An Innovative, Interdisciplinary, and Multi-Technique Study of Gilding and Painting Techniques in the Decoration of the Main Altarpiece of Miranda do Douro Cathedral (XVII-XVIIIth centuries, Portugal)

IRINA CRINA ANCA SANDU,[1]* ELSA MURTA,[2]* RITA VEIGA,[1] VÂNIA SOLANGE F. MURALHA,[3] MANUEL PEREIRA,[4] STEPANKA KUCKOVA,[5] AND TITO BUSANI[6]

[1]*REQUIMTE and Department of Conservation and Restoration, Faculty of Sciences and Technology (FCT), Nova University of Lisbon (UNL), 2829-516, Caparica, Portugal*
[2]*José de Figueiredo Laboratory, General Direction of Cultural Heritage, Rua das Janelas Verdes, Lisbon, Portugal*
[3]*Research Unit VICARTE: Vidro e Cerâmica para as Artes, Faculty of Sciences and Technology, Nova University of Lisbon (UNL), 2829-516, Caparica, Portugal*
[4]*Centro de Petrologia e Geoquímica do Instituto Superior Técnico / CERENA, Technical University of Lisbon (UTL), Av. Rovisco Pais 1, 1049-001, Lisbon, Portugal*
[5]*Department of Biochemistry and Microbiology, Institute of Chemical Technology, Technická 3, 166 28 Prague 6, Czech Republic, S. Kuckova*
[6]*CENIMAT, Faculty of Sciences and Technology, NOVA University of Lisbon, Portugal*

KEY WORDS gilded altarpiece; polychrome materials and techniques; muti-technique; interdisciplinary study; historical and technical documentation; restoration intervention

ABSTRACT The research results presented in this paper are part of a larger study on the materials and techniques used in polychrome altarpieces of gilded woodcarving decoration ("talha dourada") in Portugal. The paper focuses on a narrative Portuguese Altarpiece from Miranda do Douro, considered one of the masterpieces of "talha dourada" among all the retables of the Iberian Peninsula in XVIIth and XVIIIth centuries. Although on the Portuguese territory, the altarpiece was made by artists from the Royal Spanish school of Valladolid, under a mannerist style. Thus the study opens a window on the artists' circulation between Spain and Portugal and influences of the Spanish schools in Baroque epoch on the Portuguese "talha". During its history this altarpiece underwent several transformations and extensive conservation treatments in 1989. On this occasion more than 50 samples were collected and analyzed using an interdisciplinary multi-technique methodology. 27 of these samples are chosen for this study in order to investigate the chromatic palette, the materials and techniques used in the polychromy of the retable. A novel protocol of investigation using different conventional and unconventional analytical techniques (OM + fluorescent staining tests on cross-sections, Raman microscopy, XRD, XRF, X-ray micro-CT, SEM-EDX, MALDI-TOF-MS and LC-MS/MS) was established within an innovative research project (http://sites.fct.unl.pt/gilt-teller/) and applied on these samples. This protocol is necessary to confirm the results obtained in the 1989 campaign and to have further insight into the gilding and polychrome decoration materials and techniques and the additional information reported in the historical documents. The material and technical history of this important altarpiece will be thus re-documented from a scientific perspective, meant to confirm and bring new information on the decorative technique used in the creation of this complex Portuguese monument. *Microsc. Res. Tech. 76:733–743, 2013.* © 2013 Wiley Periodicals, Inc.

INTRODUCTION

Miranda do Douro Cathedral was raised in Miranda do Douro city, which is located on the right bank of the Douro river, in the international region that separates the Portuguese province of Trás-os-Montes from the Spanish province of Castilla y León. The first stone of the cathedral was laid in 1552 and was consecrated in 1566. The architect and military engineer Miguel de

*Correspondence to: Irina Crina Anca Sandu, REQUIMTE and Department of Conservation and Restoration, Faculty of Sciences and Technology (FCT), Nova University of Lisbon (UNL), 2829-516, Caparica, Portugal. E-mail: irina.sandu@fct.unl.pt and Elas Murta, Laboratório José Figueiredo, Direcção Geral do Património Cultural, Lisboa, Portugal. E-mail: elsa.murta@gmail.com

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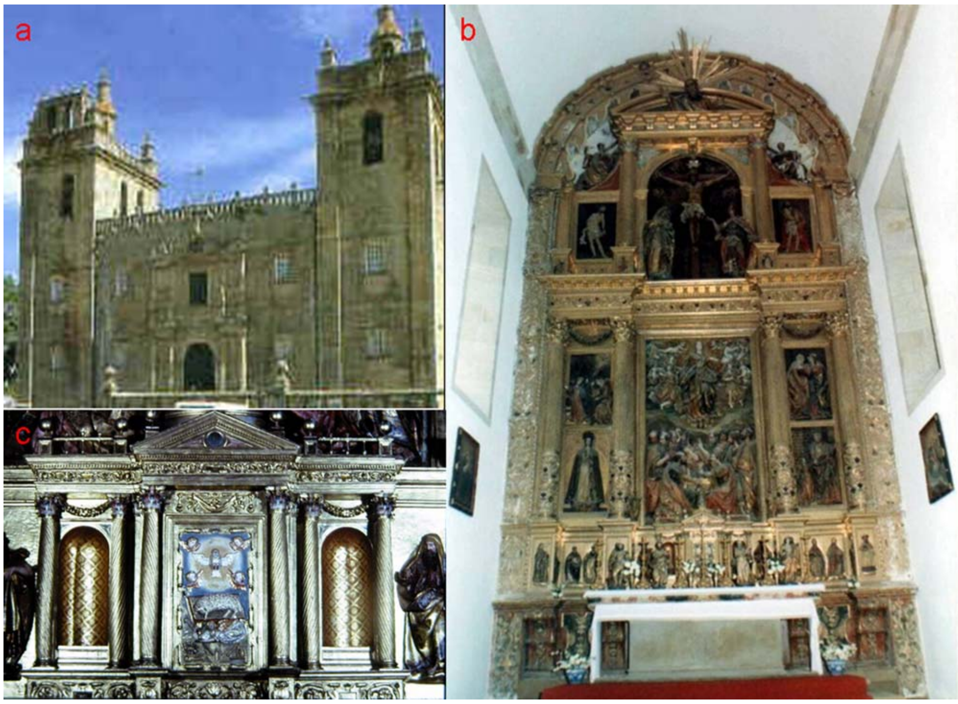

Fig. 1. The Miranda de Douro Cathedral: (**a**) view of the main façade; (**b**) the main altarpiece; (**c**) detail of the sacrary of the altarpiece. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Arruda was the author of the cathedral's plan. The main altarpiece of the Cathedral (Fig. 1) was built between 1610 and 1614 by order of the religious responsible ("cabido") and paid by the Factory of the Cathedral (Rodrigues Mourinho, 1988).

Technical, legal (contracts) and historical documents (Rodrigues Mourinho, 1988a,b) report the transformations that the retable suffered from its creation and also the authors (sculpture master, gilder and painter), money amounts and time necessary for each work (from carving the wood, decorating the panels with painting and gilding the sculptures and the wood surfaces). Legal and historical contract documents from 1610 reveal contract details imposed to Juan de Muniategui and his brother Francisco de Velázquez with Gregorio Fernandez by the amount of *38.800 reis,* to carve the altarpiece. In 1633 the sculptor Gregorio Fernandez calls for Jerónimo de Calabria (probably of Italian origin), a painter of altarpieces from Valladolid (Rodrigues Mourinho, 1988a). For the total amount of *640.000 reais (16.000 silver reales)* the altarpiece would be "*painted, gilded, estofated, engraved and incarnated in all its perfection*", under the supervision of the sculptor master, Gregorio Fernandez. The legal contract, with 14 conditions/clauses, was imposed to the artist to gilt the altarpiece, to embellish the sculptures with "sgraffito" and "brocade" decoration techniques and create perfect flesh tones.

Besides the presence and contract made with artists from Valladolid School in Spain the historical sources speak also about the use of an "evaluator" (as competent official figure), Teodósio de Frias ("conceituated person, coming from a noble family") to assess the quality of the final work (Rodrigues Mourinho, 1988a).

Between 1633, year when the entire carved structure was finished, and 1749 there is no historical document attesting any other intervention on this retable (Rodrigues Mourinho, 1988a). Between 1749 and 1754 the Cathedral was extended in length and this allowed a change in the framing of the original retable structure (Rodrigues Mourinho, 1988a) and a "refreshment" of the polychrome decoration.

In 1989 the altarpiece underwent major restoration interventions carried out by specialists from the Laboratory José de Figuereido from Lisbon. On this occasion more than 50 samples were collected before and during the restoration interventions in order to perform a study on polychrome materials and techniques and to establish best practice for treatments to be performed (JCHb Special Issue, 2012). 27 samples among the overall amount were selected and further analyzed using a novel methodology of investigation involving different conventional and unconventional analytical techniques (Pinna et al eds, 2009; Sandu et al., 2011; Sandu et al., 2012). These samples come from "predela", the frontal lower part of the retable, composed of 16 polychrome sculptures and the Sacrary (Fig. 2).

Thus, optical microscopy (OM) and fluorescent staining tests on cross-sections, Raman microscopy, X-ray fluorescence (XRF), and X-ray diffraction (XRD), X-Ray micro-computerized tomography (micro-CT), scanning electron microscopy coupled with energy dispersive

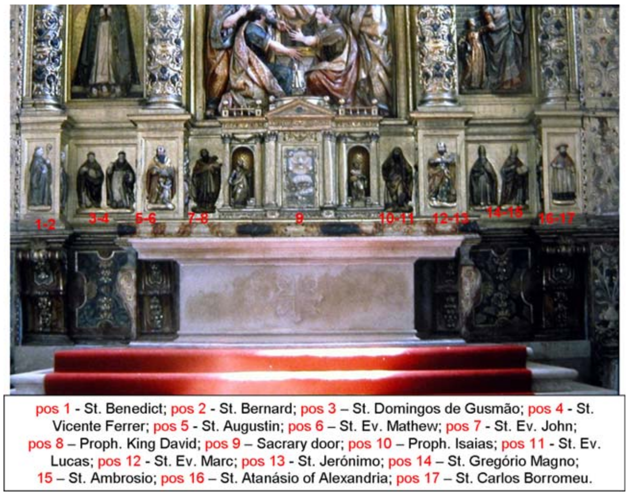

Fig. 2. Detail of the lower part of the altarpiece with the positions of sampling. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

X-ray spectrometry (SEM-EDX), proteomic mass spectrometric techniques (MALDI-TOF-MS and LC-MS/MS) were used to complement and assess the historical information on the altarpiece. This investigation was necessary to confirm the results obtained in the 1989 restoration campaign and to have further insight into the gilding and polychrome decoration materials and techniques and the contractual information reported in the available documents.

SAMPLING

This article will focus on only 27 samples of the total number that were collected from the altarpiece. These samples were taken before the restoration intervention in order to characterize the materials and techniques of the "predela," the bottom raw of polychrome carved wood decoration from the altarpiece, corresponding to the Sacrary and Saints of the Church (Evangelists, Prophets, Doctors of the Church, Bishops and Popes) (Hall, 1998). Table 1 gives the main characteristics of the 27 samples and sampling positions as illustrated in Figure 2.

MATERIALS AND METHODS

Optical Microscopy and Cross-Sections Analysis

Cross-sections were obtained using a polyester embedding resin (Crystal) with hardener. After curing, the resin blocks were cut and polished to reveal the 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 (Sandu et al., 2009, 2012).

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 (Sandu et al., 2013), was applied on some cross-sections for mapping the proteinaceous binders in the ground, bole layer and

TABLE 1. Sampling positions and description of sampling areas

Sample	Sampling position	Color and description of sampling area
PT-AM-MD_1	Pos 6	Red from the mantle of St. Mathew
PT-AM-MD_2		Angel's aisle with polychromy near St. Mathew
PT-AM-MD_3	Pos 7	Green from the mantle's border
PT-AM-MD_4	Pos 8	Green from the mantle's decoration of Prophet David
PT-AM-MD_5	Pos 9	Gold leaf decoration from the Sacrary door
PT-AM-MD_6		Mantle of the angel sustaining the flag with the lamb from the Sacrary Door
PT-AM-MD_7	Pos 10	Red from the mantle's decoration
PT-AM-MD_8		Green from the mantle's border
PT-AM-MD_9	Pos 11	Foot carnation
PT-AM-MD_10		Cover of the book
PT-AM-MD_11	Pos 12	Blue from the mantle's decoration
PT-AM-MD_12		Red from the mantle's decoration
PT-AM-MD_13	Pos 17	Red from the hat's decoration of St. Carlos Borromeu
PT-AM-MD_14		Dark or black from the mantle's decoration
PT-AM-MD_15		White from the mantle's decoration
PT-AM-MD_16	Pos 1	Black from the mantle's decoration
PT-AM-MD_17	Pos 13	White from the mantle's decoration
PT-AM-MD_18	Pos 13	Red, hat's decoration
PT-AM-MD_19	Pos 14	Black, cover of the book
PT-AM-MD_20	Pos 14	Green, mantel with decoration
PT-AM-MD_21	Pos 15	Red from mantle's decoration
PT-AM-MD_22	Pos 15	Green from the inner side of the mantle
PT-AM-MD_23	Pos 16	Blue, from the mantle's decoration
PT-AM-MD_24	Pos 4	Red, book's leaves
PT-AM-MD_25	Pos 3	Red from the mitra's decoration
PT-AM-MD_26	Pos 4	Green from the mitra's decoration
PT-AM-MD_27	Pos 5	Ochre, decoration from the mantle

paint layers (Sandu et al., 2006, 2008). 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.

microRaman Analysis on Cross-Sections

The equipment used was a Labram 300 JobinYvon spectrometer, equipped with a He-Ne laser of 17 mW power operating at 632.8 nm and a solid state laser operating at 532 nm. The laser beam was focused with a 50x or 100x Olympus objective lenses. The laser energy was filtered up to 10% using a neutral density filter for all analyses. The attribution of the Raman spectra was made using databases of reference materials reported in the literature (Bell et al., 1997; Burgio et al., 2001).

Mass Spectrometric Techniques

Specific Cleavage With Trypsin. These two techniques are widely used in the proteomics field (Fremout et al., 2011; Kuckova, 2007; Sandu et al., 2009; Tokarski et al., 2007) for the identification of protein-based materials and in our study were useful to detect the proteinaceous content of the binders in the paint layers. Both mass spectrometric techniques (MALDI-TOF-MS and LC-MS/MS) need the following samples preparation.

Approximately 5–50 mg of each sample placed into 20 μL 50 mM NH_4HCO_3 (Lachema Brno). Digestion was carried out in 50 μL of solution of 10 μg/mL sequencing grade trypsin (Promega) in 50 mM NH_4HCO_3 at room temperature for 2 h. The solution containing released peptides was desalted using ZipTips (Millipore Corporation, Bedford, MA) packed with reversed phase (C18) resin.

MALDI-TOF-MS. The first half of fragments in the weights of approximately 5–50 mg was digested in 20 μL of 50mM NH_4HCO_3 (Lachema Brno) containing ~10 μg/mL of trypsin ((TPCK) from Promega Corporation) at room temperature for two hours. After the trypsin digestion, the samples were purified on reverse phase ZipTip (Millipore Corporation, Bedford, MA). An aliquot of the obtained peptide solution (2 μL) was mixed with 4 μL of 2,5-dihydroxybenzoic acid (DHB) (Sigma) solution (18 mg of DHB in 1 mL of mixture of acetonitrile (Lachema Brno)/0.1% trifluoracetic acid (1/2 [v/v] (Sigma)). The resulting mixture (2.8 μL) was spotted on the stainless steel MALDI target and dried on air. Mass spectra were acquired by Bruker-Daltonics Biflex IV MALDITOF mass spectrometer equipped with standard nitrogen laser (337 nm) in positive reflector mode with mass accuracy 0.2 Da; at least 200 laser shots were collected for each spectrum. The spectra were analyzed using the XMASS (Bruker), mMass software (Kuckova et al., 2007) and a home-made database of reference proteinaceous binders (Tokarski et al., 2006).

LC-MS/MS. Mass spectrometry and protein identification LC-MS/MS was performed using an Acquity UPLC system coupled to an ESI-Q-ToF Premier tandem mass spectrometer (Waters, UK). Prior to the analysis, protein digests were solubilized in 0.1% formic acid and loaded onto a Symmetry C18 trapping column (180 μm i.d. x 20 mm length, particle size 5 μm, reverse phase); with a flow rate of 15 μL/min for 1 minute. Trapping was followed by a reverse phase HPLC with a flow rate of 0.4 μL/min through a BEH 300 C18 analytical column (75 μm i.d. x 150 mm length, particle size 1.7 μm, reverse phase; Waters, UK). A linear gradient (initial 3% B, 1 min - 40% B, 60 min) was followed by a cleaning step (85% B, 62 min; 85% B, 67 min; 3% B, 70 min; solvent A was 0.1% formic acid in water and solvent B was 0.1% formic acid in acetonitril). Peptides eluted from the column flowed directly into the ESI source. A collision energy ramp from 15 V to 30 V was used for peptide fragmentation. Protein identification was carried out using PLGS 2.3 software (Waters, UK) by searching a species specific, non-redundant Uniprot protein database with the following search parameters: 2 missed cleavages; acetyl N-term, carbamidomethyl C and oxidized M as variable modifications, peptide accuracy 50 ppm, and MS/MS fragment mass accuracy 0.2 Da.

X-Ray Diffraction

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.

X-Ray Fluorescence

As cited previously, qualitative XRF was performed, when needed, to complement the XRD analysis. No preparation of the samples is needed. The equipment used is a Phipps PW148 XR Spectrometer (Rh anode tube). Four scans were performed including all the elements with atomic mass equal or higher than Na. This technique is particular useful in the detection of metallic elements present in the gilded layers, namely Au, Cu, Ag, Pb, Hg (Sandu et al., 2010, 2011).

X-Ray Micro-Computerized Tomography

X-ray microtomography allowed a three-dimensional (3D) observation of the samples without sample preparation or chemical fixation (Sandu et al., 2011). Digital radiographs have been acquired with a μCT SkyScan 1172 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 specimen using a constant source power (10W): highly opaque pieces were investigated with source voltage and

TABLE 2. Analyses performed on 27 samples

Sample ID	SM	MO-Vis	MO-UV	Sypro	SEM-EDX	X-Ray micro-CT	XRD	Micro-Raman	MALDI-TOF-MS	LC-MS/MS
PT-AM-MD_1	x	X	x	x	x	x	x		x	x
PT-AM-MD_2	x				x	x			x	
PT-AM-MD_3	x	X	x							
PT-AM-MD_4	x	X	x	x			x	x	x	
PT-AM-MD_5	x	X	x	x	x	x	x	x	x	
PT-AM-MD_6	x	X	x	x					x	
PT-AM-MD_7	x	X	x							
PT-AM-MD_8	x	x	x	x					x	
PT-AM-MD_9	x	x	x	x			x	x	x	x
PT-AM-MD_10	x	x	x							
PT-AM-MD_11	x	x	x						x	
PT-AM-MD_12	x	x	x	x				x		
PT-AM-MD_13	x	x	x							
PT-AM-MD_14	x	x	x						x	
PT-AM-MD_15	x	x	x			x	x			
PT-AM-MD_16	x	x	x	x				x	x	x
PT-AM-MD_17	x	x	x					x	x	x
PT-AM-MD_18	x	x	x					x		
PT-AM-MD_19	x	x	x	x			x			
PT-AM-MD_20	x	x	x						x	x
PT-AM-MD_21	x	x	x	x					x	
PT-AM-MD_22	x	x	x				x	x	x	
PT-AM-MD_23	x	x	x					x		
PT-AM-MD_24	x	x	x					x	x	
PT-AM-MD_25	x	x	x							
PT-AM-MD_26	x	x	x				x	x		
PT-AM-MD_27	x	x	x	x				x	x	

current of, respectively, 100 kV and 100 μA, and using downstream 0.5 mm aluminum filtration increase beam penetration in the samples in order to prevent "beam hardening", a nonlinear X-ray absorption effect; less opaque were inspected with lower source voltages, without the use of a filter. The acquisition was performed by rotating the specimen 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 (m^{-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 3D 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 3D reconstructions. Slice reconstructions have been obtained with the NRecon 1.6.3 routine and volumetric visualization has been achieved with *DataView,* which integrate the instrument software packages. Rendering program allows the 3D virtual visualization (image or video) of the samples.

Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

A ZEISS Auriga working at 5 KeV at a working distance of 9 mm was used for the scanning electron images. The elemental mapping was obtained using an Oxfordx-act detector operating at 10 KeV and at 5.5 mm working distance in order to map the Kα and the Lα peak of the element of interest. The operating conditions were chosen in order to prevent the typical C coating that usually is required (Sandu et al., 2006, 2009, 2011) to image nonconducting samples similar to the ones presented in this article.

RESULTS AND DISCUSSIONS

The analyses performed on each of the 27 samples are given in Table 2. The stratigraphic observation under visible and fluorescent light microscopy and the chemical characterization of the constituents in the polychrome layers allowed to identify the inorganic and organic components and also to assess to which point the artists respected the legal conditions of the work.

As the legal contract mentions, the altarpiece displays a series of technical and artistic characteristics which the analytical data revealed. Although the study limited to only 27 samples, these cover the chromatic palette used in the polychrome decoration of the Sacrary and biblical figures representing saints, prophets, bishops and popes, doctors of the Church.

The ground layers, forming a thick preparatory basis (200–1000 μm), were made with gypsum and anhydrite (the presence of gypsum can be associated to the *gesso fine/mate* while the anhydrite is considered to be the main constituent of *gesso grosso*), sometimes with traces of kaolinite (detected by XRD and microRaman, Table 3) and animal glue (identified by MALDI-TOF-MS) and applied directly on the wooden support (Fig. 3b) (Rodrigues Mourinho, 1988).

The polychrome decoration is made of different colors (red, pink, green, blue, ochre, white, black, shiny gold) that usually consists of several layers (1–4) of

TABLE 3. microRaman and XRD results for each layer constituting the polychrome composites in 15 samples

Sample	Preparation	Red bolus	1st color layer/gilding	2nd color layer
PT-AM-MD_1	Anhydrite, Gypsum	—	Red lead, Vermillion	—
PT-AM-MD_4	Gypsum, Anhydrite, Anatase	Anatase, Hematite	Azurite, Lead white	—
PT-AM-MD_5	Gypsum, Anhydrite	Goethite	Goethite	Hematite, Graphite, Gold leaf
PT-AM-MD_9	Anhydrite, Gypsum	—	Lead white	Vermilion, Lead white
PT-AM-MD_12	-	Red bolus: hematite, quartz; Brown bolus: graphite	Vermilion, Red lead, Massicot	—
PT-AM-MD_15	Gypsum, Anhydrite, Kaolinite	Lead white, Red ochre	Gold leaf	—
PT-AM-MD_16	Gypsum	Anatase, Goethite, Hematite	Gold leaf	Carbon-based black compound
PT-AM-MD_17	Gypsum	Hematite, Anatase	Gold leaf	—
PT-AM-MD_18	Gypsum	Hematite, Anatase	Gold leaf	Vermilion
PT-AM-MD_19	Gypsum, Anglesite Kaolinite	Hematite	Gold leaf	—
PT-AM-MD_22	Gypsum, Anatase	Anatase, Hematite	Gold leaf residues Cu-sulphate (probably Brochantite)	Azurite
PT-AM-MD_23	Anhydrite	Anatase, Hematite	Gold leaf, Azurite	—
PT-AM-MD_24	Gypsum	Hematite	Gold leaf, Carbon-based black compound	Vermilion
PT-AM-MD_26	Gypsum	Rutile, Anatase, Hematite, Gypsum and weddelite	Gold leaf, Lead white	Azurite
PT-AM-MD_27	Anhydrite	Hematite	Gold leaf, Lead white	—

paint overlapped or intercalated by gold leaf (Figs. 3a, 3c, and 3d). MicroRaman analysis identified several pigments and inorganic compounds that are usually encountered in painted and sculpted works of art from the same époque: vermillion, red lead, yellow (goethite) and red (hematite) ochres, massicot, lead white, red lead, carbon-based black pigments, azurite (and a copper sulphate, identified as brochantite ($CuSO_4{\cdot}3Cu(OH)_2$), for sample 22) (Table 3).

For the samples with only gold leaf as polychrome layer (PT-AM-MD_2, 5, 6, 13) and also for other samples (e.g., 12, 14, 16, 17, 20) where the leaf is interposed between layers of paint the bolus displays a dark red color. Its main component was identified as being hematite (red ochre), sometimes mixed with carbon black or a light ochre/orange color (goethite and anatase being identified). The presence of Ti (anatase) can be related with the geological origin of the clay minerals (mainly kaolinite) contained in the bole layers (Barata et al., 2011; Costa, 1986; Grygar et al., 2003). Clays with similar characteristics to the traditional Armenian Bole can be also found in Portugal (Barata et al., 2011; Costa, 1986), being known in publications from XVI-XVIIIth centuries as a high quality bole.

Animal glue was identified in the ground layers and also in the bole layer for the gilded samples. The paint layers were bonded with egg tempera. MALDI-TOF-MS methodology allowed to identify the presence of proteinaceous materials directly on cross-section (Sandu et al., 2013) and the fluorescent stain (Sypro Ruby) complemented the identification by mapping the distribution of proteins (from animal glue or tempera) on each layer of the polychrome composites (Fig. 4) (Sandu et al., 2012). The presence of animal glue was also confirmed by LC-MS.

From the eighth condition of the contract we know that incarnation (Figs. 5a and 5b) had to be made as much as resembling the natural flesh tones, the final result being a flat, smooth polychrome surface.[#] The stratigraphic and compositional analysis show the presence of a mixture of pigments: white lead and Vermillion tempera on a thin ochre layer over a thick ground (Fig. 3b).

The fourth condition (Figs. 5b, 5c, and 5d) speaks of the garment's decoration using *sgrafito* or *brocade* techniques[†] (Gonzalez Lopez, 2000; Le Gac, 1999; Nodal Monar and Calvo, 2008) to imitate the appearance of precious textiles.

The stratigraphic sequence of the garments illustrate several layers of different colors over the ground layer (Figs. 3a, 3c, 3d, and 3e) sometimes with gold

[#]((. . .) encarnações de todas as figuras (. . .) a polimento m.to lisas (. . .) que imita ao natural).

[†]Aode collorir todas as figuras de bulto com finas cores (. . .) de tellas como de brocados ao natural e picados de grafio.

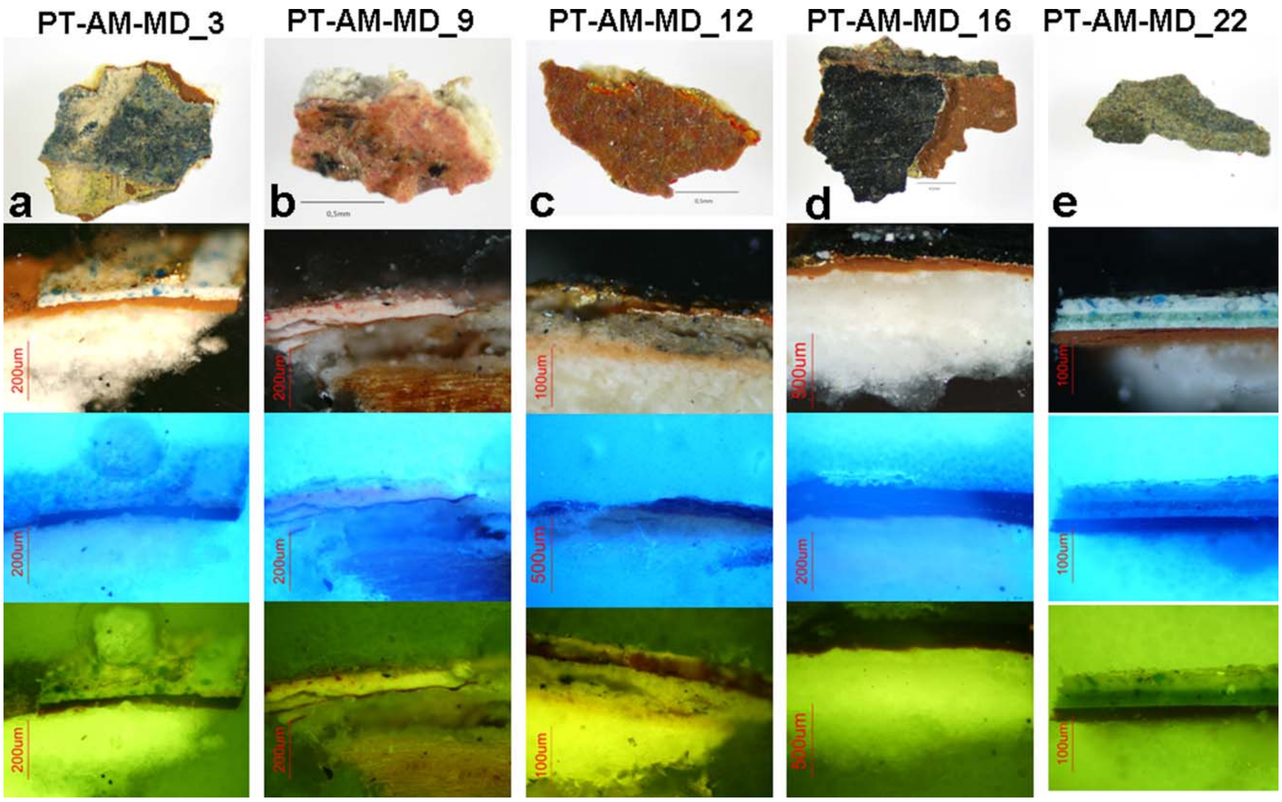

Fig. 3. Selection of cross-sections from five samples showing the sequence of layers and the Vis-UV pattern under OM observation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

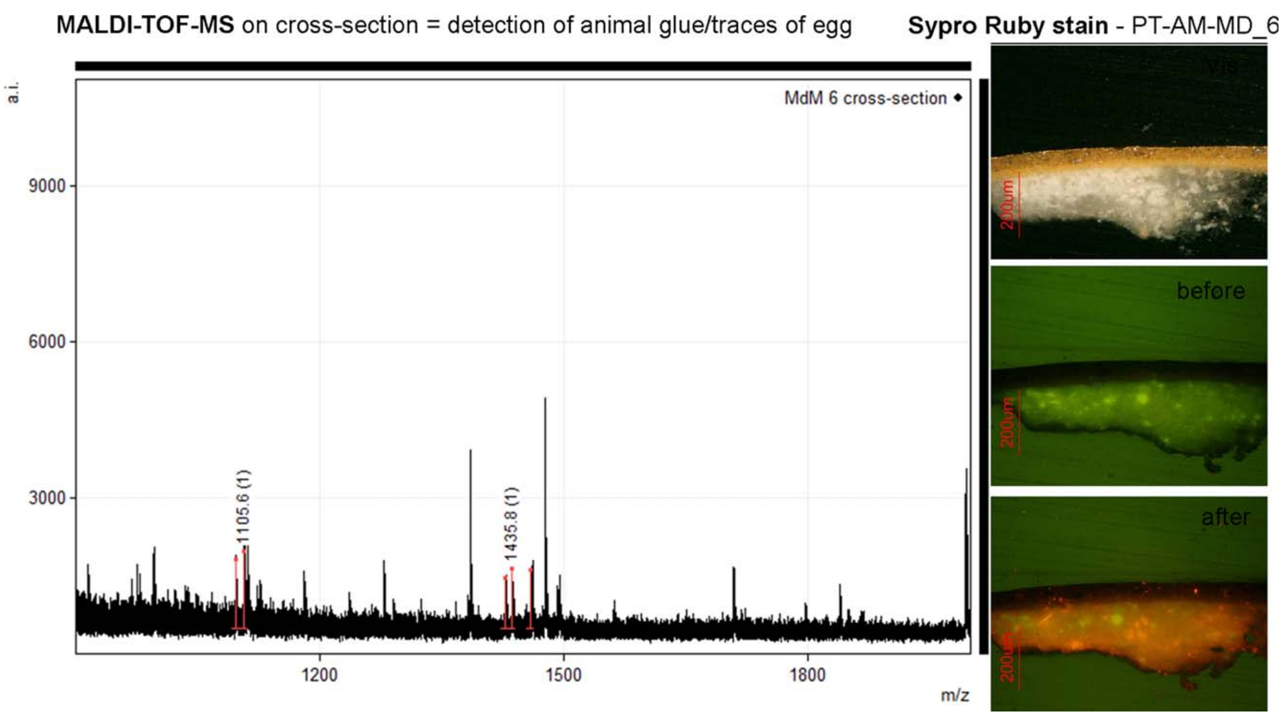

Fig. 4. Complementary methodology for identification of protein-based materials on cross-section using MALDI-TOF-MS and Sypro staining. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Fig. 5. Details from the samples areas: (**a**) Saint Atanásio of Alexandria (pos 16); (**b**) Saint Ambrosio (pos 15); (**c**) *brocade* decoration on the garment of Saint Ambrosio (pos 15); (**d**) *sgrafito* technique on the garment of Saint Augustin (pos 5). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

leafs in between. The presence of gold leaf within the polychrome layers is also defined as a composite technique known as *estofado (sgraffito of a tempera layer over gold)* (Nodal Monar and Calvo, 2008), well diffused in Spanish and Portuguese wooden polychrome sculpture (GCI Proceedings, 2002; IPCR Proceedings, 2002; Studies in Conservation Special Issue, 1970; Belda Navarro, 1996–1997; Gonzalez Lopes, 2000).. Figures 3 and 5 give examples of application of gold leaf within the paint layers to form a complex polychrome composite, illustrating a high level of technical and artistic skills.

Figure 6 shows a sample taken from the Sacrary door containing gold leaf decoration. Several studies performed on Baroque altarpieces from Portugal (Bidarra et al., 2008, 2009, 2010, 2011; Le Gac et al., 2008, 2009; Le Gac, 1999; Pombo Cardoso, 2006) indicate the use of pure gold (fine gold, known in Portuguese as "ouro subido ou moido") in ancient times and alloys of gold with other metals (Ag, Cu) in more recent times. Nevertheless, the identification of the pure gold or highly containing god alloy is considered as being almost a mark of authenticity and good quality of the craft in gilding the altarpieces.

SEM mapping on the surface of sample 5 (Fig. 6) and its stratigraphic analysis revealed the pattern of the *esgrafitad*" decoration and the sequence of layers used to make the gilding: very thin gold leaf was applied over a layer of bole (light ochre color) made of goethite, hematite and graphite applied over a ground made of anhydrite and gypsum. As the second and fifth condition of the contract says, the gold decoration should be made with fine, clean (pure) gold, well burnished and with colors.[‡] The appearance, thickness and compactness of the gold leaf in the stratigraphic sequence of cross-sections (Figs. 3, 4, and 5) confirm the contract's condition on the use of burnished gold leaf (water gilding technique).

The inner structure of some samples was also investigated using X-ray micro-CT technique (Sandu et al., 2011) in order to better understand the properties of the layers composing the polychromy. Figure 7 shows comparative rendering in black-white and color visualization in three directions of three samples.

The images, although represent a virtual reproduction of the sample, sectioned by X-ray at different heights and in three directions, have a good resolution and allow to distinguish between phases and the size and shapes of the pores or fractures present in the sample's structure. For example, sample MD_1 displays big holes and pores at the level of the ground, represented in purple fake color and variable thickness of the upper layer of gilding (bole + leaf), represented in lighter, gray colors. The preparation has two distinguished types of layers: one at the bottom, with more pores and one at the top, below the bole layer, more compact. Correlating these data with the XRD results, where anhydrite and gypsum were identified in the ground, we can say that micro-CT helps in distinguishing between layers of *gesso grosso* (mainly made of anhydrite) and *gesso matte* (mainly made of gypsum). Sample MD_5 is imaged both in gray-scale and colored sections and this allows to see the difference between phases in the stratigraphy of the gilded composite, as it is the case of the intermediate layer vs. the surrounding ground layers. This intermediate layer appears colored in purple and in a darker gray in the Figure 7, corresponding to a lighter chemical composition (e.g., organic binder, see other techniques) and/or less massive texture. The shape/size/orientation of pores (spherical or irregular) or mineral grains, and other physical parameters can be also correlated to the degree of craftsmanship and the nature of the applied materials.

The simple analysis of the radiographs can provide very useful information concerning the distinct elements composing the samples, including the wooden support. Unfortunately, in the reconstructed slices, of

[‡](. . .) Outras de brutesco sobre ouro limpo com finas cores e abulltadas; O ouro será mais subido de cor e de mais corpo que se possa achar. A arquitectura a de ser de ouro limpo (. . .) bem brunido.

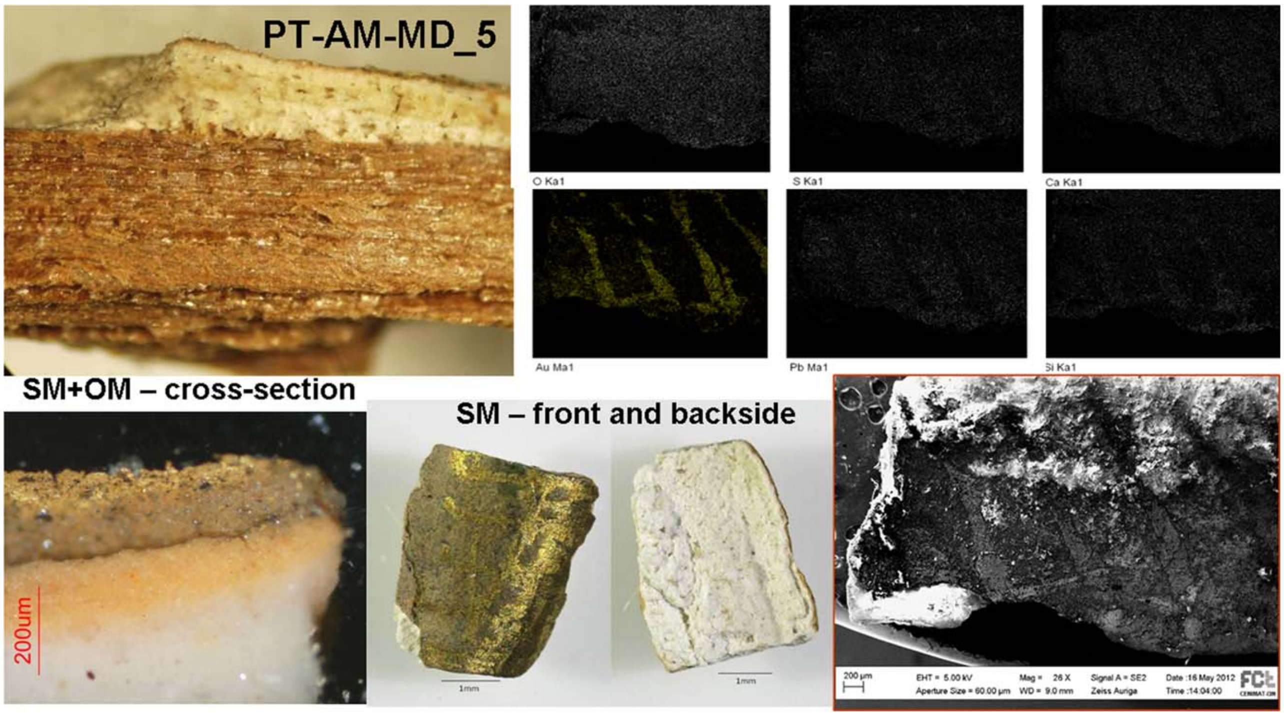

Fig. 6. Gold leaf decoration from the Sacrary door. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

combined wood/polychromy composition, the wood became "transparent" due the extreme contrast of phases (metal rich layers, such as Au, Cu, Fe, Pb, vs. organic materials). On other hand, the separated tomographic study of the wood supports constitutes a powerful tool for the recognition of the species and for the characterization of conservation/restoration problems (Le Gac et al., 2012; JCHa Special Issue, 2012).

CONCLUSIONS

The multi-technique scientific approach presented in this paper aimed to reveal the congruence between the contract's conditions published on the main altarpiece of the Miranda do Douro Cathedral and the polychrome/gilding materials and technique analytically identified and characterized. The imaging techniques, such as OM (Vis-UV), micro-CT and SEM, were complemented by molecular and spectrometric/mass spectrometric techniques (microRaman, XRD, EDS, MALDI-TOF-MS, LC-MS/MS) in order to make a full characterization of inorganic and organic materials inside the polychrome samples.

The 27 samples taken before the restoration intervention were useful to give a comprehensive view on the chromatic palette and also on the technical and material peculiarities of the polychrome decoration from the lower part of the altarpiece, pointing mainly on incarnates and garments's gilded decorations. Besides the artistic quality, attributed, according the contract, to artists from the Valladolid School, the quality of materials and of the polychrome technique is also confirmed through this study: gypsum and anhydrite (*gesso grosso* and *gesso mate*) as constituents of the preparatory layers, compact red-ochre bolus layer and burnished gold leaf applied in water gilding technique, and egg tempera mixed with pigments of different provenance (lead white, red and yellow ochres, azurite, vermillion and red lead, carbon black etc.) for recreating the sumptuous decoration of brocades on the garments.

The microCT technique, complemented by stratigraphic observation under OM, allows also to image in dynamic mode (as sequence of images through the samples) the different degradation and deterioration forms, suggesting a high degree of ageing and decay mechanisms.

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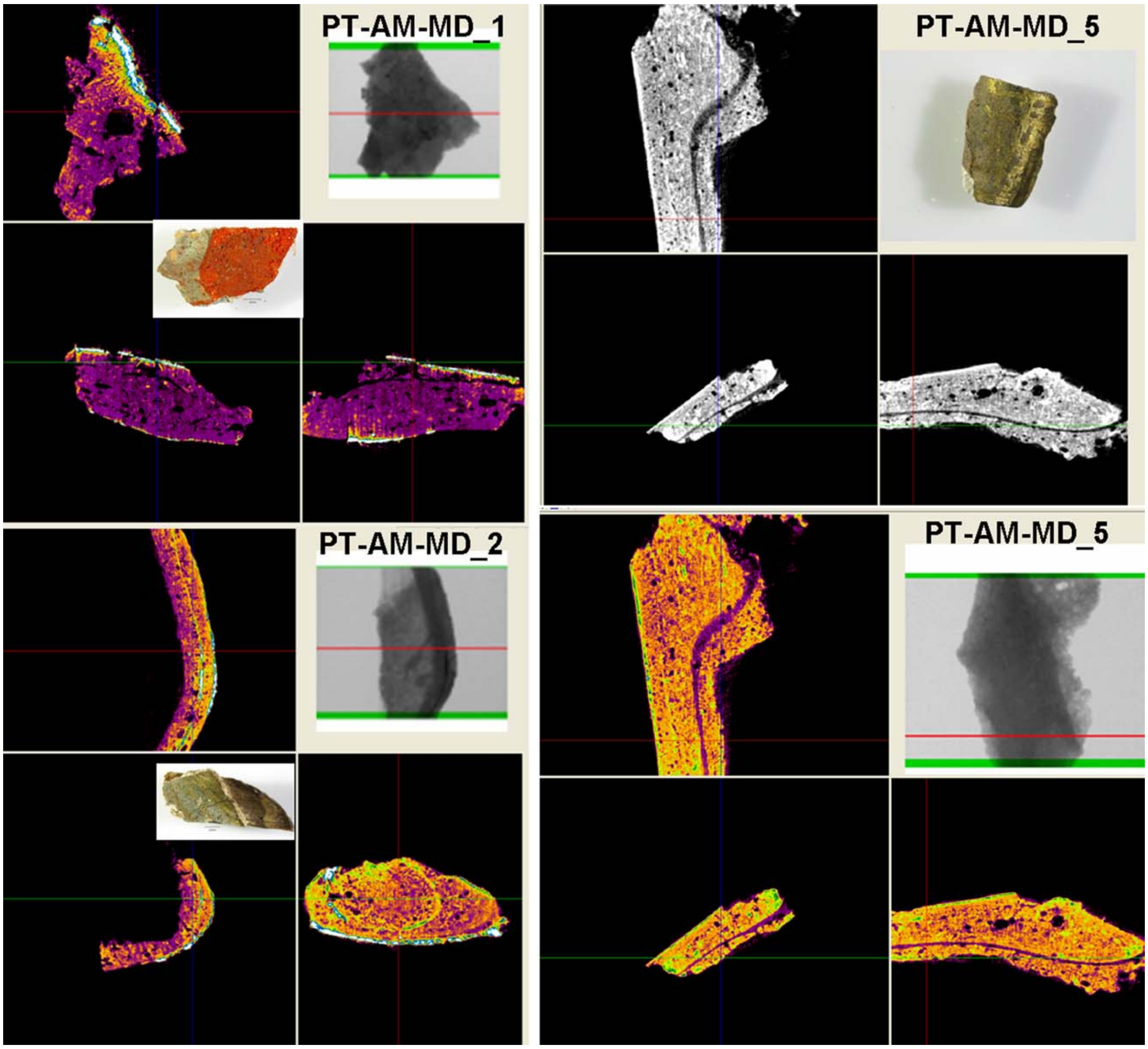

Fig. 7. Selection of X-Ray micro-CT reconstructed slices (XY, XZ, and YZ perspectives) of three samples, 1, 2 and 5, as colored and gray-scale images. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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