Redox-driven alterations of lead chromate and cadmium sulfide pigments in oil paintings: an experimental and computational study

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Abstract

The chemical alteration of artists' pigments in paintings, leading to color changes, such as darkening or fading, is a major challenge in heritage science. These alterations, often linked to physical paint degradation (flaking, crumbling, chalking), require a comprehensive investigation into pigment properties and the external factors driving their transformation to develop effective preservation strategies of artworks in museums.

The alteration of specific inorganic pigments, namely chrome yellows ($PbCr_{1-x}S_xO_4$, with $0 \leq x < 1$), cadmium yellows and cadmium reds ($Cd_{1-x}Zn_xS$ and $CdS_{1-x}Se_x$, with $0 \leq x < 1$), is driven by redox reactions. These processes generate secondary products that usually manifest as superficial layers and/or localized aggregates, with dimensions generally below 100 µm, within the paint stratigraphy. Such restricted distribution complicates their full characterization.

This problem can be addressed through a systematic, multi-scale, and multi-technique study of paintings, related micro-samples, and laboratory-prepared paint models (both before and after artificial aging) (Fig. 1). The approach combines molecular, nano-micro, and macroscopic analyses, employing a wide range of state-of-the-art techniques and computational simulations. Notably, electron microscopy and synchrotron radiation-based X-ray imaging methods (µ-XRF, µ-XAS, and µ-XRD), coupled with electronic and vibrational (micro)spectroscopies (UV-Vis-NIR, IR, and Raman), allows for obtaining spatially resolved information on the atomic, molecular, and optical properties of both the original pigment and its degradation products, down to nanometer length scales. Combining these analyses with macro-scale, non-invasive investigations (spanning the IR to X-ray range), using portable devices performed *in situ* on paintings, provides the capability to visualize and map areas where lead chromate- or cadmium sulfide-containing paints are at the highest risk of degradation or where alterations are currently developing. Furthermore, computational modeling based on DFT methods enables us to gain further insight into the structural and electronic properties of the starting pigment in relation to its surrounding chemical environment.

This lecture will present an overview of the alteration processes affecting chrome yellows, cadmium yellows, and reds in late 19th- to early 20th-century oil paintings. These findings, obtained through the experimental and computational approach described above, will be discussed in terms of their potential contribution to developing models and digital tools for the virtual reconstruction of original colors and the prediction of their changes over time.

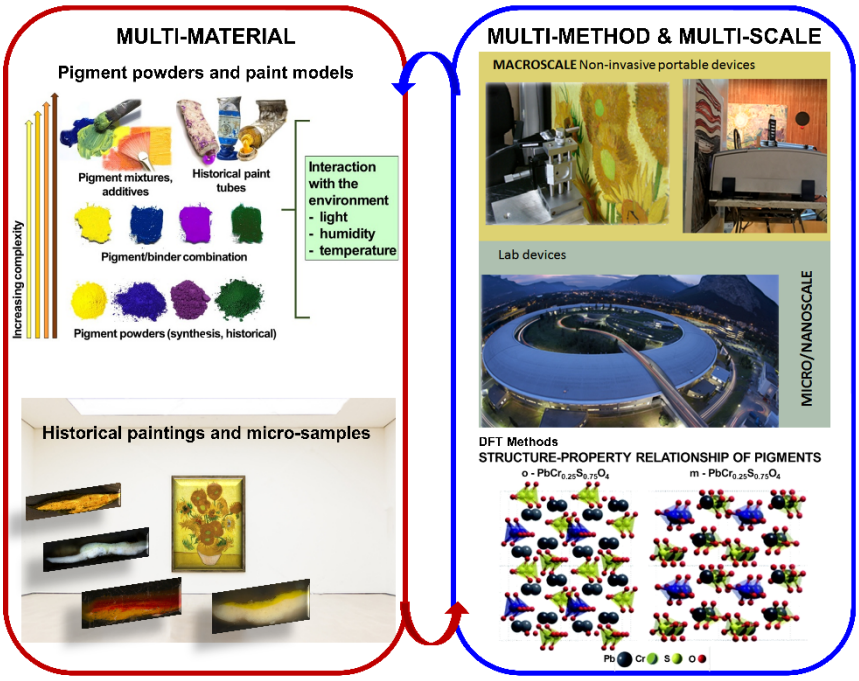


Figure 1. Scheme of the multi-material, multi-method, and multi-scale approach used to investigate alteration pathways of lead chromate and cadmium sulfide pigments within late 19th- to early 20th-century oil paintings.

Short bio.

Letizia Monico is a senior researcher at the Institute of Chemical Sciences and Technologies "Giulio Natta" (SCITEC) of the National Research Council (CNR) and a visiting scientist in the AXIS research group of the Physics Department at the University of Antwerp.

Since earning a joint PhD in Chemistry from the Universities of Perugia and Antwerp in 2012, she has established herself as a specialist in the study of alteration processes and the characterization of artists' materials, particularly inorganic pigments in paintings, using vibrational and synchrotron-based X-ray microspectroscopies. She is a member of MOLAB, an infrastructure for in-situ non-invasive measurements of cultural heritage objects within the European Research Infrastructure for Heritage Science, and a co-coordinator of the Historical Materials BAG at the European Synchrotron Radiation Facility in Grenoble.

She is (co-)author of over 45 peer-reviewed papers and book chapters.

From 2013 to 2022, her research on the alteration processes of pigments received numerous awards, including the Eric Samuel Award from the Microscopy Society of America, the SILS-SPECS PhD Award from the Italian Synchrotron Radiation Society, the Primo Levi Prize, and the Rossi Manaresi Medal, both from the Italian Chemical Society.

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