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Short Report

Gilded Wood from the Organ of the Church of Santa Cruz (Coimbra)

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A talha dourada é uma parte importante do patrimônio cultural português. Aproveitando uma intervenção no órgão da Igreja de Santa Cruz (Coimbra) procedeu-se à caracterização da talha dourada da sua decoração. Fontes históricas indicam que o órgão data dos séculos XV-XVI, tendo posteriormente sofrido várias intervenções. As amostras foram recolhidas em diferentes locais da parte central do órgão e foram caracterizadas por microscopia óptica e eletrônica de varredura, microanálise, difração de raios-X e espectroscopia de infravermelho com transformada de Fourier. A sequência estratigráfica e as análises química e mineralógica permitiram elucidar as técnicas de douramento usadas. A técnica que os artistas portugueses trouxeram da China, introduzindo caulim na composição do *bolus*, foi identificada em todas as amostras. O uso de gesso (*gesso mate* e *gesso grosso*) na camada de preparação está evidente em algumas amostras, indicando o uso da técnica desenvolvida na Itália e em Flandres no século XIV e largamente usada no século XVII.

Gilded wood is an important part of Portuguese cultural heritage. We profit an intervention in the organ of the Church of Santa Cruz (Coimbra) to make a study on its gilded wood decoration. Historical sources indicate that the organ dates from the XV-XVI centuries, although it has suffered several restoration works over the centuries. Samples were collected from different places of the central part of the organ. Scanning electron microscopy combined with energy dispersive X-ray spectroscopy, optical microscopy, X-ray diffraction and Fourier transform infrared spectroscopy were the techniques used in this work to analyze the samples. Stratigraphical sequence and global chemical and mineralogical analysis data allowed the identification of the gilding techniques. All the samples exhibit the typical technique brought by Portuguese artists from China, with kaolin in the *bolus* composition. Some samples present a typical Italian and Flemish technique developed in the XIV century, and used in the XVII century, with gypsum (*gesso mate* and *gesso grosso*) in the preparation layer.

Keywords: gilded wood, optical microscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy, X-ray diffraction, Fourier transform infrared spectroscopy

Introduction

The conservation and preservation of the cultural heritage has deserved considerable attention in the recent years and gilding wood is not an exception. Several works have been focused on the characterization of the original and restoration materials as well as on the gilding techniques on wood or on stone.[1-8]

The so-called gilding technique consists on applying a gold leaf to a previously treated wood surface. Portugal is a rich country in what concerns examples of gilded wood, which can be found in a great number of monuments. The gilding technique was introduced in our country in the middle age and with the influence of Flemish artists it was widely spread since the XVcentury.[9] Due to the brightness and splendor of gilded decorations, the most relevant works of gilded wood are to be found in religious monuments, such as churches. An important part of these works were made with Brazilian gold brought to Portugal mainly during the XVIII century.

Due to the metal's scarcity and price, the use of thin leafs become an economical way of suggesting the appearance of solid gold.[1] Gold with the addition of an alloying metal such as silver or copper can be beaten extraordinarily thin.

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To prepare the wood surface for the gilding, several coats are previously applied to the wood surface, namely a glue based layer, a preparatory coat and a clay mixture or *bolus*.[1] The first layer consisted, in general, of an animal glue. The second layer or preparatory coating was a mixture of glue with pigments such as gypsum or calcite depending on the availability of the materials. While in northern Europe countries calcite was used, in the southern countries the use of gypsum was more common. The third layer or *bolus* was formed by animal glue, kaolin and iron oxide. Several pigments could also be added. The way gold leaf was attached to the *bolus* made the difference between oil and water gilding. The gold leaf could be applied over the *bolus* with an adhesive or mordant, giving the so-called oil gilding. On another process *i.e.* water gilding, an aqueous mixture was applied over the *bolus* to improve the adhesion of the gold leaf.[1]

The present work is focused on the gilded wood of the organ of the Church of Santa Cruz in Coimbra. A conservation intervention in the organ taken under the responsibility of IPPAR (Direcção Regional de Coimbra) made possible the study of the gilded wood described in this paper.

Although the church was built during the XII century, it was only in the XV-XVI centuries that an organ was installed.[10] Different parts of the organ were submitted to several restoration works in the XVII, XVIII and XIX centuries.[11] The major intervention during the XIX century included cleaning and painting of some gilded areas. Figure 1a shows a photograph of the actual aspect of the organ.

The aim of the present study was to obtain chemical and mineralogical compositions of the samples, in order to elucidate some details of the gilding process. Samples were observed using optical (OM) and scanning electron microscopy (SEM). Optical microscopy enables the observation of the structure of individual layers (stratigraphic analysis) while SEM is a technique used for topological examination. Electron microscopy combined with energy dispersive X-ray spectroscopy (EDS) provides spectra of X-ray frequencies that were used to identify constituent elements. X-ray powder diffraction (XRD) was also applied to identify the different mineral phases present in the samples. The results were complemented by the Fourier transform infrared (FTIR) analysis of the samples.

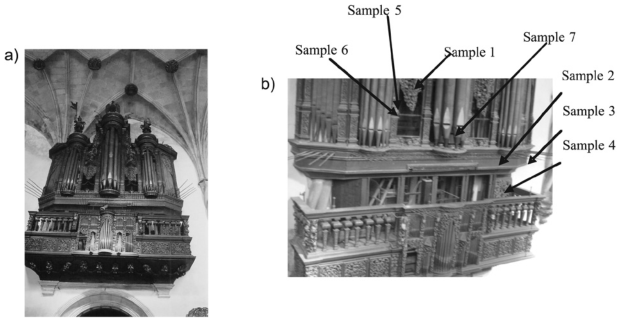

Figure 1. Organ of the church of Santa Cruz: (a) General view and (b) detailed aspect (arrows indicate the location of the samples).

Experimental

Seven samples, representative of the area studied, were taken from various places of the gilded decoration of the organ (Figure 1b) and will be named by the numbers indicated in the Figure. Another sample (sample 8) was collected from gilded motifs found on a stone that was covered by the lower part of the organ box. Samples were removed with a pointed scalpel being their larger dimension, in general, around 5 mm.

The optical microscopy observations were performed in an Olympus CK40M optical microscope equipped with an Olympus C5060 digital camera. Samples were previously mounted in a resin. Grinding and polishing operations were performed with a Metaserv equipment using Si-C papers with increasing granulometries (320, 500, 600 and 800 μm) and two alumina pastes. Scanning electron microscopy was carried out using a Hitachi S2400 microscope equipped with X-ray energy dispersive system. The samples were coated with a gold layer before SEM-EDS analysis was performed. Observations were made with secondary electrons using an accelerating voltage of 20 kV. X-ray powder diffraction analyses were recorded on a Philips PW 1710 diffractometer using $CuK\alpha$ (λ = 1.5406 Å) graphite-monochromatised radiation. Patterns were obtained on oriented films by step scanning from 5° to 60° 2θ, with a step size of 0.05° 2θ, a time *per* step of 0.5 s and 40 kV and 40 mA in the X-ray tube. To prepare the oriented films, the samples (after crushed to powder in an agate mortar) were dispersed in distilled water under ultrasonic at room temperature, deposited on a silicon "zero background" sample holder and allowed to evaporate. The identification of the crystal phases was made by means of the diffraction data collected by International Center for Diffraction Data (ICDD).[12]

For the FTIR essays, samples were crushed to powder in an agate mortar. The absorbance spectra were recorded at room temperature using a Mattson spectrometer in the 4000-550 cm^{-1} range. Data were collected using KBr wafers, with a resolution of 4 cm^{-1} and with 40 scans.

Results and Discussion

Figures 2a to 2h present optical micrographs of samples 1 to 8 from which the stratigraphical sequence was inferred.

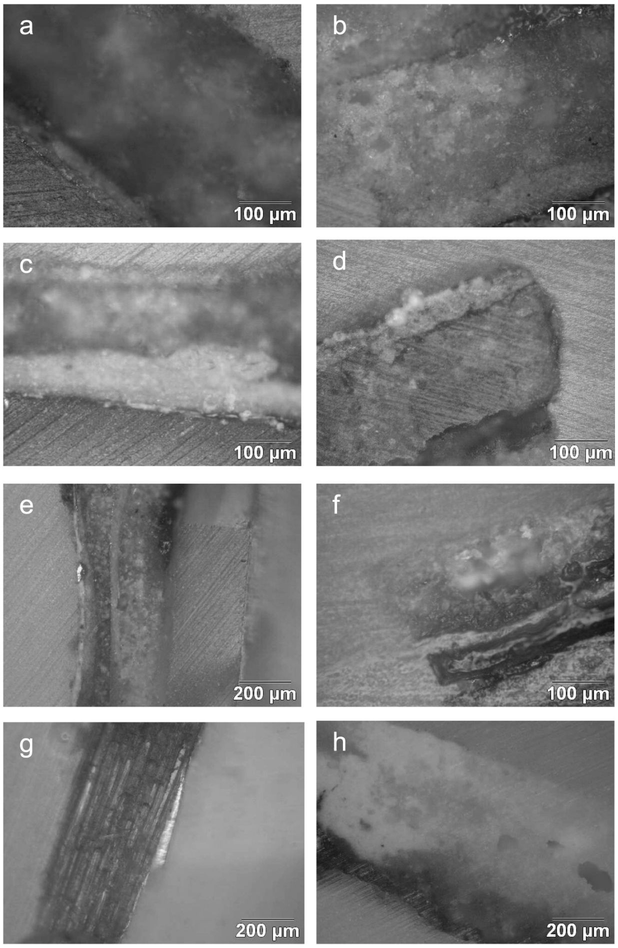

Figure 2. Optical micrographs of samples 1 to 8, respectively, from (a) to (h) sample location.

In the following, we detailed the stratigraphical sequences of samples 1 and 3, but a similar analysis was made for all the other samples. Notice that this would be possible to see in the colour photographs, not shown here, but available as Supplemenatry Information, SI, at http://jbcs.sbq.org.br, as a PDF file. In sample 1, we can identify, from top to bottom, four layers, respectively, a glue based mixture (dark brown), a preparatory coating (light brown), the *bolus* (red) and gold (only small points). The stratigraphical sequence of sample 3 is formed by two layers of preparatory coating (grey) and one layer of *bolus* (beige). No golden points were observed.

The global chemical compositions of all the samples determined by SEM-EDS are indicated in Table 1.

These results show that gold only appears in samples 4, 5 and 8, what may be explained by the small dimensions of the samples. In general, gold was not used in its pure state, but associated with other metallic materials such as silver and copper. Chlorine was detected in several samples. A similar result was previously reported by Souza[6] in a study centered in the gilded decoration of a Brazilian church. The author related the presence of chlorine with silver, and it seems to be also the case of the results obtained in the present study. Elements such as Si, K, Al, Mg and Mn have their origin on the clays that form the *bolus*. The presence of Pb is related with the pigment white lead ($2PbCO_3 \cdot Pb(OH)_2$) present in the *bolus* and the red pigment minium (Pb_3O_4), associated with the red paint. The Ti detected in some samples is probably related with the

Table 1. Global chemical composition (mass %)

Element	Sample							
	1	2	3	4	5	6	7	8
Mg	2.17	1.66	1.35	1.16	3.22	2.07	3.73	1.50
Al	5.40	5.15	-----	1.18	3.71	2.72	6.15	0.64
Si	17.62	17.15	4.82	2.25	11.48	5.96	7.74	1.23
P	2.72	-----	3.01	-----	1.05	-----	3.24	-----
S	17.62	11.65	44.18	-----	-----	28.37	34.48	-----
Cl	5.44	3.16	-----	-----	4.21	-----	-----	3.07
K	4.19	3.04	3.85	1.60	3.76	2.80	2.12	1.13
Ca	37.86	39.30	42.79	9.49	22.69	45.89	31.81	14.29
Ti	2.15	1.94	-----	-----	2.23	-----	-----	-----
Mn	-----	-----	-----	-----	-----	-----	-----	0.50
Fe	4.84	8.48	-----	2.15	4.69	12.18	5.17	2.04
Cu	-----	7.12	-----	1.06	1.78	-----	5.57	1.28
Ag	-----	1.36	-----	9.56	5.07	-----	-----	5.69
Au	-----	-----	-----	29.44	16.89	-----	-----	44.56
Pb	-----	-----	-----	42.11	19.20	-----	-----	24.07

kaoline used in the *bolus*. Iron which appears in almost all the samples is responsible for the red coloration of some preparatory layers. Calcium is related with the presence of calcium carbonate or calcium sulfate in the preparatory layer. The presence/absent of sulfur gives the indication of the appearance or not of gypsum.

Figures 3a and 3b exhibit the X-ray powder diffraction patterns of samples 1 and 3, respectively. Sample 1 presents gypsum, also called *gesso mate* ($CaSO_4 \cdot 2H_2O$; ICDD 33-311), anhydrite, also called *gesso grosso* ($CaSO_4$; ICDD 37-1496), calcite ($CaCO_3$; ICDD 5-586), hematite (Fe_2O_3; ICDD 33-664) and quartz (SiO_2; ICDD 33-1161). Sample 3 shows the presence of gypsum, anhydrite, calcium sulfate with undetermined hydration degrees, kaolinite ($Al_2Si_2O_5(OH)_4$; ICDD 14-164) and quartz (SiO_2). The presence of cerussite ($PbCO_3$), hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) and minium (Pb_3O_4) were identified using, respectively, the ICDD 5-417, 13-131 and 8-19 files. The presence of gold, silver and copper was confirmed considering the data of files ICDD 4-784, 41-1402 and 4-836, respectively. Table 2 displays the mineralogical composition of all the analyzed samples with X-ray diffraction. Due to their very small dimensions, samples 6 and 7 were not analyzed by DRX.

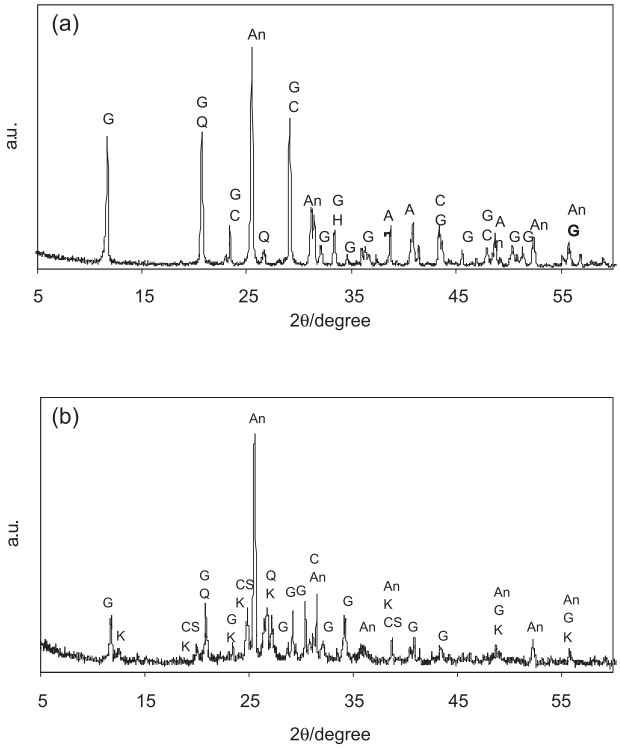

Figure 3. X-ray powder diffraction patterns of samples (a) 1 and (b) 3. G-gypsum (ICDD:33-311); An: anhydrite (ICDD: 37-1496); CS: calcium sulfate with undetermined hydration degrees (ICDD: 21167); C: calcite (ICDD: 5-586); H: hematite (ICDD: 33-664); Q: quartz (ICDD: 33-1161); K: kaolinite (ICDD: 14-164).

Table 2. Crystalline materials identified from DRX patterns

Sample	Crystalline materials
1	Gypsum; Anhydrite; Calcite: Hematite; Quartz
2	Gypsum; Anhydrite; Calcite; Kaolinite; Hematite;Quartz; Copper
3	Gypsum; Anhydrite; $CaSO_4 \cdot xH_2O$; Kaolinite; Quartz
4	Cerussite; Hydrocerussite; Minium; Calcite; Hematite; Quartz; Copper; Silver; Gold
5	Cerussite; Hydrocerussite; Calcite; Kaolinite; Hematite; Quartz; Copper; Silver; Gold
8	Cerussite; Hydrocerussite; Calcite; Quartz; Copper; Silver; Gold

FTIR analysis was made on all the samples. Before starting a detailed examination of the results it is important to mention that the interpretation of the FTIR spectra of this type of materials is very complex. Among other reasons there are a great number of compounds present, in different amounts. As a result, band overlapping will not allow an undoubted band assignment. For instance, if calcite is present there will be a strong band centered at 1492-1429 cm^{-1} which is the absorption region of some characteristics functional groups.[13,14] The unquestionably understanding of the organic medium present, and consequently the type of gilding used, became then very difficult, if not impossible. Additionally, it is also important to note that ageing may cause significant changes in the infrared bands of certain binding media.[13] A detailed discussion of the identification of binding media from FTIR can be found in the study developed by Meilunas *et al.*[15]

Figure 4 illustrates two examples of the FTIR spectra, respectively of samples 1 and 4. The strong band around 1120 cm^{-1}, and the stretching mode of Si-O-Si assigned to the stretching vibration modes of SO_4^{2-}, indicates the presence of gypsum, anhydrite and also quartz, confirming the existence of all these mineral phases in sample 1 and the presence of quartz in sample 4. The two well defined bands at 600 and 690 cm^{-1} are also assigned to SO_4^{2-} vibration modes. The broad band near 1400 cm^{-1}, observed for sample 1, and the well defined band at 1410 cm^{-1}, detected for sample 4, is attributed to stretching vibration modes of CO_3^{2-} groups and accounts for the existence of calcite. In the case of sample 1, the kaolinite identified in the XRD pattern is recognized only by the small shoulder at 1009 cm^{-1}; all the remain bands characteristics of this mineral are not observed since they are overlapped by the strong band due to SO_4^{2-} groups of gypsum and anhydrite. It is interesting to note that in the DRX pattern of sample 1 the peaks correspondents to these last mineral phases are the most intense. The bands at 1033 and 1118 cm^{-1} assigned to kaolinite are more defined in sample 4. The bands at 1621 and 1684 cm^{-1} in the spectrum of sample 1, and at 1545 and 1623 cm^{-1} in the spectrum of sample 4, can be attributed to the vibration of N-H groups of the proteins aminoacids, indicating the use of animal glue. The presence of oil could be disclosed only in samples 4 and 6, attending to the bands at 2925 and 2852 cm^{-1} (see spectrum of sample 4 in Figure 4b).

The FTIR analysis of samples 6 and 7, which were not study by XRD, exhibited bands that indicate the presence of gypsum, kaolinite and calcite, in agreement with the data of the global chemical analysis previously discussed.

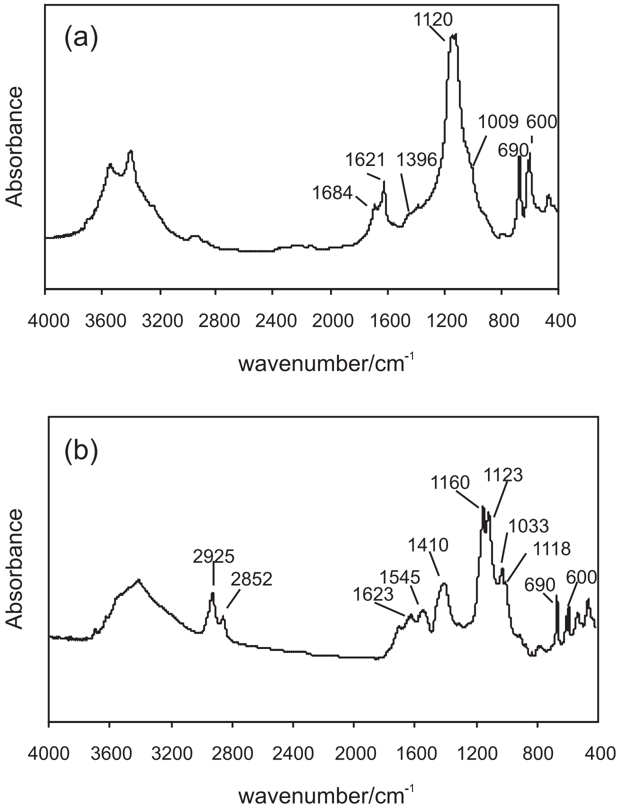

Figure 4. Fourier transform infrared spectroscopies FTIR of: (a) sample 1 and (b) sample 4.

Table 3. Composition of the different layers present in the samples

Sample	Preparatory layer	Bolus	Gold leaf	Paint
1	Gypsum Anhydrite Calcite	Kaolinite Hematite Quartz		
2	Gypsum Anhydrite Calcite	Kaolinite Hematite Quartz	Cu Ag	
3	Gypsum Anhydrite CaSO4.xH$_2$O	Kaolinite Quartz		
4	Calcite White lead	Kaolinite Hematite Quartz	Au Cu Ag	Minium White lead
5	Calcite White lead	Kaolinite Hematite Quartz	Au Cu Ag	
6	Gypsum Calcite	Kaolinite Hematite Quartz	Cu	
7	Gypsum	Kaolinite Hematite Quartz		
8	Calcite White lead	Kaolinite Quartz Hematite	Au Cu Ag	

The combination of all the results obtained in this study allowed us to propose an interpretation of composition of the layers observed in optical microscopy, which we summarize in Table 3. In sample 1, we can assume that the preparatory layer has a mixture of calcite and *gesso mate* and *gesso grosso*. The *bolus* has iron oxide, quartz and kaolinite. Although from OM, we observed small golden points, gold was not detected by SEM-EDS, most probably due to the small size of the sample. In sample 3, several hydration states of calcium sulfate are present in the preparatory layer. The *bolus* has kaolin and traces of quartz, but no iron oxide was detected, which explains the beige coloration.

Regarding the preparatory layer, there are differences between the samples. Samples 3 and 7 present gypsum in the preparatory layer, which is characteristic of the Italian and Flemish technique developed in the XIV century and used during the XVII century. This technique was described by C. Ceninni[16] and also by Nunes.[17] Samples 1, 2 and 6 present, in the preparatory layer, calcium carbonate and gypsum which was a technique developed for paintings in Italy during the XV century and used later on gilding.[6] In samples 4, 5 and 8 the preparatory coat is a mixture of calcite and of white lead (no gypsum was detected). This may correspond to an intentional procedure to increase the brightness of the final gilding, as it was detected by other authors.[4,18] The presence of the white lead pigment in sample 4 may have two possible sources. It could be a filler of the red paint that covers the original gilding, or, most probably it was originated from an uncompleted transformation of white lead during the calcinations made for the preparation of minium. The introduction of kaolin in the mixture that forms the *bolus* is present in all the samples, indicating that this procedure, brought by Portuguese artists from China, was used.

In the present study, it was not possible to distinguish between oil gilding and water gilding. On the other hand, several discrepancies between the global analysis and the optical microscopy observations occurred. The authors intend to continue this work with the analysis of the organic compounds by means of other techniques.

Conclusions

Using the optical and electron microscopy, X-ray powder diffraction and Fourier transform infrared spectroscopy we attempted to correlate the results obtained on 8 samples of the organ of the Church of Santa Cruz (Coimbra) with different gilding techniques. As the organ had suffered various conservation interventions along the centuries we expected to identify diverse techniques. We were able to determine several features associated with the gilding procedures dated from the XVI, XVII and XVIII centuries. In samples 3 and 7 a XVI century technique was followed, while in samples 1, 2 and 6 a technique first developed for paintings was used. Finally, samples 4, 5 and 8 present all the same composition, which is different from the others. Due to the motifs of sample 8 (a phoenix), the gilding can be attributed to the Baroque period (XVII-XVIII centuries).

Acknowledgments

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Supplementary Information

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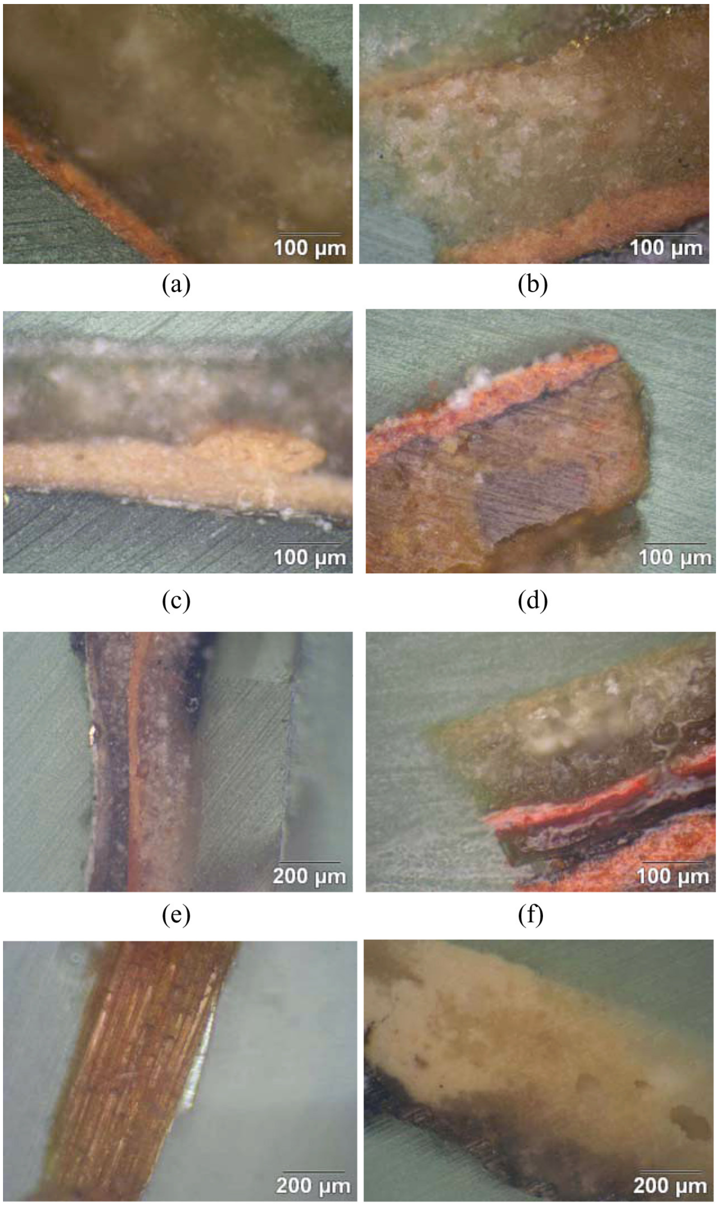

(a) (b)

(c) (d)

(e) (f)

(g) (h)

Figure S1. Optical micrographs of samples 1 to 8, respectively, from (a) to (h) sample location.

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