EUROPEAN SYNCHROTRON RADIATION FACILITY

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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

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:** Formation mechanism of PbO2 (plattnerite) by oxidative blackening of lead white in/on mural paintings by Cimabue (13th C.), Assisi Cathedral, Italy	**Experiment number**: HG-105
Beamline: ID16b	**Date of experiment**: from: 20-05-2017 to: 23-05-2017	**Date of report**: 25/02/2020
Shifts: 12	**Local contact(s)**: Jussi-Petteri Suuronen	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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1. INTRODUCTION

Lead white, a mixture of hydrocerussite [2 $PbCO_3 \cdot Pb(OH)_2$] and cerussite ($PbCO_3$) is a pigment that has been observed to blacken over time in mural paintings. This blackening can often be attributed to the formation of plattnerite (β-PbO_2).[1-2]
This phenomenon has been observed in a series of Cimabue's 13th century mural paintings of *San Francesco Basilica* in Assisi, Italy. After an earthquake in 1997 fragments of these mural paintings were collected which show that originally white brushstrokes have blackened (Figure 1).[3]
The aim of this research is to better understand the mechanism behind the oxidation of lead white and which factors influence it. For this part of the experiment a series of model samples have been analyzed which were made by exposing lead white to different conditions such as pH and oxidizing agents.

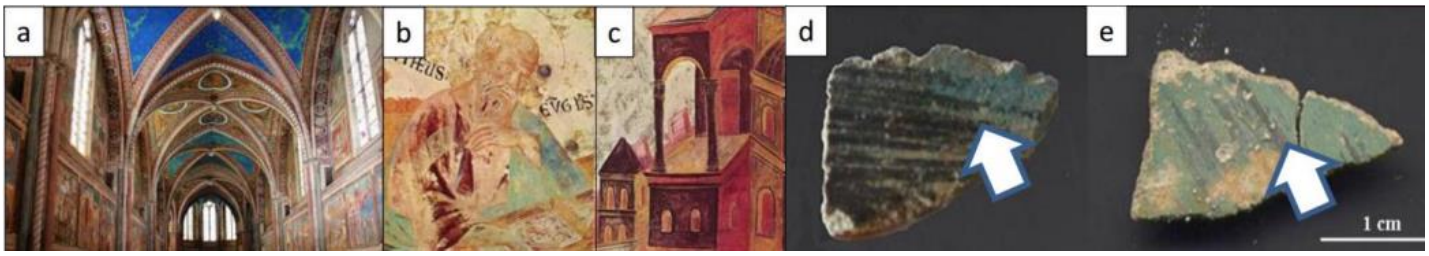


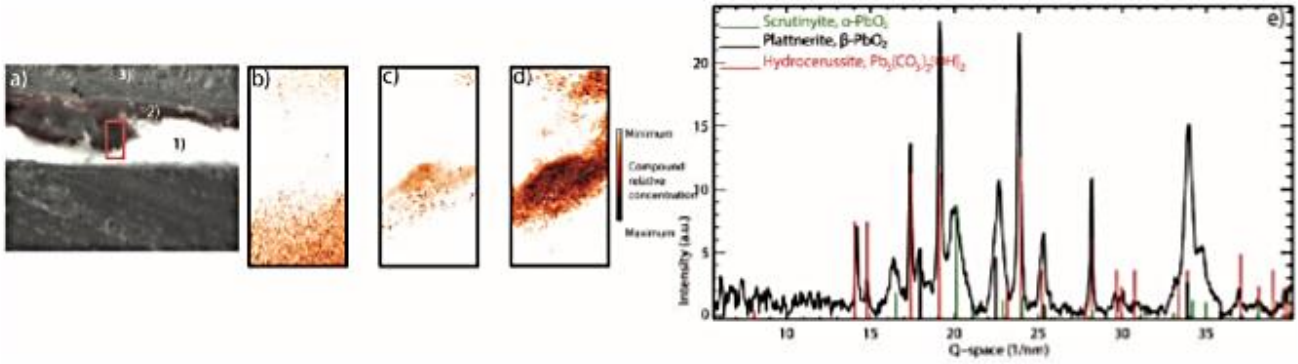
Fig. 1 (a) Assisi Cathedral (b, c) details of mural paintings damaged during the earthquake (d) fragment showing a strong amount of blackening (e) fragment showing a slight amount of blackening.

2. EXPERIMENTAL

Submicroscopic SR-based XRPD measurements were performed at beamline ID16b of the European Synchrotron Radiation facility, which uses a hard Xray beamline intended for 2D or 3D analysis of micro- and nano-scaled materials. Measurements were performed on mock-up paint samples, prepared as 20 and 50 µm thick cross sections. The clearest diffraction patterns were obtained from the thicker mock-up samples (50 µm). These were acquired in transmission geometry by means of an X-ray beam with a spot size of 60 × 85 nm^2, at the energy of 29.6 keV. Oil-based paint was prepared from two different kinds of lead white by mixing them with boiled linseed oil and for the pigment A (rich in hydrocerussite) also the fresco technique was used (with slaked lime as binding medium, in a 2:1 lime/lead white ratio). The resulting paints were applied on polycarbonate slides before the start of the oxidation treatment. The reaction between the sodium hypochlorite solution (~13% free chlorine, i.e., all chlorine present in the water as Cl_2(g), HOCl(aq) and OCl^- (aq), pH ~13) and the powdered mixtures A and B (i.e. without the presence of any binding medium) was studied first. The treatment was performed by submerging the powdered pigments into NaOCl solution in a dark and sealed environment for one week. After drying, the model paint samples (mock-ups) were exposed to the same sodium hypochlorite solution as mentioned above by dipping them into the solution. The mock-ups were dipped in the solution for one, three and six days. In some cases, treated samples were given a post-treatment by exposing them to a solution of diluted hydrochloric acid (~3%) to facilitate the XRPD analysis. After the exposure, the mock-ups were prepared for the analysis: some mock-ups were embedded in acrylic resin.

3. RESULTS

In general, the presence of PbO_2 could not always be detected after one day NaOCl exposure. NaOCl-induced degradation of pigment B (rich in cerussite) never gave rise to any positive identification of plattnerite. This is likely caused by the overlap between the diffraction lines of cerussite and plattnerite. However, scrutinyte was detected to be abundantly present. This is highly suggestive of a secondary maturation reaction in which α-PbO_2 is gradually converted to β-PbO_2. To better understand the formation process of plattnerite and scrutinyte, different parameters such as the composition of the starting material or the pH and dissolved inorganic carbon in the exposition solution should be considered and carefully monitored during the reaction process.



a) cross-sectional micrograph of the scanned area - red rectangle indicates location of maps (81.5 × 39 µm², 164 × 40 pixels, step size 0.5 × 1 µm²); 1) lead white paint layer (pigment A), 2) blackened region after treatment in NaOCl, 3) embedding resin; b) distribution map of hydrocerussite; c) distribution map of plattnerite; d) distribution map of scrutinyite; e) averaged X-ray pattern

References

[1] S.M. Lussier, G.D. Smith, Rev. Conserv. 8 (2007), 41-53.
[2] T. Rosado et al., Color Res. Appl. 41 (2016), 294-298.
[3] M. Vagnini et al., Vib. Spectrosc. 98 (2018), 41-49.