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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.

ESRF	**Experiment title: Effect of Chlorine on the oxidative degradation of minium by Cl-K/Pb-M45-edge XANES and scanning XRPD**	**Experiment number**: HG-79
Beamline: ID21	**Date of experiment**: from: 04/05/2016 to: 13/05/2016	**Date of report**: 25/10/2016
Shifts: 24	**Local contact(s)**: Marine Cotte, W. De Nolf	*Received at ESRF:*

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1. INTRODUCTION

We proposed to examine samples from degraded minium (Pb_3O_4) from the Roman-Egyptian period and the Middle ages, showing blackening/formation of Plattnerite (PbO_2) with the aim of elucidating the (oxidative) role of Cl. Both original samples and model samples were be examined via Cl-K/Pb-$M_{4,5}$ edge XANES and XRPD mapping. Based on the literature [1], the following reactions/equilibria may (not all) be responsible:

(1) Alkaline reaction of Pb^{2+} with oxidizing Cl-species, e.g.: $Pb^{2+} + OCl^- + 2OH^- \Leftrightarrow Cl^- + PbO_2 + H_2O$ [2]

(2) Acidic precipitation of litharge with NaCl: $PbO + Cl^- + H_3O^+ \rightarrow Pb(OH)Cl\downarrow + H_2O$ [3]

(3) Disproportionation of minium, $Pb_3O_4 + 2CO_2 \Leftrightarrow 2PbCO_3 + \beta\text{-}PbO_2$ [4]

(4) Heat/light-induced multi-step lead oxide transformation: $\beta\text{-}PbO_2 \rightarrow Pb_2O_3 \rightarrow Pb_3O_4 \rightarrow \beta\text{-}PbO$ [5]

Our current hypothesis to explain the presence of the great variety of secondary Pb^{2+}-, Pb^{4+}- and Cl-containing compounds is that both reducing and oxidising influences may be at work here: in the absence of light and the presence of oxidising Cl species, either reactions (1) or (2) are expected to dominate: depending on the redox/pH circumstances either plattnerite (black) or laurionite (white) are mainly formed. On the other hand, under photo-activation conditions, next to the pathway described in [1], disproportionation reaction (3) and/or reaction sequence (4) may induce the co-existence of Pb_3O_4 with PbO_2 (+ Pb-carbonates) [1], possibly leading to both white ($PbCO_3$) and black (PbO_2) secondary products.

2. EXPERIMENTAL

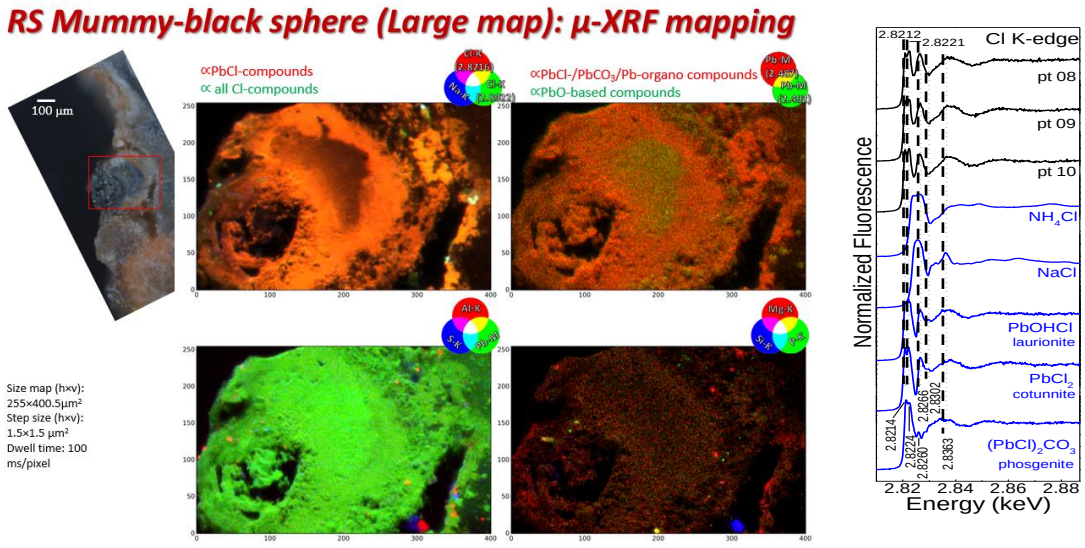
XANES spectra were acquired in XRF mode by scanning the primary energy around the Pb-$M_{4,5}$ edge (2.45-2.65 keV) and Cl K-edge (2.82-2.86 keV) with energy step of 0.2 eV. Investigations under vacuum (10^{-6} mbar) were performed both in unfocused mode (collimated beam, 0.2 mm diameter) and by means of a focused X-ray beam [0.5 x 0.9 μm^2 diameter (hxv)]. Energy calibration was performed with respect to the first inflection point of a Pb metal foil, which was determined by its first derivative.. During the μ-XRF mapping experiments, the fluorescence signals were generated by employing a monochromatic primary beam of fixed energy (around the Cl and Pb-$M_{4,5}$ edges). Maps of the same area were recorded at two different excitation energies close to the Cl K-edge: (a) at 2.8216 keV, favoring the excitation of specific Cl-species such as $PbCl_2$, $(PbCl)_2CO_3$ and PbOHCl but disfavoring that of NH_4Cl, NaCl, MgCl2, KCl, CaCl2 etc. (b) at 2.8922 keV (all Cl species) to obtain a Cl−K_α fluorescence intensity map that is proportional to the total Cl content at a given position (i.e., irrespective of its oxidation state). Maps of the same area were recorded at two different excitation energies close to the Pb-$M_{4,5}$ edge: (a) at 2.492 keV and (b) at 2.8470 keV (all Pb species) to obtain a Pb−M_α fluorescence intensity maps that allow to discriminate between PbCl/PbCO3/Pb-carboxylate species. Contrari to the expectation, these energies proved to be not informative for distinguishing between Pb(II) and Pb(IV)

compounds. The program PyMca was used to fit the fluorescence spectra and separate the different elemental contributions [6].

3. RESULTS

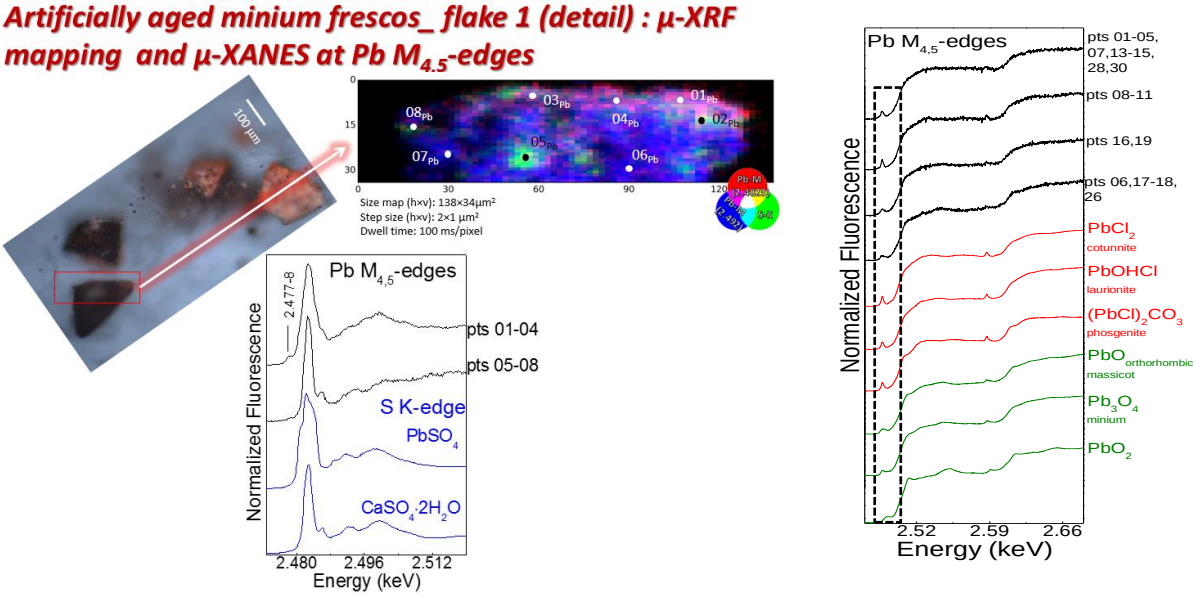
3.1 µ-XRF/µ-XANES maps and spectra obtained from Red Shroud Mummy samples

Overview of the µ-XRF maps at various relevant primary energies, obtained from sample #1:



The corresponding Cl K-edge XANES data show the presence of a mixture of PbOHCl, $PbCl_2$ and a third component. Similar spectra and images were collected from other samples of similar origin.

3.2 µ-XRF/µ-XANES maps and spectra obtained from Medieval Fresco samples



In Pts 1-4, mainly $PbSO_4$ is observed, possible together with reduced S-species. In Pts5-8 mainly gypsum is present. It is not possible to determine the origin of the S-species present.

3.3 The corresponding XRD data, which is much more rich in data and compound signatures, is still being elaborated.

References:

- [1] F. Vanmeert, G. Van der Snickt, K. Janssens, *Plumbonacrite Identified by X-ray Powder Diffraction Tomography as a Missing Link during Degradation of Red Lead in a Van Gogh Painting, Angew. Chemie-Int. Ed.* **54** (2015) 3607-3610.
- [2] D. Guo et al., Role of Pb(II) Defects in the Mechanism of Dissolution of Plattnerite (β-PbO2) in Water under Depleting Chlorine Conditions, *Environ. Sci. Technol.* 48 (2014) 12525−12532.
- [3] *I. Tapsoba* et al., Finding Out Egyptian Gods' Secret Using Analytical Chemistry: Biomedical Properties of Egyptian Black Makeup Revealed by Amperometry at Single Cells, *Anal. Chem.* 82 (2010) 457–460.
- [4] E. Kotulanová et al., Degradation of lead-based pigments by salt solutions, J. of Cultural Heritage 10 (2009) 367–378; Walter P. et al., Making make-up in Ancient Egypt, *Nature* 397 (1999) 483-484.
- [5] L. Burgio et al., Raman spectroscopy as a means for the identification of plattnerite (PbO2), of lead pigments and of their degradation products, *Analyst* 126 (2001) 222–227
- [6] V. A. Solé, E. Papillon, M. Cotte, Ph. Walter, and J. Susini, *Spectrochim. Acta Part B 26*, 63-68 **(2007).**