



	Experiment title: μ XRF and μ XANES to unequivocally disclose the nature of the black phases and Hg-Cl and Hg-S-Cl species on blackened Roman cinnabar fresco paintings	Experiment number: HG-184
Beamline: ID21 and BM23	Date of experiment: from: 10/03/2022 to: 03/06/2022	Date of report: 29/07/2022
Shifts: 48	Local contact(s): Marine Cotte (ID21) and Olivier Mathon (BM23)	<i>Received at ESRF:</i>
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Report:

The aim of this experiment was to refine the understanding of the chemical reactivity leading to the darkening/blackening of cinnabar (α -HgS) pigment on Roman cinnabar fresco paintings by μ XRF and μ XANES at S and Cl edges and μ HERFD-XANES at Hg edge. Initially, 21 shifts (12 in BM23 and 9 in ID21) were allocated. However, in order to finish with the study of specific samples, the local contact of ID21 increased the number of shifts. Due to technical problems, it was however only possible to take the advantage of around additional 15 shifts.

In ID21, we investigated 12 Hg-reference compounds (powders), 13 cross-sections of 9 and 4 mural painting samples from the archaeological site of Pompeii (Italy) and Maison de Aiôn (France). 7 samples from both locations were also analyzed as unmounted (sub-)millimetric fragments. The deriving results were compared with a wide range of mock-ups (53) that mimic cinnabar decorated Roman frescoes subjected to ageing experiments. The list of samples analyzed by μ HERFD-XANES at Hg edge in BM23 was more reduced (9 Hg-reference compounds, 8 aged cinnabar mural paintings mock-ups as fragments, 2 samples from Aiôn and 5 from Pompeii embedded as cross-sections). Considering that a specific and unique set-up was needed at BM23, it took some time to systematize the analytical protocol. However, pivotal results that explain the chemical reactivity of cinnabar were obtained.

The preliminary analysis of the data allowed us to conclude that, depending on the environment surrounding the cinnabar-decorated Roman frescoes, the deterioration compounds associated to the darkening of cinnabar were very different. In the samples from Aiòn (known to be prone to darken), the variety of degradation products of cinnabar is not so extensive. On the contrary, in all the Pompeian samples exposed to the volcanic eruption of Mt. Vesuvius in the 79 AD, the formation of corderoite ($\text{Hg}_3\text{S}_2\text{Cl}_2$), calomel (Hg_2Cl_2) and metallic mercury (Hg^0) was confirmed (see Figure 1). Moreover, massive sulfation (gypsum presence) of calcite, and formation of chlorides (CaCl_2) were also highlighted. Considering that, the cinnabar was randomly present in mixture with ochre pigment in the painting layers, for this specific archaeological context, the sulfation of calcite cannot be only explained by the oxidation of the S coming from the cinnabar.

During this first stage of data treatment, we performed Principal Component Analysis (PCA) on the High Resolution XANES spectra at Hg edge of the reference Hg compounds and then we projected the spectra obtained in the samples from Pompeii on the reduced space (see Figure 1 right). As can be observed, the presence of metacinnabar ($\beta\text{-HgS}$) was revealed. The rest of the measurements suggest the presence of a mixture of cinnabar and Hg^0 in the Pompeian samples exposed to the volcanic eruption. In some cases, the isolated presence of Hg^0 was also detected (see Figure 1 right).

In the Pompeian samples not exposed to the 79 AD volcanic eruption, it was challenging to identify degradation products of cinnabar, sulfation of calcite or even crystallization of chloride salts in the cinnabar pictorial layers.

The first results obtained from the data acquired from the aged mock-ups led us to hypothesize that much more aggressive conditions should be designed to simulate the extreme conditions that led to the blackening of cinnabar in Pompeii during the Mt. Vesuvius eruption. According to this, at this moment we are designing and conducting new ageing experiments on mock-ups. In the future, the study of these lasts using the same analytical approach here presented will help to clarify if all the degradation products identified in the historical samples can be obtained from the chemical routes proposed in the laboratory.

Thanks to the conclusions already extracted, we were able to present an oral contribution titled “Looking for black: From in-situ analyses to synchrotron experiments to unravel the transformation of cinnabar in the wall paintings of Pompeii” at the International Congress “Chemistry for Cultural Heritage” (4-8 July 2022, Ravenna, Italy).

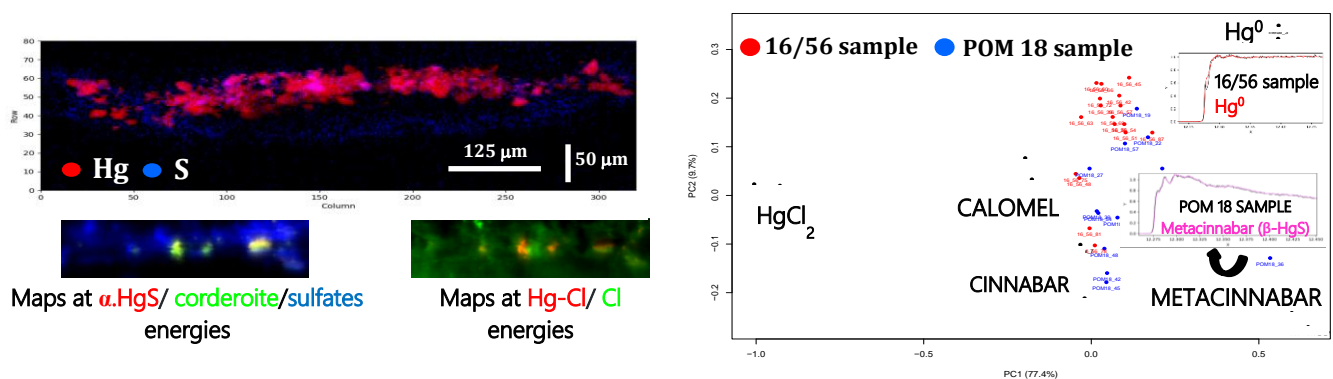


Figure 1. μXRF distribution maps of Hg and S and distribution maps at the energies of cinnabar ($\alpha\text{-HgS}$), corderoite, sulfates, Hg-Cl and Cl in sample POM 18 from Pompeii (left), and scores and loadings plot including the $\mu\text{HERFD-XANES}$ spectra of Hg-reference compounds and measurements acquired on two Pompeian samples exposed to the volcanic eruption, the $\mu\text{HERFD-XANES}$ spectra of Hg^0 and metacinnabar identified in some measurements are also presented (right).