Scanning µ-XRF/µ-XRPD investigation into the blackening of HgS in works of art

F. Vanmeert¹, M. Radepont¹,², M. Cotte³, S. Legrand¹, and K. Janssens¹

¹ Universiteit Antwerpen, Groenenborgerlaan 171, 2020 Antwerpen, Belgium
² Laboratoire d’Archéologie Moléculaire et Structurale – UMR8220 CNRS, 3 rue Galilée, 94200 Ivry-sur-Seine, France
³ European Synchrotron Radiation Facility, 6 rue Jules Horowitz, BP220-38043 Cedex 9 Grenoble, France

Since antiquity, the red pigment mercury sulfide (α-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 the alteration products remains challenging, mainly because of the micrometric size and heterogeneity of the surface layers that develop. Therefore, the full degradation pathway is not yet fully understood. In this work we have performed combined micro X-ray fluorescence and micro X-ray powder diffraction (µ-XRF/µ-XRPD) imaging experiments to further elucidate the different compounds that play a role in the blackening of α-HgS. Measurements were performed on aged model samples as well as a real paint sample taken from the mural paintings of the monastery of Pedralbes, which has been previously investigated [1][2].

Combined µ-XRF/µ-XRPD scanning experiments have been performed at the hard X-ray micro/nano-probe beam line (P06) of the PETRAIII storage ring, using a photon energy of 20.5 keV. The beam was focused to 0.4 x 0.4 µm² (hor. x vert.) employing a Kirkpatrick-Baez mirror optic. Diffraction signals were recorded in transmission geometry with a Pilatus 300K area detector. X-ray fluorescence signals were recorded using a Si-drift detector with 50 mm² active area. Elemental and phase distribution maps were collected from model and real paint samples with 1 x 1 µm² or 1 x 0.5 µm² (hor. x vert.) step size and an acquisition time of 1 sec/point. The high readout speed of the Pilatus detector (< 5 ms) allowed for fast mapping with minimal overhead time (< 1 sec).

Figure 1: Phase composition (orange) and Hg-L distribution maps (blue) obtained by combined µ-XRF/µ-XRPD scanning of a thin section (20 µm thickness) from the Pedralbes mural painting. A photograph of the thin section (top left) and an image of the combined Hg-containing crystalline phases (top right) are shown. The dashed line indicates the upper edge of the original cinnabar. Map size: 136 x 80.5 µm² (hor. x vert.).

The high spatial and angular resolution as well as the high brightness achieved at beam line P06 allowed for the localization and identification of various Hg-containing degradation products that play a role in the blackening of the red mercury sulphide (Figure 1). The µ-XRPD results clearly
show the layered structure of the alteration process with the different layers only several micrometers thick. The white calomel (Hg₂Cl₂) is located on top of the original cinnabar with γ-Hg₃S₂Cl₂ (kenhsuite) situated just below. The rare β-Hg₃S₂Cl₂, which was not found in previous studies [1][2], is shown to be present over a larger area deeper within the red HgS, indicating it as a first step in the degradation pathway. The compound responsible for the actual black colour is however still lacking. Several crystalline compounds remain unidentified due to signal overlap and the ‘grainy’ structure of the diffraction patterns acquired. It should be noted that after the mapping experiment, the samples showed heavy blackening caused by exposure to the X-ray beam. It is not yet clear if this alteration is due to damage to the organic binder of to the pigment itself.

References