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THE STUDY OF STAGES AND OPERATIONS INVOLVED IN THE PRESERVATION AND RESTORATION OF TWO XIX-th CENTURY ICONS, ON WOODEN SUPPORT

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Key words: icons, stopping xylophagous attack, consolidations, reintegration, restoration

Abstract. The paper presents the stages and the operations involved in the preservation and restoration of two icons on wooden support, from the XIX-th century, which are part of the heritage of the "Sfinții Arhangheli Mihail and Gavriil" church, from Galați. The two icon have inventory numbers as part of the collection as followed: 112 for the first icon and 113 for the second one. Both icons have the same theme, "The Grieving Mother from Rohia" and are made by anonymous painters in egg tempera, on lime wooden support, without ground. Being part of the same collection, they were deposited in the same place and as a direct consequence, they suffer from similar deteriorations and degradations that affect both the support and the painting layer. Both panels are attacked by xylophagous insects and the painting layer has detachments, gaps, cracks, clogged dirt and a cracked and degraded varnish layer. Ten samples taken from the already detached areas were analyzed by optical microscope, SEM-EDX and micro-FTIR. Based on the chemical elements identified in the EDX spectrums, the pigments used to create the painting layer are: ultramarine natural blue Na₈-10Al₆Si₆O₂₄S₂-4, carbon black, earth green, K[(Al,FeIII),(FeII,Mg)](AlSi₃,Si₄)O₁₀(OH)₂, ocher (FeO), burned or natural umber Fe₂O₃·H₂O + MnO₂·n H₂O+ Al₂O₃, lead white (2PbCO₃·Pb(OH)₂) and yellow iron oxide (Fe₂O₃·4H₂O). It was also determined that the gold leaf usually used in byzantine icons was replaced in the case of both icons: the icon number 112 has silver leaf covered with varnish, while the halo of the icon number 113 was created with yellow metallic pigments (realgar or orpiment).The pigments were also identified by determining specific peaks in micro-FTIR spectrums. For natural ultramarine blue the peaks between 628 – 724

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cm-1 were assigned; the peaks in the interval 795 – 887 cm-1 confirm the presence of carbonates (calcium and lead based). The earth green pigment (aluminum – silicates) had the peaks between 1464 – 1599, while the carbon black pigment was confirmed by the peaks in the interval 921 – 1060 cm-1. After the pigments and the materials used by the author were identified, the restoration process begun with the following stages: consolidation of the painting layer (fish glue 8% and japanese paper), stopping the xylophagous attack (encapsulation with nitrogen), consolidation of the wood supports (colophon and wax, 1:1), cleaning the painting layer (ethylic alcohol and distilled water, 1:1), filling the gaps and reintegrating the fillings in *tratteggio*, all followed by the process of varnishing the two icons.

Introduction

The two icons part of "Sfinții Mihail and Gavriil" church collection, from Moscu village, Galați, are very similar. Both icons have the same theme, and that is "The Grieving Mother from Rohia". The structural composition is the same for both icons, the only significant difference being the shape of the lower scenes of the icons: the icon number 112 has square lower scenes while the second icon with inventory number 113, has round medallions. Both icons are painted in neobyzantine style using egg tempera and the colors used are the same, the general chromatic impression offered by the two art pieces being quite similar: the cloak of the Virgin Mary is dark, surrounded by a green ocher background that becomes darker to the edges of the panels.

Although they have these similarities and are painted in the same period of time, the two icons are done by two different authors, as proven by the different technique used in painting the face of the Mother and the different writing style [1].



Fig. 1. The Grieving Mother from Rohia nr. 112: a – the front of the icon; b – the back of the icon



Fig. 2. The Grieving Mother from Rohia nr. 113: a – the front of the icon; b – the back of the icon

1. Storage environment and the state of conservation

The environment where the two icons were kept has a significant importance on their state of conservation. The high values of humidity (65% - 85%) and temperature (18° – 25°C) allowed for the xylophagous attack to begin. Also the fluctuations of these two climate factors have subjected the wood supports and the painting layers to tensions. These tensions were caused by the continuous exchange of water between the wood supports and the environment, in order to obtain a fluid balance. The repeated tensions lead to cracks in the mass of the wood and in the painting layer [2-4].

1.1. The state of conservation

Because the icons were kept in the same improper environment regarding the stability of atmospheric factors (temperature, humidity), the two icons suffer from a series of similar deteriorations and degradations that require establishing a restoration and preservation protocol.

The two icons are made on lime wooden panels: the one for the icon number 112 is made out of two boards that are kept together by two sparrows crossbeams, from side to side of the panel and the panel of the icon number 113 is made out of three boards, locked tight by a frame. Both the systems that keep the panels together and the panels themselves, have suffered, besides from the xylophagous attack, from a series of deteriorations and degradations. For example, the deteriorations are: boards distancing from each other (fig. 3), cracks, fly holes (fig. 4) support missing due to improper handling and structural weakness caused by insect attack (fig. 5) and the degradations are clogged dirt and wood changing color.

The two painting layers also suffer from deteriorations: cracks, gaps, detachments (fig. 7), fly holes and degradations like clogged dirt (fig. 6), browned varnish and blisters [6-10].

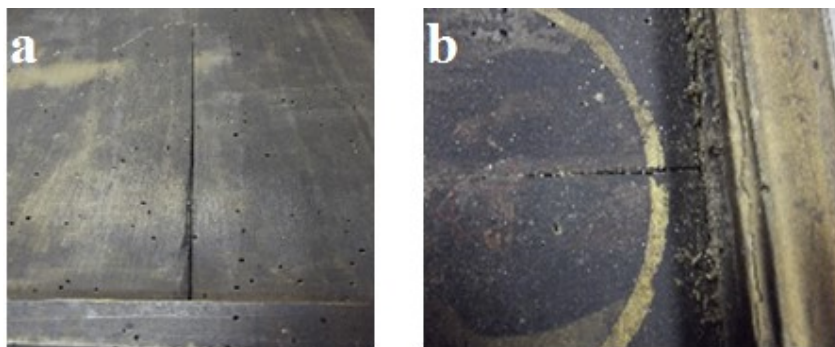


Fig. 3. The Grieving Mother from Rohia nr.113: distance between the boards of the panel: a – back, b – front;

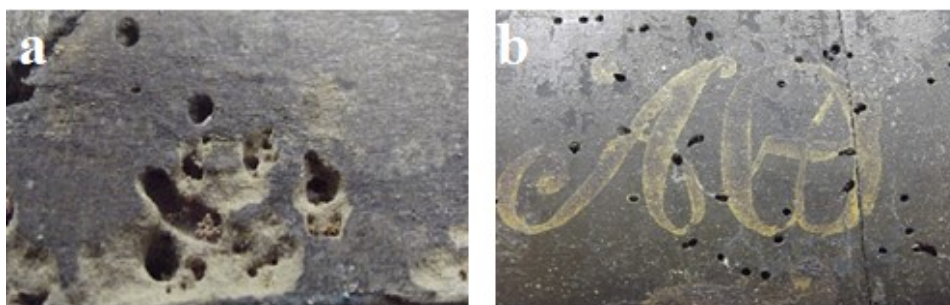


Fig. 4. The Grieving Mother from Rohia: a – xylophagous atac on the back of the icon nr. 112; b - xylophagous atac on the back of the icon nr. 113;

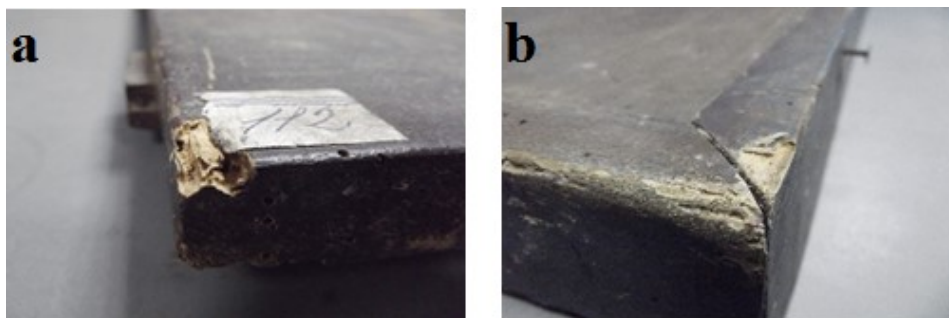


Fig. 5. The Grieving Mother from Rohia: a - support missing on the icon nr. 112; b - support missing on the icon nr.113

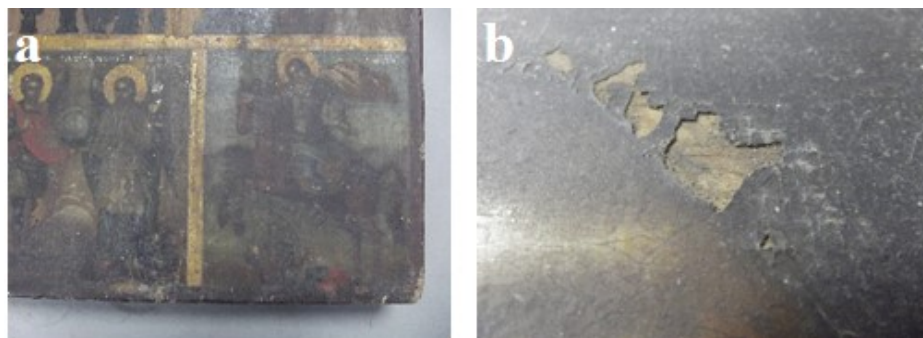


Fig. 6. The Grieving Mother from Rohia: a – dirt on the icon nr. 112; b - dirt on the icon nr. 113

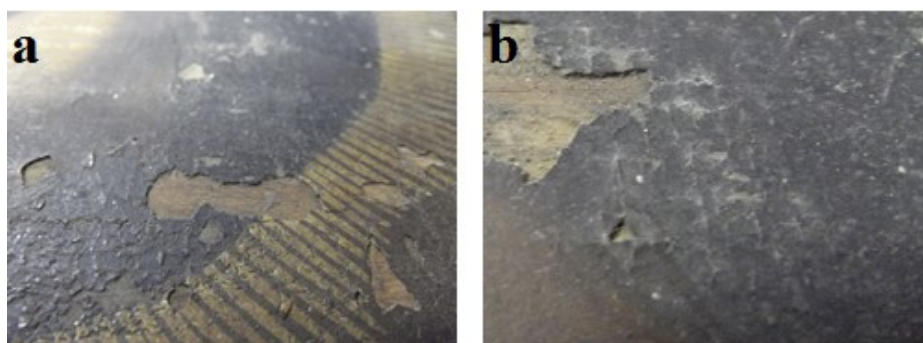


Fig. 7. The Grieving Mother from Rohia: a - cracks of the painting layer on the icon nr. 112; b - cracks of the painting layer on the icon nr. 113

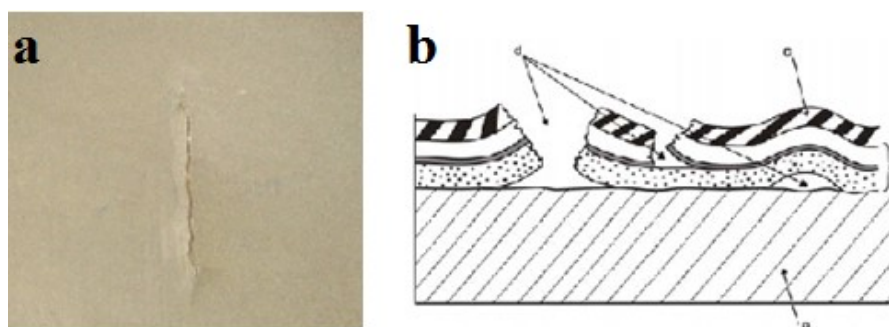


Fig. 8. The Grieving Mother from Rohia: a - detachments on the icon nr. 113b - stratigraphic structural drawing(a – wooden support, b – painting layer, c – dirt, d – detachments;)

2. Experimental part

Five samples from each painting layer of the two icons were taken as shown in the figures 9 a and b.



Fig. 9. Areas from where the samples were taken: a- Icon number 112 a) - face; b - halo; c - background; d - cloak; e – lower scene border; b) - Icon number 113 a - face; b - halo; c - background; d - cloak; e – lower scene border

The following instruments were used in analysis: CARL ZEISS AXIO IMAGER A1m microscope, with an attached AXIOCAM camera, the samples being enhanced between 50X and 500X. In order to identify chemical elements, the samples were analyzed with an electronic microscope, model VEGS II LSH, made by TESCAN, in Check Republic, coupled with an QUANTAX QX2 X-ray spectroscope, made by BRULER/PROENTEC from Germany. The Micro-FTIR spectrums were recorded with a FT-IR spectroscope coupled with a Hyperion 1000 microscope, both from Brüker Optic Equipment, Germania [11-13].

Based on the optical microscope analysis of the 10 samples taken from the two samples it was determined that the colors used to create the background and the cloaks are similar: a combination of blue, black and green for cloaks and green, ochre, umber and black for the background (fig. 11. c-h). The face is made in both cases with a mixture of white, ochre and green and black in shadow (fig. 11. a-b). The last two samples analyzed were those taken from the lower scenes borders.

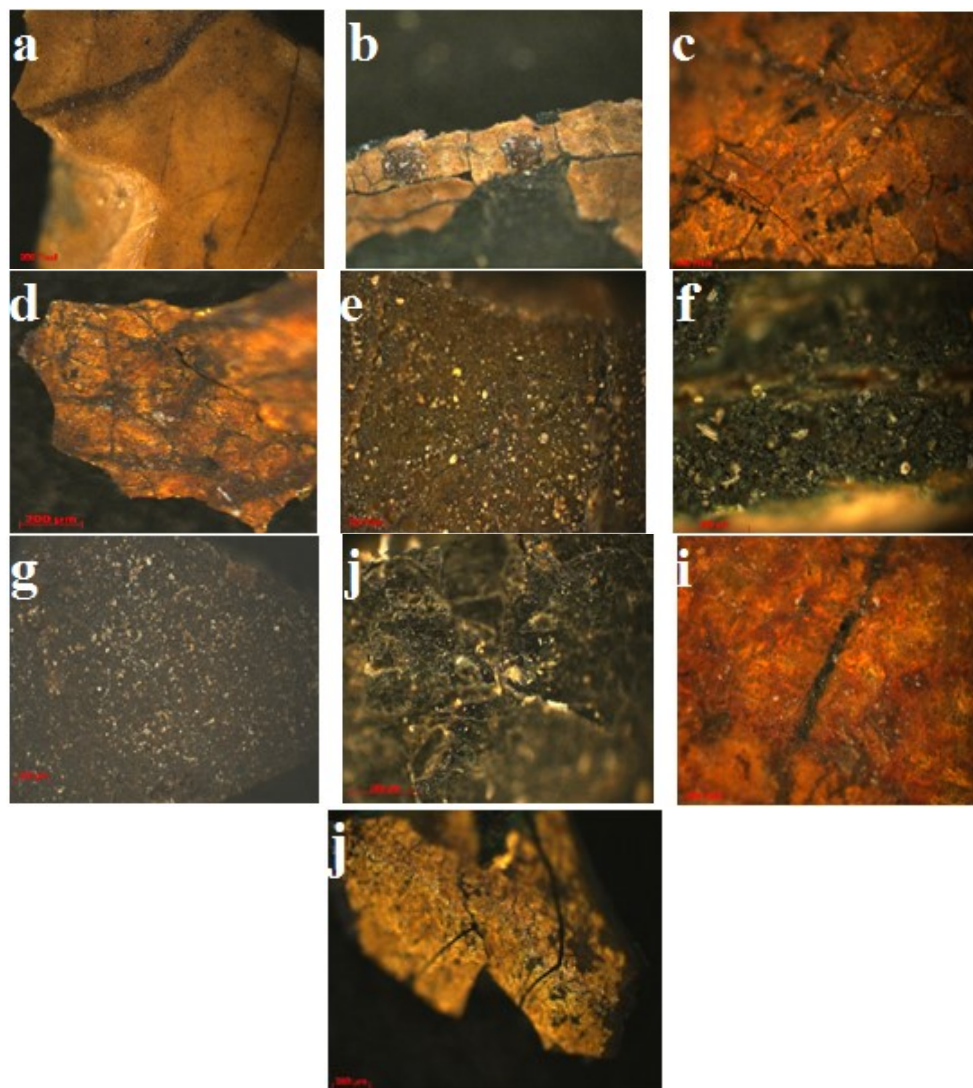


Fig. 11. Images obtained with the OM for the samples taken from different areas of the two icons: a – face from the icon nr. 112; b – face from the icon nr. 113; c -halo from the icon nr. 112; d - halo from the icon nr. 113; e – background from the icon nr. 112; f – background from the icon nr. 113; g –cloak from the icon nr. 112; h – cloak from the icon nr. 113; i - borders from the icon nr. 112; j - borders from the icon nr. 113;

The sample taken from the icon number 112 shows a metallic yellow leaf (fig. 11i). The sample taken from the border of the icon number 113 presents a yellow metallic pigment (fig. 11j). All samples show significant traces of clogged dirt and cracked varnish.

The SEM-EDX analysis was done on the same 10 sample taken from the two painting layers (fig. 12-18). One of the first conclusions was the lack of ground and canvas, which was a decisive factor in the evolution of the deteriorations and the degradations of the two icons. It was also established that the green pigment used in the painting of the backgrounds is earth green $K[(Al,FeIII),(FeII,Mg)](AlSi_3Si_4)O_{10}(OH)_2$, combined with carbon black, ocher (FeO) and burned or natural umber $Fe_2O_3 \cdot H_2O + MnO_2 \cdot n H_2O + Al_2O_3$ (fig.14-15). The cloaks were done with a mixture of ultramarine natural blue $Na_{8-10}Al_6Si_6O_{24}S_{2-4}$, mixed with carbon black and earth green (fig. 12-13)[6]. The face of The Virgin Mary on both icons was done with lead white ($2PbCO_3 \cdot Pb(OH)_2$) and yellow iron oxide ($Fe_2O_3 \cdot 4H_2O$) or mars yellow (fig. 16-17). The SEM-EDX analysis of the sample taken from the halo of the icon number 112 revealed that the metallic leaf used is silver, not gold leaf as originally believed (Fig. 18). In the case of the icon number 113, the yellow metallic pigment used was based on S, Cr și Pb (realgar or orpiment, mixed with other earth colors) (Fig. 19) [14-16].

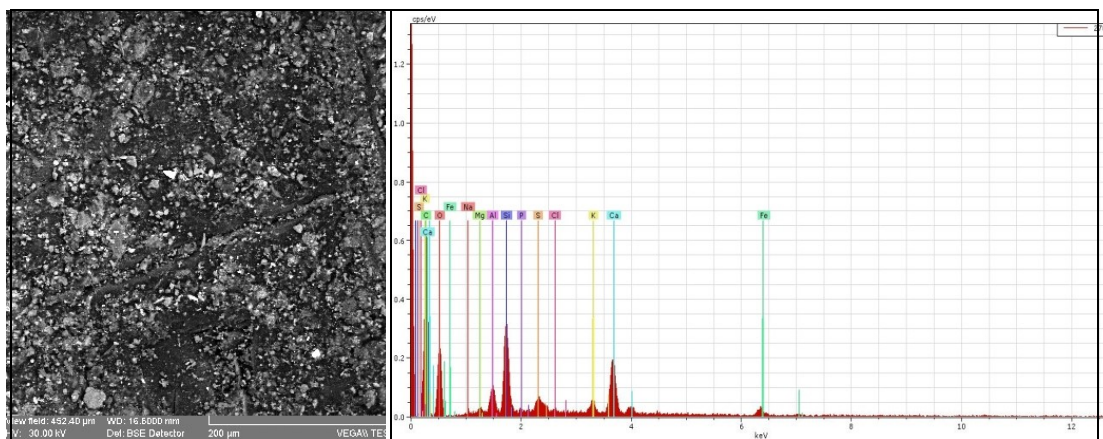


Fig. 12. SEM microphotography, BSE, 500X, EDX spectrum of the sample taken from the cloak of the icon nr. 112

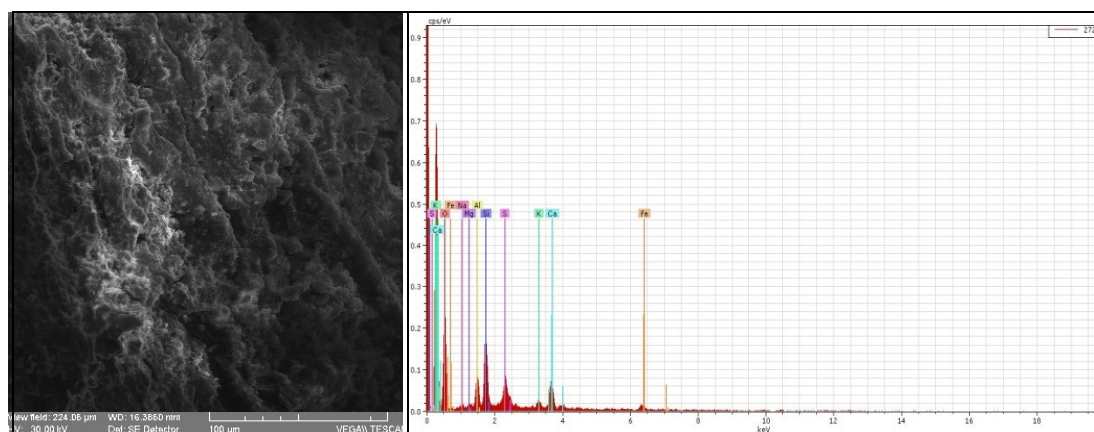


Fig. 13. SEM microphotography, SE, 1000X, EDX spectrum of the sample taken from the cloak of the icon nr. 113

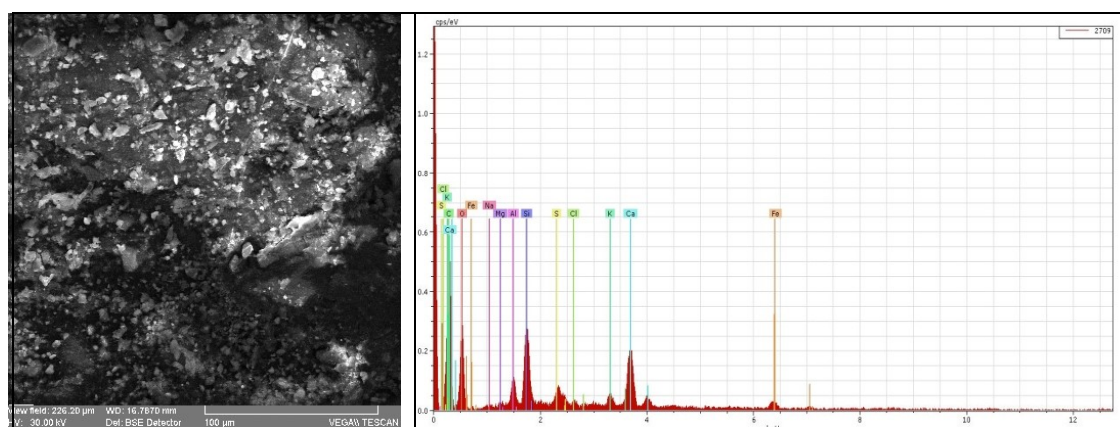


Fig. 14. SEM microphotography, BSE, 1000X, EDX spectrum of the sample taken from the background of the icon nr. 112

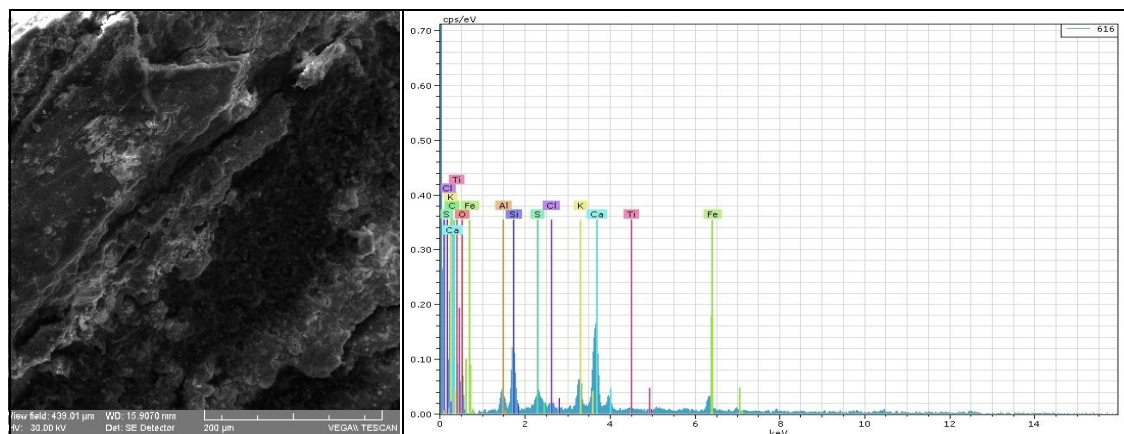


Fig. 15. SEM microphotography, SE, 500X, EDX spectrum of the sample taken from the background of the icon nr. 113

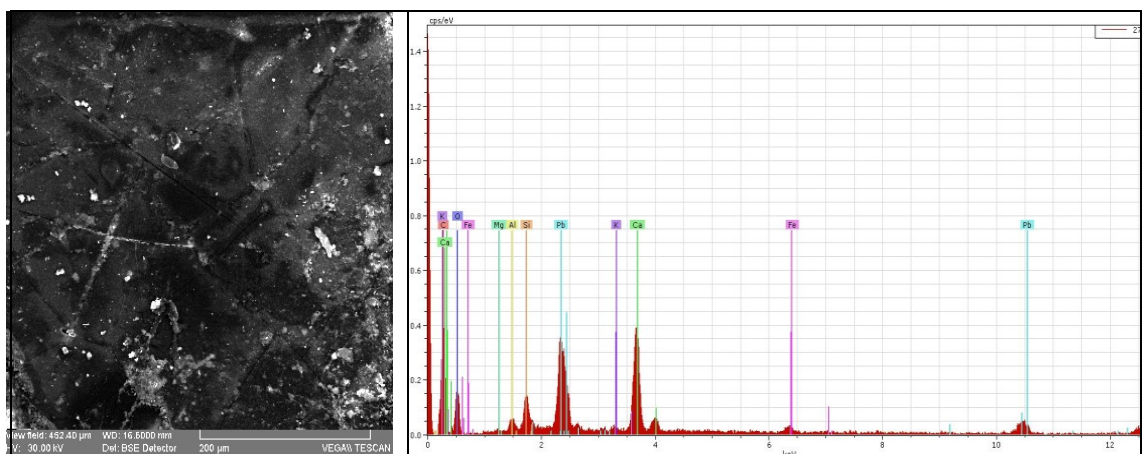


Fig. 16. SEM microphotography, BSE, 500X, EDX spectrum of the sample taken from the face of the icon nr. 112

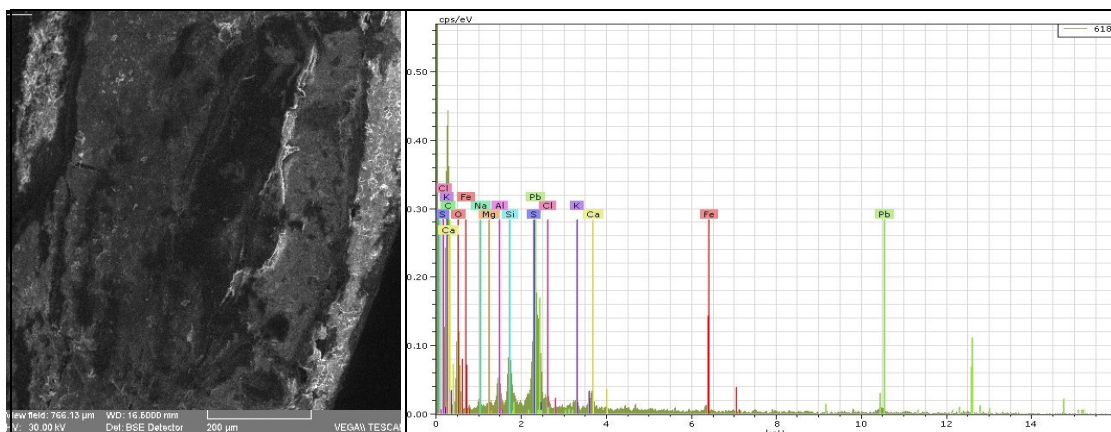


Fig. 17. SEM microphotography, BSE, 300X, EDX spectrum of the sample taken from the face of the icon nr. 113

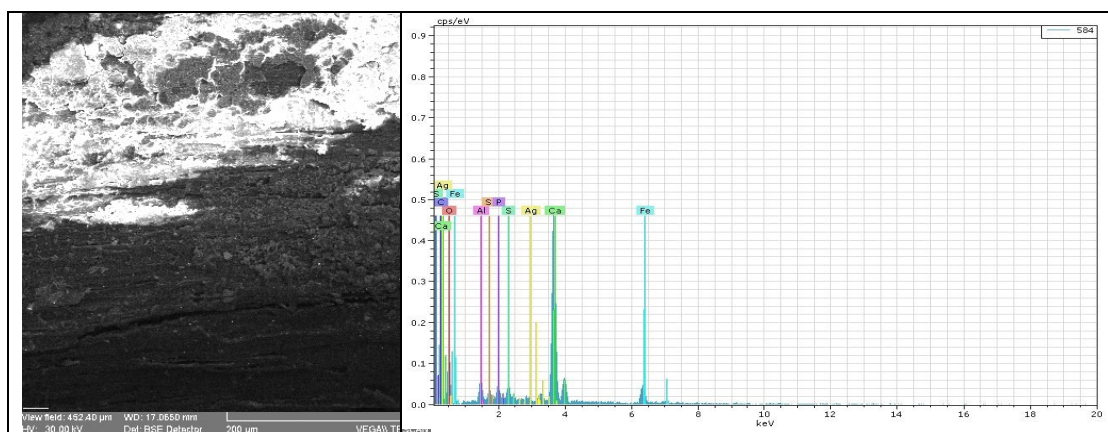


Fig. 18. SEM microphotography, BSE, 1500X, EDX spectrum of the sample taken from the halo of the icon nr. 112

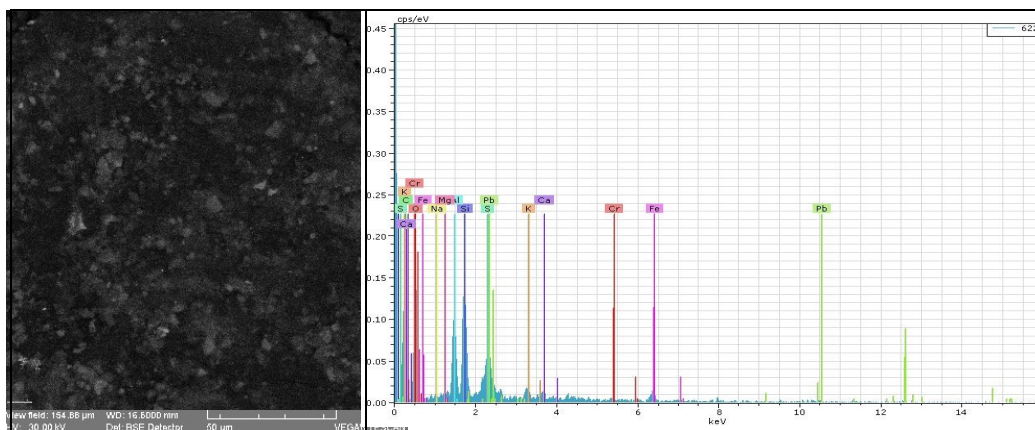


Fig. 19. SEM microphotography, BSE, 500X, EDX spectrum of the sample taken from the halo of the icon nr. 113

Tab. 1. SEM-EDX results

Nr.	Sample	Chemical elements identified	Concentration (wt.-%)	Determined pigments
1	Cloak of the icon number 112	Carbon	16.38881	ultramarine natural blue $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$, mixed with carbon black and earth green, $\text{K}[(\text{Al}, \text{FeIII}), (\text{FeII}, \text{Mg})](\text{AlSi}_3, \text{Si}_4)\text{O}_{10}(\text{OH})_2$.
		Silicon	6.172971	
		Calcium	3.941729	
		Aluminium	2.267281	
		Sulfur	1.386985	
		Iron	1.512083	
		Potassium	1.228655	
		Chlorine	0.230147	
		Magnesium	0.681442	
		Sodium	0.642462	
		Phosphorus	0.252832	
		Oxygen	65.2926	
2	Cloak of the icon number 113	Carbon	14.12818	ultramarine natural blue $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$, mixed with carbon black and earth green, $\text{K}[(\text{Al}, \text{FeIII}), (\text{FeII}, \text{Mg})](\text{AlSi}_3, \text{Si}_4)\text{O}_{10}(\text{OH})_2$.
		Silicon	6.149608	
		Calcium	2.667325	
		Sulfur	3.429675	
		Aluminium	3.294889	
		Iron	1.285284	
		Potassium	1.279955	
		Magnesium	0.828494	
		Sodium	1.508789	

3	Background of the icon number 112	Oxygen	65.42581	earth green $K[(Al,FeIII),(FeII,Mg)](AlSi_3,Si_4)O_{10}(OH)_2$, carbon black, ocher (FeO), burned or natural umber $Fe_2O_3 \cdot H_2O + MnO_2 \cdot n H_2O + Al_2O_3$
		Carbon	15.0315	
		Silicon	5.320449	
		Calcium	4.118289	
		Aluminium	2.137188	
		Sulfur	1.470609	
		Iron	1.172684	
		Potassium	0.753333	
		Magnesium	0.52451	
		Sodium	0.650922	
		Chlorine	0.261094	
		Oxygen	68.55742	
4	Background of the icon number 113	Carbon	19.01557	earth green $K[(Al,FeIII),(FeII,Mg)](AlSi_3,Si_4)O_{10}(OH)_2$, carbon black, ocher (FeO), burned or natural umber $Fe_2O_3 \cdot H_2O + MnO_2 \cdot n H_2O + Al_2O_3$
		Silicon	2.560286	
		Calcium	3.81289	
		Potassium	1.923999	
		Aluminium	0.952073	
		Sulfur	0.742888	
		Chlorine	0.174678	
		Titanium	0.393397	
		Iron	1.316699	
		Oxygen	69.1059	
5	Face of the icon number 112	Carbon	12.18437	lead white ($2PbCO_3 \cdot Pb(OH)_2$) and yellow iron oxide ($Fe_2O_3 \cdot 4H_2O$)
		Calcium	10.09271	
		Iron	1.549817	
		Aluminium	1.081189	
		Lead	22.09014	
		Silicon	2.510692	
		Magnesium	0.308795	
		Potassium	1.535387	
		Oxygen	69.08678	
			12.18437	
6	Face of the icon number 113	Carbon	10.13674	lead white ($2PbCO_3 \cdot Pb(OH)_2$) and yellow iron oxide ($Fe_2O_3 \cdot 4H_2O$)
		Calcium	8.55483	
		Iron	1.89711	
		Lead	21.52378	
		Aluminium	0.95278	
		Magnesium	0.48537	
		Silicon	2.28903	
		Potassium	1.57688	
		Oxygen	52.58347	

7	Halo of the icon number 112	Calcium	17.72147	metallic silver leaf, covered with colophon
		Carbon	12.01592	
		Iron	4.579725	
		Aluminium	1.703742	
		Silver	1.18262	
		Silicon	0.490081	
		Sulfur	0.753321	
		Phosphorus	0.71379	
		Oxygen	74.078	
8	Halo of the icon number 113	Carbon	11.3623	yellow metallic pigment based on S, Cr și Pb (realgar or orpiment) mixed with other earth colors.
		Silicon	10.86487	
		Aluminium	8.959683	
		Iron	2.591668	
		Sodium	1.848374	
		Potassium	1.477127	
		Sulfur	3.961862	
		Calcium	1.075373	
		Magnesium	1.474293	
		Lead	18.87234	
		Chromium	0.887938	
		Oxygen	36.62217	

The results obtained after OM and SEM-EDX were confirmed through micro-FTIR analysis, specific peaks being identified for several pigments and material used, as followed:

✓ natural ultramarine blue pigment 628, 655, 699 and 735cm⁻¹ in the micro FTIR spectrum of the icon number 112 (fig. 20a) and 639, 694 and 724cm⁻¹, in the spectrum of the icon number 113 (fig. 20b).

✓ For carbonates (calcium and lead based) 795, 829 and 886cm⁻¹ (fig. 20a), 816 and 883cm⁻¹ (fig. 20b), 849 and 887cm⁻¹ (fig. 21a), 812 and 845cm⁻¹ (fig. 22a), 801 and 868cm⁻¹ (fig. 22b).

✓ Earth green was identified by peaks specific to aluminosilicates: 1473 and 1581cm⁻¹ (fig. 20a), 1464, 1523 and 1599cm⁻¹ (fig. 20b), 1469 and 1599cm⁻¹ (fig. 21a), 1467cm⁻¹ (fig. 21b), 1468 and 1595cm⁻¹ (fig. 22a), 1467 and 1570cm⁻¹ (fig. 22b).

✓ The carbon black was identified by used peaks specific for tar: 1056cm⁻¹ (fig. 20a), 925 and 1060cm⁻¹ (fig. 20b), 921 and 1052cm⁻¹ (fig. 21a), 925cm⁻¹ (fig. 22a), 936 and 1015cm⁻¹ (fig. 22b). The presence of carbon black in the sample from the face of the icon number 112 is explained by the fact that the sample was taken from the shadow.

✓ For amidic group from peptides, the amino group and the carbonic group from amino acids: 1581 and 1680cm^{-1} (fig. 20a), 1523 and 1737cm^{-1} (fig. 20b), 1599 , 1678 , 1741cm^{-1} (fig. 21a), 1678 and 1739cm^{-1} (fig. 21b), 1595 and 1724cm^{-1} (fig. 22a), 1644 and 1736cm^{-1} (fig. 22b).

The colophon, with resin acids as a main component, the identification was done by the peaks specific for carboxylic, aldehydic and hidroxilic groups, as followed: in figure 20a, 1056 and 2012cm^{-1} , in figure 20b, 1060 and 2093cm^{-1} , in figure 21a, 2131cm^{-1} , in figure 21b, 1052 and 2093cm^{-1} , in figure 22a, 2090cm^{-1} and in figure 22b, 1061 and 2099cm^{-1} .

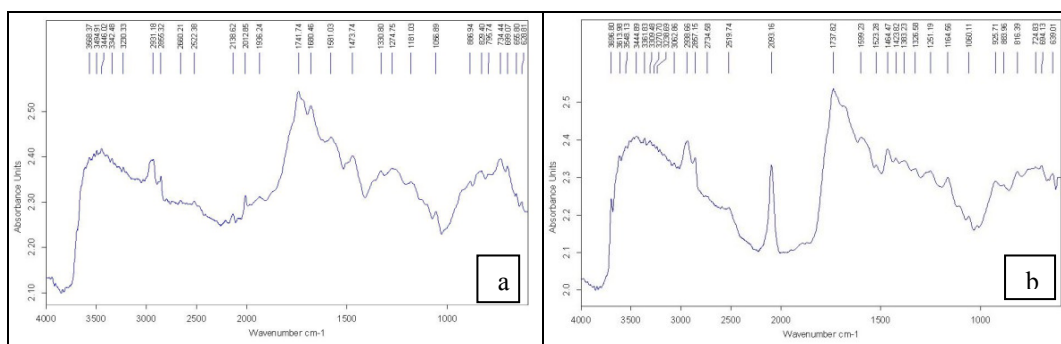


Fig. 20. Cloak micro-FTIR spectrum: a) icon number 112; b) icon number 113

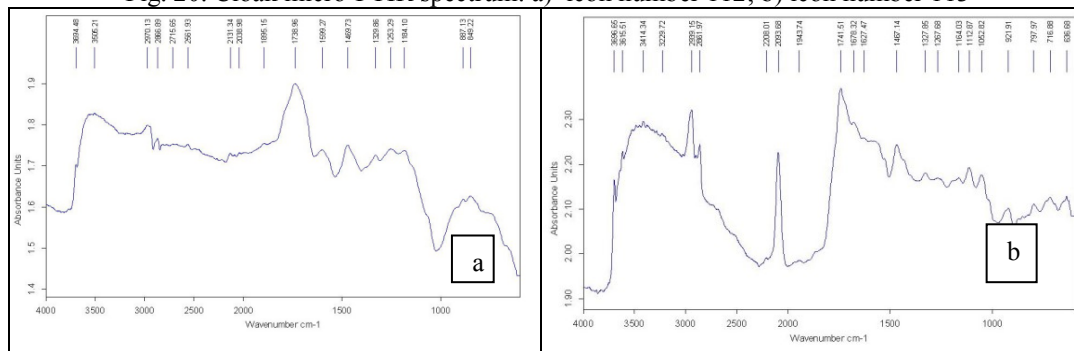


Fig. 21. Face micro-FTIR spectrum: a) icon number 112; b) icon number 113

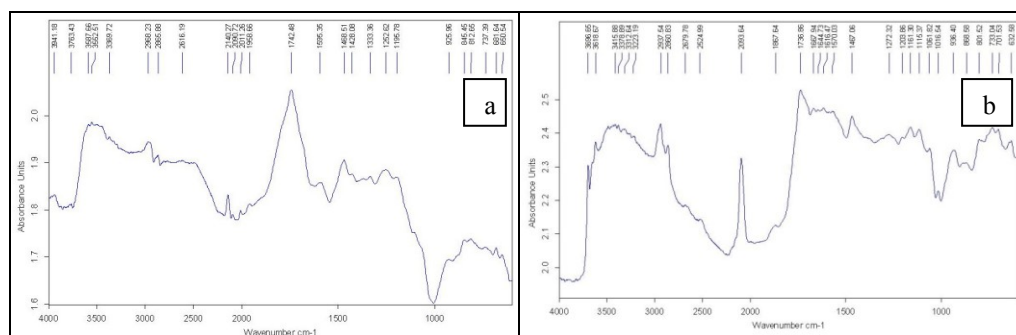


Fig. 22. Background micro-FTIR spectrum: a) icon number 112; b) icon number 113

Tab. 2. Micro-FTIR results

Nr.	Identified pigments	Peaks in sample from the cloak of icon number 112 (cm ⁻¹)	Peaks in sample from the cloak of icon number 113 (cm ⁻¹)	Peaks in sample from the face of the icon number 112 (cm ⁻¹)	Peaks in sample from the face of the icon number 113 (cm ⁻¹)	Peaks in sample from the background of the icon number 112 (cm ⁻¹)	Peaks in sample from the background of the icon number 113 (cm ⁻¹)
1	Natural ultramarine blue pigment	628, 655, 699, 735	639, 694 724	-	-	-	-
2	Carbonates (calcium and lead based)	795, 829, 886	816, 883	849, 887	-	812, 845	801, 868
3	Alumino silicates - earth green	1473, 1581	1464, 1523, 1599	1469, 1599	1467	1468, 1595	1570
4	Carbon black	1056	925, 1060	921, 1052	-	925	936, 1015
5	Amidic group from peptides, the amino group and the carbonic group from amino acids	1581, 1680	1523, 1737	1599, 1678, 1741	1678, 1739	1595, 1724	1644, 1736
6	Colophon, with resin acids as a main component	1056, 2012	1060, 2093	2131	1052, 2093	2090	1061, 2099

3. Stages of the restoration processes

The first stage of the restoration process is the consolidation of the painting layers in order to prevent the loss of other painting pieces already detached. The consolidation was done by fixing the painting layer with fish glue (8%) and Japanese paper.

The stopping of the xylophagous attack was done by encapsulating the two icons in a polyethylene bag for a period of 14 days. In the bag the value of oxygen

was reduced below 0.1% by replacing it with nitrogen (fig. 23-24). The nitrogen atmosphere in the bag was done with the help of a hose and adapter coupling. The operation of replacing the oxygen with nitrogen was repeated four times to ensure the required level of oxygen. After that the bag will be totally sealed and opened again at the end of those 14 days.

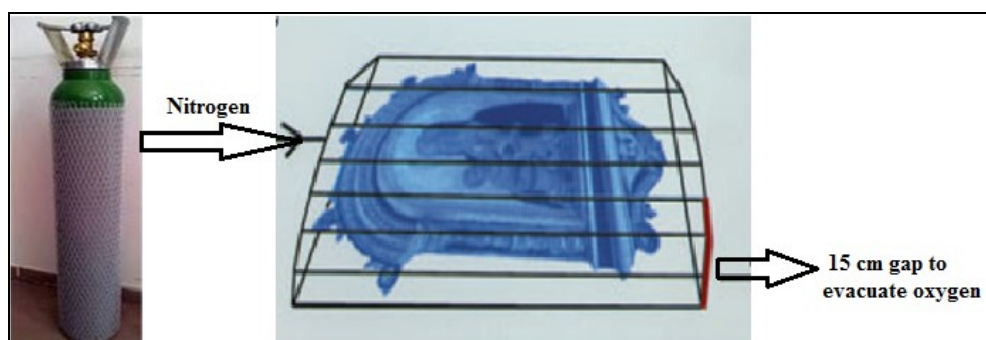


Fig. 23. The scheme of the criptoclimate



Fig. 24. Icon number 112 inside the criptoclimate

The next stage was to consolidate the two wooden panels with a mixture of colophony and natural bee wax, on a 1:1 ratio. The consolidation gave back the structural integrity that the two panels lost it as a consequence of the xylophagous attack (fig. 25) [17-19].



Fig. 25. Consolidating the wood support wiwax and colophony



Fig. 26. Cleaning test of the icon number 112

After that the painting layers were cleaned with a solution of ethylic alcohol and distilled water (1:1). This solution had the best results in the cleaning test executed as shown in the figure 26. After the clogged dirt was cleaned and the aged varnish was removed, the gaps of the two icons were also cleaned and then filled with a mixture of animal glue (8%) and charcoal. The filling will be applied in thin layers, with a window of a minimum 12 hours between applications, in order to ensure a proper exsiccation of the filled gaps. The filled gaps were sanded off and then reintegrated using *tratteggio* technique. The information obtained about the pigments used by the painters was taken into consideration in choosing the colors used for reintegration. Pigments with similar physical properties with those of the original colors were used.

After the gaps were reintegrated, the two icons were revarnished in order to ensure a proper protection against the future processes of deterioration and degradation that will affect the painting layers.

Conclusions

This study presented the stages of the restoration process of two XIX-th century icons, which are part of the cultural heritage of "Sfinții Mihail și Gavriil" from Moscu village, Galați. The icons suffer from a series of evaluative deteriorations and degradations processes, due to the improper storage environment. In order to reintegrate the two icons in the religious circuit, a restoration protocol was established and followed. A series of tests were employed, in order to determine the materials used by the painters, and then the established stages of the restoration protocol were followed: stopping the xylophagous attack by anaerobic treatment, consolidating the two wood panels and the painting layers, removing the clogged dirt and the degraded varnish, filling and sanding off the gaps, reintegration in *tratteggio* and varnishing the icons. For the chromatic

reintegration pigments with similar properties like the properties of the original colors were used. The study present the stages of the restoration process of the two XIX-th icons, that were affected by being kept in an improper environment from a climatic point of view, and the results of the analysis done in order to collect information. MO, SEM-EDX and micro-FTIR were done on five samples collected from each icon. The following pigments were identified: natural ultramarine blue, earth green, carbon black, yellow iron oxide, lead white, burned and unburned umber. It was also established that colophon was used to protect the painting layer. In both cases, the gold leaf usually used in byzantine painting was replaced with silver leaf covered with varnish (icon number 112) or with yellow metallic pigments (realgar or orpiment). The restoration process that started after the analyses had the following stages: : consolidation of the painting layer (fish glue 8% and japanese paper), stopping the xylophagous attack (encapsulation with nitrogen), consolidation of the wood supports (colophon and wax, 1:1), cleaning the painting layer (ethylic alcohol and distilled water, 1:1), filling the gaps and reintegrating the fillings in *tratteggio*, all followed by the process of varnishing the two icons.

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