



## 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 using the **Electronic Report Submission Application:**

*<http://193.49.43.2:8080/smis/servlet/UserUtils?start>*

### ***Reports supporting requests for additional beam time***

Reports can now 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.



	<b>Experiment title:</b> Micro-XRD and Micro-XANES characterization of natural and artificial degradation of mercury sulfide pigment.	<b>Experiment number:</b> EC720
<b>Beamline:</b> ID18F	<b>Date of experiment:</b> from: 05/11/2010 to: 08/11/2010	<b>Date of report:</b>  <i>Received at ESRF:</i>
<b>Shifts:</b> 9	<b>Local contact(s):</b> Dr. Gema Martinez-Criado	
<b>Names and affiliations of applicants</b> (* indicates experimentalists): <b>Marie Radepont<sup>a,b*</sup>, Marine Cotte<sup>a,c*</sup>, Koen Janssens<sup>b</sup>, Yvan Coquinot<sup>a</sup>, Wout de Nolf<sup>b*</sup>, Francesca Alberghina<sup>d*</sup>.</b> (a) Centre de Recherche et de Restauration des Musées de France, UMR 171 CNRS, Paris, France (b) University of Antwerp, Department of Chemistry, Antwerp, Belgium (c) ESRF, Grenoble, France (d) Dipartimento di Fisica e Technologie Relative, University of Palermo, Italy		

## Report:

### Purpose

Mercury sulfide is a red pigment frequently used since Antiquity but also known for its colour degradation into black or grey. The aim of this experiment was to identify the components present in the alteration layers of original work of arts and also, by analyzing artificially aged samples, to identify the factors influencing this process. X-ray diffraction is the best technique to identify cristallized compounds and considering the micrometric size of the alteration layer, ID18F seemed to be particularly relevant to answer the questions this study raises.

### Experiment

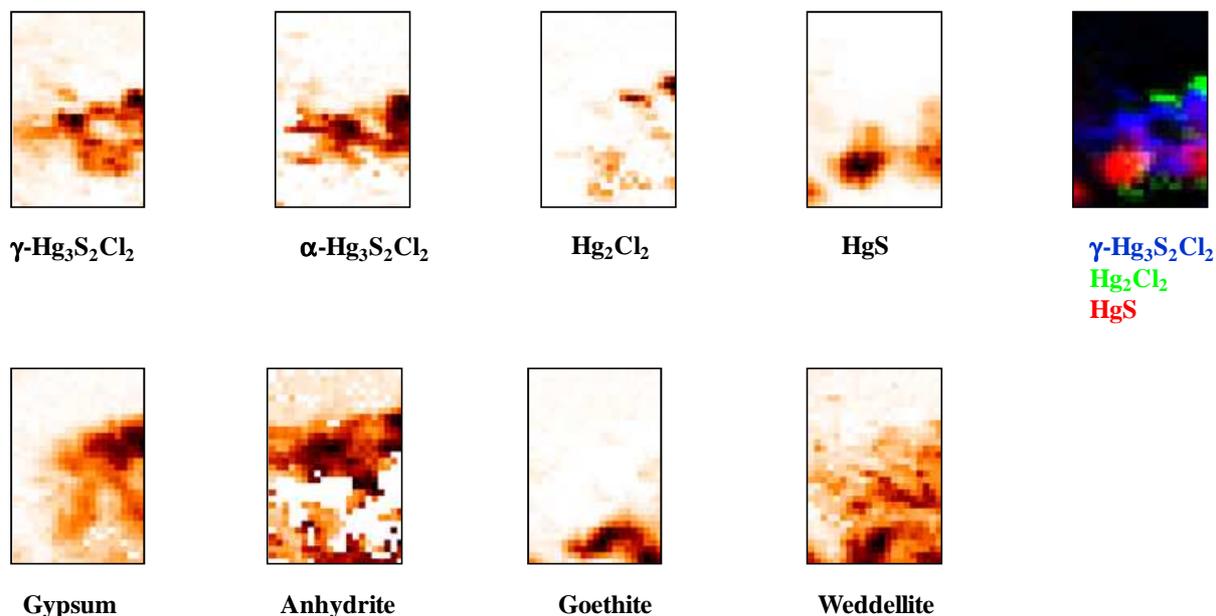
Around 10 samples were analyzed during this experiment. Five samples coming from original artworks were prepared as cross-sections in order to see their stratigraphy and then be able to differentiate different alteration layers. Among them, two coming from a frescoe in a Monastery of Pedralbes (Spain) were cut into thin sections.

The other samples were pellets containing a powder of vermilion ( $\alpha$ -HgS, Prolabo) artificially aged with UV-visible light during different periods and in two different conditions (with NaCl or NaOCl solutions). These pellets were cut and fragments of them were perpendicularly exposed to X-rays in order to have the contribution of the degradation layers without signal from vermilion.

The experiment was performed with an energy of 28 keV. The beam size was 5.3 x 1.8  $\mu\text{m}^2$  (hor x ver). Micro-X-ray diffraction patterns were collected in transmission by means of a CCD camera simultaneous to the recording of XRF spectra via an energy-dispersive Si(Li) detector. Data were then analyzed using the XRDU<sup>1</sup> software.

### Results

The XRD analyses were really relevant in this study as a new degradation product of mercury sulfide was found (kenhsuite) and as it was possible to differentiate micrometric degradation layers as one with corderoite ( $\alpha$ -Hg<sub>3</sub>S<sub>2</sub>Cl<sub>2</sub>) and kenhsuite ( $\gamma$ -Hg<sub>3</sub>S<sub>2</sub>Cl<sub>2</sub>), and one with calomel (Fig. 1), which can only be possible with a micro-beam given by synchrotron radiation.



**Figure 1** Example of results obtained after treatment of XRD data and showing the presence of degradation compounds in layers on top of cinnabar.

All the results of this experiment on ID18F are published in the following paper: *The use of microscopic X-ray diffraction for the study of HgS and its degradation products corderoite ( $\alpha\text{-Hg}_3\text{S}_2\text{Cl}_2$ ), kenhsuite ( $\gamma\text{-Hg}_3\text{S}_2\text{Cl}_2$ ) and calomel ( $\text{Hg}_2\text{Cl}_2$ ) in historical paintings*, Marie Radepont, Wout de Nolf, Koen Janssens, Geert Van der Snickt, Yvan Coquinot, Lizet Klaassen and Marine Cotte, *J. Anal. At. Spectrom.*, 2011, DOI: 10.1039/c0ja00260g.

**Abstract:** Since Antiquity, the red pigment mercury sulfide ( $\alpha\text{-HgS}$ ), called cinnabar in its natural form or vermilion red when synthetic, was very often used in frescoes and paintings, even if it was known to suffer occasionally from degradation. The paint hereby acquires a black or silver-grey aspect. The chemical characterization of these alteration products is rather challenging mainly because of the micrometric size and heterogeneity of the surface layers that develop and that are responsible for the color change. Methods such as electron microscopy, synchrotron-based microscopic X-ray fluorescence, microscopic X-ray absorption near edge spectroscopy, Raman microscopy and secondary ion microscopy have been previously employed to identify the (Hg- and S-) compounds present and to study their co-localization. Next to these, also microscopic X-ray diffraction (XRD) (either by making use of laboratory X-ray sources or when used at a synchrotron facility) allows the identification of the crystal phases that are present in degraded HgS paint layers. In this paper we employ these various forms of micro-XRD to analyze degraded red paint in different paintings and compare the results with other X-ray based methods. Whereas the elemental analyses of the degradation products revealed, next to mercury and sulfur, the presence of chlorine, X-ray diffraction allowed the identification, next to  $\alpha\text{-HgS}$ , of the Hg and S-containing compound calomel ( $\text{Hg}_2\text{Cl}_2$ ) but also of the Hg, S and Cl-containing minerals corderoite ( $\alpha\text{-Hg}_3\text{S}_2\text{Cl}_2$ ) and kenhsuite ( $\gamma\text{-Hg}_3\text{S}_2\text{Cl}_2$ ). These observations are consistent with X-ray absorption spectroscopy measurements performed at the S- and Cl-edges.

The second part of this experiment consisted in shifts at ID21 to perform Cl- and S-K edges XANES and elemental maps.



	<b>Experiment title:</b> Micro-XRD and Micro-XANES characterization of natural and artificial degradation of mercury sulfide pigment.	<b>Experiment number:</b> EC720
<b>Beamline:</b> ID21	<b>Date of experiment:</b> from: 10/02/2011 to: 15/02/2011	<b>Date of report:</b>
<b>Shifts:</b> 15	<b>Local contact(s):</b> Dr. Marine Cotte	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): <b>Marie Radepont<sup>a,b*</sup>, Marine Cotte<sup>a,c*</sup>, Koen Janssens<sup>b*</sup>, Yvan Coquinot<sup>a*</sup>.</b> (a) Centre de Recherche et de Restauration des Musées de France, UMR 171 CNRS, Paris, France (b) University of Antwerp, Department of Chemistry, Antwerp, Belgium (c) ESRF, Grenoble, France		

## Report:

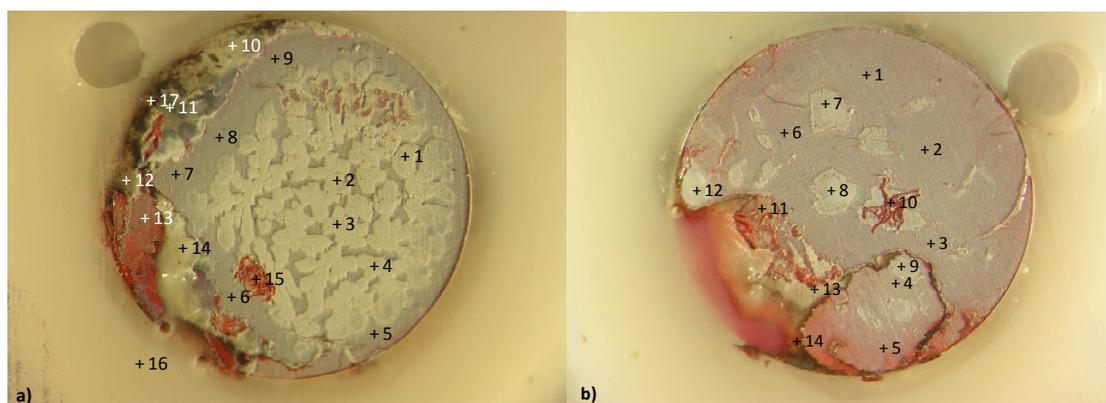
### Purpose

After the analyses on ID18F, the aim of this part of the experiment was to obtain Cl- and S-K edges XANES and chemical maps of samples containing degraded cinnabar.

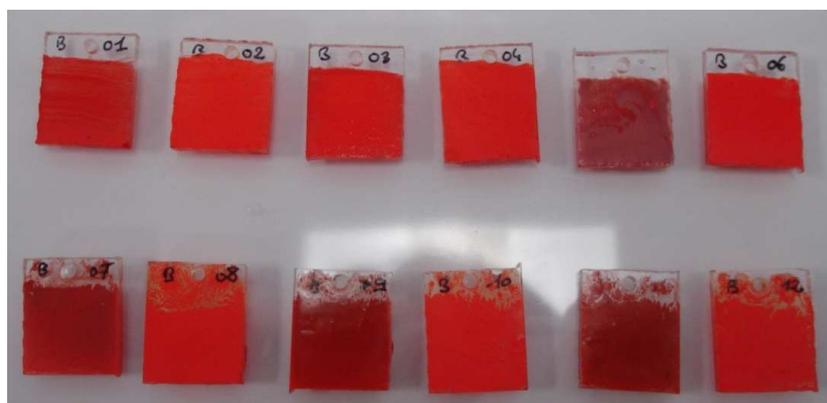
### Experiment

Around 20 samples were analyzed during this experiment. One was a cross-section of a fragment taken from a Cross painted by Giotto. This cross-section contains vermilion below a grey layer apparently containing chlorine after SEM measurements. It was decided to study carefully this sample in order to have a complete description of the alteration layers. Next to this original sample, artificially aged ones were studied. First, we looked at pellets containing only vermilion powder and aged in different conditions (Fig. 1). Then, we focused our attention on samples where vermilion was mixed with linseed oil or with lead white and linseed oil (Fig. 2). For these last samples, the exposition conditions were with or without UV-visible light, and with a H<sub>2</sub>O/NaCl/NaOCl solution.

Pellets were analyzed with a macro-beam (200µm) while a micrometric beam (1.3 x 0.2 µm<sup>2</sup> hor x ver) was necessary for the study of complex cross-sections. For each sample, chemical maps were acquired and XANES spectra at Cl- and S-K edges were collected. After acquisition, the data were analysed using PyMCA<sup>1</sup>.



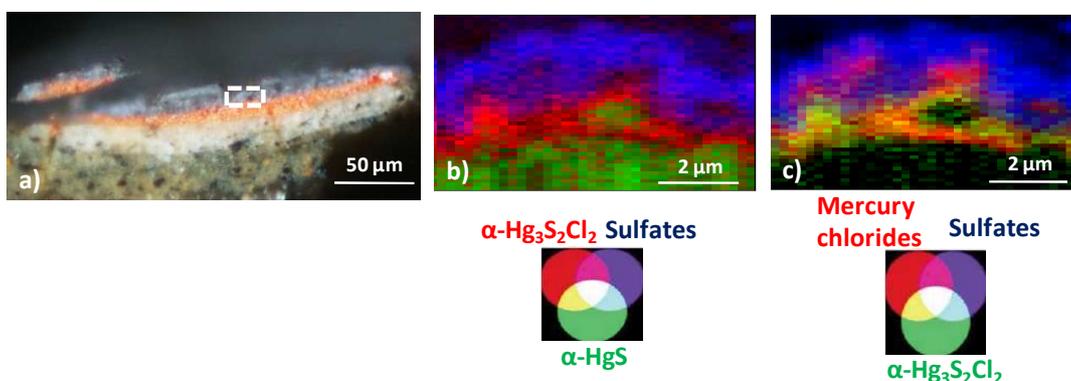
**Figure 1** Pictures of a  $\alpha$ -HgS pellet artificially aged in front of light (a: front; b: back) and in a tube containing a NaOCl solution during 741h. All the points represent where XANES spectra were collected.



**Figure 2** Picture of twelve artificially aged samples of vermilion mixed with linseed oil (01-06) and vermilion + lead white mixed with linseed oil (07-12).

### Results

For the Giotto cross-section, the elemental maps obtained (Fig.3) showed, next to the cinnabar ( $\alpha$ -HgS), the presence of  $\text{Hg}_3\text{S}_2\text{Cl}_2$  as a thin layer and on top of these two, sulfates (Fig. 3b).  $\mu$ XANES spectra at Cl- and S-K edges were collected on this sample to have a better idea of the composition of each layer. The results obtained are quite similar to the ones previously got on other naturally aged paintings.



**Figure 3** a) Picture of the Giotto sample with a dashed area corresponding to the zone where the b) and c) fluorescence maps were acquired.

The same kind of process ( $\mu$ XRF maps then  $\mu$ XANES spectra at both edges) was applied to artificially aged HgS pellets and pigment + binder mixture, in order to see if we can find the same components on artificially aged samples as we found on original ones. One of the observations is that the choice of resin used for embedding and manipulating the pellets was not the best one, conversely to what we expected. It contains relatively high amounts of chlorides and sulfates. We have also observed that the resin, in contact with the pellets, has been modified, during ageing process (whitening). We are working on an improved set-up with inert and non-contaminated material to hold the pellets.

However, one of the exciting results, on non-embedded samples, was the presence of sulfates. The absence of calcium in these models paintings raises new questions about the type of sulfates formed during artificially ageing.  $\mu$ FTIR is envisaged as a good way to identify these sulfates.

These data were acquired in Feb 2011 and are still under investigation.