



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.



	Experiment title: VARIOUS MECHANISMS INVOLVED IN CINNABAR BLACKENING STUDIED WITH COMBINATION OF μ -XANES AND μ -FTIR	Experiment number: EC-207
Beamline:	Date of experiment: from: 07/11/07 to: 13/11/07	Date of report: 21/05/08
Shifts: 18	Local contact(s): J. Susini	<i>Received at ESRF:</i>
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Report:

Purpose

The subject of this research was the analysis of a set of paintings, covering a wide geographical (France, Spain, Austria, Greece) and historical (from Roman antiquity up to 20th century) domains; but sharing a common alteration phenomenon: mercury sulphide blackening. This pigment (HgS), used in a cinnabar natural form or in a vermilion synthetic form, may turn into black or silver-grey. Up to recent times, the most advanced hypothesis was the phase transformation of red hexagonal cinnabar into black cubic meta-cinnabar by action of light.¹ Yet, other mechanisms have recently been observed. Analyses, conducted on fragments from Pompeian paintings, through the peer-reviewed experiment ME1103 and continued in house-research^{2,3} have shown that two other degradation mechanisms could be involved. On one hand, micro-X-ray fluorescence elemental maps have shown peculiar distributions of chlorine and sulphur on altered regions. On the other, X-ray absorption spectroscopy performed at both Cl and S K-edges has confirmed the presence of characteristic degradation products: i) Hg-Cl compounds (e.g. corderoite, calomel and terlinguaite), which may result from the reaction with exogenous NaCl, in grey areas, ii) gypsum, produced by the calcite sulphation, in black coatings. The purpose of the present work was to determine, over a wider set of blackening cinnabars, the frequency of the various mechanisms: metacinnabar, chlorinated and sulphated compounds. The ultimate objective was to make a connection between environmental conditions and blackening mechanisms and this way to better highlight the parameters that may favour cinnabar alteration, which is the main information requested by curators.

The lateral resolution and sensitivity offers at both the sulphur and the chlorine K-edges at the ID21 beam line were crucial for such analyses.

Experiment

Around 20 samples were studied, few being raw fragments, and most being prepared as transversal cross-sections. Macro-analysis was performed on raw fragments as well as powder references with a beam size from 50 to 200 μ m. In some cases (in particular fragments from villa Kérylos), the analysis of raw fragments was hampered by the presence of superficial organic films, which completely absorbed fluorescence from low-Z elements. In these cases, working on polished cross-sections was essential. All the analyses of transversal cross-sections were performed with a micrometer-probe (0.8 μ m(hor) \times 0.3 μ m(ver) at 2.9keV).

In a first time, analyses were conducted at the chlorine K-edge (2.9keV), in order to excite simultaneously sulphur and chlorine fluorescence. In many cases, chlorine was detected, but its distribution was not

systematically correlated to mercury distribution. μ XANES was then performed on peculiar points to provide a better identification of chlorine speciation. As was observed on Pompeian paintings, Hg-Cl compounds were clearly evidenced in many samples. In some cases, Pb-Cl compounds were also observed, probably originating from the alteration of lead pigments.

As an example, two spectra collected above a cinnabar layer (in an altered area) and below it (in the mortar), are compared to two references ($(\text{HgCl})_2$ and CaCl_2). Comparing to the previous study where analyses were limited to punctual spectra², here the protocol was pushed in order to generate chemical mappings. This approach was achievable thanks to the fact that all Hg-Cl compounds present a white line at a relative low energy, comparing the different alkaline and alkaline-earth chlorides. In other words, it was possible to selectively excite Hg-Cl compounds by exciting fluorescence with a beam of 2.8231keV (details can be found in ref 4). In Figure 1, this process reveals that Hg-Cl compounds are located only on top on the cinnabar layer, while the chlorine present in the mortar is in a different chemical environment (probably CaCl_2). This approach was conducted in several samples to get the images of the different chlorinated compounds. It offers information far much precious than punctual analyses.

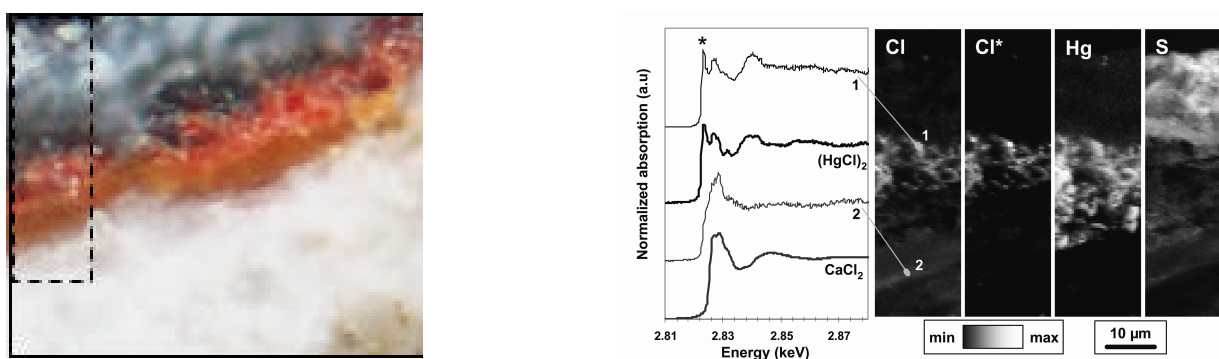


Figure1: Example of analysis by μ XRF and μ XANES at the chlorine K-edge. Left: picture of a transversal cross-section of altered cinnabar. Right, μ XANES and chemical mapping of chlorine (Cl), mercury-chlorine (Cl*), mercury (Hg) and sulphur (S). Figure are taken from ref 4.

A similar work was then conducted at the sulphur K-edge (2.5keV). In addition to cinnabar (HgS), corderoite ($\text{Hg}_3\text{S}_2\text{Cl}_2$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), other forms of sulphur were detected: among them, metacinnabar, lead sulphate (anglesite) and a still unknown sulphite form. Chemical mappings were acquired on some particular fragments, revealing sometimes very complex stratigraphy, with the presence of the various sulphur species, in multi-layered arrangement.

Results

The experiments were conducted on a relatively wide set of fragments. Due to limited schedule and to sample complexity, detailed analyses, in particular chemical mappings, were performed only for a few relevant cases. They revealed the presence of the different degradation products (metacinnabar, chlorinated and sulphated compounds), but surprisingly, these different compounds were usually simultaneously present in the same fragment, which makes difficult the establishment of a correlation between environmental conditions and degradation processes.

Other analyses, in particular isotopic, are envisaged to go deeper into the phenomena understanding, in particular to analyze the origin (endogenous or exogenous) of elements.

The ID21 X-ray microscope is particularly adapted for such studies, as it provides a unique tool to identify and to image both chlorine and sulphur compounds with a micrometer probe. Unique information could be obtained this way. Part of them are already published⁴, but work is still on going, and should lead to a more complete and dedicated article.

References

1. Gettens, R. J.; Feller, R. L.; Chase, W. T. *Stud. Conserv.* 1972, **17**, 45-69
2. M. Cotte, J. Susini, A. Moscato, C. Gratziau, A. Bertagnini, N. Metrich, *Anal. Chem.*, 2006, **78**, 7484-7492.
3. *ESRF Highlights*, 2006, 105-106
4. M. Cotte, J. Susini, V. A. Solé, Y. Taniguchi, J. Chillida, E. Checroun, P. Walter, *Journal of Analytical Atomic Spectrometry*, **23**, 820-828 (2008).