

Analysis of the Colour Traces Found on the Cloister of the Jeronimos Monastery in Lisbon

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Abstract

Traces of orange colourations found on both the exterior and interior walls of the cloister of the Jeronimos Monastery in Lisbon were analyzed and studied during the recent conservation intervention. The aim of these studies was to determine the origin of these traces since this would influence the approach taken during the intervention. The analytical results showed that the colour traces were remnants of the application of an intentional finish applied on a first layer of limewash(es). From the evaluation of all the available data it is considered that this coloured finish could have been applied as early as the beginning of the 17th century.

Keywords: colour traces, orange patina, lime-wash, calcareous deposits, analysis

Analyse der am Kreuzgang des Hieronymus Klosters in Lisabon gefundenen Farbspuren

Zusammenfassung

Im Rahmen der kürzlich durchgeführten Konservierung des Hieronymus Klosters in Lisabon, wurden orangefarbene Spuren einer Bemalung sowohl auf den Außen- wie auf den Innenwänden gefunden. Diese Farbreste wurden analysiert und untersucht. Das Ziel dieser Untersuchungen war es, die Herkunft dieser Spuren zu bestimmen, denn davon hingen die durchzuführenden Maßnahmen ab. Die analytischen Arbeiten zeigten, dass die Farbspuren von einer gewollten Farbgebung stammten, die auf einer ersten Lage aus Kalktünche aufgebracht wurde. Nach Auswertung aller zugänglichen Daten kann davon ausgegangen werden, dass diese Farbgebung bereits zu Beginn des 17. Jahrhunderts angebracht wurde.

Stichwörter: Farbspuren, orangefarbene Patina, Kalktünche, kalzitische Ablagerungen, Analyse

1 Introduction

The 16th century Cloister of the Jeronimos Monastery, one of the most important monuments in Portugal and the world, has recently undergone a conservation intervention. During the condition survey that preceded this intervention, particular attention was given to the colour traces that were found on its walls. These traces, visible in areas that were not covered by biological colonization—the major problem for the intervention—were extensive though they did not provide a uniform covering and were found both on interior surfaces as well as exterior ones. They ranged in colour from a yellowish- to a reddish-orange, and, in some specific areas, such as the columns and arch tracery of the lower gallery they reached a brown tint.

Given the high interest that orange coloured patinas have raised for the past fifteen years, particular attention was addressed to the traces found on the cloister. Thus, careful documentation was made regarding their location, followed by several sampling campaigns for their analysis. The aim of the latter was to ascertain, if possible, the origin of these colour traces. Could they be the result of a natural weathering process? Or were they the remnants of previous coloured treatments? Or could they possibly be a combination of both? Previous studies on another Portuguese Monastery showed that the latter was the most probable answer to the question but that a combination of all three possibilities could occur on different parts of the same monument [1]. While these studies were carried out mainly for scientific interest, in the case of the cloister of the Jeronimos Monastery, the studies had a more practical aim: to ascertain whether coloured treatments had been applied in the past as has been traditionally done in Portugal [2] since these results would affect the approach to be taken during the intervention [3].

2 General Background on Orange Coloured Patinas

There has been a long interest in orange coloured patinas on monuments. However, the interest in the field of conservation, mainly because of the implications the origin of these patinas could have on the approach taken during a conservation intervention, raged during the decade of the '86-'96. That year, the second symposium focusing exclusively on oxalate films was held [4]. From the many studies that have been carried out on these patinas, a clearer picture of their complex nature and origin has been achieved. This can be summarized as follows:

- not all orange coloured patinas necessarily contain oxalates [1,5] ;
- the presence of oxalates does not imply an intentional treatment [6];
- some oxalates may result from lichenic activity [7];

- but oxalates can result from the biodegradation of an intentional treatment [5];
- or from purely chemical degradation of an intentional treatment [8];
- the colouration may result from traces of an intentional pigmented treatment [9];
- or from the weathering of an intentional treatment [10];
- or from the biodegradation of an intentional treatment [9,10];
- but can also result from purely geologic weathering of some stones [1,5];
- or from purely biological activity [11];
- or from a combination of any of the above possibilities.

The above list of possibilities provides an idea of the complexity of the study. This is further complicated by the limitations of the various chemical analysis used to study these patinas.

3 Experimental

3.1 Sampling

Several sampling campaigns were carried out along the course of the project. The first three campaigns corresponded to 1998, at the time the first phase of the project, i.e., condition survey and documentation, was being carried out. Then samples were taken during the actual intervention, beginning in early 2000 and ending by November 2001, when the project was practically completed. Apart from samples of efflorescences, concretions and brownish/black air pollution originated deposits of interest in other aspects of the intervention, a total of twenty eight samples of orange coloured deposits were obtained for analysis and will be discussed in this paper. Of these, 16 were taken from interior and 12 from exterior surfaces. Finally, one red coloured sample, found in the eye of St. Lucia, a statue located on the N facade in one of the niches of the upper gallery, will also be discussed since it is of anecdotal interest. Results of the analysis of all the samples can be found in the internal reports [12,13]. The sample identification numbers used in this paper follows that of these reports: different sampling locations are denoted by the number following the general identification letter J, e.g. J1 corresponds to a different location than J2.. When the samples were subdivided into layers for analysis such as XRD, they were identified by the addition of an ending letter, e.g., J1B. When several samples were taken from one same location, these are indicated as, e.g. J14B/10, signifying that both samples 14 and 10 were taken from the same general area of the monument. The complete list of samples and their locations in the cloister is given in the Appendix to this paper.

3.2 Analytical Techniques

Different samples were analyzed in different laboratories depending both on the availability of equipment and personnel and the type of analysis to be carried out. Apart of visual examination under the microscope, both directly and polished cross sections, the analytical techniques used included: X-ray powder diffraction (XRD), X-ray fluorescence spectrometry (XRF) with a wavelength dispersive system (XRF-WDS), synchrotron radiation X-ray fluorescence (SR-XRF), gas chromatography coupled with mass spectrometry (GC-MS), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy (RS), scanning electron microscopy (SEM) coupled with an energy dispersive X-ray system (EDS).

More details about the experimental conditions used in each particular case are included in the corresponding paragraphs.

In some cases, when some anions such as silicates, oxalates and/or nitrates were not detected by XRD, their presence could be assumed from characteristic absorptions in the FTIR spectra. The presence of oxalates was inferred by the peak around 1320 cm⁻¹ [14], silicates by the absorption band around 1090-1000 cm⁻¹, and nitrates by the peak at about 1310-1405 cm⁻¹ [15]. When the presence of waxes or other organic material, such as oils or fats, was suspected from optical microscopical analysis and/or by the background pattern of the XRD spectrum it was confirmed by FTIR through the characteristic absorption peaks of organic functional groups [16]. Given the complex nature of the samples, no positive identifications could be made and therefore simply reported as “organic material”.

4 Results and Discussion

This paper reports the analysis corresponding only to the orange coloured deposits (which ranged from yellowish to reddish to brownish but that for simplicity will be called orange since this is their most frequent colour) found both in interior and exterior surfaces, thus not including the black surface crusts, where present, or the white calcareous substrate.

The mineralogical composition for twelve samples of surface deposits taken from the interior of the cloister, and ranging in colour from brown to orange to yellow, were determined by XRD and are summarized in Table 1. As stated above, in some cases the presence of silicates, oxalates and/or nitrates, when not detected by XRD, could be inferred from the FTIR spectra.

Table 1: Mineralogical composition, determined by XRD, of twelve orange deposits taken from interior surfaces of the cloister galleries. Samples' labels such as J14B/10 indicate that sample 14 was taken from the same area as sample 10.

	Colour	Calcite	Gypsum	Quartz
J1B	Ochre	•	–	–
J2A	Brownish	o	•	–
J3A	Brownish	•	o	–
J4B	Brownish	•	o	+
J5A	Yellowish	o	•	–
J10B	Ochre	•	–	–
J11A*	Brown-red.	o	–	–
J12A	Ochre	•	–	–
J14B/10	Orange	•	–	–
J15A/11	Ochre	±	–	–
J17A/3	Brownish	•	•	–
J18A/5	Yellowish	+	•	–

where: • = very abundant; o = abundant; + = present; ± = traces; – = not detected

* showed an abundant presence of Gaylussite $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$

Traces of nitrates were found only in sample J2A, and of oxalates in sample J10B. J10B also showed the presence of organic material and traces of silicates. Traces of silicates were also found in samples J1B, J3A, J11A, J12A and in a slightly higher concentration in sample J15A/11.

The elemental composition, as determined by XRF-WDS for these first eight samples is presented in Table 2. Apart from the elements listed in the table, sample J3 showed traces of Zr, and sample J11A had traces of Rb, Cu and Cr.

Table 2: Elemental composition of orange deposits taken from interior surfaces of the cloister galleries as determined by XRF-WDS

	J1	J2	J3	J4B	J5	J10B	J11	J12
Ca	•	•	•	o	•	•	•	•
Mg	+	+	±	±	±	±	o	+
Na	+	+	–	±	–	±	+	–
K	+	+	+	+	+	o	o	o
Si	+	+	+	+	+	+	o	o
Al	+	+	±	±	–	±	o	+
S	+	•	o	o	o	±	±	±
Cl	±	+	±	–	±	±	±	–
Fe	o	o	+	+	o	o	o	o
Mn	±	±	±	±	±	±	+	±
Zn	±	±	±	±	±	±	±	±
Pb	–	+	+	–	–	–	±	±
Ti	±	±	±	±	±	±	o	±
Sr	+	o	±	+	±	+	+	o

where: • = very abundant; o = abundant; + = present; ± = traces; – = not detected

The elemental composition of sample J14/10 was determined by EDS analysis. The results showed higher amounts of both Si and K in the exterior orange layer as compared to the white substrate. A similar pattern corresponds to that obtained for samples J10B, J11 and J12 (Table 2). These samples were taken from the walls of the stairs leading from the lower to the upper gallery and to the choir (Coro Alto) in the church (J10B, J14) and from the choir itself (J11, J12). The presence of higher amounts of both Si and K in these exterior orange layers has been attributed to the application of a water-glass (soluble silica) treatment. However, it is also possible that this could result from leachings running over the wall surface as a consequence of later repointings and repairs carried out with Portland cement over the surface of

the wall. This would be particularly true for those samples collected from the wall on the stairs where many repairs were carried out.

The mineralogical composition for eight of the exterior samples is presented in Table 3. In some cases, the samples from this group were subdivided into two specimens.

Table 3: Analysis of orange deposits taken from exterior surfaces of the cloister galleries. Mineralogical data was obtained by XRD. Samples' labels such as J7A/6 indicate that sample 7 was taken from the same area as sample 6.

	Colour	Calcite	Gypsum
J6A	yell.-orange	+	o
J6B	yell.-orange	+	o
J7A/6	Brownish**	±	–
J7B/6	Brownish*	±	–
J19A/6	Orange	±	●
J19B/6	Orange	–	●
J20A/6	dark brown	+	●
J21A/6	dark brown	±	–
J21B/6	brown-yell.	+	–
J22	Yellowish	±	●
J24	Yellowish	+	–
J25/22	Yellowish	●	+

where: ● = very abundant; o = abundant; + = present; ± = traces; and, – = not detected.

* colour layer showed the presence of small green dots of micro-algae, the number of asterisks indicates increasing concentration.

Nitrate was found in sample J24 and as traces in J22. This last sample also showed traces of oxalates. Weddellite was found abundantly in sample J6B while whewellite was present in sample J25/22. Silicates were found in several samples and are reported in decreasing concentration down to traces: J7B/6, J21A/6, J21B/6 > J7A/6 > J24, J25/22 > J6A. Organic matter was found present in samples J7A/6, J7B/6 and J19B/6.

Elemental composition was determined by XRF-WDS on some of these samples. The results are presented in Table 4.

Table 4: Elemental composition of orange deposits taken from exterior surfaces of the cloister galleries, as determined by XRF-WDS. Samples' labels such as J25/22 indicate that sample 25 was taken from the same area as sample 22.

	J6	J7/6	J22	J24	J25/22
Ca	o	•	•	•	•
Mg	+	+	±	±	±
Na	+	±	±	–	–
K	+	o	+	±	+
Si	+	o	+	•	+
Al	–	+	±	±	±
S	o	o	+	±	+
Cl	±	±	±	–	–
Fe	o	o	o	+	+
Mn	±	+	±	±	±
Zn	±	+	±	±	±
Pb	±	o	±	±	–
Ti	±	+	±	±	±
Sr	+	o	–	–	±

where: • = very abundant; o = abundant; + = present; ± = traces; – = not detected.

All samples presented traces of Cu, except for sample J6. Sample J7 showed the presence of P, while sample J6 only showed traces of it. Only sample J7 showed traces of Cr and only samples J7 and J22 showed traces of Ba. The ratio between the amounts of Si and K detected in most samples indicate that a potassium silicate is present, especially for sample J7 taken from the north side at the base of the column in the SE corner of the lower gallery arcade. In this particular case, the application of a water-glass treatment is the most likely explanation, since all of the lower arcades, in particular the tracery, had received various conservation treatments.

X-ray fluorescence by synchrotron radiation with an energy dispersive system was also used to analyze the coloured deposits of some samples, both from the interior (J14/10 and J17/3) and exterior (J22, J24 and J25/22). These analysis were performed using the facilities at the *Laboratoire pour l'Utilization du Rayonnement Electromagnétique* (France) on line D15 of the DCI storage ring using the microprobe mounting equipped with a Si (Li) detector. Two excitation energies were used, 8.1 keV to analyze for Fe, Mn, Ti, V and Cr, and 21 keV for Pb, Br, Zn and Ba. The analyzed area (about 0.03mm²) was selected with the aid of a microscope and focused via a laser beam using a computer-controlled micrometer stage. The results confirmed those obtained previously.

These analysis were complemented by the investigation of the nature of organic matter found in some samples. For this purpose, GC-MS analysis was carried out on one sample (J7) for which sufficient material was available. The presence of di-(2-ethyl hexyl) adipate was detected, an ester of an acid found in waxes or as an oxidation product of fatty acids, such as oleic acid. These results are consistent with the evidence of the darker hue found on the actual columns of this gallery, where the application of wax and/or oil would have been a first approach at protecting the highly carved columns and tracery. The wax coating would have served to trap more dust and other air-pollutants resulting in the darkening of the surface, a common phenomenon observed on all waxed stones exposed to the outdoors environment. The subsequent deterioration would then have prompted a nineteenth century application of water-glass.

Comparison of the results obtained from both interior and exterior samples show that these are essentially identical. Minor differences can be detected, for example, the interior samples show slightly smaller concentrations of gypsum and lead, than the exterior ones reflecting the relatively more protected environment.

The above conclusion was confirmed through optical microscopy examination of these samples, both in fracture section and in polished cross-section, revealing no significant differences between them [12,13]. Figures 1 and 2, show two different photomicrographic views of sample J10, taken from the stairs leading from the



Figure 1: Photomicrograph of a cross-section of sample J10, taken from the stairs that lead to the upper gallery and the choir in the church. The thin orange finish lies above a thicker calcitic layer showing a denser, thin, inner layer, possibly the resulting natural patina of the exposed stone, and a thicker, more porous layer resulting from a limewash application. (34x)



Figure 2: Photomicrograph showing a more general view of sample J10 showing the layered structure of the calcitic stratum suggesting that the limewash was applied in several coats. (24x)

lower to the upper gallery and into the choir (Coro Alto) of the church. The sample is composed of a thick white layer and a thin orange coating. To be noted is that the white layer can be differentiated into an inner, thin and coherent layer and a thicker porous exterior one. The former could possibly be attributed to the natural surface patina developed by the stone, while the latter one, given its variable thickness and its morphology could be the result of a lime-wash application. In parts (Fig. 2), a distinctive layering can be observed reflecting possible successive limewash applications as well as their exposure to frequent moisture, or infiltrations, to allow the development of the recrystallization process observed. The white layer is between 4 to 10 times thicker than the coloured layer.

The observed layering on the calcitic layer is similar to that noticed on samples taken from the portal of the church. Their genesis was hypothesized on the basis of water infiltration through lime-mortar joints with a contribution of biological activity in their formation, although their thickness had been a puzzling factor [17]. The presence of a limewash layer, subjected to repeated water infiltrations, would facilitate the formation of such a thick layer, and is consistent with the formation of calcareous concretions or accretions, where re-crystallized layering is observed [13, 18]. It is likely that these deposits on the portal also had an orange layer applied on top (residues of this colouration can still be observed on the walls of the church to date) but these thin layers would be hard to detect under the brownish first layer of air pollution, especially since Fe is one of the contaminants. Analysis of samples not having a black crust but having a brownish colouration were found to have an enrichment in iron and clay minerals in the coloured layer, attributed to the natural weathering of this stone [19]. However, the samples analyzed had not shown a thick calcitic layer as the ones presently analyzed. The fact that the colouration could originate from both natural weathering and intentional treatments has required that further analyses be carried out to be able to elucidate their origin.

Microscopic examination of sample #7-5 (interior, window at the lower gallery level, in the wall of the staircase leading to the upper gallery) in cross-section, showed the same morphology described above, except that the white layer was far thinner, this being consistent with their location and possible erosion through human touch (Figure 3). The red layer was below 50 μ m thick, while the white layer was around 0.2mm, but although thin, it also showed layering in parts.

Other examined samples (exterior #7-1, #7-2, #7-3 and #7-7; interior #7-4, #7-5 and #7-6) showed similar morphology with minor variations in layer thicknesses or surface texture. The most distinctive was an interior sample (#5-2) obtained from below grade of the interior N wall of the lower gallery, after some of the paving stone slabs were removed. This sample presented the peculiarity of having a thin greyish blue-ochre finish on top of the orange surface layer as can be seen in Figure 4. From



Figure 3: Photomicrograph of a cross-section of sample #7-5, taken from the interior side of the window at the lower gallery. Note that the white layer, even though thin, shows some stratification consistent with application of several limewash coats (28x).

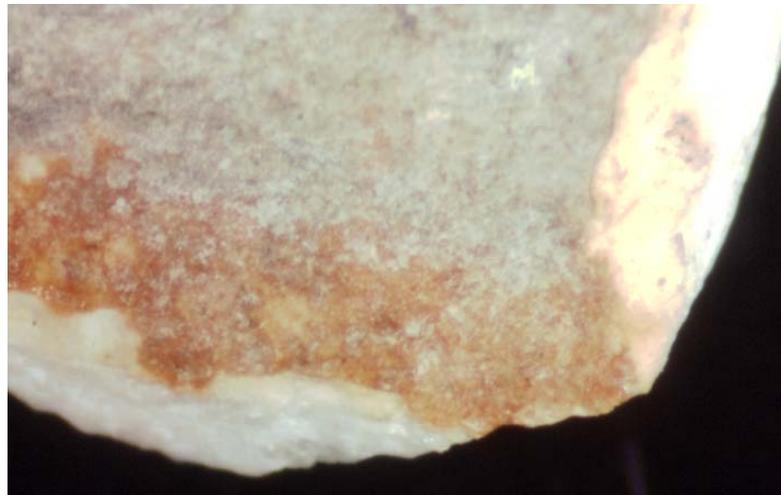


Figure 4: Photomicrograph of sample #5-2, taken from below grade of the interior N wall of the lower gallery. The orange layer has a greyish blue-ochre layer on top of the distinct orange layer. Under this layer, a thicker, white calcitic layer can be seen (14x).

cross-sections of this sample the thickness of the red layer was found to be about 50 μm , while that of the white one ranges between 0.3–0.5 mm. A more coherent internal white layer could also be observed in parts of this sample, and that ranges in thickness between 50–100 μm .

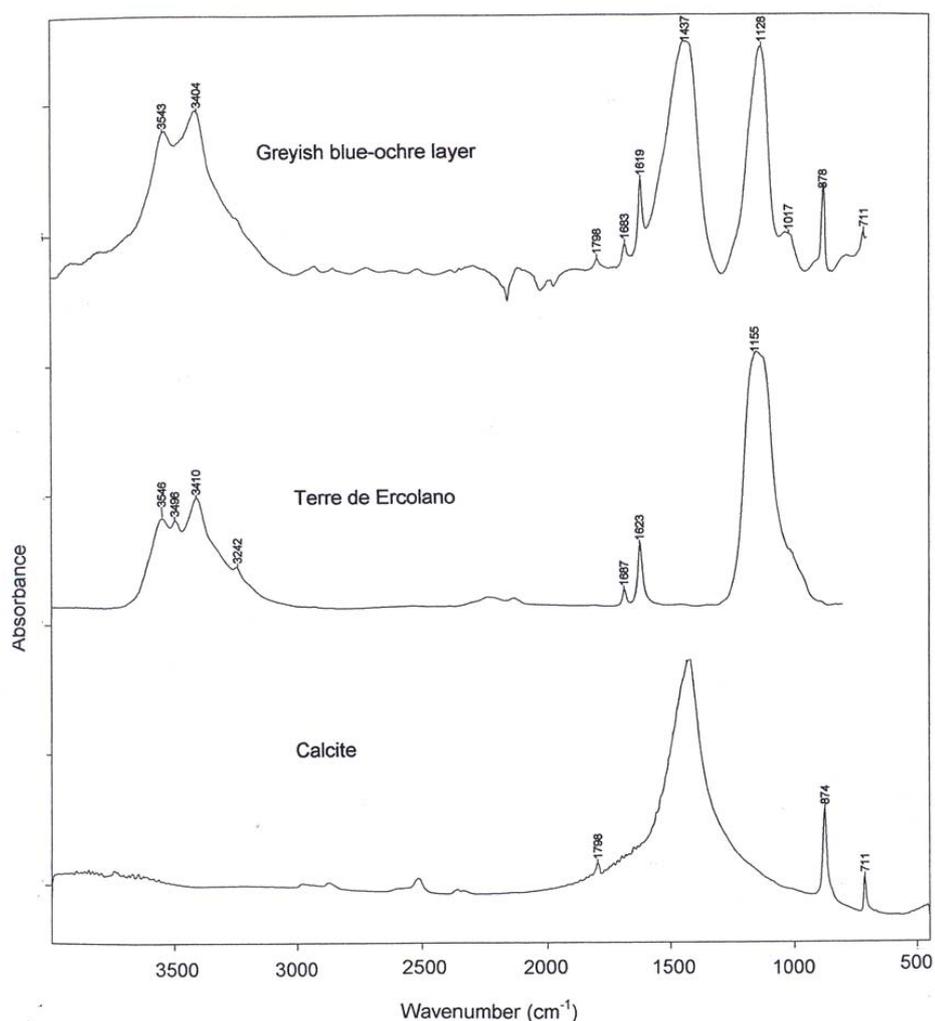


Figure 5: FTIR spectrum of the greyish blue-ochre layer on sample #5-2. The presence of the orange earth pigment, *terre di Ercolano*, was identified. For comparison reference spectra of this pigment and that of calcite are included.

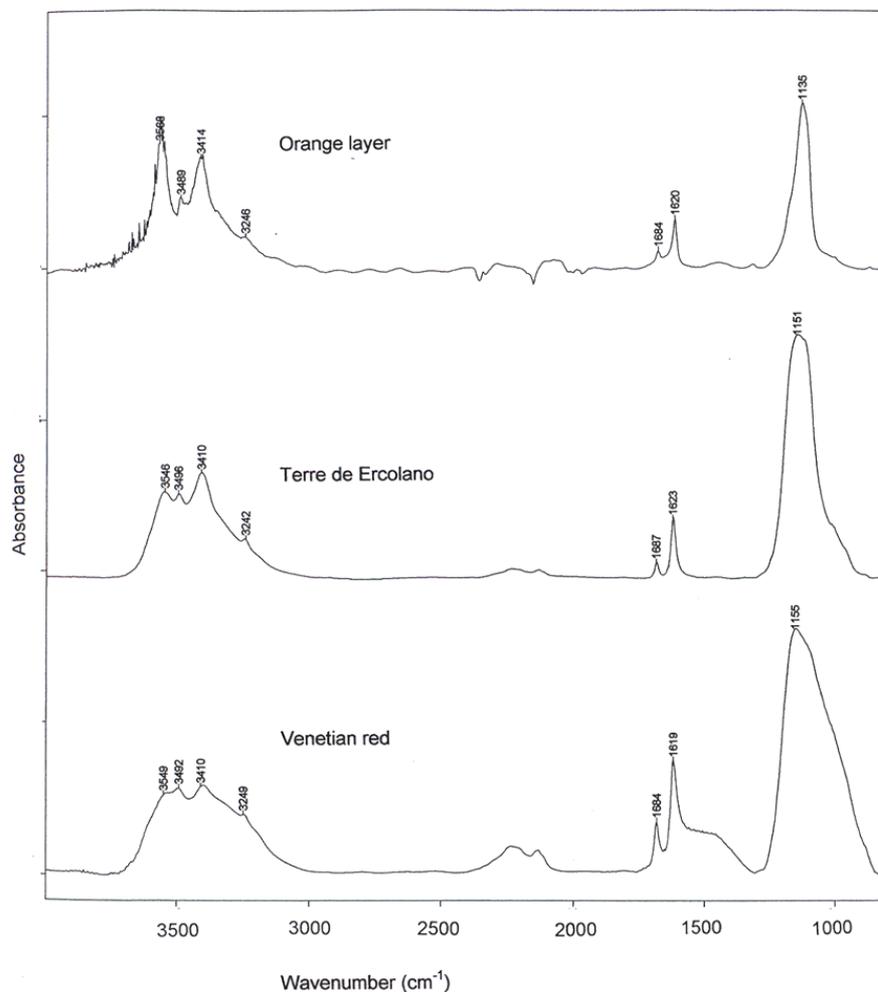


Figure 6: FTIR spectrum of the orange layer on sample #7-4, taken from the upper window of the staircase between the two galleries on the S side. The presence of *terre di Ercolano* was detected. For comparison the spectrum of the Venetian red pigment reference is also included.

FTIR analysis was carried out on this sample using a Bio-Rad FTS 30 equipped with an UMA 500 Microscope. Materials removed from the different layers of these samples were placed between the windows of a diamond anvil cell and the spectra were recorded with a 4 cm^{-1} resolution. The main objective of these analysis was to identify the origin of the colour layers in these samples. The greyish blue-ochre surface layer on sample #5-2 showed the presence of a red earth pig-

ment, identified by comparison with spectra of reference compounds as *terre di Ercolano*, a mixed orange earth (Kremer 4160), and calcite (Figure 5). The wide variety of the names given to the different red earths, reflect their origin. Venitian red has a scarlet shade, whereas Spanish red has a bluish tone from the impurities of the natural product [20].

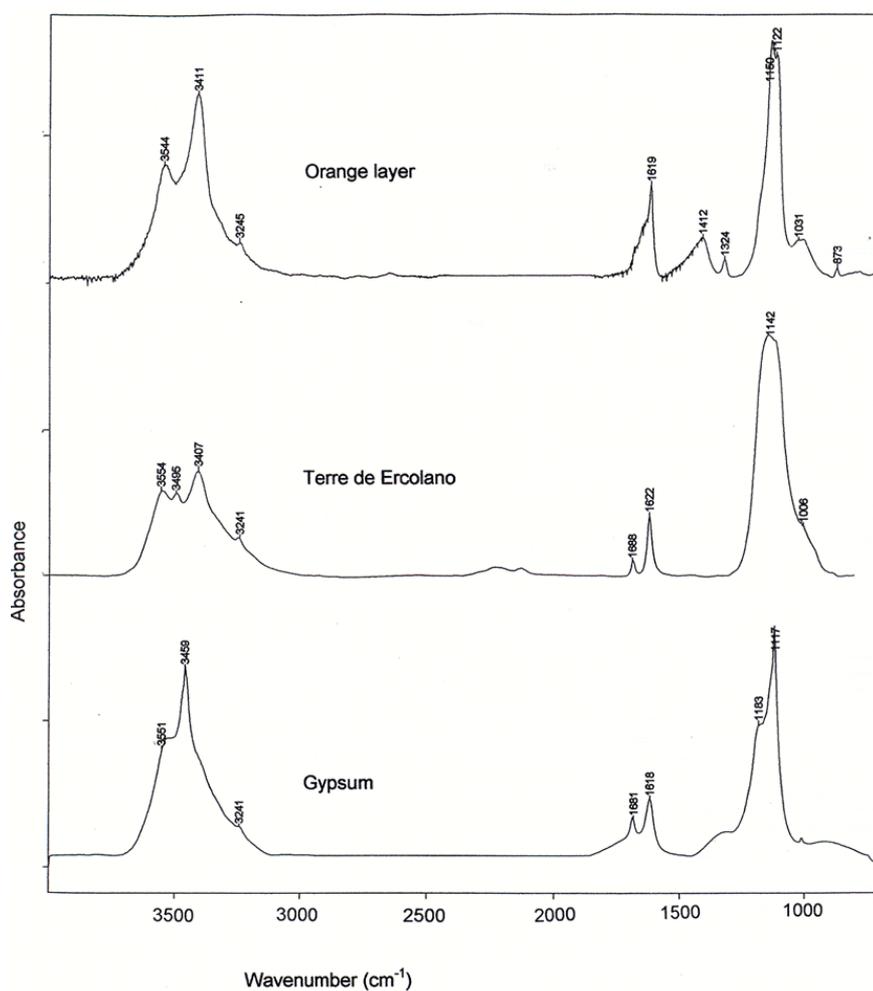


Figure 7: FTIR spectrum of the orange layer on a sample removed from the lower window of the staircase on the S side (#7-5). The presence of the *terre di Ercolano* pigment was detected along with that of gypsum. The spectra of the pigment and that of a gypsum reference samples are included for comparison.

A better match was found between the spectra of the orange layer on a small calcareous concretion from an interior sample (#7-4, window, at the upper gallery level, in the wall of the stairs leading to this gallery, S side of the cloister) and that of the *terre di Ercolano* pigment reference. For comparison, the spectrum of a Venetian red reference pigment, described as a mixture of Fe_2O_3 , CaCO_3 , and CaSO_4 (Kremer 4051) is also included in Figure 6.

Figure 7 shows the spectrum of sample #7-5 (removed from the interior of the window, at the lower gallery level, in the wall leading to the upper gallery on the S side of the cloister) where oxalates (indicated by the small peak at 1324 cm^{-1}), gypsum and *terre di Ercolano* are present. The higher concentration of gypsum can be accounted for by the relatively protected location of the sample. For comparison, the spectra of the pigment and that of a gypsum reference samples are included.

Scanning electron microscopical examination of these samples was carried out with a variable pressure SEM (Leo 1455VP). Sample #5-1 (interior, below grade, of N wall, same location as sample #5-2) clearly showed that the orange layer corresponded to a distinct surface finish that had a similar appearance to that of a wax coating

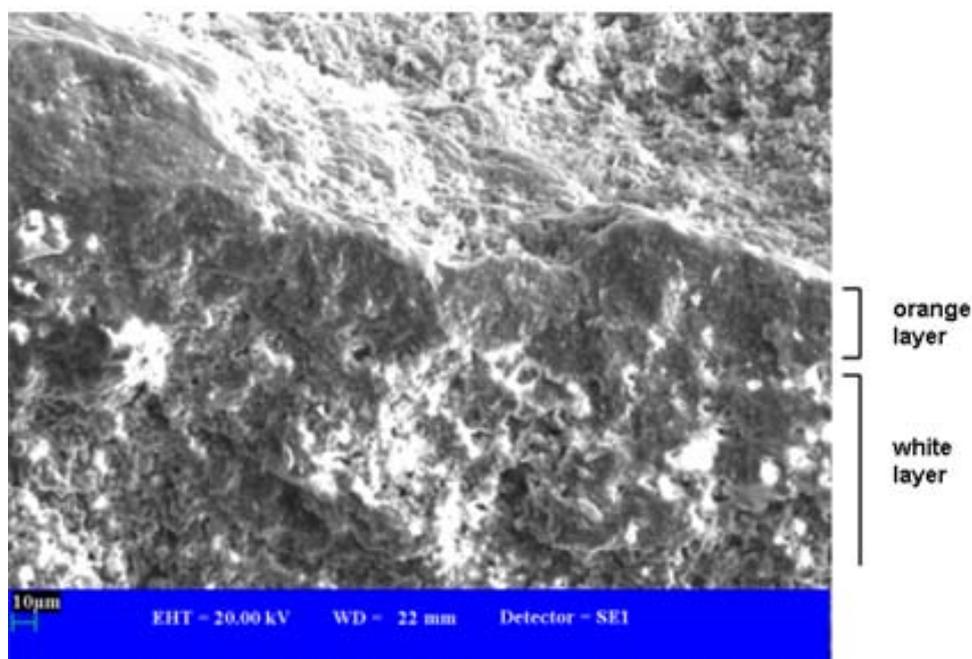


Figure 8: SEM view of the cross-section of the below grade sample (#5-1) showing the orange coloured finish, with the appearance of a wax coating above the porous calcitic layer (300x).

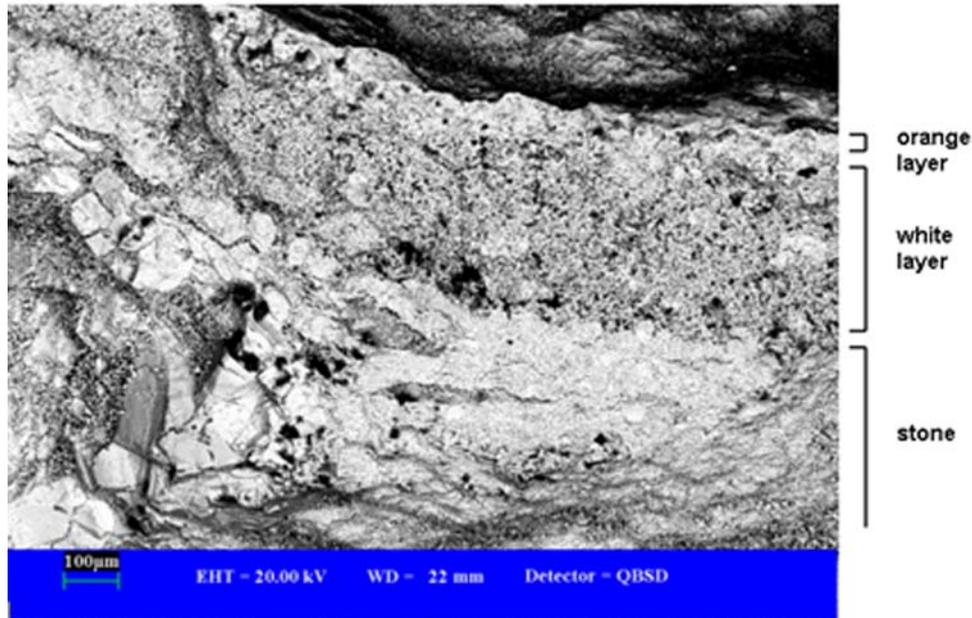


Figure 9: SEM backscattered image of a cross-section of the same sample shown in Figure 8 (#5-1). The thin orange layer is distinctly visible above the thicker white coating that lies on top of the stone, identifiable by the crystals that are best seen at the left side of the picture (75x).

[21], while the underlying calcitic strata (~0.5mm thick) is very porous and consistent with the hypothesis of a lime-wash application. Figure 8 shows a detail of what appears to be a thin wax coating (approximately some 40-50 μm thick), while Figure 9 shows a back-scattered image of the cross section of this sample.

The greyish blue-ochre surface layer proved to be very thin (some ten microns thick) having a layered structure at lower magnification (50X) and a rather granular appearance at higher magnification (500X), that was clearly different from the fairly smooth orange layer at this same magnification. EDS analysis showed that this layer was rich in S (between 4 to 10 times higher than in the orange layer) presumably present as gypsum and consistent with the observed granular appearance, and in C (around 1.5 times higher) present as CaCO_3 and confirmed by FTIR. It also showed that the Si/K ratio was slightly higher in the grayish-ochre layer as compared to the red one, whereas the Si/Na ratio showed exactly the opposite trend. Hence, it would appear, that given the location of the sample, this surface layer was formed by sulfation from air-pollution and later impregnated by run-off from Portland cement as reflected in the higher CaCO_3 content. Finally, the orange layer showed twice the amount of Fe than the grey layer.

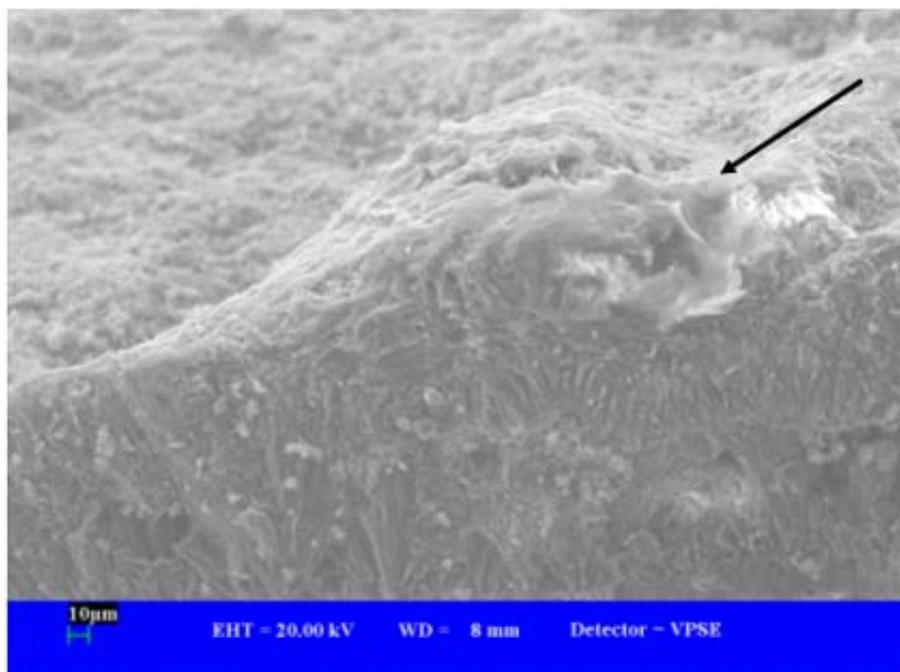


Figure 10: SEM image of a sample removed from the interior window at the upper S gallery level (#7-4). The orange layer has the appearance of an organic coating (see arrow). Note the underlying layered structure typical of calcitic recrystallizations from water infiltrations (600x).

SEM examination of the sample taken from the interior window at the upper S gallery level (#7-4) showed again that the orange layer corresponded with that of an organic coating (Figure 10). In this case, the layer appears much thinner—probably because of its location on the window where human touch may have eroded and smeared it—ranging in thickness between some 10 and 30µm. Figure 10 shows this coating and the layered structure of the underlying calcite strata consistent with the concretionary aspect of this sample, resulting from the recrystallization of successive limewash applications and water infiltrations.

For comparison, the SEM of an exterior sample (#7-1), taken from the S façade, shows that in this case the organic layer is even thinner and does not cover the surface uniformly (Figure 11). This is consistent with its exposed outdoor location. Other exterior samples examined by SEM, e.g. a sample from the W exterior façade (#7-7) showed even less traces of the organic material, consistent with its paler colour.

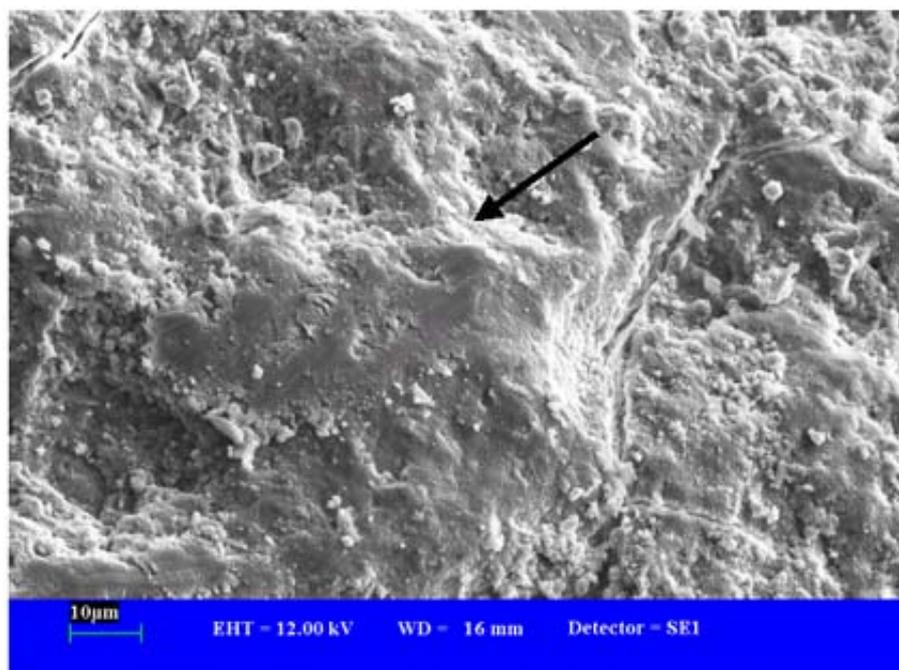


Figure 11: SEM image of an exterior sample (#7-1) taken from the S facade of the cloister. The surface of the sample shows a patchy layer of some organic material, particularly visible in the center of the photomicrograph (see arrow) (2,100x).

Raman spectroscopy was also used to identify the red pigment found in the eyes of the St. Lucia statue. Raman spectra were recorded with a Renishaw System 1000 spectrometer, using a 514nm laser. The laser beam was focused on different areas of the samples with 20x and 50x objective lenses, allowing spatial resolution of about 2 microns. Powers in the order of 1% were used, with accumulation times between 40 to 120 seconds. Calibration was carried out using the 520.5 cm^{-1} line of a silicon wafer. Identification of the materials was done by comparison of the spectra obtained with those of reference compounds. The corresponding spectrum (Figure 12) is consistent with that of a synthetic red iron oxide pigment reference (Fe_2O_3 , Forbes Collection Mars red), that has been manufactured since the mid-nineteenth century [22]. Figure 12 shows the spectrum of the sample, the spectrum the pigment reference from the Forbes Collection and that of the aroclor[®] mounting medium for the pigment reference. The presence of this pigment can be attributed as a prank from the children of the Casa Pia. Only recently (1998), the eyes of the lions at the base of the central column of the south portal of the church had their eyes also painted in red by some vandals.

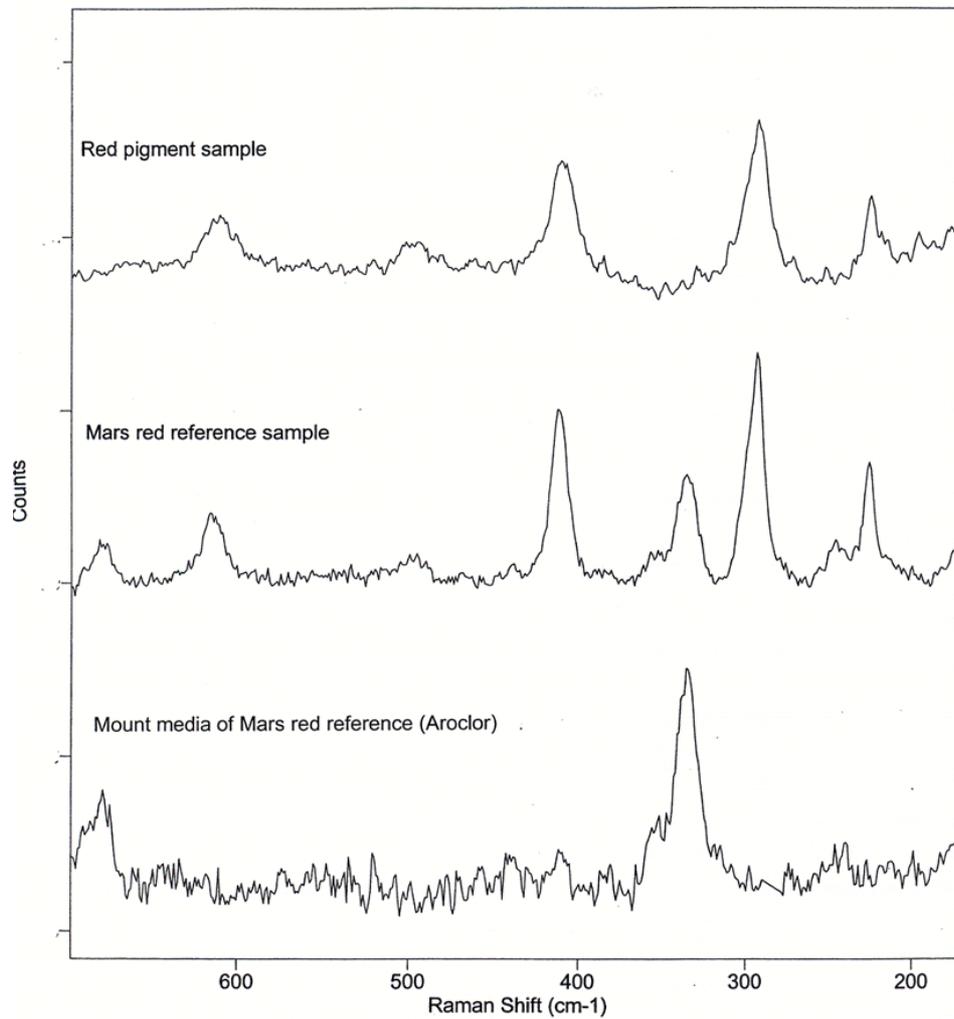


Figure 12: Raman spectrum of the red pigment found in the eyes of the St. Lucia statue (excitation wavelength: 514.5 nm). This spectrum is consistent with that of a synthetic red iron oxide reference (Mars red, Forbes Collection). The spectrum of the reference pigment mounted in aroclor,[®] and that of the mount medium alone are also included for comparison.

5 Conclusions

The analysis performed on the traces of orange coloured surface deposits on the cloister of the Jeronimos Monastery showed that these were, in most cases, the result of an intentionally applied coating. This treatment appears to coincide with a wax (or oil or tallow) treatment although a subsequent wax treatment would permeate any ochre colouration applied previously. Traditionally, the colour would have been applied as a lime paint to which tallow or oil would have been added. The thinness of this coating, ranging between 10 and 50 μm , make it difficult to provide a conclusive answer to this question. The sporadic presence of oxalates would appear to have originated from the weathering (including biodeterioration) of this organic treatment. Furthermore, it has been shown that the colour was applied on a thick limewash layer after some years to allow for the many concretionary areas to form. Given the extensive presence of lime, these concretions can form within a decade, as can be deduced from the growth rate of stalactites in newly built concrete structures. Hence, it can be considered that the colour traces could reflect a treatment applied as early as the late 16th century or early 17th century. A 1609 oil painting by Filipe Lobo, in the *Museu Nacional de Arte Antiga* shows the Church of Santa Maria de Belem with a light ochre finish would confirm these conclusions (see Figure 3 in [3]). Finally, the possibility of a last campaign where a water-glass treatment was applied has been postulated. Since this product was developed during the late 19th century, its application may be dated to the restoration work carried out at that time or even to works carried out at the beginning of the 20th century.

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APPENDIX

Location of the samples within the Cloister of the Jeronimos Monastery, Lisbon.

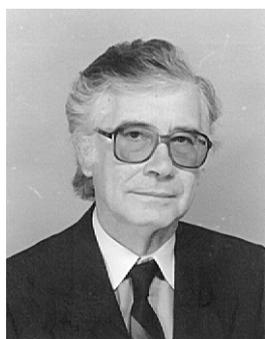
- J1 Interior. Lower gallery, S wall, 7th confessionary. Ochre spots.
- J2 Interior. Lower gallery, S wall, last confessionary from the E. Ochre layer.
- J3 Interior. Lower gallery, S wall, last confessionary from the E. Ochre layer on E side of the door jamb.
- J4 Interior. Lower gallery, S wall, last confessionary from the E. Ochre layer on mortar.
- J5 Interior. Lower gallery, S wall, 5th confessionary, yellowish layer on tympanum.
- J6 Exterior. SE corner of cloister facing the garden, N side. Orange-yellow thin layer.
- J7/6 Same location. Brownish layers.
- J10 Interior. Lower S gallery. Stairs leading to the upper gallery and Upper Choir in the Church. Ochre layer.
- J11 Interior. Upper Choir in the Church, side of the Evangelum, to the left. Ochre powder removed from wall irregularities.
- J12 Interior. Upper Choir in the Church, ochre layer.
- J14/10 Interior. Lower S gallery. Stairs leading to the upper gallery and Upper Choir in the Church. Ochre layer.
- J15/11 Interior. Upper Choir in the Church, side of the Evangelum, to the left. Ochre powder removed from wall irregularities.
- J17/3 Interior. Lower gallery, S wall, last confessionary from the E. On E side of the former door. Brownish layer.
- J18/5 Interior. Lower gallery, S wall, 5th confessionary, yellowish layer on tympanum.
- J19/6 Exterior. SE corner of cloister facing the garden, N side. Orange powder and thin layers with white interior.
- J20/6 Exterior. SE corner of cloister facing the garden, N side. Dark brown crusts with yellowish-orange interior.

- J21/6 Exterior. SE corner of cloister facing the garden, N side. Brown fragile crusts with yellowish interior (sometime greenish).
- J22 Exterior. NE corner of the cloister facing the garden. Thin, hard yellowish flakes.
- J24 Exterior. NE corner of the cloister facing the garden. Thin yellowish flakes.
- J25/22 Exterior. NE corner of the cloister facing the garden. Thin, hard yellowish flakes.
-
- #5-1 Interior. Below grade of the interior N wall of the lower gallery.
and #5-2 Pieces of limestone with successive white, orange and grey-ochre layers.
- #7-1 Exterior. Lower S gallery. Orange layer on stone.
- #7-2 Exterior. S side of the cloister. Orange layer on a calcareous concretion.
- #7-3 Exterior. S side of the cloister. Orange powder.
- #7-4 Interior. S side of the cloister, window at the upper gallery level in the wall of the stairs leading to this gallery. Orange layer on a concretion.
- #7-5 Interior. S side of the cloister, window at the lower gallery level in the wall of the stairs leading to the upper gallery.
- #7-6 Interior, S side of the cloister. Orange layer on stone.
- #7-7 Exterior, W side of the cloister. Second buttress from N, under a gargoyle.
Yellowish deposit on stone.n



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