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RECIPES FOR PIGMENT MANUFACTURING IN GREEK POST-BYZANTINE PAINTING MANUALS

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ABSTRACT

Greek post-Byzantine (post-1453 AD) painters were often using painting manuals in order to retrieve information relevant to their discipline; yet rather few pertinent texts survive today. The renowned "*Hermeneia of the art of painting*" is a manual compiled at circa 1730 AD by the hieromonk and icon painter Dionysios of Fourna. It contains both iconographical dictations and technical instructions; the latter include seven recipes for the manufacturing of pigments as well as four recipes describing the conversion of gold leaf to powder ("*chrysography*"). Here, we compare the Dionysios of Fourna "*Hermeneia*" pigment recipes with pertinent recipes found in three other Greek painting manuals, namely the Panteleimonos monastery codex 259 (late 16th century), the Holy Metropolis of Samos codex 61 (1783 AD) and the Pagonis' "*Hermeneia*" of painting (1803 AD). Pioneering European painting manuals such as the Cennino Cennini "*Il libro dell' arte*" and the Theophilus Presbyter "*De diversis artibus*" are also considered. Revealed correlations between the manuscripts in consideration as well as to spot the possible sources of the "*Hermeneia*" pigment manufacturing recipes are reported. In order to highlight various pigment-related issues, data deriving from the analytical investigation of micro-samples originating from five post-Byzantine Greek icons have been also included, through OM, SEM-EDX and μ-Raman. Original data are presented deriving from the replication of a unique and hitherto unpublished pigment manufacturing recipe. It is thus shown that the recipes found in the Greek painting manuals do indeed largely reflect the materials employed by contemporary icon painters. It has been proved that most of the renowned Dionysios' "*Hermeneia*" pigment manufacturing recipes originate from substantially earlier Greek sources, while related material is also found in medieval European texts. It is shown that a deviant body of relevant recipes exists in less known -and mostly unpublished- Greek painting manuals, revealing that the Dionysios' painting manual is by no means an exhaustive account of the technical information available to post-Byzantine painters at about the time of Dionysios. Moreover, the potential trend considered herein for the very first time is the diffusion of Persian technical knowledge among late post-Byzantine Greek painters.

KEYWORDS: cinnabar, verdigris, lead white, lake, Hermeneia, bianco San Giovanni, SEM-EDX, μ-Raman.

1. INTRODUCTION

There are strong hints indicating that ancient craftsmen were occasionally using technical texts in the frame of their duties. Besides, the oldest pertinent texts that survive today are the second millennium BC cuneiform script recipes on glassmaking from Mesopotamia (Brill 1972). However, there do exist several other ancient texts that include either scattered or comprehensive technical dictations, such as the Theophrastus' "*On stones*" ("*Περί λiθων*", ca. third century BCE, Θεόφραστος 1998), the Dioscorides' "*On materials of Medicine*" ("*Περί ὑλης Ιατρικής*", 1st century AD, Διοσκουρίδης 2000), and the "*Natural History*" of Pliny the Elder ("*Naturalis Historia*", 1st century AD, Πλίνιος 1998). Following the emergence of alchemical texts such as those contained in the early 4th century AD Leyden and Stockholm papyri (Caley and Jensen 2008), extensive technical manuals started circulating among craftsmen during medieval times. Undoubtedly one of the most comprehensive such texts is the early 12th century "*De diversis artibus*" ("*On divers arts*") by Theophilus Presbyter that contains detailed directions pertaining to the disciplines of painting, metalwork and glass manufacturing (Theophilus 1979). The somewhat later (ca. 1400 AD) "*Il libro dell' arte*" by Cennino d' Andrea Cennini (Cennini 2015) largely focuses on painting and provides one of the most comprehensive accounts on painting materials and techniques, that stands out from the tens of surviving European painting manuals (Clarke 2001).

Despite the fact that there exist hundreds of medieval and later European painting manuals (Clarke, op. cit.) there is a notable scarcity of relevant Greek sources. Indeed, the oldest Greek text to contain technical instructions pertaining to painting is a short mid-14th century passage that deals with the rendering of faces and vestments (Parpulov et al. 2010). Also, shortly after the beginning of the 15th century, Isidore of Kiev wrote down some recipes dealing with the making of ink and starch glue, as well as with chrysography (i.e. writing in powdered-gold) (Νούσια 2008). In addition to the latter short text, one should consider some tenths of scattered recipes that deal mainly with inks and chrysography and were recently spotted in several byzantine (12th to 15th c.) manuscripts (Oltrogge 2011). Nevertheless, there is no evidence to support the existence of detailed Greek painting manuals before 16th century AD. Besides, the oldest pertinent text is the codex No259 of St Panteleimonos monastery (Mount Athos) that is dated to the late 16th century and was recently published by K. Vafiades (Βαφειάδης 2017). Note however, that the latter text deals largely with the description of holy figures and scenes and embodies a very limited amount of technical information. It is only much later that a comprehensive Greek technical text on painting emerged: Dionysios of Fourna, a hieromonk and icon-painter himself, gathered material from various sources and, around 1730 AD, compiled the renowned "*Hermeneia of the art of painting*" (from now on "*Hermeneia*") (Διονύσιος 1997). After a relatively lengthy introduction that occupies the first part of the manual, Dionysios describes in detail the materials and technique of icon and wall painting; the third and most extensive part of this work is devoted to iconographic descriptions (see for instance Şarlak and Onurel 2014). The structure and content of the "Hermeneia" certainly denotes that the text was compiled in order to be used as a handy painting manual by craftsmen (Clarke 2001).

Soon after its compilation, "*Hermeneia*" gained wide circulation among painters all around Balkans and beyond, and its wide distribution might well be traced by the tenths of relevant copies that survive today (Kakavas 2008). The text attracted the interest of early 19th century European scholars, and it soon ended up translated and published (Kakavas 2008). However, some of the first "*Hermeneia*" editions were based on a falsified version of the text, and it was not before 1900 that an edition of the genuine Greek text appeared; the latter edition was the result of the tireless efforts made by the important scholar Athanassios Papadopoulos-Kerameus, who spotted and restored all the falsified parts of the previous Greek "*Hermeneia*" editions (Διονύσιος 1997). In addition to the Dionysios' text, Papadopoulos-Kerameus published five earlier texts that apparently have contributed substantially to the compilation of his "*Hermeneia*". On the basis of comparison between the latter text and the former sources, it becomes obvious that Dionysios' enriched considerably the iconographical part of the pre-existing texts, yet added little, if any, original materials to the technical part (Διονύσιος 1997, Kakavas 2008).

A recent study (Kakavas 2008) has shown the survival of several tens of manuscripts bearing Greek post-byzantine (i.e. post-1453 AD) painting manuals. Many of the latter are catalogued as mere copies of the Dionysios' "*Hermeneia*", while some manuscripts are simply marked as "*Hermeneia*" deviants (Kakavas, op. cit.). However, recent studies of unpublished manuscripts have shown the existence of at least two groups of manuscripts that deviate substantially from the Dionysios' text in terms of technical content, and this indicates that the "*Hermeneia*" is by no means an exhaustive account of its contemporary technical knowledge (Mastrotheodoros & Beltsios 2019, 2021).

In the present study the authors survey the pigment manufacturing recipes found in four painting manuals; the Dionysios' "*Hermeneia*" serves as the reference point and its pigment recipes are compared to those spotted in the following three manuscripts:

i) The late-16th century codex No259 of Panteleimonos monastery in Holy Mount Athos that contains (among miscellaneous passages) a rather small technical part (Βαφειάδης 2017). The editor of the manuscript finds that a large part of its content originates from various earlier sources, and interprets the text as an early attempt to formulate a painter's manual (Βαφειάδης, op. cit.).

ii) A 1783 AD, hitherto unpublished copy of the Dionysios' "Hermeneia" that is nowadays kept in the Holy Metropoly of Samos library (Inv. Num. 61) (Μπάλπης 1783). In this case, the Dionysios' "*Hermeneia*" text was copied by the Cretan priest Ioannis Balpis who added certain original recipes to the technical part (Mastrotheodoros & Beltsios, 2019). Note that a slightly earlier Balpis copy of the "*Hermeneia*" is kept in the Benaki Museum library (Inv. Num. 141, see: Χατζοπούλου 2017).

iii) A 1803 AD painting manual owned by the painter Ioannis Pagonis who was active in the area of Pilio Mountain (central Greece) during the first decades of the 19th century. This manuscript deviates substantially in terms of structure and content from the Dionysios' "*Hermeneia*"; it was recently published by A. Varsamidis (Βαρσαμίδης 2020).

Here we proceed to a comparison between the pigment manufacturing recipes of the four aforementioned Greek manuscripts in order to explore possible correlations between them. Besides, it must be highlighted that scholars have hitherto regarded Dionysios' "*Hermeneia*" as a comprehensive textbook that includes a rather exhaustive account of its contemporary technical knowledge on painting. Nevertheless, the current work offers strong clues indicating that this view must be discredited. Moreover, in order to highlight specific issues that pertain to the use of pigments by Greek post-Byzantine icon painters, we present analytical data deriving from the technical investigation of five post-Byzantine Greek icons. Besides, several works dealing with the analytical investigation of post-Byzantine icons have recently emerged (e.g. Abdel-Ghani 2015, Mastrotheodoros et al. 2018, Bratitsi et al. 2019, Karydis et al. 2019, Christopoulou et al. 2020, Mastrotheodoros et al. 2021), shedding thus light on the materials and techniques employed by post-medieval Greek painters. The analytical methodology employed in the current study is presented in detail below. It should be clarified that only the recipes that pertain to the manufacturing of pigments to be used in painting will be herein considered; therefore, recipes dictating the preparation of inks (either plain or gold) for writing purposes will not be included in the discussion that follows. Finally, authors present the results of the replication of a unique and hitherto unpublished recipe found in the Fr. Ioannis Balpis' "*Hermeneia*" copy along with data collected from the preliminary analytical investigation of the corresponding products.

2. ANALYTICAL METHODOLOGY

Micro-samples were collected from five Greek post-Byzantine icons (i.e. religious paintings executed on properly prepared wooden panels) that are currently exhibited in the Ioannina Byzantine Museum (Ioannina, NW Greece). Samples of minimum dimensions (~ 1mm^2) were exclusively removed from areas of pre-existing paint losses using surgical scalpels. Subsequently, samples were examined below a binocular stereoscope and embedded in polyester resin. Upon resin's curing the blocks were subjected to grinding and polishing in order to expose samples' cross-sections; the latter were then examined through an optical microscope (OM, Leica, DMRPX) at magnifications up to 200x. The products of the Ioannis Balpis' artificial copper pigment manufacturing recipe (see sections 3.3 & 4.2) were examined under OM and scanning electron microscopy (SEM) in the as-received state (un-embedded in resin/ non carbon-coated). The SEM investigation was conducted using a FEI, Quanta Inspect D 8334 SEM-EDX device; in order to improve conductivity, samples cross-sections were carbon-coated using a Balzers' CED030 carbon vaporizer prior to SEM probing. Elemental compositions were estimated using the built-in 'Genesis-Spectrum' software (EDAX Company), in a standard-less quantification mode that incorporates ZAF matrix corrections (Heinrich, 1991). Also, selected samples were examined through a Renishaw, inVia μ-Raman using a low power (~0.01-1mW) 514nm laser; corresponding spectra were collected through a 100x magnification lens in the range of 60–3200 wavenumbers. It should be noted that the analytical data that pertain to icons' micro-samples analysis were acquired in the framework of G. P. Mastrotheodoros' PhD thesis (Mastrotheodoros 2016), while data pertaining to the analysis of the Balpis' pigment recipe products were acquired in the frame of the current study. All figures are for the first time published herein.

3. PIGMENT MANUFACTURING RECIPES IN GREEK PAINTING MANUALS

In the next subsections the pigment manufacturing recipes that are found in the four Greek painting manuals in consideration will be presented. The "*Hermeneia*" of Dionysios that serves as the reference text, will be discussed first.

3.1. Dionysios' "Hermeneia" (ca. 1730 AD)

The technological part of the Dionysios' "*Hermeneia*" contains eight recipes that deal with the manufacturing of pigments. The first one corresponds to §37 in the standard "*Hermeneia*" edition (Διονύσιος 1997, 28) and is entitled "*How to dissolve gold leaf*": gold leaves are mixed with a rather thick plant gum water solution in a small porcelain pot and the mixture is stirred until finely grinded. The excess of gum is then removed through successive washings with water and the powdered gold is left to dry; prior to using it, the gold dust is once more mixed with a bit of gum. It is worth noting that at the end of the recipe Dionysios makes explicit reference to the employment of this material in icon painting (Fig. 1a). Passage §41 dictates the manufacturing of a "fine" kermis lake (Διονύσιος 1997, 29-30): this recipe is very detailed and describes the typical process for kermis dye extraction and lake precipitation, yet it makes reference to the employment of two obscure ingredients, namely "*τζουγάν/tzugan*" and "*λωτούρ/lotur*"; according to Mastrotheodoros et al., (2021) the latter terms probably refer to *saponaria officinalis* and the roots of lotus tree (genus *diospyros*) respectively.

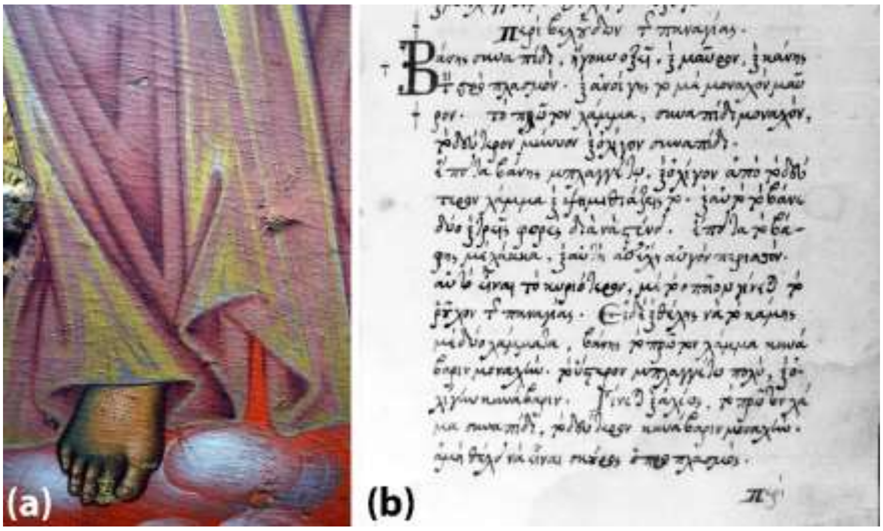

Figure 1. (a) Details of a 1773 AD icon from Ioannina, Greece, showing extensive use of gold powder; Byzantine Museum of Ioannina, Inv. Num.: 27 (Jesus Christ the Judge). (b) Detail of Samos MS no61 folio 24r, that dictates the rendering of Virgin Mary's cloth.

A recipe on the making of verdigris ("*βαρδάραμον/vardaramon*", §42, Διονύσιος 1997, 30) follows: here Dionysios calls for the immersion of thin copper sheets in vinegar stored within a copper pot; the pot is covered and exposed to sun during hot summer days, a process that leads to the formation of verdigris (Scott 2002). Recipe §43 dictates the preparation of artificial cinnabar/vermilion (Διονύσιος 1997, 31) through a seemingly variant of the dry process (Gettens et al. 1993a), while recipe §44 (Διονύσιος 1997, 31) describes the manufacturing of lead white ("*πλακούντι/plakunti*") by a variant of the stack process, i.e., by placing thin lead sheets over vinegar (Gettens et al. 1993b). The next two recipes deal with the manufacturing of blue pigments: the first one describes the extraction of blue dye from cloth shearings and the precipitation of the corresponding lake (§45, Διονύσιος 1997, 31-32), while the second (§46, Διονύσιος op. cit., 32) dictates the production of the so-called "lime-blue" pigment (Krekel & Polborn, 2003). The last pigment-manufacturing recipe appears amid general directions for wall painting and contains a brief description of the preparation of calcium carbonate white to be used exclusively for wall painting (§59, Διονύσιος 1997, 39).

3.2. Codex 259 of Panteleimonos Monastery (late 16th c.)

The late 16th century Panteleimonos Monastery codex 259 contains only four passages pertaining to pigment manufacturing. The first one (f34r) describes the preparation of gold-powder and at first sight appears very similar to the equivalent of Dionysios (§37, Διονύσιος 1997, 28). However, the Panteleimonos MS recipe calls for the grinding of gold leaf with honey instead of gum (Dionysios); upon completion of the grinding process, the excess of honey is removed through washing and the gold powder is mixed with "gum of Alexandria" prior to its use. At the end, the recipe in consideration declares that the decorative elements rendered in this substance should be burnished with a "*dog-tooth burnisher*" in order to show up (Βαφειάδης 2017, 187).

The next recipe of codex 259 appears in the verso of folio thirty-four (f34v) and pertains to the manufacturing of lead white (Βαφειάδης, op. cit. 188-189); it is very similar to the corresponding recipe of Dionysios (Διονύσιος 1997, 31) and can be viewed as a predecessor (or a close relative to predecessor) of the latter. Immediately after the lead white recipe (f34v, Βαφειάδης, op. cit. 189-190), the manuscript contains a passage dictating the preparation of verdigris which is in fact practically identical to Dionysios' §42 (Διονύσιος 1997, 31); however, in the Panteleimonos text there is the following additional instruction at the end: "*and when you wish to render a vestment or background, apply a primary paint layer of lead white before verdigris*". Finally, a recipe dealing with the manufacturing of blue or red lake from cloth shearings, equivalent to that found in the Dionysios' painting manual (§45, Διονύσιος 1997, 31-32), appears in folios 36r and 36v (Βαφειάδης op. cit., 191-192).

3.3. *Fr. Ioannis Balpis' "Hermeneia" copy (1783 AD)*

While the text of Balpis resembles a facsimile of the Dionysios' "*Hermeneia*", careful comparison reveals that the former contains several additional passages. In particular, Balpis has enriched his copy mainly by adding detailed dictations as regards the rendering of various items as for example the "*velvet*" vestments of Virgin Mary (Μπάλπης 1783, f24r, Figure 1b). However, apart from additional instructions pertaining to painting technique, Balpis has included a remarkable recipe for the making of a copper-based green pigment that is not found in the Dionysios' "*Hermeneia*" (Μπάλπης 1783, f35v, Fig. 3a). This particular recipe calls for the placement of yoghurt in a copper vessel, the latter being explicitly described as "*not tinned*" in order for the yoghurt to be able to interact with the metallic copper. The yoghurt is stirred twice per day up until it turns all green, then is removed and placed in a shadowy place to dry; a transcription of the recipe and further details are provided in 3.2.

The other pigment manufacturing recipes of the Balpis text are in fact copies of the recipes found in the Dionysios' "*Hermeneia*". Nevertheless, the passage describing the synthesis of artificial cinnabar shows some notable deviations: although both recipes call for the use of the same raw materials (i.e. sulfur, mercury, and "*murtasangki*", see next for details), in the case of the Balpis recipe (Μπάλπης 1783, f36r-v) these ingredients are first mixed and then heat treated, while Dionysios dictates that they should be first roasted separately and then mixed prior to receiving a second round of thermal treatment (§43, Διονύσιος 1997, 31-32). Similarly, the details of the kermis lake recipe of Balpis (Μπάλπης 1783, ff35r-35v) deviate substantially from those of the corresponding recipe of Dionysios (§43, Διονύσιος 1997, 31).

3.4. *Pagonis' "Hermeneia of sacred icons" (1803 AD)*

The text in consideration contains six pigment-manufacturing recipes and the title of a seventh one whose body is missing (presumably it was never copied). It is of some significance that the recipes in discussion appear in a completely different order compared to that in the reference text (Διονύσιος 1997). The recipe dictating the preparation of gold powder is practically identical to that of the corresponding Dionysios' one (§37, Διονύσιος 1997, 28-29). However, the recipe of Pagonis contains an additional short sentence that provides directions regarding the application of the gold powder on panel painting ("*icons*"): "*and dissolve gum from Alexandria, or skin glue, and work (it) on the icons by brush, and when the icon is dried, lay on it a leaf of paper and burnish the gold from above*" (Βαρσαμίδης 2020, 652-655).

What follows is a recipe dealing with the manufacturing of lead white (Βαρσαμίδης 2020, 660-661), which is in fact identical to that of Dionysios (§44, Διονύσιος 1997, 31). The next passage describes the preparation of verdigris ("*vardaramon*") (Βαρσαμίδης 2020, 660-663) in a manner more or less similar to that found in the corresponding Dionysios' recipe. However, the Pagonis' recipe shows some notable differences from the latter, including alternative spellings and adopted syntax. In addition, at the end of the Pagonis recipe there is a recommendation mentioning "*…and when you wish to render a vestment or background, first apply lead white and on this the vardaramon*" (Βαρσαμίδης 2020, 662-663); note that the same recommendation is found in the corresponding Panteleimonos MS recipe.

Finally, within the technical part of the Pagonis "*Hermeneia*" two recipes for lake pigment manufacturing exist. The first one describes the manufacturing of a blue pigment ("*lazouri*") from cloth shearings (Βαρσαμίδης 2020, 662-663) and the second the making of red lake from kermis ("*krimezi*") (Βαρσαμίδης op. cit., 680-681). Both recipes show an overall similarity with the corresponding Dionysios ones (§45 & §41 respectively, Διονύσιος 1997, 31-32 & 29-30), yet they also exhibit some notable differences suggesting that Pagonis did not copy these particular recipes from Dionysios' "*Hermeneia*".

A summary of the pigment manufacturing recipes found in the herein discussed texts is presented in Table 1.

Table 1. A summary of pigment manufacturing recipes in the painting manuals in consideration

Recipe	Painting manual			
	Panteleimonos codex 259 (late 16th c.)	Dionysios "Hermeneia" (ca. 1730)	Fr. I. Balpis "Hermeneia" (1783)	Pagonis' "Hermeneia" (1803)
Gold powder (for painting purposes)	●	●	●	●
Verdigris (Cu + vinegar)	●	●	●	●
Artificial Cu- green (Cu + yoghurt)	-	-	●	-
Artificial cinnabar	-	●	●	●[1]
Lead white	●	●	●	●
Lake(s) from cloth shearings	●	●	●	●
Kermis lake	-	●	●	●
Lime blue	-	●	●	-
$CaCO_3$ white	-	●	●	-

4. DISCUSSION

4.1. *Gold powder*

All four studied painting manuals contain recipes that describe the conversion of gold leaves to gold powder (Table 1). However, a detailed inspection of these very recipes reveal that the Pagonis recipe is strongly reminiscent of the Panteleimonos' MS259 recipe as both call for the mixing of gold powder with "*gum of Alexandria*" and its subsequent burnishing. One shall also highlight here the reference to "*dog tooth burnisher*" of Panteleimonos MS259 and the description of the burnishing process in Pagonis' text, where the gold powder is covered by a paper sheet prior to its burnishing; both these references are unique amid the known Greek painting manuals and offer important insights as for the implements and methods used for burnishing by Greek painters. In addition, it must be noted that the explicit reference to the employment of gold powder in icons' painting is not found in the late 16th century Panteleimonos text, yet it exists in all the other, considerably later, texts. Interestingly, a recent study has shown that the pertinent pigments are indeed mostly found on post-byzantine Greek icons that are dated from 18th century onwards (Mastrotheodoros et al. 2018). Note however, that earlier examples of highlights rendered in gold are occasionally spotted as well; a pertinent example is shown on Fig. 2 where the cross-section of a sample collected from a 17th century Greek icon and a corresponding EDX spectrum are shown.

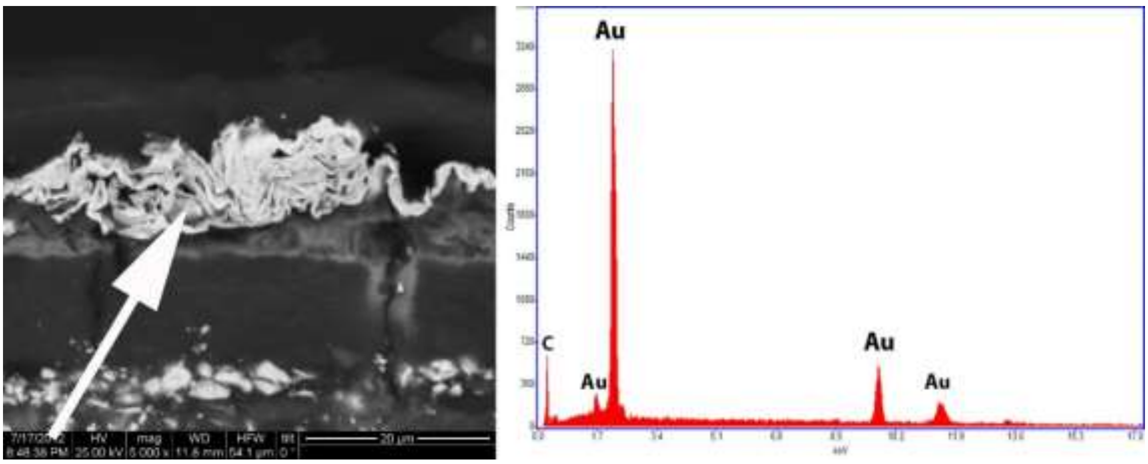

Figure 2(a) Arrow indicates gold leaf highlight placed on top of a mordant (gray substrate); 17th century icon, Ioannina Byzantine Museum Inv. Num.: 25 (Royal Doors). SEM-BSE, 5000×. (b) EDX spectrum collected from the gold leaf shown on the left; the carbon is detected due to the presence of the conductive carbon layer (see "Analytical Methodology").

[1] Only title, the body of the recipe is missing.

4.2. *Artificial copper green*

The recipes dealing with the synthesis of artificial copper green pigments are more or less of similar content, and presumably they all lead to the same product (Scott 2002). However, the Panteleimonos codex 259 and the Pagonis "*Hermeneia*" recipes contain a final admonition for the proper application of the pigment on a lead white substrate, which is not to be found in the Dionysios and Balpis texts. This is a hint that indicates a possible ancestor-successor correlation between the Panteleimonos (late 16th c.) and the Pagonis (1803) text.

On the other hand, of special interest is the recipe dealing with the manufacturing of "*another* (copper green)" that employs a copper vessel and yoghurt and appears only in the Balpis text (Μπάλπης 1783, f35v, Fig. 3a). The corresponding recipe is for the first time transcribed and translated here:

Έτερον. Βάλε γιγούρτι εις ένα αγγείον χαλκωματένειον, το οποίον πρέπει να είναι αγάνοτον, διά να παίρνει τον ίγιοτα να πρασινίζει. Άφες το να κάμη ημέρας πολλάς, (σφίγκοντάς το πρώτον, να εύγη όλον το υγρόν) κ' ανακάτωνέ το με μίαν βέργα, δύο φοραίς την ημέραν. Και όταν ιδής ότι πρασίνησε καλά, τότε το ευγάνης ατο χάλκωμα, κ' το ξηραίνεις εις τον ίσκιον.

Another. Place yoghurt in a copper vessel which must not be lined with tin so that formation of green surface-rust is possible, and let it stand for many days (but first have it well strained so that all of its liquid is removed). Stir yoghurt with a stick twice a day. And when you see that it has turned green properly, you remove it from the copper vessel, and you let it dry in the shadow.

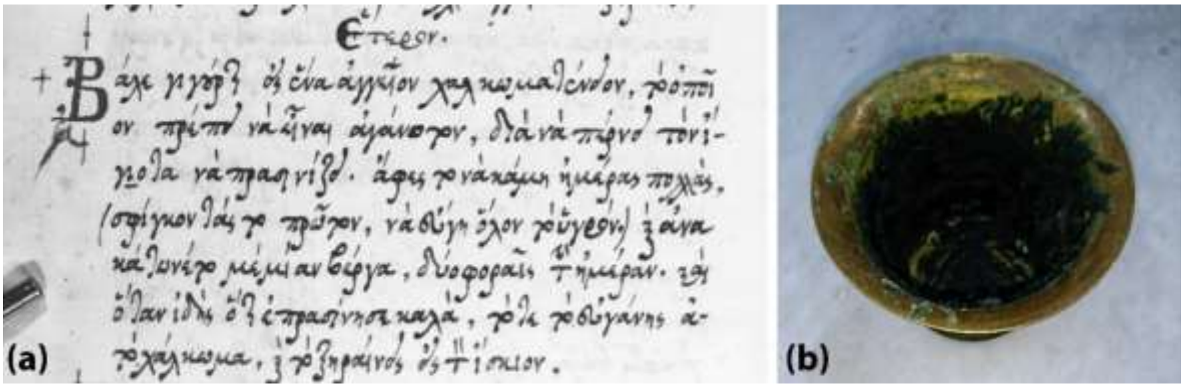

Figure 3(a) Detail of folio 35v of the Samos Holy Metropolis library MS No61 (b) Photograph of the transformed-to-green yoghurt after several days in a brass container.

To the best of authors' knowledge, no recipe of this kind exists in pertinent European texts (Scott 2002, 271); yet sporadic references to the employment of a number of organic corrosives of copper (e.g., wine lees or curdled milk) do exist (see Scott, op. cit.). Nevertheless, yoghurt is recommended as an alternative to vinegar in certain Persian verdigris manufacturing recipes that are dated from mid-15th to early 20th centuries (Barkeshli 2017, 190). Therefore, the existence of this very recipe in a Greek late 18th century painting manual suggests the possibility of a hitherto undocumented route of technological exchanges between Greek and Persian craftsmen during the late pre-industrial period.

On the basis of its unique –among Greek "Hermeneiae"- character, the recipe in consideration is under study by the present authors. Replication experiments of this particular recipe[2], that are for the first time conducted by the current authors and reported herein, show that the recipe is indeed applicable, as a series of intensively colored substances are readily produced regardless the exact type of vessel (i.e. made of pure copper or brass) (Fig. 3b). However, upon the SEM-EDS investigation of the corresponding products it turned out that the type of the starting vessel affects the composition of the product. For instance, it is evident that the product made in the brass vessel bears a considerable amount of zinc (Table 2), while it appears that there might also be some differentiations as regards the micromorphology of the two products (Fig. 4a-b). On the other hand, both products contain amounts of various other elements that apparently pertain to the composition of the employed yoghourt (e.g., Ca, Cl, Mg, see Table 2). However, readers should keep in mind that the recorded elemental compositions correspond to single grain analyses, therefore they may not precisely reflect the gross composition of the products. In fact, the analytical investigation of the recipe products is currently in progress, and further analyses will be conducted in due time (including XRD & μ-FTIR).

[2] Recent bibliography shows few examples of relevant replication experiments (see e.g. Katsaros et al. 2010).

Table 2. EDX analyses of "yoghourt green" recipe products; data are normalized to 100 wt%.

Type of vessel	Detected elements (wt%)							
	Mg	P	S	Cl	K	Ca	Cu	Zn
Cu-Zn	3.6	16.4	4.7	7.2	7.7	17.8	17.0	25.6
Cu	2.8	5.2	2.6	12.8	9.4	14.3	53.0	n.d.

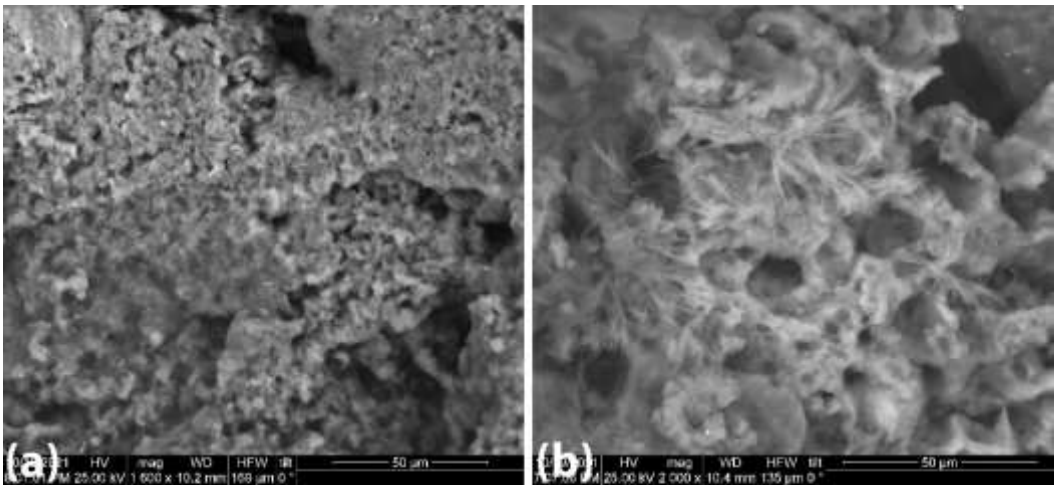

Figure 4(a) SEM-BSE image of the copper vessel product, 1600×. (b) SEM-BSE image of the brass vessel product, 2000×.

4.3. *Artificial cinnabar*

Artificial cinnabar (vermilion) manufacturing recipes are only found in the Dionysios' "*Hermeneia*" and the relevant copy made by Balpis (the Pagonis' text bears only the title of the recipe) (Table 1). In fact, both these recipes correspond to versions of the dry process which was typical of that period (Gettens et al. 1993a). Note however that the Balpis recipe deviates substantially from that of Dionysios (see section 3.3) and this clearly indicates that Balpis did elaborate on his source material. In addition, one should note that both recipes call for the employment of another substance in addition to mercury and sulfur, the so-called "*mourtasangki*" which is further specified as "*molivochoma*" by Balpis. This term has been misinterpreted in the key-English translation of the "*Hermeneia*" text (Dionysius 1974) and other pertinent publications, as discussed recently in some detail by Mastrotheodoros et al., (2021).

Cinnabar/vermillion (i.e., the synthetic analogue of the natural mineral) was indeed very frequently employed by Greek post-byzantine icon painters (Mastrotheodoros et al., 2021), and its presence on icons can be readily verified by either the detection of mercury and sulfur through elemental analysis techniques (e.g., EDS on micro-samples or spot XRF analysis) or through the micro-Raman analysis of corresponding samples cross-sections. A relevant example is presented in Fig. 5a where a micro-Raman spectrum collected from vermillion grains spotted on a micro-sample from a late 17th-century post-Byzantine icon is shown; the spectrum in consideration bears the characteristic cinnabar Raman shifts (Bell et al., 1997). Moreover, investigation of this cross-section under the SEM showed that the pigment grains are of rather small diameters, implying thus intensive grinding (Fig. 5b).

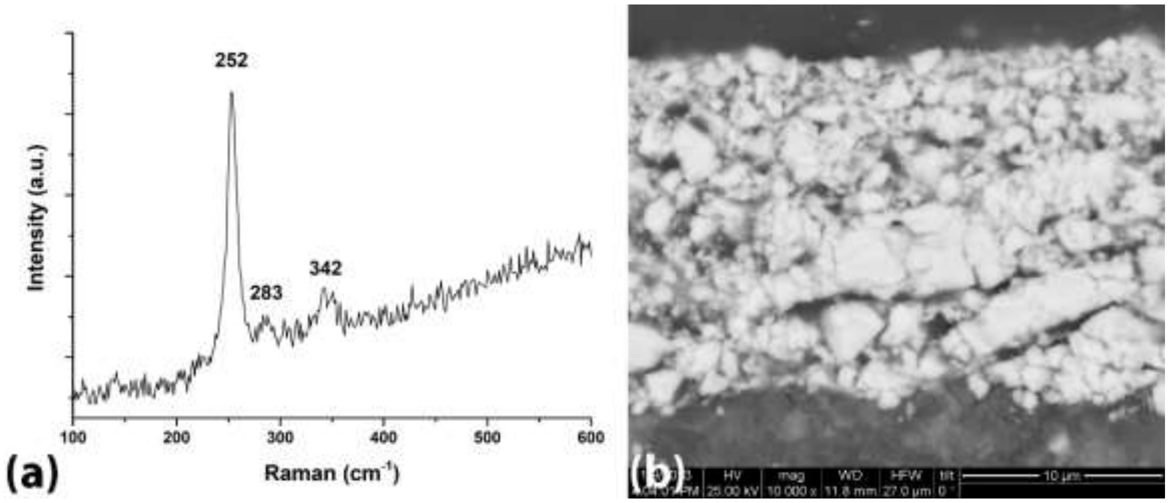

Figure 5(a) Raman spectrum from the cinnabar grains shown on Figure 5b. (b) Cinnabar grains from a late 17th century Greek icon from Epirus territory (Ioannina Byzantine Museum, no Inv. Numb., Jesus Christ Enthroned); SEM-BSE, 10000×.

4.4. *Lead white*

Lead white manufacturing recipes are found in all of the studied texts (Table 1). All these recipes are very similar and in fact describe a variant of the stack process (Gettens et al., 1993b). However, they all call for the sealing of the vessel, which is a condition that might have hindered carbon dioxide, an important component of the reaction, from entering the container. Thompson (1998, 112) states that there do exist several medieval recipes dictating the placement of sealed vessels within dung, yet in most of these cases the product (presumably lead acetate) was roasted in mild fire, and, hence, it was transformed to basic lead carbonate. Also, Harley (2001, 166) notes that in cases where sealed vessels were indeed employed, the product was subsequently roasted in the sun, and a relevant recipe appears already in the 14th century "Liber diversarum arcium" (Clarke 2011, 111). Therefore, it appears that the product of the Greek "Hermeneiae" recipes was transformed to basic lead carbonate upon its exposure (/drying) to open air. Note however that lead white was in massive production in Europe since much earlier; hence it is improbable that Dionysios and his contemporaries relied, at least exclusively, in home-made versions of this pigment. Besides, there is a relevant passage in the Dionysios' "*Hermeneia*" that clearly indicates procurement of the pigment through trade as the reader is asked to use "*Venetian* (lead) *white or from the fine Frankish one, which are* (sold) *in the form of lumps wrapped in paper sheets*" (§18, Διονύσιος 1997, 20).

It is worth noting that lead white is a pigment present virtually everywhere in icon painting. Besides, lead white is extensively used to render white and in general light hues, and it is also occasionally mixed with various pigments in order to impart body and luminosity. Upon the examination of icon samples' cross-sections through the use of the backscattered electrons (BSE) detector of the SEM, lead white grains are readily recognized due to their intense bright appearance. A relevant example is shown on Figure 6a where a cross-section from an early 18th century icon is depicted. In particular, the cross-sectioned microsample originates from the depiction of a gray bone that lays on top of the brown soil just below St Georgios (arrow, Fig. 6b). Under OM (insert on Figure 6a) the sample shows evidently two distinct paint layers, namely a brown (soil) and a light gray one (bone); BSE probing (Fig. 6a/background) revealed that lead white grains (white spots) predominate in the upper paint layer yet abound in the brown layer as well.

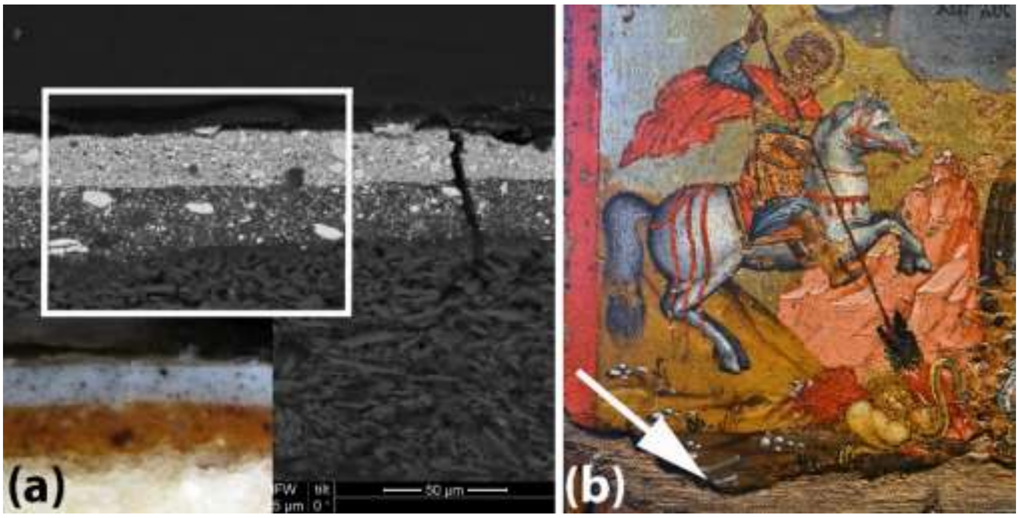

Figure 6(a) Background: cross-section of a sample from the spot shown in Figure 6b, SEM (BSE) 1200×. Insert figure: same sample, OM, 200×. (b) Detail of an early 18th century Greek icon; Ioannina Byzantine Museum Inv. Num.: 187 (Holy Communion with Saints). Arrow indicates the sampling position.

4.5. Kermis lake & lake(s) from cloth Shearings

The kermis lake recipe does not exist in the relatively early Panteleimonos codex, yet it appears in the other three texts considered herein (Table 1). Upon comparison of the latter texts it becomes apparent that neither Balpis nor Pagonis copied their recipes from Dionysios. This is particularly important in the case of the Balpis "*Hermeneia*"; while Balpis did view the Hermeneia of Dionysios as the reference text he added or modified some material whenever he felt that this would be a valid contribution.

On the other hand, the Balpis recipe dictating the manufacturing of lake from cloth shearings is in fact a facsimile of the Dionysios recipe; only minor spelling differentiations between the two texts can be spotted and the same is true for the corresponding Pagonis recipe. Here it shall be noted that similar recipes do exist in European painting manuals dating back to at least the early 14th century AD, a relevant example being the Bolognese MS (Merrifield 1849, 431-435). Moreover, some scholars have suggested that until the 17th century most of the lake pigments circulating among European painters had been manufactured by these methods (Kirby et al., 2005, 74; Kirby et al., 2007, 73). Interestingly, upon the SEM-EDX examination of samples from Greek post-byzantine icons authors were able to spot various lake grains that are notably rich in sulfur (S), which according to the literature (Kirby et al. 2005) implies manufacturing through dye extraction from clothes (Fig. 7).

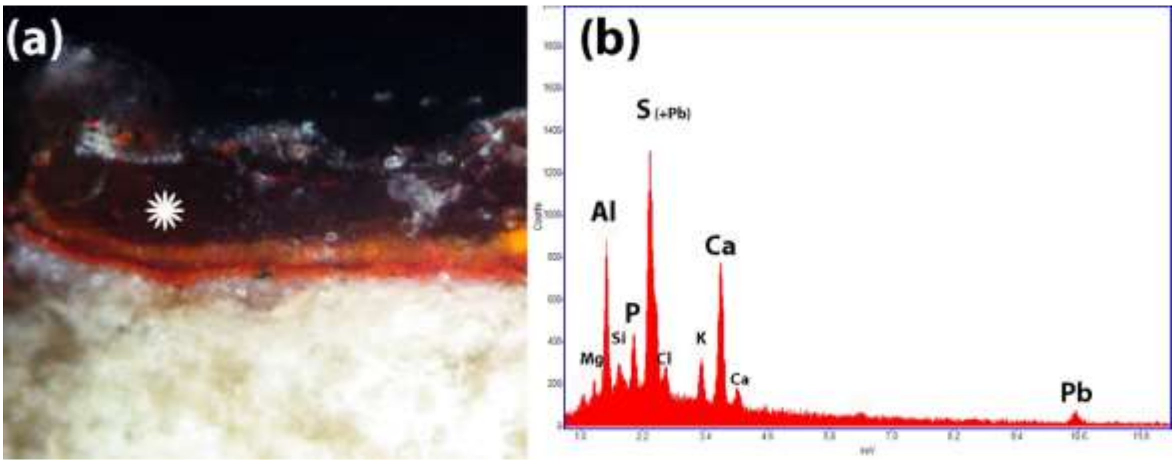

Figure 7(a) Cross-section from a 16th century Greek icon (Ioannina Byzantine Museum Inv. Num.: 599, Virgin Mary Hodegetria); OM, 200×. Asterisk marks the lake-containing paint layer from which the S-dominated EDX spectrum shown on (b) was collected.

4.6. *Lime blue & calcium carbonate-based pigments*

The recipes dictating the manufacturing of the so-called *"lime blue"* and "*white for wall painting*" are found only in the Dionysios "*Hermeneia*" and its version by Balpis (Table 1). As for the former recipe, note that the oldest pertinent example exists in the Mappae Clavicula (Smith and Hawthorne 1974, 26), a text compiled between 8th and 12th centuries, while versions of it re-emerged in several later medieval texts (Orna et al., 1980, 57). Given this array of older lime-blue recipes, one can assume that the farthermost ancestors of the Dionysios' recipe can be traced down to the early medieval alchemical texts and this is definitely an important observation. However, it is worth noting that the Dionysios recipe deviates from the aforementioned ones in that it introduces a pre-treatment stage: the pot containing a lime plus vinegar mixture (~1:2 v/v) is placed on fire and boiled until the vinegar is exhausted; only then new vinegar is added (1:1 v/v to treated lime), the pot is sealed and buried in horse-dung (§46, Διονύσιος 1997, 32). Experimentation with lime-blue recipes has shown that the exact type of the product depends largely on production conditions (Krekel and Polborn, 2003, 176), therefore one may assume that the pre-treatment dictated by Dionysios could indeed affect the outcome.

As for the "*white for wall painting*" recipes, it is obvious that the Balpis passage is in fact a facsimile of the Dionysios one. Regardless the alternative routes described within the recipe, the outcome is always primarily composed of calcium carbonate, while calcium hydroxide can be also present. Apparently the recipe in consideration is closely relevant to the "*bianco di sangiovanni*" of Cennino Cennini, which is manufactured with a rather similar process (Cennini 2015); experimental reproduction of the latter recipe has shown that the product contains always a considerable fraction of calcium hydroxide (ca. 30%) (Denninger 1974, 186).

Finally, it shall be noted that in both cases (Dionysios & Balpis texts) the aforementioned $CaCO_3$-based white is explicitly mentioned as a pigment to be used exclusively in wall painting, and it appears that the lime blue pigment was also particularly appropriate for wall painting use (Krekel and Polborn, 2003, 180). Therefore, it might not be a coincidence that the corresponding recipes have not been included in the Panteleimonos codex and the Pagonis painting manual as neither of them deals with wall painting materials and techniques.

5. CONCLUSIONS

On the basis of a comparative study of four Greek post-byzantine painting manuals it is shown by critical assessment and some selective analytical measurements that most of the pigment manufacturing recipes found in the renowned Dionysios "*Hermeneia*" painting manual originate from considerably earlier sources. In addition, the corresponding recipes are strongly relevant to recipes found in earlier European painting manuals. However, various modified and additional recipes exist in some less known –and mostly unpublished- Greek painting manuals, and this clearly indicates that the Dionysios "*Hermeneia*" is by no means an exhaustive account of the contemporary technical knowledge. Besides, it is shown that there exist at least two additional "branches" of technical knowledge, one represented by the 1803 AD Pagonis' "*Hermeneia of the sacred icons*" that appears to be relevant to the late 16th century Panteleimonos monastery codex No259, and a second emerging in a Dionysios "*Hermeneia*" copy made by father Ioannis Balpis on 1783 AD. The in-depth study of the latter text suggested the possibility of diffusion of Persian technical knowledge among late post Byzantine Greek painters, a potential trend considered herein for the very first time.

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