MS114.O01

Multimodal investigation of Pb- and As-based pigment degradation

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Many painting materials employed by artists in different historical periods, ranging from the Antique period to the modern era, are subject to spontaneous degradation [1]. Usually, a combination of physical and chemical factors in the environment of the works of art exert an influence on the durability of the pigments originally employed. This can lead to a loss of mechanical strength of the paint as a whole but can also take milder forms such as a discoloration. Often discoloration phenomena are caused by redox transformation of original pigments.

In the recent past, we have examined the degradation of various sulfide-based pigments such as vermillion red (HgS), cadmium yellow (CdS) and chrome yellow (PbCrO4). All these substances are semi-conductor materials that upon illumination with light of sufficient energy can release electron-hole pairs that in their turn can promote oxidation and reduction reactions, either of the semi-conductor material itself or of materials in its immediate vicinity.

In this presentation, the attention will be focussed on the degradation of lead and arsenic based pigments employed by artists and craftsmen in different period. Minium aka as red lead) is a mixed-valence oxide of lead that can be converted to various lead carbonates, hereby losing its characteristic red-orange color. Another pigment used in many historical periods is orpiment (As2S3), an arsenic sulfide of limited durability that may first convert into arsenolite (As2O3) and upon further oxidation to arsenate compounds while the sulfidic anions form sulfates.

The degradation pathways of these pigments can be elucidated as a function of environmental conditions by means of a combination of (X-ray based) analytical imaging methods such as X-ray fluorescence, X-ray diffraction and X-ray absorption spectroscopy. Macroscopic forms of these methods [2] are employed to characterize and explore the affects works of art in their totality while microscopic variants are useful for more detailed (speciation) analysis of minute paint samples taken from these artworks [3].

The information obtained in this manner is useful to optimize/redesign the conditions in which important works of art are stored for extended periods of time. This will enable a more durable way of preserving precious and often unique works of art for the following generations.

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Keywords: minium, orpiment, degradation