On the application of Optical Coherence Tomography as a complimentary tool in an analysis of the 13th century Byzantine Bessarion Reliquary

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ABSTRACT

This work presents the results of an application of Optical Coherence Tomography (OCT) to examine a 13th century Byzantine reliquary of unparalleled artistic and historical value. The aim of this work, performed at the initial stage, before the restoration, was focused on the resolution of cleaning procedures regarding both the thick, old varnish and the gold leaf details finely applied on the painted parts of the artwork by means of an integrated approach of non-invasive and invasive analyses and diagnostics.

The results allow definition of the thickness of the varnishes, their inner morphology and establishes the presence (or absence) of secondary layers of gold leaf upon the original ones. Knowledge of varnish thickness and in-depth localisation of the secondary gold leaf allowed the restoration procedure of cleaning and thinning of the altered varnish to be performed safely and effectively in order to recover the wonderful pristine sight of a precious and ancient byzantine work of art.

KEYWORDS

OCT, altered varnish, Byzantine art, reliquary, multidisciplinary examination, non-invasive methods

HIGHLIGHTS
The structure and composition of thick varnish layer is revealed.
Evidences of 15th century restoration are disclosed and examined.
The locations of gold leaf decorations (primary and secondary) are given.
The character and in-depth location of delaminations within the varnish are described.

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1. INTRODUCTION

There are several artworks which have a complex structure, reflecting the magnificent craftsmanship of their creators. One of them is the reliquary of Cardinal Bessarion, a very precious masterpiece of extraordinary value in its artistic, historic and religious aspects.

The present work relates only to the painted part of the object (scenes of the Passion of Christ), particularly the precarious condition of the painted surface which had been affected by several alterations and deterioration of the thick layer of varnish. Treatments such as cleaning, thinning and removal of ancient finishing layers are the most delicate phases of the overall conservation project [1]. In order to plan the restoration work and resolve the best means of achieving a good result, one needs to know all possible information about the superficial materials, including their morphology, stratification and condition.

During the preliminary studies and analyses preceding the restoration steps[1], many diagnostic and analytical techniques were applied in order to reveal both the materials used and the artist's techniques. Apart from the lid and metal elements, the conservation state and decay of the superficial materials of the polychrome part (scenes of the Passion of Christ) were assessed with the aid of optical coherence tomography (OCT) in addition to the routine methods.

Problems related to the examination of varnishes need to be considered in the context of restoration: because certain signs of the age of such objects are especially characteristic (some broad cracks, decreased transparency, scarce yellow nuance), the appropriate way to operate is on the principle of minimum intervention [2]. In the present case, this implies thinning the thick varnish in order to eliminate its deleterious effect on the original visual impression of the painting. The methods used traditionally to study varnish layers are both invasive (and therefore not extensively applicable), such as examining the cross sections of samples taken from the object, which allows determination of varnish thickness, transparency and defects, as well as its chemical composition (by FTIR and GC-MS), and non-invasive, including optical methods, such as confocal microscopy, microprofilometry, UV-excited luminescence and IR imaging, which give partial information about varnish morphology and thickness. OCT yields both morphological and structural information on the thickness of varnish layers and can be applied to as many spots on the object as necessary. The OCT technique, used in this case exclusively at the decision-making stage before the restoration, was therefore employed in the present case for non-invasive multi-spot confirmation of conclusions derived by classical local analyses. The information gathered allowed the restorers to identify precisely the state of the alterations and deteriorations, their localisation in depth and their morphology. This knowledge was used for making some crucial decisions concerning the varnish thinning.

2. THE OBJECT EXAMINED

2.1 The Bessarion Reliquary

Since 1437, Cardinal Bessarion, a Roman Catholic Bishop and the titular Latin Patriarch of Constantinople, had been living in exile in Italy. As a close associate and ambassador of Byzantine

[1] The restoration was coordinated by Daniela Poletto and Serena Bidorini (MiBACT - Ministero dei beni e delle attività culturali e del turismo, soprintendenza di Venezia). Cinzia Ortolani and Mary Yanagashita, under the direction of Clarice Innocenti, restored the metal details and the jewellery, Francesca Bettini and Andrea Santacesaria, under the direction of Marco Ciatti, restored the painted parts and the wooden structure (MiBACT, OPD Florence).

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Emperor John VIII Palaeologus he was promoting a reunion between the Catholic and Orthodox churches as well as seeking Italian support in a war against the Byzantine Empire. In 1463, Bessarion donated the reliquary of the True Cross to the Venetian Scuola di Santa Maria dei Battuti della Carità as a political gesture. The reliquary was officially transferred to Venice in 1472, a little while before Bessarion's death. The ceremony was portrayed by Gentile Bellini in a painting now residing in the National Gallery in London (Fig. 1a).

Fig. 1. (a) *Cardinal Bessarion and Two Members of the Scuola della Carità in prayer with the Bessarion Reliquary* by Gentile Bellini, about 1472-3: egg tempera with gold and silver on a panel, National Gallery, London (with permission); (b) Bessarion Reliquary, 13th century, Galleria dell Academia, Venice in its renaissance form, after the adjustment ordered by Bessarion in the second half of the 15th century, before last restoration; (c) central part of the reliquary (icon) with the following scenes: *The Capture of Christ* (1), *The Mocking of Christ* (2), *Christ Ascending the Calvary* (3), *The Flagellation of Christ* (4), *Christ Ascending the Cross* (5), *The Descent from the Cross* (6), and *The Entombment of Christ* (7). The lid, relics and metal elements have been removed for restoration. Photos (b, c): Marco Brancatelli OPD.

The Bessarion Reliquary (Fig. 1) is an object of great significance to the history of Venice, as well as a splendid example of Byzantine art._The central part (Fig. 1) consists of a wooden chest containing a couple of fragments of the wood of the Holy Cross and a couple of pieces of the fabric of Christ's tunic behind rock crystal windows, two embossed plates with the Archangels Michael and Gabriel and two fine portraits in gold of the Emperor Constantine and his mother, St. Helen. In the centre, bolted into the wood, is a finely chiselled cross with triple cross-pieces entirely covered in marvellous silver-gilt filigree. The icon is framed in a monstrance-shaped mounting of silver-gilt adorned with gems and stained glass.
The large frame of the relics' chest is painted with seven scenes of The Passion of The Christ: *The Capture of Christ (*It.: *Cattura)*, *The Mocking of Christ (Derisione di Cristo)*, *Christ Ascending the Calvary (Salita al Calvario)*, *The Flagellation of Christ (Flagellazione)*, *Christ Ascending the Cross (Salita alla croce)*, *The*

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Descent from the Cross (Deposizione dalla croce), and *The Entombment of Christ (Deposizione nel sepolcro)*. An inserted lid depicts the Crucifixion. There is an evident correlation between the holy relics and the subject of the painted scenes relating to The Passion of The Christ.

The reliquary was executed in the 13th century and bears signs of a later renovation, which may be linked to an order of Cardinal Bessarion [3-5]. It is likely that the reliquary was refurbished and presented in a procession before being transferred from Bologna to Venice on May 24th, 1472.

2.2 State of preservation and problems to be resolved

The aim of this contribution is to focus on issues affecting the polychrome parts of the reliquary only. Conservation of the painting was mostly concerned with the secondary (applied on top of the primary, original layer in course of past renovations) varnish layers. An initial observation of the surface gave the impression of a very thick, cracked and pale yellow-shaded varnish; this impression was confirmed by stereo-microphotography (Fig. 2a).

The appearance of the secondary 15th century varnish is very unusual, but it should be remembered that very few artefacts with such ancient and aged varnish have survived to the present day: most surviving paintings of comparable age have undergone several restoration treatments in the past, often incorporating quite brutal cleaning procedures (sometimes using strong alkaline mixtures [6]), so it is rather rare to find such very old varnishes preserved and in good condition. The result of the application of a thick layer of secondary varnish is extraordinary, considering the elapsed time: transparency is very high, yellowing is mild, the embedding of dirt particles in the varnish surface is infinitesimal and the overall thickness is the greatest ever seen on an old painted surface, at least in the authors' more than thirty years of experience.

Stereo-microscopic observation revealed that the drawing in gold, executed in gold leaf, originates from two sources of different technological and chronological provenance (Fig. 2b): the later, brighter, upper gold leaf decorations appear to be floating within the bulk of the varnish, above the more matte and tarnished primary ones below the varnish.

In specific areas of the reliquary, precisely the two left upper scenes, the upper part of the Crucifixion lid and the upper scene on the right, the legibility of the painting has decreased dramatically because of an "iridescence" occurring within the varnish (Fig. 2a). The destruction described affects the transparency, obscuring the legibility of the intricate composition, as well – critically – as posing serious problems related to the conservation and restoration of the images.
One of the most creditable hypotheses, albeit not definitively demonstrable, is that this effect was due to countless photo-induced stresses produced as a result of prolonged exposure to direct sunlight. This has created problems in terms of restoration: how deep is this phenomenon? Is it homogeneous or random in structure? Is it possible to remove it?
Certainly these questions are not capable of resolution by means of the sampling approach, and it was thus necessary to approach the problem using a non-invasive structural diagnostic technique.

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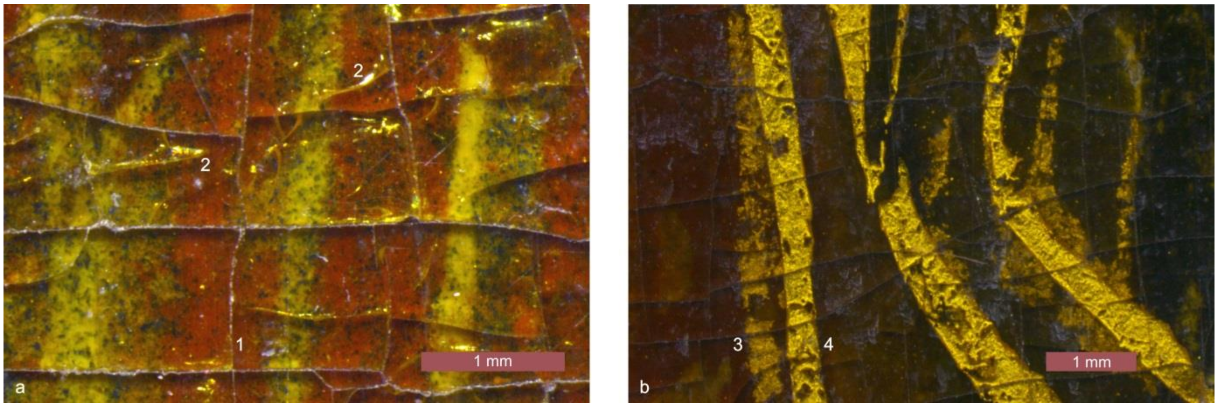

Fig.2 Microphotographs of the surface of the reliquary before conservation-restoration. (a) Thick cracked varnish exhibiting the “iridescence” phenomenon (scene: *The Capture of Christ*) with (1) – craquelure; (2) – internal cracks. (b) Two layers of gold leaf: (3) the primary one (13th century) appears slightly darker and is localised under the thick layer of varnish, while (4) the secondary (from the second half of the 15th century) is brighter, submerged in the varnish and partially superimposed on the more ancient one (scene: *Christ Ascending the Cross*). Photos: Francesca Bettini, OPD.

3. EXAMINATION METHODS AND INSTRUMENTATION

3.1 Visual inspection

Initial examination of the reliquary was performed with a Leica M 205C stereo-microscope with an LED diffuse light source using a Leica DFC 295 (LAS 24.8) camera.
Routine pre-analysis of UV-induced fluorescence[2] of the polychrome parts did not yield very much new information, since fluorescence of the thick secondary varnishes obscured that of the layers underneath. Neither the problem of the superimposed gold embellishments nor the inner iridescence of the varnish was resolved by this method.

3.2 Analytical methods

Bessarion’s reliquary was examined with a broad set of analytical methods, both non-invasive and micro-invasive. The presentation of all results is beyond the scope of this report. In direct relation to further presented OCT results were XRF point-wise examinations[3] with the portable LITHOS 3000 XRF instrument from ASSING SpA, Italy. More than 150 XRF spectra were collected from the painted surfaces, the glass, metal details and the gems to help characterize the pigment palette, the alloys used, corrosion products and the precious stones. To characterise a binder used for gilding, the micro-invasive approach has been adopted, namely Gas Chromatography Mass Spectrometry (GC-MS) and Pyrolysis GC-MS analyses[4]. The complex procedure of analysis and the equipment adopted are described elsewhere [7]. Briefly: after routine GC-MS analysis, material for the further analysis was acquired by ultra-selective micro-sampling [8]: collection of a very small amount of material of a single layer in the wall of the craquelure.

[2] performed by Giuseppe Zicarelli, OPD

[3] performed by Simone Porcinai and Andrea Cagnini, (Laboratorio di Chimica 2, OPD, Florence)

[4] performed by Maria Perla Colombini, Anna Lluveras Tenorio and Alessia Andreotti (SCIBEC - Laboratorio di Scienze Chimiche per la Salvaguardia dei Beni Culturali, Pisa University)

To enhance and clarify doubts concerning the stratigraphy of primary and secondary layers, two micro-samples were taken from two already existent paint losses in the right (scene of *The Mocking of Christ*) and bottom part of the reliquary chest (scene of *The Entombment of Christ).* The samples were embedded in polyester resin, grounded and polished to obtain cross-sections. Images both in diffuse light and of UV-induced fluorescence were photographed using a Zeiss Axiophot optical photo-microscope with a 10x eyepiece/ocular and nosepiece revolver fitted with 2.5x, 5x, 10x, 20x and 50x epifluorescent objectives. A diffuse light source halogen bulb (100 W) was used for dark-field mode visual light observations. For UV-induced fluorescence, an Osram HBO mercury-vapour lamp with filter 330WB80 was employed as the excitation source. A Canon PhotoShot G6 (7 Mpixel) photo-camera with barrier filter 450DF65 was utilised to record the observations. For presentation in this paper (Fig. 4a,b in the Results chapter) the results obtained from the sample collected near one of the OCT examination spots (No. 3 in Fig. 3b) was chosen.

After VIS/UV examination of the cross-sections, the samples were analysed by SEM-EDS with a Zeiss EVO 25 scanning electron microscope equipped with secondary electron and back-scattered electron detectors and coupled with an Oxford X-Max SDD EDX microprobe detector (80 mm^2 detector area). The cross-sections were mounted on aluminium stubs, sputtered with graphite and analysed under high vacuum conditions (2 x 10^{-6} atm) at 20 keV, 200 pA, with a 30 s collection time, and EDS analysis software integrated with AZtecEnergy SEM acquisition both from Oxford Instruments was used. The SEM-EDS analysis provided information on the elemental composition of each layer of the cross-section and thus the composition of the paint and finishing layers.

A very small amount of pulverised material and/or microscopic fragments were collected in a selective way and analysed with a THERMO NICOLET NEXUS™ Fourier transform infrared (FTIR) spectrophotometer in order to characterise the varnish layer components. The powder or fragments were ground with KBr following the technique for obtaining micro-pellets (Ø 1.5 mm). During the examination, 128 spectra were collected with a resolution of 4 cm^{-1} and averaged. OMNIC™ “Specta” software developed by Thermo Fisher Scientific was employed for elaboration of the data.

It is worthwhile to note that in addition to abovementioned examinations, performed before the restoration process, the varnish removal was additionally monitored with laser scanning micro-profilometry and laser scanning confocal microscopy.[5] In this study, published already [9], the method of direct assessment of the varnish thinning process is presented.

3.3 Optical Coherence Tomography

Optical coherence tomography (OCT) is a non-invasive technique which originates from medicine diagnostics, where it is considered a mature technique useful mostly in ophthalmology, especially for examination of the retina [10]. It has been in use for structural examination of cultural heritage (CH) objects since 2003 [11-14]. Until today, the technique has been utilised in the analysis of easel paintings [15-20], wall paintings [21, 22] as well as reverse painting of glass [23]. Among other objects, those made of jade, porcelain, and faience [24-26] were investigated most. Some attention has been given also to objects of historic glass and stained glass [27, 28]. OCT can be also used for material studies – in closest relation to CH objects are those of sandstone properties [29] and wood coatings [30]. Previously we showed that OCT may be combined with other methods to increase significantly – due to the effect of

[5] performed by Raffaella Fontana, Enrico Pampaloni and Marco Barucci (Istituto Nazionale di Ottica, CNR – INO Firenze);

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synergy – their analytic power, namely with Laser Induced Breakdown Spectroscopy (LIBS) for easel paintings [31] and with macroXRF technique for historical manuscripts [32].

OCT is an interferometric technique, usually built around the Michelson interferometer. In its most popular spectral domain modality, the object under examination terminates one arm of the interferometer, and the mirror – held in a fixed position – the other. The emission from a broadband light source is passed through a single-mode optical fibre to ensure high spatial coherence of the probing beam. This is a narrow beam of light penetrating the object essentially perpendicularly to its surface, and is formed by a collimator attached to the fibre end. Both light which is back-scattered and that which is reflected at discontinuities of refractive index within the object, is collected back into the object arm of the interferometer and brought to interference with the light in the reference arm. Detection of the interferometric signal is performed in the spectrograph, and structural information about the object along the probing beam (A-scan) is retrieved by means of Fourier transformation. By translating the probing beam to adjacent positions along a given line, a cross-sectional image of the object (B-scan) is obtained.

The B-scan is the most common way of presenting the results of OCT examination. In the present contribution, B-scans are shown in a false colour scale in which non-scattering media like air, as well as glass and some varnishes are represented in black. Low-scattering media are shown in blue to green, whereas high scattering/reflecting ones are displayed in warm colours (yellow to red). It should be noted that areas not accessible to probing light (e.g. within and below the layer of opaque paint) are also seen as black. Since the OCT cross-sectional images usually cover a relatively large area (from a few to 15 mm), the axial (in-depth) scale is elongated compared to the lateral one. Additionally, the distances along the probing beam are seen in OCT as optical ones and this must be taken into account when true axial distances within the object structure are measured. Usually it is accomplished by dividing a distance obtained with scale bar by the refractive index (i.e., estimated here as 1.5). However, in figures 4 and 6-8, two vertical scales are shown for the convenience of the reader: one to be used in air to describe the surface of the cross-section, the other in the material (n_R=1.5) for measurements within the varnish layers.

Data for this contribution were accumulated by collection of 100 adjacent B-scans to form a 3-D cube comprising scattering intensities for all voxels. This data can be further processed with the technique called *gate imaging* described in detail elsewhere [16]. Briefly: from the 3-D cloud of points the slice of voxels of a given thickness (further referred to as the *width of the gate*) and from a given depth under the surface of the object examined (further referred to as the *depth of the gate*) has been extracted. This way the slice is always parallel to the surface of the painting, independent of its tilt (necessary to avoid specular reflections of the probing OCT beam during the examination). Data from the given lateral position in the slice were then averaged and presented in the same false colour scale as OCT tomograms forming 2D maps. This data presentation modality is especially well suited for the imaging of range of overpaintings [16, 19] as well as of structural details under a thick layer of varnish [33].

The performance of the instrument is mainly determined by the spectral properties of the light source. To ensure high sensitivity of detection, only sources with high spatial coherence are acceptable. Simultaneously, a very low temporal coherence is needed to attain a high axial resolution, and sources with bandwidth of about 200 nm are often used. Inconveniently, the in-depth resolution decreases with the square of the central wavelength, whereas the absorption of many pigmented layers and other materials constituting objects of art usually reaches a minimum at wavelengths of about 2 µm [34, 35]. Therefore, also limited by the availability of sources, the most useful radiation is that from the near infrared region which enables axial resolutions in the range 1 µm – 2 µm to be achieved [18].

In the present study, a portable high-resolution instrument was used. It comprises a broad-band light source made up of superluminescent LEDs emitting in a band of 770-970 nm. The intensity of radiation at

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the object never exceeded 800 µW, and due to fast scanning it was focused at any given spot on the object for only 40 ms. The lateral imaging resolution was about 13 µm, whereas the axial one was 3 µm in air, with an axial imaging range of 1.4 mm. As mentioned above, all of the axial distances should be corrected for the refractive index of the medium. Thus, the axial resolution in the transparent varnish layer (n_R=1.5) may be estimated to be 2 µm. The distance to the object from the most advanced element of the device was 43 mm, and during a single measurement structural information from an area of (8 × 8) mm^2 was acquired in 300,000 A-scans in about 12 s.
The OCT examination (Fig. 3) of the Bessarion Reliquary was performed in the Opificio delle Pietre Dure in Florence in 2012, preceding the conservation-restoration of the artwork.

Fig. 3. Scenes from the reliquary's border: (a) *The Capture of Christ*; (b) *The Mocking of Christ*; (c) *Christ Ascending the Cross.* 1-5: areas of OCT examination shown in Figs. 4 and 6-8. Squares delineate areas of volume scanning, whereas lines denote single cross-sectional scanning. Arrow marks place of collection of the sample shown in Fig. 6a,b and examined by SEM-EDS and GC-MS. Photos: Francesca Bettini, OPD.

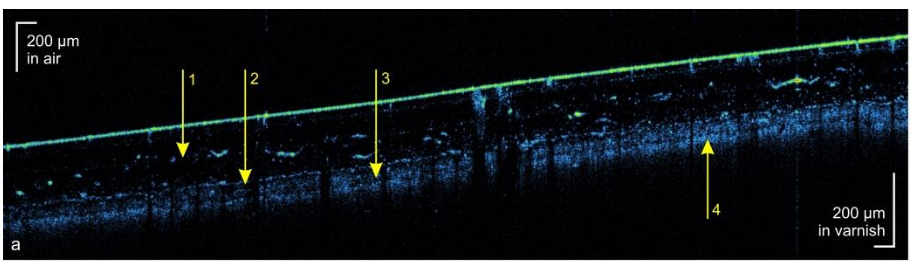
4. RESULTS

4.1 Inspection of original 13th century layers/ painting technique

The layering of the ground, the paint and the varnish films demonstrate the following stratification: a thick, compact ground composed of gypsum and animal glue is applied onto a wooden panel, followed by a second and extremely fine layer to level the surface. Due to the excellent flatness of the ground layer, the paint layer is extremely thin and smooth. This enhances the legibility of the intricate details of the composition by reducing the scattering of the light at paint-varnish interface. In some areas, the paint layer is worn and the residues of the original varnish are scarcely visible. The stratigraphy was

resolved by means of VIS/UV and SEM-EDS examination of the cross-sections – the results obtained for one of the OCT-tested spots are given in Fig 6.
The pigment palette, as identified by means of XRF, was found to be in accordance with a Byzantine painting technique, using traditional pigments such as lead white, minium, cinnabar, green earth, wine black, and red and yellow ochres. The pigments were probably applied with egg tempera (an accurate sampling to perform a GC-MS dedicated to the binder characterisation was considered inopportune and detrimental to the integrity of such a small, unique and precious object). Moreover, on small details of the surface some gold leaf decorations were present, according with the technique of mordant gilding [36].

In order to extend the above conclusions, driven from point-wise invasive examinations, there arose the need for a non-invasive method of structural inspection of the painting. Optical coherence tomography imaging is not able to visualize all the strata that are discernible in the classical sample analysis (e.g., ground and opaque paint layers). However, in cases of paintings with many transparent and semi-transparent layers, it has proved to be useful in resolving the character and sequence of layers, as well as in measuring their thickness non-invasively [15].
The strongest uppermost line in the OCT tomogram represents the surface (air – varnish interface) of the painting examined. It is yellowish in false-colour presentation due to the greatest change in refractive index, whereas the internal interfaces of the layers, with only small refractive index changes, are usually visible as weak (blueish) lines, in so far as there is no delamination present. Transparent varnishes are seen as black stripes and semi-transparent paint layers as blue stripes with a well-defined lower boundary. The last visible structure is the upper surface of the opaque paint/ground layer.
Despite the deterioration of the secondary varnish layers, the OCT tomograms shown in Fig. 4 clearly reveal the structure of the primary paint and varnish layers.



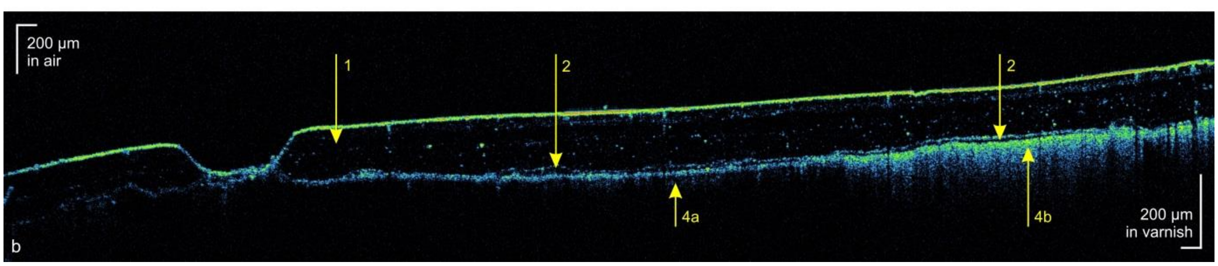


Fig. 4. OCT scans of the Bessarion Reliquary. (a) *The Capture of Christ*, spot 1 in Fig. 3a; (b) *The Mocking of Christ*, spot 2 in Fig. 3b. Sequence of layers from the top: (1) secondary resinous varnish from the 15th century; (2) primary 13th century varnish; (3) primary semi-transparent paint layer – glaze; (4, 4a, 4b) primary non-transparent paint layers of different optical properties.

In the area close to the Christ's feet in the scene of *The Capture of Christ* (Fig. 3a, spot 1, Fig. 4a), under the thick layer of secondary varnish (1), a single transparent paint layer of even thickness – glaze (3) is

visible under the preserved primary varnish (2). The layer which is non-transparent to near-infrared radiation (4) is localised under the glaze (3).
In the tomogram recorded in *The Mocking of Christ* (Fig. 3b, spot 2, Fig. 4b), the stratigraphy of the painting is similar to that described above. The difference is in the type of paint-layers under the thin layer of primary varnish: there is no glaze layer and two kinds of opaque paints are discernible – a strongly absorbing one on the left-hand side of the tomogram (layer 4a in Fig. 4b; green paint in Fig. 3b, spot 2) and a scattering one on its right-hand side (layer 4b in Fig. 4b; red paint in Fig. 3b, spot 2).

4.2 Inspection of the 15th century renovation

4.2.1 Examination of the secondary varnish and gilding

The microscopically inspected cross-sections showed a high level of integrity of the primary and secondary layers: no decohesion or inhomogeneity is appreciable. The only phenomenon was some extensive breakup of the varnish layers (square-shaped craquelure) caused by slow rearrangement of the outer face over the centuries. The thickness of secondary varnish acquired from the cross-sections was ca. 150 µm.
Fourier transform infrared spectroscopy (FTIR) established that the secondary varnish was composed of – a polysaccharide gum, very probably derived from a *Prunus* tree species: apricot, cherry, or plum (Fig. 5).

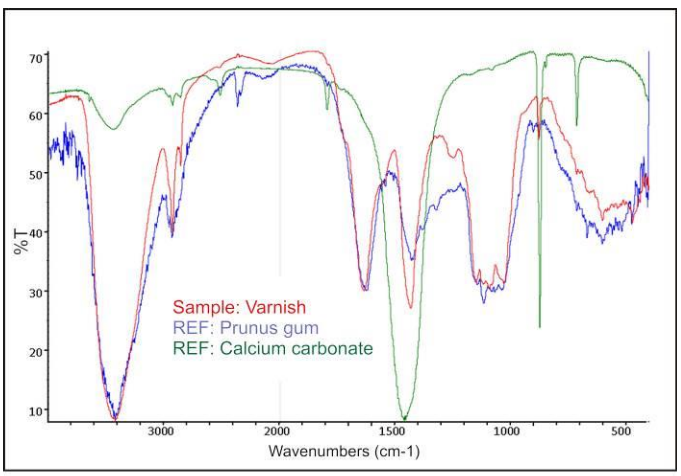


Fig.5. Infrared spectrum of the varnish. The spectral profile matches well with a reference standard of *Prunus* gum (apricot, cherry, or plum) containing traces of calcium carbonate.

Adhesives for the secondary gold leaf were identified by means of GC-MS. The results show the presence of a drying oil, probably linseed, and a small amount of conifer resin (rosin), according to the warm orange tone of the UV fluorescence, typical of these organic substances.
Stereo-microscope observation (Fig. 2b) and cross-section analyses (Fig. 6a,b) revealed successive layering of gold leaf corresponding with the ancient one overlaid by the former. The local character of these observations does not illustrate either the overall condition of the varnish or its thickness. In fact the thickness of the later varnish is not uniform over the surface, and the depth of the newly applied gold leaf in this varnish varies. Thus a non-invasive way to investigate the varnish with in-depth resolution in many locations over the surface, in order to resolve its alterations and thickness, is a key requirement ensuring that the cleaning during restoration can be performed effectively and safety.

In order to evaluate the representativeness of the sample, volume OCT data were collected from an area of 16x16 mm close to the region from which the sample had been excised. A typical tomogram from this set is shown in Fig. 6c. In the region examined, the overall thickness of all varnish layers taken together varies over a broad range: from 120 µm to 205 µm. The equivalent thickness obtained locally from cross-sections is more constant, – varying from 127 µm to 155 µm. Moreover, the thin remnants of the primary varnish layer (8 – 12 µm) are clearly visible in the OCT tomogram, whereas this layer is not discernible at all in the microphotograph.

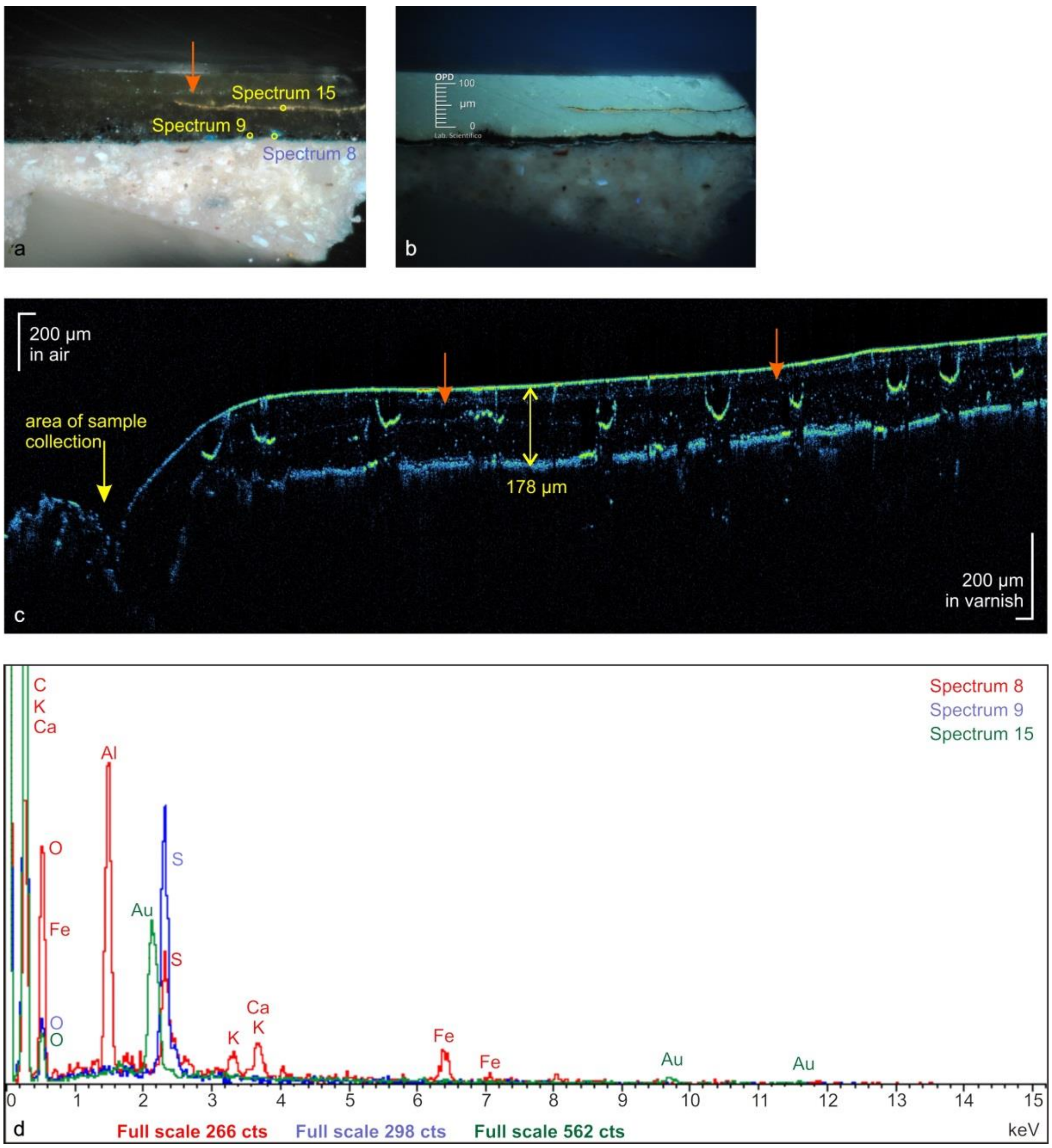


Fig. 6. Examination of *The Mocking of Christ*. (a) Microphotography of a cross-section of the sample taken from the spot marked with a magenta arrow in Fig. 3b located at the edge of the hole visible to the left of the spot 3. Gilding is seen in the middle of varnish layer. Red arrow (also in Fig. 6c) points to the boundary between two uppermost varnish layers, yellow circles mark locations of SEM-EDS spectra given in Fig. 6d; (b) UV-excited fluorescence from the same cross-section. The cold blue hue of the fluorescence excludes the presence of an oil-resinous varnish. At about 2/5 of the thickness of the varnish layer, a gold leaf is present (the black horizontal line on the right), adhered by means of an oil mordant. This leaf it is the second varnish layer, applied during the 15th century

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restoration, and exhibits a warm orange fluorescence due to the mordant. Photos: Carlo G. Lalli, OPD; (c) OCT cross-section from the same area (spot 3 in Fig. 3b) – the gold leaf is seen as strong lines within the varnish layer with no signal (shadow) below; note the approximately four-fold contraction of horizontal scale of the OCT image as compared to photographs (a) and (b); (d) SEM-EDS spectra of spots indicated in photograph (a), materials identified as rock alum used as a substrate for blue lacquer in Spectrum 8, bituminous black in Spectrum 9, gold leaf (secondary) in Spectrum 15.

The secondary gold leaf seems to be floating in the varnish layer, and some visible trace of dual layering of varnish is present above the gold leaf (which is visible both in VIS microphotography and the OCT tomogram).This implies that the final varnish layer was applied in two coats (red arrows in Fig. 6a,c), immediately after the application of the additional gold leaf.
The procedure used in the 15th century restoration is traceable in the OCT tomograms (Fig. 7a). The painting was not heavily overpainted, which used to be a common practice in past ages. Instead, some local retouching had been carried out (structure 3 in Fig. 7a, green area in Fig. 7e) on the surface of the primary varnish (structure 4 in Fig. 7a). Then a thick layer (ca. 100 μm) of *Prunus* tree gum was applied, the primary drawing in gold (structure 5 in Fig. 7a) was repeated (structure 2 in Fig. 7a) and the whole surface varnished again with a thick secondary varnish (layer 1 in Fig. 7a). The inspection of OCT tomograms reveals no signs of a distinct boundary between two secondary varnish layers at the depth of the additional gold leaf. Such a boundary, which would be seen as a thin continuous line, should be present if the two layers had different refractive indices, or if there was enough time for dust to be deposited on the lower one. The conclusion which must therefore be drawn, is that both layers are of the same kind of varnish and were applied in a short time, in one chronological phase.

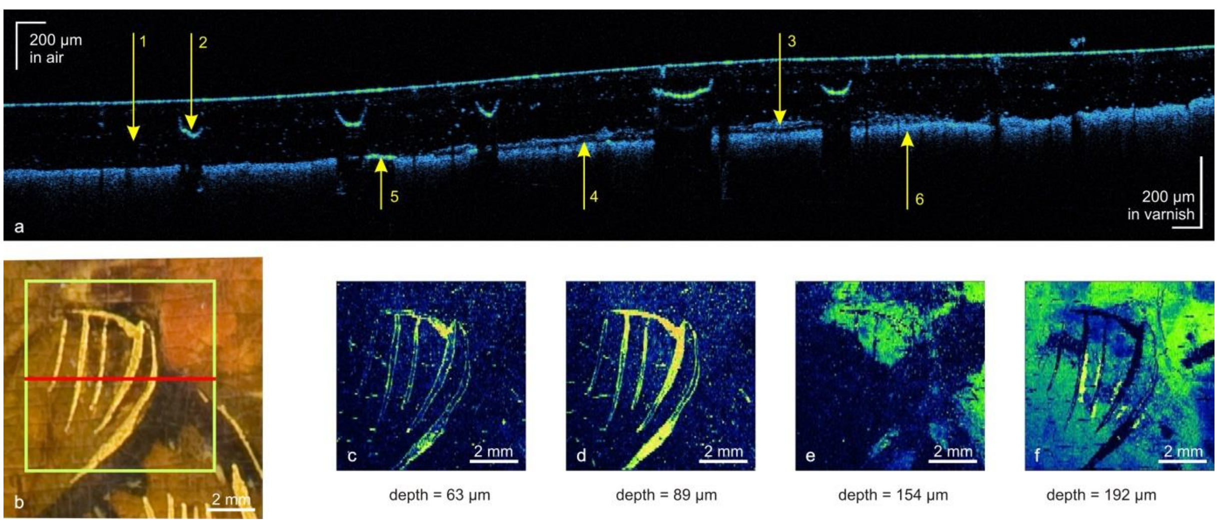

Fig. 7. OCT scans of the Bessarion Reliquary (scene: *Christ Ascending the Cross,* spot 4 in Fig. 3c). (a) The tomogram obtained in the area of cloth of the man in right upper corner of the composition. Sequence of layers, from the top: (1) secondary resinous varnish from the 15th century; (2) secondary drawing in gold; (3) retouching; (4) primary 13th century varnish; (5) primary drawing in gold; (6) primary non-transparent paint layer. (b) Microscopic photograph of the area examined: the red line marks the position of the tomogram. Photo: Francesca Bettini, OPD. (c, d, e, f): Gated images of the scanned area. The depths indicated refer to the mean locations of the gates of width 15 μm.

It was probably the poor legibility of the primary drawing in gold that led to this kind of renovation. The secondary gilding is sharper and more distinct (Fig. 7b). Both OCT tomograms (Fig. 7a) and gated images (Fig. 7c,d,f) enable clear differentiation between the primary and secondary gold drawings. The structure

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of the painting underneath the gold is, however, not visible since the gold absorbs the OCT probing beam, casting shadows onto the structures below.

4.2.2 Examination of specific deterioration of the secondary varnish

The preliminary analyses and observations of the polychrome parts of the reliquary indicated that the secondary varnish was of high transparency except for some areas showing “flake-like” opalescence. The microscopic photographs (Fig. 2a, 8b) revealed that the damage had probably occurred within the structure of the thick varnish and was not correlated with its craquelure. It was not possible to examine this phenomenon, suspected to be some kind of internal delamination, by sampling analysis due to problems with both collection and preparation of the cross-sections from the samples.
It was important to establish which layer was affected. During the 15th century, renovation, two layers of secondary varnish were applied onto the surface with an overall thickness exceeding 200 µm.

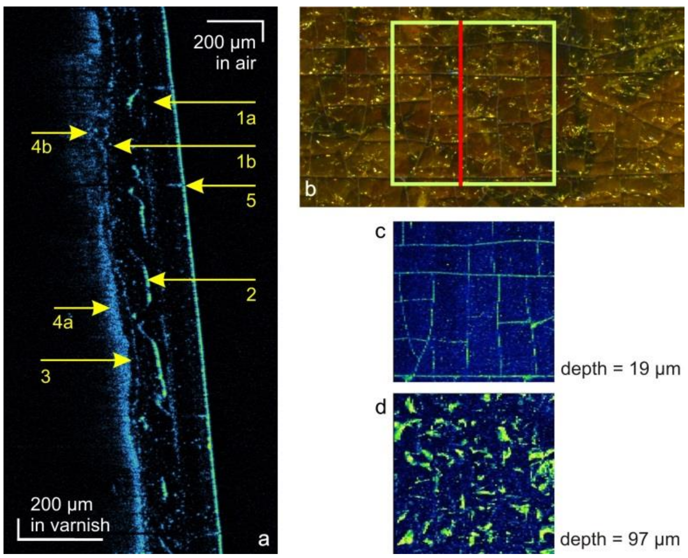

Fig. 8. OCT scans of the Bessarion Reliquary (scene: *The Capture of Christ*), spot 5 in Fig. 3a. (a) The tomogram obtained in the area of the feet of Christ. Sequence of layers, from the top: (1a) upper layer of the secondary resinous varnish from the 15th century; (1b) lower layer of the secondary resinous varnish from the 15th century; (2) delamination in the secondary varnish layer; (3) primary 13th century varnish; (4) primary non-transparent paint layer; (5) craquelure. (b) Microscopic photography of the area examined: the red line marks the position of the tomogram, the white square marks the location of gated images. Photo: Francesca Bettini, OPD. (c, d) Gated images of the scanned area: the depths indicated refer to the mean locations of the gates of width 15 µm.

While the OCT tomogram (Fig. 8a) confirmed the existence of delaminations (2) within the secondary varnish layer, it was unexpectedly discovered that the delaminations were localised, not at the boundary between the upper (1a) and lower (1b) layers of secondary varnish or between the original (3) and secondary varnishes, but within the bulk of the lower layer of secondary varnish.
Delaminations within the structure of paint layers and varnishes are clearly visible in the OCT tomograms due to a substantial change in refractive index at the interface of the detached layers. The intensity of the radiation scattered at such lateral discontinuities in the structure is found by the OCT instrument to be comparable to or greater than the intensity of the signal coming from the upper surface of the object examined. Unlike the metallic foils and the pigments, which are also easily discernible in the OCT

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tomograms (as yellowish lines), the delaminations do not absorb the probing beam and thus do not obscure the legibility of the layers underneath.
The gated imaging revealed the exact depth of the deterioration phenomena. In Fig. 8c the craquelure of the upper varnish layer is shown to be limited to the upper ¼ of the overall varnish thickness (ca. 50 µm), whereas in Fig. 8d it is seen that the delamination pattern – visible as yellowish areas – is localised at a depth of ca. 97 µm below the surface. Most important information, obtained from this examination was that the delaminations were present at certain depth with non-deteriorated varnish underneath. This finding justified the decision of thinning the varnish layer, down to well preserved layer (Fig. 9).

5. CONCLUSIONS

Due to the limited permeability of paint layers to near-infrared radiation, optical coherence tomography cannot be regarded as a universal tool for examination of painting technique in easel paintings. However, in the case of multilayer paintings executed in a classical manner, it is usually possible to determine the internal structure of the object to some extent, since varnishes and glaze layers are transparent or semi-transparent in the visible range. Moreover, it should be emphasized that primary varnish layers are seldom discovered in historical paintings due to the overly aggressive restoration practices of past ages [37, 38].

Fig. 9. Scene of *Christ Ascending the Calvary* from the Bessarion Reliquary before (left) and after (right) the 2012 restoration. The result of varnish thinning is clearly visible: the "iridescence" effect and the craquelure have disappeared, and the painting is fully revealed again in its pristine glory. Photos: Giuseppe Zicarelli, OPD.

The results of the examination of the Bessarion Reliquary (Fig. 2) are therefore to be deemed the more interesting, given the fact that, not only the secondary layers, but also the primary ones, including preserved primary varnish, could be discerned in the OCT tomograms.

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The current trend in cultural heritage diagnostics is strongly oriented towards non-invasive techniques. Generally speaking, invasive analyses are conclusive in reference to a finite small area, but sometimes the extrapolation of such results does not provide the necessary precision needed for an accurate restoration intervention. On the other hand, non-invasive techniques alone, even when coupled with each other, are not in all cases able to provide answers to all of the questions posed by a complex artwork such as Bessarion's reliquary. Thus, the application of both approaches is significant, as it enhances both the accuracy and the reliability of surface analyses and allows extrapolation of the results of invasive analyses, even if those are carried out by selecting only relatively few micro-samples, thus reducing dramatically the sampling impact.

In the present scenario, OCT has demonstrated its remarkable power to illustrate and expand "vision through" the varnish in such a way that it was possible to determine exactly the varnish layer thickness, the depth of "floating gold leafs" and the in-depth localisation of the deterioration of the varnish layer. The use of OCT, coupled with a few collected samples analysed in the traditional manner, allowed the obtention of a very complete description of the aged, altered and layered varnishes, at the same time minimising damage to the surface of this important artwork.

Concerning the optical alterations that had occurred in the upper left part of the object, the OCT observation allowed precise localisation of these phenomena within the structure, confirmed their character (delaminations), and correlated them with photo-induced stress due most probably to improper maintenance over the ages (display condition, exposure to the sun light, etc.). In addition, OCT fulfilled the restoration necessity both of having the precise positioning of secondary gold leafs, which must be preserved, as well as of elimination of defects due to delamination by careful thinning of the varnish layer.

Armed with the results of this complementary examination technique, the restorer is aware of the condition of the material and the way in which – and to what extent – the varnish could and should be thinned in order to optimise recovery of the legibility of the painting considered, thus to a great extent additionally avoiding unnecessary removal of and substitution for the historically original materials.

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