MetOx
Metal-oxalates in the 15th to 17th Century Southern Netherlandish oil paintings

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SUMMARY

Context
For more than two decades, heritage science has striven to describe the complex physicochemical mechanisms governing oil binder and pigment transformations as oil paintings age through time. Metal oxalates constitute one of the families of ionic species that have recently been identified as a new type of alteration products in numerous oil paintings. These coordination complexes are considered highly problematic when they precipitate on the paint surface, forming a thick, opaque, highly insoluble crust, which radically modifies the visual properties of an artwork and alter its readability. However, unlike metal soaps, the mechanistic aspects of metal oxalate formation within oil paintings had been much less investigated at a fundamental level until they were systematically addressed by the MetOx project.

Objectives
The MetOx project was based on the correlation of three major research axis: (i) the multi-instrumental, microanalytical characterization of cross-sections belonging to major Southern Netherlandish oil paintings produced from the 15th to the 17th centuries; (ii) the non-invasive and non-destructive macroanalysis of a selection of historical Southern Netherlandish oil paintings belonging to the study group; and (iii) the macro-to-micro characterization of the alteration phenomena in different collections of model systems of varying materialities and ageing conditions. These research endeavours pursued a trifold objective:

i. To develop an analytical protocol comprising a macro-to-microscale approach allowing to localize and quantitatively evaluate the presence of metal oxalates formed in oil paint surfaces and strata.

ii. To propose and experimentally verify a mechanism for metal oxalate formation from the results of the analyses of the selected Southern Netherlandish 15th to 17th century paintings and from modelling and fabrication of equivalent mock-up samples, that will be subjected to accelerated ageing and macro-to-microanalysis.

iii. To propose preventive conservation-restoration guidelines allowing to reduce the rate of formation of metal oxalates in Southern Netherlandish oil paintings on the basis of the information obtained by application of the developed analysis protocol.
Conclusions
By interlinking results obtained at the macro and microscales, both in historical paintings and model systems, we have identified that certain pigments (e.g. red lakes, verdigris, smalt and ultramarine), fillers (e.g. calcium carbonate) or driers (e.g. zinc vitriol) unequivocally favour the formation of specific metal oxalates within oil paint layers. Furthermore, we have been able to prove that, in the presence of the above-stated materials, the oxalate anion is produced through a humidity-mediated, photochemical degradation of the oil binder, thus offering novel insights on the transformation processes that lead to the formation of metal oxalates within oil paint layers as they age.

Keywords
Southern Netherlandish Painting - Metal-oxalates – Oil paint alteration