

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>

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.



	Experiment title: Elucidation of the degradation mechanism of minium (red lead) by means of submicroscopic XRPD mapping and tomography	Experiment number: HG-50
Beamline: ID16B-NA	Date of experiment: from: 12/03/2015 to: 18/03/2015	Date of report: 07/10/2015
Shifts: 18	Local contact(s): Jussi-Petteri Suuronen	<i>Received at ESRF:</i>

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Report:

Introduction:

Red lead (used in metal anti-corrosion coatings) is an artists' pigment, employed in all historic periods (including the 19th C), that is known both to darken (due to oxidative formation of PbO₂, plattnerite or PbS, galena) and to whiten (either to PbCO₃ or PbSO₄). In our previous work, a protrusion from a painting by Van Gogh was studied using μ XRPD imaging, revealing at least three white lead compounds: the commonly encountered hydrocerussite (2PbCO₃.Pb(OH)₂) and cerussite (PbCO₃) but also the more exotic compound plumbonacrite (3PbCO₃.Pb(OH)₂.PbO) which was linked to the degradation of the red lead pigment.[1]

The focus of this experiment was to gain further insights into the degradation mechanism that takes place in red lead containing paints. We have therefore performed several controlled degradation experiments on minium (Pb₃O₄) powders (both commercial and self-synthesized) as well as on common red lead impurities, such as litharge (*t*-PbO) and massicot (*o*-PbO). The powders were exposed to sodium carbonate buffer solutions (0.01 M NaHCO₃/Na₂CO₃) at various pH (8-9-10) as well as to a chlorine rich solution (0.01 M NaCl). These controlled degradation experiments were carried out on paper screen printed electrodes to be able to study the redox behavior of the powders during artificial degradation. The coated electrode surfaces were irradiated with a blue laser (405 nm) for approximately 4 hours.

To visualize the layer stratigraphy and reduce the contribution of barite (BaSO_4), which is an additive in the paper screen printed electrodes, the electrodes were cut with a scalpel to about 1 – 1.5 mm thickness. The different layers of the sample were positioned parallel with the incoming beam.

Experimental:

A monochromatic primary beam with a photon energy of 28.9 keV was produced using a double crystal monochromator. Initially, the incident beam was focused using a Kirk-Patrick Baez mirror optic down to a diameter of $95 \times 105 \text{ nm}^2$ (hor. \times vert.). However, to increase the incoming flux the beam was defocused to $165 \times 185 \text{ nm}^2$ by opening the secondary horizontal gap (s2hg) from 0.1 to 0.3 mm. This change also improved the quality of the powder diffraction patterns as a larger amount of crystallites is sampled. XRF signals were collected using a Vortex-EX SDD detector in the horizontal plane at an angle close to 90 degrees with respect to the incoming beam. Diffraction patterns were collected using a FReLon $2k \times 2k$ CCD detector placed in transmission geometry. Combined XRF/XRPD experiments were performed with a dwell time per point between 1.5 – 3 s. XRF spectra were analyzed with the PyMCA software package, while the diffraction data was treated using XRDUA.[2-3]

Results:

The results obtained from the XRPD imaging experiments show three different layers (see Figure 1):

- Layer I: paper substrate containing barite
- Layer II: graphite electrode active area
- Layer III: mixture of the deposited minium with various alteration products: hydrocerussite, $2\text{PbCO}_3 \cdot \text{NaOH}$ and $3\text{PbCO}_3 \cdot \text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3$ (Sanromanite)

These results show the successful alteration of minium (containing both Pb^{IV} and Pb^{II}) to lead(II) species following the above described artificial alteration treatments. However, several ‘mixed’ compounds are formed because of the buffer solution needed to provide the necessary CO_2 . Although the transformation of minium was successful, no evidence of the rare plumbonacrite compound is found. For future experiments, more mild ageing conditions should be explored in order to better identify the various steps in the alteration reaction of red lead, better illustrating the gradual uptake of CO_2 as shown in the following equilibrium [4]



In several cases it was difficult to align the layered structure of the sample parallel to the incoming X-ray beam due to the thickness of the samples (1 – 1.5 mm). Better sample preparation strategies should be explored, e.g. embedding of the treated electrodes, which should allow us to cut thinner section without disturbing the layer stratigraphy.

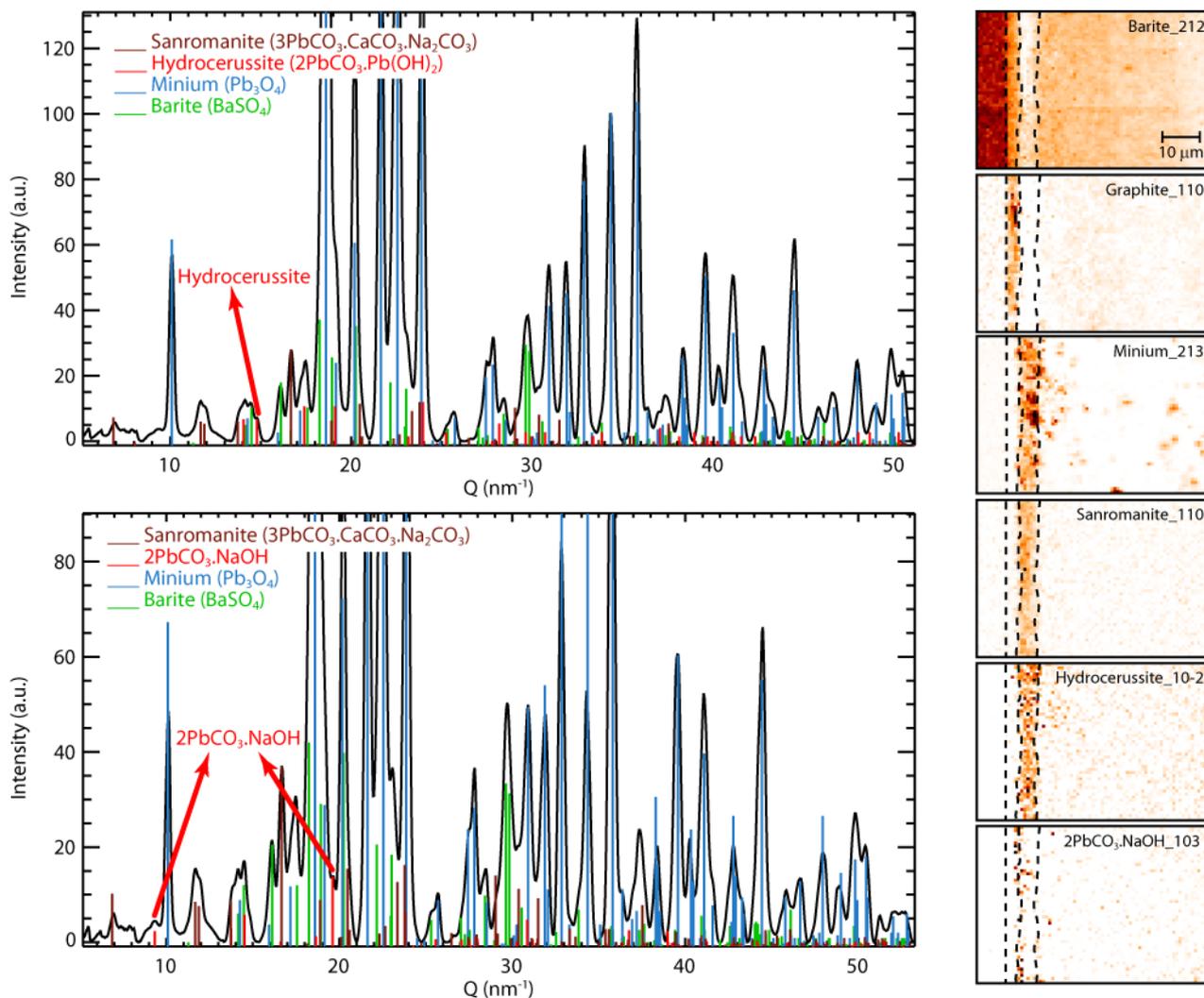


Figure 1: Diffractograms showing the limited presence of hydrocerussite (Top) and $2\text{PbCO}_3\cdot\text{NaOH}$ (bottom) in sample B16 (minium exposed to 0.01 M sodium carbonate buffer at pH 9). (Right) The 2D distribution images show the layered structure of the sample and the various alteration products found on sample B16.

References:

- [1] F. Vanmeert, G. Van der Snickt, K. Janssens, *Angewandte Chemie-International Edition* **2015**, *54*, 3607-3610.
- [2] V. A. Sole, E. Papillon, M. Cotte, P. Walter, J. Susini, *Spectrochim. Acta, Part B* **2007**, *62*, 63-68
- [3] W. De Nolf, F. Vanmeert, K. Janssens, *J. Appl. Crystallogr.* **2014**, *47*, 1107-1117.
- [4] P. Taylor, V. J. Lopata, *Can. J. Chem.* **1984**, *62*, 395-402