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Material Aspects of Icons. A Review on Physicochemical Studies of Greek Icons

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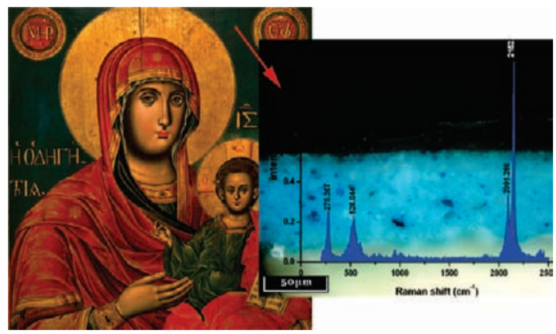
CONSPECTUS

Holy icons created in the Byzantine era are a vital entity in Orthodox Christianity, a living tradition unbroken over more than 1500 years. The importance of these symbolic representations has inspired interdisciplinary studies to better understand the materials and process of their construction. Researchers from a variety of fields are working together to place icons in their proper historical and cultural framework, as well as to develop long-term conservation strategies. In this Account, we review very recent analytical results of the materials and painting methods used in the production of Byzantine iconography.



The care of icons requires particular attention because of their function; icons are objects of veneration and, for the most part, still stand in today's churches to serve ritual practices. Accordingly, they are affected by random, fluctuating environmental conditions aggravated by public access. Because of the holiness of the icons, the typical tradition of the church is to periodically restore the depicted scenes, either by retouching any defects or by partial or complete overpainting. These interventions greatly increase the complexity of the paint stratigraphy. To reveal the extent and quality of the original painting under several historical overpaintings or dirt overlays on the icon, researchers usually pursue a manifold approach, combining complementary multispectral imaging and spectroscopic techniques nondestructively.

Unfortunately, a visual and exhaustive spectroscopic examination of a minimum number of cross-sectional microsamples is almost always necessary to clarify the structure of the paint layers and map the constituent materials identified therein. A full understanding of these details is critical for assessing the painting methods, stylistic conventions, and compositional concepts that render the different iconographic details. Cross-sectional micro-Raman spectroscopy, although time-consuming, now affords the direct identification of the distinct grains of almost all of the inorganic pigments and inert components included in the paint layers. Micro-Raman studies are complemented and cross-checked by micro-FTIR and scanning electron microscopy−energy dispersive spectroscopy (SEM−EDS) studies. This approach is essential in documenting the evolution of the materials and techniques used in creating icons over the centuries.

Analytical data on Greek icons are now available for comparison with similar results from other important schools of iconography, such as in the eastern Mediterranean, the Balkans, or Russia, or, further, with Western schools of painting. The research constitutes a reference base for identifying and solving analytical problems, such as those related to the organic materials found in icons that have not yet been systematically studied. Moreover, the results on icons are also generally applicable to important analytical issues encountered in studying any multilayered paint stratigraphies.

1. Introduction

Byzantine iconography constitutes a fundamental chapter in the history of Greek art and of Eastern European−Mediterranean cultural heritage and is studied as an integral component of painting of the medieval period. The tradition of icon painting is alive in the orthodox world up to the present day, since icons are not just objects of art expression but are chiefly sacred objects involved in worship. Therefore their study refers not only to the analysis of museum or private collections but equally and importantly to the investigation of icons currently standing as liturgical objects in churches.

From an aesthetic point of view, certain elements of icon painting derive from the classical and hellenistic plastic art, regarding the rendering of the drapery and the way it unfolds around the knees or the elbows, the postures, the model-

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ing of the flesh tones, the use of shade, and more generally the rendering of light. However the light in Byzantine art is used to reinforce the two-dimensionality of the image. This is achieved by multiplying the sources of light all over the entire composition and by creating lightings and shadings for each figure independently. Thus any reference to physical space is canceled; on the contrary, the composition refers to a symbolic, aspatial and atemporal, bidimentional, antirealistic world. On the other hand, the depiction of firm, sober characters and fixed archetypal, immaterial postures and gestures evokes the inner spiritual life of the figures recalling the art of the Fayium portraits.[1]

Byzantine iconography has along the centuries progressively set up a typical technique and corresponding style that were crystallized in its apogee, from the 13th to the 15th centuries; though outstanding masterpieces preserved in museums and churches date back to the 12th and 13th centuries. Icons of the Byzantine period are characterized by a limited palette consisting of mineral, mostly earth pigments and frugal color shades that are employed following iconographic conventions to signify the holy figures rather than describe the garments or make obvious the physical shape of the bodies. The lightings and shadings in the garments are thereby not modeled; rather they are schematically designed and rendered by superposition of gradual flat lighter or darker tones. However, despite the certain compliance to "acceptable ways" for the depiction of the Saint figures and conformity to stereotypical painting techniques, such discipline did not prevent across the centuries the iconographers, monks or secular,- in their majority anonymous, from creating an intuitive art.

Icons have been extensively studied from the historical, theological, iconographic, and stylistic points of view in the context of theological and archeological disciplines.[2] However it is only in the past decade that "multispectral" light was shed to material aspects of icons.[3] Systematic investigation of a large number of Greek icons representative of different periods and provenance has demonstrated through multidisciplinary studies the close interdependence among materials, stylistic features, geographical—historical context, and semantic content.[4–6] There are historical documents that provide descriptions of the materials and techniques used in the creation of icons of different periods and styles.[7] However there are currently concerns about the accuracy of the technical information contained in them. This is due either to a certain vagueness or insufficiency in technical details, or more often to difficulties in the interpretation of these early quotations. There is a clear need for verification of the technical information in order to further explore the importance of these early texts for the identification of icons.

The aim of this Account is to review the results of analytical investigations carried out in a systematic manner into the techniques employed in the creation of Greek icons. We considered worthwhile to present a synthetic review of, in large part, published data on material aspects of icons that derived from detailed technical studies carried out in "Ormylia" Art Diagnosis Centre, during the last 15 years, contributing to the introduction of a multitechnique methodology for the study of Byzantine Iconography, being previously only fragmentarily approached. Early results are here reviewed with reference to more recent related studies.

2. Multitechnique Approach to Materials Identification and Painting Techniques Investigation

Past years′ research on cultural heritage objects and specifically on paintings is oriented toward technical advancements to improve the performance of nondestructive *in situ* studies in a view to fully compensate or at least to reduce the extent of microdestructive analyses.[8] Imaging or scanning spectroscopic techniques are preferable since they allow visualization of the forms or mapping of the distribution of the materials not only on the surface but often also in the underlayers.[9] There are several case studies demonstrating the potentiality of a nondestructive analytical approach comprising complementary spectroscopic techniques for the understanding of the painting methods and of the pathology of large wall compositions in Byzantine churches.[10,3] Furthermore comprehensive studies of Byzantine illuminations were accomplished noninvasively by putting the sheets of manuscripts under microscopes interfaced to lab spectrometers.[11] However, in the case of icons painted on wooden panels, due to the complexity of their sratigraphy, the acquisition of exploitable information through nondestructive methodology is efficient only as a preliminary yet indispensable stage that guides further investigation of materials and painting techniques on an adequately selected and properly treated minimum number of microsamples. Therefore, although innovative nondestructive techniques have been experimented on icons with some promising results, examples of well-established methodology applied for the study of paintings are rather presented here as better highlighting particular traits of icons.

2.1. Support Structure. Composite high-resolution X-radiographs produced by X-ray tubes at a range of voltages

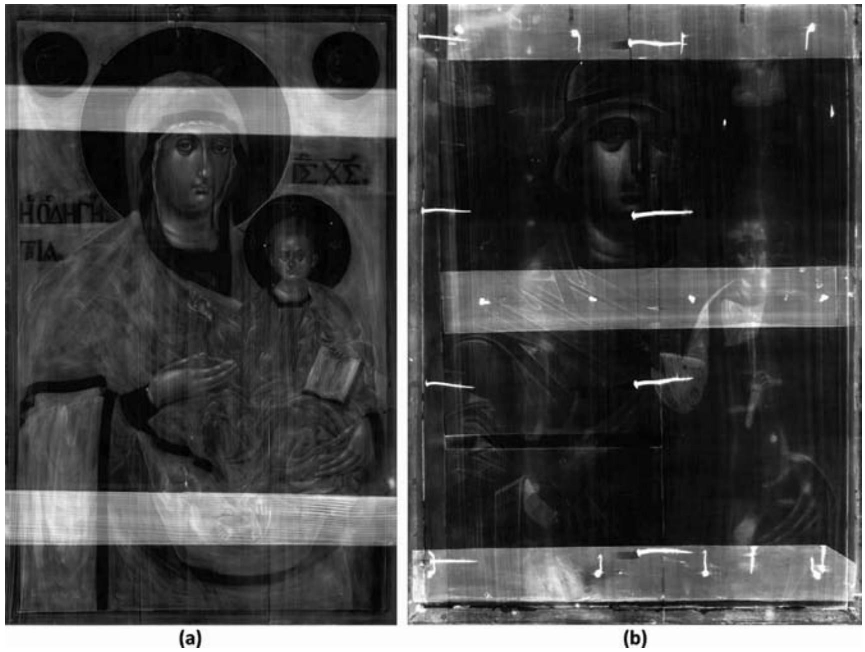

FIGURE 1. Composite X-ray radiographs putting in evidence construction details of the wood of the two icons of the "Mother of God, Hodegetria" (a) 1835, School of Galatista,[6] and (b) 16th century, Cretan School.[3] In panel a, there is evidence of the technical skill of the artist, accurately fitting three panels together and reinforcing them with appropriately positioned transverses without using any metallic nail. In panel b, a secure adhesion of the three wooden panels of the support was obtained using four iron nails to grip those on the left and center, while four others link the middle panel to the one at its right. The nails had been inserted from left to right, slightly inclined toward the facing side of the icon, without any trace of detail on the rear side.

5−50 kV, adaptive to the thickness or the kind of the wooden support of icons under examination, are appropriate for the visualization of features essential for the recognition of the nature and structure of the board (single panel or assembly) and of the method of manufacture (with or without metallic parts; a preparation with or without canvas glued under the ground) (Figure 1). On the other hand, X-radiography allows the study of the preservation state of the support often subjected to worm attacks or other kind of damage as well as of any intervention for its conservation or restoration. It gives also clues on the painting technique through the recognition of certain pigments that contain heavy elements like lead, mercury, etc., in a nondestructive manner.

2.2. Preparatory and Final Drawing. Infrared high-resolution composite reflectograms acquired with interference filters in the spectral region of 1700−2000 nm often in combination with X-radiographs are essential for the documentation of the underdrawing of icons.[4,6] Furthermore, stylistic details that characterize the final drawing of icons of different periods, generally outlined with carbon black, are viewed in enhanced contrast under infrared light penetrating through the superficial dark layer of soot, which progressively veils the original drawing and colors of the paintings (Figure 2).

2.3. Multilayered Paint Structure. Results obtained with nondestructive analysis assist to optimize the adequate choice of the points for microsampling with respect to the painting technique traits and the stylistic conventions for rendering the different iconographic details. The examination of the cross sections including typical stratigraphies from relevant iconographic details in the composition using a polarizing microscope provides high-resolution color images, which constitute the visual reference for any further chemical study (See Figures 3, 4, and 6).

2.3.1. Inorganic Pigments as Prevailing Coloring Materials. Micro-Raman spectroscopy, thanks to its high spatial ($\leq 1\ \mu$m) and spectral (≤ 1 cm^{-1}) resolution, specificity, high reproducibility, and excellent sensitivity has been proven the most accurate and suitable technique for the identification of pigment mixtures applied in the multilayered stratigraphies of icons.[12] The technique applicable in a microsampling cross-section configuration has the advantage of focusing through high-magnification objective lenses (50×, 100×) on the micrometer-sized particles of the pigment mixtures in the different paint layers of icons of 5−50 μm average layer-thickness. The incident laser excitation beams mostly used in the study of inorganic pigments are provided by cw air-cooled He−Ne red (632.8 nm) and argon ion green (514.5 nm) laser

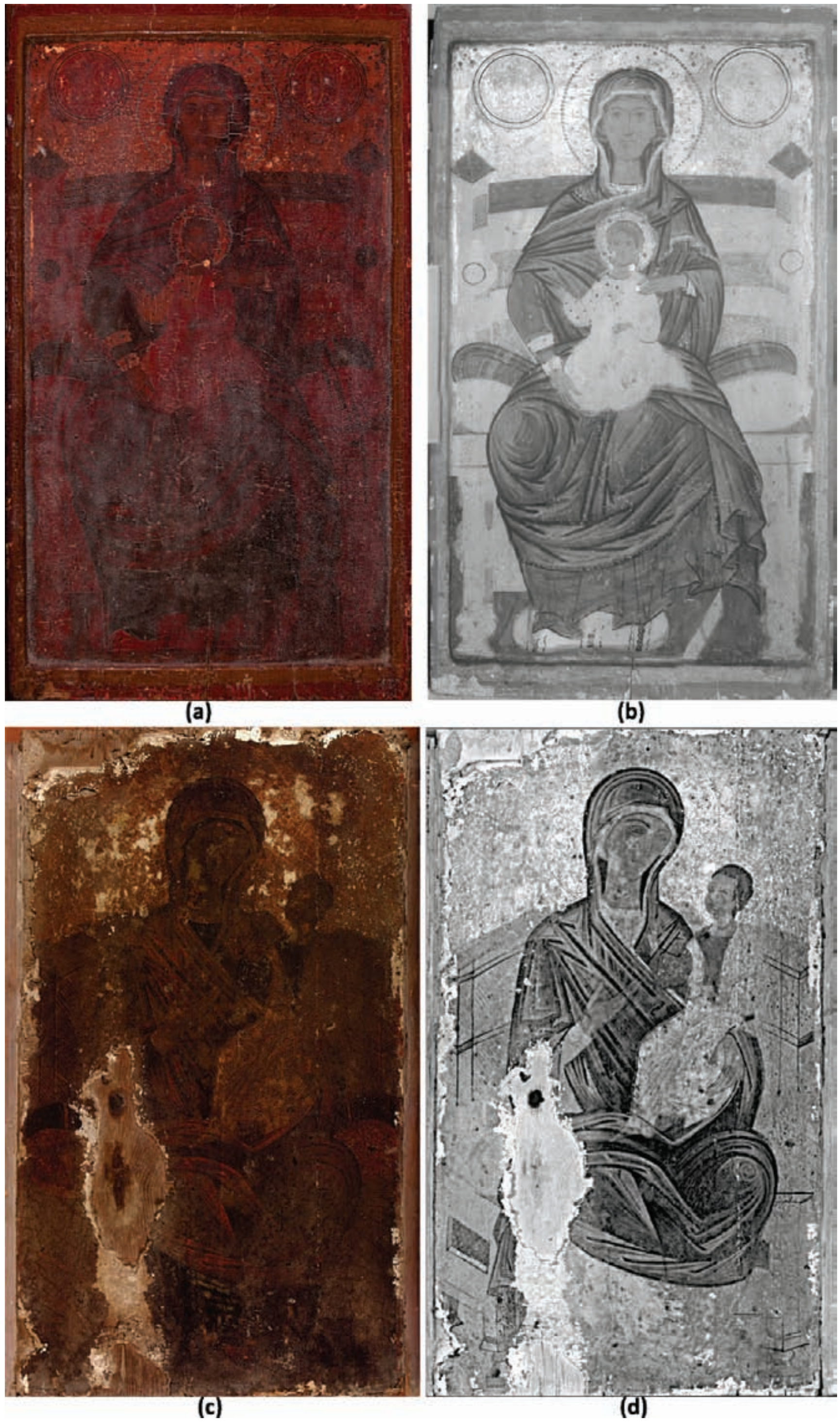

FIGURE 2. (a, b) Mother of God with the child, enthroned, icon preserved at St Nicolas' church of Galatista, in Chalkidiki. First half of the 17th century. (c, d) The Immaculate Virgin, icon preserved at St Dimitrios' church of Athytos, in Chalkidiki. First quarter of the 17th century (From ref 4, pp. 210−223). Panels a and c are photographs in the visible, and panels b and d are composite infrared reflectograms at the 1800 nm. Stylistic details are viewed in enhanced contrast under infrared light penetrating through the superficial dark layer of soot, which progressively veiled the original drawing and colors of the paintings.

sources, in low laser power at the sample, usually between 0.05 and 0.7 mW, and long integration times of 5−100 s multiplied by 5−30 accumulations. Moreover, the technique applied *in situ* has been appropriate for studying manuscripts or small sized, simply layered icons handled on the stage of the microscope.[11] Micro-Raman spectroscopy applied on cross sections can lead to direct identification of distinct grains of almost all the inorganic pigments or inert inorganic compounds included in the stratigraphy, pertinently complemented or cross-checked by micro-FTIR and SEM−EDS studies.[13] However when micro-Raman measurements are applied directly on paintings, often the acquisition of an exploitable spectrum is disabled due to the high fluorescence of the materials on the dirt and protective multilayered varnish accumulated over the paint surface. For *in situ* applications, micro-Raman has been interestingly combined with techniques providing rapid elemental information assisting the screening of pigments. Micro-Raman has been applied in combination with laser-induced breakdown spectroscopy (LIBS) in different types of paintings including icons. Elemental analysis obtained with LIBS on the same spots where Raman spectra were acquired on the surface of the object with a resolution corresponding to the typical focusing conditions and respective probed area, estimated around 1−10 μm deep and 100 μm wide, was proven valuable for the secure identification of the top-layer pigment mixtures.[14] However, the microdestructive character of LIBS must be taken into account, given the even minimal removal of material corresponding to the dimensions of a laser single pulse, due to the nature of the ablation process involved. A prototype micro-Raman/micro-XRF assembly developed in the framework of the PRAXIS project has been also validated for the study of icons.[15] Raman and XRF spectra were collected from the same positions in order to extract, respectively, complementary structural and elemental information relevant for the identification of the pigments. An $X-Y$ scanning option was attached to the instrument in order to enable mapping of pigments on the studied surface, overcoming the limitation of spatial resolution discrepancy between the two analytical components (with a measuring spot ~25 μm wide and a penetration depth depending on the materials for the X-ray beam and a spot ~2.5 μm wide/~6 μm deep for the laser beam). However, the great penetration depth of the XRF analyzer, offering the possibility to extract information from both the top and underlayer materials, would be proven extremely valuable in the study of the multilayered structure of icons only in condition that this elemental information was depth-resolved. The depth resolution capability of recently developed 3D micro-XRF instruments realized by a confocal setup of the X-ray optics is still only tentatively experimented in the investigation of stratified paint layer composition in a noninvasive manner.[16]

2.3.2. Organic Pigments Selective Use. A methodology of dye extraction and analysis with HPLC-DAD and complementarily with MS has been applied by Karapanagiotis et al.[17] to give accurate results for the identification of the species used in the preparation of organic pigments applied in icons. HPLC analysis combined with Raman analysis and optical white light and fluorescence microscopy applied in cross sections allowed documentation in detail of the different techniques of application of red lakes in the stratigraphy of the icons, demonstrating an evolution in the selection of the raw materials but also in their application techniques. The recent investigation of lakes in the painting of icons belonging to the Cretan School and preserved either in churches and monasteries or in the collections of the Benaki Museum allowed the establishment of a first set of data as a reference for the further extension of related studies.[5,17]

2.3.3. Binding Media. The identification of the binding media in paintings in general has been widely approached with the application of gas chromatography coupled with highly sensitive MS detectors. Furthermore, thanks to recent advances in mapping and linear imaging FTIR spectroscopy[18] and in immunofluorescence techniques[19] applied in cross section configuration, there are promising results in the identification of organic materials and in particular of binding media, which may be resolved layer by layer. The analysis of the icons' binding media has not been systematically approached up to now, although it is highly important for our understanding of the Byzantine artists' painting technique. There are only few analytical works carried out with different gas chromatography/MS methods on derivatives of samples taken from the paint layers of Byzantine iconographic artworks. In the case of wall paintings, the focus of analysis was put on the identification of proteinaceous binders, thus on the determination of their distinct amino acid composition (egg, animal glue, casein).[20] In the case of post-Byzantine panel paintings from the Ionian Islands, Kouloumpi et al.,[21] applied a chromatographic methodology based on the simultaneous derivatization and determination of amino acids and fatty acids aiming at determining the exact composition of the binder as egg yolk or egg/oil emulsion. Characterization of binding media in the icons of post-Byzantine period would also enable researchers to investigate the validity of common assumptions about the influences of the Venetian style on Greek icon painting techniques from the 16th to the early 19th century, which up to now have been based mostly on information in artists' handbooks.[7]

Micro-FTIR spectroscopy applied on a systematic basis prior or supplementarily to chromatographic analysis assists the interpretation of the GC/MS results because it permits mapping of the spatial distribution of the identified components. Conventional micro-FTIR spectroscopy in reflectance mode was combined with selective staining with amido-black/pH 7 applied on embedded samples viewed in cross section under

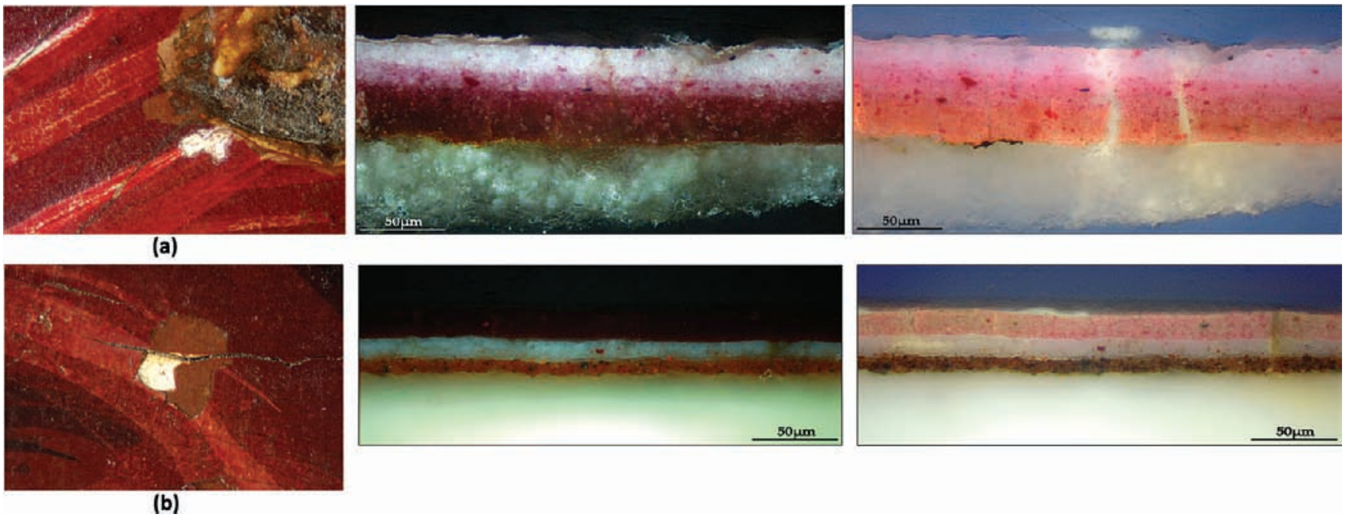

FIGURE 3. Photomicrographs in white reflected light and of the ultraviolet fluorescence response of cross sections from light gradations in the maphorion of the Mother of God and respective macro details (on the left) of the samples' positions (under stereomicroscope) on two icons belonging to the Cretan school (16th century). Characteristic fluorescence response of kermes (identified through HPLC/DAD[17]) applied either in the paint of the underlay in mixture with redwood, madder lake, and lead white (top) or pure in a thick layer of glaze over the red garments (red ochre and carbon black in the underlay; lead white in the light gradations) (bottom).

the microscope by Daniilia, Sr., et al.,[5] for the screening of the binding media in the paint and in the ground layers of the microsamples taken from icons by the hand of Angelos, Cretan style, 15th c. Layers of different concentrations of animal glue in mixture with gypsum ground were identified as a preparation for the painting with egg yolk binder, while, alternatively, in the final layers, oil and natural resin were identified in the mixture of animal glue with gypsum ground as a preparation for the painting with an emulsion of egg yolk containing stand oil and a natural resin.

3. Evolution of Materials and Techniques in the Painting of Icons from the Byzantine Style to the Late Centuries

Post-Byzantine icons belonging to the Cretan style (15th−18th centuries), being actually widely abundant[2] and therefore the most studied regarding materials and techniques, are relevant for the understanding of the devolvement of iconography from the pure Byzantine style to the post-Byzantine and laic styles up to the late 19th century. This is because following the fall of Constantinople there has been an exponential increase of production by Cretan artists who, thanks to their privileged status in the Venetian-ruled Crete, could travel in the whole Byzantium but also in Italy and particularly in Venice, exerting mutual exchanges on materials and painting methods with western artists. Post-Byzantine icons remain very respectful to tradition in particular as regards the composition of the palette; however the Cretan school of iconography has notably developed the Byzantine style through the integration and progressive development of certain technical achievements of the Italian painting. Although there was a certain enrichment in the palette, this remained relatively confined, with the only remarkable innovation in the employed materials being the introduction of lake pigments, for which natural organic dyestuffs obtained from various plant or insect sources are adsorbed onto or coprecipitated with an inert, semitransparent inorganic substrate in order to be used as pigments. Red lakes prepared mostly from kermes and cochineal but also from madder and redwoods are applied either in the paint of the underlay in mixture with lead white (and indigo or azurite) to produce bright rose, orange-red, and purple shades (Figure 3a) or, most interestingly, in a thick layer of glaze producing a translucent veil over the red garments of the saint figures (Figure 3b).

A recent extensive study of icons in the Cretan style dated from the middle of the 15th to the end of 17th century,[18] has demonstrated that while madder and redwoods are in continuous use, after the middle of the 16th century there is a clear substitution of kermes by cochineal. The dexterity in the technique of red lakes combined with the adoption of the *tempera grassa* technique, which both maybe attributed to the exchange with Italian painting techniques, lend a transparency in the paint layers and respective effects in the aesthetic result characteristic of the Cretan school. The use of organic pigments is, however, restricted to the red lakes, in contraposition of the Italian paintings whereas yellow lakes have been also introduced in the palette of panel or easel paintings already from the 14th century applied in mixture with inorganic pigments either in certain yellow or green shades.[22]

El Greco, although educated in the Byzantine tradition of the 16th century Cretan workshops of icon painting, he quickly developed his personal style highly influenced by the Venetian masters. Already in his early works, before leaving his homeland Candia (Heraklion), Crete, there are personal traits announcing his glorious creative path first in Venice and Rome and later in Toledo. The study of the Baptism of Christ dated to 1567 (the year in which El Greco moved from Candia to Venice) has been essential to demonstrate that even though the practices of Italian Renaissance painters already prevail in Greco's personal style, elements of traditional Byzantine iconography are still not completely absent:[23] The ground layer consists of gesso and animal glue, a typical preparation in icons. Traces of bole and gold, detected on the left side of the panel, confirmed that the Baptism formed the inner side of the right-hand panel of a triptych, the frame of which was executed with a traditional burnished gilding technique. For the blue hues (lapis lazuli), the red clothes (cochineal lake), the green garments and the flora (copper resinate), and the yellow shades in the sky (lead−tin yellow), El Greco employed an oily binder in paint layers applied over a layer of white imprimatura containing powdered glass (a practice of Venetian painters). However, he has also used egg tempera for both the yellow-brown garments and the earth in the paint layers consisting of earthy pigments (such as yellow ochre and brown umber), applied directly over the white gesso ground. Detailed study of the binding media was not possible due to the minimal quantity of the samples that were available. However, in the cross sections examined under UV-light, the layers containing oil exposed a strong fluorescence in contrast with the ones containing egg.

After the post-Byzantine period (15th−18th), a decisive role in the evolution of Greek iconography was played by the so-called Galatistan school, recently systematically studied.[6] The founder, Makarios, a monk in Mount Athos, was directly influenced by the iconographic and literary work of the 18th-century Dionysios of Fourna. Although Makarios and his disciples generally followed the directions in Dionysios' Manual,[7] which became a handbook for the continuation and regeneration of the Byzantine iconographic tradition from the early 18th century onward, they progressively introduced elements from folk, baroque, and rococo styles worked out in their own manner. Their palette was gradually enriched with a great number of synthetic pigments such as Prussian blue, ultramarine blue, indigo, copper resinate, emerald green, cinnabar (in extensive use), cochineal lake, chrome yellow, naples yellow, minium, and gold shell, shedding intense and shining colors when mixed with lead white. The traditional gold in the background was substituted with intense color (blue or green) (Figure 4). Gold leaf was strictly confined to haloes and to specific decorative surfaces, while gold paint was extensively used in lighting the wealthy drapery of the garments. The Galatistan artists respected the traditional technique of using egg tempera; however they tended to apply pure pigments and rich in medium layers searching to create effect analogous to those of oil painting techniques.

4. Overpainted Icons

High-definition X-radiography and IR reflectography, as well as spectroscopic techniques like mid-IR spectroscopy and X-ray fluorescence spectroscopy, based on radiation that penetrates through the superficial layers and interacts with the inner layers, have been proven very informative in the study of icons. Wall paintings, as well as icons preserved in churches, are exposed without any effective system of temperature, humidity, light, and pollutant control and thus are affected by highly and randomly fluctuating environmental conditions, aggravated under the enhanced public access, and subjected to the practices of the liturgy, for example, candle lighting and incense burning. In fact, an obvious common impact on the murals and icons is the superficial dark layer of soot that progressively veils the original drawing and colors of the paintings (see Figure 2).

In addition to the overlay of soot, several superposed overpaintings as a result of interventions retouching the surface of icons have been undertaken in the past not by conservators but by iconographers, not with the intention of conservation of the artistic value of the icon but for the restoration of its iconographic and aesthetic integrity in order to continue to serve its function as liturgical object. In such cases, without removing the existing partially damaged original painting, completions or overpainting of the whole drawing have been applied. Consequently the study of icons subjected to several overpaintings demands particular attention in order to distinguish the different layers belonging to different stages of painting dated to different periods affirmed by different techniques and styles.[24] Infrared reflectograms and complementarily X-radiographs, acquired without touching the object, reveal the extent and quality of the original painting preserved under the several historical overpaintings or dirt overlays on the icon, providing essential data to the further investigation or intervention on the objects.[25]

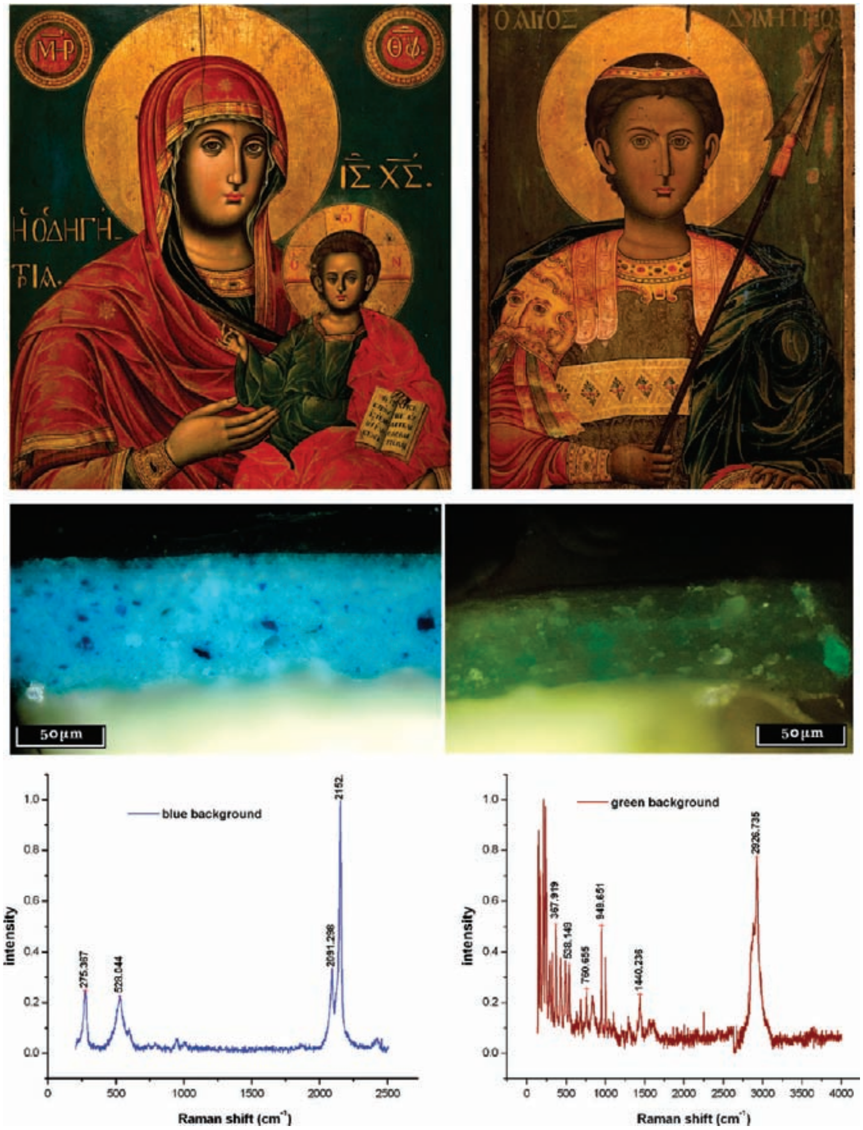

FIGURE 4. Prussian blue (a) and emerald green (b) were identified by micro-Raman spectroscopy in the paint layer of the background of the icons of Mother of God Hodegetria and of St Demetrius, respectively. The two icons, belonging to the School of Galatista, are dated to 1835 and attributed to the same iconographer.[6]

In the overpainted Icon of Athanasios the Athonite (Figure 5), strong absorption of X-rays by lead white, the dominant pigment used for the highlights of the original painting, resulted in clear readings even of the finest brushstrokes in the face and the folds of the garments, allowing estimatation of the state of preservation and the extent of the surviving original painting underlaying the paint surface. In contrast, the corresponding IR reflectograms up to 1900 nm have not been useful in reading the original painting concealed by the overpaint consisting of highly IR absorbing pigments (see Figure 6). The identification of the pigments of the stratigraphy has been crucial for the understanding of the original-16th century-painting technique as well as for the discrimination of different paint layer sets that belong to different stages in the painting and overpainting of the icon. For the underpaint of the face and hands, a mixture was used comprising yellow ochre, carbon black, green earth, and a few grains of lead white. In the gradations of the flesh tones lead white with scattered grains of cinnabar and yellow ochre have been identified. In the overpainting (Figure 6, layer e), lithopone, a mixture of $BaSO_4$ and ZnS (SEM−EDX evidence) predominates while grains of carbon black, ultramarine blue, and minium are added in the paint mixture unevenly applied. The identification of lithopone, first circulated commercially in 1874 AD, allows dating of the overpainting not earlier than the last quarter of the 19th century. For the identification of the binder, the FTIR spectra acquired from the overpainting and

FIGURE 5. Icon of Saint Athanasios the Athonite, detail of the upper part of the icon in the visible and respective composite X-radiograph taken at 37 kV, 6 mA, and exposure time of 105 s on a Kodak MX-Industrex film (from ref 25). Strong absorption of X-rays by lead white, the dominant pigment used for the highlights of the underlying original painting, resulted in clear readings of the brushstrokes in the face and the folds of the garments, allowing estimation of the state of preservation and the extent of the surviving original, underlying painting.

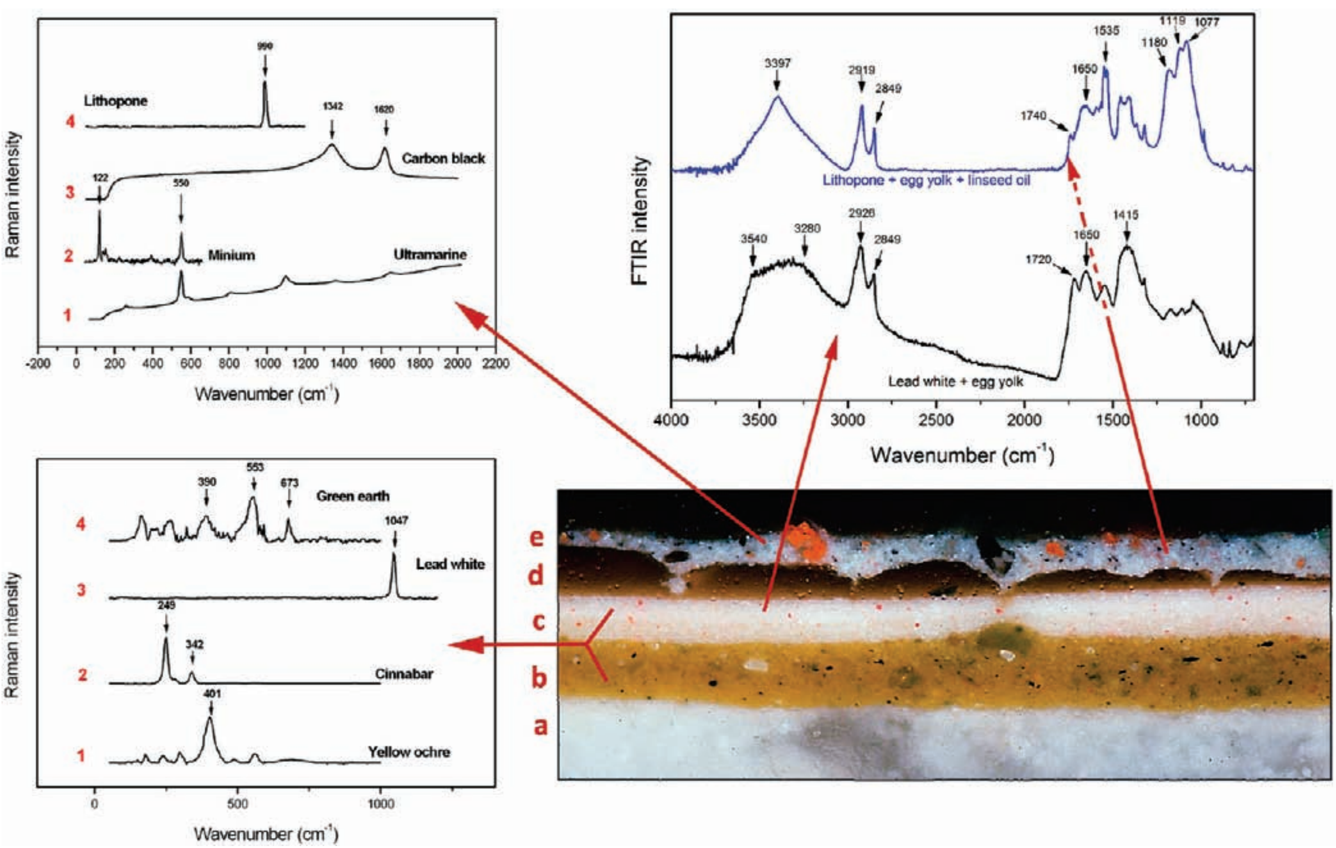

FIGURE 6. Cross-section in the flesh tone of the face, microphotograph under white light. The pigments have been identified in the stratigraphy through micro-Raman spectra acquired with a 632.8 nm laser source, as follows: Original painting, (a) gesso ground, (b) underpaint of yellow ochre, carbon black, green earth, and grains of lead white, (c) flesh tone of lead white, grains of cinnabar, and yellow ochre, (d) varnish; overpainting, (e) lithopone, carbon black, grains of ultramarine blue, and minium. The FTIR spectrum of the overpainting layer displays features attributable to some oil content in the egg binder.[25]

from the highlight of the original painting were compared. The absorption at 1650 cm^{-1}, similarly present in both spectra, can be assigned to the protein amide I band ($\nu_{C=O}$ stretching) suggesting the identification of egg. However, the observed shift to higher wavenumbers of the maximum of the broad band (3500−3000 cm^{-1}, ν_{C-H} stretching) from 3280 to 3397 cm^{-1} and of the characteristic carbonyl peak ($\nu_{C=O}$ stretching) from 1720 to 1740 cm^{-1} is considered to be linked to the addition of some oil in the binder of the overpainting.

5. Concluding Remarks

The identified pigments, their combination in simpler or more complex mixtures or layers, and their resulting chromatic contrasts in the painting composition of icons characterize the period, the geographical provenance, and the style, even though there is a noticeable general tendency through the centuries for the enrichment of the drawing detail and of the color intensity and variety that is beyond any geographical or stylistic context. Is the aesthetic research that had induced the enrichment of the color palette or is the progressive availability in the market of new colors by that time already applied in the West that had as consequence the evolution in the aesthetics of Byzantine art? It is difficult to give a definite answer to such queries; nevertheless, physicochemical investigation provides a wealth of supporting data to study through a multidisciplinary approach the interdependency of the materials, styles, iconographic content, and artistic context.

From the analytical point of view, advancements are expected in the next future studies in identifying and understanding the use of organic materials either as binding media or as protective surface layers. Next to chromatographic analysis, complementary or cross-informational spectroscopic techniques coupled with microchemical imaging may contribute to our knowledge of differential use of natural polymers either as binding media or as protective surface layers depending either on the pigment mixture or on the phase of the painting. Egg tempera use, identified with the traditional technique of icon painting, has been always respected by iconographers from the Byzantine period until today. However through the centuries, under the influence of the West, icon painters experimented either with adding a small amount of oil in the egg binder or, when remaining faithful to the exclusive use of the egg yolk, with attaining similar aesthetic effects to the oil painting in luminosity and transparency by varying the proportion and dilution of the egg binder in the paint. Indicative studies of icons mostly belonging to the Cretan School prompt further systematic analytical studies for the investigation of the binders in icons.

On the other hand, our understanding on the interactions between organic and inorganic compounds of the stratigraphy and their consequence in the aging of the icons in different environmental conditions may allow development of new, more efficient conservation methods (cleaning and consolidation treatments) and long-term strategies to preserve and protect them from further damage taking into account the specificities of their hostile environment, in the majority of the cases, being the interior of a living church.

The results of our group reviewed in this paper were obtained through a collaborative work with our colleagues at "Ormylia" Art Diagnosis Centre whose names are cited in the references. We are grateful for their important intellectual and experimental work.

BIOGRAPHICAL INFORMATION

Sophia Sotiropoulou, Physicist, Ph.D. in chemical engineering, is senior scientist at Ormylia Art Diagnosis Centre. Her field of research includes characterization of paint surfaces (studying optical, chemical, and perceptible properties) and integration of analytical data into the conservation and documentation of artworks and archeological objects.

Sister Daniilia, Chemist and icon painter, is senior scientist at Ormylia Art Diagnosis Centre. Her research interests include the deepening into the materials and techniques applied in the Byzantine Art, in reference to the semantic content and historical context of the artwork.

FOOTNOTES

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