

## THE STUDY OF RED LEAD DEGRADATION IN *LORVÃO APOCALYPSE*

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The mechanisms of red lead degradation were studied in a medieval Portuguese codex, "Lorvão Apocalypse" (1189), by Raman microscopy ( $\mu$ -Raman) and  $\mu$ -X-ray diffraction ( $\mu$ -XRD). To determine the main factors affecting red lead degradation, a set of accelerating ageing experiments was designed to assess the influence of extenders and of the two other pigments, vermilion and orpiment. The experiments were followed by  $\mu$ -Raman,  $\mu$ -EDXRF and XRD.<sup>1</sup>

Raman microscopy results for the simulation of degradation of red lead, in the presence of orpiment, are in agreement to what was found in the "Lorvão Apocalypse", and it was concluded that galena, a lead sulphide, was the major degradation product. Despite the several degradation patterns observed in the manuscript, the Raman spectra detected the same products, in agreement with a sequence of reactions occurring in the solid state. The results obtained by Raman microscopy for the samples aged in laboratory, were compared with the ones in the manuscript, the spectra being very similar. Besides galena, in the spectra appeared a Raman band at ca. 810 cm<sup>-1</sup>, tentatively assigned to a lead arsenate, eq. 1. In addition, XRD analyses of one year reaction of red lead with orpiment identifies an arsenic trioxide, As<sub>2</sub>O<sub>3</sub>, as a product and a species with a structure related to Pb<sub>2</sub>O<sub>3</sub>, as a reaction intermediate. The experimental evidence gathered enables to state that in "Lorvão Apocalypse", the degradation of red lead was a result of its reaction with orpiment. The understanding of the red lead degradation will make possible the design and testing of new conservation strategies that hopefully will enable a better conservation and access of "Lorvão Apocalypse", an extraordinary human achievement almost millenary in age.



(1) A study on red lead degradation in the medieval manuscript, Lorvão Apocalypse (1189)", Catarina Miguel, Ana Claro, António Gonçalves, V.S. F. Muralha, Maria J. Melo, J. Raman Spectrosc (2009) (DOI: 10.1002/jrs.2350).

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