Probing the alteration pathways of artists' pigments by synchrotron radiation-based X-ray methods and vibrational spectroscopy techniques

Letizia Monico,[1,2,3,*] Marine Cotte,[4,5] Koen Janssens,[3,6] Wout De Nolf,[4] Steven De Meyer,[3] Frederik Vanmeert,[3,7] Gert Nuyts,[3] Aldo Romani,[1,2] Laura Cartechini,[1] Francesca Rosi,[1] Gerald Falkenberg,[8] Jan Garrevoet,[8] Lucia Amidani,[4,9] Pieter Glatzel,[4] Costanza Miliani[10]

[1] CNR-SCITEC, via Elce di Sotto 8, 06123 Perugia (Italy), [2] SMAArt Centre and Department of Chemistry, Biology and Biotechnology, University of Perugia, via Elce di Sotto 8, 06123 Perugia (Italy), [3] AXES Research Group, NANOlab Centre of Excellence, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp (Belgium), [4] ESRF, Avenue des Martyrs 71, 38000 Grenoble (France), [5] LAMS, CNRS UMR 8220, Sorbonne Université, UPMC Univ Paris 06, Place Jussieu 4, 75005 Paris (France), [6] Rijksmuseum, Conservation & Restoration—Scientific Research, Hobbemastraat 22, 1071 ZC Amsterdam (The Netherlands), [7] Laboratories of the Royal Institute of Cultural Heritage (KIK-IRPA), Parc du Cinquantenaire 1, 1000 Bruxelles (Belgium), [8] DESY, Notkestraße 85, 22607 Hamburg (Germany), [9] Rossendorf Beamline at the ESRF, HZDR, Institute of Resource Ecology, Dresden 01314 (Germany), [10] CNR-ISPC, via Cardinale Guglielmo Sanfelice 8, 80134 Napoli (Italy)

*Corresponding author e-mail: letizia.monico@cnr.it

Cultural heritage objects are multilayered and heterogeneous systems composed of organic and inorganic materials with either amorphous or crystalline structure, that are subject to complex chemical transformations over time. Such degradation processes are typically promoted by a number of environmental factors, such as light, humidity and temperature.

In this context, the color change of artists' pigments is one of the grand challenges of heritage science. Darkening or fading, often accompanied by flaking, crumbling and chalking of the paint, affect a large number of polychrome artworks in museums and collections, with serious risks for their understanding, preservation, and management.

For a number of inorganic pigments, the alteration involves redox reactions. [1] These processes lead to the formation of secondary products that are usually distributed as layers and/or aggregates of limited size (below 100 µm) at the painted surface. Thus, the use of analytical tools that are able to provide spatially resolved elemental speciation and structural information down to the (sub)micrometer scale length, such as synchrotron radiation (SR)-based µ-XRF, XANES and µ-XRD techniques (in point analysis and mapping/imaging mode), is required for studying this kind of processes. The combination of such methods with vibrational spectroscopy techniques (e.g. IR and Raman) permits to gather complementary insights into the molecular nature of the newly formed compounds. [2,3]

In this contribution, an overview of our research activities aimed at unravelling the degradation pathways of selected artists'pigments in paintings (i.e., chrome yellows, cadmium yellows, arsenic sufildes and Prussian blues) will be provided. [4-13] SR-based X-ray data acquired at beamlines ESRF-ID21/-ID26 (Grenoble, FR) and PETRA III/DESY-P06 (Hamburg, DE), in combination with vibrational spectroscopy results obtained from the analysis of artificially aged mock-ups, original artworks and related paint micro-samples will be presented. [4-15] Issues related to SR X-ray induced damages of the painted surface and strategies for mitigating such damage will be also discussed.

References

[1] C. Miliani et al., Angew. Chem. Int. Edit. **54** (2018), 7324; [2] K. Janssens et al., Top. Curr. Chem. **374** (2016), doi: 10.1007/s41061-016-0079-2; [3] M. Cotte et al., J. Anal. Atom. Spectrom. **32** (2017), 477; [4] L. Monico et al., Angew. Chem. Int. Edit. **54** (2015), 13923; [5] L. Monico et al., Anal. Chem., **85** (2013), 851; [6] L. Monico et al., Anal. Chem., **83** (2011) 1214; [7] L. Monico et al., Anal. Chem., **85** (2013) 860; [8] L. Monico et al., J. Anal. At. Spectrom., **30** (2015) 1500; [9] L. Monico et al, Microchem. J. **124** (2016), 272; [10] L. Monico et al., Anal. Chem., **83** (2011), 1224; [11] L. Monico et al., Anal. Chem. **86** (2014), 10804; [12] L. Monico et al., J. Anal. At. Spectrom., **30** (2015), 613; [13] L. Monico, ACS *Omega*, 4 (2019), 6607; [14] L. Monico et al., *Chem. Eur. J.* **24** (2018), 11584; [15] L. Monico et al., *Sci. Adv.*, **6** (2020), eaay3514.