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| | Experiment title: Revealing ultramarine pigment qualities in Middle ages paintings by a combination of Synchrotron-based μ XRF/ μ XANES/ μ XRD | Experiment number: HG139 |
| Beamline: ID21 | Date of experiment: from: 17/10/18 to: 20/10/18 | Date of report: 15/11/19 |
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The main objective of the project was to gather information on the mineral and elemental composition of the various grades of ultramarine pigment used by Old Masters, notably French painters of the 14th c. Submicronic XRF and XANES mapping (ID21) were combined to detect markers of the pigment ancient elaboration processes. Ultramarine was the most highly-valued painting material during the Middle Ages. It is a deep blue pigment, naturally obtained from the mineral lazurite ($\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{S}_n$), the main component of the lapis lazuli stone. During the Middle Ages, the preparation of ultramarine was a complex process, involving numerous steps, notably possible heating of the lapis lazuli rock (up to 800°C) [1]. Historical treatises reveal that several grades of ultramarine were then obtained according to the synthesis refinement, and sold at very different prices on colour markets. Painters selected carefully between those grades before using them in their artworks. Today, determining markers of the synthesis of ultramarine pigments within historical paintings is of great importance to our understanding of artist's use of what was one the most precious materials of their time.

During this beamtime, a corpus of about 10 historical micro-samples collected on paintings commissioned by the Duchy of Burgundy under the reign of Philip the Bold, around 1400, and conserved in the *Louvre* museum, were studied. X-ray absorption near-edge structure spectroscopy (XANES) at the sulfur K-edge in microbeam was employed at ID21 to monitor the changes in the sulfur species within lazurite following treatments. Our working hypothesis was indeed that the different grades of ultramarine differ by the speciation of sulfur anions, sensitive to heat treatments [2].

Experimental

Paint samples under the form of cross-sections (resin blocks containing microscopic paint fragments) were mounted within the ID21 vacuum chamber.

In a first time, XRF maps were collected with an incident X-ray energy of 2.5 keV, with a beam size of $0.6 \times 1.0 \mu\text{m}^2$ (flux of 4.3×10^8 photons s^{-1} , attenuated using a $6 \mu\text{m}$ aluminum filter). This rendered possible the probing of individual pigment particles (usually dispersed in a lead-based matrix) in the historical samples. Points-of-interest were chosen over the samples based on the Al, Si, and S distribution in these maps, and μXANES spectra were collected. All XANES spectra were acquired by scanning the energy across the sulfur K-edge from 2.46 to 2.53 keV.

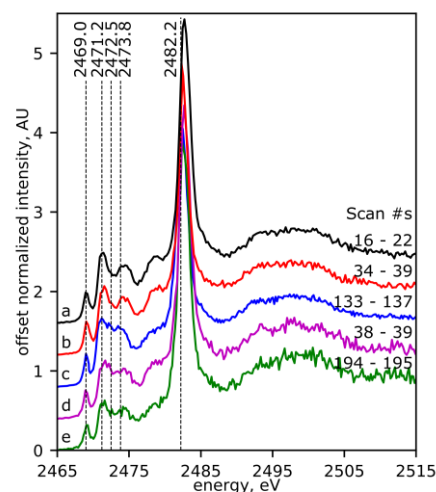
In this focused moden without attenuation, radiation damage was observed during consecutive μXANES acquisition. Decreasing the flux using attenuators and accumulating single spectra from several points per pigment particle was implemented as a mitigation. Besides, to evaluate pigment heterogeneity, analyses were performed over several (>10) particles per historical samples.

Results

In preparation of this work, an extensive laboratory research was performed by A. Gambardella to assess the effect of heating on ultramarine pigments. All the results are presented in a recently published work by A. gambardella et al. [3]. This work showed that the sulfur signature was uniquely dependent on the temperature of heat-treatment. In particular, peaks at 2469.0 and 2471.2 eV, attributed to contributions from the trisulfur radical ($\text{S}_3^{\cdot-}$), which is responsible for the blue color of lazurite, increase in relative intensity with heat of treatment $\geq 600 \text{ }^\circ\text{C}$, paralleled by an intensified blue hue.

In all of the historical samples analyzed at the ESRF during this beamtime, some particles exhibited characteristic spectra for lazurite from heat-treated lapis lazuli (a selection is shown in Figure 1).

Notably, these spectra have peaks of higher intensities at 2471.2 eV relative to those at both 2472.5 and 2473.8 eV, with those from Bellechose (Figure 1a) and Maelwael (Figure 1b) also exhibiting clear local minima at 2472.5 eV. The spectral similarity of these historical pigment particles to those from the pigments prepared from heat-treated lapis lazuli rock (not shown in this report) strongly suggests that each of these artists used ultramarine pigment containing lazurite derived from heat-treated lapis lazuli rock. An interesting result was also the correlation in some particles between the intensity of the blue color and the relative contribution of the trisulfur radical species to the spectral profile. All the obtained results of experiment HG-139 are detailed in [3].



Conclusion and perspectives

The results of this beamtime permitted to identify sulfur speciation using μXANES spectroscopy at the sulfur K-edge as a reliable marker for the preparation of the ultramarine pigment from heat-treated lapis lazuli rock. An immediate output of the beamtime was a publication [3]. Future perspectives include to complete this extensive XANES work with XRD analysis. Indeed, we expect that the different grades of ultramarine also differ by their composition : various crystalline phases in addition to lazurite, notably sodalite $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$, diopside $\text{CaMgSi}_2\text{O}_6$, albite $\text{NaAlSi}_3\text{O}_8$ and other silicate could be present according to the post-synthesis employed in the past. Identifying those crystalline phases and map their distribution at the microscale, using synchrotron μXRD (for example on beamline ID13) would strongly complement the present study.

References

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