More than gold – an interdisciplinary, complementary study of gilding materials and techniques in Baroque altarpieces from Portugal

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Resumo

O artigo apresenta um estudo interdisciplinar e multi-técnico dos materiais e das técnicas de douramento em vários retábulos Portugueses da época Barroca, desenvolvido durante um projecto de investigação financiado pela Fundação para Ciência e Tecnologia em Portugal (PTDC/EAT-EAT/116700/2010).

Foram usadas técnicas microscópicas, em conjunto com difracção de raios X, microtomografia computadorizada de raios X, espectroscopias de microFTIR e microRaman para caracterizar a estrutura estratigráfica de 49 amostras provenientes de 7 retábulos das áreas de Lisboa/Cascais e de Santarém. A investigação pretende ser também um estudo comparativo entre materiais e técnicas de douramento utilizados em retábulos do mesmo período histórico, mas provenientes de duas áreas geográficas diferentes.

Palavras-chave

Materiais e técnicas de douramento, retábulos Portugueses, época Barroca, estudo interdisciplinar

Abstract

The paper deals with an interdisciplinary and multi-technique study of gilding materials and techniques in several Portuguese altarpieces during the Baroque period, developed within a research project funded by the Portuguese Foundation for Science and Technology (PTDC/EAT-EAT/116700/2010).

Different microscopic techniques together with X-ray diffraction, X-ray micro-CT, micro-FTIR and micro-Raman spectroscopy were used to characterize the stratigraphic structure and gilding techniques of 49 samples taken from 7 altarpieces in the Lisbon/Cascais and Santarém areas. The research is also a comparative study between the gilding materials and techniques used in altarpieces from the same historical period but in two different geographical areas.

Keywords

Gilding materials and techniques, Portuguese altarpieces, Baroque époque, interdisciplinary study

Resumen

El artículo presenta un estudio interdisciplinar y multi-técnico de los materiales y de las técnicas de dorado en varios retablos portugueses del periodo Barroco, desarrollado durante un proyecto de investigación financiado por la Fundação para Ciência e Tecnologia en Portugal (PTDC/EAT-EAT/116700/2010).

Técnicas microscópicas junto con la difracción de rayos X, tomografia microcomputerizada, espectroscopias de micro-FTIR y micro-Raman fueron empleadas para caracterizar la estrutura estratigráfica de 49 muestras procedentes de 7 retablos de las áreas de Lisboa/Cascais y Santàrem. La investigación pretende también constituir un estudio comparativo entre materiales y técnicas de dorado utilizadas en retablos del mismo periodo histórico aunque de áreas geográficas diferentes.

Palabras-clave

Materiales y técnicas de dorado, retablos Portugueses, periodo Barroco, estudio interdisciplinar

Introduction

Within the Gilt-Teller (www.gilt-teller.pt), a research project funded by FCT (Portuguese Foundation for Science and Technology), an interdisciplinary team is studying from three different perspectives (historically, technically and analytically) the gilding materials and techniques [1] in the gilded woodcarved decoration ("talha dourada") from Portuguese churches during three centuries (ca. 1500-1800) [2].

The art known as "talha dourada", of a great scenographical component reinforced by the dogmas instituted after the Trento Council (1545-1563), was a privileged art, transversal to different stylistic époques not only in Portugal but also in all the countries of Portuguese expansion and influence [3-4]. The most florishing expression of this art occurred during the Baroque époque, namely between the XVIIth and XVIIIth centuries. Portuguese Baroque talha can be attributed to two different stylistic moments: one that generally corresponds to the reign of Pedro II (designated as "national style"), and another that is usually associated to the reign of his son, João V – hence its designation of "Joanin style" [5].

The "national style" altarpiece was widely accepted throughout the country, from the larger, most relevant cities, to the smaller, more isolated towns of inland Portugal. In these churches the altarpiece is projected as an individual entity, a closed-up and powerful space. It makes use of spiral-like columns, that tend to prolong themselves way into the top of the retable. At the centre, a void space with premeditated dimensions is created, in order to place the eucharistic throne, usually in the shape of a pyramid. The use of concentric archivolts, the profusion of sculpture attached to the structure, and the presence of spiral-like columns that prolong themselves into the arches produces a dynamic composition, resulting in an overall sense of movement and dazzlement.

The definition of altarpiece (retable) comes from Latin: *retro* - behind, and *tabula* – table (panel), indicating the sacred place where the Eucharistic mass is celebrated and the panel behind the altar or around it, creating visual and spiritual motivations for celebrating the religious cult. It is the place as excellence where the eyes of the faith are centered. For this reason the embellishment with gold leaf of retabular surfaces, sculptures or other artistic works served as symbol of magnificence and devotion shown by the artists with the purpose of worshiping God. This form of art will create true schools where art craft masters specialized themselves in carving, gilding and applying the polychrome layers on the wood.

A classical stratigraphic structure of gilding on wood [6-7] in watergilding technique was made of the following components: a sizing animal glue layer (added with some garlic pieces, mixture named "alhada" in the XVIIIth century) applied still hot by brush, to impermeabilize the support; a white preparation, made of *gesso* (name given to the ground layers made of Ca sulfates) and in some cases with addition of chalk, frequently *gesso grosso* (usually made of anhydrite) overlapped by *gesso fino or mate* (dihidrated calcium sulfate or gypsum), bound with animal glue, in a total of 1 to 5 layers each; a bole reddish colored layer, made of argillous materials or mixed with ochres, traditionally named *Armenian bole*, bound by animal glue and applied by very soft brushes (known as *pituá*) in 3 to 5 layers; good quality gold leaves (*ouro de lei*), that could be made of pure gold or alloyed with silver and/or copper, applied over the bole with very diluted animal glue solution (*água de cola*); final polishing of the gilded leaf with agate burnishers; polychromy obtained by overlapping layers of tempera color (pigments mixed with an egg-based binder) where the drawings were left visible (using a sharp tool, *sgraffito) or estofado technique*, showing vegetal, zoomorphic or geometric motives outlined with a fine brush [8-10]. In the more hidden carved areas of the retables or sculptures the gilding could also be done using a mordant, being a method more immediate and less expensive than the water gilding. The mordant gilding can be also applied sometimes in visible areas to produce different optical effects.

The research pretends to be also a comparative study between the gilding materials and techniques used in altarpieces from the same historical period (*national Baroque* with the exception of the altarpiece in Salvaterra de Magos identified stilistically as belonging to the *proto-Baroque*) but in different geographical areas, not very far one from another. Four main altarpieces (one from the church of Our Lady of Purification in Bucelas, Loures - PT-AM-NSPLx; one from Our Lady of Victory in the Cidadela Palace, Cascais - PT-AM-

-PCC; one from the parish church of Tancos, Santàrem - PT-AM-Ta and another from the parish church of Salvaterra de Magos, Santàrem – PT-AM-Sal) and three lateral altarpieces (lateral altarpiece from Our Lady of Sorrow in Lisbon - PT-AL-NSPLx, right lateral altarpiece of Our Lady of Glory - PT-AL-NSCSt and left lateral altarpiece of Our Lady of Conception - PT-AL-SGSt, both in the Cathedral of Santàrem) were taken into study (Figure 1 and Table 1). The lack of work contracts providing information on gilding materials and techniques justified the need for undertaking a close observation of the retables during sampling and to perform a complex analytical investigation on the collected samples. With the exception of the lateral altarpiece in the Church of Pena (Lisbon) all the other were subject to posterior interventions of re-gilding (partially or totally), over-painting or conservation-restoration (mainy cleaning and filling of lacunas).

Figure 1 – The 7 studied altarpieces.

Geographical area	Altarpiece acronym	Dates	Work contract	Names of artists/ craftsmen	Other comments
Lisbon, Pena	**PT-AL-NSPLx**	XVIIIth century	no	no	-
Loures, Bucelas	**PT-AM-BULx**	XVIIIth century	no	no	Posterior interventions of restoration and punctual re-gilding
Cascais	**PT-AM-PCC**	XVIIIth century	no	no	Posterior interventions of over-painting
Santàrem, Tancos	**PT-AM-Ta**	1696 (carving)	yes	José Ramalho (carver)	Re-gilding (imitation of gold) intervention in some areas
Santàrem, Salvaterra de Magos	**PT-AM-Sal**	1666 (carving)	no	Afonso Vaz de Castro ? (marketer and carver)	Posterior intervention of restoration
Santàrem, Sé (Cathedral)	**PT-AL-NSCSt**	1703 (carving)	yes (carving contract)	Manuel Álvares (carver)	1994-1996 – intervention of conservation and restoration
	PT-AL-SGSt	1705 (structure, the *24 Ancients from Apocallipse*) 1709 – 1710 (carving)	yes (carving)	António Martins Calheiros (carver - structure) Matias Rodrigues de Carvalho (carver) José Pereira Lobo (carver)	

Table 1 – Main data on the sampled altarpieces.

Materials and methods

Different microscopic techniques (stereomicroscopy, optical microscopy and scanning electron microscopy) together with X-ray diffraction, micro-computerized tomography (micro-CT), microFTIR and microRaman spectroscopy were used to characterize the stratigraphic structure and gilding techniques of 49 samples taken from the 7 eucharistic and devotional altarpieces in the area of Lisbon and Santàrem previously identified (Table 2). The sampling areas cover different surface decoration techniques (gilding, estofado, flesh polychromy) and positions on the lower part of the altarpieces, such as tabernacles, throne, columns, decorative vegetal motives on *predela* and antropomorphic representations (Table 3)[4].

Altarpiece acronym	No of samples	Optical microscopy (Vis, UV)	Sypro staining	SEM-EDX	u-CT	XRD	u-Raman	u-FTIR
PT-AL-NSPLx	4	X	X	X	X	X		X
PT-AM-BULx	10	X		X	X	X		X
PT-AM-PCC	6	X	X	X			X	
PT-AM-Ta	6	X		X		X		
PT-AM-Sal	6	X		X				
PT-AL-NSCSt	9	X		X			X	
PT-AL-SGSt	8	X		X			X	

Table 2 – Analyses performed on the 7 altarpieces.

The microscopic observation under visible light was complemented with UV fluorescence on cross-sections and with a specific stain for proteins (Sypro Ruby) useful to map and identify the presence of animal glues in the different layers of the gilded composites [11]. The SEM and micro-CT imaging [12] contributed to the characterization of the layers morphology and peculiarities of technique (such as the difference between *gesso grosso* and *gesso mate* in the ground layers), while the energy dispersive X-ray spectrometric elemental analysis (EDX) mapped the constitutive elements for each layer and identified the karat values for the gold leaves. Inorganic (inert charges, pigments) materials were identified using XRD, SEM-EDX, microFTIR and microRaman techniques, while for the organic (binders and varnishes) components mainly staining tests on cross-section and microFTIR spectroscopy were applied [12].

- ***Optical microscopy (OM) complemented by staining test with Sypro Ruby***

Cross-sections were obtained using a polyester embedding resin (Crystal) with hardener. After curing, the resin blocks were cut and polished to reveal the gilding/paint/ground composite in cross-section. The cross-sections were dry polished with successively finer grades of Micro-mesh abrasive cloths (600, 800, 1200 and 4000 mesh). A felt was used for the final polishing. Water or other aqueous-based liquids were avoided during polishing since they could dissolve the proteinaceous component in the samples [13-14]. The cross-sections were observed at different magnifications (from 50x to 500x) using an Axioplan Zeiss 2 imaging binocular microscope and the images were acquired using a Nikon DXM1200F digital camera, coupled to the microscope. The filter blocks used for observing the fluorescence were filter 8 (G 365, FT 395 and LP 420) and filter 6 (BP 450-490, FT 510 and LP 515). Visual light observations (illumination position for dark field observation, abbreviated as f2) were performed in reflection geometry.

A fluorescent stain, Sypro Ruby [11], was applied on some cross-sections for mapping the proteinaceous binders in the ground, bole layer and paint layers [15-16]. The procedure is easy to apply (1 drop is applied directly on the cross-section surface using a Pasteur pipette) and has a very good detection limit (nanogram order), being preferred to other stains commonly used in the conservation field for protein detection and mapping.

- ***X-ray diffraction (XRD)***

Powder and/or flat samples were submitted to XRD analysis using a X´PERT Panalytical difractometer, with Cu Kα radiation, in order to characterize the existent crystalline phases. Special attention was done to the mineral composition of the preparation mixtures and different polychrome samples. The analysis of the results is performed with the X´PERT PLUS program using a PDF2 data base. The interpretation of the diffractograms obtained by direct incident beam in the small flat fragments (non destructive analysis) could be rendered difficult by the limited size/amount of the samples or by preferential orientation. Therefore, complementary qualitative elemental information, provided by XRF analysis, has been used in phase determination.

- ***Scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDX)***

A Bruker X'Flash 5010 X-ray energy spectrometer coupled to a Hitachi S-3700N electron microscopy was used to obtain the backscattering images, point analysis and chemical mapping data on cross-sections. The equipment operates a 20KV in order to get the Kα and the Lα peak of the element of interest and with a working distance of 10mm. The cross-sections were previously coated with graphite.

- ***Micro-computerized tomography (μ-CT)***

X-ray microtomography allowed a three-dimensional (3-D) observation of the samples without sample preparation or chemical fixation [17]. Digital radiographs have been acquired with a μ-CT SkyScan 1172 (Brucker) instrument using an X-ray cone incident on a rotating specimen. The instrument comprehends a 1.3 Megapixel camera and is able to reach spatial resolutions of 5 μm with a detail detectability of 2 μm. The maximum object diameter is 20 mm for standard operation and 37 mm with a camera offset. Due to the sample variable size and composition the experimental conditions have been optimized for each sample using a constant source power (10W). Highly opaque pieces were investigated with source voltage and current of, respectively, 100kV and 100 μA. Downstream 0.5 mm aluminum filtration was used to increase beam penetration in the samples in order to prevent "beam hardening", a nonlinear X-ray absorption effect. The acquisition was performed by rotating the sample over 180° with variable rotational step. The pixel size is chosen according the size of the analyzed objects and the final magnification of the radiographic images. The data set after acquisition consisted of transmission X-ray images saved as 16 bit TIFF files and presented in Hounsfield units (HU) or attenuation coefficient units (mm^{-1}); the number of images acquired depended on the rotation step selected. The gilded samples radiographs showed relatively high contrast due to the difference in X-ray absorption between layers. A modified Feldkamp cone-beam algorithm (http:\\skyscan.com) has been used to reconstruct 3-D representations of the internal microstructure with mitigation of beam hardening and ring artifacts. Two sets of vertical slices (coronal and sagital) could be generated by default in 3-D reconstructions. Slice reconstructions have been obtained with the NRecon 1.6.3 routine and volumetric visualization has been achieved with DataView and CTvox programs, which integrate the instrument software packages. The CTvox allows the 3D virtual visualization (image or video) of the samples.

- ***Fourier Transform Infrared Micro-spectroscopy (μ-FTIR)***

A Nicolet Nexus spectrophotometer interfaced with a Continuum microscope with a MCT-A detector cooled by liquid nitrogen was used. The spatial resolution is 100 mm, the spectra being obtained with a resolution of 4 cm^{-1} and 256 scans, in transmission mode, in an interval between 4000 and 650 cm^{-1}, using a Thermo diamond anvil compression cell.

- ***Raman micro-spectroscopy (μ-Raman)***

For microRaman analysis a microspectrometer HORIBA XPlora equiped with a 785 nm laser was used. The spectra were acquired in extended scanning mode, in the region 100-2000 cm^{-1}. The laser beam was focused with lens of 50x from Olympus, with a laser power on the sample's surface of 1.1 mW (5 seconds of exposure, 15 cicles of accumulation).

Results and Discussion

The multi-technique and multi-layer approach was aimed to answer to several issues related with gilding materials and techniques, such as: differentiation between *gesso grosso* and *gesso mate* in the structure and composition of the ground layers; differentiation between ground, bole layers and metal leaf and their elemental characterization; identification and mapping of inorganic and/or organic phases in the whole composite.

As shown in the Figure 2, there is a certain similarity in the structure, appearance and composition of gilding layers for all the altarpieces with few exceptions where two gilding phases or later over-painting were detected.

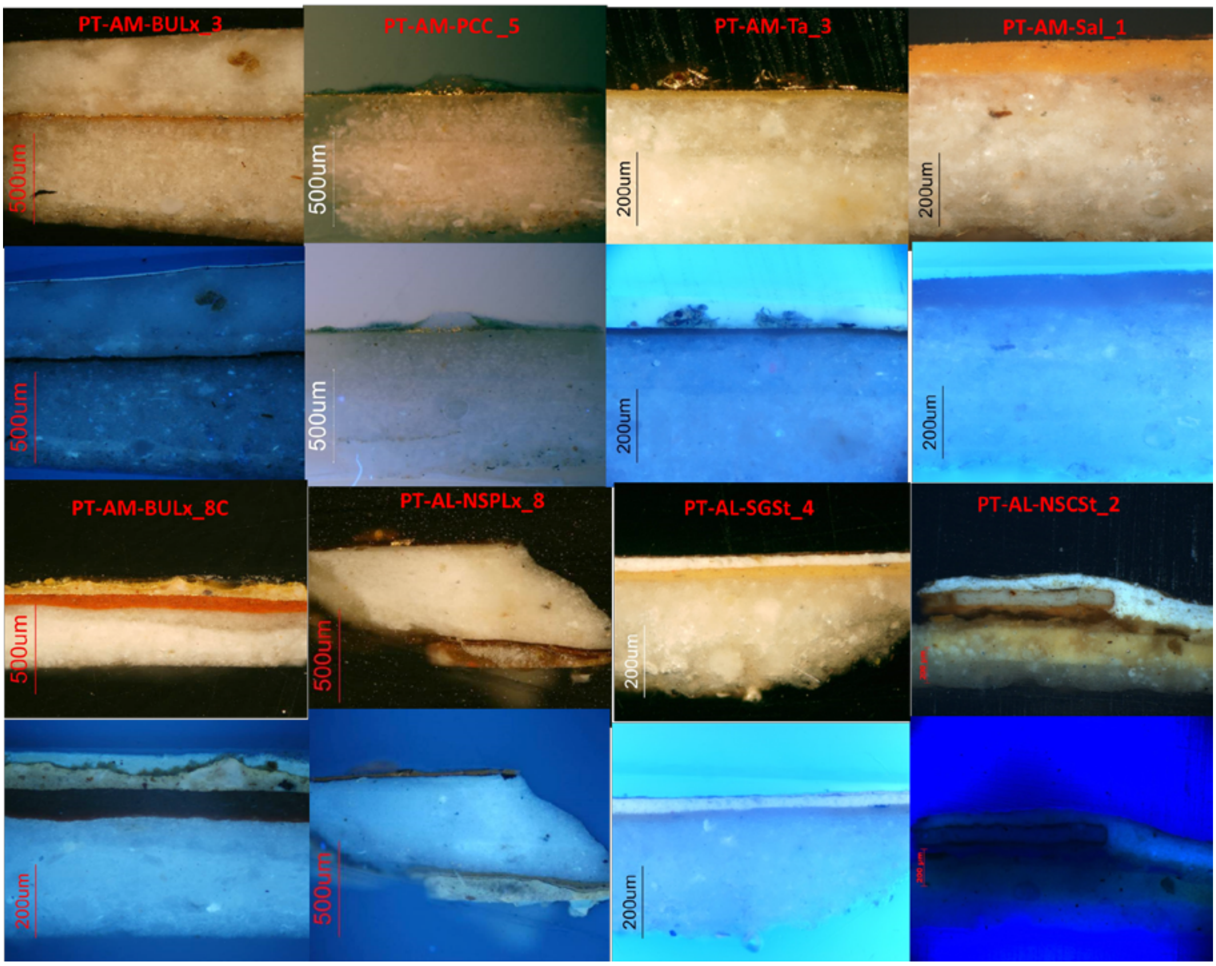

Figure 2 – Examples of the stratigraphy of the gilding layers in the 7 altarpieces, observed by optical microscopy in Vis and UV light.

The stratigraphy is generally made of *gesso grosso/gesso fino* layers (anhydrite/gypsum) of ground (variable thickness, from 200 μm to ca. 600 um) (Figure 3), red or yellow ochre bole layers (with variable thickness, from 20 μm to few μm – Figures 2 and 4) and the metal leaf, just few micrometer thickness. Chalk (calcite) was identified in few samples (PT-AM-BULx_7 and 8; PT-AM-PCC_2) in mixture with gypsum. As the micro-CT and SEM techniques show in Figure 3 the *gesso grosso* layers present a coarser and heterogenous granulometry while the *gesso mate* layers are composed of finer and more homogenous crystals.

The bole layers are mainly made of iron oxides (Fe) and clay minerals (XRD analysis identified kaolinite, quartz and muscovite in layers of yellow ochre). Generally each sample has only one color of bole, with the exception of PT-AM-BULx_8 where a first layer of red bole is present, overlapped by a second yellow layer (Figure 2). In this specific case, based on the pattern of the stratigraphic components and leaf regularity the presence of two techniques of gilding was identified, water gilding over the red bole and mordant gilding over the yellow layer.

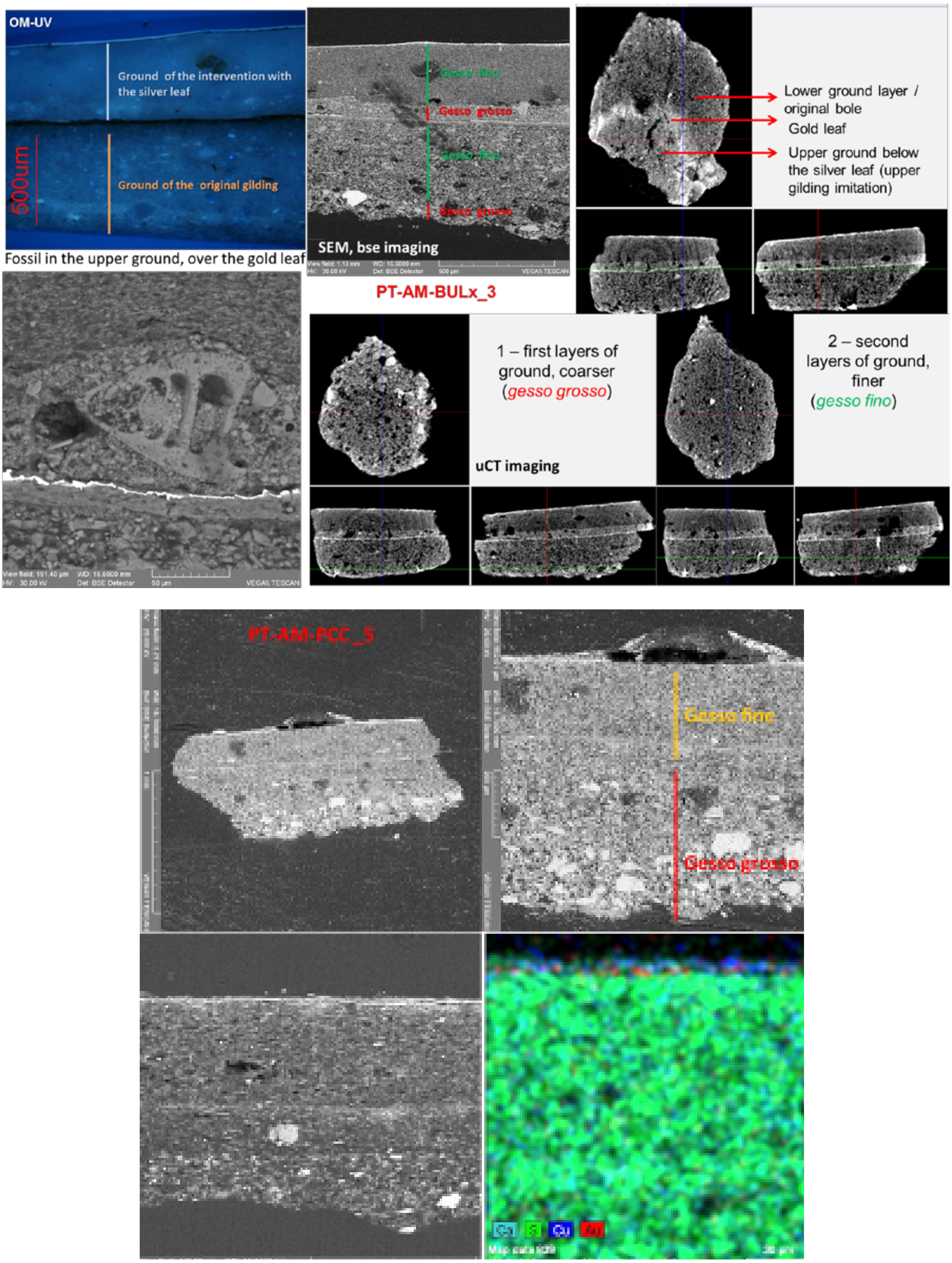

Figure 3 – The *gesso grosso/gesso fino* technique in the ground layers using μ-CT and SEM-EDS imaging, samples PT-AM-BULx_3 and PT-AM-PCC_5.

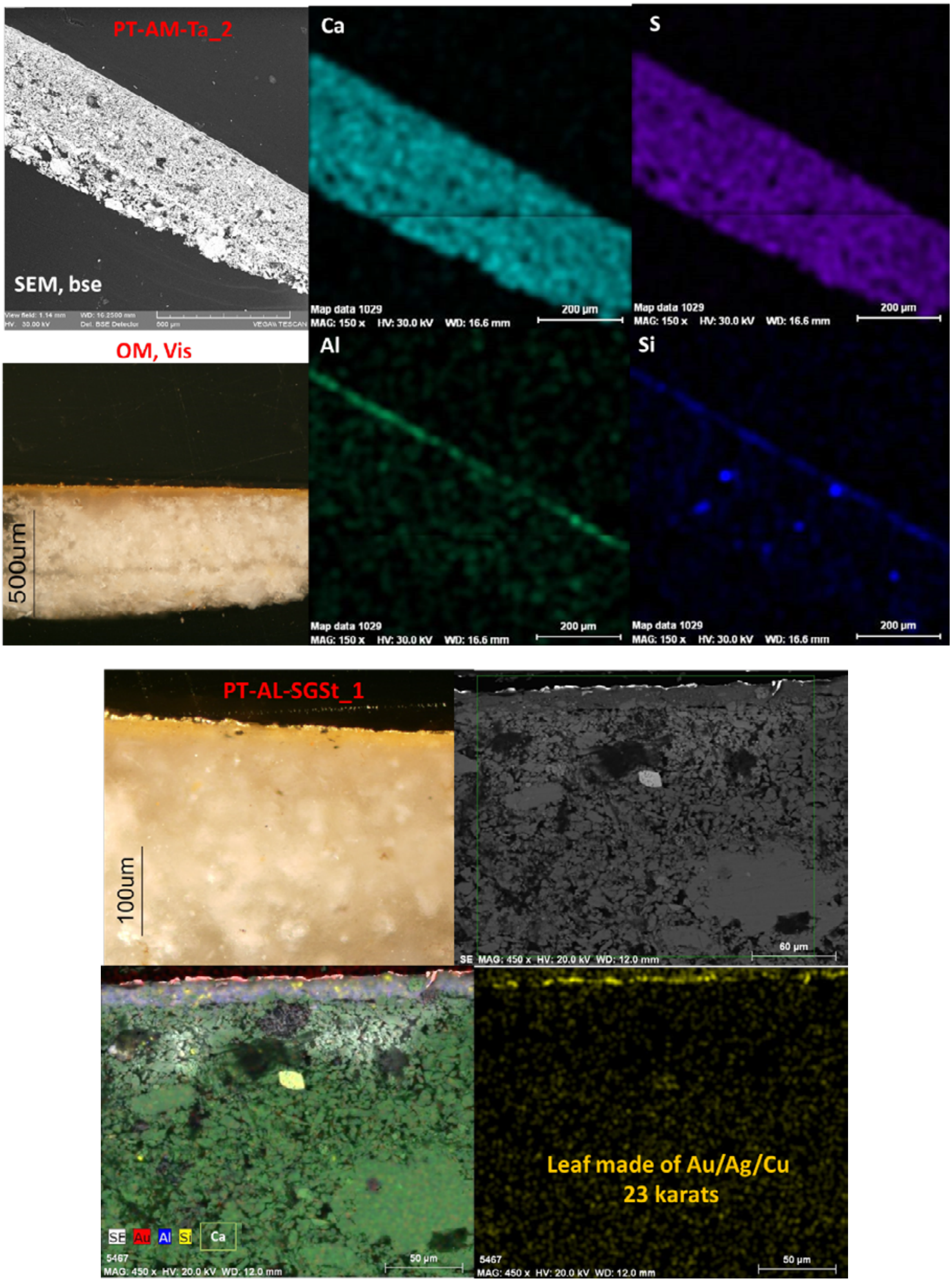

Figure 4 – SEM-EDS elemental mapping of ground and gilding layers in the samples PT-AM-Ta_2 and PT-AL-SGSt_1.

In some samples (e.g. PT-AM-BULx_3, PT-AM-PCC_6), two phases of gilding were identified, the upper layers being probably from later interventions of re-gilding (the leaf being of poorer quality than in the lower layers of gilding or an imitation of the gold leaf with Cu-Zn leaf as it is the case of PT-AM-Ta_3, Figure 5). Generally the gold leaf was identified to be an alloy of Au with Ag and Cu (from 21 to 23 karats purity – Table 3) applied with the water gilding technique (Figure 6). These results are consistent with other studies performed on gold leaf from Portuguese retables [9-10, 18].

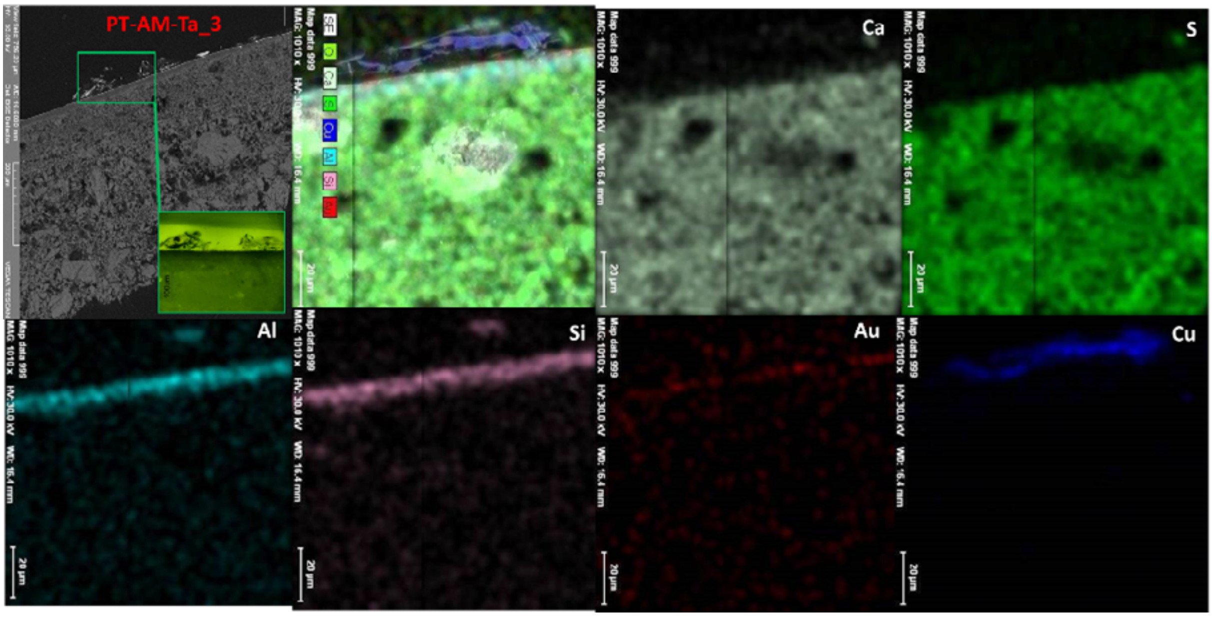

Figure 5 – Elemental EDS mapping of sample PT-AM-Ta_3.

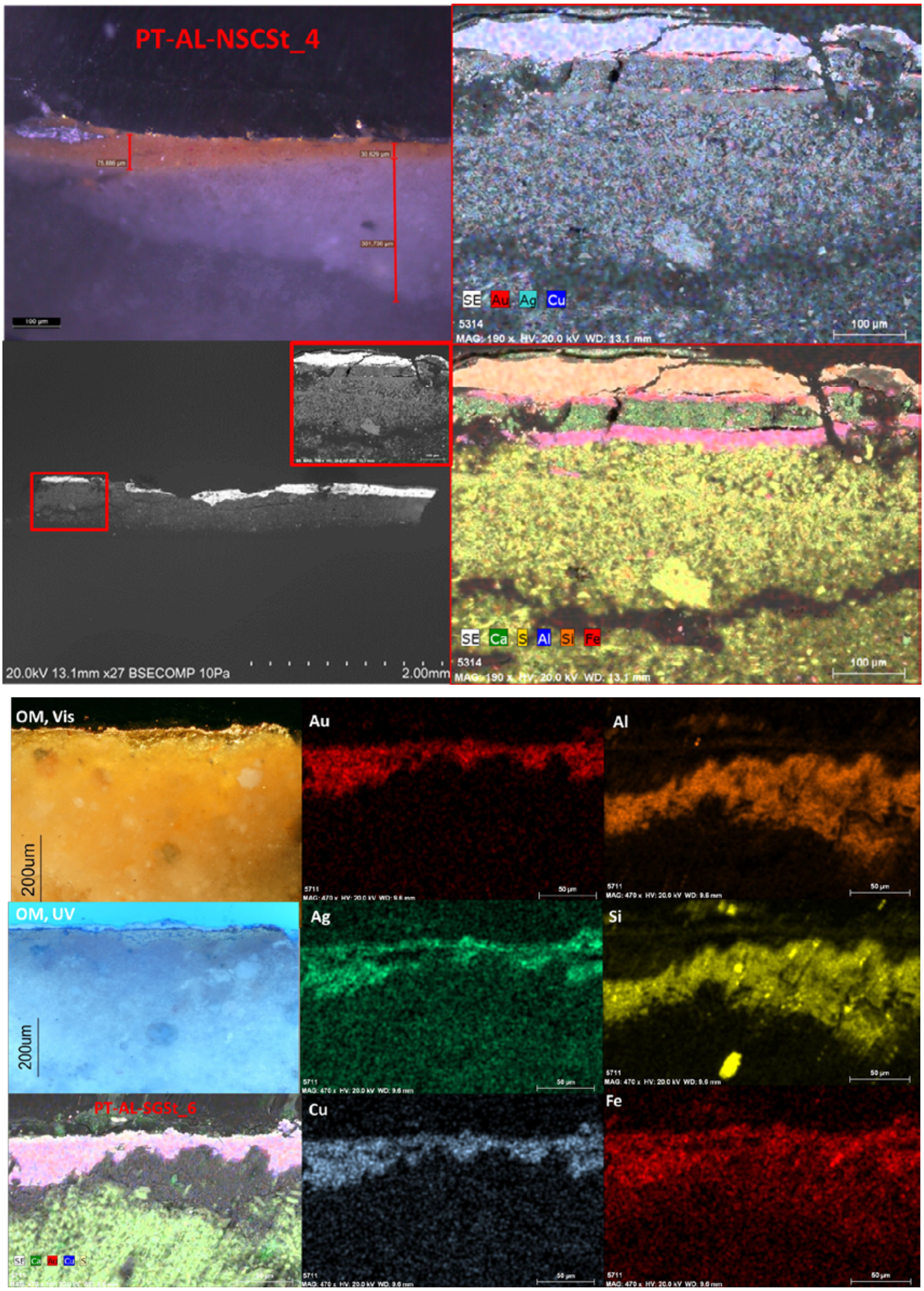

Figure 6 – OM imaging and EDS elemental mapping for cross-sections of samples collected from 2 altarpieces from the same church (PT-AL-NSCSt_4 and PT-AL-SGSt_6).

Only in a sample from *estofado* area (PT-AM-Ta_6) Au and Cu were detected in the composition of the leaf but this can be due to an error in the detection of Ag in this case as other samples from the same areas/technique of gilding showed an alloy composition of Au/Ag/Cu.

Silver leaf was also identified in the case of the lateral altarpiece of the Nossa Senhora da Pena church in Lisbon and as upper layer for the Bucelas main altarpiece (Table 3).

Altarpiece acronym	**Sample acronym**	**Sampling area**	**Leaf composition**	**Karats** (average value)
PT-AL-NSPLx	PT-AL-NSPLx_7	Silver leaf (?), burnished and in good conservation state from a volute of the left side of the altarpiece	Ag	-
	PT-AL-NSPLx_8	Silver leaf (?) with mate appearance, in bad conservation state, with many lacunas with dark borders from a volute of the left side of the altarpiece	Ag	-
PT-AM-BULx	PT-AM-BULx_3	Fragment of wood with gilding layers (silver?) from the backside of the main altarpiece	Ag (superior gilding)	-
			Au/Ag (inferior gilding)	21
	PT-AM-BULx_4	A fragment from an area with bole and gold leaf	Au/Ag/Cu	22
	PT-AM-BULx_6	B fragment from an area with “sgraffito” decoration	Au/Ag/Cu	23
	PT-AM-BULx_8	C fragment from another area with an yellow varnish over the leaf that has the appearance of wax	Au/Ag/Cu	23
PT-AM-PCC	PT-AM-PCC_5	Throne of Main altarpiece - right side of Putti’s hair	Au/Ag/Cu	22-23
	PT-AM-PCC_6	Throne of Main altarpiece - left side, nose of Putti	Ag/Cu (superior gilding)	73-89% Ag
			Au/Ag/Cu (inferior gilding)	23

Altarpiece acronym	Sample acronym	Sampling area	Leaf composition	Karats (average value)
PT-AM-Ta	PT-AM-Ta_3	Gilded fragment from carved area with lacunas in the ground and visible intervention of re-gilding	Cu/Zn (superior gilding)	-
			Au/Ag/Cu (inferior gilding)	21
	PT-AM-Ta_5	Blue "estofado" fragment from the tabernacle's angel aisle	Au/Ag/Cu	22-23
	PT-AM-Ta_6	Red "estofado" fragment from the tabernacle's angel aisles	Au/Cu	23
PT-AM-Sal	PT-AM-Sal_2	Fragment from an area of the in between panels of the left side column	Au/Ag/Cu	23
	PT-AM-Sal_6	Fragment from the right side of the altarpiece, with white and grey over-painting	Au/Ag/Cu	23
PT-AL-NSCSt	PT-AL-NSCSt_1	White polychrome area over the altarpiece table, previously gilded	Au/Ag/Cu	23
	PT-AL-NSCSt_4	Gilding from a predela's volute of the right side of the altarpiece	Au/Ag/Cu	23
PT-AL-SGSt	PT-AL-SGSt_1	Gilding from a predela's carved flower	Au/Ag/Cu	23
	PT-AL-SGSt_5	Gilding in "estofado" technique from the clouds of the tabernacle's door	Au/Ag/Cu	22-23
	PT-AL-SGSt_6	Gilding in "estofado" technique from the red garment of Christ of the tabernacle's door	Au/Ag/Cu	23

Table 3 – Composition of metal leaf in the analysed retables.

In case of PT-AL-NSPLx the silver leaf presents a coating, identified as shellac varnish (according its typical color of fluorescence and micro-FTIR analysis, Figure 7). This is the only altarpiece entirely covered with silver leaf in a church where the main altarpiece presents gold leaf (www.gilt-teller.pt) and the presence of shellac as its coating shows the intention of imitating the appearance of the gold leaf with this technique. Silver was also identified in the sample from the backside of the main altarpiece from Bucelas (PT-AM-BULx_3 – Figure 3a) and its presence is pointing on the intention of covering a surface not immediately visible to the eye with a poorer quality leaf.

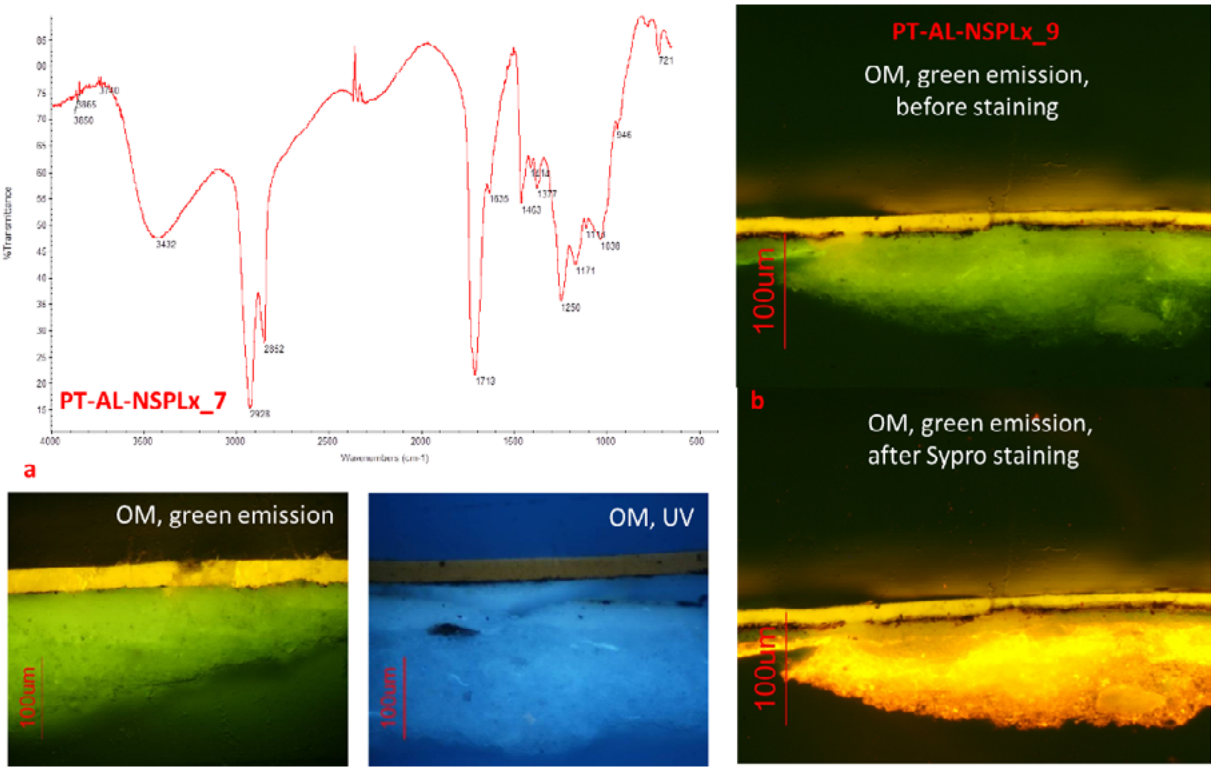

Figure 7 – Two examples of the organic materials identified and mapped in the stratigraphic layers: a) shellac varnish for silver leaf protection in samples from PT-AL-NSPLx identified by μ-FTIR and OM fluorescence; b) Sypro staining for mapping animal glue in the ground layers of sample PT-AL-NSPLx_9.

The ground and “bole” composition in these two cases shows similarities: Ca, S, O were detected for both gold and silver leaf composites and Al, Si (Fe only for the ochre bole in the lower original gilding in the sample from Bucelas altarpiece) for the layers beneath the leaf (Figure 8). In case of the sample from Bucelas the difference between *gesso grosso* and *gesso fino* layers is more obvious in the upper part of the stratigraphy, over the original gold leaf, while the ochre bole is present in the lower part, beneath it (Figures 3a and 8a). The *gesso grosso* layers of the upper composite includes fossils remnants visible in the bse SEM image (Figure 3a) and the elemental mapping (Figure 8a) shows a higher concentration of Ca in this layer. These two findings would possibly indicate a mixture of Ca-based materials (calcite and Ca sulphate). As the XRD analysis on other samples from the same altarpiece (e.g. sample 7) identified the presence of calcite in the ground this assumption can be considered correct.

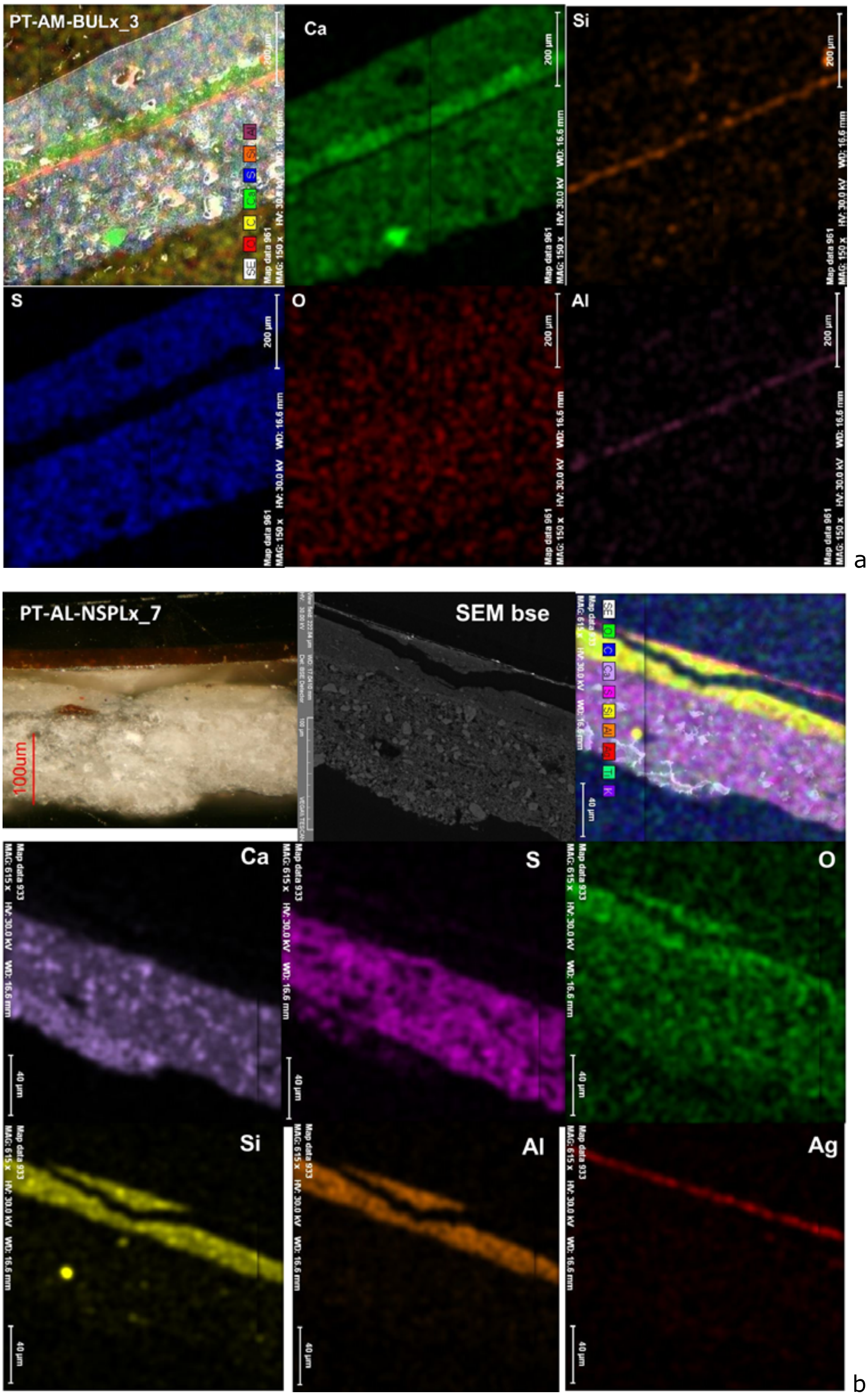

Figure 8 – Elemental mapping by SEM –EDX on two samples with silver leaf: PT-AM-BULx_3 (a) and PT-AL-NSPLx_7 (b)

The presence of organic materials as protective or aesthetic coating over the leaf was identified in case of some altarpieces (PT-AL-NSPLx – shellac, Figure 7; PT-AM-PCC – wax, Figure 9), for the others their absence possibly indicating cleaning or other restoration interventions. In some cases in Santarem (PT-AL-NSCSt; PT-AL -SGSt; PT-AM-Sal) these interventions were documented [19-20] while for others (e.g. Bucelas) the visual assessment of conservation state of the altarpiece decoration and the interview with the parish of the church confirmed them.

For the main altarpiece of Cidadela Palace in Cascais, residues of an waxy protective material (with aproximately 50 µm thickness and with no specific florescence answer to the protein staining with Sypro Ruby) with fissures and cracks along its thickness are observed in cross--section. In this layer the SEM mapping detected the presence of Zn, probably a zinc oxide contamination from a posterior intervention on the altarpiece (Figure 9).

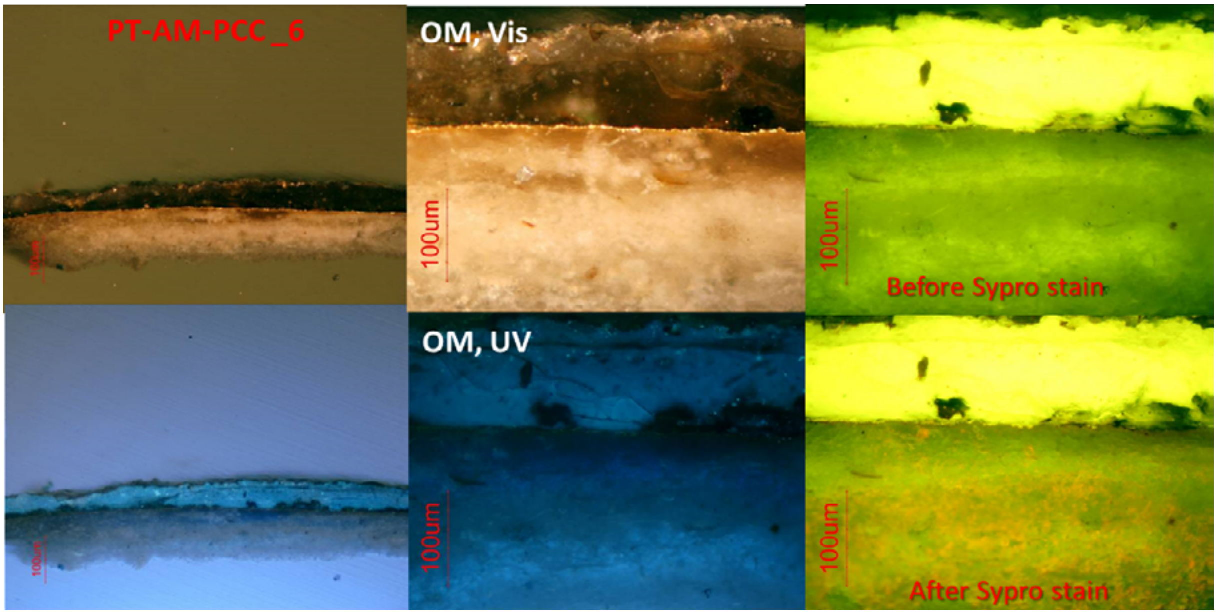

Figure 9 – OM characterization of waxy-material as protective layer in case of sample PT-AM-PCC_6.

Polychrome layers were also detected in some samples in correspondence of flesh tones in the anthropomorphic representations on taberbacle's doors or as part of the columns decorations or other colored areas such as in the *marmoreado* technique applied above the altarpiece tables in Santàrem (PT-AL-NSCSt_1 and 2) and in the altarpiece of Cidadela Palace (PT-AM-PCC_2). In few cases (e.g. PT-AL-NSCSt; PT-AM-PCC) their presence testify some intervention using recent pigments, such as barite (Figure 10) and zinc white (Figure 9). Traditional inorganic materials, such as calcite (e.g. white layers in samples PT-AL-SGSt_4); lead white (identified as cerrusite by µ-Raman in samples PT-AL-NSCSt_2 – Figure 10, PT-AL-SGSt_4, PT-AM-Ta_4 and PT-AM-Ta_5) and cinnabar (PT-AM-Ta_6, PT-AL-SGSt_4 and PT-AL-SGSt_8) were also detected in the polychrome decorations.

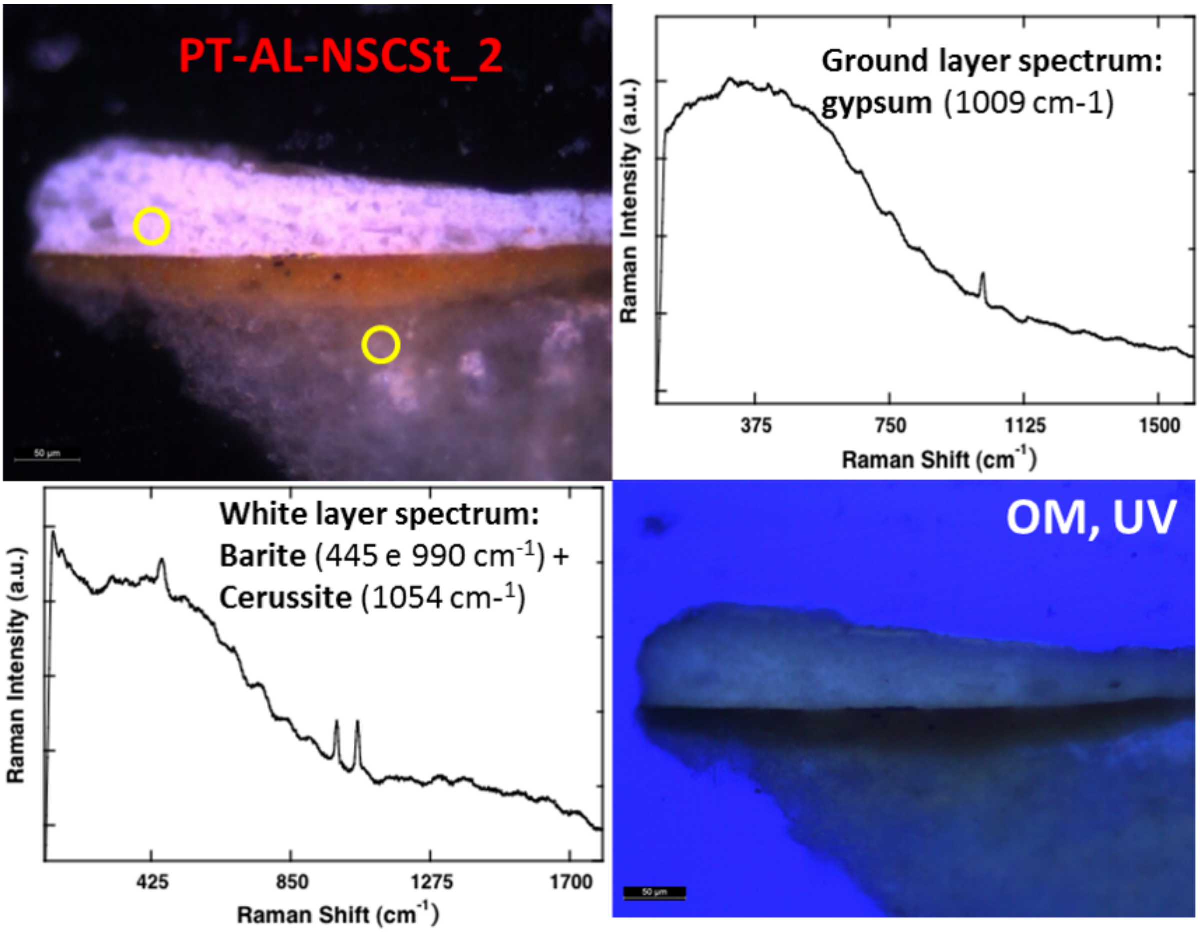

Figure 10 – OM and µ-Raman results for sample PT-AL-NSCSt_2.

Conclusions

The results show the characteristics of a stratigraphic pattern used in water gilding technique (ground layers of variable thickness, bole layers of different colours - red or yellow ochres, and the thin metal leaf) and the use of gold leaf (made of Au alloyed with Cu and Ag; 21, 22 and 23 karats) in most of the cases studied in the present paper. The most common value for gold leaf purity is 23 karats which indicates a high quality of the leaf used for gilding both for tabernacle and decorative elements and also for "estofado" decorations. The PT-AL-NSPLx is the only altarpiece entirely covered with silver leaf in a church where the main altarpiece presents gold leaf (www.gilt-teller.pt) and the presence of shellac as its coating shows the intention of imitating the appearance of the gold leaf with this technique.

In few altarpieces the imitation of gold leaf appearance was done with silver leaf (as pure silver or alloyed with copper) and a varnish with an orange color or with copper-based leaf. The presence of Cu/Zn based leaf for the main altarpiece in Tancos (PT-AM-Ta), Ag/Cu leaf for the main altarpiece in Cidadela Palace (PT-AM-PCC) and Ag leaf with shellac varnish for the main altarpiece in Bucelas church (PT-AM-BULx) in the layers overlapping previous original gilding layers points on later interventions of imitation of the gold leaf.

The original gilding technique is the water gilding using ochre bole layers but in one case mordant gilding is supposed to be applied over other layers made with a water gilding recipe (sample PT-AM-BULx_8).

The gesso (*gesso grosso* and *gesso fino*) grounds are common for all the altarpieces, with the exception of Bucelas and Cidadela-Cascais altarpieces where chalk/calcite (containing fossils in case of Bucelas ground layers) was identified in mixture with the Ca sulfates.

In some cases polychromy can be found, especially in the representation of ornamental antropomorphic (e.g. angels, Christ from the tabernacle's scene of Ressurection) or vegetal motives and traditional materials were identified such as calcite, lead white and cinnabar for white and pink/red areas. Polychrome layers belonging to more recent over-painting (containing barite and zinc white) were also found in one lateral altarpiece in Santárem (PT-AL-NSCSt) and in the main altarpiece of Cidadela Palace (PT-AM-PCC).

These results on the material composition and stratigraphic pattern of gilding layes and techniques are consistent with other studies performed on Portuguese retables in the same historical period.

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