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Editorial for Special Issue "Historical Mineral Pigments"

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The physical–chemical characterization of natural and synthetic historical inorganic and mineral pigments, which may be found embedded in paintings (real or mock-ups), glass, enamel, ceramics, beads, tesserae, etc., as well as their alteration under different decay scenarios, is a demanding line of investigation. This field of research is now both well established and dynamic, as revealed by the numerous publications in high-quality journals of varied scientific disciplines. Likewise, pigment research has adapted to the current challenge faced by other fields of study related to minerals, by including interdisciplinary scientific approaches and the use of complementary, cutting-edge, and/or innovative analytical techniques or methods.

In recent decades, the analysis of pigments in artworks and archaeological artifacts has been more and more frequently accomplished by interdisciplinary teams conjoining Sciences (Mineralogy, Crystallography, Chemistry, Physics, or Mathematics) and Humanities (History, Archaeology, and Conservation/Restoration, to mention a few). The goal is to obtain the most and best information to assist in characterizing pigments, coloring compounds, and their degradation forms and mechanisms due to interactions with other pigments, impurities, or binders. In such a manner, questions and analyses can be properly tackled, and the correct results attained, offering crucial information to historians, archaeologists, and conservators/restorers to determine pigment origin (natural or synthetic), manufacturing process, fingerprints for author/schools/region adscriptions, chronology, authentication, or trade routes. Special attention is given to the precise identification of clay- and earth-pigments, a group of mineral pigments traditionally neglected during in-depth analysis of painting-heritage case studies. Furthermore, results enable identification of the best intervention strategies or preventive conservation of the colored artworks and archaeological items containing pigments.

As mentioned above, to attain the desired objectives, there are several recommendations in Conservation Science and Archaeometry and, particularly, in the investigation of historical pigments. First, one should use an array of analytical techniques that provides complementary data; second, innovative analytical strategies are demanded; and third, noninvasive in situ or ex situ techniques are called for, due to the exclusive artistic and historical value of the examined materials. However, noninvasive methods often are done in synergy with micro-destructive analyses performed in laboratory via well-established robust techniques such as scanning electron microscopy–energy dispersive X-ray spectrometry (SEM-EDS), which offers unique and irreplaceable information regarding the paintings´ structure and colored archaeological artifacts, as well as chemical–mineralogical and morphological features of pigments at the micro- or nanoscale.

Another recent and highly valuable trend in investigating ancient pigments is to apply multivariate methods such as chemometric tools (e.g., fuzzy logic and principal component analysis) to spectral data acquired from diverse analytical techniques. These can be applied to real paintings or mock-ups, enamels, glass tesserae, etc., in order to correctly identify inorganic pigments as well as their state of conservation or origin. Moreover, statistical probabilistic techniques such as Monte Carlo simulations are used in the field of painted

artworks, ceramics, or mosaics to optimize acquisition and refine analytical protocols. Similarly, in the past few years, two more subjects have gained importance in relation to pigment research, namely, the radiation damage during analysis and, consequently, the investigation of the related mineral phase transitions. In this regard, ample studies deal with the adequate acquisition parameters to permit harmless pigment analysis using varied analytical techniques such as Raman spectroscopy. The impact of urban air pollution on the decay of open-air painted artwork is also a trending topic. Remarkably, scientists have verified that the damaging effects of gases and particulate matter such as carbonaceous particles are enhanced by climate change. The most notable side-effect of the pollution-induced deterioration of paintings is color variation (fading or blackening). To investigate the damage forms and mechanisms, researchers use paint mock-ups (model paint samples) that simulate the structure and composition of historical paintings, which are subsequently subjected to natural and/or accelerated aging tests to evaluate the impact of pollutant gases and mineral particles, UV/Vis radiation, temperature, or relative humidity.

This special volume covers the themes described above. Although we are aware that other specific subjects related to historical inorganic/mineral pigments (shown in the Special Issue information) are of great interest and deserve in-depth investigation, we hope that the works here presented are valuable to both beginners and experts in the exiting world of ancient pigments and that they will serve as bases for further research.

The first article of this volume represents a collaboration between the Department of Crystallography, Mineralogy, and Agricultural Chemistry of the University of Seville (Spain) and the Department of Biological, Geological, and Environmental Sciences of the University of Bologna (Italy). Martín and colleagues show that, whatever the new applied analytical techniques in the field of historical paintings, SEM-EDS is still one of the most suitable (and used) tools to analyze at micro- and nanoscale the chemical composition and morphology of inorganic pigments [1]. However, they point out that in order to obtain correct quantitative chemical data, analytical simulation strategies should be performed to establish the most suitable measurement setups. They illustrate the application of a Monte Carlo SEM-EDS simulation to the compositional micro- and nano-characterization of the Egyptian blue mineral pigment. Their results demonstrate the effects of thickness, size (0.1–10 μm) and geometrical shape of the examined grain pigments, as well as the sample holder (carbon or aluminum) and SEM-EDS instrumental parameters (e.g., electron beam energy, probe size, and position with respect to the sample, type, geometry, and angles of EDS detector, etc.) on the obtained X-ray intensity which, consequently, influences the correct pigment analysis and quantification.

The next article by Costantini and co-workers [2] from the Department of Analytical Chemistry of the University of Basque Country (Spain) and the Department of Mathematical, Physical, and Computer Sciences of the University of Parma (Italy), investigates the phase transition of plattnerite (β-PbO_2 lead (IV) oxide) in both historical paintings and commercial pigments due to laser impact of Raman spectroscopy, including a confocal Raman microscopy coupled to a temperature-controlled stage, proving the robustness of this technique in identifying minerals and their transformation. Two types of lasers were used, i.e., 633 and 785 nm, operating at different laser power. Plattnerite laser-induced degradation yields the formation of red lead (Pb_3O_4), litharge (α-PbO), and massicot (β-PbO). Nonetheless, results show dissimilar response of irradiated pigments whether embedded in historical paintings (frescoes) or commercial pigments, which is due to pigment–binder interactions or the effect of other pigments. In particular, new phases of lead oxide are found in commercial plattnerite (identified via X-ray diffraction, XRD); additionally, commercial pigments show better stability with increasing laser power than do historical ones. All the degradation pathways of the lead oxides are discussed, thus improving our knowledge regarding thermally induced degradation phenomena. The final aim of this work is to prevent incorrect interpretation of Raman results, given that the identified Raman features could allow for discernment between secondary minerals produced by plattnerite decomposition versus pigments intentionally added to historical paintings.

The two companion papers that follow are by Pozo-Antonio and co-workers from the University of Vigo (Department of Natural Recourses and Environment Engineering) and the University of Granada (Department of Mineralogy and Petrology) from Spain in collaboration with the University of Lisbon (CERENA). Both are dedicated to improving knowledge on the physical–chemical damage of tempera paint mock-ups composed of one pigment out of lapis-lazuli, smalt, azurite, and malachite mixed with either egg yolk or rabbit glue, when exposed to an SO_2 accelerated aging test. Special focus is put on the pigment–binder interaction effect and on pigment chemical structure and grain size in the forms and mechanisms of alteration. The works were conducted combining eight analytical techniques to decipher the macro- and micro-scale characteristics of the paintings, pigments, and binders. The first article is dedicated to lapis-lazuli- and smalt-based paintings [3]. Results indicate that precipitated white sulfate-rich salts occur in both paint mock-ups, and that the pigment alteration depends on its nature, with lapis-lazuli being more resistant to SO_2 impact than smalt. Whereas in the lapis lazuli pigment the origin of the hydrated salts is attributed to its impurities (calcite and diopside), leaving the blue lazurite crystals intact, K^+ leaching from the smalt glass induced both anhydrous salt precipitation and blue pigment discoloration. In the second paper of this research series, azurite- and malachite-based paintings are studied [4], with results showing that both pigments undergo chemical alteration regardless of both crystal size and the binder present in the tempera, as confirmed by crystallization of copper-sulfate salts. However, rabbit-glue-based paints are more prone to SO_2 damage than are egg-yolk-based paints, thus revealing the crucial role played by binders and pigment–binder interactions in the weathering of paintings in general, and particularly in air-pollution-induced decay. Preventive conservation recommendations are provided.

The next article focuses on an investigation done by a multidisciplinary research team from France (IRAMAT-CEB, CNRS/University of Orleans, and CEMHTI-CNRS) and Spain (University of Castilla-La Mancha, Department of Ancient History) that deals with the first comprehensive archaeometry study of Roman mosaic from the Iberian Peninsula, most precisely conducted on the mosaic glass tesserae from the 4th century Roman villa of Noheda (Spain) [5]. The work sheds light on the raw pigments and compounds used in the color palette of the tesserae and their opacifiers. It was performed using SEM-EDS, XRD, and laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS); this last was combined with statistical methods and principal component analysis (PCA) considering that 420 pieces were examined. The identification of the main coloring pigments and elements, opacifiers, and their associated trace elements allowed the authors to suggest novel and noteworthy archaeological outcomes. Among the varied conclusions, the uniform composition of the tesserae base glass (mixing Roman antimony and manganese) points out that the glasses result from an effective recycling process of older Roman material, thus providing new insights into the organization of tesserae production and trade. Furthermore, the distinct and varied features of specific tesserae in relation to their pigment composition and trace elements revealed diverse glass-coloring and opacifying recipes, different times and/or sources of the raw materials, as well as productions sites, including an Egyptian origin.

Lastly, the volume wraps up with a review done by the multidisciplinary research team of Hradil and colleagues from the ALMA Laboratory (Czech Republic) regarding clay-based and iron oxide pigments in European paintings of the Mediaeval and Baroque periods [6]. This paper, which is based on case studies performed by the authors, highlights that a detailed and systematic characterization of clay minerals found in historical paintings is crucial to resolving the so-called "provenance analysis" that aims to assess the origin of the pigment and, so, its regional source, as well as to refine the dating or workshop attribution of artworks. Likewise, this article emphasized, on the one hand, the importance of using precise terminology since ochre, earth, and clay pigments are not synonyms, and, on the other hand of applying the correct analytical methodology to unequivocally identify clay pigments. Despite some limitations, this technique is undoubtedly powder X-ray

micro-diffraction, which is capable of determining clay structures. However, it should be further supported by other micro- and trace-element analyses combined with mineralogical and geological methods and by a good art-historical context. This review also includes a notable brief synopsis of earths, ochres, Armenian bole, Bohemian green earth, white and red earths, and pottery clays.

Conflicts of Interest: The authors declare no conflict of interest.

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