

Article

# By the Hand of Angelos? Analytical Investigation of a Remarkable 15th Century Cretan Icon

Georgios P. Mastrotheodoros <sup>1,2,\*</sup> , Marios Theodosis <sup>3</sup>, Eleni Filippaki <sup>2</sup> and Konstantinos G. Beltsios <sup>4</sup>

<sup>1</sup> Conservation of Antiquities and Works of Art Department, West Attika University, Agiou Spyridonos, 12243 Aegaleo, Greece

<sup>2</sup> Institute of Nanoscience and Nanotechnology, NCSR ‘Demokritos’, Patr. Gregoriou E & 27 Neapoleos Str, 15341 Agia Paraskevi, Greece; e.filippaki@inn.demokritos.gr

<sup>3</sup> Greek State Archives, D. Solomos Square, 29100 Zakynthos, Greece; mariostheodosis3@gmail.com

<sup>4</sup> School of Chemical Engineering, National Technical University, Iroon Polytechniou 9, 15780 Zografou, Greece; kgbelt@mail.ntua.gr

\* Correspondence: g.mastrotheodoros@inn.demokritos.gr

Received: 23 October 2020; Accepted: 13 November 2020; Published: 16 November 2020



**Abstract:** A 15th century St Theodoros icon of outstanding quality is on display at the Zakynthos Ecclesiastical Art Museum. On the basis of certain stylistic characteristics, this icon has been attributed to the legendary Cretan painter Angelos Akotantos. In order to explore the latter attribution, the icon was subjected to examination via multispectral imaging, while microsamples were investigated through an optical microscope (OM), a scanning electron microscope coupled with an energy dispersive analyzer (SEM-EDX),  $\mu$ -Raman and X-ray diffraction (XRD). The data were evaluated in the light of the findings of recent analytical studies conducted on several genuine Angelos icons. Identified materials include gypsum, gold leaf, bole, natural ultramarine, lead white, charcoal, green earth, red lake, minium, cinnabar, and red and yellow ochres. The identified materials resemble those employed by Angelos, while the identification of ultramarine is of particular significance, as this extremely expensive and rather rare pigment was very often used by the particular painter. Moreover, multispectral imaging reveals notable painting technique similarities between the icon in consideration and known Angelos icons, while cross sections of corresponding samples exhibit almost identical structures. Overall, the present work considerably strengthens the suggestion that the St Theodoros icon in consideration was painted by Angelos and also widens our knowledge regarding the late Byzantine painting.

**Keywords:** pigment identification; preliminary drawing; gilding; Byzantine

## 1. Introduction

Religious panel paintings (“icons”) are an essential part of the Eastern Orthodox Christian Church ritual practices; hence, such artifacts have been continuously manufactured for more than 17 centuries [1]. In case of the artistry developed in the region of modern-day Greece, this long period is divided into three sub-periods, namely the Byzantine (330–1453), post-Byzantine (1453–1830) and modern periods (post-1830). The marking year 1453 corresponds to the capture of Constantinople (Byzantine Empire capital) by the Ottoman Turks, while 1830 corresponds to the declaration of the autonomy of the Greek state.

During the late 14th and early 15th centuries, icons of notably high quality were produced in the island of Crete (south Aegean Archipelago). As this artistic trend bears several idiomorphic characteristics, it has been designated as the “Cretan School of iconography”, and it is well known that

it considerably affected the development of the Orthodox religious painting throughout Greece and the Balkans [2]. Among the highlights of the Cretan painting stand several early 15th century icons of exquisite painting quality that bear the inscription “Χεῖρ Ἀγγέλου” ((by) “the hand of Angelos”). Interestingly, in the early 1960s M. Manoussakas spotted a Cretan painter’s will in the Venice State archives that is dated to the early 15th century (probably 1436) [3]; the testator was named Angelos Akotantos, and he made his will on the occasion of a trip to Constantinople. Soon after the Manoussakas publication, it was proven that the Angelos of the will was the painter of the aforementioned famous icons [4,5]. In order for the reader to get an idea of the importance of Angelos’ work, it is essential to note that the Cretan painting scholars acknowledge that he was indeed an outstanding painter of the 15th century and also that he “established and crystallized a large number of iconographic subjects in Cretan painting through his own work” [6]. Also, as for Angelos’ productivity, it is indicative to mention that more than 30 icons bearing his signature survive today, while some others are ascribed to him on the basis of pronouncedly idiomorphic stylistic characteristics [2,6].

The St Theodoros icon in consideration (Figure 1) dates from the second quarter of the 15th century (1425–1450) and has been recently ascribed—on the basis of stylistic criteria—to Angelos [7,8]. The icon originates from Crete and was once placed in the church of the Strofades monastery, from which it was later transferred to Zakynthos Island. It is worth noting that in 1953, the area of Zakynthos was struck by a series of strong earthquakes that destroyed many dwellings and infrastructures, including churches and monasteries. Unfortunately, during this event many of the Zakynthos icons were either destroyed by the fire that followed the earthquakes or “disappeared”; however, several hundred icons were rescued as a result of the tireless efforts of M. Chatzidakis and his co-workers [9]. St Theodoros icon survived this terrific disaster and is currently displayed at the Zakynthos Ecclesiastical Art Museum.



**Figure 1.** St Theodoros icon, Zakynthos Ecclesiastical Art Museum; the sampling spots are marked on the figure. Note that the painting has been transferred onto a new wooden panel.

The present work demonstrates how the analytical investigation of this very icon strengthens its assignment to Angelos Akotantos using a combination of technical evidence reported herein with related findings of other workers who previously studied several genuine Angelos icons [10–15]. The materials employed in the St Theodoros icon were identified through the meticulous investigation of microsamples’

cross sections, while the assessment of various technical aspects (pigment mixing, preliminary drawing, etc.) was assisted by the complementary use of multispectral imaging. Thus, authors managed to considerably strengthen the hypothesis that the St Theodoros icon is a work of Angelos, and also to widen the understanding of important details of late- Byzantine painting.

## 2. Materials and Methods

The icon (dimensions: 148.2 × 58.7 cm) was initially pictured using a MuSIS-MS multispectral camera (FORTH-Photonics, Heraklion, Greece) in the 1000 nm and the false-color infrared (IRFC) modes. Micro-samples (~1 mm × 1 mm) were removed from damaged areas using surgical scalpels (Figure 1), and, after preliminary stereoscope investigation, they were embedded in polyester resin, cross-sectioned and subjected to grinding and polishing (Pedemin-2, DAP-7, Struers, Ballerup, Denmark). Cross-sections were examined under an optical microscope (OM, DMRXP, Leica Microsystems, Wetzlar, Germany) at magnifications up to 200×, and, upon carbon coating (for conductivity purposes, using a Balzers' CED030 carbon vaporizer, Leica Microsystems, Wetzlar, Germany), through a scanning electron microscope coupled with an energy dispersive analyzer (SEM-EDX, Quanta Inspect D 8334, FEI, Hillsboro, Oregon, USA). Elemental compositions were estimated by using the built-in 'Genesis-Spectrum' software (EDAX Company, Mahwah, NJ, USA), in a standard-less quantification method mode that incorporates ZAF matrix corrections [16], and in combination with high accelerating voltage (25 kV) and optimal spectra collection parameters (a high count rate, long collection times, adequate DT%, etc. leading to high elemental peak to background ratios). Through the analysis of multi-elemental standard targets, it was demonstrated that this approach results in quantitative analysis with errors of circa ±3% for high concentration elements, and ±20% for low concentration ones (<5%). For each distinct pigment/phase, at least three EDX analyses were undertaken, targeting on different grains/areas; results were automatically normalized to 100% and the mean values were calculated. Due to the presence of the conductive carbon layer, carbon was not quantitatively estimated in organic/lake-type pigments. Micro-morphological characteristics were recorded using the SEM's backscattered electron detector (BSE), which permits for the differentiation of the observed phases on the basis of their atomic number. Also, the size of the various pigment grains along with the thickness of the gold leaves and the pertinent adhesives were determined using a built-in image processing tool of the SEM device (Table 1). Samples cross-sections were further examined under a μ-Raman device (inVia, Renishaw, Wotton-under-Edge, UK) using a low power (~0.01–1 mW) 514 nm laser; spectra were collected through a 100× magnification lens with repeated acquisitions of varying durations, and recorded in frequencies of 100–1800 cm<sup>-1</sup>. A minor ground/gesso sample (<1mg) was pulverized and analyzed by using X-ray diffraction (XRD, 'D500', SIEMENS, Munich, Germany, equipped with a Cu-Kα anticathode, diffraction pattern recorded in the range of 2–90° (2θ) with a step size of 0.04° and a scan speed of 2 s per step). Note that during older conservation interventions, the painting and ground layers of the icon were detached from their original wooden substrate and placed onto a new one [7]; therefore the present authors did not employ techniques that pertain to wooden panel identification (e.g., x-ray radiography).

**Table 1.** EDX elemental analysis results, wt%, normalized to 100%. Abbreviations: n.d.: not determined.

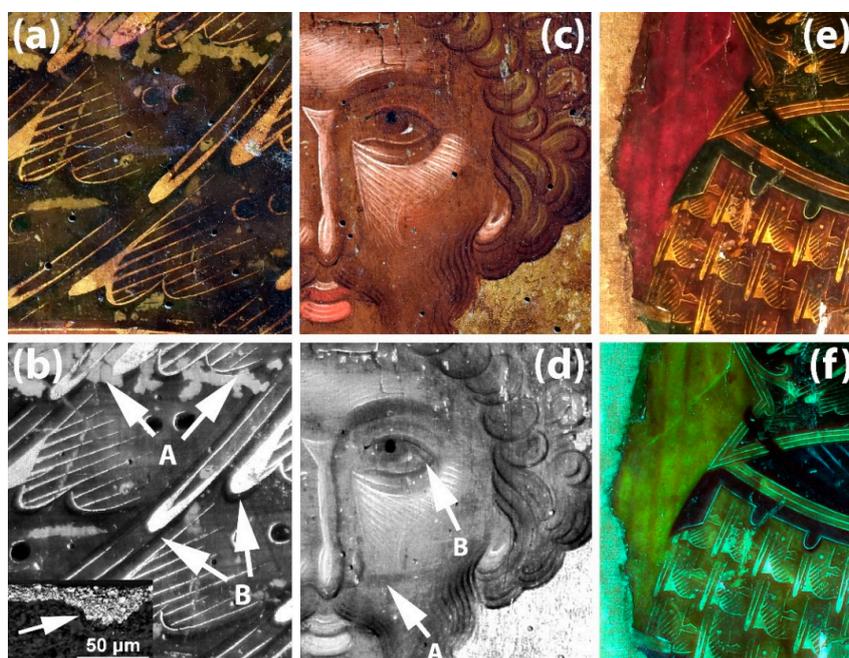
| Phase/Pigment        | EDX Analysis Results (Elements, wt%) |     |                    |      |      |     |      |          |                                  |      |                | Grain Size ( $\mu\text{m}$ )      |
|----------------------|--------------------------------------|-----|--------------------|------|------|-----|------|----------|----------------------------------|------|----------------|-----------------------------------|
|                      | Na                                   | Mg  | Al                 | Si   | S    | Cl  | K    | Ca       | Fe                               | Pb   | Other          |                                   |
| Gesso/ground         | 0.1                                  | 1.0 | 0.3                | 1.6  | 38.8 |     |      | 58.3     |                                  |      |                | n.d.                              |
| Lazurite             | 13.5                                 |     | 21.9               | 39.0 | 14.8 | 2.0 | 0.8  | 8.1      |                                  |      |                | 4–22                              |
| Green earth          |                                      | 5.1 | 2.9                | 45.2 |      | 1.3 | 12.5 | 4.3      | 28.7                             |      |                | 6–23                              |
| Red lake             | 1.6                                  | 1.4 | 44.1               | 6.8  | 10.5 | 9.2 | 4.0  | 15.9     | 2.4                              |      | P (4.1)        | n.d.                              |
| Red iron ochre       |                                      | 2.1 | 9.1                | 16.5 |      | 6.1 | 1.0  | 15.7     | 45.9                             |      | P (3.6)        | 4–5                               |
| Cinnabar             |                                      |     |                    |      | 14.7 |     |      |          |                                  |      | Hg (85.3)      | 0.8–7.0                           |
| Orange iron ochre    | 0.5                                  | 1.3 | 17.9               | 34.5 | 2.5  | 1.1 | 2.4  | 8.7      | 29.5                             |      | P/Ti (1.4/0.2) | 1–5                               |
| Lead white           |                                      |     |                    |      |      |     |      |          |                                  |      | 100.0          | 0.4–8.0                           |
| Minium               |                                      |     |                    |      |      |     |      |          |                                  |      | 100.0          | 2–9                               |
| Charcoal             |                                      |     |                    |      |      |     |      |          |                                  |      |                | ~0.5–2.0                          |
| Gold leaf adhesives  |                                      |     |                    |      |      |     |      |          |                                  |      |                |                                   |
|                      | Na                                   | Mg  | Al                 | Si   | S    | Cl  | K    | Ca       | Fe                               | Pb   | Other          | Layer thickness ( $\mu\text{m}$ ) |
| Yellow bole (campus) | 0.4                                  | 1.4 | 18.3               | 35.1 | 5.8  | 0.6 | 1.8  | 13.6     | 22.8                             |      | Ti (0.3)       | 3–8                               |
| Mordant (highlights) | 0.7                                  | 1.0 | 2.4                | 4.1  |      | 3.9 | 1.3  | 13.0     | 4.0                              | 65.8 | P (3.8)        | 2.5–7.0                           |
| Gold leaves          |                                      |     |                    |      |      |     |      |          |                                  |      |                |                                   |
|                      | Spot                                 |     | EDX (elements wt%) |      |      |     |      |          | Leaf Thickness ( $\mu\text{m}$ ) |      |                |                                   |
|                      |                                      |     | Ag                 | Cu   | Au   |     |      |          |                                  |      |                |                                   |
|                      | Background/“campus”                  |     | 0.1                | 0.3  | 99.6 |     |      | ~0.4–0.6 |                                  |      |                |                                   |
|                      | Gilded highlights on vestments       |     | 0.0                | 0.3  | 99.7 |     |      | ~0.4–0.6 |                                  |      |                |                                   |

### 3. Results

First, we present the results of the multispectral imaging, and the data that pertain to materials identification follow. The latter are presented in terms of the stratigraphy of a typical icon [17]: first the data on the ground/preparatory layer are presented, then the pigment palette is disclosed through the paint layers analysis results, and finally the data that pertain to gilded decorations are discussed.

#### 3.1. Multispectral Imaging

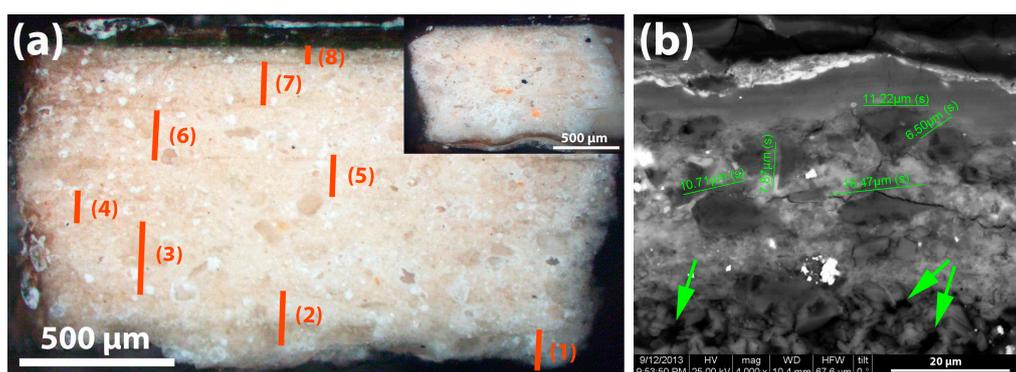
The potential of infrared radiation to penetrate through the upper layers of paintings has been exploited in order to reveal layers that are invisible to the naked eye (such as underdrawings) [18,19] as well as for pigments identification [20]. In case of the St Theodoros icon, the inspection at 1000 nm revealed a wealth of information pertaining to the painting technique. The preliminary drawing is of a notably confident character, created by employing two techniques, namely brushstrokes and extremely thin (<30  $\mu\text{m}$ , see next) incisions (Figure 2a,b). It is worth noting that in the case of the Saint's face and curly hair (where accuracy in sketch is of utmost importance), the drawing was rendered through thin brushstrokes (no incisions), while only few minor sketch-corrections were spotted in the corresponding areas (Figure 2c,d, arrow B). The preparatory paint layers that followed drawing (base colors/underpaintings [17]) were freely applied onto the ground (Figure 2d, arrow A), while the subsequent lighter tones and highlights were rendered with extremely accurate/skillful and fine brushstrokes (Figure 2). On the other hand, IRFC photography gave some hints on the employed pigments. For instance, the red mantle is rendered in an intense yellow-orange false color, thus implying the presence of cinnabar, while the differences in the false color of the "greenish" armor parts and the underwear garment around the Saint's waist indicate employment of different pigments (Figure 2e,f) [21].



**Figure 2.** (a) Visible macro-detail of the armor. (b) Same area as in (a), pictured at 1000 nm. Preliminary drawing executed by incision (arrows "A") and brushstrokes ("B"); insert picture (lower left corner) shows an incision cross-section (scanning electron microscope (SEM), backscattered electron detector (BSE), 2000 $\times$ ). (c) St Theodore face, detail on visible light. (d) Same area as in (c), infrared (1000 nm). Arrow "A" points on preliminary paint layer brushstrokes, "B" on a minor sketch correction. (e) Detail, visible light. (f) The area figured in (d) as it was pictured in the false-color infrared (IRFC) mode.

### 3.2. Ground/Gesso

During the microscopic probing of the cross-sections, it was observed that the preparatory ground layer consists of up to eight distinct sub-layers of ~50–150  $\mu\text{m}$  thickness, which correspond to the successive gesso coatings applied onto the wooden panel (Figure 3a). XRD and  $\mu$ -Raman analyses revealed that the inorganic ground component is gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), which was probably mixed with an organic gluing agent [17]. For instance, the relevant  $\mu$ -Raman spectrum shows a characteristic shift at  $\sim 1008 \text{ cm}^{-1}$  that corresponds to the  $\nu_1$  ( $\text{SO}_4$ ) symmetric stretching mode of gypsum (Figure 4a) [22]. In addition, the ground layer contains minor admixtures of black, red and yellow pigments (see insert on Figure 3a).

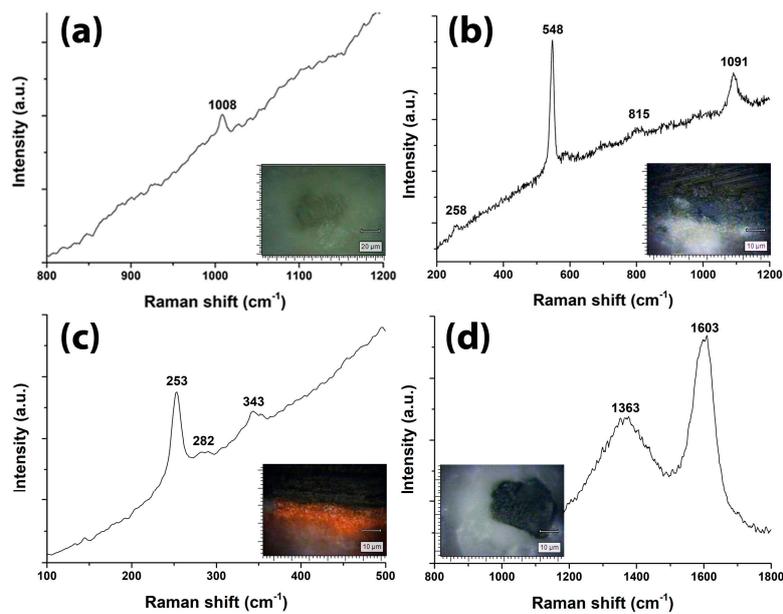


**Figure 3.** (a) Multiple ground layers, optical microscope (OM), 50 $\times$ . The insert picture shows scattered grains of black and yellow pigments in the ground (OM, 50 $\times$ ). (b) Natural ultramarine grains and their maximum dimensions; arrows point on charcoal particles that lay into the lazurite substrate (SEM, BSE, 4000 $\times$ ).

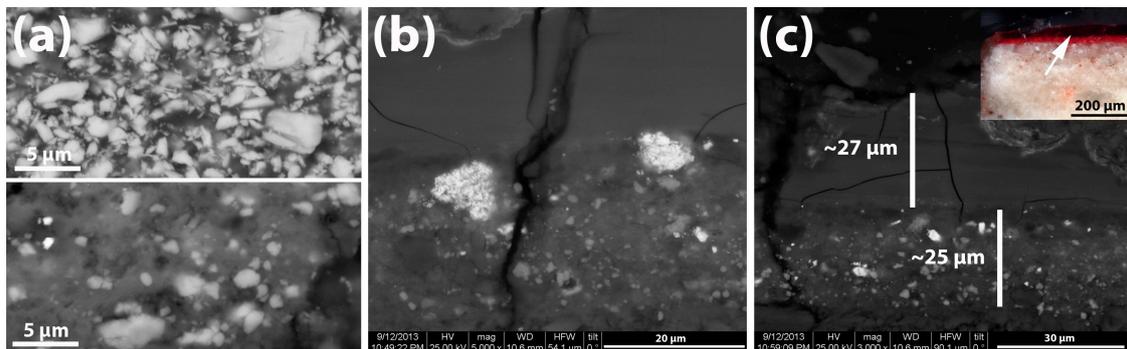
### 3.3. Paint Layers

Pigments employed in the St Theodoros icon were identified through SEM-EDX and  $\mu$ -Raman spectroscopy (Table 1 and Figure 4). Thus, a palette consisting of nine distinct pigments was revealed: natural ultramarine, green earth, two types of iron ochre, cinnabar, minium, red lake, charcoal and lead white (Table 1 and Figure 4). The extremely expensive and rather rare ultramarine pigment was identified through its characteristic Raman spectrum ( $\nu_1$  stretching vibration mode and  $\nu_2$  bending vibration mode of  $\text{S}_3^-$ , at  $548 \text{ cm}^{-1}$  and  $258 \text{ cm}^{-1}$ , respectively [23]) and its elemental composition (Table 1), while the characteristic conchoidal fracture features of the relevant grains and the detection of minor calcite (natural impurity) verify the natural origin of the particular pigment (Figures 3b and 4b, Table 1) [23,24].

In the case of the green pigment, authors were unable to collect Raman spectra. However, the EDX analysis revealed that the pertinent grains are mainly composed of silicon, iron, potassium and magnesium, and this elemental composition evidently shows employment of green earth (Table 1) [28,29]. Similarly, the use of two iron ochre varieties was attested to through SEM-EDX analyses, as the deep-red and the yellowish ochre differ drastically in terms of elemental composition (especially as regards the content of iron, calcium, silicon and chlorine, see Table 1). In addition, the grains of these two pigments are of a notably small size (0.5–5  $\mu\text{m}$ ), and this is so in the case of cinnabar and lead white as well (0.5–8  $\mu\text{m}$ , see Figure 5a). Note that a cinnabar Raman spectrum is displayed on Figure 4c; the characteristic shifts at  $253$ ,  $282$  and  $343 \text{ cm}^{-1}$  originate from a totally symmetric  $\text{A}_1$  and degenerated E transverse modes ( $\text{E}_{\text{TO}}$ ) respectively [30]. The employment of these thin-grained pigment fractions reflects intense grinding and suggests meticulous pigment preparation.

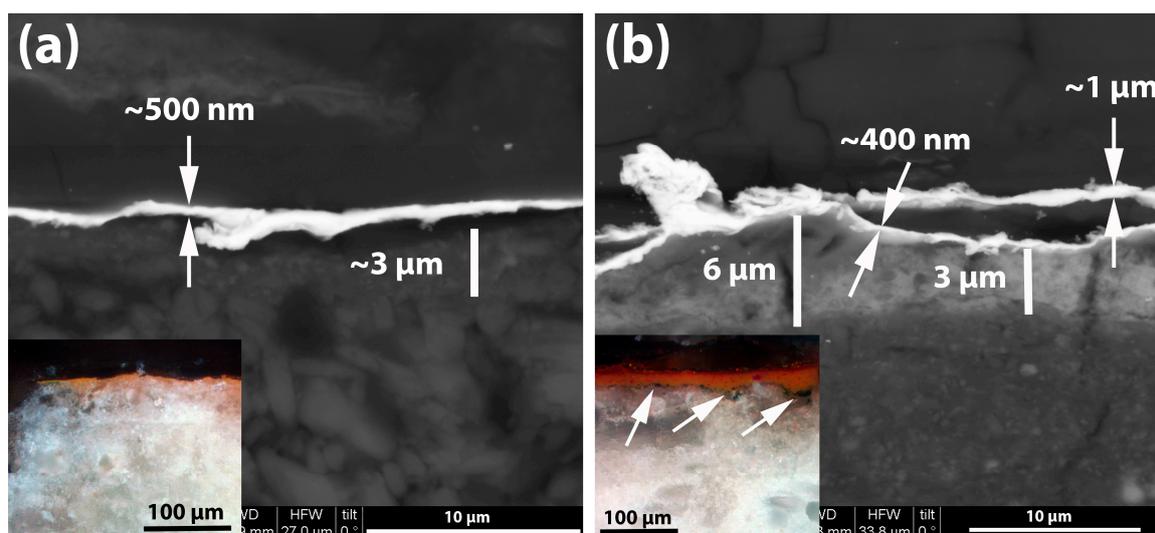


**Figure 4.** Characteristic  $\mu$ -Raman spectra of St Theodoros icon ground and pigments. (a) Gypsum, characteristic peak at  $1008\text{ cm}^{-1}$ . (b) Natural ultramarine, Raman shifts at  $258$ ,  $548$ ,  $815$  and  $1091\text{ cm}^{-1}$ . (c) Cinnabar, shifts at  $253$ ,  $282$  and  $343\text{ cm}^{-1}$ . (d) Carbon black, characteristic shifts at  $1363$  and  $1603$  wavenumbers. Insert figures show indicative individual pigment grains that were analyzed. For libraries of pigment Raman spectra, the reader is directed to [25–27].



**Figure 5.** (a) Notably small grains of ochre (bottom) and cinnabar (up); SEM, BSE,  $10,000\times$ . (b) Minium grains (big bright particles) among ochre (gray particles); SEM, BSE,  $5000\times$ . (c) Lake glaze (upper layer, uniform) on top of an ochre and lead white substrate (bottom layer, spotted) (SEM, BSE,  $3000\times$ ). Insert picture: the same sample under OM, the arrow points on the glaze ( $100\times$ ).

On the other hand, a few minium grains were spotted among red ochre particles, therefore it seems probable that the minium was added in order to slightly adjust the hue of the ochre (Figure 5b). Of special interest is the case of the deep-red lake, which was used as a glaze (translucent paint layer) that covers an ochre plus lead white paint layer (Figure 5c), which is in fact a technique quite commonly applied in Cretan icons [31]. Here the lake organic coloring compound could not be identified, yet the elevated phosphorous (4.1 wt%) is compatible with the employment of insect dye [32]. Finally, charcoal of plant origin was applied as a preliminary paint layer in the areas rendered in lazurite (Figure 3b) and as a minor addition in various paint layers. Charcoal was also used to render the preliminary drawing (Figure 6b), while a minute amount of the same pigment was included in the ground layer/gesso (Figure 3a). The corresponding Raman spectra show the typical G and D bands of carbon at  $\sim 1600\text{ cm}^{-1}$  and  $\sim 1360\text{ cm}^{-1}$ , respectively [33].



**Figure 6.** (a) Background image: thin gold leaf (bright layer) on a bole substrate (dark gray substrate, 3.12  $\mu\text{m}$  marker); BSE, 10,000 $\times$ . Insert picture: same sample, OM, 200 $\times$ ; note the yellow bole layer. (b) Background image: Double gold leaf (uppermost bright layers) on a lead-mordant (bright substrate); BSE, 8000 $\times$ . Insert picture: same sample under OM, arrow points on charcoal grains that lay on the white gesso and correspond to preliminary drawings (200 $\times$ ).

### 3.4. Gilded Pictorial Elements

The icon background (“campus”) along with the highlights of the armor and certain vestment details (e.g., bracelets) are rendered in gold tones. Micro-samples investigation revealed that these particular pictorial elements are in fact gilded with high purity ( $\text{Au} > 99 \text{ wt } \%$ ) and extremely thin ( $< 1 \text{ micron}$ ) gold leaves (Figure 6, Table 1). The latter have been applied by employing two distinct gluing agents, a yellow iron-rich clayey bole in case of the background and a lead-containing mordant in the highlights (Table 1). These adhesives pertain to the two most common—in the framework of painting—gilding techniques, namely water and mordant/oil gilding, respectively [34,35]. It shall be mentioned that the gold leaf thickness determination was achieved through inspection of high magnification SEM images, using a built-in image processing software (Figure 6) therefore some overestimation is possible [35,36].

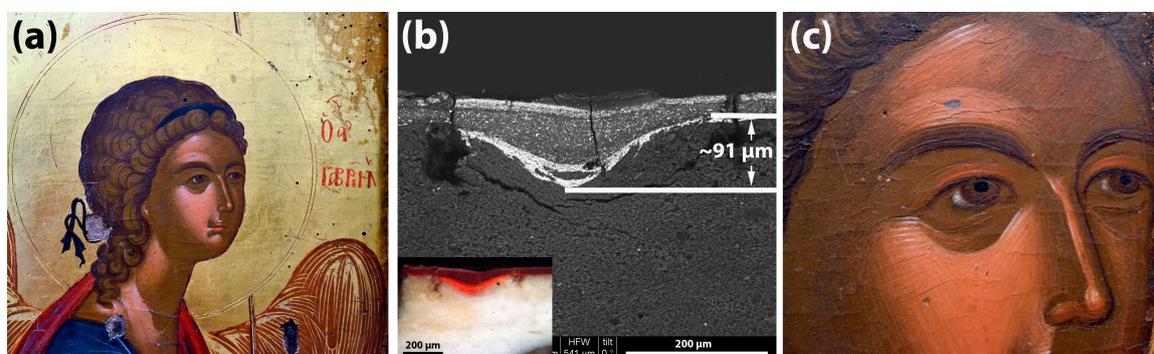
## 4. Discussion

Through the analytical investigation of the St Theodoros icon, authors were able to identify the employed painting materials (except of the organics) and techniques, and now, a crucial question arises: how can these data contribute towards the assessment of painter’s identity? To this end, the analytical data were compared to the findings of previous studies of Angelos’ known (signed) works [10–12,14,15], and evaluated in the light of analytical investigations of other high-quality Cretan icons [31,37–39]. It is thus shown that the icon in consideration can indeed be assigned to Angelos.

According to the pertinent studies, Angelos’ works show a series of specific technical characteristics, that when seen as a whole constitute a rather idiomorphic painting manner. In detail, the gypsum grounds contain always a bit of charcoal and ochres [11,32] (probably added for the purpose of modifying the gesso color) and this is also the case for the St Theodoros icon (Figure 3a), though the incorporation of pigments in grounds is an uncommon practice for post-Byzantine painting [39,40]. As for the gilded backgrounds, Angelos always used a yellow bole substrate to apply the gold leaves on [10,11,15], and yellow is the bole of the St Theodoros icon as well (Figure 5a). Yet, it seems that the red-colored boles were extensively used during 15th century [38], and, hence, the employment of a yellow bole is a very important component of Angelos’ ‘fingerprint’.

Angelos' palette comprised of 11 pigments, including common ones such as charcoal, ochres and green earth, as well as some valuable and less frequently used ones, such as lazurite and azurite [10,11,13,15]. At first sight, it appears that there is no relevance between this palette and the idiomorphic character of Angelos' paintings. However, the use of natural ultramarine deserves special attention. It is well known that this very pigment was circulating in various grades, the best of which possessed an extremely high cost [24,41]. As is evident by the photomicrographs in Daniilia et al. [11], Angelos' paintings bear first-grade lazurite with grains that usually measure above 10 microns, and this is also the case for the St Theodoros lazurite (Figure 3b). On the other hand, previous analytical studies have shown that lazurite was rather rarely employed in icon painting [29,31] and this indeed adds much value to the identification of ultramarine in the St Theodoros icon.

On the other hand, Angelos' paintings show some idiomorphic technical characteristics that resulted in the typical extremely skillful manner detected by archaeologists. In detail, Angelos always rendered the preliminary drawing/sketch by combining thin brushstrokes and very shallow incisions [10,12]. Sometimes the incised drawing could be rather extensive [15]; however, the facial features and the details of flesh and hair parts were always rendered by thin and extremely skillful brushstrokes, they were never incised [10,12,15], and this is regarded a typical characteristic of Angelos' work [14]. Therefore, the fact that the same technique has been applied in the St Theodoros icon is regarded as a notable clue towards assigning the icon to Angelos (Figures 2 and 6b). For comparison purposes, we present an example of preliminary drawing on another high-quality Cretan icon. The artifact in consideration (which is of a slightly later date, i.e., the early 16th century) is the left wing of a Royal Doors pair depicting the Annunciation of Virgin Mary that is currently on display at the Byzantine Museum of Ioannina (BMI), Greece (Figure 7a). In this case, the preliminary drawing incisions are considerably deeper than those of St Theodoros icon (~90  $\mu\text{m}$ /Figure 7b versus ~20  $\mu\text{m}$ /Figure 2d, respectively), while the facial characteristics and hair details are pronouncedly incised (Figure 7c).

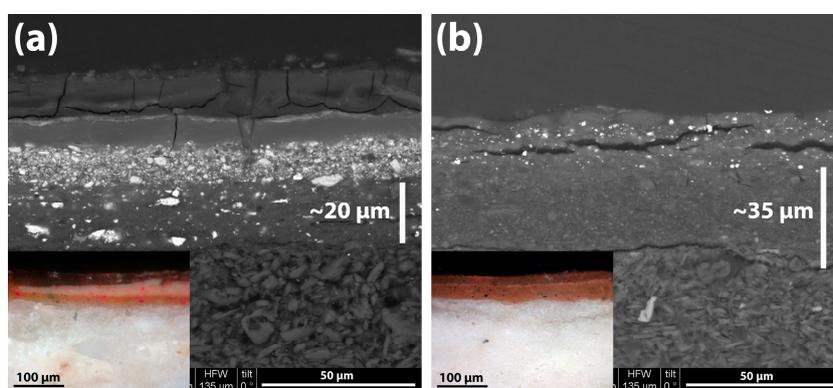


**Figure 7.** (a) Royal Doors, BMI, detail of Archangel Gabriel, left wing. (b) Background image: deep preliminary drawing incision (~91 microns) BSE, 500 $\times$ . Insert picture: same sample under OM, 100 $\times$ . (c) Detail of Archangel Gabriel face, sketch incisions on the facial characteristics are evident.

What is more, the St Theodoros icon shows notable similarities to the Angelos' works as regards the pigment mixtures and paint layer stratigraphy/application methods employed to render specific pictorial elements. In order to highlight the importance of this aspect, it should be kept in mind that the art of Eastern Orthodox iconography is based on a series of rules and dictations that more or less define the materials and techniques to be used when painting an icon. For instance, there are several post-Byzantine painting manuals that offer detailed recipes for the preparation of specific underpaint colors and the corresponding lighter tones [17,42]. Hence, the materials and techniques 'fingerprint' of a Late-Byzantine or Early Post-Byzantine icon painter cannot contain too many unusual features.

In the flesh parts, Angelos used a preparatory paint layer (underpainting/"proplasma") consisting of yellow ochre, cinnabar, hematite, lead white and charcoal, that was freely applied onto the ground

in the form of thin layers [10,11]. It is worth mentioning that the latter rarely exceed 25  $\mu\text{m}$  in thickness [10,13], and that the freehand application of this underpainting is a characteristic that is documented on all Angelos icons [10]. In case of the St Theodoros icon, IR photography (Figure 2) revealed that the flesh underpainting was applied with an identical manner to the one seen on Angelos' paintings. In addition, the cross-section of a corresponding microsample (St Theodoros left hand) shows intriguing similarities in the stratigraphy and composition level with flesh samples from Angelos' icons [10,11,13]. The underpainting in St Theodoros flesh consists of yellow ochre, cinnabar, red ochre, lead white, charcoal and a bit of green earth (Figure 8a). Older studies of Angelos paintings had failed to spot green earth in flesh underpaints, thus leading some scholars to conclude that this is a notable deviation of Angelos from his contemporary painting trends [10]. Nevertheless, this pigment was recently identified in a genuine Angelos icon [13] and in the icon studied herein, implying thus that some parts of the full spectrum of Angelos materials and techniques might still be unknown; in addition, certain features might be specific to particular artistic periods of Angelos.



**Figure 8.** (a) Sample from the flesh section of St Theodoros, cross-section. Background image: BSE, 2000 $\times$ ; perpendicular line marks the underpainting that contains numerous cinnabar grains (bright particles). Insert picture: same sample, OM, 200 $\times$ . (b) Sample from the Annunciation icon, flesh part. Background image: BSE, 2000 $\times$ . The perpendicular line marks the underpainting, note the absence of cinnabar. Insert picture: same sample under OM, 200 $\times$ .

Finally, in order to highlight the rather idiomorphic character of Angelos' flesh painting manner (which is documented in the St Theodoros icon), the icon discussed herein was compared to a relevant high-quality Cretan icon (Annunciation, royal doors, Figure 7). Cross-sections from flesh parts of the two works are shown in Figure 8. The layered structure of St Theodoros sample (Figure 8a) is practically identical to the stratigraphy seen in samples from several Angelos paintings (see for instance the figures in row "a" of Table 1, pages 102–103 in [10]). The characteristic features in both cases (St Theodoros icon and signed Angelos paintings) are the following: (a) the thinness (usually  $\sim 20 \mu\text{m}$ ) and color of the underpainting (pale yellowish-brown); (b) the consistent addition of cinnabar in the latter; and (c) the application of only one—yet significantly brighter—middle tone (lead white + cinnabar + ochre) on the base color. The final touches/highlights consist of pure lead white and are applied directly on the middle tone [10,13]. In contrast, the sample from the Annunciation icon shows an underpainting of moderate thickness ( $\sim 35 \mu\text{m}$ ) that contains no cinnabar (Figure 8b), while the lighter flesh tones were built with at least two brighter (containing more lead white) paint layers (only the first is shown in Figure 8b).

## 5. Conclusions

By critically assessing the data acquired through the analytical investigation of the St Theodoros icon, it was documented that the painter of this high-quality icon employed materials and painting techniques which are remarkably similar to those characterizing works of the renowned Angelos painter. In brief, the preliminary drawing was rendered in the typical Angelos manner, namely through

a combination of brushstrokes and notably thin incisions; the facial characteristics were rendered through extremely skillful drawing. Similarly, flesh parts were painted with the same technique as the one encountered in Angelos' works. Other common features of the studied artifact and Angelos' icons include the addition of pigments in the gesso ground, the employment of high-grade lazurite for rendering blues and the use of yellow bole for gilding backgrounds. Although some of these techniques/materials do characterize icons of other Cretan painters of the same period, their simultaneous appearance in a single icon, along with the corresponding stylistic characteristics (archaeological perspective), collectively constitute a safe fingerprint of an Angelos painting.

**Author Contributions:** Conceptualization, G.P.M.; methodology, G.P.M., M.T. and E.F.; validation, G.P.M. and K.G.B.; formal analysis, G.P.M.; investigation, G.P.M. and K.G.B.; resources, G.P.M.; data curation, G.P.M. and M.T.; writing—original draft preparation, G.P.M.; writing—review and editing, G.P.M., K.G.B. and E.F.; visualization, G.P.M.; supervision, K.G.B.; project administration, G.P.M.; funding acquisition, G.P.M. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Acknowledgments:** G.P.M. expresses his gratitude towards the Alexander S. Onassis Public Benefit Foundation for providing a Ph.D. scholarship. His eminence Dionysius, Metropolitan of Zakynthos, and the Abbey and the Abbot of the Monastery of St Dionysius in Zakynthos, along with the General Directorate for the Restoration, Museums and Technical Works and the Directorate for Byzantine and Post-Byzantine Antiquities (both are divisions of the Greek Ministry of Culture and Sports) are sincerely acknowledged for providing sampling permissions. Special thanks are due to George Mitrikas (INN, NCSR 'Demokritos') for providing access to  $\mu$ -Raman. Finally, G.P.M. thanks Giannis Kefallinos for providing accommodation during field-work in Zakynthos island.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Vokotopoulos, P. *Byzantine Icons*; Ekdotiki Athinon: Athens, Greece, 1995.
2. Χατζηδάκης, Μ. *Ελληνες ζωγράφοι μετά την Αλωση (1450–1830)* [*Greek Painters After the Fall of Constantinople (1450–1830)*]; Kentro Neoellinikon Ereunon: Athens, Greece, 1987.
3. Μανουσάκας, Μ. Η διαθήκη του Αγγέλου Ακοτάντου (1436), αγνώστου κρητικού ζωγράφου (πίν.52–53). *Δελτίον Χριστιανικής Αρχαιολογικής Εταιρείας* **1962**, *20*, 139. [[CrossRef](#)]
4. Cattapan, M. I pittori Pavia, Rizo, Zafuri da Candia e Papadopulo dalla Canea. *Thesaurismata* **1977**, *14*, 199–238.
5. Vassilaki, M. *The Painter Angelos and Icon-Painting in Venetian Crete*; Ashgate/Variorum: Farnham, UK, 2009.
6. Vassilaki, M. *The Hand of Angelos: An Icon Painter in Venetian Crete*; Lund Humphries: Farnham, UK, 2010.
7. Μυλωνά, Ζ. *Μουσείου Εκκλησιαστικής Τέχνης Ιεράς Μονής Στροφάδων και Αγίου Διονυσίου* [*Museum of Ecclesiastical Art of the Holy Monastery of Strofades and Saint Dionysius*]; Αποστολική Διακονία της Εκκλησίας της Ελλάδος: Athens, Greece, 2011.
8. Αχειμάστου-Ποταμιάνου, Μ. *Εικόνες της Ζακύνθου* [*Icons of Zakynthos*]; Ιερά Μητρόπολη Ζακύνθου και Στροφάδων: Athens, Greece, 1997.
9. Ζήβας, Δ.Α. *Ζάκυνθος 1953–2003* [*Zakynthos 1953–2003*]; Περίπλους: Athens, Greece, 2003.
10. Milanou, K.; Vourvopoulou, C.; Vranopoulou, L.; Kalliga, A.E. Angelos painting technique. A description of panel construction, materials and painting method based on a study of seven signed icons. In *Icons by the Hand of Angelos: The Painting Method of a Fifteenth-Century Cretan Painter*; Milanou, K., Vourvopoulou, C., Vranopoulou, L., Kalliga, A.E., Eds.; Benaki Museum: Athens, Greece, 2008; pp. 19–114.
11. Daniilia, S.; Minopoulou, E.; Andrikopoulos, K.S.; Karapanagiotis, I. Analysis of organic and inorganic materials and their application on icons by Angelos. In *Icons by the Hand of Angelos: The Painting Method of a Fifteenth-Century Cretan Painter*; Milanou, K., Vourvopoulou, C., Vranopoulou, L., Kalliga, A.E., Eds.; Benaki Museum: Athens, Greece, 2008; pp. 115–150.
12. Alexopoulou, A.; Kaminari, A. Study and documentation of an icon of Saint George by Angelos using infrared reflectography. In *Icons by the Hand of Angelos: The Painting Method of a Fifteenth-Century Cretan Painter*; Milanou, K., Vourvopoulou, C., Vranopoulou, L., Kalliga, A.E., Eds.; Benaki Museum: Athens, Greece, 2008; pp. 151–162.

13. Milanou, K.; Vourvopoulou, C.; Vranopoulou, L.; Kalliga, A.E. A technological examination of Cretan icons dating from the end of the 14th to the middle of the 15th century. *Μουσείο Μπενάκη* **2016**, *13–14*, 251–272, (In Greek, with English abstract).
14. Μιλάνου, Κ.; Βουρβοπούλου, Χ.; Βρανοπούλου, Λ.; Καλλιγά, Α. Ο άγιος Νικόλαος με υπογραφή ‘Χειρ Αγγέλου’. Παρατηρήσεις σχετικές με τα υλικά κατασκευής και την τεχνική του έργου [Saint Nikolaos (icon) signed ‘By the hand of Angelos’. Observations on the materials and techniques of the artifact]. In X.A.E. *28ο Συμπόσιο Βυζαντινής και Μεταβυζαντινής Αρχαιολογίας και Τέχνης*; Simmetria: Athens, Greece, 2008; pp. 62–63.
15. Stassinopoulos, S. An icon of St Nicolaos with scenes from his life by the painter Angelos. Conservation and technical analysis. *Μουσείο Μπενάκη* **2016**, *13–14*, 223–250, (In Greek, with English abstract).
16. Heinrich, K.F.J. Strategies of electron probe data reduction. In *Electron Probe Quantitation*; Springer: Berlin/Heidelberg, Germany, 1991; pp. 9–18.
17. Dionysios of Fournā. *The “Painter’s Manual” of Dionysius of Fournā: An English Translation [from the Greek] with Commentary of cod. gr. 708 in the Saltykov-Shchedrin State Public Library, Leningrad*; Oakwood: London, UK, 1996.
18. Cosentino, A. Infrared technical photography for art examination. *e-PRESERVATION Sci.* **2016**, *13*, 1–6.
19. Boer, J.R.J.V.A.D. Infrared Reflectography: A Method for the Examination of Paintings. *Appl. Opt.* **1968**, *7*, 1711–1714. [[CrossRef](#)]
20. Cosentino, A. Identification of pigments by multispectral imaging; a flowchart method. *Heritage Sci.* **2014**, *2*, 8. [[CrossRef](#)]
21. Moon, T.; Schilling, M.R.; Thirkettle, S. A Note on the Use of False-Color Infrared Photography in Conservation. *Stud. Conserv.* **1992**, *37*, 42. [[CrossRef](#)]
22. Sarma, L.P.; Prasad, P.S.R.; Ravikumar, N. Raman Spectroscopic Study of Phase Transitions in Natural Gypsum. *J. Raman Spectrosc.* **1998**, *29*, 851–856. [[CrossRef](#)]
23. Osticioli, I.; Mendes, N.; Nevin, A.; Gil, F.P.; Becucci, M.; Castellucci, E. Analysis of natural and artificial ultramarine blue pigments using laser induced breakdown and pulsed Raman spectroscopy, statistical analysis and light microscopy. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2009**, *73*, 525–531. [[CrossRef](#)]
24. Plesters, J. Ultramarine blue, natural and artificial. In *Artist’s Pigments, Vol. 2*; Ashok Roy, Ed.; National Gallery of Art: Washington, DC, USA, 1993; pp. 37–65.
25. Bell, I.M.; Clark, R.J.; Gibbs, P.J. Raman spectroscopic library of natural and synthetic pigments (pre- ≈ 1850 AD). *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **1997**, *53*, 2159–2179. [[CrossRef](#)]
26. Burgio, L.; Clark, R.J.H. Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2001**, *57*, 1491–1521. [[CrossRef](#)]
27. Caggiani, M.; Cosentino, A.; Mangone, A. Pigments Checker version 3.0, a handy set for conservation scientists: A free online Raman spectra database. *Microchem. J.* **2016**, *129*, 123–132. [[CrossRef](#)]
28. Grissom, C.A. Green earth. In *Artists Pigments: A Handbook of Their History and Characteristics*; Feller, R.L., Ed.; National Gallery of Art: Washington, DC, USA, 1986; pp. 141–168.
29. Mastrotheodoros, G.P.; Beltsios, K.G.; Bassiakos, Y. On the blue and green pigments of post-Byzantine Greek icons. *Archaeometry* **2020**, *62*, 774–795. [[CrossRef](#)]
30. Botticelli, M.; Maras, A.; Candeias, A.  $\mu$ -Raman as a fundamental tool in the origin of natural or synthetic cinnabar: Preliminary data. *J. Raman Spectrosc.* **2019**, *51*, 1470–1479. [[CrossRef](#)]
31. Karapanagiotis, I.; Lampakis, D.; Konstanta, A.; Farmakalidis, H. Identification of colourants in icons of the Cretan School of iconography using Raman spectroscopy and liquid chromatography. *J. Archaeol. Sci.* **2013**, *40*, 1471–1478. [[CrossRef](#)]
32. Kirby, J.; Spring, M.; Higgitt, C.; National Gallery. The Technology of Red Lake Pigment Manufacture: Study of the Dyestuff Substrate. Available online: [www.nationalgallery.co.uk](http://www.nationalgallery.co.uk) (accessed on 10 October 2020).
33. Tomasini, E.; Siracusano, G.; Maier, M. Spectroscopic, morphological and chemical characterization of historic pigments based on carbon. Paths for the identification of an artistic pigment. *Microchem. J.* **2012**, *102*, 28–37. [[CrossRef](#)]
34. Mactaggart, P.; Mactaggart, A. *Practical Gilding*; Archetype: London, UK, 2002.
35. Mastrotheodoros, G.P.; Beltsios, K.G.; Bassiakos, Y.; Papadopoulou, V. On the Metal-Leaf Decorations of Post-Byzantine Greek Icons. *Archaeometry* **2017**, *60*, 269–289. [[CrossRef](#)]

36. Mastrotheodoros, G.P.; Anagnostopoulos, D.F.; Beltsios, K.G.; Filippaki, E.; Bassiakos, Y. Glittering on the Wall: Gildings on Greek Post-Byzantine Wall Paintings. In *Communications in Computer and Information Science*; Springer: Berlin/Heidelberg, Germany, 2019; Volume 962, pp. 397–404. [[CrossRef](#)]
37. Valianou, L.; Wei, S.; Mubarak, M.S.; Farmakalidis, H.; Rosenberg, E.; Stassinopoulos, S.; Karapanagiotis, I. Identification of organic materials in icons of the Cretan School of iconography. *J. Archaeol. Sci.* **2011**, *38*, 246–254. [[CrossRef](#)]
38. Karapanagiotis, I.; Minopoulou, E.; Valianou, L.; Daniilia, S.; Chryssoulakis, Y. Investigation of the colourants used in icons of the Cretan School of iconography. *Anal. Chim. Acta* **2009**, *647*, 231–242. [[CrossRef](#)]
39. Mastrotheodoros, G.P. Pigments and Various Materials of Post-Byzantine Painting. Ph.D. Thesis, University of Ioannina, Ioannina, Greece, 2016.
40. Mastrotheodoros, G.P.; Beltsios, K.G.; Bassiakos, Y.; Papadopoulou, V. On the Grounds of Post-Byzantine Greek Icons. *Archaeometry* **2015**, *58*, 830–847. [[CrossRef](#)]
41. Cennini, C. *The Craftsman's Handbook*; Dover Publications: Mineola, NY, USA, 1954.
42. Mastrotheodoros, G.P.; Beltsios, K.G. Sound Practice and Practical Conservation Recipes as Described in Greek Post-Byzantine Painters' Manuals. *Stud. Conserv.* **2018**, *64*, 42–53. [[CrossRef](#)]

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).