

Synergy or protection? Physicochemical study of minium–vermilion mixture degradation in the context of medieval manuscripts

A. Scientific context of the project (max. 2,5 pages)

The Mont Saint-Michel abbey had an active scriptorium that produced numerous manuscripts from the end of the 10th to the 13th centuries. These manuscripts represent a unique corpus of great scientific value as it concerns a large number of manuscripts, produced over a period of a few centuries, well-dated for its earliest production, and has remained mainly undisturbed. As part of the vast material analysis project “Materials study of the ancient manuscripts from the Mont Saint-Michel”, the different materials used to produce these manuscripts are being investigated since 2019: parchment (animal species and thickness)¹, inks (vitriol composition) and colouring materials. The study of this corpus brought new insight into the production practices in this scriptorium at the time and more widely in the Normandy region.

Regarding colouring materials, some visible degradations were seen, and especially for the orange-red pigments where a blackening or a metallic lustre could be present, visually contrasting with the original colour. Blackening can be very partial, fairly extensive or complete within a letter, with occurrences where the border or central area of the letter is preferentially attacked. Visual alterations were seen for the three main types of red identified: minium (Pb_3O_4), vermilion (α -HgS) and mixture of both. Initial statistical analyses seem to show preferential degradation of certain pigments and could corroborate ancient writings claiming that mixtures of these pigments could slow down the degradation of paint layers.

The deterioration of these materials, particularly vermilion, has been known since ancient times and has been studied by researchers for over 20 years in order to understand the mechanisms of deterioration. But until now, studies have focused on minium or vermilion separately and in contexts and environments that are often very different from manuscripts², particularly in oil paintings and frescoes displayed outdoors. This PhD therefore aims to study the mechanisms and kinetics of degradation of minium-vermilion mixtures in protein binders - such as those identified in the scriptorium of Mont Saint-Michel - in order to see whether the mechanisms of degradation are similar to those of pure materials or whether there is synergy between the two, with the binder, and with possible fillers (as lead white or calcite).

This project will be organized into two main parts, one concerning the study of the degradation of these red-orange materials through artificial aging on model mock-ups, and the other concerning the study of a historical corpus, in particular through chemical and exhaustive statistical analyses. This project therefore proposes a multidisciplinary study of the mechanisms of deterioration of these complex mixtures of materials in the context of heritage conservation.

¹ Robinet L. et al., *Journal of Cultural Heritage* 67, p. 452-460, 2024.

² Zou W. et al., *Studies in Conservation*, p. 1-17, 2025; De Seauve T. et al., *Technè* 56, p. 80-88, 2023 ; Aze S. et al., *European Journal of Mineralogy* 19(6), p. 883-890, 2007.

The first phase of this project focuses on aging reference samples in a climate chamber in order to control both the environmental conditions and the materials used in the mock-ups. The detailed laboratory characterization of the colouring materials currently available on the market using a range of analytical techniques (XRF, XRD, FTIR, Raman spectroscopy, reflectance spectroscopy, XPS, etc.) will yield valuable information on their impurities. This first consideration is of great importance as it has been shown that chlorine impurities might affect the photosensitivity of cinnabar (natural vermilion)³. In addition to pigment impurities, the question of the influence of mixtures with other pigments used as fillers, such as lead white or calcite, on the degradation will be approached. Observation of the practices of the Mont Saint-Michel scriptorium has also led to questions about the influence of the support on pigment degradation, such as the presence of lipid materials in low quality sheepskin parchments. Light appears to be a determining factor in the degradation of mixtures but parameters such as temperature, humidity, or the presence of pollutants may also be tested. It is therefore essential to study the photoreactivity of these systems. Based on initial results obtained in the CRC light chamber, we may call upon the LAMS photodegradation platform currently being set up in order to have a better monitoring of the effect of light on the mixtures. A detailed characterization of the degradation products will be carried out using the aforementioned analysis techniques, as well as colorimetric monitoring to see how these two parameters correlate. The use of MONARIS Raman spectroscopy instruments (PLASVO platform) will be particularly favoured as these can be configured in low frequency mode in order to be adapted to the sensitivity of the mercury containing pigment vermilion⁴, and environmental cells can be used to follow the progression of degradation in situ in a controlled system. To better understand the degradation mechanisms involved, techniques such as XPS could be explored, which would require adapting the experimental measurements, likely involving working under environmental conditions due to vermilion presence. In order to perform kinetic monitoring, the implementation of a quantitative analysis of the degradation products with XRD and the Rietveld method will be explored. Depending on the results obtained with all these laboratory techniques, additional corresponding analyses might be conducted with synchrotron sources in order to access different scales and resolutions, for example on the Nanoscopium (Soleil) or ID21 (ESRF) beamlines.

The other phase of the project, which will be carried out partly in parallel, involves studying a corpus of damaged historical manuscripts. Obviously, the study will begin with the corpus of manuscripts from the Mont Saint-Michel scriptorium in order to compare the laboratory results with historical reality. First, a detailed characterization of red pigments will be undertaken early in the thesis to help choose the model materials to be tested. Since the objective is to observe the influence of mixtures on degradation, it is essential to be able to quantify the proportions of minium and vermilion in the mixtures. The work currently underway at the CRC shows that this issue poses a challenge with the techniques used to date (FORS and XRF) and will require the implementation of a specific methodology. Then, the degradation products will also be characterized (XRF, FORS, XRD...). We also wish to explore the idea of a statistical observation of degradation across the entire corpus in order to see whether the conclusions drawn in the laboratory for kinetics of alteration as a function of pigment proportions hold true for this historical corpus. This will certainly be done using visual criteria that have yet to be established (estimation of the extent of the damages and their surface area) and occasionally compared with a quantification of degradation products. Depending on the progress of the thesis and the issues raised, other corpora from different scriptoria, particularly in Normandy, may be considered.

³ McCormack J.K., *Mineralium Deposita* 35, p. 796-798, 2000.

⁴ Pouli P. et al., *Journal of Cultural Heritage* 4, p. 271-275, 2003

This type of study is essential for gaining an in-depth, theoretical understanding of the mechanisms of degradation of these materials in the context of illuminated manuscripts. The richness of this project lies in its ability to compare the results with a widely explored historical corpus. Armed with these results, conservators will be able to better understand the variability of the degradation observed on manuscripts and, where possible, adapt the conservation conditions for these exceptional productions.

The lack of studies on the degradation of mixtures of these pigments and the preliminary tests allow us to consider with confidence that the results of this study will be significant. The main risk is the multiplication of aging parameters, none of which have been properly explored in our study context and all of which have a potential impact on degradation. Beyond the durability of these pigments, understanding these mechanisms could also be a subject of interest in issues related to mercury and lead pollution in different contexts.

The doctoral student will benefit both from the expertise of these supervisors in the field and from the laboratory equipments available for this project. The CRC has expertise in the study of the degradation of coloured materials and of the FORS and XRF analyses of ancient manuscripts, and one of the supervisors wrote her PhD thesis on the degradation of vermilion⁵. The project leader, Anne Michelin, undertakes to pass her HDR during the course of this thesis. In the meantime, Christine Andraud, a specialist in optics and colour measurement, will supervise the PhD thesis. MONARIS, through Ludovic Bellot-Gurlet (co-director), has a great expertise in Raman spectroscopy analyses of sensitive materials, especially concerning the mercury containing vermilion which will require the implementation of a specific methodology. Various collaborations are already underway for specific techniques such as with the Institut Néel (Grenoble) through Pauline Martinetto for portable XRD (expertise in analyzing pigments in historical manuscripts) and synchrotron analyses, and the LCPMR through Jean-Jacques Gallet for XPS.

Research plan with provisional calendar (max. 0,5 page)

PhD supervision team: C. Andraud (dir., CRC), A. Michelin (co-sup until her HDR defence 70%, CRC), M. Radepont (co-sup, CRC), L. Bellot-Gurlet (co-dir. 30%, MONARIS).

	Task/quarter	1	2	3	4	5	6	7	8	9	10	11	12
Study of mock-up	Research and characterization of mock-up materials	■	■										
	Preparation of mock-ups		■	■									
	Ageing			■	■	■							
	Characterization of aged mock-ups (laboratory)				■	■	■	■	■				
	Characterization of aged mock-ups (synchrotron)							■	■				
Study of historical painting	Minium/vermilion quantification				■	■							
	Characterization of degradation products						■	■	■				
	Statistical analysis of visible degradation in the corpus			■	■	■							
PhD follow-up and project valuation	Writing articles								■		■		
	Preparation/participation in conferences						■	■					■
	PhD writing and defense											■	■
	PhD follow-up meetings	■	■	■	■	■	■	■	■	■	■	■	■

⁵ Radepont M., *PhD thesis*, Universiteit Antwerpen and Université Pierre et Marie Curie, 2013.