

Lead calcium phosphates in Cultural Heritage objects: an integrated analytical approach for studying their origin and formation

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Lead calcium phosphates have been reported in few historical artistic materials, such as paintings and inks. The origin of these compounds is not completely understood. Some authors propose that they are present as a natural pigment [1], while others attribute them to degradation reactions [2].

Interestingly, other researches in the field of environmental science have focused on the reactivity of hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; hereinafter named "HA"] for the treatments of toxic metal in different environmental matrices [3]. They showed that HA can immobilize Pb^{2+} ions, giving rise to a series of solid solutions of lead and calcium phosphate [$\text{Pb}_x\text{Ca}_{(10-x)}(\text{PO}_4)_6(\text{OH})_2$], where Pb^{2+} ions are mostly occupying Ca^{2+} sites. If Pb^{2+} ions are substituting all the calcium available in the structure, a compound called "hydroxypyromorphite" ($\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$) is obtained [4].

The present project aims to investigate the spectroscopical properties of different solid solutions and the physico-chemical and environmental conditions that promote the formation of lead calcium phosphates in various kind of cultural heritage objects, and to define how they may evolve over time.

As a first step, a series of lead calcium hydroxyl phosphates of different Pb:Ca stoichiometry will be synthesized according to previous studies. Then, characterized by means of SEM-EDX, FT-IR, Raman and UV-Visible spectroscopies as well as a number of X-ray methods (with conventional and synchrotron radiation sources), including XRF, XRD and XANES spectroscopy at the P K- and Ca K-edges.

As a second step, the physico-chemical stability of these synthesized compounds will be assessed by studying the effect of pH and different binding media. Furthermore, accelerated aging experiment will be performed for evaluating the influence of moisture, light and/or temperature on their reactivity.

In parallel, mock-up paints and ink model samples will be prepared in laboratory to verify and compare the composition and morphology of the synthesized lead calcium phosphates with those found in different original artworks.

References

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