



## MA-XRF investigation of a 17th century icon by the renowned painter Theodoros Poulakis

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### ABSTRACT

Eastern Orthodox religious panel paintings (“icons”) are continuously manufactured since the dawn of Christianity and are still being used in the framework of pertinent rituals and worship. In the current work, an important Greek icon is investigated through non-invasive macroscopic X-ray fluorescence (MA-XRF) analysis to reveal the employed painting materials and techniques. The artifact in consideration was painted by the renowned icon painter Theodoros Poulakis who was active during the 17th century (ca. 1622–1692). Poulakis’ work is characterized by the extremely skillful painting and played a major role in the stylistic developments of Greek religious painting; additionally, more than one hundred icons that either bear Poulakis’ signature or are attributed to his hand on stylistic basis are spotted today. Through the MA-XRF investigation of the icon in consideration authors were able to identify the materials employed in its manufacturing and revealed interesting technical details, including some peculiar –and possibly idiomorphic– characteristics. In particular, the identified pigments include vermilion, lead white, minium, at least two distinct ochre pigments, a copper-based blue (presumably azurite) and two distinct (in terms of composition) copper-based green pigments, along with a deep-red organic lake. Poulakis used extensively high-purity gold leaves for gilding the background and the haloes of the figures, while MA-XRF allowed for the identification of inferior (in terms of purity) gold leaves that were used for rendering gilded highlights on various details. The analytical data allowed for an in-depth investigation of the materials and techniques employed by Poulakis in this particular painting and led to the spotting of some rather idiomorphic technical characteristics, such as the presence of a copper green pigment that contains Zn–As–Ba impurities and the combination of multiple colors for highlighting red vestments. The results are evaluated under the light of other relevant studies and aim primarily at setting a sound foundation for a forthcoming, extensive and thorough investigation of the materials and techniques employed in other Theodoros Poulakis paintings.

### 1. Introduction

Icons –i.e. Eastern Orthodox religious panel paintings– have been manufactured since the dawn of Christianity. The infancy of icon production has been occasionally linked with the production of Egyptian funerary mummy portraits (“fayum portraits”) (Vokotopoulos, 1995), yet this relation has been disputed (Κόρδης, 2001). The Iconoclastic Controversy (726–842 CE) was of decisive importance for the establishment of the use of icons within the framework of Christian Orthodox rituals, and after this period, the art of icon painting experienced a great

boost and spread all around the Byzantine Empire and beyond (Evseeva & Cook, 2005). Interestingly, even after the conquest of a significant part of Byzantine/ Greek territories by Ottoman Turks (15th century CE) Christians remained more or less able to practice their Orthodox rituals, therefore icon painters did not refrain from painting. Additionally, although the technique of oil painting on canvas supports gradually prevailed in contemporary European painting (DeGhetaldi, 2016), post-15th century icon painters kept on manufacturing their paintings by employing (or adapting) medieval techniques. Indeed, they kept on rendering Holy Figures and Scenes on primed (gessoed) wooden panels

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using pigments mixed with egg yolk, while they very often embellished the backgrounds (campuses) and various details of their paintings by gold leaves (Dionysios of Fourni, 1996). The activity of the so-called post-Byzantine (i.e. ~1453–1830 CE) painters accounts for the majority of the thousands of Greek icons that are nowadays preserved in collections and worshiped in churches, convents and in private in Greece and abroad.

During the last decades a growing interest on these paintings has emerged among scholars, which has triggered efforts to reveal the materials and techniques employed for their manufacturing through analytical investigation by employing various invasive and non-invasive techniques such as optical and scanning electron microscopy, Fourier transform infrared and Raman spectroscopies etc. (Alexopoulou & Kaminari, 2008; Karapanagiotis et al., 2009; Sotiropoulou & Daniilia, 2010; Valianou et al., 2011; Mastrotheodoros et al., 2022). However, during the last decades a new, non-invasive and extremely powerful analytical tool became available for implementing such studies. This is the case of macroscopic (or scanning) X-ray fluorescence analysis (MA-XRF) that was recently developed to a level that allows for the rapid scanning of relatively large areas ( $\sim 1 \times 1 \text{ m}^2$ ) and the subsequent creation of elemental distribution maps (Alfeld et al., 2013). This technique allows scholars to gather crucial data pertaining to the materials and techniques, as well as to the state of preservation of paintings (Alfeld et al., 2013; Mazzinghi et al., 2021; Alfeld, 2020). However, most of the pertinent studies are focused on the investigation of Western European panel and canvas paintings, and only a limited number have been conducted on icons (Walczak et al., 2019; Gerodimos et al., 2022; Mastrotheodoros et al., 2023). Despite being still relatively few, the latter works have highlighted the extreme potentialities of MA-XRF for the investigation of icons.

In the current work authors present the results of the MA-XRF study of a post-byzantine icon that was conducted by using the first MA-XRF instrument installed in Greece. In particular, the study has been focused on the investigation of an important late 17th century icon of St John the Forerunner with scenes from his life (Fig. 1-left). The central part of the icon depicts St John as an angel standing in front of a rather arid landscape while on the bottom of this scene St John the Chrysostom and St Spyridon are depicted. The central part is surrounded by ten scenes from St John's life; starting from bottom left upwards the depicted scenes include a) the Annunciation to Zachariah, b) the

Embracement of Anna and Zachariah, c) the Birth of St John, d) St John preaching, e) the Baptism of Jesus Christ by St John, f) St John judging Herod, g) St John imprisoned, h) the Beheading of St John, i) Herodias presenting St John's head, and j) the Entombment of St John (Fig. 1, left). This icon is currently exhibited in the Byzantine Museum of Ioannina (henceforth BMI) and is regarded as of particular importance because it is a signed work of the renowned icon-painter Theodoros Poulakis (ca. 1622–1692) who was born on the island of Crete (south Aegean Archipelago). Poulakis' work is characterized by the extremely skilful painting that quite often includes stunning micrographic scenes (see Fig. 1, right) and the incorporation of western European elements (in particular elements deriving from Flemish copper prints, see (Πηγάπουλος, 1979). Moreover, the artistic legacy of Theodoros Poulakis is considered to have played a notable role in the stylistic developments of Greek religious painting during late 17th and 18th centuries as many painters were influenced by its idiomorphic characteristics (Χατζηδάκης, 1987). Additionally, Poulakis was very productive: indeed, more than one hundred and thirty icons that either bear its signature or are attributed to his hand, are known to exist today (Χατζηδάκης & Δρακοπούλου, 1997).

The MA-XRF investigation of the icon in consideration aims primarily at the identification and detailed documentation of the materials and techniques employed in this work, and at the assessment of the potentialities of MA-XRF analysis for the investigation of icons. Through the evaluation of the analytical data under the light of earlier pertinent studies (Karapanagiotis et al., 2013; Mastrotheodoros et al., 2020; Mastrotheodoros et al., 2021; Christopoulou et al., 2020) authors try to reveal potentially idiomorphic technical characteristics of this particular Poulakis' painting. Ultimately, the current work aims to form the basis for a subsequent, extensive technical investigation of additional –either signed or attributed– Poulakis icons, in search of potential technical fingerprints on his works.

## 2. Materials and methods

The studied icon measures  $52.7 \times 42.0 \times 2.7 \text{ cm}^3$  and is displayed in the permanent exhibition of the BMI. Following the issue of a license from the authorities in charge, the artifact was transferred (under the escort of conservators and archaeologists of the Ioannina Ephorate of Antiquities) to the XRF Lab premises (Dept. of Materials Science and



**Fig. 1.** Left: St John the Forerunner with scenes from his life, by Theodoros Poulakis (late 17th century CE). Right: detail of a micrographic scene from the upper part of the icon showing the Baptism of Christ; note the scale bar.

Engineering, University of Ioannina) for the analysis. The MA-XRF investigation was conducted by using the M6-Jetstream instrument (Bruker), which is equipped with a 30 W Rhodium anode X-ray tube (maximum voltage: 50 kV) with polycapillary optics and a silicon drift detector (active area: 30 mm<sup>2</sup>). Limitations imposed by the rather short-term availability of the artifact led to the proper manipulation of the experimental set up. In particular, five distinct scans were performed on the painting: scan “A” corresponds to the whole of the icon while scans “B”, “C”, “D” and “E” correspond to various details (Fig. 2). In the case of the scans “A” and “B,” the X-ray beam spot size was set to 100  $\mu\text{m}$  (Mo K $\alpha$  transition). Scans “C”, “D,” and “E” were conducted by employing a spot size of approximately 35  $\mu\text{m}$  (Mo K $\alpha$  transition) which was attained by adjusting the distance between the studied object and the spectrometer accordingly. The X-ray tube was operated in a voltage and current setting of 50 kV and 600  $\mu\text{A}$ , respectively, and measurements were conducted in air. Elemental distribution maps were generated via the built-in M6-Jetstream software.

### 3. Results and discussion

Based on the evaluation of the scan “A” sum-spectrum (i.e. the sum of all the corresponding  $\sim 2.500.000$  spectra) (Fig. 3), the elemental distribution maps of the major and minor detected elements were generated. Note that, following a previous pertinent discussion (Mastrotheodoros et al., 2023), in most of the current cases the elemental distribution maps were displayed using an RGB intensity gradation scale (black: zero counts/red: maximum counts); a grayscale was however preferred in selected elemental distribution maps of scans B and C (see next).

The element calcium (Ca, Fig. 4) is detected all over the scanned icon except from the areas where lead (Pb), mercury (Hg), copper (Cu) and zinc (Zn) exist (Fig. 4), while Ca seems to fade in areas of high iron (Fe) and manganese (Mn) intensities (Fig. 4). Given that the photons of Ca are of rather low energy (Ca K $\alpha$  = 3.69 keV), they cannot penetrate through layers that are rich in pigments comprising of heavier elements such as those mentioned before. Therefore, it is assumed that the detected Ca originates primarily from the substrate of the painting, and in particular from the preparatory layer/ground that is customarily applied on the wooden panels in the framework of Greek post-byzantine painting (Dionysios of Fournia, 1996; Mastrotheodoros & Beltsios,

2022). Besides, the fact that Ca shows a strong correlation with sulfur (S) –in particular in areas of cracks where the substrate is revealed– corroborates this assumption as calcium sulfate compounds were used for priming panels in the latter framework (Mastrotheodoros & Beltsios, 2022). However, some of the high-Ca intensity areas (orange-red in the relevant map, see Fig. 4 do not show a correspondingly high S intensity; this is the case of the flesh preparatory color (“proplasmos”/ shadowy areas of flesh parts, see e.g. the face of St John in the central scene, Fig. 4) for which a Ca- and Fe-rich ochre pigment has been presumably employed.

A comparative inspection of the elemental distribution maps of Fe and Mn allows for the distinction of two Fe-rich ochre-type pigments: a) a high-Mn, brownish pigment (presumably umber) used to render St John’s wings, his beard and hair, along with the hair of most of the depicted figures and other dark-brown pictorial elements, and b) a low-Mn yellowish-brown pigment used to paint pale-brown vestments (e.g. St John’s tunic)(Eastaugh et al., 2008). In fact, Fe-rich earth pigments were excessively used in post-byzantine icon painting and previous studies have shown employment of a wide range (in terms of composition and color) of relevant materials in icon painting, while many of these pigments were found to contain Mn too (Bikiaris et al., 2000; Mastrotheodoros et al., 2021; Mastrotheodoros et al., 2022). Interestingly, the Mn-rich areas on the St John icon show enhanced potassium (K) as well which presumably reflects presence of K-rich component (s) in this particular earth pigment: indeed, it is well documented that earthy pigments often contain K-bearing substances such as illite and other phyllosilicate minerals (Fuster-López et al., 2016; Hradil et al., 2003). It is worth noting that considerable K is also detected on the bare wood –i.e. on areas of the panel that have been revealed due to loss of paint and ground/ground– which is something logical given that this element is essential to wood growth (Fromm, 2010).

However, minor amounts of Fe are also detected on the gilded areas of the icon such as the campus (background), the haloes of the holy figures and some vestments (Fig. 4). In these areas titanium (Ti) shows up too; the coexistence of Fe and Ti most probably pertains to the bole/poliment that has been used for attaching the gold leaves (Mactaggart & Mactaggart, 2002), as it is well documented that the various bole-like clayey substances used in this framework were very often Ti-bearing (Grygar et al., 2003; Mastrotheodoros et al., 2018). At this point it is worth noting that the post-byzantine craftsmen used almost exclusively



Scan	Scan parameters					
	Size (mm)	Spot size ( $\mu\text{m}$ )	Step ( $\mu\text{m}$ )	Dwell time (ms/pixel)	Total pixels	Scan time (h)
A	533.0×419.4	100	300	4	2.482.469	3:21
B	104.0×83.3	100	150	4	384.615	0:33
C	60.5×87.9	35	100	5	531.795	0:51
D	20.0×25.5	35	50	5	204.000	0:25
E	4.3×4.9	35	15	8	94.214	0:15

Fig. 2. Left: The areas of MA-XRF scans (rectangles). Right: MA-XRF scan parameters.

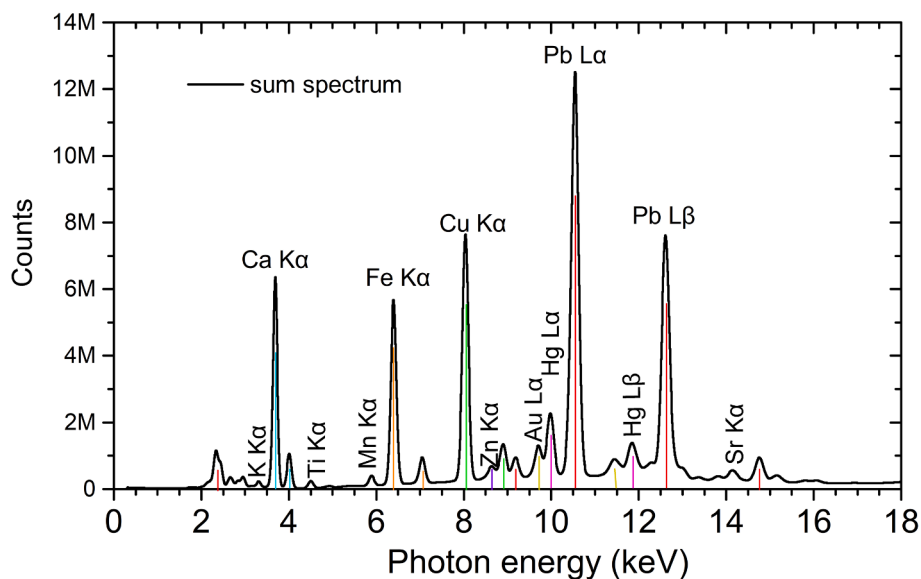


Fig. 3. Sum spectrum, scan A (2.482.469 spectra).

the “water gilding” techniques for embellishing their panel paintings with gold leaves (Dionysios of Fourni, 1996; Mastrotheodoros et al., 2018), while “oil gilding” methods were employed in the corresponding wall paintings (Katsibiri & Howe, 2010; Mastrotheodoros et al., 2019b; Mastrotheodoros et al., 2019).

Mercury (Hg) is detected in most of the intense red areas of the painting (Fig. 4), and the coexistence of S in these very areas clearly suggests employment of red mercury sulfide/ cinnabar, a pigment excessively used in Greek post-byzantine religious painting (Daniilia et al., 2008; Karapanagiotis et al., 2013; Mastrotheodoros et al., 2019a; Mastrotheodoros et al., 2021). Here it is interesting to highlight that the stick kept by St John is rendered in cinnabar, not only in the central figure of the icon, but also in the two small scenes where St Johns is depicted holding it (scenes d & f, see Introduction). Additionally, Hg is detected in various parts of the painting that do not appear red; although under specific circumstances HgS ( $\alpha$ -HgS) can alter to the black-colored metacinnabar ( $\beta$ -HgS) (Gliozzo, 2021), in the current case it seems more probable that minute cinnabar quantities were mixed with various other pigments to render specific pictorial elements (see e.g. the brown wings of St John). Also, minor Hg is detected on the red margin line that surrounds the painting, yet in this case lead (Pb) prevails suggesting that Poulakis opted for the use of a mixture of cinnabar and minium ( $Pb_3O_4$ ) for rendering the margin. The employment of the latter pigment is clearly revealed in the elemental distribution maps because the pictorial elements that are rendered in the –typical for minium– bright orange-red hue show only Pb (FitzHugh, 1986). However, Pb is primarily associated with white/ whitish hues such as the highlights of the flesh parts and the vestments, the walls of the dwellings etc., and probably relates to the excessive use of lead white, which practically was the sole white pigment in use in the pre-18th century panel painting (Eastaugh et al., 2008; Gettens & Stout, 1966; Bomford et al., 1989). The detail of scan “A” that is shown in Fig. 5 highlights graphically the side-by-side use of Pb-white and minium over a cinnabar substrate: the elemental distribution maps of Pb and Hg suggest that the curtain on the right has been painted on cinnabar (HgS) and highlighted using two different colors, i. e. Pb-white and Pb-red. The fact that Poulakis chose this rather complex way for highlighting a very small detail of the icon (note the scale bar in Fig. 5, left) highlights that he was extremely skilled and painted minutely even the smallest details.

In fact, the examination of the data collected through the high-resolution scans of specific scenes/ iconographic details of the artifact allowed for an in-depth understanding of the technical and materials

characteristics of Poulakis painting. To this view, the elemental distribution maps of scene “d” (St John preaching) revealed a couple of very important technical details (Fig. 6). The distributions of Hg and Pb reveal the use of cinnabar, lead white and minium, and highlight some aspects of Poulakis painting manner, such as the rendering of the inscription in HgS, the partial projection of Pb in areas rendered in Pb-free pigment (see e.g. the bush leaves) etc. The Au distribution shows some high intensity areas of irregular shape that correspond to areas of successive gold leaves overlap (Mastrotheodoros et al., 2023). Nevertheless, the cross that embellishes the top of St John’s stick shows a very sharp and characteristic shift in the Au intensity, indicating that this particular pictorial element had received a second gilding in order to be highlighted and differentiated from the gilded background. It is worth noting that partial loss of the second Au leaf has revealed a black-colored substrate (Fig. 6, upper-left) that does not contain elements pertaining to linseed oil mordants (e.g. Pb). Therefore it is assumed that the second Au leaf was attached by employing an organic mordant like processed garlic juice (presumably colored by carbon black), whose production is described in detail in the 18th century “Hermeneia” painting manual (Dionysios of Fourni, 1996). Interestingly, the same black substance is observed on the trunk of the bush where minor Au is detected as well, indicating thus that the trunk had received similar gilded highlights (Mastrotheodoros et al., 2019b). Finally, although the gilded background shows no copper (Cu), in both the aforementioned Au-highlighted details (cross and trunk) minor Cu is detected (Fig. 6, bottom-left) and this is regarded as a sound indication that Poulakis used Au leaves of inferior purity for highlighting purposes; besides, this practice has been already attested in the framework of post-byzantine icon painting (Mastrotheodoros et al., 2018).

The elemental distribution map of Cu is also of high interest as it allows for the differentiation of three distinct Cu-based pigments/ colors: a) a blue used to render the bluish animal skin worn by St John and the vestment of the elder man on the right (crowd), b) a bright green applied over gold leaves in details of the vestments (figures of the crowd on the right), and c) a dark green used to render the bush and the other plants. Interestingly, the two green pigments differ significantly in terms of elemental composition as only the dark green used for rendering the plants contains detectable zinc, barium and arsenic (Fig. 6, bottom). This finding is considered important because these elements may be related to the provenance of this pigment: indeed, it has been already documented that various mineral Cu-based pigments bear detectable trace elements (Smieska et al., 2017; Švarcová et al., 2009; Mastrotheodoros

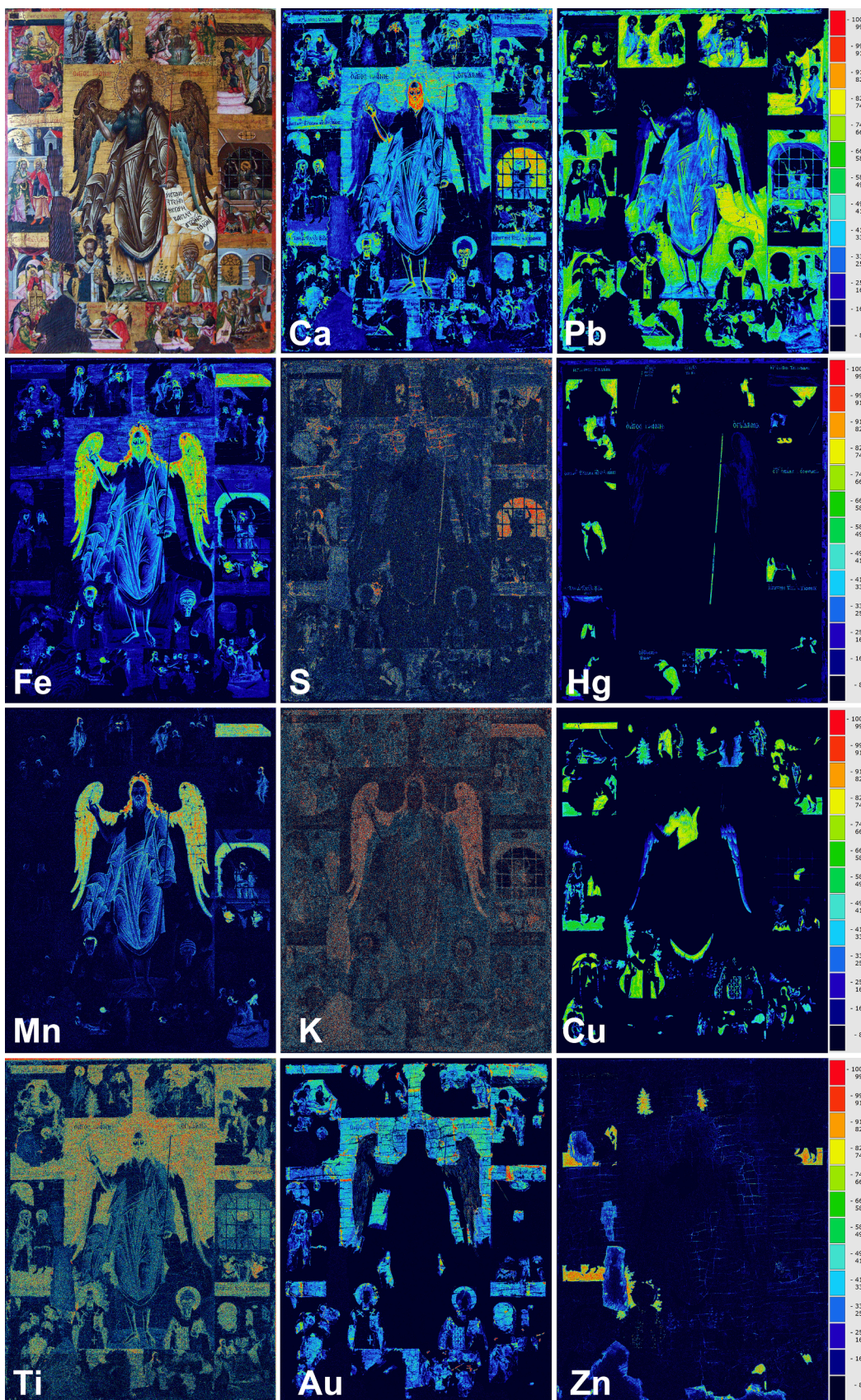


Fig. 4. Scan "A". From upper left to bottom right: the icon under investigation (upper left) and the elemental distribution maps of Ca, Pb, Fe, S, Hg, Mn, K, Cu, Ti, Au and Zn respectively.

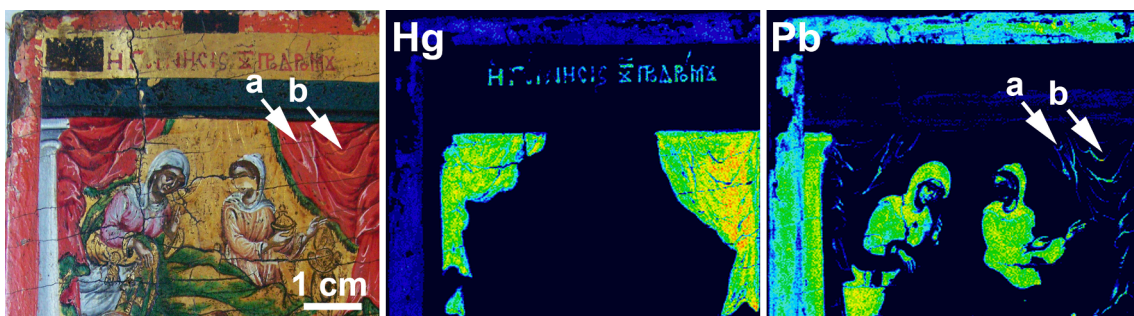


Fig. 5. Left: detail of scene “c” (St John Birth), upper left corner. Middle and right: details of the corresponding elemental distribution maps of Hg and Pb (scan “A”).

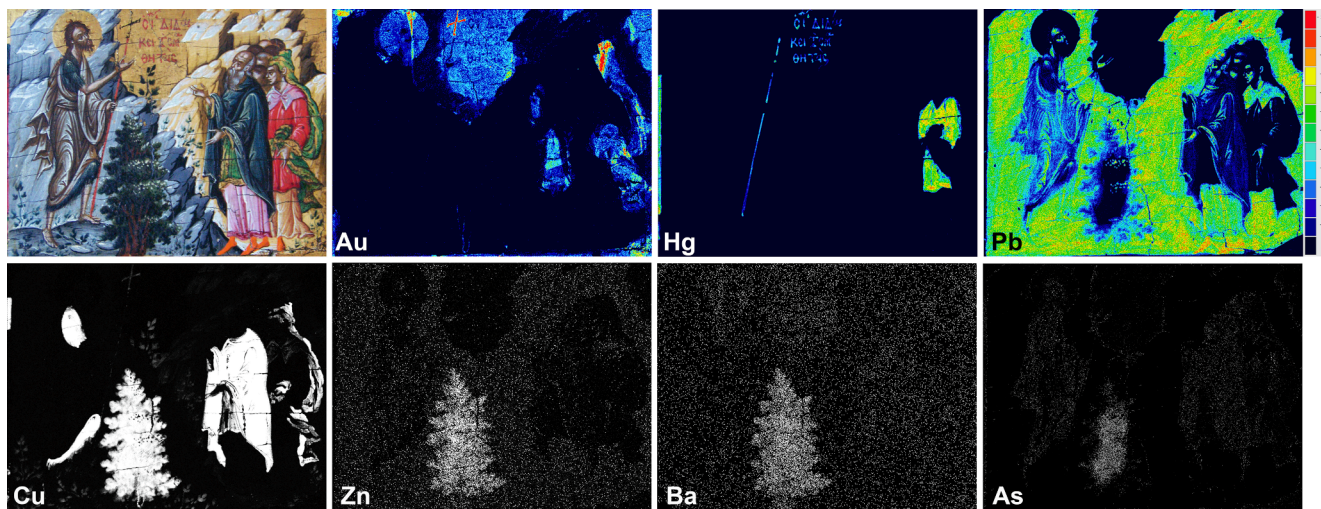


Fig. 6. Scan “B”. From upper left to bottom right: detail of scene “d” and the elemental distribution maps of Au (note the bush trunk), Hg, Pb, Cu (note the cross), Zn, Ba and As.

et al., 2020). On this basis, the detection of trace elements on Cu-based green (and blue) pigments needs to be explored further by examining more paintings, as it may eventually be used for fingerprinting paintings that are ascribed to particular artists or group of artists.

Furthermore, the detection of Zn deserves a special note. As already mentioned, this element is detected in all the dark green Cu-rich areas of

the painting, yet minor Zn is also detected on all the major cracks of the paintings as well as in the areas of paint and gesso losses, where the bear wooden panel has been exposed (Figs. 4 & 7). Interestingly, in the latter areas the Zn distribution shows a strong correlation with the paint losses’ margins and does not show an even distribution on the surface of the wooden substrate. To the authors view, the rather peculiar distribution

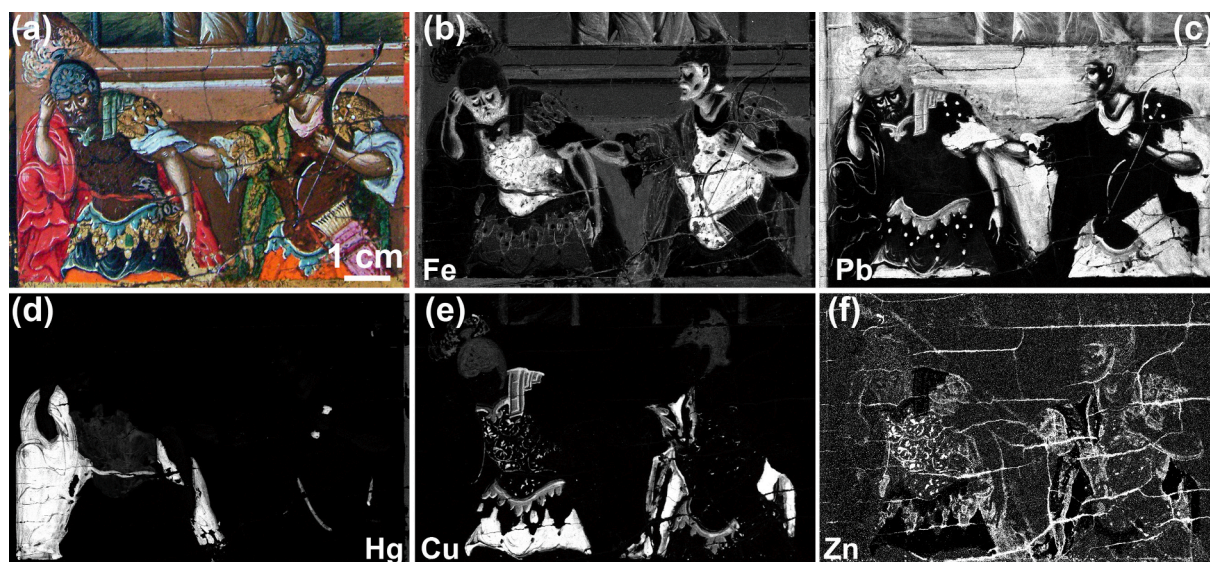


Fig. 7. Scan “C”. (a): detail of scene “g”. (b–f): the corresponding elemental distribution maps of Fe, Pb, Hg, Cu and Zn.

of Zn indicates that its detection pertains to a Zn-bearing conservation material like a consolidant that has been used for stabilizing the edges of the decaying painting. In fact, various Zn components are occasionally used as additives in various commercial animal skin glues and their derivatives (Buck, 1990; Brandis, 2023) which are substances often used for consolidating purposes in the framework of paintings conservation (Schellmann, 2007).

Of interest are also the elemental distribution maps of a small detail of scene “g” (scan C) that depicts two soldiers guarding the imprisoned St John (Fig. 7). The maps of Fe and Pb (Fig. 7b, c) show graphically that Poulakis used a rather detailed incised preliminary drawing, which is revealed thanks to the settling of various pigments within the relevant tracks; the filling of the incisions by paint resulted in a local increase of the paint layer thickness, hence a higher intensity of the corresponding characteristic X-rays (Mastrotheodoros et al., 2023). Yet, on the upper part of the Pb elemental distribution map one may observe that Poulakis did not always follow precisely the preliminary drawing, as the forms of the final highlights (Pb-rich) on St John vestment do not follow precisely the underdrawing. Additionally, the very fine brushstrokes by which Poulakis rendered even the finest details of his painting are highlighted by the elemental distribution maps of details like the one of Hg shown on Fig. 7d. On the latter one may observe that the cords of the sheath, the quiver and the handle of the arrow were all rendered in vermilion. In line with the previous observations about Cu-based pigments, in scan C employment of all the three distinct pigments is documented as well, i.e. a Cu-blue, a Cu-green and a Cu/Zn-green. In particular, the MA-XRF data revealed that the armours of the soldiers had been decorated by the latter green pigment as it is evident by the corresponding elemental distribution maps (Fig. 7e, f); besides, the distribution of Cu and Zn on the armour of the left soldier clearly reveals the very fine and skilfully executed plant motives that are currently invisible to the naked eye.

Furthermore, thanks to the proper evaluation of the MA-XRF data, the employment of at least one type of organic lake pigment has been documented. In fact, the use of lake pigments can be assumed through the macroscopic observation of the painting as there are a series of deep red hues that are strongly reminiscent of organic lakes; this is the case for instance, of the shadowy areas on the red cloak of the left soldier on Fig. 7a. The fact that these areas do not show Fe allows for the exclusion of the use of ochre-type pigments and is indeed an important hint for the employment of lake. In order to further investigate the nature of this dark red pigment, the sum spectra corresponding to two areas that include the same number of pixels (i.e. spectra) were thoroughly compared and revealed that the dark red pigmented area shows considerably enhanced Ca and K (Fig. 8). Both these elements are indeed characteristic of lake pigments as potash alum was one of the most common ingredients for lake pigment manufacturing, while Ca is also very commonly detected in significant amounts in the substrates of these

pigments (Kirby et al., 2005).

Finally, the elemental distribution maps generated through the processing of scan “D” data allowed for a better assessment of the state of preservation of the painting and its conservation history. In fact, the distribution of Cu reveals the existence of a rather extensive crack network on the Zn-free Cu green pigment that has been applied over gold leaf (Fig. 9), while the rather extensive losses of this paint layer appear filled with the aforementioned Zn-bearing substance (probably a consolidant). Moreover, thanks to the very high resolution of this scan, in case of the strontium (Sr) distribution map individual Sr-rich grains can be observed (Fig. 9d). These grains can be probably identified as Celestine ( $\text{SrSO}_4$ ) which is a mineral associated with gypsum (Franceschi & Locardi, 2014), the latter being the typical preparatory material in the framework of post-byzantine iconography (Mastrotheodoros et al., 2016; Mastrotheodoros et al., 2023).

#### 4. Conclusions

The MA-XRF analysis of the Poulakis St John the Forerunner icon in consideration allowed for a thorough investigation of the materials and techniques employed in its manufacturing. The identified pigments include vermilion, lead white, minimum, two distinct ochre pigments, a copper-based blue (possibly azurite), two distinct copper-based green pigments, and a deep-red organic lake. High-purity gold leaves were applied on a bole substrate (water gilding technique) for gilding the background and the haloes of the figures; on the contrary, an organic-based mordant was used to attach inferior (in terms of purity) gold leaves on various details (gilded highlights). Additionally, authors were able to spot some rather idiomorphic technical characteristics, such as the employment of a particular copper-green pigment containing Zn–As–Ba impurities. Also, although the painting is currently considered to be in a very good state of preservation, the MA-XRF data showed that it does suffer from the (partial) loss of some subtle details, like the extremely thin/ small decorative motives and the gilded highlights, which were presumably affected by previous cleaning interventions. Such details are considered extremely important because they can contribute considerably towards assessing the quality and character of Poulakis work. It shall be highlighted that the in-depth investigation of the materials and techniques employed by Poulakis in this painting was achieved through a non-invasive methodology thanks to the extraordinary capabilities of the employed state-of-the-art MA-XRF set-up and the proper handling of the corresponding data. The results collected so far are of utmost importance towards understanding Theodoros Poulakis’s work and set a sound foundation for a forthcoming, extensive, and thorough investigation of the materials and techniques employed in other Poulakis paintings.

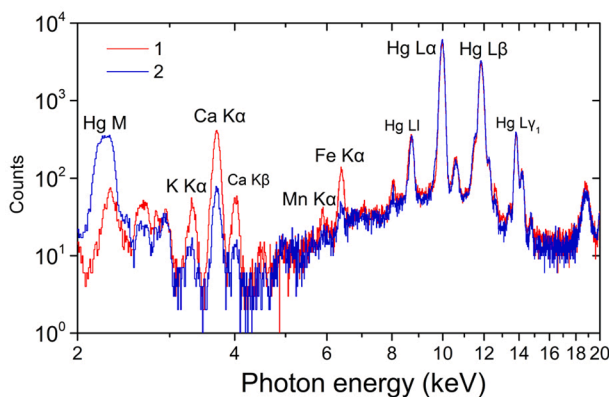


Fig. 8. Left: Overlap of the elemental distribution maps of Pb (white) and Hg (red); the green-highlighted areas 1 & 2 correspond to the areas of the sum spectra shown on the right. Right: sum spectra from areas 1 (red line) and 2 (blue line) shown on the left.

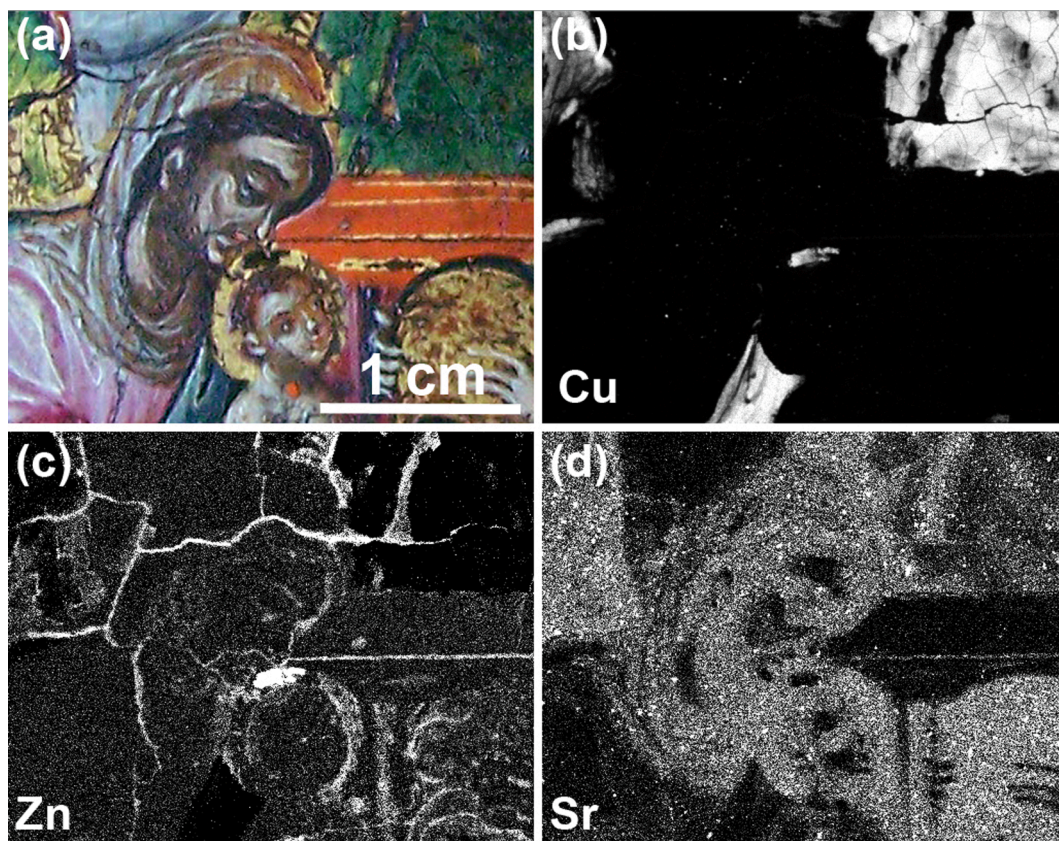


Fig. 9. Scan “C”. (a): macro photo of the scanned area. (b–d): the elemental distribution maps of Cu, Zn and Sr.

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## CRediT authorship contribution statement

**Georgios P. Mastrotheodoros:** Conceptualization, Methodology, Validation, Writing – original draft, Writing – review & editing. **Anastasios Asvestas:** Investigation, Data curation, Visualization, Formal analysis, Validation. **Theofanis Gerodimos:** Investigation, Data curation, Validation. **Anastasia Tzima:** Validation. **Varvara Papadopoulou:** Resources, Validation. **Dimitrios F. Anagnostopoulos:** Resources, Methodology, Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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