Archaeological and Anthropological Sciences (2019) 11:2821–2836
https://doi.org/10.1007/s12520-018-0732-5

ORIGINAL PAPER

Probing the birthplace of the "Epirus school" of painting: analytical investigation of the Filanthropinon monastery murals—Part I: pigments

Georgios P. Mastrotheodoros[1] · Eleni Filippaki[1] · Yannis Bassiakos[1] · Konstantinos G. Beltsios[2] · Varvara Papadopoulou[3]

Received: 23 June 2018 / Accepted: 3 October 2018 / Published online: 22 October 2018

Abstract
The Filanthropinon monastery church is regarded the birthplace of the "Epirus/NW Greece School" of painting as it bears the oldest wall paintings of this very school. Surviving inscriptions bear no painter name(s), yet they testify that the murals were executed in three phases between 1531/2 and 1560. The bulk of the technical and typological characteristics of the latter paintings are typical of post-Byzantine religious art, while OM, SEM-EDX, and micro-Raman probing reveals the existence of a number of idiomorphic characteristics that might be viewed as part of the microscopic fingerprint of the "Epirus school." A microscopic fingerprint of the school is important because current attributions of relevant works to specific painters are mostly stylistic ones, as pertinent signatures are rare. The latter characteristics include the application of a "charcoal plus blue smalt" substrate in the paintings' background and the employment of a possibly local (: Epirus), unusual ochre pigment. Sophisticated segregation of pigment grains, employment of glauconite, and the extensive use of San Giovanni white were also documented. Analytical data support the following scheme as regards artistic identities: the 1531/2 nave paintings were executed by a single painter, possibly assisted by a pupil who also contributed to the 1542 paintings. The paintings of the 1542 and 1560 phases are apparently the outcome of another—yet related to the nave painter—workshop; there are clues which indicate employment of Georgios and Frangos Kontaris in both of these commissions. Finally, remnants of four different overpaintings were also revealed: pertinent pigments indicate successive interventions during an extended period of time, which reflect the will of Filanthropinon votaries to retain the murals vivid.

Keywords Wall painting · Post-byzantine · Pigment · OM · SEM-EDX · Kontaris

Introduction

During the Byzantine period (330–1453 AD), Orthodox Christian churches were routinely embellished by wall paintings or/and mosaics. Constantinople was the unambiguous art center of that period, as artistic innovation was triggered off, formed, and embraced therein (Acheimastou-Potamianou 1994), and the Fall of Constantinople to Ottoman Turks (1453) corresponds to the end of the Byzantine period. Nonetheless, painting flourished during the "post-Byzantine" period as well, because the inhabitants of former Byzantine territories mostly retained their Orthodox faith despite the Ottoman conquest. Besides, Ottomans accepted and made use of the Orthodox Church administration system, and, thus, during this period, new churches were built and painted (Chatzidakis 1987).

Short before the "Fall," many Constantinople craftsmen were moving to Crete—a Venetian-ruled island of the Aegean Archipelago—and this migration led to a boost of the local painting. Soon, Crete became the major painting center of the Greek territories and remained so up until the late seventeenth century (op. cit.). Cretan painting of this period exhibits several idiomorphic characteristics that allow for its designation as the "Cretan School of painting" (op. cit.). Moreover, Cretan icons were distributed to mainland Greece and elsewhere, while local painters were commissioned to

✉ Georgios P. Mastrotheodoros
g.mastrotheodoros@inn.demokritos.gr; mastroteog@yahoo.gr

1 Institute of Nanoscience and Nanotechnology, NCSR 'Demokritos', Aghia Paraskevi, 15310 Attiki, Greece

2 Department of Materials Science and Engineering, School of Sciences, University of Ioannina, 45110 Ioannina, Greece

3 Ephorate of Antiquities of Arta, 47100 Arta, Greece

paint churches in places outside Crete too; thus, the Cretan idiom was very widely spread (op. cit.).

More or less simultaneously, a new, substantially deviating (and with different stylistic routes) trend was developed in the Ottoman-ruled mainland Greece (Acheimastou-Potamianou 1995; Georgitsoyanni 1999). Commonly named "Epirus/Northwest Greece School," this idiom bears all the characteristics of a distinct painting trend (iconographic repertoire, distinct palette, impact on oncoming artists etc.), and it initially flourished in the area of Ioannina (Epirus, NW Greece). The first pertinent paintings are found in the katholikon (: main church) of the Filanthropinon monastery which is located on the islet of the Ioannina ("Pamvotis") lake (Acheimastou-Potamianou 1995). An inscription testifies that the church received a renovation on 1291/92. Yet, the oldest wall paintings that survive today are those covering the lower parts of the main church (nave[1]) walls, which are dated to 1531/32 and mark the beginning of the "Epirus school" of painting (op. cit.) (Fig. 1a). A few years later (1542), the wooden roof of the nave was replaced by a taller, built one, while simultaneously the new upper part of the nave and the inner narthex walls ("litē," from now on "narthex") were painted (Fig. 1b); the three exonarthexes were the last to receive paintings in 1560 (Acheimastou-Potamianou 1995, 1999) (Fig. 1c). Unfortunately, the Filanthropinon inscriptions bear no painter names; nonetheless, taking into account stylistic and iconographic features along with the characteristics of other signed paintings, scholars suggest the following: (i) the first phase (lower part of nave walls, 1531/32) may not be attributed to a specific artist; (ii) the legendary painter Frangos Katelanos may have worked in the second phase (nave upper part/narthex, 1542), possibly assisted by the brothers Frangos and Georgios Kontaris (reportedly pupils of Katelanos); (iii) the third and final phase (1560, exonarthexes) is regarded a work of the Kontaris brothers (Acheimastou-Potamianou 1995, 1999; Deligianni-Dori 1999; Koilakou 2001).

In the absence of written evidence, the visual/stylistic study needs to be supplemented by an archaeometric investigation of the works. Such an investigation would reveal possible differences in technical and material level among the various Filanthropinon painting phases, which are unperceivable by the naked eye.[2] Indeed, analytical studies of Greek wall paintings have revealed the materials and techniques employed in their manufacture (e.g., Zorba et al. 2006; Pavlidou et al. 2006; Daniilia et al. 2007; Bianchin et al. 2008; Iordanidis et al. 2014). Moreover, such investigations have occasionally traced evidence for a "materials evolution" taking place side by side with the perceivable stylistic developments, while in some instances, they revealed idiomorphic characteristics—in terms of materials and techniques—in the works of specific artists (Pavlidou et al. 2006; Civici et al. 2008; Daniilia et al. 2008a, b; Katsibiri and Howe 2010). In order to fully estimate the contribution of analytical investigation in understanding the technical aspects of post-Byzantine painting, one shall bear in mind the scarcity of pertinent painting manuals. Indeed, up to today, the one and only published Greek text that includes a systematic description of the materials and techniques of wall painting is the ca. 1730 Dionysius of Fourna "Hermeneia of the art of painting" (Dionysius 1996, 1997).

In this framework, microsamples collected from the three Filanthropinon painting phases were subjected to analytical investigation through OM, SEM-EDX, micro-Raman, XRD, and FTIR; for comparison purposes, samples from an earlier (Byzantine?), semi-destroyed depiction—which was revealed upon removing a superficial painting layer during conservation, Fig. 1d (Acheimastou-Potamianou 1995)—were also examined. Analytical data are evaluated in the framework of pertinent published studies; in addition, they are predestined to serve as a base for the authors' ongoing investigation of several other wall paintings assigned to the Epirus school. In view of the range and volume of collected data, the material is presented in two parts: the pertinent to Filanthropinon pigments analytical results are presented and discussed in part I, while in the second part (to be submitted), the mortars, gildings, and painting technique(s) are considered.

Methodology

Initially, paintings were thoroughly examined in order to properly select spots appropriate for sampling. Subsequently, minute size samples were collected exclusively from damaged areas, taking into account the following: (a) each sample should comprise of the complete painting stratigraphy [including both or part of the plaster layers (surface and base/"arriccio" and "intonaco" respectively) and all the subsequent paint layers], (b) in order to strengthen the comparative character of the study, samples from the same iconographical elements were preferentially picked up (e.g., from backgrounds/"campus," red vestments, red bordering lines etc.), and (c) areas that correspond to post-sixteenth century additions/interventions were distinguished and not sampled. In total, 45 samples were collected and examined: 42 come from the three main painting phases and three from the

[1] From now on, the word "nave" will be exclusively used as a term relevant to the analyzed, lower-part paintings (1531/2 painting phase). No material from the later (1542), upper part of the nave paintings is included in the study; instead, the present authors have studied several samples from the inner narthex decorations that also belong to the 1542 painting phase (see the "Methodology" section).

[2] In the early 1990s samples from the Filanthropinon wall paintings were analyzed by P. Behlis and E. Photou-Jones. Yet up today only a short pertinent paper has been published, where the analytical data accumulated through the analysis of only two Filanthropinon samples are presented; this paper contains data pertinent to a few samples collected from other relevant monuments too (Behlis and Photos-Jones 1999).

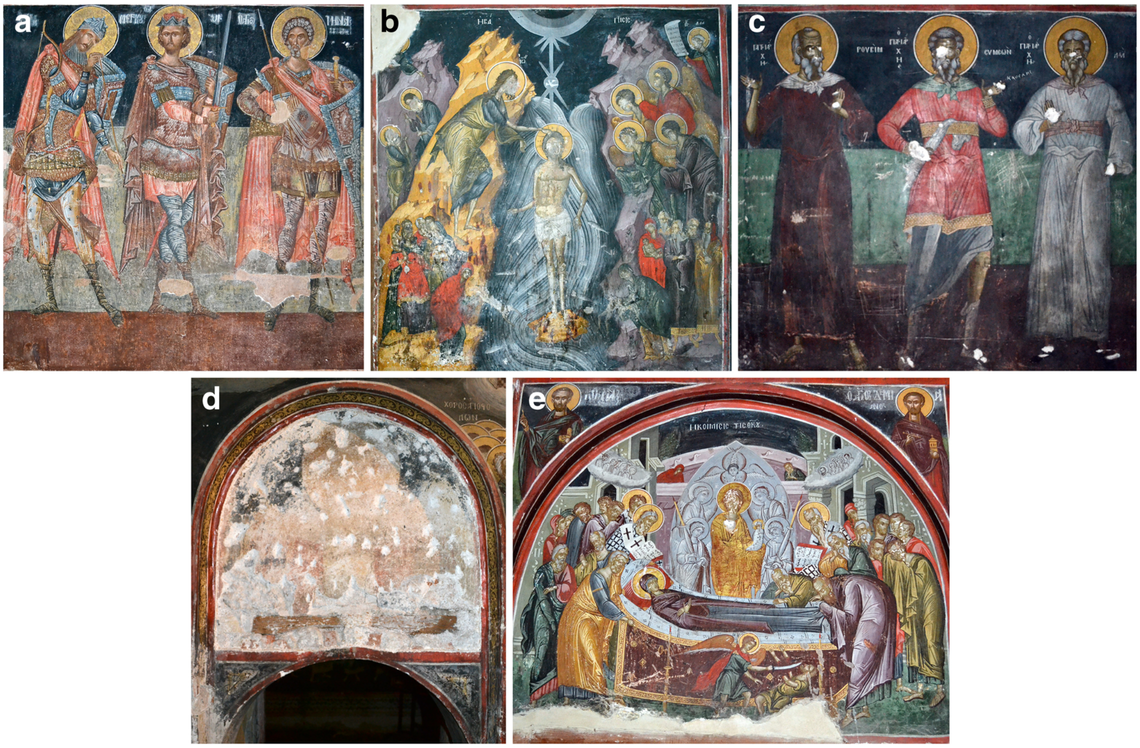

Fig. 1 **a** Warrior Saints, first (1531/2) painting phase, nave. **b** The Baptism, narthex; second phase (1542). **c** Three Old Testament Patriarchs; north exonarthex, third phase (1560). **d** Semi-destroyed depiction on the south exonarthex lintel; earlier phase (Byzantine?). **e** The Dormition of the Virgin, narthex

remnants of the earlier (Byzantine?) depiction (Table 1). Samples were thoroughly examined and photographed under a binocular stereoscope and subsequently embedded into polyester resin. Upon grinding and polishing, samples' cross sections were examined and pictured under a polarizing optical microscope (Leica, DMRXP) at magnifications up to × 200. Afterwards, samples were carbon-coated by a sputtering device (Balzers, CED-030) for conductivity purposes and thoroughly examined under a scanning electron microscope coupled with an energy-dispersive X-ray analyzer (SEM-EDX, FEI, Quanta-Inspect D-8334). For the estimation of the pigments' compositions, EDX spectra from at least four individual pigment grains were collected. Spectra were processed by using the SEM's built-in "Genesis-Spectrum" software (EDAX Company) following a standard-less quantification method which incorporates ZAF matrix corrections (Heinrich 1991). In addition, the morphological characteristics of the samples were recorded by using the SEM's backscattered electron (BSE) detector which permits visual differentiation of the various phases on the basis of their atomic number contrast (Goodhew and Humphreys 1988). On the basis of the cross-section analysis data, the surfaces of selected samples were subsequently subjected to SEM-EDX analysis as well. Finally, upon conductive carbon coating removal, sample cross-sections were further studied through micro-Raman spectroscopy (inVia microscope, Renishaw). In particular, samples were irradiated with a 514-nm laser and corresponding spectra were collected through a × 100 objective lens, with repeated acquisitions (2–6) of varying durations (10–40 s). Spectra were recorded in frequencies that ranged among 100–1800 cm^{-1}, while for each different type of pigment/phase, several individual grains were analyzed.

Results and discussion

The number of pigments employed in the Filanthropinon wall paintings was initially estimated on the basis of OM observations conducted on the samples' cross-sections. Subsequently, several individual pigment grains were examined under the SEM-EDX in order to fully assess their morphological features and elemental compositions, while decisive identification was achieved through micro-Raman spectroscopy. This methodological approach revealed the presence of white, black, red/deep red, yellow(/brown), green, and blue pigments, which in several instances have been intermixed in order to achieve specific hues. The pertinent data are summarized in Table 2 and discussed in detail below, while indicative Raman spectra are shown in Figs. 6 and 7.

Black and white

The one black pigment found in the examined paintings is charcoal that was manufactured via carbonization of plant

Table 1 Sampling spots and corresponding serial numbers

s/n	Main church/nave
Fm1	Deep red/brown ground, St Petros, west wall
Fm2	Red bordering line, St Petros, west wall
Fm3	Pale brown garter, St Georgios, north wall
Fm4	Greenish ground, St Petros, west wall
Fm5	Deep red garter, St Prokopios, south wall
Fm6	Intense red vestment, St Heleni, west wall
Fm7	Deep red/purplish vestment, St Nikitas, south wall
Fm8	Gilded halo, St Artemios, south wall
Fm9(a-b)	Dark campus, St Pavlos, west wall
Fm10	Gilded relief medal, St Theodoros Tiron, north wall
Fm11	Yellow-brown epimanikion (maniple), St Kyrillos, apse, east wall
Fm12	Red bordering line, north wall-iconostasis joint
Fm13	Base plaster ("arriccio"), St Merkurios, north wall
Fm14	Dark campus, St Gregorios, apse, east wall
s/n	Inner narthex ("Liti"/"narthex")
Fin1	Dark campus, The Baptism, east wall
Fin2	Red bordering line, St Provos, south wall
Fin3	Greenish ground, >>
Fin4	Deep red/brown ground, >>
Fin5	Intense red vestment, St Panteleimon, west wall
Fin6	Yellow-orange vestment, St Longinos, north wall
Fin7	Purplish vestment, The Baptism, east wall
Fin8	Yellow hallo, >>
Fin9	Yellow band, decorative podea (apron), St Provos, south wall
Fin10	Black band, >>
Fin11	Masonry mortar, >>
Fin12	Base plaster, >>
Fin13	Gilded vestment, Jesus, The Dormition of the Virgin, east wall
Fin14	Greenish ground, >>
Fin15	Red bordering line, >>
s/n	North Exonarthex
Fen1	Red bordering line, St Theofanis, south wall
Fen2	Greenish ground, >>
Fen3	Dark red/brown ground, >>
Fen4	Intense red vestment, St Simeon, south wall
Fen5	Yellow hallo, St Kiprianos, north wall
Fen6	Purplish vestment, St Markos, north wall
Fen7	Black band, decorative podea (apron), window, north wall
Fen8	Surface plaster ("intonaco"), St Prokopios, south wall
Fen9	Base plaster, >>
Fen10	Masonry mortar, >>
Fen11	Dark campus, St Simeon the stylite, south wall, east face of a pessary
Fen12	Intense green, decorative podea, window, north wall
Fen13	Dark campus, St Flavianos, south wall
s/n	South Exonarthex/Hyperthyron (lintel)
Fes1	Dark campus, hyperthyron (lintel), north wall
Fes2	Traces of red, >>
Fes3	Base plaster, >>

Table 2 Summary of the pigment-analysis EDX results, expressed as wt% elements (normalized to 100%)

Red/deep red pigments												
Nave												
	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Mn	Fe	Other
Fm1,2,5,7a	0.5	1.9	3.1	7.8	1.0	0.7	1.3	13.4	0.3	1.6	64.0	P/Cu/Pb (1.4/tr/2.9)
Fm2	0.3	0.7	26.0	34.3	0.4	0.6	1.0	11.6	3.6	0.2	20.7	P (0.6)
Fm7b	0.3	0.7	0.7	1.4	0.1		0.2	9.1			86.6	P/Pb (0.1/0.8)
Fm6,12					16.7			1.6				Hg (83.3)
Narthex												
	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Mn	Fe	Other
Fin2,5,12,15					16.4			0.5				Hg (83.1)
Fin4,7	0.7	1.4	5.4	11.1	0.3	1.0	1.4	7.7	0.3	1.3	68.9	P/Pb (0.2/0.4)
Fin4,7,14		1.3	1.5	3.6	0.7	0.3	0.4	10.2		2.0	79.1	P/Cu/Pb (0.2/0.3/0.5)
North exonarthex												
	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Mn	Fe	Other
Fen1,4					16.6							Hg (83.5)
Fen2,3,6a	0.2	1.2	1.7	17.8	0.5	0.3	0.5	6.9	tr	1.7	69.0	P/Cu (0.1/tr)
Fen6b		0.8	0.4	5.4				7.5			85.5	P (0.4)
South Exonarthex												
Fes2		0.5	2.5	14.3	0.5	0.2	0.7	16.0		0.8	64.0	P (0.5)
Yellow/yellow-brown												
Nave												
	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Mn	Fe	Other
Fm3,4	0.2	2.1	3.6	8.7	0.4	0.5	1.4	21.4	0.5	1.6	58.7	P (0.9)
Fm11	1.2	2.4	3.5	13.1		1.9	1.6	8.2	0.2	2.5	64.8	P (0.6)
Narthex												
	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Mn	Fe	Other
Fin3,6,8,14	0.5	2.0	3.0	6.8	1.2	0.8	1.0	18.3	0.5	0.4	63.6	P/Pb (1.1/1.0)
North exonarthex												
	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Mn	Fe	Other
Fen2,5	0.5	1.7	1.9	18.5	0.3	0.6	0.6	19.4	0.3	tr	55.8	P (0.6)
Fen5		1.2	0.8	7.0		0.5		2.3		tr	87.6	P (0.6)
Green												
Nave												
Fm4	Yellow ochre + carbon black											
Narthex												
	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Fe	Cu	Other
Fin3	0.3	2.7	9.0	49.2	0.3	0.6	10.9	7.2	0.4	19.0	0.3	
Fin14		5.1	0.9	1.8	0.1	0.8	0.3	6.0		0.7	77.2	Zn/As (4.0/3.0)
North exonarthex												
Fen2,12	0.1	4.3	7.7	47.5	2.1	1.6	7.3	12.3	0.2	16.8		
Blue												
Nave												
	Na	Mg	Al	Si	S	Cl	K	Ca	Co	Fe	Cu	Other/Comment
Fm7			0.2	0.2	0.6			1.4		0.6	94.3	P/Zn/Pb (0.1/0.9/1.6)
Fm9a	9.5	3.1	1.5	54.5	0.6	1.9	5.8	19.2	0.2	1.4	0.1	P/Mn/Pb (0.1/2/0.2)
Fm9a			2.2	2.1		0.1	0.3	3.9		0.9	88.8	P/Pb (0.1/1.5)
Fm9b		1.4	11.2	26.6		2.1	5.2	14.3		9.3	1.9	P/Ti/Pb (1.5/1.7/24.9)
Fm14	8.7	0.2	13.6	21.0	21.2	0.4	4.2	19.9		1.1		Pb (9.9)
Narthex												
Fin1a	10.0	3.0	1.2	55.7	1.2	2.2	4.1	17.8	0.3	2.0	1.4	Mn (1.0)

Table 2 (continued)

Red/deep red pigments											
Fin1b	Charcoal										micro-Raman identification/Fig. 6a
North exonarthex											
Fen11/13	10.7	3.0	1.3	49.6	0.8	1.5	3.5	26.3	0.2	1.0	P/Mn/Pb (0.2/1.6/0.4)
South Exonarthex											
Fes1	Charcoal										micro-Raman identification

In Table 2, only the EDX data that are relevant to pigments are presented; gilding and mortar elemental compositions are given in Part II. Few samples were examined through OM, SEM, and/or micro-Raman but not via EDX and hence they do not appear in Table 2 (e.g., sample Fen7)

materials. Indeed, the micro-Raman analysis of several black grains revealed the characteristic D and G shifts of charcoal (~ 1350 and ~ 1600 cm^{-1} respectively, see, e.g., Coccato et al. 2015) (Fig. 6a). In the majority of the pertinent samples, particles with dimensions well below 20 μm were seen, implying a rather intense grinding step prior to application. Yet in a few instances, grains of enhanced dimensions do exist, which quite often retain the characteristic plant tissue structure of the parent material (Fig. 2a). On the other hand, no phosphorous was detected through EDX analysis and, hence, the possibility of ivory/bone black employment is excluded. It is worth noting that similar plant-derived carbon black pigments have been found in many other Byzantine and post-Byzantine wall paintings (Zorba et al. 2006; Daniilia et al. 2007; Hein et al. 2009).

White highlights (Figs. 2b and 4b) were found to consist of calcium carbonate as in the pertinent Raman spectra the typical calcite major shift at ~ 1087 cm^{-1} was observed (Bell et al. 1997) (Fig. 6b). The latter layers of paint appear rather homogeneous; hence, it is assumed that they had been originally applied by brush in the form of lime putty ($Ca(OH)_2$ finely dispersed in water) and were subsequently gradually carbonized through reaction with atmospheric carbon dioxide. Apart from the white highlights, in several instances, well-defined, calcium-dominated (: EDX) grains of rather enhanced dimensions were spotted dispersed into layers of various colors.

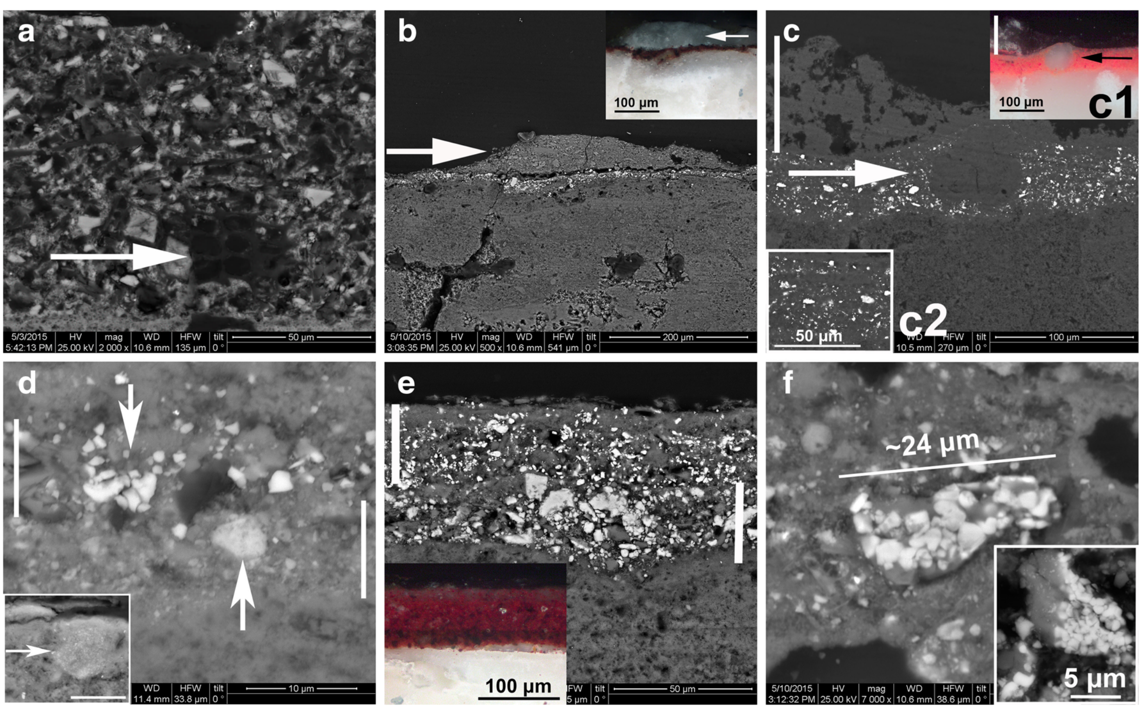

Fig. 2 **a** Carbon black layer; arrow indicates grain with anatomic characteristics of the parent plant. Sample Fm9a, BSE, × 2000. **b** Calcium carbonate highlight (Fin7, BSE, × 500); a pertinent OM picture is inserted (× 200). **c** $CaCO_3$ grain in a HgS paint layer; HgS grains range among 0.5–10 μm (Fen1, BSE, × 1000); inserted picture: OM, × 200. Perpendicular lines denote a superficial efflorescence layer, commonly seen in many samples (gypsum, characteristic Raman shift at ~ 1010 cm^{-1}/Fig. 6c). **d** Three distinct iron-ochre pigments. Background picture: moderate-iron (lower layer) and high-iron grains (upper layer), Fm7, × 8000. Inserted picture: low-iron red, Fm2, × 6000. Horizontal lines = 10 μm. **e** Two overlapping layers of red ochre; the lower contains coarse grains and appears darker than the upper (Fen6, × 2000, inserted picture OM × 200) **f** Double-phase ochre grains; background: sample Fin7, × 7000; inserted: Fen3, × 10,000

These grains were identified as calcium carbonate as well (: micro-Raman) and appear with rather angular contours and occasionally with smoother ones; hence, it is suggested that they have been formed through grinding of a calcitic raw material (Fig. 2c).

Lime was indeed the only white pigment to be used by Byzantine and post-Byzantine wall painters, not only in the Greek lands but in adjacent areas as well (Pavlidou et al. 2006; Daniilia et al. 2007, 2008a, b; Sakellariou et al. 2010; Holclajtner-Antunović et al. 2016; Marič-Stojanovič et al. 2018). Yet, to the authors' best knowledge, this is the very first time that the presence of the grinded calcite grains in non-white/highlighting paint layers is noted. Besides, it is well known that both Cennino Cennini and Dionysius of Fourna describe the preparation of an artificial, calcium carbonate white pigment that was to be exclusively used in wall painting (Dionysius 1997; Broecke 2015). On this basis, the white calcite particles that are seen in the Filanthropinon paint layers shall be identified as an artificial calcium carbonate white, equivalent to the "bianco San Giovanni" of Cennini.

Finally, it shall be noted than in several instances, superficial, whitish, and semi-transparent Ca–S-containing (: EDX) layers were spotted (Fig. 2c). Upon micro-Raman analysis, the latter layers were found to be gypsum (major shift at ~ 1009 cm^{-1}, Fig. 6c) (Bell et al. 1997), and it is hence assumed that they correspond to decay products. Besides, gypsum is the most common degradation product spotted on wall paintings (see, e.g., Daniilia et al. 2008b; Holclajtner-Antunović et al. 2016).

Red/deep red

Two types of red pigments have been identified in the Filanthropinon wall painting samples, namely, cinnabar and natural iron ochre(s). Cinnabar/vermilion grains are readily discernible due to their bright appearance upon backscattered electron (BSE) observation (Fig. 2c) and distinct elemental profile (major elements detected: Hg and S, Table 2), as well as through the characteristic Raman shifts at 253 and 345 cm^{-1} (Fig. 6d) (Bell et al. 1997; Burgio and Clark 2001). This pigment was identified in several samples from all three Filanthropinon painting phases, namely in samples Fm6/12, Fin2/5/12/15, and Fen1/4. Natural mineral cinnabar has been used since antiquity, while its synthetic equivalent is manufactured since the first millennium AD (Gettens et al. 1993). The latter gained wide popularity only after the thirteenth century, and it is believed that it very soon replaced completely the costly natural product. The scarcity of pure forms of the mineral and the wide distribution of artificial cinnabar (vermilion) during the period in consideration (sixteenth century AD) strongly suggest that the Filanthropinon pigment is of artificial rather than mineral origin. Besides, one may also note the fractured-appearance of the grains (which is regarded a characteristic of artificial HgS produced by the dry method, see Gettens et al. 1993) and the absence of—the typical for natural cinnabar—stibnite (Sb_2S_3) and quartz admixtures (Eastaugh et al. 2008).

In the studied samples, cinnabar appears mostly as rather thin grains with dimensions well below 5 μm, while quite often a significant fraction of the pigment appears in the form of even smaller particles (< 1 μm, Fig. 2c). This extremely thin fraction brings in mind a passage from the "Il libro dell'arte," where Cennini suggests that the more the cinnabar is grinded, the better (in terms of hue) it becomes (Broecke 2015). Relevant is also a "Hermeneia" extract in which Dionysius suggests the application of differential sedimentation for the separation of smaller from larger cinnabar grains to be used in another application (Dionysius 1997).

HgS grains are occasionally seen in several paint layers, yet cinnabar has been used as the base color ("proplasmos") for the intense red vestments in all three painting phases, and for rendering the bordering lines in narthex and exonarthex paintings (samples Fin2-Fen1, Fig. 2c). On the contrary, the nave bordering lines bear a single red ochre layer (sample Fm2), which is only partially covered by coarse cinnabar (grain diameter d: 10 $\mu m < d < 55$ μm) in case of sample Fm12. However, among the two layers (red ochre/cinnabar), a thin accumulation layer exists, hence the presence of the coarse cinnabar in this very sample may be assigned to a latter overpainting intervention.

On the other hand, iron-containing ochre-type pigments were identified in samples of all three phases; the presence of these pigments was verified on the basis of their high iron and aluminosilicate contents (EDX—Table) as well as through their characteristic Raman spectra (Fig. 6e, Bikiaris et al. 1999; Bouchard and Smith 2003). In the case of Filanthropinon wall paintings, red ochres have been rather commonly employed for rendering red and purple hues (upon mixing with carbon black), and they were also used as minor admixtures in paint layers of several other hues (e.g., in olive-green substrates, see samples Fin3 and Fin14, Tables 1 and 2). Based on their elemental profile, Filanthropinon red ochre grains may be divided in three distinct subgroups: (i) high iron (Fe~79–87%), (ii) moderate iron (Fe~64–69%), and (iii) low iron, clayey ones (Fe < 25%) (Table 2; Fig. 2d). Nave is the only phase that bears all three ochre pigments as no low-iron clayey grains (iii) were spotted in narthex and exonarthex samples. On the other hand, the elemental profile and microstructure of the high-iron grains [(i), common in all painting phases] allow for their characterization as "caput mortum," a pigment that was rather frequently employed in Byzantine and post-Byzantine painting (Bikiaris et al. 1999; Daniilia et al. 2002; Ganitis et al. 2004).

Interestingly, in several samples, the well-known dependence of pigment hue to grain size was clearly visualized (Mastrotheodoros et al. 2010). A pertinent example is the two-layered sample Fen6: both paint layers contain high-iron grains of comparable compositions, which nevertheless differ significantly in terms of grain size: deep-red, upper-layer grains range among 0.3–3 μm, while the lower layer contains significantly larger grains (2–15 μm) which appear obviously darker (Fig. 2e). This extraordinarily fine partition of a single pigment implies employment of a very selective segregation process.

Another notable finding was the revealing of several double-phase ochre grains in samples from both the narthex and the north exonarthex wall paintings. Upon BSE observation, these very grains appear to consist of a gray matrix in which bright particles are dispersed (Fig. 2f). EDX analyses revealed that the bright particles contain mostly iron, while the matrix contains varying amounts of the elements Ca, Si, and Al, along with several minor admixtures including manganese. Similar gains have been recently documented in post-Byzantine panel paintings ("icons") executed in the same geographical region (Epirus-SW Greece) (Mastrotheodoros 2016), and on the basis of their elemental profile, it may be said that they are vaguely reminiscent of compositions of manganese-containing iron occurrences that are not uncommon in Epirus. To the best of the authors' knowledge, ochre grains with these distinct characteristics have not been reported before in the pertinent literature and they might represent pigment from an unknown local (: Epirus) source; yet, a separate systematic investigation is needed for the determination of the identity/provenance of the pigment in consideration.

Yellow/yellow-brown

All yellow grains are of a characteristic elemental profile (major component: iron, moderate aluminosilicate content, Table 2), while corresponding micro-Raman spectra exhibit the typical shifts of limonite (Bikiaris et al. 1999) (Fig. 6f); hence, it is concluded that the only yellow pigment employed in Filanthropinon wall paintings is iron ochre. Ochre was extensively used for rendering halos, yellow/pale brown vestments (e.g., maniples, upon mixing with red ochre or/and carbon black), and olive-green grounds (mixed with black and occasionally with a small amount of red) (Fig. 3a, b). Pertinent grains appear homogeneous/single-phased under OM/SEM and usually with rounded contours, a characteristic that indicates either intense grinding or prolonged flowing-water action on a natural raw material (Fig. 3a). In a couple of samples, among the yellow grains appear a few pale-brown ones (Fig. 3a); the latter are of enhanced iron and lower calcium contents in comparison to the former (Table 2), yet they are limonitic too (Raman spectra retain the intense limonite shifts). To the authors' opinion, these very grains shall be regarded as natural admixtures of the ochre pigment, rather than craftsmen's intentional additions.

Remarkable characteristics of all the analyzed ochre grains are their enhanced iron content and the presence of minor manganese admixtures (Table 2), which bring in mind the compositions of "sienna"-type yellow earth pigments (Helwig 2007; Eastaugh et al. 2008). Moreover, the majority

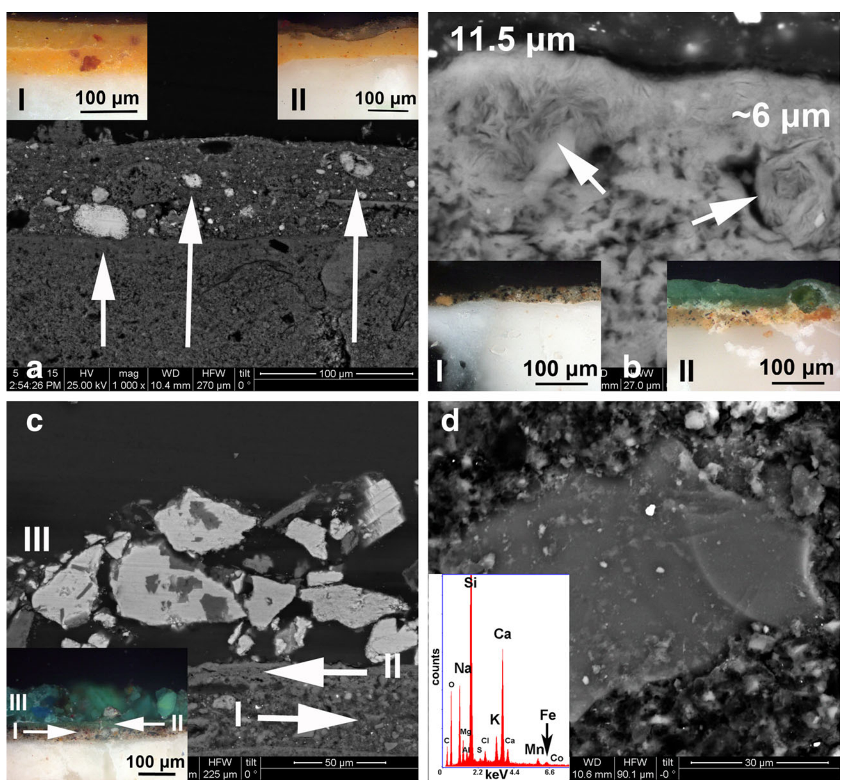

Fig. 3 **a** Background: rounded ochre grains, (Fen5, BSE, × 1000). Inserted pictures: I: distinct pale-brown grains dispersed in an ochre matrix (Fen5, OM, × 200). II: Ochre on plaster (Fin8, OM, × 200). **b** Background: Green-earth grains (arrows) (Fin3, BSE, × 10,000). Inserted: I: black + ochre olive-green layer (Fm4, OM, × 200). II: green-earth on olive-green substrate (black + ochre, Fen2, OM, 200×) **c** Three-layered green, Fin14. Substrate (I): black + ochre + red/ Intermediate (II): green-earth/surface (III): coarse malachite. Gray inclusions on malachite correspond to Ca–Mg phases. Background: BSE, × 1200. Inserted: OM, × 200. **d** Smalt grain with conchoidal-fracture features (Fm9a, BSE, × 3000). Inserted: relevant EDX spectrum

of the studied red and yellow Filanthropinon earth pigments exhibit a similar minor element profile (Mn, P and, occasionally, Pb) and a common geological origin is possible. The assumption that both red and yellow Filanthropinon ochres come from a single—possibly local—source is intriguing, yet the pigment-quality earths abound in earth's crust (Hradil et al. 2003); hence, this hypothesis deserves further consideration on the basis of extensive local geological probing.

On the other hand, the absence of deep-brown, umber-type pigments from the palettes of all three Filanthropinon painting phases is noticeable. Analytical data revealed that in order to compensate for this shortage, Filanthropinon craftsmen used quite often charcoal plus red/yellow ochre mixtures (samples Fm1, Fin4, Fen3), while in a few instances, more sophisticated routes for rendering brown were employed: this is the case of St. George's brown garter (sample Fm3), which has been rendered by applying a thin carbon-black wash over a red-yellow substrate (Fig. 4a, b).

Green

Green had been extensively used in all three Filanthropinon phases for rendering the upper part of the ground on which the depicted figures stand (Fig. 1c, e), yet it was rather rarely encountered in other parts of the paintings. For this reason, samples from the green grounds of the nave, narthex, and exonarthex were comparatively studied, along with a pertinent sample from the narthex hyperthyron Dormition portrayal (Fin14). Interestingly, analytical data revealed no presence of a green pigment in the nave sample, as for rendering the greenish ground a mixture of carbon black plus yellow ochre has been used (Fig. 3b). On the contrary, both the narthex and exonarthex samples exhibit a rather similar structure: on an olive-green substrate (carbon black + yellow ochre), a layer containing lime and green grains has been applied (Fig. 3b). The latter exhibit the compositional trends of green earths (enhanced Si–Fe contents, elevated Mg, Al and K, see Grissom 1986; Deer et al. 1992; Hradil et al. 2003) (Table 2), and the relevant fibrous microstructure (Fig. 3b) (Buckley et al. 1978; Moretto et al. 2011); the subtle compositional differentiations among the narthex and exonarthex pigments (e.g., minor copper admixtures in the latter) may indicate that materials of different origins have been employed.

Celadonite and glauconite are the most widely used (in painting context) members of the mica group, yet distinction between these two species is not a trivial task. Nonetheless, several scholars have exploited elemental-composition variations towards this goal. On this basis, both the Filanthropinon narthex and exonarthex green earths seem to be of glauconitic origin, as they are characterized by $Si/Al < 10$ and $Mg/Al < 1$, while in addition, the silicon, aluminum, and magnesium concentrations show the common glauconite trend ($Si > Al > Mg$) (Ospitali et al. 2008; Moretto et al. 2011; Perez-Rodriguez et al. 2015). On the other hand, implementation of micro-Raman analysis posed serious difficulties as the analyzed green grains are very finely dispersed into a calcitic matrix: besides, it is well known that when green earths are mixed with other pigments such as San Giovanni white, they may be hardly detectable (Bersani et al. 2005). Nonetheless, the authors were able to collect spectra that indeed exhibit the characteristic Raman shifts of glauconite, namely those at $\sim$264, 458, 548, 595, and 700 cm^{-1} (Fig. 7a) (Ospitali et al. 2008; Moretto et al. 2011; Wang et al. 2015).

The employment of glauconite is of some significance when it comes to considering green earths identified in other Byzantine/post-Byzantine monuments, as in the majority of the pertinent published works, green earths are identified as celadonite (Daniilia et al. 2000, 2008a; Pavlidou et al. 2006; Zorba et al. 2006; Sotiropoulou et al. 2008; Sakellariou et al. 2010; Pelosi et al. 2013; Cheilakou et al. 2014; Kakoulli et al. 2014; Holclajtner-Antunović et al. 2016); on the contrary, glauconite was recently identified in the fourteenth century Ruthenian-Byzantine mural paintings in the Wawel Cathedral (Krakow, Poland) (Rafalska-Lasocha et al. 2010). Another interesting feature of the Filanthropinon samples is the fact that green earths were always laid on top of an intermediate olive-green substrate that consists of charcoal plus yellow ochre (Fig. 3b, c), yet this deserves further discussion (see Part II).

On the other hand, green-ground sample Fin14 is more complicated as it is composed of three distinct layers: on an

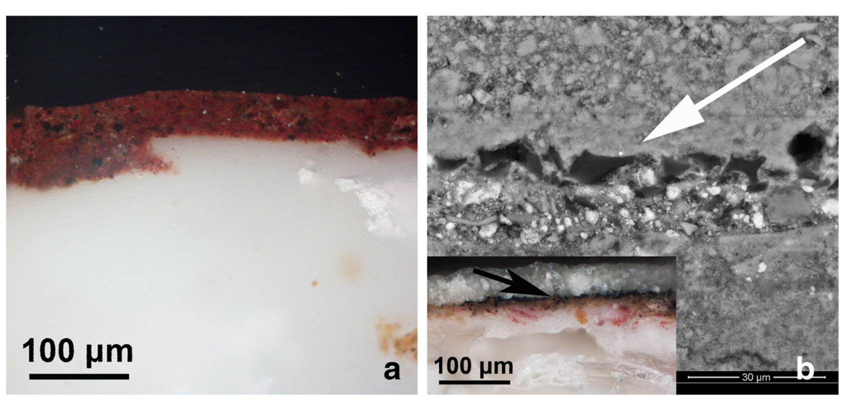

Fig. 4 **a** Dark red/brown ground, sample Fen3; paint layer consists of deep red ochre plus C-black. OM × 200 **b** Background: C-black wash (arrow) covering a red + yellow ochre substrate (bright grains); the uppermost layer is a white highlight. BSE, × 3000. Inserted image: same sample, OM, × 200; arrow indicates C-black wash

olive-green substrate (black + ochre) lays a green earth layer, which has been covered by grains of a rather coarse pigment (Fig. 3c). The latter are only partially preserved, and their extensive loss is most probably related to the fact that they were applied by a secco painting technique (for pertinent details see Part II). Under high magnification, these very grains exhibit conchoidal-fracture features, while EDX analysis revealed that their major component is copper; these characteristics indicate employment of malachite (Gettens and Fitzhugh 1993b), an assumption verified through micro-Raman analysis (Bell et al. 1997; Bouchard and Smith 2003) (Fig. 7b). Besides, the microstructure of grinded malachite allows for its distinction from artificial copper pigments, as the grains of the latter are mostly spherulite-like (Naumova et al. 1990; Scott 2002). Moreover, the detection of various admixtures such as Ca–Mg (probably dolomite-related, spotted as scarce grains and inherent inclusions on individual grains, Fig. 3c), azurite, and hematite grains, further highlights the natural origin of the Filanthropinon pigment, as the aforementioned are rather common malachite impurities (Palache et al. 1951; Daniilia et al. 2008b). In addition, EDX data indicate the presence of significant zinc and arsenic levels in the Filanthropinon malachite grains (Table 2), which are probably related to admixtures of olivenite [$Cu_2(AsO_4)(OH)$] and adamite, [$Zn_2(AsO_4)(OH)$], two minerals commonly associated with natural azurite and malachite (Švarcová et al. 2009). However, the presence of scarce azurite grains (Figs. 3c and 7c) may lead someone to suppose that the nowadays observed malachite is a degradation product of—presumably originally applied—azurite. Yet, this hypothesis may be readily objected as (a) the pictorial element in consideration (: ground depiction) is rendered with green in all three Filanthropinon painting phases, and (b) the presence of two successive greenish underpainting layers indicate that the craftsman intended a green hue.

Blue

Following the common Byzantine/post-Byzantine tradition, in all the studied painting phases, the extended background/campus areas have been rendered by a rather dark blue hue (Fig. 1). In case of the south exonarthex sample Fes2 (Byzantine phase), OM, SEM-EDX, and micro-Raman inspection revealed nothing but charcoal particles embedded into the surface plaster. On the contrary, in the samples from the nave, narthex and north exonarthex, among the abundant carbon-black particles, few non-charcoal grains appear too. EDX analyses revealed that the major component of the latter grains is silicon (Si > 50%), while they also contain moderate calcium (~ 17%), sodium (~ 10%), and potassium (~ 5%), and various other minor elements including manganese (~ 1.5%), aluminum (under 1.5%), and cobalt (~ 0.3%, Table 2, Fig. 3d). This elemental profile along with the characteristic glassy microstructure of the pertinent grains (Fig. 3d) allow for their identification as smalt, an artificial glassy pigment (Mühlethaler and Thissen 1993).

Yet, one may note a few peculiar characteristics of the Filanthropinon smalt composition, namely the enhanced presence of sodium (rather than potassium), the low cobalt content, and the elevated manganese (Table 2, Fig. 3d). Although rarely, sodium-containing smalt is indeed reported in the literature (Spring et al. 2005), while smalt grains with low cobalt content (< 1%) are occasionally reported too (Robinet et al. 2013; Janssens et al. 2016). Besides, it is well known that even a small cobalt addition (< 1%) is sufficient to color intense blue a silicate glass (Colomban 2013), yet the higher the cobalt load, the smaller the particles that preserve the intense blue color. As for manganese, we note that when oxidized, it imparts a purple color in glass, and thus its addition in iron-containing glasses may result in a counterbalance of the yellow-brown color induced by Fe(III) ions (Gratuze et al. 1996). In this perspective, the detection of elevated iron in the Filanthropinon smalt grains favors the hypothesis that manganese was intentionally added in order to compensate for iron. At this point, it is noted that smalt has been occasionally detected in other Byzantine (Gettens and Stout 1958) and post-Byzantine mural paintings as well (Daniilia et al. 2008b; Daniilia and Minopoulou 2009). Nonetheless, in these instances, smalt was found on top of a carbon black layer (not intermixed with it) and its composition proved to be similar to that of "common" smalt (potassium-rich, elevated cobalt etc.). Hence, the Filanthropinon smalt may be regarded as an unusual one, both in terms of composition and the method employed for its application (: mixing with C-black).

Despite the verified smalt presence in the carbon-black layer, the Filanthropinon backgrounds appear dark bluish/black (Fig. 1); this could be well explained by the limited smalt addition or/and by the smalt discoloration, a phenomenon commonly treated in the pertinent literature (Spring et al. 2005; Daniilia and Minopoulou 2009; Robinet et al. 2013). Nonetheless, the existence of blue patches on the vaults and on other high, currently inaccessible parts of the nave paintings implies that another blue pigment may had originally existed on top of the pre-discussed dark layers. Besides, the application[3] of blue pigments on top of carbon-black substrates was a common practice in Byzantine and later painting, and scholars have often noted the rather extended loss of these surface blue pigments (Gettens and Stout 1958; Winfield 1968; Pavlidou et al. 2006; Zorba et al. 2006; Daniilia et al. 2008a, b; Sotiropoulou et al. 2008; Holclajtner-Antunović et al. 2016; Marič-Stojanovič et al. 2018). Bearing in mind the latter piece of information, the surfaces of several Filanthropinon campus samples were thoroughly examined in order to reveal possible

[3] For details on application technique and the related terms, "fresco"/"secco" reader is addressed to Part II

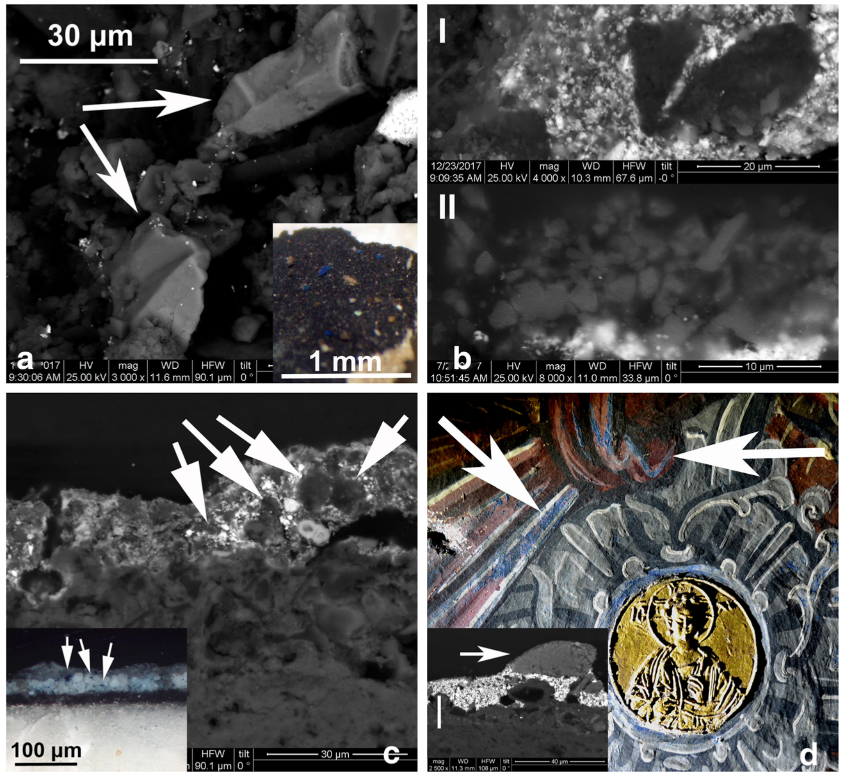

Fig. 5 **a** Background: azurite grains on campus (Fm9a, BSE, × 3000); inserted: same sample, stereoscopic view (× 40). **b** I: Remnants of surface overpainting (Prussian blue+Pb-white), Fm9b, × 4000; II: grains of artificial ultramarine, overpainting (Fm14, BSE, × 8000). **c** Indigo-type grains (arrows) among Pb-white, overpainting covering carbon-black + smalt substrate. Background: BSE, × 3000. Inserted: OM, × 200. **d** Overpainting remnants on St Nikitas garment, nave. The gilded relief medal is also pictured (raking light). Inserted figure: remnants of azurite (arrow) + Pb-white overpainting that covers St Nikitas vestment (perpendicular line: original deep red paint layer) (Fm7, BSE, × 2500)

blue-pigment remnants. The intensive study of the pertinent material revealed the existence of original blue paint layer remnants only in case of a nave sample (Fm9a), while various latter overpainting remnants were documented on nave and narthex samples (Fm7, Fm9b, Fm14 and Fin1b respectively, for details see next); on the contrary, no coloring substance beyond intermixed charcoal and smalt was detected in case of the north exonarthex samples.

In detail, upon the meticulous stereoscopic inspection of the sample Fm9a surface, a few grains of intense blue color were spotted, which proved to be coarse-grinded natural azurite (Fig. 5a; Table 2). Presumably, azurite was originally applied on top of the "black plus smalt" substrate in order to achieve an intense blue color, yet it was subsequently gradually lost leaving only scarce grains. This might very well be the case in inner narthex and exonarthex wall paintings as well, although in the relevant samples, no azurite remnants have been traced up today; the several restoration and "cleaning" interventions which took place during past centuries have probably contributed to this loss.[4]

On the contrary, surface examination of sample Fm9b revealed the presence of a few white patches with occasional blue grains. EDX and micro-Raman analysis revealed that the white pigment is lead white (detection of Pb and major lead carbonate Raman shift at ~ 1050 cm^{-1} respectively, see, e.g., Bell et al. 1997; Burgio and Clark 2001) (Fig. 7d). As it has been already demonstrated (see the "Black and white" section and references therein), in the framework of Byzantine and post-Byzantine mural painting, the only white pigment to be employed was calcium carbonate; hence, superficial lead white layers shall be obviously assigned to a later overpainting/"reparing" intervention. The blue grains that exist in the lead white layer are of a rather homogeneous microstructure (Fig. 5b(I)), and they were found to contain no sulfur, a low level of copper (< 2%), and a moderate level of iron, thus suggesting the employment of Prussian blue, the artificial iron-based pigment that was first manufactured in the early eighteenth century and became a popular solemn-blue pigment within two or three decades (Kirby 1993; Berrie 1997; Kirby and Saunders 2004). It is worth noting that Prussian blue has been recently identified as a restoration material in other Byzantine paintings (Holclajtner-Antunović et al. 2016).

Remnants of yet another blue overpainting were documented on the background ("campus") sample Fm14: on a thin lead white layer, several extremely small, bright blue grains are laid (Fig. 5b(II)). EDX analyses revealed notably high sulfur and sodium contents yet no copper, while the corresponding Raman spectrum shows the characteristic lazurite shifts at 262, 547, 809, and 1092 cm^{-1} (Clark and Franks 1975; Plesters 1993; Bell et al. 1997; Burgio and Clark 2001) (Fig. 7e). Natural lazurite grains exhibit conchoidal fracture

[4] It is indicative to note that during the twentieth century, two conservation interventions took place, namely on 1964 and 1973–1974, while authors traced evidence of at least three other, significantly earlier interventions (see next).

characteristics and are always accompanied by various impurities (Plesters 1993; Holclajtner-Antunović et al. 2016). Nevertheless, both latter features are absent in the case of the Fm14 sample grains, which also belong to the 1–3 μm size range and, overall, the findings are compatible with low-cost synthetic lazurite (/artificial ultramarine).

Similarly, in the case of the background sample Fin1 (narthex), the original black + smalt paint layer is partially covered by a rather thick overpainting that consists of coarse lead-white and a few blue grains which are rather uniform in shape (Fig. 5c). EDX analysis revealed absence of the elements Cu, Fe, S, and Co from the latter grains, implying thus employment of an indigo-type pigment, an assumption that was subsequently verified through micro-Raman analysis (Fig. 7f). It is worth noting that indigo was one of the most widely used pigments in Byzantine and post-Byzantine panel painting (Mastrotheodoros 2016), yet it has been only rarely found in pertinent murals (Gettens and Stout 1958).

Of special interest is sample Fm7, which was collected from St Nikitas deep red/purplish vestment (nave south wall, Table 1). Macroscopic and OM observations revealed the presence of bluish overpainting remnants, and further analyses verified the existence of a thick lead white + azurite layer that covers the original lime-highlighted deep red garment (Fig. 5d). These azurite grains differ slightly from the ones that originally covered the nave background (sample Fm9a) in terms of composition,[5] indicating thus employment of two different pigments. One may note that the covering of St Nikitas deep red vestment with a blue overpainting seems meaningless, and such an intervention may only be interpreted in the framework of a “restoration” executed in a rather distant period of the past, when the perception of restoration and the esthetic criteria differed significantly from the modern ones. Yet, one clue for the date of this overpainting is offered by its very constituents: in European painting, the use of natural azurite is known to drastically decrease from seventeenth century onwards and practically ceased during eighteenth century (Gettens and Fitzhugh 1993a; Kirby 1993), and this trend was recently verified in case of Greek portable icons too (Mastrotheodoros 2016). Hence, mid-eighteenth century must be regarded a “terminus ante quem” for the aforementioned overpainting intervention.

Thanks to the several blue overpainting remnants, one may draw a rough sketch of the post-manufacture interventions in case of the Filanthropinon wall paintings. In detail, azurite (sample Fm7) was probably used in an intervention executed before mid-eighteenth century, while Prussian blue (Fm9b) and artificial ultramarine (Fm14) allow for the determination of two “terminus post quem,” namely ca. 1710 and 1830 respectively. On the other hand, the employment of the “indigo-type” pigment in sample Fin1 does not allow for any particular chronological assumption, as indigo was a pigment widely used from antiquity up until recently. However, such an intensive overpainting activity indicates that the people who were practicing their spiritual duties in Filanthropinon church were concerned about retaining the vivid appearance of the wall paintings, as the latter were obviously regarded an indispensable part of their everyday ritual life.

Further considerations

When it comes to comparison between the various Filanthropinon painting phases, one may proceed on several interesting observations. First of all, in all three painting phases, the Filanthropinon dark campuses/backgrounds bear an unusual, in terms of composition, blue smalt intermixed in the lime + charcoal layer. This has served as a substrate for blue pigments (that are largely lost) and to the authors’ best knowledge has not been documented in any other relevant monument up today[6]; hence, it may be regarded as an idiomorphic characteristic of these very paintings. The employment of this mixture in all three Filantropinon painting phases obviously suggests a characteristic of certain painters who shared common materials (and technical) background. On the other hand, a few characteristic points of differentiation were revealed. Indicative is the case of the red bordering lines (which are a constituent element of byzantine wall painting, see Fig. 1): nave lines have been rendered by red ochre, while narthex and exonarthex borders bear cinnabar (Fig. 3c). Moreover, the unusual double-phase red ochre grains and green earths were detected in samples from both the narthex and exonarthex (Fig. 3f) yet not in nave, while the latter paintings are the only to bear the low-iron, clayey red ochres (type “iii”/Table 2). Further on, green grounds have been rendered by two successive paint layers (green earth on olive-green substrate) in narthex and exonarthex, while the same pictorial element has been painted by using a single, olive-green paint layer[7] in the nave (Fig. 4b).

The revealed variations and similarities of the three Filanthropinon phases contribute substantially to the assessment

[5] Fm7 sample azurite grains (overpainting) contain minor Zn admixtures (probably related to adamite, see the “Green” section and Švarcová et al. 2009), an element not detected in Fm9a sample azurite (original).

[6] Neither on the “bluish” background sample which was collected from the Filanthropinon south exonarthex lintel semi-destroyed depiction (sample Fes1, Fig. 1d). This clue, along with the fact that the corresponding plasters differ from those of the three main painting phases (see Part II), strengthens archeologists’ view according to which this very painting is of an earlier date (possibly Byzantine).

[7] In few samples, the remnants of—largely lost—superficial pigment layers were detected (including malachite/sample Fin14), and it is not impossible that the nave olive green ground was originally covered by malachite which is not preserved today.

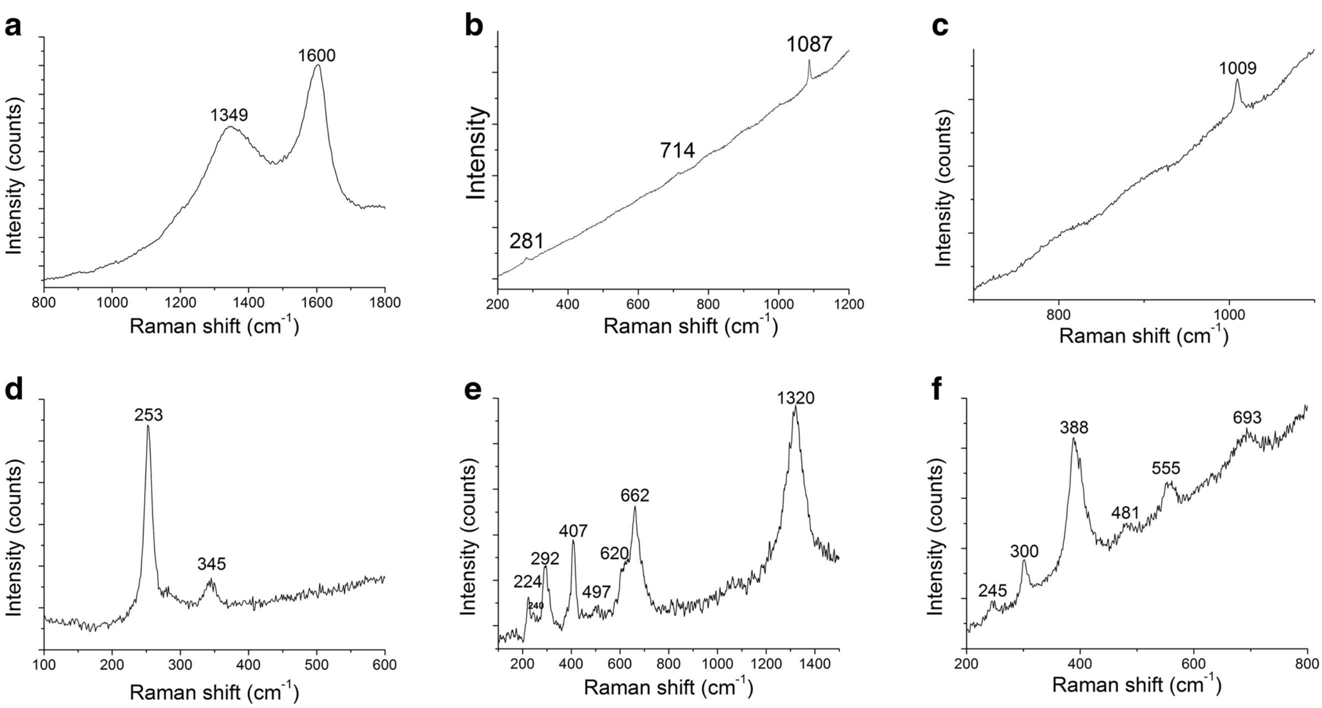

Fig. 6 Indicative micro-Raman spectra of various Filanthropinon pigments. **a** Black/plant charcoal, sample Fin1. **b** Calcite/"San Giovanni" white, sample Fm11. **c** Gypsum accumulation, sample Fin8. **d** Cinnabar/HgS, sample Fin2 **e** Red ochre (hematite), sample Fen 6. **f** Yellow ochre (limonite), sample Fen5

of artistic identities, as there are no inscriptions/archival records to testify the names of the employed painters. However, on the basis of stylistic and iconographic features, archeologists have hypothesized that the nave painter worked alone (in 1531/2) and did not take part in the painting of the other two phases (Acheimastou-Potamianou 1995, 1999; Deligianni-Dori 1999). The latter hypothesis is strongly supported by microscopic findings presented herein, as the samples from the nave paintings

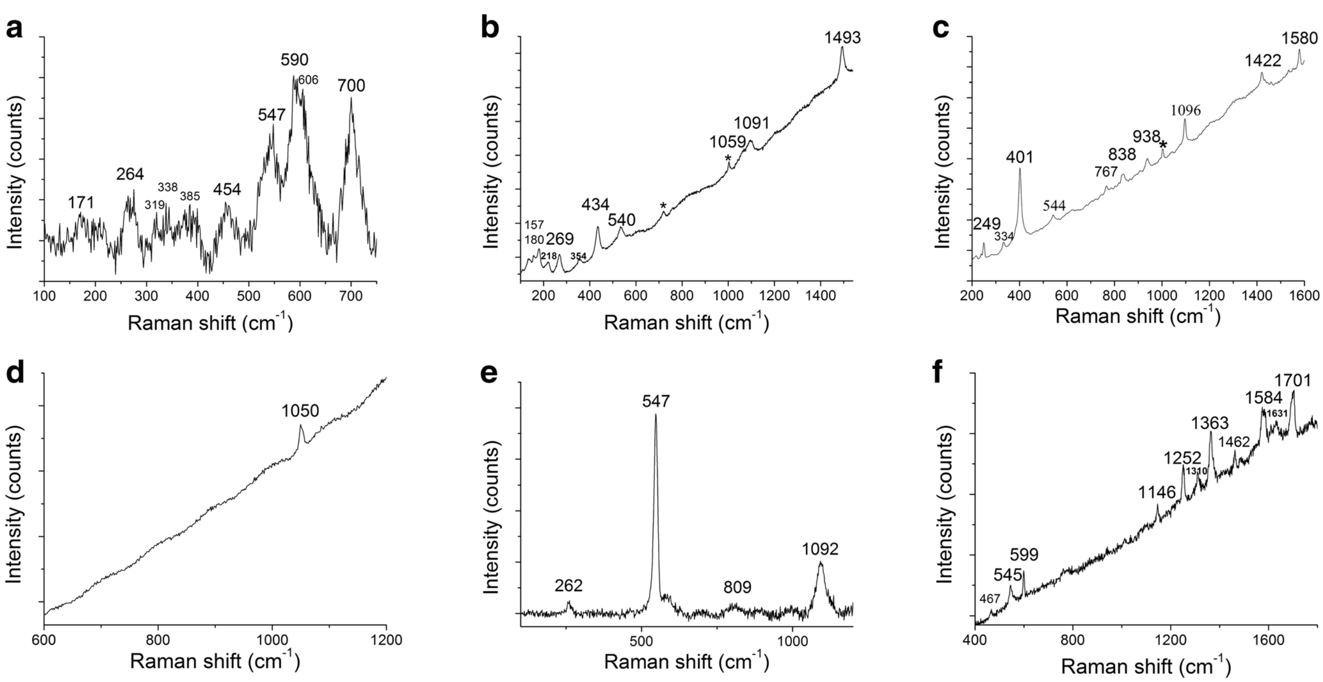

Fig. 7 Selected micro-Raman spectra. **a** Glauconite, sample Fin3. **b** Malachite, sample Fin14; asterisks mark gypsum peaks (decay product). **c** Azurite, sample Fin14; asterisk marks gypsum shift. **d** Lead white, sample Fm11. **e** Artificial ultramarine (lazurite), sample Fm14. **f** Indigo, sample Fin1

exhibit idiomorphic characteristics, absent in the narthex and exonarthex samples (e.g., the rendering of bordering lines with red ochre—rather than cinnabar—and the use of the low iron clayey ochre).

On the other hand, narthex and exonarthex paintings exhibit notable similarities, the most characteristic of which are the employment of a very peculiar (in terms of microstructure) red iron ochre and the use of a glauconitic green earth. Of special interest is also the rendering of green grounds by applying two successive paint layers. Archeologists have argued that the legendary painter Frangos Katelanos had presumably worked in the narthex (1542) with the assistance of Georgios and Frangos Kontaris (who were reportedly his pupils), while the exonarthex paintings (1560) are ascribed to the Kontaris brothers alone (Acheimastou-Potamianou 1995, 1999; Deligianni-Dori 1999). Indeed, the highlighted similarities among the two painting phases are strong enough to indicate the employment of a single workshop. Besides, work in progress on samples from two churches that bear Kontaris inscriptions ("St Nikolaos" in Krapsi village and "Transfiguration" in Klimatia, Epirus) has revealed very similar (in terms of stratigraphy) green grounds (for a preliminary relevant discussion, see Mastrotheodoros et al. 2018). Hence, it seems probable that the Kontaris brothers had indeed taken part in the decoration of both the Filanthropinon narthex and exonarthex decoration.

Finally, the unusual employment of "charcoal plus minor smalt" substrate on the dark backgrounds of all three Filanthropinon phases deserves a further comment. As it has been already stated, this very mixture has not, up today, been documented elsewhere. However, ongoing study on other Kontaris inscribed churches revealed the presence of the same paint layer on the campus samples of at least one pertinent church (Mastrotheodoros G.P., unpublished data), and this finding strengthens the hypothesis that an idiomorphic characteristic of the Epirus/NW Greece school has been detected. In this view, it may be assumed that this innovation first appeared in the Filanthropinon nave painting (1531/2) and from there was disseminated—probably through apprenticeship—in the Filanthropinon narthex and exonarthex paintings as well as in other monuments that were subsequently painted in the framework of the Epirus school of iconography.

Conclusions

Through the in-depth OM, SEM-EDX and micro-Raman investigation of Filanthropinon wall paintings samples, the pigments employed by the artists were revealed. A rather limited palette has been employed: plant-derived charcoal was the only black pigment, while for the whites, lime and a "bianco San Giovanni"-type pigment were employed; the latter is for the first time documented in Greek murals. Reds have been rendered by various natural iron ochres and cinnabar, and yellows by limonitic ochre, while dark browns lack. Green earths (glauconite) and malachite, along with a very peculiar smalt and azurite have been also identified in original paint layers. The identification of different grain-size fractions of given pigments along with the existence of extremely thin-grained pigments (< 3 μm) imply employment of sophisticated grinding and segregation methods. Moreover, in a few instances, analytical data revealed the employment of an idiomorphic red iron ochre which was collected from an unidentified, possibly local, source. Dark campuses were found rendered with a remarkable mixture of charcoal and smalt; analytical data suggest that this dark layer was originally covered by blue pigment(s). As this very mixture has not been documented elsewhere, it is assumed that it might have been invented by the Filanthropinon nave painter and passed through apprenticeship to subsequent craftsmen (including the two Kontaris brothers). Hence, a potentially important part of a microscopic fingerprint of the Epirus/NW Greece school of painting emerges.

On the other hand, the existence of several differences has emerged upon examining samples from the three Filanthropinon painting phases, which turned to be an extremely valuable tool for the assessment of artistic identities. In detail, on the basis of analytical data, it is evident that the first Filanthropinon painting phase (the lower part of the nave/1531–2) was decorated by a painter of individual character, while the narthex (1542) and the exonarthexes (1560) were painted by craftsmen of a single workshop. The archeological hypothesis that the two Kontaris brothers contributed to both the 1542 and the 1560 phases has been very much strengthened. On the other hand, the fact that the idiomorphic "charcoal plus smalt" substrate was employed in all three Filanthropinon phases (1531–1532, 1542, 1560) indicates that at least one of the narthex painters had taken part—presumably as a pupil—in the earlier decoration of the nave. Although the identification of this person with the legendary Frangos Katelanos is tempting, current analytical data offer no pertinent clue.

Finally, artificial lazurite/ultramarina, Prussian blue, indigo, and azurite (yet different from the azurite of the original paintings) have been identified in remnants of latter "renovation" interventions; on the basis of the employed pigments, it seems that the latter have been repeated several times, with the earliest taking place most probably shortly after the end of seventeenth century.

Acknowledgments The personnel of the Ioannina Ephorate of Antiquities and especially the archeologists P. Dimitrakopoulou, E. Katerini, and D. Rapti, along with the conservation personnel are sincerely thanked for their support. Special thanks are due to the General Directorate for the Restoration, Museums and Technical Works and the Directorate for Byzantine and Post-Byzantine Antiquities (both divisions of the Greek Ministry of Culture and Sports) for sampling permissions. Dr. G. Mitrikas (INN, NCSR 'Demokritos') is sincerely thanked for providing access to a micro-Raman facility, while Dr. S. Chaitoglou (INN, NCSR 'Demokritos') is acknowledged for his help during micro-Raman analyses.

Funding information This research has been integrated through an Greek State Scholarships Foundation (IKY) scholarship program and co-financed by the European Union (European Social Fund-ESF) and Greek national funds through the action entitled "Reinforcement of Postdoctoral Researchers," in the framework of the Operational Program "Human Resources Development Program, Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) 2014-2020 (grant number: 2016-050-0503-7689).

References

Acheimastou-Potamianou M (1994) Greek art: byzantine wall paintings. Ekdotike Athenon, Athens

Acheimastou-Potamianou M (1995) The Filanthropinon monastery and the first phase of the post-byzantine painting (in Greek), second edition, Archaeologicon Deltion 31. Fund of Archaeological Proceeds, Athens

Acheimastou-Potamianou M (1999) Wall paintings of the Filanthropinon monastery (in Greek). In: Garidis M, Paliouras A (eds) Monasteries of the Ioannina islet. 700 years 1292–1992, Ioannina, pp 17–36

Behlis P, Photos-Jones E (1999) Laboratory analyses of pigments from post Byzantine wall paintings: the monasteries of the island of Ioannina (in Greek). In: Garidis M, Paliouras A (eds) Monasteries of the Ioannina islet. 700 years 1292–1992, Ioannina, pp 597–612

Bell IM, Clark RJH, Gibbs PJ (1997) Raman spectroscopic library of natural and synthetic pigments (pre- ~ 1850 AD). Spectrochim Acta A 53:2159–2179

Berrie BH (1997) Prussian blue. In: FitzHugh EW (ed) Artist's pigments: a handbook of their history and characteristics, vol 3. National Gallery of Art, Washington, pp 191–217

Bersani D, Lottici PP, Casoli A (2005) Case study: micro-Raman and GC-MS of frescoes. In Edwards HGM, Chalmers JM (eds) Raman Spectroscopy in Archaeology and Art History, Royal Society of Chemistry, Cambridge, pp 130–141

Bianchin S, Casellato U, Favaro M, Vigato PA, Colombini MP, Gautier G (2008) Physico-chemical and analytical studies of the mural paintings at Kariye Museum of Istanbul. J Cult Herit 9:179–183.

Bikiaris D, Sist D, Sotiropoulou S, Katsimbiri O, Pavlidou E, Moutsatsou AP, Chryssoulakis Y (1999) Ochre-differentiation through micro-Raman and micro-FTIR spectroscopies: application on wall paintings at Meteora and Mount Athos, Greece. Spectrochim Acta A 56:3–18

Bouchard M, Smith DC (2003) Catalogue of 45 reference Raman spectra of minerals concerning research in art history or archaeology, especially on corroded metals and coloured glass. Spectrochim Acta A 59:2247–2266

Broecke L (2015) Cennino Cennini's Il libro dell'arte. Archetype publications, London

Buckley HA, Bevan JC, Brown KM, Johnson LR, Farmer VC (1978) Glauconite and celadonite: two separate mineral species. Mineral Mag 42:373–382

Burgio L, Clark RJH (2001) 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 A 57:1491–1521

Chatzidakis M (1987) Greek painters after the fall of Constantinople (1450–1830), (in Greek), vol 1. Institute of Historical Research/ National Hellenic Research Foundation, Athens

Cheilakou E, Troullinos M, Koui M (2014) Identification of pigments on Byzantine wall paintings from Crete (14^{th} century AD) using non-invasive fiber optics diffuse reflectance spectroscopy (FORS). J Archaeol Sci 41:541–555

Civici N, Anastasiou M, Zorba T, Paraskevopoulos KM, Dilo T, Stamati F, Arapi M (2008) Studying wall paintings in Berati castel (Albania): comparative examination of materials and techniques in XIVth and XVIth century churches. J Cult Herit 9:207–213

Clark RJH, Franks ML (1975) The resonance Raman spectrum of ultramarine blue. Chem Phys Lett 34(1):69–72

Coccato A, Jehlicka J, Moensc L, Vandenabeele P (2015) Raman spectroscopy for the investigation of carbon-based black pigments. J Raman Spectrosc 46:1003–1015

Colomban PH (2013) The destructive/non-destructive identification of enameled pottery, glass artifacts and associated pigments-a brief overview. Arts 2:77–110

Daniilia S, Minopoulou E (2009) A study of smalt and red lead discolouration in Antiphonitis wall paintings in Cyprus. Appl Phys A Mater Sci Process 96:701–711

Daniilia S, Sotiropoulou S, Bikiaris D, Salpistis C, Karagiannis G, Chryssoulakis Y, Price BA, Carlson JH (2000) Panselinos' Byzantine wall paintings in the Protaton church, Mount Athos, Greece: a technical examination. J Cult Herit 1:91–110

Daniilia S, Bikiaris D, Burgio L, Gavala P, Clark RJH, Chryssoulakis Y (2002) An extensive non-destructive and micro-spectroscopic study of two post-Byzantine overpainted icons of the 16^{th} century. J Raman Spectrosc 33:807–814

Daniilia S, Tsakalof A, Bairachtari K, Chryssoulakis Y (2007) The Byzantine wall paintings from the Protaton church on Mount Athos, Greece: tradition and science. J Archaeol Sci 34:1971–1984

Daniilia S, Minopoulou E, Demosthenous D, Karagiannis G (2008a) A comparative study of wall paintings at the Cypriot monastery of Christ Antiphonitis: one artist or two? J Archaeol Sci 35:1695–1707

Daniilia S, Minopoulou E, Andrikopoulos KS, Tsakalof A, Bairachtari K (2008b) From Byzantine to post-Byzantine art: the painting technique of St Stephen's wall paintings at Meteora, Greece. J Archaeol Sci 35:2474–2485

Deer WA, Howie RA, Zussman J (1992) An introduction to the rock-forming minerals, 2nd edn. Longman, England

Deligianni-Dori E (1999) On the Kontaris workshop. Contribution in the search on the apprenticeship in wall painting and the establishment of painters' workshops (in Greek). In: Garidis M, Paliouras A (eds) Monasteries of the Ioannina islet. 700 years 1292–1992, Ioannina, pp 103–150

Dionysius of Fourna (1996) The 'Painter's Manual' of Dionysius of Fourna, translated in English by P. Hetherington. Oakwood Publications, California

Dionysius of Fourna (1997) The interpretation of the art of painting (in Greek), edited and published by a. Papadopoulos-Kerameus, Petersburg, 1909, reprinted in Athens by K. Spanos

Eastaugh N, Walsh V, Chaplin T, Siddall R (2008) Pigment Compendium. Butterworth-Heinemann, Oxford

Ganitis V, Pavlidou E, Zorba F, Paraskevopoulos KM, Bikiaris D (2004) A post-Byzantine icon of St Nicholas painted on a leather support. Microanalysis and characterization of technique. J Cult Herit 5:349–360

Georgitsoyanni EN (1999) Les rapports des peintures murales des monastères des Philanthropinon et Diliou avec "L'atelier de Kastoria" de la fin du XVe s., (in Greek with French abstract). In: Garidis M, Paliouras A (eds) Monasteries of the Ioannina islet. 700 years 1292–1992, Ioannina, pp 85–101

Gettens RJ, Fitzhugh EW (1993a) Azurite and blue verditer. In: Roy A (ed) Artist's Pigments: A handbook of their history and characteristics, vol 2. National Gallery of Art, Washington, pp 23–35

Gettens RJ, Fitzhugh EW (1993b) Malachite and green verditer. In: Roy A (ed) Artist's pigments: a handbook of their history and characteristics, vol 2. Oxford University Press, New York, pp 183–201

Gettens RJ, Stout GL (1958) A monument of Byzantine wall painting: the method of construction. Stud Conserv 3(3):107–119
Gettens RJ, Feller RL, Chase WT (1993) Vermilion and cinnabar. In: Roy A (ed) Artist's pigments: a handbook of their history and characteristics, vol 2. National Gallery of Art, Washington, pp 159–182
Goodhew PJ, Humphreys FJ (1988) Electron microscopy and analysis, 2nd edn. Taylor & rancis, London
Gratuze B, Soulier I, Blet M, Valauri L (1996) De l'origine du cobalt : du verre à la céramique. Rev Archéométrie 20:77–94
Hein A, Karatasios I, Mourelatos D (2009) Byzantine wall paintings from Mani (Greece): microanalytical investigation of pigments and plasters. Anal Bioanal Chem 395:2061–2071
Grissom CA (1986) Green earth. In: Feller RL (ed) Artist's pigments: a handbook of their history and characteristics. Cambridge University Press, National Gallery of Art, pp 141–167
Heinrich KFJ (1991) Strategies of electron probe data reduction. In: Heinrich KFJ, Newbury DE (eds) Electron probe quantitation. Plenum Press, New York, pp 9–18
Helwig K (2007) Iron Oxide Pigments. In Berrie BH (ed) Artist's Pigments: A handbook of their history and characteristics', vol 4. National Gallery of Art, Washington and Archetype publications London, 1–37
Holclajtner-Antunović I, Stojanović-Marić M, Bajuk-Bogdanović D, Žikić R, Usković-Marković S (2016) Multi-analytical study of techniques and palettes of wall paintings of the monastery of Žiča, Serbia. Spectrochim Acta A 156:78–88
Hradil D, Grygar T, Hradilová J, Bezdička P (2003) Clay and iron oxide pigments in the history of painting. Appl Clay Sci 22:223–236
Iordanidis A, Garcia-Guinea J, Strati A, Gkimourtzina A (2014) A comparative study of pigments from the wall paintings of two Greek byzantine churches. Anal Lett 47:2708–2721
Janssens K, Van Der Snickt G, Alfeld M, Noble P, van Loon A, Delaney J, Conover D, Zeibel J, Dik J (2016) Rembrant's 'Saul and David' (c. 1652): use of multiple types of smalt evidenced by means of non-destructive imaging. Microchem J 126:515–523
Kakoulli I, Prikhodko SV, King A, Fischer C (2014) Earliest evidence for asbestos composites linked to byzantine wall paintings production. J Archaeol Sci 44:148–153
Katsibiri O, Howe RF (2010) Microscopic, mass spectrometric and spectroscopic characterization of the mordants used for gilding on wall paintings from three post-byzantine monasteries in Thessalia, Greece. Microchem J 94:83–89
Kirby J (1993) Fading and colour change of Prussian blue: occurrences and early reports. Natl Gallery Tech Bull 14:63–71
Kirby J, Saunders D (2004) Fading and colour change of prussian blue: methods of manufacture and the influence of extenders. Natl Gallery Tech Bull 25:73–99
Koilakou C (2001) Identification of wall-paintings by the workshop of the Theban painters Georgios and Frangos Kontaris, in the area of their birthplace (in Greek). Delt Christ Archaeol Soc 22:191–208
Lampakis D, Karapanagiotis I, Katsibiri O (2017) Spectroscopic investigation leading to the documentation of three post-byzantine wall paintings. Appl Spectrosc 7(1):129–140
Marič-Stojanovič M, Bajuk-Bogdanovič D, Uskokovič-Markovič S, Holclajtner-Antunovič I (2018) Spectroscopic analysis of XIV century wall paintings from patriarchate of Peć monastery, Serbia. Spectrochim Acta A 191:469–477
Mastrotheodoros GP (2016) Pigments and various materials of post-Byzantine painting (in Greek), PhD Thesis, Department of Materials Science and Engineering, University of Ioannina, Ioannina
Mastrotheodoros G, Beltsios KG, Zacharias N (2010) Assessment of the production of antiquity pigments through experimental treatment of ochres and other iron based precursors. Mediterr Archaeol Archaeom 10(1):37–59
Mastrotheodoros GP, Filippaki E, Bassiakos Y, Beltsios KG (2018) Post-byzantine monumental pictorial art: painting materials and techniques in the church of the Transfiguration of our Savior in Klimatia (Epirus, NW Greece). In: Zezza F, Koui M (eds) 10th International Symposium on the Conservation of Monuments in the Mediterranean Basin, Springer. https://doi.org/10.1007/978-3-319-78093-1_47 (in press)
Moretto LM, Orsega EF, Mazzocchin GA (2011) Spectroscopic methods for the analysis of celadonite and glauconite in Roman green wall paintings. J Cult Herit 12:384–391
Mühlethaler B, Thissen J (1993) Smalt. In: Roy A (ed) Artist's pigments: a handbook of their history and characteristics, vol 2. Oxford University Press, New York, pp 113–130
Naumova MM, Pisareva SA, Nechiporenko GO (1990) Green copper pigments of old Russian frescoes. Stud Conserv 35:81–88
Ospitali F, Bersani D, Di Lonardo G, Lottici PP (2008) 'Green earths': vibrational and elemental characterization of glauconites, celadonites and historical pigments. J Raman Spectrosc 39:1066–1073
Palache C, Berman H, Frondel C (1951) The system of mineralogy, vol 2, 7th edn. John Wiley & Sons, New York
Pavlidou E, Arapi M, Zorba T, Anastasiou M, Civici N, Stamati F, Paraskevopoulos KM (2006) Onoufrios, the famous XVI's century iconographer, creator of the "Berati school": studying the technique and materials used in wall paintings of inscribed churches. Appl Phys A Mater Sci Process 83:709–717
Pelosi C, Agresti G, Andaloro M, Baraldi P, Pogliani P, Santamaria U (2013) The rock hewn wall paintings in Cappadocia (Turkey): characterization of the constituent materials and a chronological overview. e-Preserv Sci 10:99–108
Perez-Rodriguez LJ, Del Carmen Jimenez de Haro M, Siguenza B, Martinez-Blanes JM (2015) Green pigments of Roman mural paintings from Seville Alcazar. Appl Clay Sci 116-117:211–219
Plesters J (1993) Ultramarine blue, natural and artificial. In: Roy A (ed) Artist's pigments: a handbook of their history and characteristics, vol 2. National Gallery of Art, Washington, pp 37–65
Rafalska-Lasocha A, Lasocha W, Grzesiak M, Dziembaj R (2010) X-ray powder diffraction investigations of Ruthenian-byzantine frescoes from the royal Wawel cathedral (Poland). Powder Diffract 25(3): 258–263
Robinet L, Spring M, Pagès-Camagna S (2013) Vibrational spectroscopy correlated with elemental analysis for the investigation of smalt pigment and its alteration in paintings. Anal Methods 5:4628–4638
Sakellariou E, Zorba T, Pavlidou E, Angelova S, Paraskevopoulos KM (2010) The byzantine church of "40 holy martyrs" in Veliko Turnovo, Bulgaria: pigments and techniques. In: Angelopoulos A, Fildisis T (eds) 7th International Conference of the Balkan Physical Union, AIP Conf Proc 1203: 501–506
Scott DA (2002) Copper and bronze in art: corrosion, colorants, conservation. Getty Publications, Los Angeles
Sotiropoulou S, Sr D, Miliani C, Cartechini L, Papanikola-Bakirtzis D (2008) Microanalytical investigation of degradation issues in byzantine wall paintings. Appl Phys A Mater Sci Process 92:143–150
Spring M, Higgitt C, Saunders D (2005) Investigation of pigment-medium interaction processes in oil paint containing degraded smalt. Natl Gallery Tech Bull 26:56–70
Švarcová S, Hradil D, Hradilová J, Kočí E, Bezdička P (2009) Microanalytical evidence of origin and degradation of copper pigments found in bohemian gothic murals. Anal Bioanal Chem 395:2037–2050
Wang A, Freeman JJ, Jolliff BL (2015) Understanding the Raman spectral features of phyllosilicates. J Raman Spectrosc 46:829–845
Winfield DC (1968) Middle and later byzantine wall painting methods. A comparative study. Dumbart Oak Pap 22:61–139
Zorba T, Pavlidou E, Stanojlovc M, Bikiaris D, Paraskevopoulos KM, Nikolic V, Nikolic PM (2006) Technique and palette of XIIIth century painting in the monastery of Mileseva. Appl Phys A Mater Sci Process 83:719–725