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An extensive non-destructive and micro-spectroscopic study of two post-Byzantine overpainted icons of the 16th century

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This work is an extensive study of two post-Byzantine icons, 'Our Lady, the Life-giving Spring' and 'Saint Athanasios the Athonite,' both painted during the 16th century and now kept at Saint Modestos's Church in Kalamitsi, Chalkidiki, Greece. The icons were examined using non-destructive and microanalytical techniques, namely fluorescence photography under UV light, x-radiography and optical microscopy, in addition to micro-Raman and micro-Fourier transform IR spectroscopy. This study allowed the assessment of the current state of preservation of these icons, revealed prior damage and identified in detail the pigments and materials used in the original paintings and overpaintings. Moreover, it confirmed the usefulness of this approach to the detailed evaluation of icons in general and provided significant structural data on representative portable icons of Cretan-style religious painting. The palette for the original paintings of the two icons consists of the natural pigments caput mortuum, yellow ochre, carbon black, azurite, green earth, cinnabar, white lead, red lake and copper resinate; egg yolk was used as the binder. By contrast, the rather elementary overpaintings are of low tonality, consisting predominantly of mixtures of minium and carbon black, and also the synthetic pigments ultramarine blue, "chrome green" (Prussian blue + lead chromate), chrome yellow and lithopone. A blend of linseed oil and egg provided the binder for the pigments used. The same artist is understood from art historians to have overpainted both icons at the beginning of the 20th century.

INTRODUCTION

The identification by physico-chemical analysis of the materials used in the production of the *original* icons of 'Our Lady, the Life-giving Spring' and 'Saint Athanasios the Athonite' (two post-Byzantine icons painted during the 16th century and now kept at Saint Modestos's Church in Kalamitsi, Chalkidiki, Greece) would provide us with significant new information which is otherwise unobtainable from the sparse literature on Byzantine and post-Byzantine portable icons and wall paintings.[1–3] The availability of such analytical results would be extremely helpful to art historians and archaeologists for their better understanding of the evolution of painting techniques and of the modifications that have occurred with time to the substances used, including, pigments, vehicles, binders and varnishes.

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Conservators and restorers would then be able to decide upon the most appropriate procedures to be followed for the purposes of restoration; other courses of action may cause irreversible damage.

The aim of this study was to determine (a) the current state of preservation, (b) the scale of prior damage, (c) the number and nature of the overpaintings, (d) the characteristics of the structural materials and (e) the artistic techniques that distinguish from others the inspired iconographic works of the 16th century Cretan School. To these ends, the two icons specified above were examined using non-destructive and micro-analytical techniques, namely fluorescence photography under UV excitation, x-radiography and optical microscopy, and also micro-Raman and micro-Fourier transform (FT) IR spectroscopy.

EXPERIMENTAL

Description of the icons

The icon of the Life-giving Spring (Plate 1), 94 cm high and 54 cm wide, is one of the few extant religious paintings that records precisely the year of its being painted. The three letters $\zeta\nu\alpha'$, found on the rear side, date its completion to AD 1543 ($\zeta\nu\alpha' = 7051$ years since the creation of the world according to the Fathers of the Church). What we have, therefore, is a post-Byzantine icon fashioned in the Cretan style—a style whose artistic features had become well established by that time, especially in the works of Theophanes the Cretan, one of the greatest representatives of this School and one who in the mid-16th century was at the peak of his career. Although the icon's wooden support is in an excellent state of preservation, its painted surface bears extensive damage and signs of subsequent, partial intervention: areas of overpainting can be clearly distinguished, especially in the bottom half of the work.

The Virgin, 'the Life-giving Spring,' is depicted with the Christ Child on her lap: she sits in a fountain with water flowing from faucets into a water tank. Christ bestows a blessing with His right hand, while in His left hand He holds a scroll. Two Archangels in the upper area of the gold background are shown in a reverent posture on either side of the central figures. The inscriptions ΜΗΡ ΘΥ, Η ΖΩΟΔΟΧΟΣ ΠΗΓΗ, Μ(ΙΧΑΗΛ), Γ(ΑΒΡΙΗΛ) can be distinguished.

The icon of 'Saint Athanasios the Athonite' (Plate 2), 93.5 cm high and 59 cm wide, is painted on a single piece of recessed wood. The authentic icon is a rare work of art with characteristics of the Cretan style, although what survives has suffered extensive damage. Inartistic overpainting has concealed the greater part of the underlying original artwork, which has remained well preserved. There is, however, flaking in various parts of the paint layers over the entire painted surface, and this significantly affects the aesthetic value of the icon.

Saint Athanasios wears a hooded monastic mantle. His right hand is raised in blessing and in his left hand he holds an open scroll on which is written the inscription 'ΕΙ ΚΑΙ ΠΑΤΕΡΑ ΚΑΛΕΙΝ ΜΕ ΘΕΛΕΤΕ ΜΙΜΕΙΣΘΕ ΜΟΥ ΤΑΣ ΠΡΑΞΕΙΣ' (If you wish to call me 'Father' imitate my works). The inscription 'Saint Athanasios' is written in capitals near the top of the painting.

Procedures

Ultraviolet fluorescence photographs were taken using a Hasselblad 205 FCC camera and an illuminating system comprising four high-pressure mercury lamps, on a Kodak EPR 64 ASA daylight, colour reversal film (code No. 6117). A Kodak 2E Wratten gelatin filter was placed in front of the camera lens.

X-radiographs were obtained by means of an Andrex BW Smart 160 x-ray portable unit (0.5–6 mA, 10–160 kV), supplied with a EP-100 dosimeter, on a Kodak MX-Industrex film which was then developed using a Kodak M35 x-ray film processor. X-radiographs were taken at 20 kV, 6 mA and exposure times of 25 s.

Special attention was paid to obtaining a representative sampling of the artefact under consideration and to avoiding further irreversible damage to it. Samples were mounted in polyesteric transparent resin so that their cross-sections would provide, after grinding and polishing using a Struers Planopol-V machine, all relevant information from the existing stratigraphy.

Cross-sections were observed under a Leica DM RXP research polarizing microscope equipped with a quartz halogen and a UV excitation light source in addition to an automatic photography device.

Initially, a Bruker RFS 100/S FT-Raman microscope was employed at UCL to acquire Raman spectra of the samples and the cross-sections. It was equipped with an Nd:YAG laser as the excitation source which operated at 1064 nm through a Nikon microscope. Most of the spectra were collected in Ormylia on a Renishaw System 1000 Raman spectrometer comprising an Olympus BH-2 imaging microscope, a grating monochromator and a charge-coupled device (CCD) Peltier-cooled detector (576×384 pixels). The incident laser excitation was provided by an air-cooled He–Ne laser source, operating at 632.8 nm. The power at the exit of a $\times 100$ objective lens was varied from 1 to 3 mW, depending on the stability of the pigments identified. Spectra were recorded with a resolution of 4 cm^{-1}, at a collection time of 30 s, and after an accumulation of 10 scans. In order to avoid undesirable Rayleigh scattering, two 100 cm^{-1} notch-filters were employed to cut off the laser line. Pure silicon was used for the calibration of the instrument (to ± 2–3 cm^{-1}).

FTIR spectra were obtained using a Biorad FTS-45A FTIR spectrometer, connected to a UMA 500 microscope and equipped with a mercury cadmium telluride (MCT) detector cooled by liquid nitrogen. For the purpose of analysing the different components in every paint layer of the samples collected, a small amount from each was removed using a micro-scalpel. The particle was then placed on the surface of a freshly prepared KBr pellet. For each spectrum 250 consecutive scans were recorded with a resolution of 4 cm^{-1} using a $\times 15$ objective lens. The sample collection area was adjusted with the upper aperture of the microscope. All spectra were collected in the transmission mode and converted afterwards into absorbance spectra. As background, the spectrum of the KBr pellet was used.

RESULTS AND DISCUSSION

'Our Lady, the Life-giving Spring'

Current state of preservation of the original painting and subsequent interventions

Damage to the gold background had been caused in the past by an unsuccessful attempt to remove in part the surface varnish and dirt. The places where this cleaning had been undertaken were noted with extraordinary clarity in the fluorescence photograph under ultraviolet light [Plate 3(A)]. On the faces of the Mother of God and Christ, on Christ's

Plate 1. 'Our Lady, the Life-giving Spring' (AD 1534). Egg tempera on wood, 94 × 59 × 3.3 cm. Positions of sampling before cleaning.

Plate 2. 'Saint Athanasios the Athonite'. Egg tempera on wood, 93.5 × 59 × 3.3 cm. Positions of sampling before cleaning.

Plate 3. 'Our Lady, the Life-giving Spring'. (A) Fluorescence photograph under UV light; (B) composite x-radiograph (computerized synthesis with image enhancement).

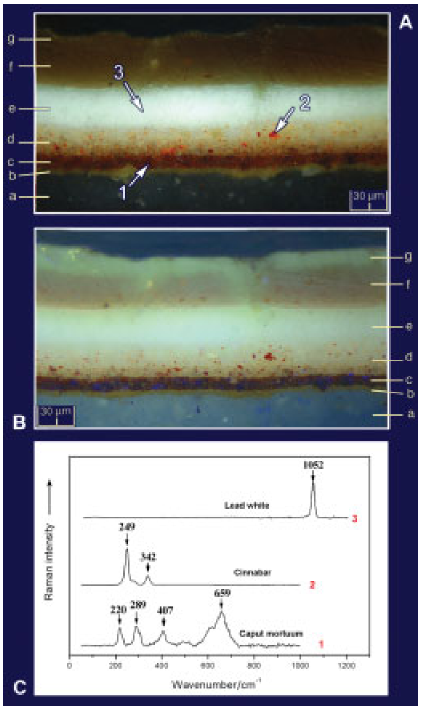

Plate 4

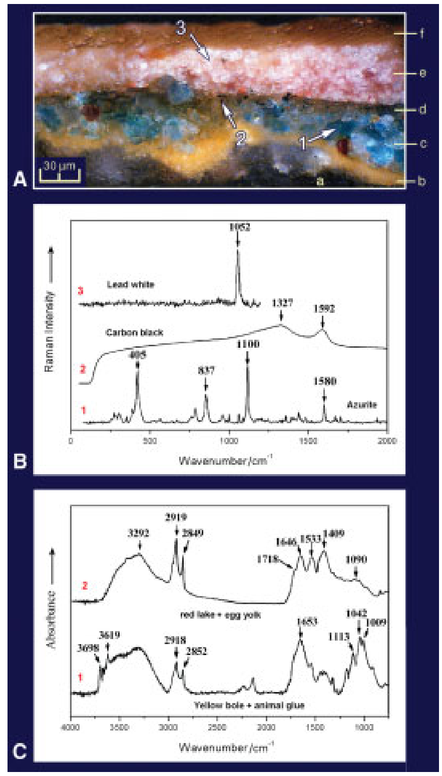

Plate 5

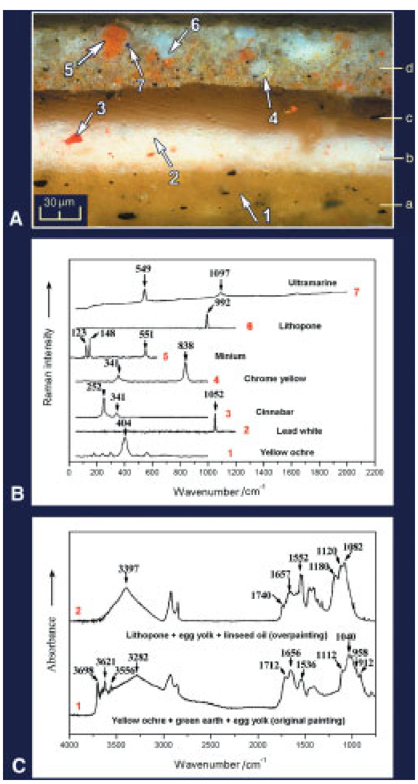

Plate 6

Plate 4. Cross-section of a light from the Virgin's mantle. Photography via a microscope. (A) Reflected light; (B) fluorescence under UV light; (C) micro-Raman spectra. a, gesso ground; b, yellow bole; c, underlayer, caput mortuum; d, highlight, lead white, cinnabar and caput mortuum; e, white highlight, lead white; f, glaze of red lake; g, varnish.

Plate 5. (A) Cross-section from the Archangel Gabriel's cloak. Photography via a microscope in reflected light, (B) micro-Raman spectra and (C) micro-FTIR spectra. a, gesso ground; b, yellow bole; c, underlayer of tunic, azurite and grains of red and yellow ochre; d, principal line of tunic, carbon black and grains of azurite; e, underlayer of cloak, red lake and lead white; f, varnish.

Plate 6. (A) Cross-section of the underlayer from the Virgin's right hand. Photography via a microscope in reflected light, (B) micro-Raman spectra and (C) micro-FTIR spectra. Original painting: a, underlayer, yellow ochre, carbon black, grains of lead white and of green earth; b, flesh tone, lead white, grains of yellow ochre and cinnabar; c, varnish. Overpainting: d, chrome yellow, minium, lithopone, carbon black and grains of ultramarine blue.

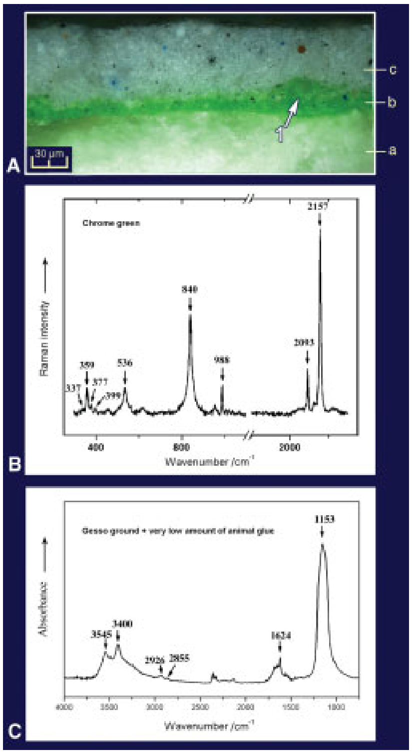

Plate 7

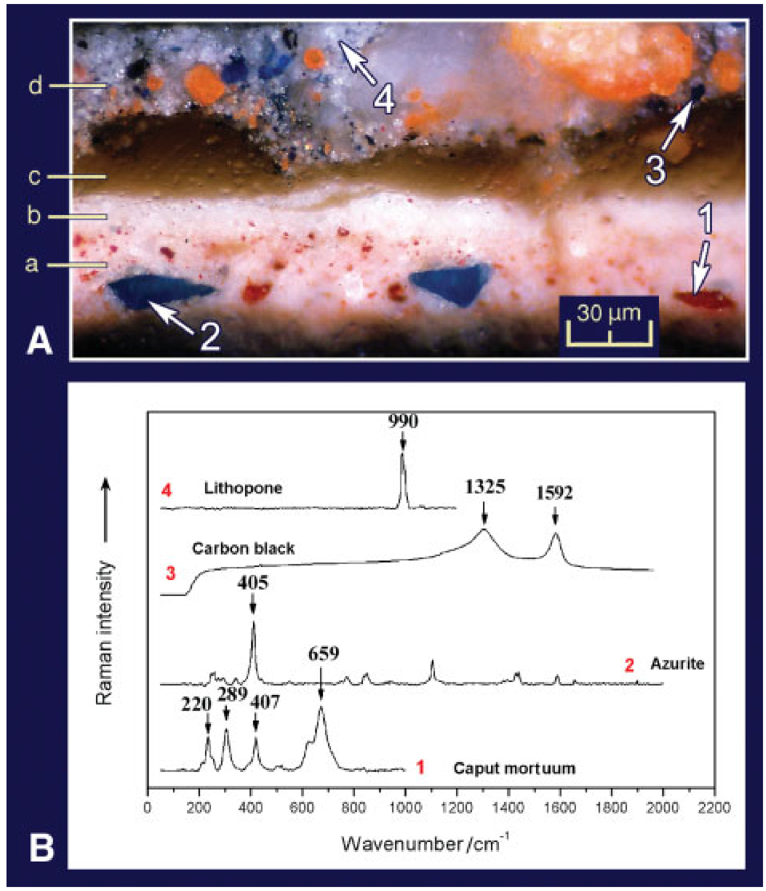

Plate 9

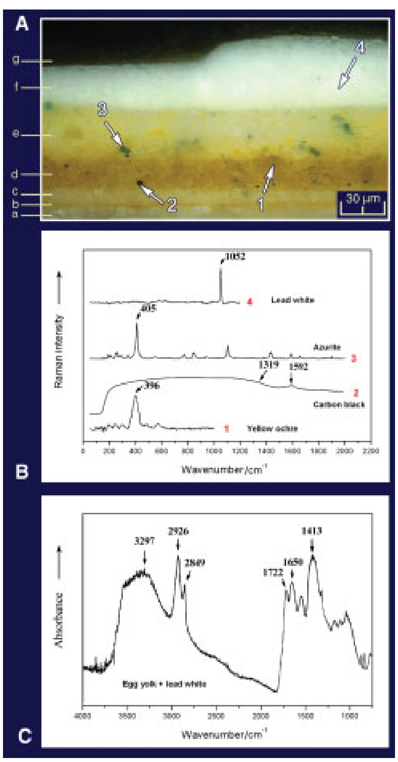

Plate 8

Plate 7. (A) Cross-section of the underlayer from the fountain's basin. Photography via a microscope in reflected light, (B) micro-Raman spectra and (C) micro-FTIR spectra. Original painting: a, gesso ground. Overpainting: b, chrome green and grains of lithopone; c, lithopone, grains of carbon black and ultramarine blue.

Plate 8. (A) Cross-section from a light in the monastic mantle. Photography via a microscope in reflected light, (B) micro-Raman spectra and (C) micro-FTIR spectra. a, Gesso ground; b, yellow bole; c, imprimatura, lead white and grains of yellow ochre; d, underlayer, yellow ochre, carbon black, grains of lead white and of red ochre; e, two gradations of highlights, lead white, yellow ochre and grains of azurite; f, white highlight, lead white; g, varnish.

Plate 9. (A) Cross-section from the monastic habit. Photography via a microscope in reflected light, (B) micro-Raman spectra. Original painting: a, underlayer, caput mortuum, lead white, grains of azurite, red lake and yellow ochre; b, light, lead white and grains of caput mortuum; c, varnish. Overpainting: d, ultramarine blue, minium, lithopone and carbon black.

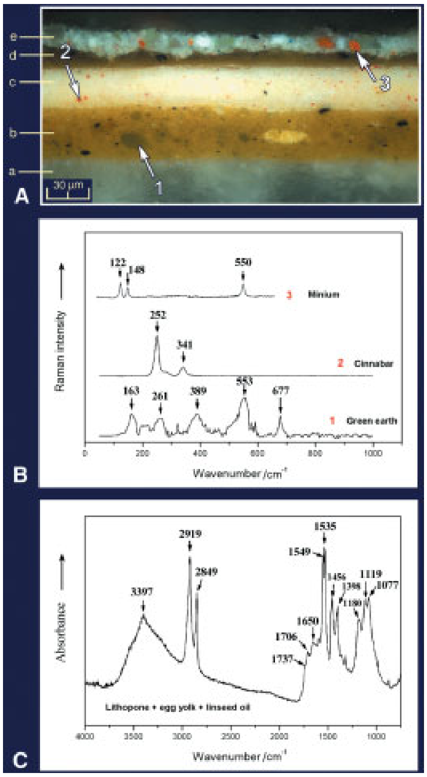

Plate 10

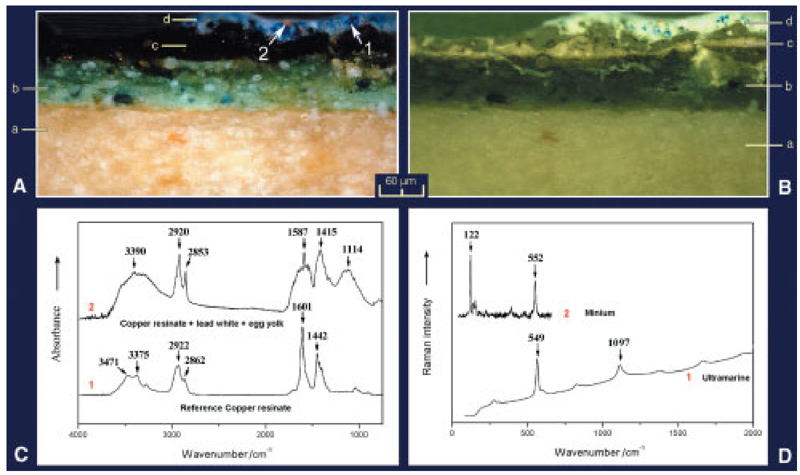

Plate 11

Plate 10. (A) Cross-section from the flesh tone of the face. Photography via a microscope in reflected light, (B) micro-Raman spectra and (C) micro-FTIR spectra. Original painting: a, gesso ground; b, underlayer, yellow ochre, carbon black, green earth and grains of lead white; c, flesh tone, lead white, grains of cinnabar and yellow ochre; d, varnish. Overpainting: e, lithopone, carbon black, grains of ultramarine blue and minium.

Plate 11. (A) Cross-section from the bottom end of the background. Photography via a microscope in reflected light, (B) fluorescence under UV light, (C) micro-FTIR spectra and (D) micro-Raman spectra. Original painting: a, gesso ground; b, earth's surface, copper resinate and lead white; c, varnish. Overpainting: d, lithopone, ultramarine blue, minium and carbon black.

halo, in some areas around it, on the Virgin's mantle, and on the three gold stars, barely discernable on the Virgin's mantle (head and each shoulder), the fluorescence was of the same yellowish hue as that of the Archangels, a circumstance verifying that the original icon had been preserved in these areas. The occasional brushstrokes at the perimeter of the Virgin's face, above her right eye and below her nose, identify points where minor interventions over the varnish of the original painting have been made. Christ's hair, His garments, His left hand holding the scroll, and both of His feet have been completely overpainted. In order to respond to the critical questions of whether and, if so, to what extent, the original painting has been preserved beneath the inartistic, dark and uneven layers of the overpainting, the most significant evidence would be expected to be derived from examining x-radiographs [Plate 3(b)] and cross-sections of appropriately selected samples. However, the high absorption of x-rays by minium, the main component of the paint layers of the overpainting, has precluded the possibility in most places of obtaining information on the underlying painting from x-radiography. In particular, minium was used both for the Virgin's mantle and for Christ's cloak. There are, however, certain small places visible in the x-radiograph where the preserved sections of the original painting can be traced, e.g. in Christ's tunic and clavus. Of significance is the discovery of a surviving part of the fountain to the right and left of the Mother of God.

Materials and techniques of the original painting and the overpainting

The analytical techniques of micro-Raman and micro-FTIR spectroscopy were employed to identify the pigment composition of both the original and the overpainting and also the binders that were used.[4–8]

The painting technique observed in the Virgin's mantle and visible in a cross-section of this area [Plate 4(A), position 1 in Plate 1] is of interest. The sample taken comes from an area next to Christ's halo, which has not been overpainted. The underlayer (paint layer c) consists of iron(III) oxide (largely caput mortuum in view of its hue), as confirmed by its micro-Raman spectrum [Plate 4(C), 1], which yields characteristic peaks at 220, 289, 407, 615 and 659 cm^{-1}. The upper two tones of the highlights had been rendered by mixing different amounts of lead white, with its characteristic peak at 1052 cm^{-1} arising from the CO_3^{2-} group[9,10] [Plate 4(C), 3], caput mortuum and grains of cinnabar [Plate 4(C), 2], which contributed a reddish hue to the mixtures. In the highlight, pure lead white was used.

When the same cross-section is observed under a UV source of light [Plate 4(B)], it becomes possible to identify a paint layer over the lead white, one that exhibits a different fluorescent hue from that of the upper varnish layer. It is in fact a richly bound layer of red lake (Plate 4, layer f) which had been applied in the form of glaze over the paint layers of the mantle. The artist, having painted the mantle, rather than choosing a pale violet hue for a final aesthetic touch, covered the surface with glaze of red lake. Owing to its high transparency, the lake lent a softer and warmer tone to all underlying gradations by slightly reducing the brilliance of the highlights. This layer emits strong fluorescence typical of many organic materials, and it was not possible to collect its Raman spectrum. FT Raman spectroscopy failed to overcome the problem.[11,12]

Cross-sectional photography from the border between the cloak and the tunic of the Archangel Gabriel allows recognition of the layer structures of each [Plate 5(A), position 2 in Plate 1]. Heavily grained and richly coloured azurite, which exhibits strong Raman bands at 405, 837, 1100 and 1580 cm^{-1} [Plate 5(B), 1], was used for the blue tunics of the two Archangels. The thin intermediate layer (d) belongs to a principal line and consists of scattered carbon black with two peaks at 1327 and 1592 cm^{-1} [Plate 5(B), 2]. The violet cloaks contain lead white [Plate 5(B), 3] mixed with red lake.

The coating of the underlying yellow bole [layer b, Plate 5(C), 1], which originates from the adjacent gilt background, consists of hydrated iron oxide and large amounts of kaolinite producing the characteristic FTIR peaks of the outer OH groups at 3698 cm^{-1} and of the inner groups at 3619 cm^{-1}. The strong peaks between 900 and 1100 cm^{-1} are attributed to the Si—O, Si—O—Si, Si—O—Al and Al—OH groups.[13,14] The peak at 1653 cm^{-1}, in conjunction with the strong peaks at 2852 and 2918 cm^{-1} attributed to methylene groups, are believed to belong to a proteinaceous material. In line with Byzantine tradition, animal glue was mixed with yellow bole in order to attach the superimposed gold leaf to the icon. Peaks detected in the FTIR spectrum of the red pigment layer [Plate 5(C), 2] are attributed to a protein, the most intense of which arise from methylene groups at 2919 and 2849 cm^{-1}, the amide carbonyl group (—CO—NH—) at 1646 cm^{-1} and the NH stretch at 3292 cm^{-1}. Egg yolk had undoubtedly been used as the binding material.[15] The peak at 1409 cm^{-1} is due to lead white and that at 1090 cm^{-1} to red lake. It is well known that many lakes can be precipitated from solution by treatment with aluminium compounds to produce materials which exhibit the same behaviour as pigments.[16] The absence of any paint layer over the surface varnish of the sample suggests that the original painting of the Archangels has been preserved intact.

In a cross-section taken from the Virgin's right hand, the paint layers both of the original painting and of the overpainting were revealed [Plate 6(A), position 3 in Plate 1] even though non-destructive methods did not provide positive indications for the preservation of the original painting. Dominant in the dark olive-green coating of the underlayer are yellow ochre, with its characteristic strong broad band at $\sim$400 cm^{-1} [Plate 6(B), 1], and carbon black, with grains of green earth and lead white; the warm-shaded flesh tones reveal lead white mixed with cinnabar [Plate 6(B), 2 and 3, respectively] and small amounts of yellow ochre.

Above the layer of varnish and dirt, the pigment mixture of the overpainting was found to consist of chrome yellow grains which give rise to strong Raman peaks at 341 and 838 cm^{-1} [Plate 6(B), 4], minium [Plate 6(B), 5] and lithopone, a mixture of barium sulphate and zinc sulphide (SEM–EDX and light microscopy evidence) [Plate 6(B), 6], which gives rise to a characteristic peak at 992 cm^{-1}. In the same paint layer, carbon black and grains of ultramarine blue [Plate 6(B), 7] can also be detected.[17–19] The latter may be distinguished microscopically from lazurite by the size (small and uniform) and shape (rounded) of its grains.

FTIR spectra were collected in order to identify the binder used both in the original painting and in the overpainting. In the spectrum of the original painting, peaks of yellow ochre and green earth [Plate 6(C), 1] were identified, in addition to characteristic peaks of a proteinaceous binder similar to egg yolk. The spectrum of the overpainting [Plate 6(C), 2] displays great similarities to that of the original but also some small differences. Thus an amide band occurs at $\sim$1657 cm^{-1} in the spectrum of each, suggesting that in both paintings egg yolk was used as the binder. However, the broad peak between 3000 and 3500 cm^{-1} is at a higher wavenumber in the spectrum of the overpainting (3397 cm^{-1}) than that of the original painting (3282 cm^{-1}). The same has occurred for the carbonyl peak, which in the overpainting occurs at 1740 cm^{-1} but in the original is at 1712 cm^{-1}. These differences suggest that a small amount of linseed oil together with egg yolk were used, a practice very common in Western painting.[5] The three peaks identified between 1050 and 1200 cm^{-1} in the spectrum of the overpainting are attributed to lithopone.

Because of extensive damage, the original painting of the lower part of the fountain did not survive, as is apparent from the corresponding cross-section [Plate 7(A), position 4 in Plate 1]. In the course of the overpainting, a covering of ''chrome green'' (a mixture of Prussian blue and lead chromate) had been applied: the characteristic Raman bands of the pigment at 536, 2093 and 2157 cm^{-1} are attributed to Prussian blue and those at 337, 359, 377, 399 and 840 cm^{-1} to lead chromate [Plate 7(B)]. Some scattered grains of lithopone and ultramarine blue in this paint layer give rise to the intense green colour of the earth's surface. Owing to the high fluorescence of this layer, the Raman spectrum was collected using the lowest power of the laser beam and after the accumulation of 120 spectra. The entire collection time for the spectrum was more than 5 h. On what would have been the top surface of the cross-section, a grey layer (a mixture of lithopone, carbon black and grains of ultramarine blue) was detected.

The preparation layer of the icon consists of a mixture of anhydrite and gypsum, which can be identified on the basis of the FT-Raman spectrum. In the FT-IR spectrum [Plate 7(C)] the peak at 1153 cm^{-1} is attributed to sulphate groups (SO_4^{2-}) while those at 3545, 3400 and 1624 cm^{-1} are attributed to water molecules.[20] The peaks at 2926 and 2855 cm^{-1} are ascribed to methylene groups of the organic binder (animal glue) of the preparation layers.

Following from this discussion of the cross-sections, one can appreciate the obvious high quality of the artistry in what survives of the original painting. Its palette mostly comprises the earth pigments yellow ochre, caput mortuum and green earth, but natural cinnabar and azurite were also employed. A red lake was found as a glaze in the Virgin's mantle and in the Archangels' cloaks where it is mixed with lead white. Carbon black and lead white complete the simple palette of this icon.

The chief pigments of the unimaginative and poorly coloured overpainting are minium, ultramarine blue, carbon black, chrome green, chrome yellow and lithopone. The last, a white synthetic pigment—a mixture of ZnS and $BaSO_4$—first became commercially available in 1874, a fact that fixes the earliest period to which the overpainting could belong.

Significant is the presence of a different kind of medium in the colour layers, egg yolk for the original painting and a mixture of linseed oil and egg for the overpainting.

'Saint Athanasios the Athonite'

State of preservation

The painting of Saint Athanasios (Plate 2) shows structural and drawing differences from those of other icons on the same sanctuary screen. Here, the figure of the Saint stops short at his knees—unusual in the representations of isolated figures—whereas other saints are bust portraits. What is therefore evident is that the top and bottom extremities of the icon have been shorn, undoubtedly to enable it to be set into a space of limited dimensions on the sanctuary screen. Taken together, these particulars lead us to the certain conclusion that Saint Athanasios had originally been depicted full-size and not as it appears today.

In order to estimate its original height, the underlying drawing was studied from the exposure on the x-radiograph [Fig. 1(A)]. According to the norms of Byzantine iconography and following conventional proportions, the length of a saint is portrayed as being 7–8 times greater than that of his head. In this particular icon, the length of the head is approximately 15 cm, hence the original extent of the figure was probably around 110 cm. From the size of the halo and of the two border ends (upper and lower), the combined length of the icon would have reached 120 cm. The extant piece is 93.5 cm high, and we estimate the upper covered part of the wood to have been 8 cm high and the lower part 18 cm. In Fig. 1(B) an attempt is made to re-create the original shape and structural details of the wooden board. For the parts that no longer exist, the lines are drawn based on the drawings of other similar icons of the same period.

The original painting can be identified with the naked eye only in a few places, viz. the right hand, the folds of the tunic and the mantle below, the Saint's left hand and the open scroll. There are also several spots on the face, on the monastic mantle, and on the cowl over the Saint's shoulders, where it is possible to trace the presence of brushstrokes from

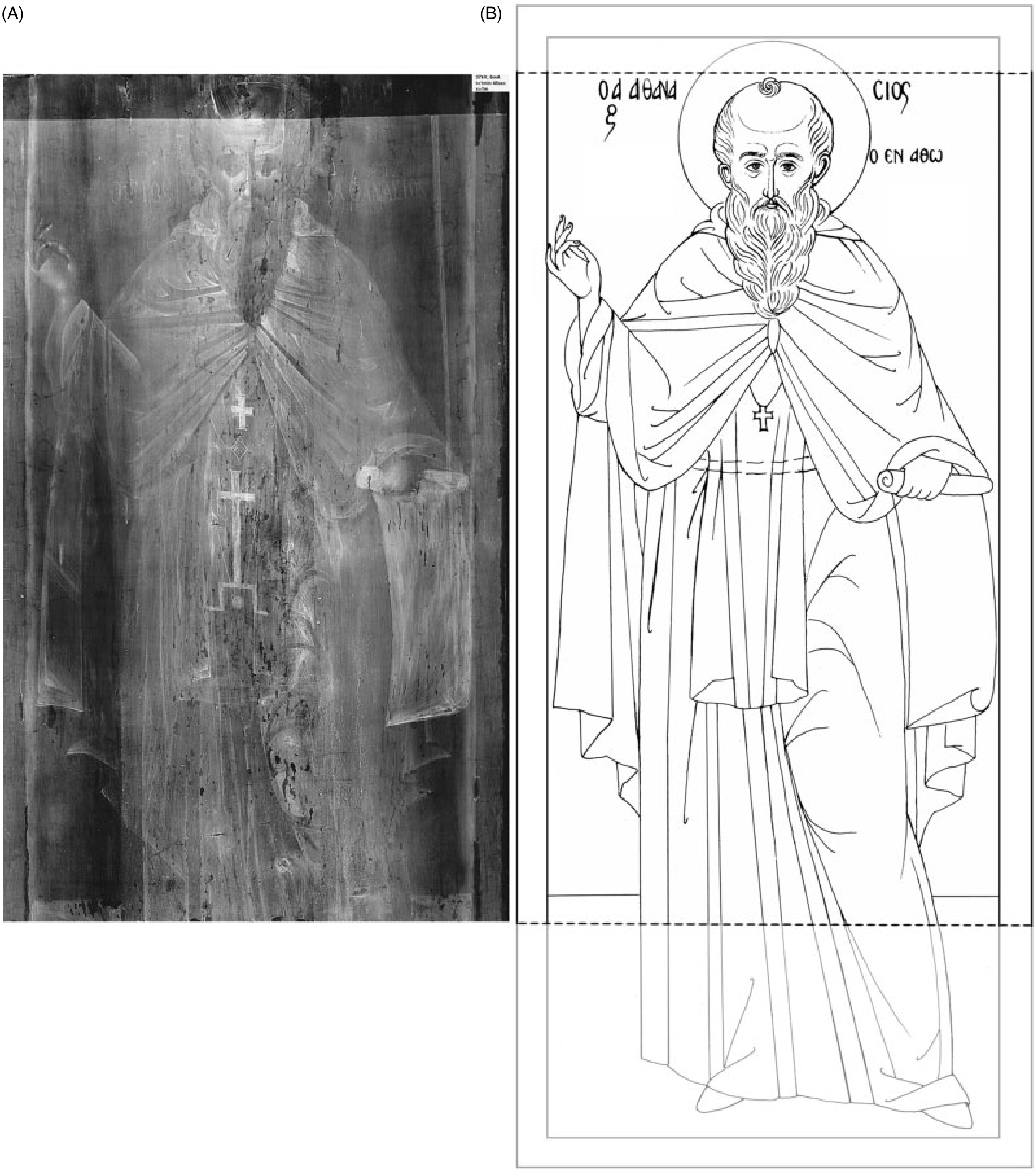

Figure 1. 'Saint Athanasios the Athonite'. (A) Composite x-radiograph (computerized synthesis with image enhancement). (B) Approximate reconstruction of the original drawing of the icon of Saint Athanasios.

the original painting not concealed by the superimposed painted layers.

At the upper end of the icon and on either side of the halo, several letters from the underlying inscription are faintly discernible. In the x-radiograph the inscription becomes very readable: Ο Α(ΓΙ)ΟC ΑΘΑΝΑ/CIOC/Ο ΕΝ ΑΘΩ (Saint Athanasios of Athos). The exposure of the underlying painting in the icon's x-radiograph is striking. Strong absorption of x-rays by lead white, the dominant pigment used for the highlights, resulted in clear readings even of the finest brushstrokes in the face and the folds of the garments.

At the bottom of the icon, to the right and left of the tunic, there are two narrow horizontal bands which exhibit high x-ray absorption. Conforming to Byzantine tradition for full-sized representations of saints, the gold background stops at the height of the knees and from there down an even paint layer is revealed, usually of a greenish hue, which represents the earth's surface. This detail further supports the view that the original portrait of Saint Athanasios was full-sized. Indeed, in the cross-section lifted from the lower end of the icon (see later), the presence of a green layer (a mixture of copper resinate and lead white) was identified.

Pigments and layer structure of the original painting and overpainting

An examination of the region of the folds (not overpainted)—more precisely of a border position between the mantle and the adjacent original gold background—reveals a cross-sectional layer structure which is impressive [Plate 8(A), position 1 in Plate 2]. Over the white gesso a thin layer of yellow bole could be distinguished, the latter having penetrated to that position from the neighbouring background. This superimposed, thin, yellowish coating (imprimatura), containing lead white and a small quantity of yellow ochre, had been applied in order to facilitate the effective adhesion of the paint layers at the boundary between the painted surface and the gold background. In the uppermost layer of the underlayer the dominant pigment is yellow ochre [Plate 8(B), 1] mixed with carbon black [Plate 8(B), 2] and a few grains of lead white. For the next two gradations of light, one can see yellow ochre mixed with lead white and finely ground azurite [Plate 8(B), 3] which gives a cooler tone to the mixture. The final white brushstrokes of the highlights were rendered in pure lead white [Plate 8(B), 4], which accounts for the clear impressions in the x-radiograph [Fig. 1(A)]. Egg yolk was used as binder since the characteristic peaks of protein were recorded on the FTIR spectrum together with the strong peak of lead white at 1413 cm^{-1} [Plate 8(C)].

Red pigments dominate in a cross-section from the monastic habit [Plate 9(A), position 2 in Plate 2], viz. caput mortuum [Plate 9(B), 1] and some red lake mixed with lead white. The addition to this mixture of a small quantity of finely ground azurite [Plate 9(B), 2] has introduced a violet hue to the final aesthetic result. The first highlight exhibits a slightly pink hue, where pure lead white has been mixed with a few grains of caput mortuum (layer b). Above the layer of varnish and dirt there is an overpainting which consists of a mixture of ultramarine blue, minium, carbon black [Plate 9(B), 3] and lithopone [Plate 9(B), 4].

For the first paint layer of the face and hands [Plate 10(A), position 3 in Plate 2] a mixture was used comprising yellow ochre, carbon black, green earth [Plate 10(B), 1]—the most characteristic peaks being at 163, 389 and 553 cm^{-1}—and a few grains of lead white. Some green earths may emit strong fluorescence in Raman microscopy and the collection of their spectra is possible only by focusing on large grains for an extended period of time. The gradations of the flesh tones are formed from lead white together with scattered grains of cinnabar [Plate 10(B), 2] and yellow ochre. The strong contrast in hue and brightness between the underlying dark colouring of the underlayer and the gradations of the flesh tones underscores the protruding points of the face which have been rendered with tight flesh tones in icons of this period. In the overpainting (layer e), lithopone predominates while a few grains of carbon black, ultramarine blue and minium [Plate 10(B), 3] were also found. The FTIR spectrum of this layer [Plate 10(C)] is similar to that of the overpainting on the 'Life-giving Spring' icon. It is obvious that egg yolk mixed with linseed oil was used as the binding material of the overpainting for these two icons.

Especially revealing was the discovery in the original painting of the use of copper resinate mixed with lead white for the earth's surface [Plate 11(A), position 4 in Plate 2]. In the fluorescence photograph of the same cross-section [Plate 11(B)], the layer of copper resinate appears to be extremely dark in comparison with the characteristic high fluorescence of the overlying varnish. This fluorescence made it impossible to collect the Raman spectrum of the copper resinate even after prolonged laser irradiation; however, it was easy to collect its FTIR spectrum [Plate 11(C), 1]. Aside from the peaks attributed to the methylene and hydroxyl groups, reference copper resinate also has two strong peaks at 1442 and 1601 cm^{-1}. The peak at 1442 cm^{-1} in the spectrum of the paint layer on the icon [Plate 11(C), 2] was hidden by the stronger peak at 1415 cm^{-1} attributed to lead white. Another strong peak at 1587 cm^{-1} is at a lower wavenumber than that of the reference, possibly due either to compositional changes of the material on aging or to interactions between the latter and the protein binder. Ultramarine blue [Plate 11(D), 1], minium [Plate 11(D), 2] and lithopone were identified in the overpainted layer.

The colour gradations in the overpainting of the various fields differ slightly, a circumstance that arises from mixing the same pigments each time but in dissimilar proportions. It appears that only four pigments were used: minium, ultramarine blue, lithopone and carbon black. The binder consists of a mixture of linseed oil and egg, while it was impossible to locate any surface varnish.

Finally, spectral data for the pigments in the two icons are summarized in Table 1.

CONCLUSIONS

The icon of the 'Life-giving Spring' from the year 1543 is a work of high artistic value, the quality of its creativity being apparent in the technical features of the extant original painting. Pre-existing, widespread damage to the lower part of the icon has been hidden by layers of overpainting which extend

Table 1. Names and compositions of pigments in the icons and characteristic wavenumbers and intensities of the observed Raman bands

Plate	Name and composition	Band wavenumber/cm^{-1} and relative intensity[a]
4(C)	Lead white [4], $2PbCO_3{\cdot}Pb(OH)_2$	1052 vs
	Cinnabar [4], HgS	249 vs, 342 m
	Caput mortuum [8], Fe_2O_3	220 ms, 289 s, 407 m, 615 s, 659 vs
5(B)	Lead white [4], $2PbCO_3{\cdot}Pb(OH)_2$	1052 vs
	Carbon black [4], C	1327 s vb, 1592 s b
	Azurite [4,11], $2CuCO_3{\cdot}Cu(OH)_2$	405 vs n, 760 m, 837 s, 1100 vs n, 1580 m
6(B)	Ultramarine blue [4], $Na_6[Al_6Si_6O_{24}]S_n$	549 vs, 1097 ms
	Lithopone [4], $ZnS + BaSO_4$	992 s
	Minium [4], Pb_3O_4	123 ms, 148 s, 551 m
	Chrome yellow [4], $PbCrO_4$	341 m, 838 vs
	Cinnabar [4], HgS	252 vs, 341 m
	Lead white [4], $2PbCO_3{\cdot}Pb(OH)_2$	1052 vs
	Yellow ochre [8], $Fe_2O_3{\cdot}H_2O$	404 vs b
7(B)	''Chrome green'', $Fe_4[Fe(CN)_6]_3{\cdot}14H_2O + PbCrO_4$	337 w, 359 s, 377 w, 399 w, 536 s, 840 vs, 2093 s, 2157 vs
8(B)	Lead white [4], $2PbCO_3{\cdot}Pb(OH)_2$	1052 vs
	Azurite [4], $2CuCO_3{\cdot}Cu(OH)_2$	405 vs, 837 m, 1100 s, 1580 m
	Carbon black [4], C	1319 s vb, 1602 s b
	Yellow ochre [8], $Fe_2O_3{\cdot}H_2O$	396 vs
9(B)	Lithopone [4], $ZnS + BaSO_4$	990 vs
	Carbon black [4], C	1325 s b, 1592 s b
	Azurite [4,11], $2CuCO_3{\cdot}Cu(OH)_2$	405 vs, 837 m, 1100 s
	Caput mortuum [8], Fe_2O_3	220 s, 289 s, 407 ms, 659 vs
10(B)	Minium [4], Pb_3O_4	122 s, 148 m, 550 s
	Cinnabar [4], HgS	252 vs, 341 m
	Green earth	163 s, 261 s, 389 s b, 553 vs, 677 s
11(D)	Minium [4], Pb_3O_4	122 vs, 148 w, 552 s
	Ultramarine blue [4]	549 vs, 808 m, 1097 m b, 1351 w, 1646 w b

[a] s, Strong; vs, very strong; m, medium; w, weak; n, narrow; b, broad.

to areas where the original painting has been preserved, e.g. the cloak of Christ and a part of the fountain. Dispersed minor interventions have been discovered even in the upper section of the icon, on the face and mantle of the Virgin, on Christ's hair and probably on the hair of the Archangels.

The surviving icon of Saint Athanasios the Athonite has suffered extensive damage owing to the severance of two large sections from the upper and lower ends of the painting (~8 and ~18 cm high, respectively) to enable it to fit into the fixed dimensions of a sanctuary screen. Originally, the Saint had been depicted full-size against a gold background but, from the knees down, the background was painted green to simulate the earth's surface. Overpainted layers almost completely cover the original painting, except for the right hand, the folds of the tunic and the mantle below, the Saint's left hand, and the open scroll. As a result of these interventions, only the general outlines of the figure of the Saint have been preserved while substantial changes in the colourings of the icon were introduced. With the exception of occasional flaking of the paint layers, the artistic value of the underlying painting is preserved.

A palette consisting of the natural pigments caput mortuum, yellow ochre, carbon black, azurite and green earth, together with red lake and copper resinate in an egg yolk medium characterizes the original paintings of the two icons. The mixtures are simple and the paint layers have been applied evenly. Lead white is dominant in the finely worked highlights. By contrast, the drawing of the overpaintings is rather elementary, the pigments used being mainly synthetic with complex mixtures of unequal thickness predominating. A mixture of linseed oil and egg was used as the binder for the pigments. Both icons were overpainted by the same artist at the beginning of the 20th century, according to art historians.

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