-175
Beamline: BM08	**Date of experiment**: from: 01/12/2021 to: 06/12/2021	**Date of report**: 19/02/2022
Shifts: 15	**Local contact(s)**: Francesco d'Acapito	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Experimental details

The aim of the experiment was to investigate the Pb speciation at the surface (0.1-0.2 μm) and in the bulk (several μm) of lead based wall painting mock-ups treated with chemical and physical treatments (cold plasma and others) and compare the artificial alteration with naturally altered lead pigments coming from hystorical wall paintings. All of the investigated samples consist of lead pigments applied with a casein binder on a lime based mortar substrate (dimensions 2 x 2 x (0.2-0.5) cm^3). Three different lead based pigments where investigated:

1) lead white ($2PbCO_3 \cdot Pb(OH)_2$) with a thickness of ca. 30-50 um;
2) red lead (Pb_3O_4) with a a thickness of ca. 100 um;
3) plattnerite (PbO_2), which is a common lead pigments alteration, with a thickness of ca 200 um.

The case studies consist of a small fragment of 2 x 2 x 1 mm^3 and a powder (measured in a borosilicate glass capillary of 1mm diameter) of altered lead pigment from a 17^{th} century wall painting from Sicily.
The samples were allocated in the experimental chamber in dark condition and inert He at 0.5 bar and the experimental investigation proceeded operating X-ray Absorption Spectroscopy in Fluorescence mode with the simultaneous acquisition in Total Electron Yield mode (TEY) carried out at the Pb L_3 edge (13035 eV). For TEY a specific sample holder was used and carbon tape was applied at the edges of the paint mock-up to ensure electrical conduction between the paint layer and the sample holder. A Pb foil was located in a second experimental chamber for energy calibration purpose. No particular experimental issues occurred. During the experiment, some artifacts in the TEY acquisition connected to the refill procedures of the electron beam were noticed. Accordingly, a time constrain was inserted, so all the measurements where set to start just after the hourly refill. Measurement duration was optimised consequently. All the samples were successfully investigated (21) as well as a set of relevant standards (14). For some of the samples, although the very thick Pb layer, (with the paint layer between 100-200 um) the transmission signal was also detected and registered.

List of the investigated samples

Sample name	Sample type	Type and number of measurements	Sample name	Sample type	Type and number of measurements
MC-TQ	Pristine paint	3 TEY-FLUO-TR	BC-4hO2_V	Alteration	3 TEY-FLUO-TR
PC-TQ	Pristine paint	3 TEY-FLUO-TR	BC-12hO2_V	Alteration	3 TEY-FLUO-TR
BC-TQ	Pristine paint	3 TEY-FLUO-TR	BC-8mO2_N	Alteration	3 TEY-FLUO-TR
BA-P-1	Case study 1	3 TEY-FLUO-TR	BC-1hO2_N	Alteration	3 TEY-FLUO-TR
BA-P-2	Case study 2	2 Capillary. FLUO	BC-4hO2_N	Alteration	3 TEY-FLUO-TR
MC-1hO2	Alteration	4 TEY-FLUO-TR	BC-12hO2_N	Alteration	3 TEY-FLUO-TR
MC-4hO2	Alteration	3 TEY-FLUO-TR	PC-PLN	Reconversion	8 TEY-FLUO-TR
MC-12hO2	Alteration	3 TEY-FLUO-TR	PC_CH3%	Reconversion	2 TEY-FLUO-TR
BC-8mO2_V	Alteration	3 TEY-FLUO-TR	PC-CW	Reconversion	6 TEY-FLUO-TR
BC-1hO2_V	Alteration	3 TEY-FLUO-TR			

Preliminary survey of the obtained results

For the lead oxides (both red lead and plattnerite mock-ups) the preliminary analysis of the XANES spectra provided significant insights. These spectra are, however, of difficult interpretation as the XANES of all the most significant lead oxides compounds for our experiment are very similar **(FIG1a**). These similarities makes the evaluation difficult, so these samples will be the object of a further beamtime request at beamlines which provide higher energy resolution. Never the less even if small changes are observed, the difference between fluorescence and TEY on the red lead samples treated with plasma (with TEY spectrum often shifted towards higher energy levels) may suggest a partially more enriched layer of lead(IV) on the surface compared to the bulk (**FIG1b**), which is in agreement with the type of plasma treatment applied.

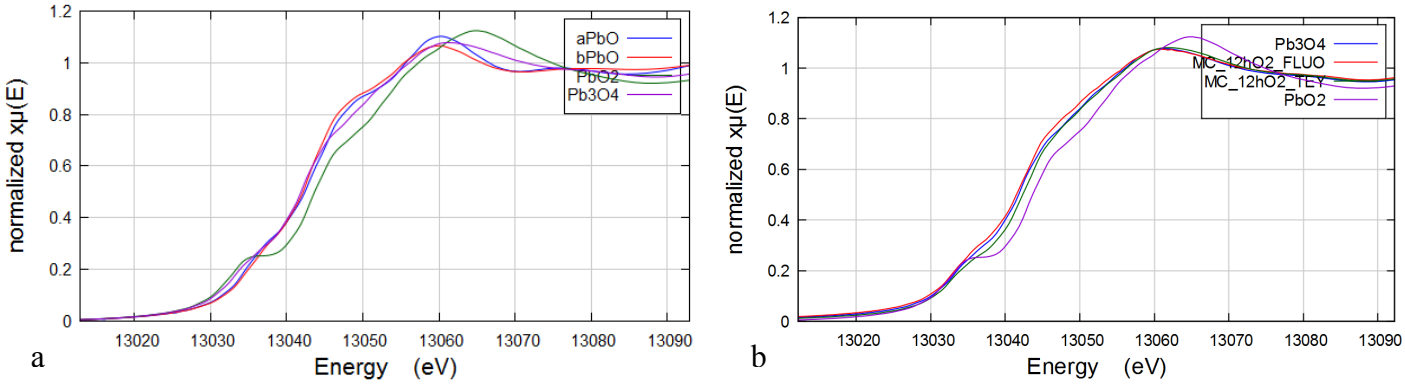

Figure 1. a) the standard lead oxides of interest; b) XANES spectrum both in fluorescence and TEY mode of red lead treated with oxigen plasma (sample MC-12hO2) and the pristine red lead and plattnerite for comparison.

In the case of basic lead carbonate mock-ups both XANES and EXAFS give significant information suggesting a structural change of the carbonate to oxides maintaining the lead(II) oxidation state (**Fig.2**), so it seems that the artificial alteration do not cause the formation of plattnerite. Regarding the case study with potentially altered hydrocerussite there are no features suggesting the presence of Pb(IV) as alteration product of lead white but it could be present in a very small percentage below the detection limit.

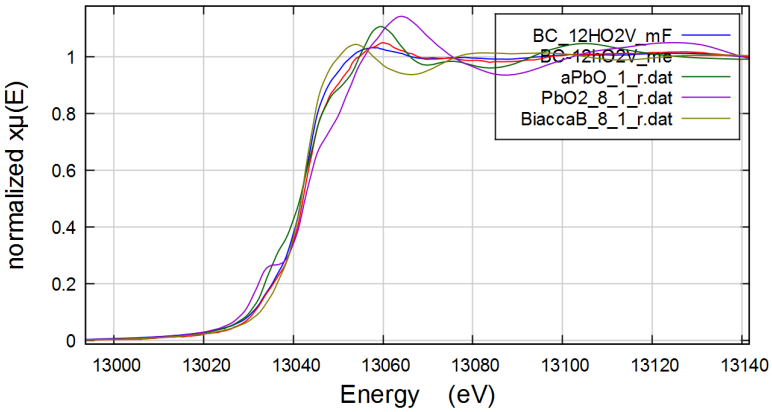

Figure 2. Fluorescence and TEY XANES spectrum of lead white treated with oxigen plasma (sample BC-12hO2V) and the reference of lead white (Biacca), litharge(a-PbO) and plattnerite (PbO_2) for comparison.

Preliminary conclusions

Performing XAS on the treated mock-ups provided description of the structure and chemical nature of Pb to cheracterize the effects of physico-chemical artificial and natural lead pigments alteration. The comparison of the fluorescence and TEY signals combined with the complementary in-house XPS measurements on the mock-up suggests a higly superficial action of the plasma and different alteration products depending on the starting lead based pigment. However for some samples a higher resolution and additionally a lower detection limit is required to better interpret the spectra where very small differences were detected.