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Purple for the δῆμος: Art and Luxury in Greek Coroplastic Polychromy of the 4th–3rd century B.C.

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Abstract

Over recent years, through in-depth technical and art historical studies, the predilection for vibrant colours in Greek art of the Late Classical and Early Hellenistic periods has become evident. The luxurious taste for colour and shine, which makes use of particularly precious varieties of pigments and colourants, has been the subject of several studies; examples include conichalcite and malachite for green, cinnabar and madder for red, gold for yellow, and even shellfish dye for purple. While supports such as plaster, marble, and ivory have been more intensively studied, terracotta has thus far received less attention. This contribution draws attention to polychrome coroplastic production of mainland Greece (Athens, Boeotia and Corinthia) during the 4th and 3rd cent. B.C. Purple, a coveted symbol of divine splendour, heroic value and aristocratic power, appears to be particularly emblematic of this revolution of ‹colour and shine›. Organic colourants, other than brominated compound from shellfish, appear to have been used to produce a palette of luminous, intense purple-red and purple-blue hues. This paper focuses on the use of purples in coroplastic production, including Athenian plastic lekythoi and Tanagra-type statuettes, held in the collections of the National Archaeological Museum in Athens, the Archaeological Museum of Thebes, and the Louvre Museum. The paper presents and discusses the results of the analytical investigations (microscopy, multi-spectral imaging, Raman, XRD, XRF, FORS, FTIR, SEM-EDX, HPLC-MS and LDI-MS), which characterized the materials used on the figurines. In particular, it explores the relationship between the recent finding of an organic purple colourant on the Parthenon sculptures and a 4th–3rd cent. B.C. trend that witnesses a ‹democratization› of the colour purple, which was found to have been used for the representation of clothing of reputedly low-value terracotta figurines.

Keywords: colourant, shellfish, Athens, Boeotia, Tanagra, plastic lekythos, terracotta figurine, madder, Egyptian blue, FORS

Introduction

A symbol of divine splendour, heroic virtue, wealth and power, the colour purple has been coveted for millennia. In the ancient Mediterranean world, the most desirable source of purple was shellfish[1], or, as an ancient Greek audience would have likely called it, *halourgos*, *phoinix* or *alethinoporphyros* (true purple)[2].

While colour terminology is a notoriously complex topic, which falls beyond the scope of this paper,

1 Shellfish such as *hexaplex trunculus*, *bolinus brandaris* and *stramonita haemastoma*.

2 Bogensperger 2017; Brøns 2017.

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many shades of purple are mentioned in the literature and many recipes for their production described in primary sources (e. g. the Leyden and Stockholm papyri)[3]. For example, the juxtaposition between *alethinoporphyros* and *pseudoporphyros* (pseudopurple) or *koinoporphyros* (common purple) is normally interpreted as the evidence for a hierarchy of values, which places shellfish purple at the very top of the scale; true purple could be imitated, but not equalled, by using other sources of purple. The preference for shellfish purple was likely due to its relative colourfastness and intense colour, especially when used to dye textiles[4]. The uses of true purple were, however, not only limited to textiles, and more and more cases of its use as a pigment in painting are coming to light in the archaeological record[5]. The colour purple, alongside other ‹precious colours›, has been discussed in relation to large-scale wall painting production and luxury objects, revealing its privileged role in society[6]. Therefore, given the monetary value and, among other aspects, social, cultural, and political power associated with true purple, it is generally believed that all other sources of purple can only be considered as more economical imitations[7]. However, a more nuanced reading of the primary sources, as well as that of the archaeological record presented in this paper, appears to reveal a more subtle scenario.

As scientific and archaeological discoveries throw light on the cultural nuances of the ancient world, it seems plausible that other sources of purple were appreciated in their own right, for a variety of reasons, and it may be reductive to interpret them as mere surrogates of true purple. The complexity of the analysis lies in understanding the different values associated with the use of different purple sources. One of the issues we encounter when interpreting the ancient record is its scarcity – hardly representative of the complexities of geographically and temporally diverse cultures – even if broadly described under the general umbrella term ‹classical›.

Coroplastic production spans vast expanses of time and space and was used by the commoner and the elite alike, providing a powerful transversal tool to analyse several aspects of societal priorities. Terracotta figurines represent a category of ‹small objects› that were historically held in low esteem by past scholarship on account of their small scale, cheap production technology (clay pressed into moulds and fired at low temperature) and, above all, their mass-production in repetitive series created by anonymous craftspeople. Their polychromy has also been under-investigated by scholars, often described as simplistic, reliant on inexpensive pigments and even carelessly applied. Recent research on ancient Greek coroplastic polychromy contradicts these views and reveals instead a different picture, as shown by the Pilina project, a collaborative project between the Louvre, the Center for Research and Restoration of the Museums of France (C2RMF) and the French School at Athens, and directed by B. Bourgeois and V. Jeammet. Results have proved that these objects were often produced by highly skilled artists; some examples are still remarkably well preserved[8]. In the course of the Pilina project, it became unexpectedly apparent that the colour purple was ubiquitously found across the spectrum of ancient Greek coroplastic production, from archaic seated korai to expensive plastic lekythoi, as well as elegant statuettes of draped figurines of the so-called Tanagrean style. This paper provides a summary of the investigations of a number of terracotta objects from the Archaic to the Hellenistic period and focuses on objects held at the National Archaeological Museums in Athens and Thebes[9]. As comparanda, it also includes objects kept in the Louvre Museum[10].

3 Jensen 2008. Ancient terminology related to colour is notoriously complex. Even modern terminology is not always straightforward. Spectral information will be provided as an objective colour measurement, instead of using descriptive terminology. When necessary, however, and to reduce subjectivity, the only distinction made here will be between purple-red and purple-blue, indicating hues where either blue or red appear dominant. Terms such as violet, which instead denotes a spectral colour, as well as mauve, lilac, lavender, etc. will be avoided for the sake of simplicity. See, for example, Martínez García 2013 for the complexities related to the interpretation of ancient terminology.

4 Daniels 2007; Cardon 2007; Kalaitzaki et al. 2017.

5 Karapanagiotis 2019; Verri et al. 2019.

6 Brecoulaki 2014.

7 E. g. Martínez García 2013.

8 For a more detailed presentation of the *Pilina* project, see Bourgeois et al. in this volume. See also Bourgeois –Jeammet 2020 and Bourgeois et al. 2019.

9 Objects in Athens National Archaeological Museum are designated by EAM and inv. number.

10 Bourgeois et al. in the same volume.

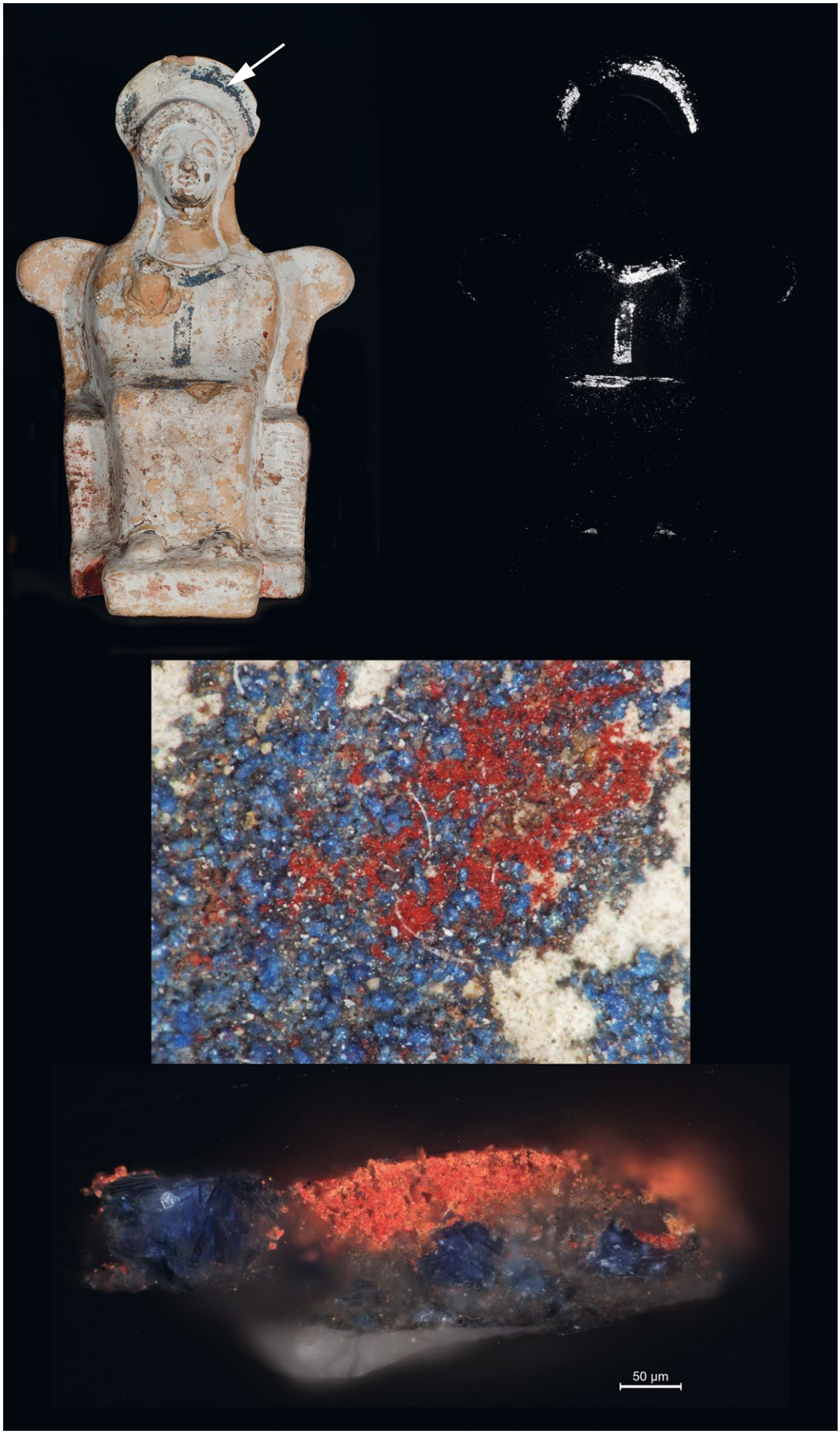
Presentation of the Results

Based on the analytical investigation, two categories of purple were identified: 1) an optical purple, obtained by mixing or layering blue and red compounds, and 2) purple colourants, divided into four types (unidentified types I, II, III, and an anthraquinone of vegetable origin) according to their Raman and apparent absorbance spectra. For each category and type, a number of significant cases are presented here. Figures 1–14 show the figurines that were found to contain a purple colour, alongside details of the paint layer and, where available, a cross section, SEM-EDX and XRD information. Figure 15 shows instead the apparent absorbance spectra, stacked for clarity, of the purple paint layers, divided by type. Finally, Figure 16 shows three representative Raman spectra for the compounds identified as Types I, II and III; all other Raman spectra of objects belonging to each group are virtually identical. The apparent absorption and Raman spectra were compared with solid-state standards of known composition and which were possibly available in Greece in antiquity[11], but no convincing comparisons were found: these include shellfish purple[12], folium[13], orchil[14], alkanet[15], cochineal[16], kermes[17], lac[18], madder[19], safflower[20], anthocyanins[21], betacyanins[22], and carotenoids[23]. One sample (EAM 4999) was successfully identified as an anthraquinone of plant origin, as presented below. Although unlikely, the presence of gold is currently being tested using a synchrotron[24].

In the following descriptions, the term ‹matrix› is used to describe a very fine-grained structure identified here as the binding medium, in reference to the ‹limewater technique›, in which calcium hydroxide in water (?) is used to bind pigment particles, as described by Bourgeois et al. in the same volume. By contrast, pigment particles made of carbonate compounds will be identified as such, to differentiate them from the finely grained neoformed calcium carbonate created by using the limewater technique. Carbonate particles correspond to the deliberate addition of crushed carbonate compounds of geological origin, such as limestone or marble, or biogenic origin, such as aragonite from seashells.

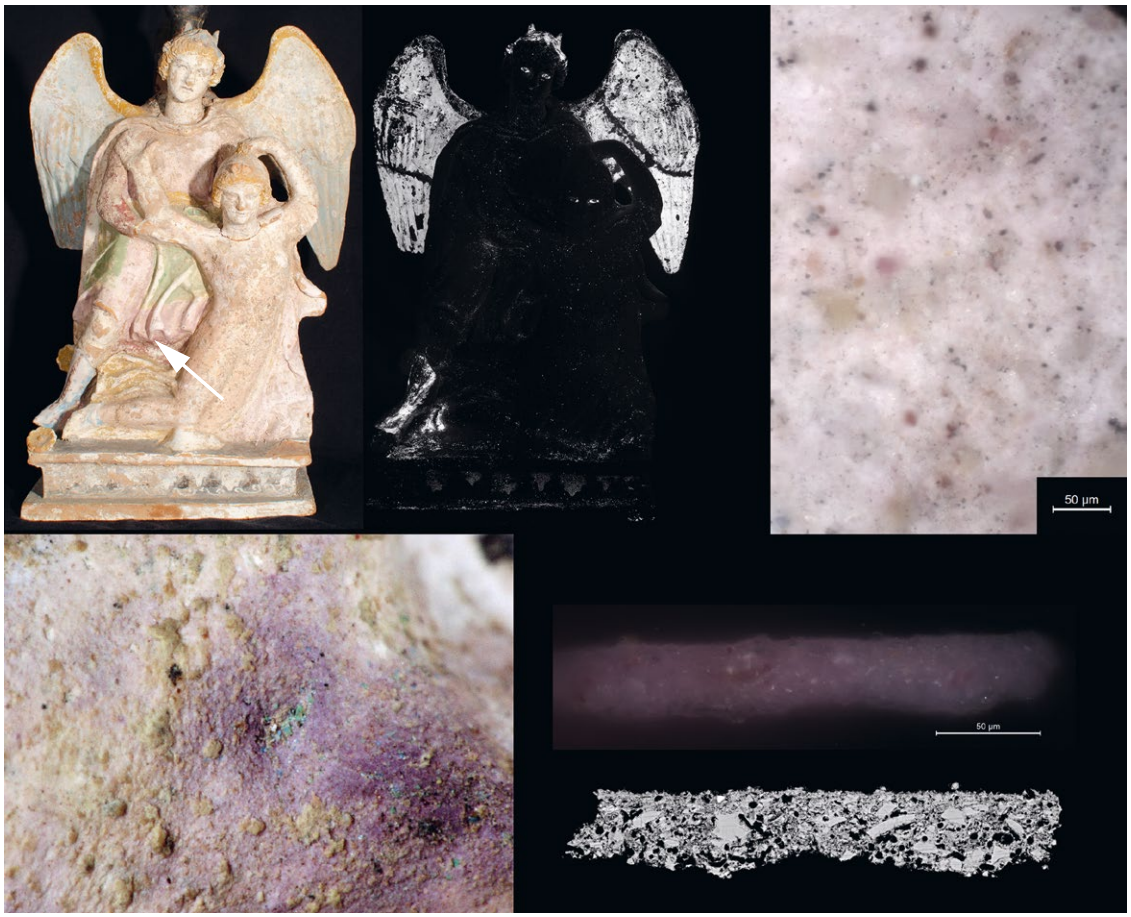
No bromine was detected with XRF and SEM on any of the samples analysed, making true purple an unlikely candidate in all cases presented below.

11 Aceto et al. 2020; Aceto et al. 2014; Spantidaki 2016.
12 Mostly 6,6'-dibromoindigo.
13 *Chrozophora Tinctoria* (L.) *A. Juss.*
14 *Roccella Tinctoria* and *Lassalia Pustulata*.
15 *Alkanna Tinctoria* (L.) *Tausch*.
16 *Porphyrophora Hamelii Brandt*.
17 *Kermes Vermilio* and related species.
18 *Kerria Lacca* and related species.
19 *Rubia Genus*.
20 *Carthamus Tinctorius* L.
21 Pelargonidin, Cyanidin, Peonidin, Delphinidin, Petunidin, Malvidin. Although non-lightfast and not purple in alkaline environments, anthocyanins can show absorptions at c. 550 nm (Melo 2008). Elderberry was found on the Codex Rossaniensis (Bicchieri 2014) and various plant materials are mentioned in the Stockholm papyrus (e. g. ‹moron›, which is possibly bilberry [*Vaccinium Myrtillus* L.], in Recipe 100).
22 E. g. Betanin Group in *Beta Vulgaris*.
23 E. g. Axtaxanthin, as found on many organisms, including marine.
24 In addition to the options listed above, the presence of gold nanoparticles of a purple colour was initially considered as a possibility. Deterioration of metallic gold, such as gold foil, has been reported on archaeological objects (Piening 2013; Spadavecchia et al. 2014; Albéric et al. 2015). Nanoparticles of gold can show absorption spectra similar to the ones observed in this paper. However, the spatial distribution, morphological characteristics of the paint layer and the absence of gold in the XRF and SEM-EDS spectra (it should be noted that if present in very small concentration, gold may not be detectable with these techniques) do not support the presence of degraded gold. Nonetheless, although highly unlikely, the presence of gold is currently being tested using a synchrotron.

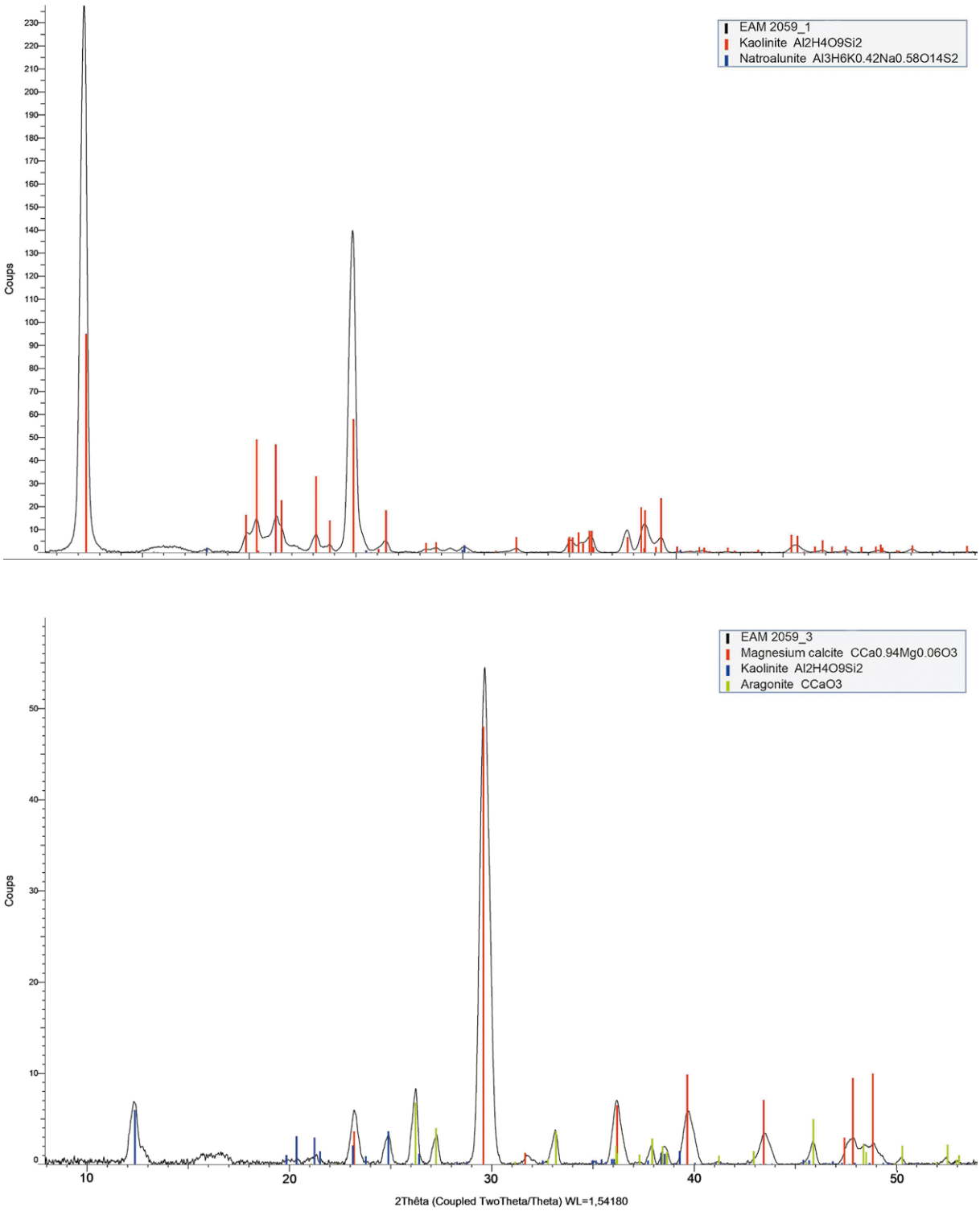


1 EAM 3972, Seated woman and detail under magnification. Visible and visible-induced luminescence images. The arrow indicates the sampling location for the cross section.

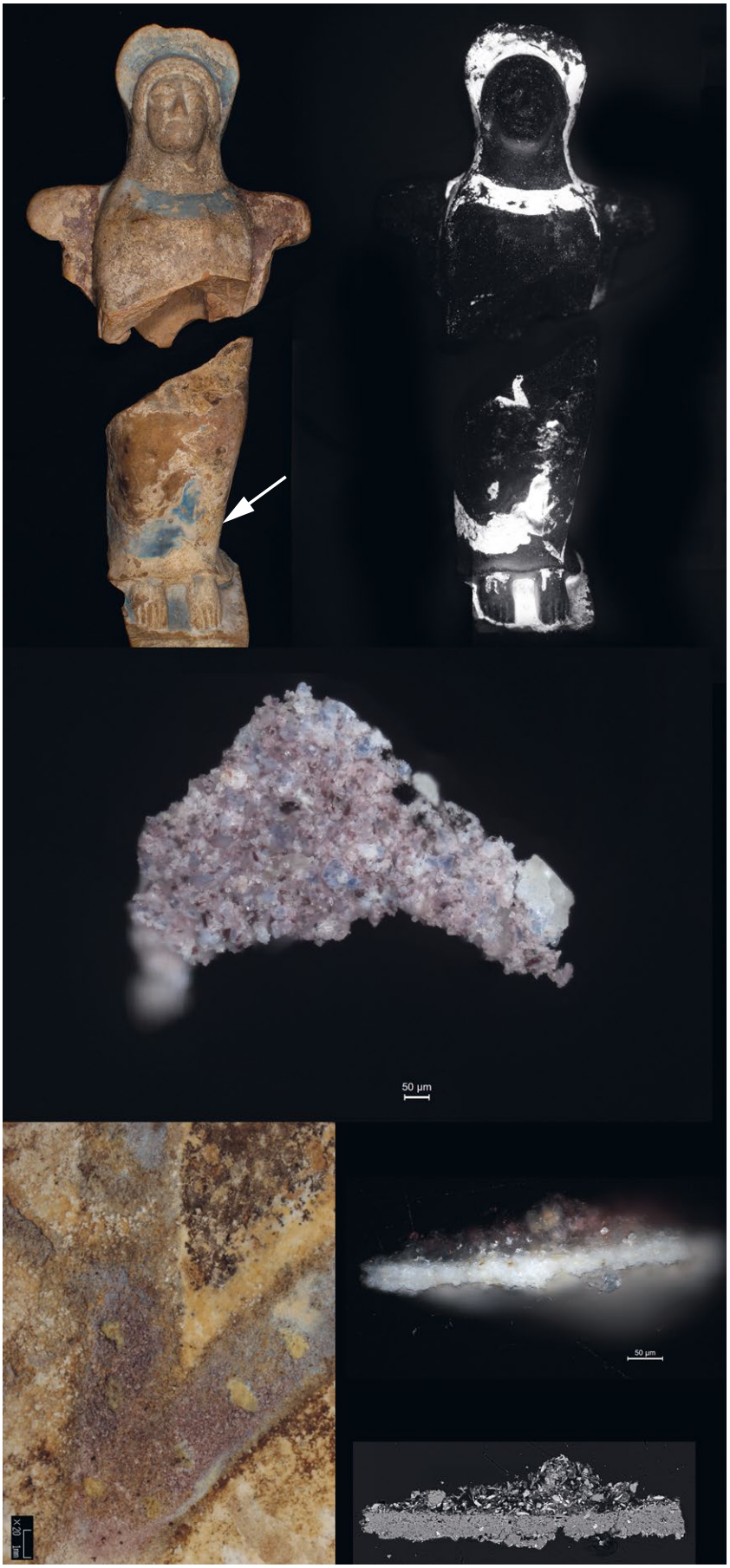
2 EAM 4999, Aphrodite leaning on an archaizing sculpture and detail under magnification. Visible and ultraviolet-induced luminescence images. The arrow indicates the sampling location for the cross section.



3 EAM 2059, *Daimon* abducting a woman and details under magnification. Visible and visible-induced luminescence images. The arrow indicates the sampling location for the cross section, which was also analysed with an SEM.



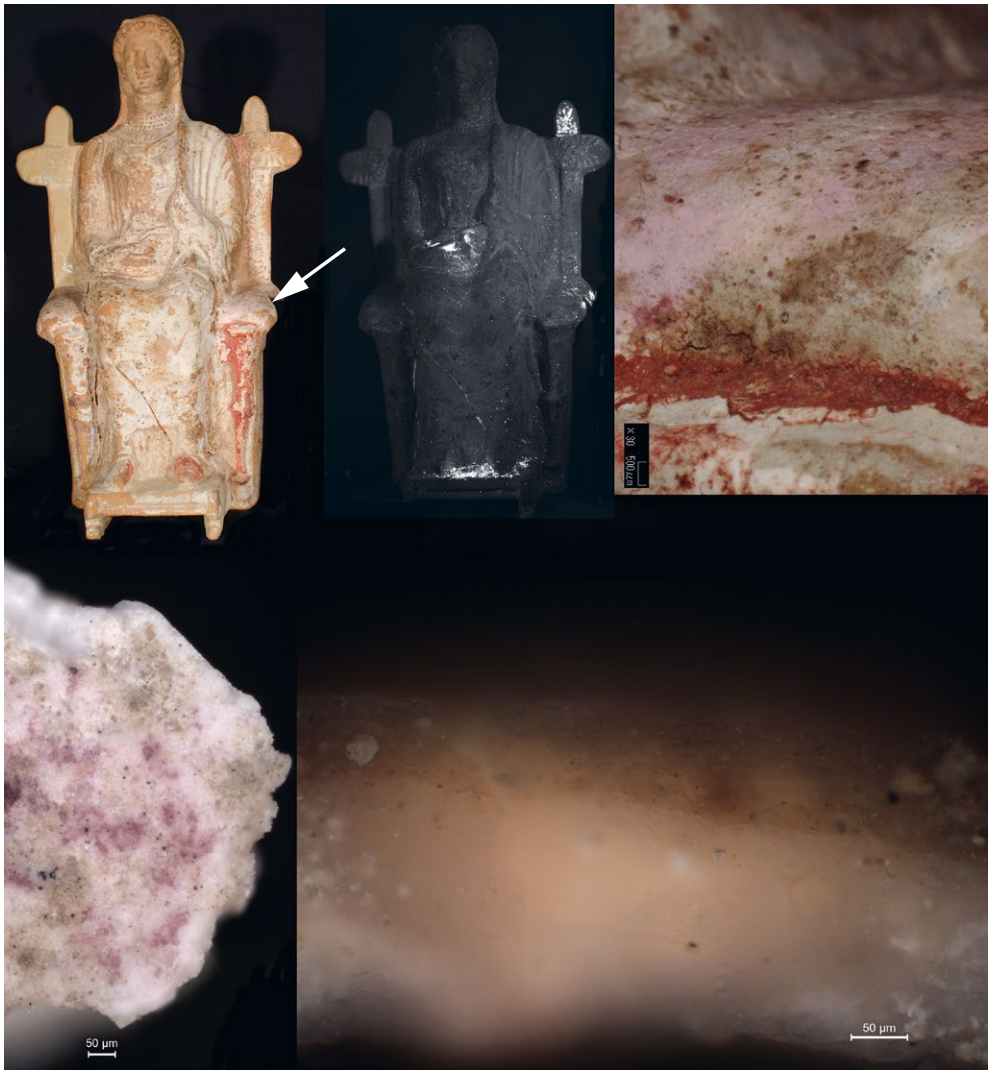
4 EAM 2059, XRD analysis of (top) a pink and (purple) particle



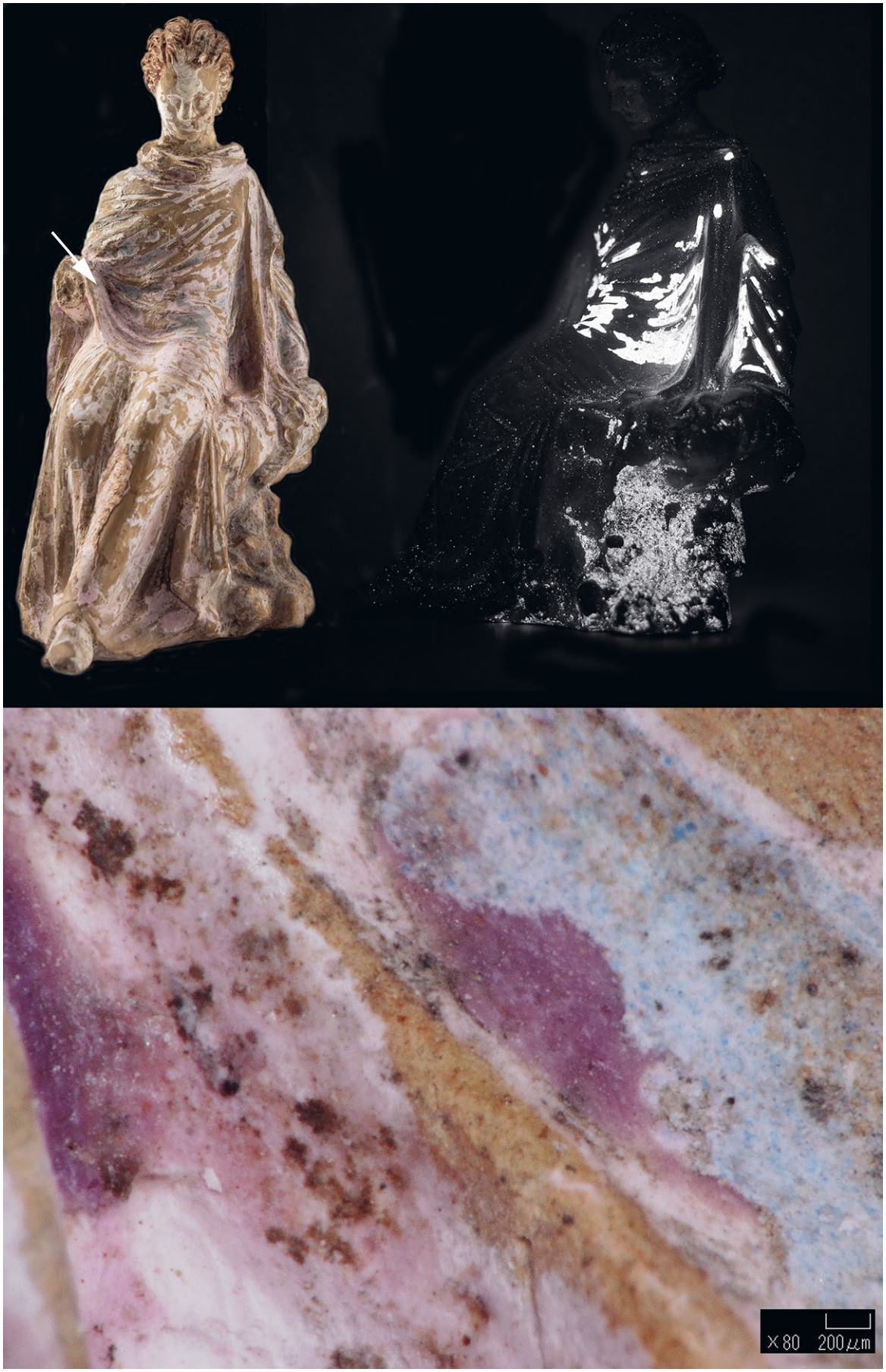
5 EAM 32064–32067, Seated woman and detail under magnification. Visible and visible-induced luminescence images. The arrow indicates the sampling location for the cross section, which was also analysed with an SEM.

6 EAM 2060, Aphrodite in a shell and detail under magnification. Visible and visible-induced luminescence images

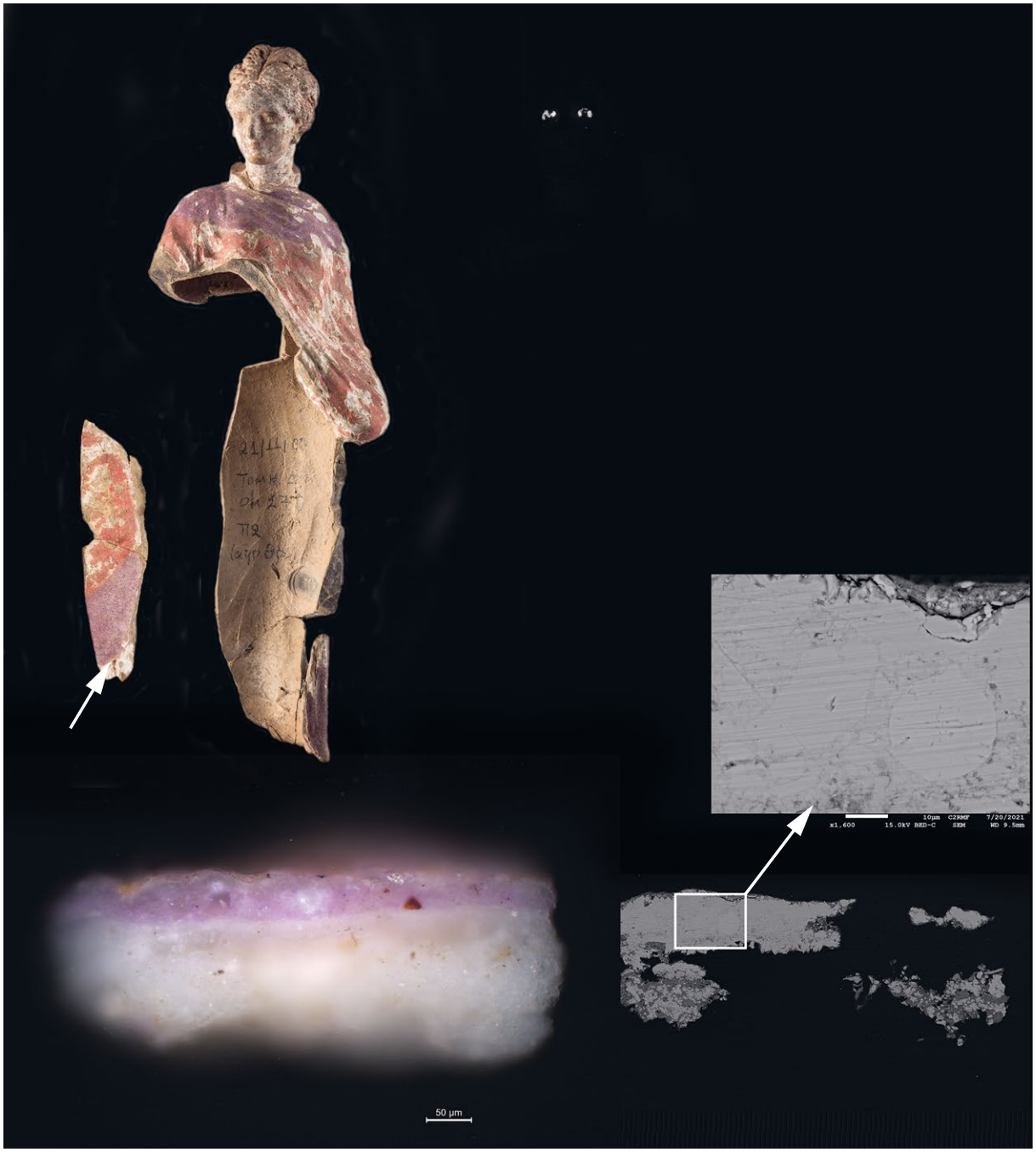
7 EAM 4163, Aphrodite leaning on a pillar and detail under magnification. Visible and visible-induced luminescence images



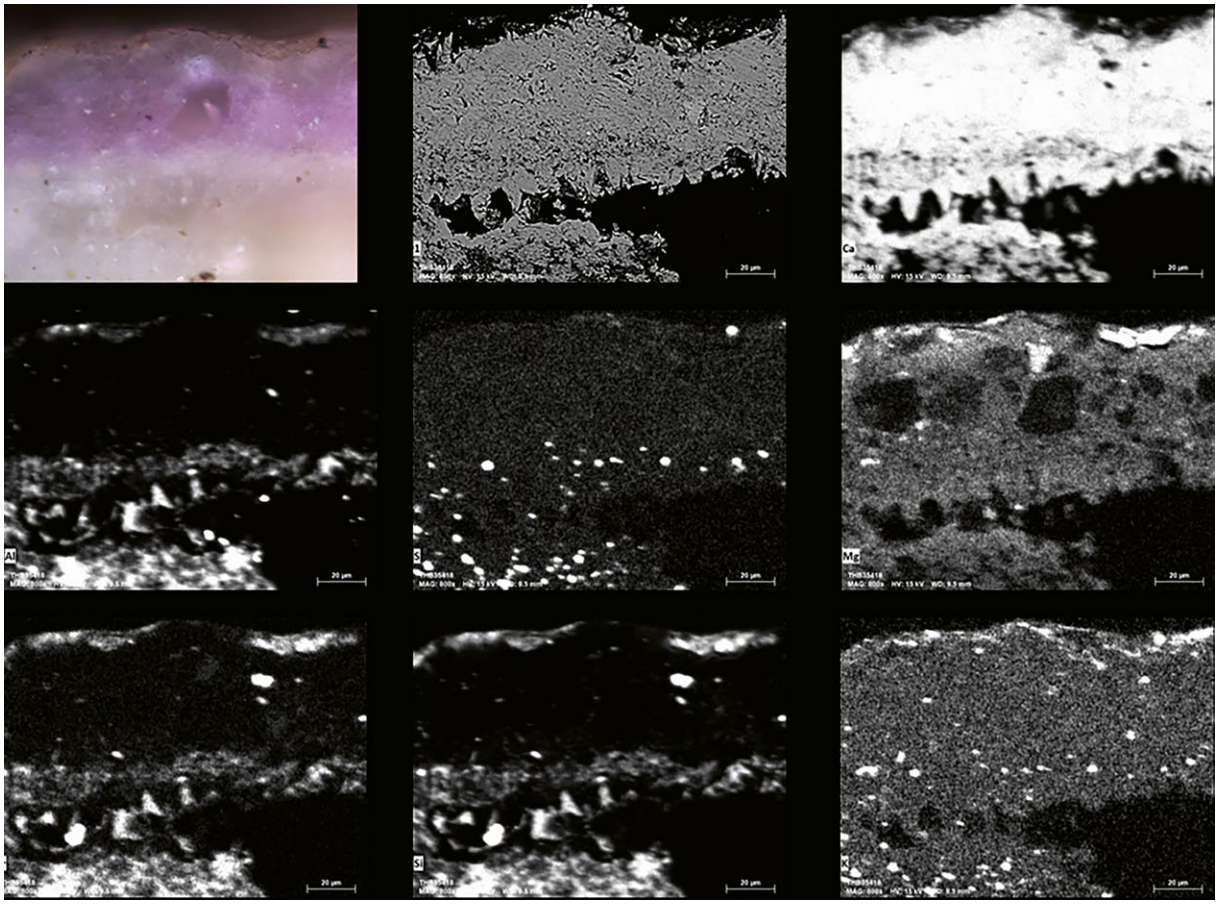
8 EAM 19367, Enthroned Aphrodite and detail under magnification. Visible and visible-induced luminescence images. The arrow indicates the sampling location for the cross section.



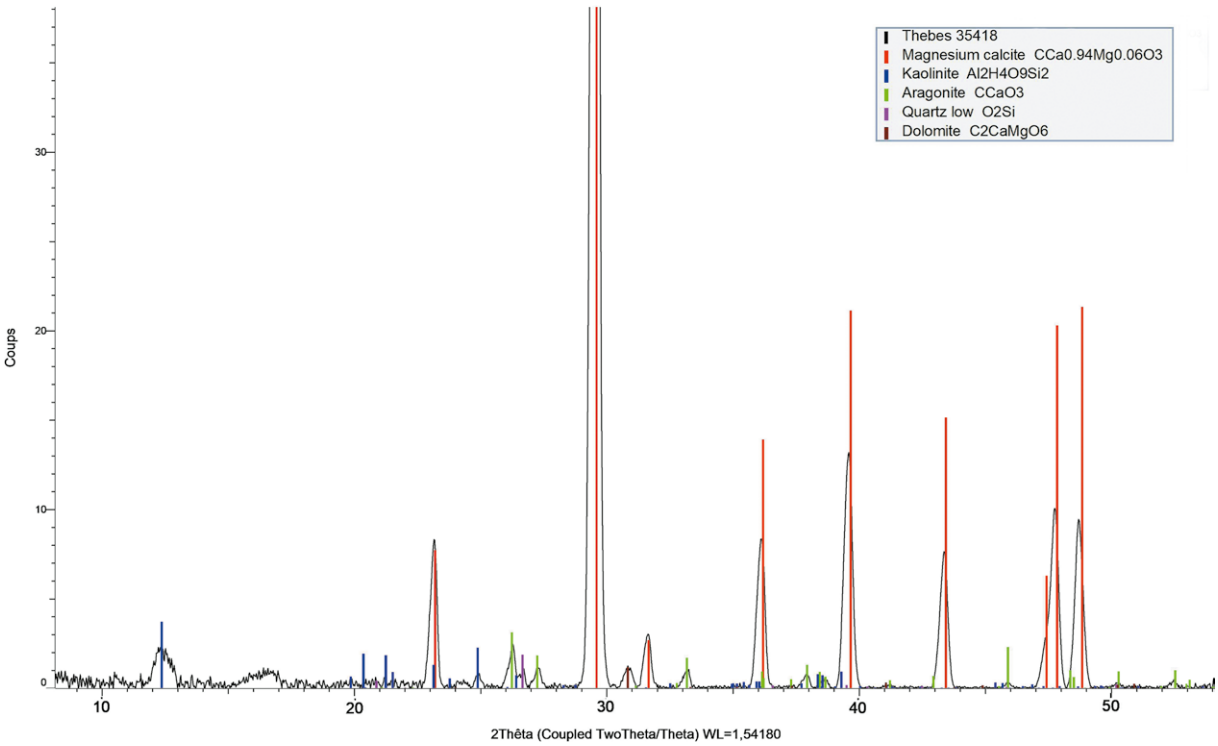
9 EAM 4041, Seated woman and detail under magnification. Visible and visible-induced luminescence images. The arrow indicates the area of the detail.



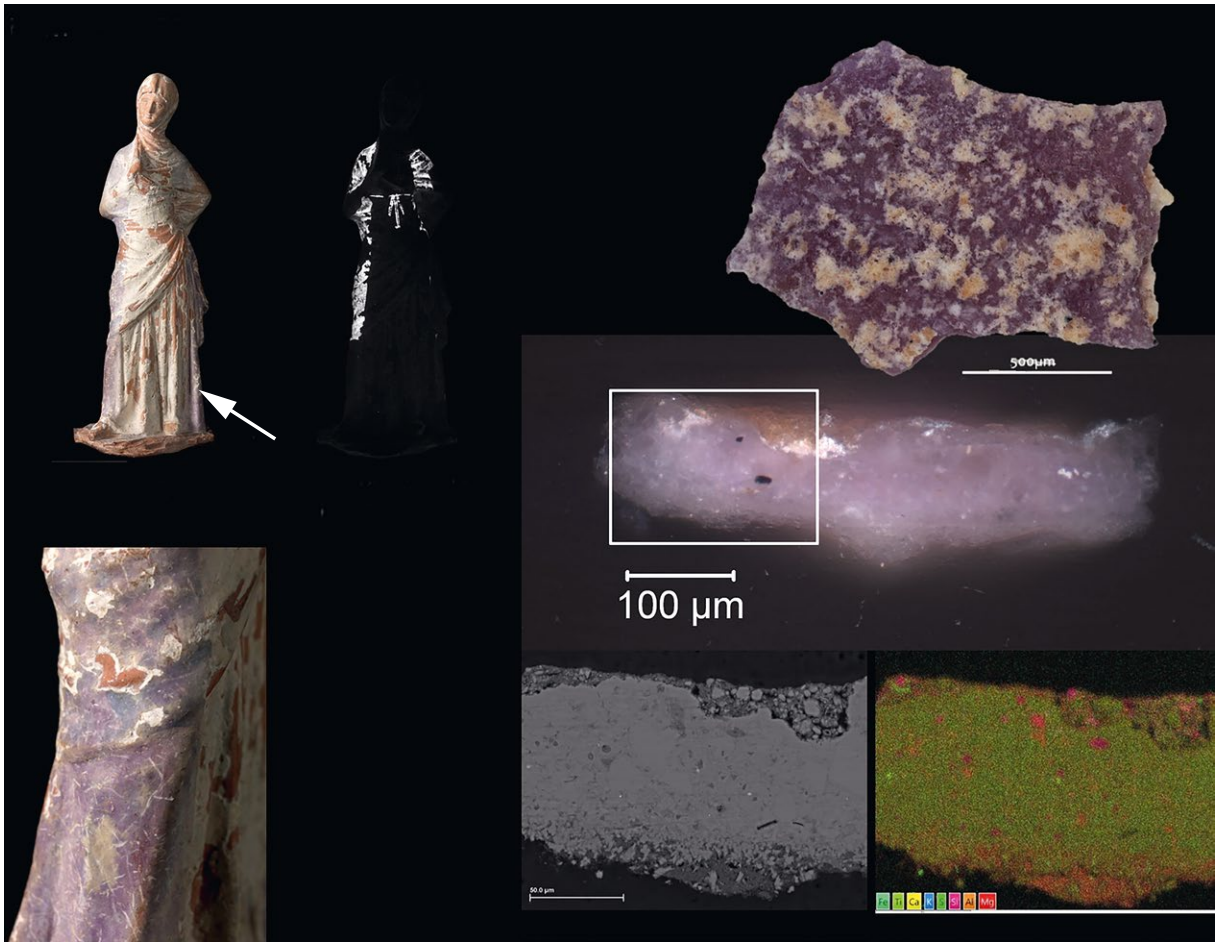
10 Thebes 35418, Standing woman and detail under magnification. Visible and visible-induced luminescence images. The arrow indicates the sampling location for the cross section, which was also analysed with SEM.



11 Thebes 35418, Standing woman. SEM-EDS maps of the cross section: (from top to bottom and left to right) visible, backscattered-electron image, calcium, aluminium, sulphur, magnesium, strontium, silicon and potassium.



12 Thebes 35418, Standing woman. XRD spectrum of the purple layer



13 Louvre MNB 584, Standing woman and detail under magnification. Visible and visible-induced luminescence images. The arrow indicates the sampling location for the cross section, which was also analysed with SEM. A colour-coded EDS map of the cross section is also reported.

Category 1: ‹Optical Purple›

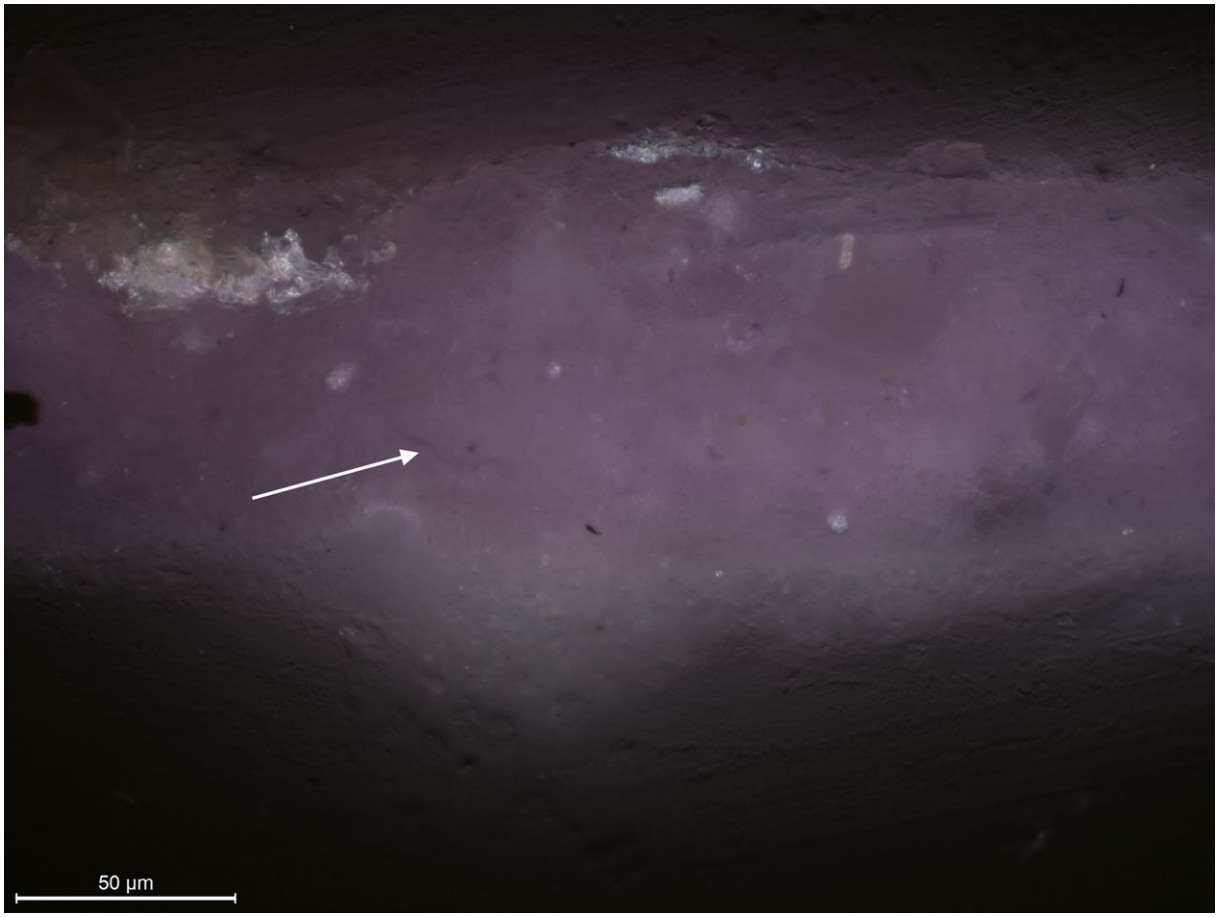
Of the approximately 260 artefacts examined and/or analysed, only a handful of figurines bear traces of purple that resort to this type of painting process. Some examples will be discussed in what follows.

EAM 3972 (Fig. 1), found in a necropolis near Eretria, attributed on stylistic grounds to an Attic workshop and dated to 520–490 B.C., represents a seated woman (a goddess?), wearing a dress decorated with blue and purple borders and a polos, also enriched with a purple band[25]. The purple colour was achieved by applying a fine-grained layer of cinnabar mixed with calcium carbonate particles and some quartz grains, over coarsely ground Egyptian blue, which is also applied as a mixture with calcium carbonate particles. These paint layers are applied over a white preparation layer, made of calcium-magnesium carbonate particles with aluminosilicates.

The so-called Sophoclean Lady at the Louvre shows a similar type of optical purple (not presented here). This large statuette of a standing woman draped in a broad mantle is attributed to a Tanagra workshop and dated to the years 330–300 B.C. (Louvre, inv. MNB 585)[26]. In spite of the poor condition of its polychromy, it was possible to observe under the microscope traces of a purple border on the mantle. SEM analysis showed a layer of Egyptian blue, mixed with some grains of car-

25 Vivliodetis – Avronidaki 2013, 9 f.

26 Jeammet 2010, 112 f. no 83. In the same volume, see Bouquillon et al., 228–231. 269 for the clay analysis and the attribution to a Tanagra workshop.



14 Louvre MNB 584, Standing woman. Cross section showing filament-like concentrated purple colourant.

bon black and kaolinite, covered by a purple-red layer containing kaolinite and an organic colourant, possibly madder, based on its distinctive orange emission when illuminated with ultraviolet radiation.

Mixtures, as opposed to layers, of red and blue particles were another way of producing optical purples. This practice was popular during the Late Hellenistic period. A particularly good example can be found in a bust of Aphrodite (not presented here), produced in Myrina (present day Turkey) during the 2nd cent. B.C. and now held in the Louvre (inv. Myrina 661)[27]. The thin chiton of the goddess was painted with a vibrant purple-blue colour, made of a mixture of Egyptian blue and madder[28].

Small and medium-size marble sculpture of the 2nd and 1st cent. B.C. in Delos (Cyclades) also show the frequent use of such mixtures[29]. Later on, this type of purple is commonly found in paintings, such as for example in mummy portraits from Egypt, where madder and indigo or Egyptian blue were used to achieve an optical purple, especially for the representation of textiles[30].

27 From the excavations of Myrina necropolis, conducted by E. Pottier and S. Reinach in the years 1880–1882. See Besques 1963, 34.

28 Jeammet et al. 2010; Jeammet et al. 2007 (Raman spectra).

29 Bourgeois et al. 2007; Bourgeois – Jockey 2010.

30 E.g. Verri 2009.

Category 2: Purple Colourant

In the corpus of objects studied within the framework of the Pilina project, the use of organic colourant(s) is much more frequent than the use of optical purple. It involves a well-known colourant already mentioned, madder, and a still unidentified colourant(s) (or mixture of colourants?).

Unidentified Purple Colourant

A number of objects were found to have been painted with a pale-to-intense purple paint, whose composition will be discussed here. Objects in this category belong to various iconographical types of different periods. They include a Late Archaic figurine of a seated woman or goddess (EAM 32064 and 32067; Fig. 5), a late 5th cent. B.C. statuette of an enthroned Aphrodite (EAM 19317; Fig. 8), 4th cent. B.C. plastic lekythoi such as EAM 2059 (Fig. 3) and 2060 (Fig. 6), as well as Louvre CA 1131 (not reported here). Additionally, numerous draped female figurines of the early Tanagrean style, for example, a seated woman (EAM 4041; Fig. 9), standing women Thebes 35418 (Figs. 10–12), and standing women Louvre MNB 495, MNB 572, MNB 581, MNB 584 (Figs. 13. 14)[31].

Raman and absorption spectroscopies allow for this group to be subdivided into three types (Type I, Type II and Type III) with similar Raman bands, which are possibly related to one or more organic compounds, whose origin could not be identified (Figs. 15. 16). The similarity of the spectra is tentatively interpreted here as possibly corresponding to a single compound, or a family of similar compounds, perhaps colourant(s) extracted or prepared in different ways from the original source(s), which might explain the slightly different position of Raman and absorption bands. Chemical degradation could also be involved. However, it remains unclear if the compound(s) do correspond to a purple colourant or some other compound extracted or mixed with (?) the colourant that imparts the purple colour. Further characterization of the compound(s) is based on other investigations, as discussed below.

Type I

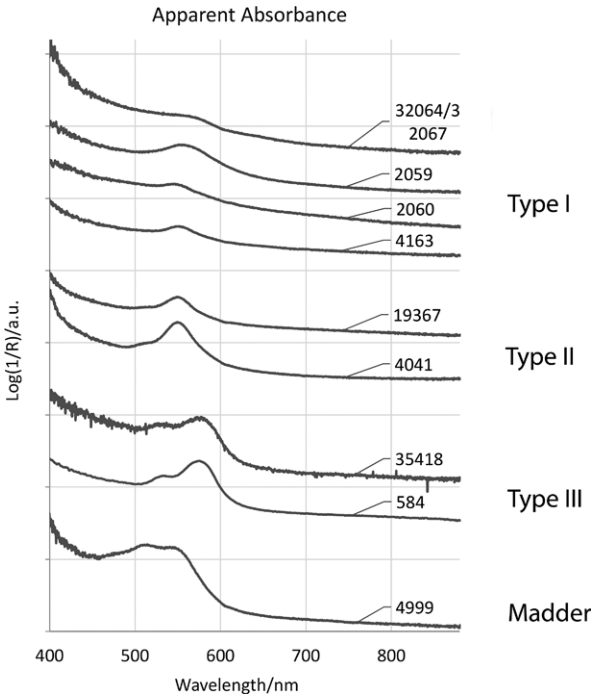
Four examples of unidentified purple Type I are presented here. While this purple colour is most accurately described by its absorption spectrum, which shows a major absorption peak at c. 550 nm, it appears as a light purple red (Fig. 15).

Fragments EAM 32064 and 32067 (Fig. 5) show a female (goddess?) figure from Eleusis (?), dated to 520–490 B.C., wearing a dress with elaborate blue and light purple-red bands, embellished by a white meander pattern. A light purple red was found on two elaborate Attic plastic lekythoi unearthed from the same tomb in Tanagra[32]. EAM 2059 represents a winged *daimon* abducting a woman, while EAM 2060 depicts Aphrodite *anadyomene* (Figs. 3. 6); both are dated to c. 400–375 B.C. The *daimon* wears a light purple-red and green tunic, while Aphrodite is surrounded by a light purple-red textile billowing behind her, as she emerges from the wavelets of the sea. EAM 4163 (Fig. 7), produced in Corinth, and dated to c. 350–300 B.C., represents a standing Aphrodite leaning on a pillar. She wears a broad mantle decorated with light purple-red bands.

In all cases, the light purple red is characterized by small, glossy and translucent particles similar in visual appearance to an organic colourant, without any perceivable UV-induced luminescence.

In the case of EAM 2059 (Fig. 3), unidentified purple Type I is applied in two layers: a pale purple underlayer containing kaolinite and a dark purple layer within a calcium carbonate-rich matrix, containing small amounts of magnesium, some grains of kaolinite with other impurities (iron and titanium oxides), and the presence of aragonite[33]. The latter can nucleate in several circumstances (geological spar, rocks, sediments, organisms, wood ash, and lime plaster). However, as it corresponds here to the larger and mostly angular individual particles (between 10 µm and 20 µm) with trace amounts of strontium and no traces of magnesium, the presence of aragonite could be interpreted as related to the use of seashells or snails fragments. Whether the presence

31 On the Louvre objects CA 1131, MNB 495, MNB 572, MNB 581 and MNB 584, see Bourgeois et al. in this volume.
32 Karouzou 1971; Trumpf-Lyritzaki 1969, FV 132.
33 Aragonite is the orthorhombic polymorph of calcium carbonate; see Toffolo 2020 for detailed discussion on archaeological carbonates.



15 FORS Spectra of the various types of purple characterized in this study

of aragonite is related to the purple colour or not remains unclear. The presence of a calcite-rich matrix likely corresponds to the use of a lime-based painting technique, as discussed by Bourgeois et al. in this same volume.

In the case of EAM 32064–32067 (Fig. 5), the purple paint layer is composed of a mixture of purple particles with Egyptian blue, aluminosilicates, quartz, and few particles of sodium aluminosilicates. The purple layer is applied over an aluminosilicate-rich preparation layer. In this case, where a carbonate-rich matrix was not observed, an organic binder was probably used to apply the purple mixture.

When looking at a larger artistic context outside the coroplastic field, it is worth mentioning that purple Type I was used on Classical marble pyxides (A11372, and likely on A11363; not presented here), also in the collections of the National Archaeological Museum of Athens[34], for both the representation of textiles and vegetation.

Type II

Unidentified purple Type II shows a Raman spectrum very similar to that of purple Type I, perhaps indicating that the two types are chemically related, or that they contain a common compound responsible for the Raman spectrum. The absorption spectrum is also very similar to Type I, with a major apparent absorption at c. 550 nm, but with the addition of a small shoulder at c. 515 nm (Fig. 15).

EAM 19367 (c. 400 B.C.; Fig. 8) and EAM 4041 (c. 330–200 B.C.; Fig. 9) show an Attic enthroned Aphrodite and a seated woman from Tanagra, respectively. In the case of EAM 19367, Aphrodite is sitting on a cushion decorated with light purple-red and white stripes, while the woman represented in EAM 4041 is elegantly wrapped in a light purple-blue mantle bordered in a vivid purple-blue colour.

While the application of the purple colour is extremely thin for EAM 19367, microscopic examinations of EAM 4041 clearly reveal that the colourant is used as a thick but translucent purple glaze, applied above a pink paint layer. Purple-blue areas on the same figurine are the result of the layering of Egyptian blue above the purple colourant. It can be noted that the c. 515 nm absorption is located where one of the two characteristic absorptions of anthraquinones of plant origin, such as madder, is observed[35]. The presence of this absorption may therefore be indicative of a mixture of colourants, including madder. However, this interpretation is not conclusive, as the shoulder at c. 515 nm may also be the result of a different extraction method from the same source as Type I, resulting in a slightly different hue and a more structured apparent absorption. At this stage of the research, it remains impossible to unequivocally identify the colouring matter.

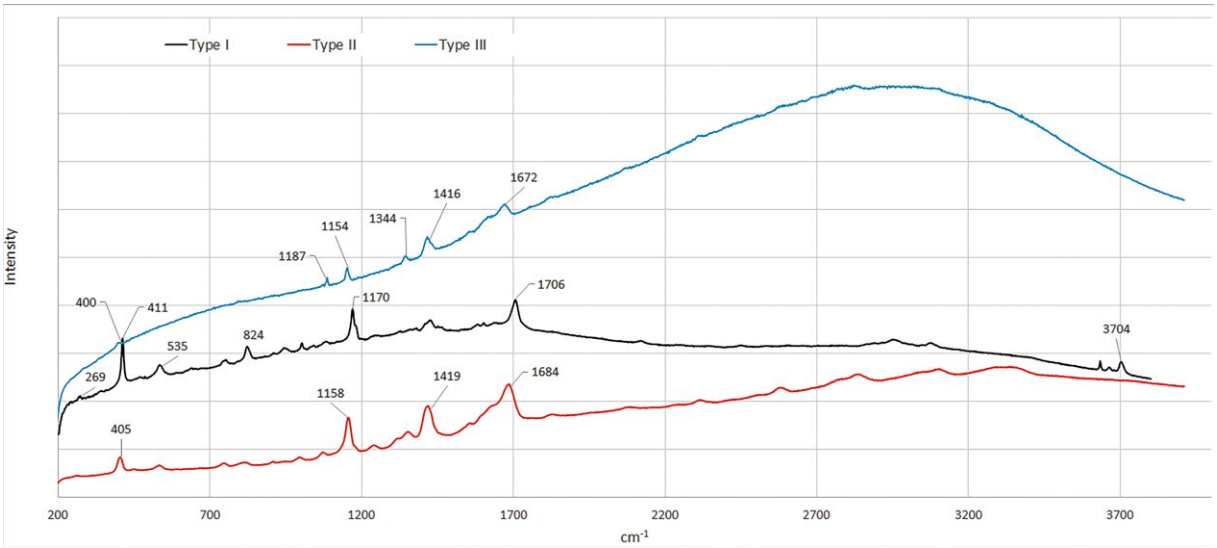
Type III

Two examples of unidentified purple Type III are illustrated here. While this purple colour is most accurately described by its absorption spectrum, which shows two major absorption peaks at c. 535 nm and 575 nm, it appears as a vivid purple blue. The Raman spectrum of Type III shows similarities to Type I and II, albeit with some differences in the position of the peaks (Figs. 15. 16).

Thebes 35418 (Figs. 10–12) represents a standing woman wrapped in a voluminous red mantle bor-

34 Brecoulaki – Verri forthcoming; Brecoulaki et al. 2014.

35 Bisulca et al. 2008.



16 Representative Raman spectra for the three types of purple: Type I (EAM 2059), Type II (EAM 19367) and Type III (Thebes 35418)

dered in a vivid purple-blue colour. Found in the recent Greek excavations of a Theban necropolis, in Tomb B 158, the figurine is likely from a Boeotian workshop and is dated to c. 300–250 B.C.[36]. Another probably Theban piece, said to have been found in Tanagra in the late 19th century and now in the Louvre collection (inv. MNB 584), represents a standing veiled woman wearing a dress and mantle ornamented with lateral purple bands; a date around 330–300 B.C. has been suggested on the basis of technical and stylistic features (Figs. 13. 14)[37].

As for the previous type, purple Type III is glossy and translucent, similar in visual appearance to an organic colourant, without any perceivable UV-induced luminescence. The paint layer is applied above a white preparation layer, rich in kaolinite with calcium and magnesium carbonate particles. Similarly to EAM 2059, the purple colour in Thebes 35418 is dispersed (?) in a dense carbonate matrix, containing magnesium, which was once again likely applied with the same lime-based technique described by Bourgeois et al. Large grains of calcium carbonate, mostly angular in shape, without magnesium but in some cases with trace amounts of strontium, are also found in the purple paint layer. These certainly correspond to aragonite, as identified by XRD (see Figs. 10–12). Aluminosilicates and concretions, likely the results of burial, are found atop the purple layer. The red of the mantle is painted with cinnabar applied over a kaolinite layer. The red layer, like the purple, is bound with a lime-based mineral binder.

The purple layer of Louvre MNB 584 is composed of a matrix of calcium and magnesium carbonate over kaolinite with aluminosilicates, aragonite, and few particles of calcium carbonate. A sample from Louvre MNB 584 was taken for LDI-MS and HPLC-DAD and -MS analysis[38].

None of the samples prepared for HPLC in the case of Louvre MNB 584, as indicated in the methodology section below, showed the presence of significant peaks above blank level, except for the HPLC-ESI-Q-ToF chromatogram of the extract after HCl/MeOH treatment, where one peak whose mass spectrum features are attributable to halogenated substituents was detected. More investigations are needed to fully interpret these results.

The negative-ion LDI mass spectrum of Louvre MNB 584 showed the presence of ions at m/z 240 and m/z 239, which could correspond to radical alizarin ion [A]- (or to an isomer) and its deprotonated molecule, [A-H]-. In addition, ions at m/z 211 and m/z 183 would be caused by the loss of one and two carbon-monoxide molecules, respectively, from the deprotonated m/z 240 molecule, and they would confirm the presence of ali-

36 Harami – Jeammet 2015.

37 Jeammet 2010, 99 no. 72.

38 The negative-ion LDI mass spectra of the two reference materials (K37202and Z2200E) showed several ions formed from the madder components, with an ion at m/z 503 that corresponds to the complex including two alizarin molecules bridged by aluminium (C14H6O4)2Al-, [2(A-2H)+Al]-), one of the structures proposed for the complex (Kiel – Heertjes 1963). Other characteristic ions at m/z 240, m/z 239, m/z 256 and m/z 255 corresponded to radical alizarin ion [A]-, deprotonated alizarin molecule [A-H]-, purpurin ion [P]- and its deprotonated molecule, [P-H]-.

zarin or other madder components with molecular mass 240 Da. The more intense ion, at m/z 225, also noted in the reference spectra, may have come from a by-product or fragmentation of the anthraquinones. This ion was observed as a fragmentation of the m/z 271 quinalizarin ion and the m/z 253 rubiadin ion[39], and they could be present in the mass spectrum of the sample as minor components.

The positive-ion LDI mass spectrum of the pigment would also confirm the presence of madder components, together with other unknown ions. In the mass spectrum of the ancient sample, double-protonated alizarin $[A+2H]^+$ (m/z 242) was detected. Moreover, potassiated alizarin $[A+K]^+$ (m/z 279) and sodiated alizarin ($[A+Na]^+$ [m/z 263] and $[A+2H+Na]^+$ [m/z 265]) were observed. The ion at m/z 279 could also correspond to a calcium complex $[A-H+Ca]^+$, and the peak at m/z 265 may be caused by the m/z 225 fragment linked to calcium $[225+Ca]^+$. In this LDI mass spectrum, an unidentified positive ion at m/z 326 was also observed; even though it was not justified, it seems to be present in a positive-ion MALDI-ToF mass spectrum for madder lake[40].

According to all the analytical tests, alizarin (or another compound with molecular mass 240 Da) seemed to be the detected component of the colourant.

To the authors' knowledge, the spectral features obtained with Raman and absorption spectroscopy from the purple compound(s) are not consistent with known alizarin-related compounds. Like most natural organic colourants, alizarin, its salts and complexes are generally fluorescent and not easily detected with standard Raman spectroscopy – hence the frequent use of SERS for their identification. In our case, however, SERS analysis was inconclusive in all cases. While it may not be impossible that a particular molecular configuration of an alizarin-containing salt or complex would return a Raman spectrum, the spectral features found in this study do not support an attribution to an alizarin-containing compound. Therefore, it seems that the Raman spectrum is likely unrelated to the presence of alizarin. While the absorption spectra are related to the colour of the unknown purple compound (as mentioned, however, no convincing matches could be found among the sources listed above, which includes alizarin-based compounds), the Raman spectra may or may not correspond to the molecule responsible for the purple colour. The discrepancies between the analytical results could be ascribed to the presence of a mixture of purple colourants, of which alizarin is only one component. If this interpretation is correct, the Raman and absorption spectra may be related to the presence of another, yet unidentified, purple compound with which alizarin is mixed. More generally, three options may be entertained at this stage:

1. The Raman spectra correspond to an unknown purple compound. Further studies are necessary to identify the chemical compound responsible for the purple colour, which is in our instance used in combination with alizarin.
2. The Raman spectra do not correspond to the unknown purple compound. Instead, they correspond to a compound that is found concomitantly with the unknown purple compound and not in other instances (e. g., on other non-purple paint layers, as could be the case for, for example, a binder, a varnish or a fluidifying agent). In this case, the Raman spectra could result from a non-purple compound, which has been intentionally or accidentally extracted from the same source as the purple compound or added for the preparation of the purple colour.
3. The Raman spectra are related to the presence of an unidentified synthetic modern material (e. g., a consolidant) and not the purple colour. However, the same spectra are found across collections and apparently only where purple is present, making this interpretation perhaps less likely.

In all cases, the results are largely inconclusive, as the absorption and Raman spectra do not support the use of alizarin alone as the sole source of the purple colour. Whether the Raman spectra correspond to the purple compound or not will be determined if a spectral match will be found through comparisons with standards of known composition.

The presence of aragonite in the purple paint layer may offer a further interpretative clue, related to the use of a purple colour of marine origin, where aragonite is formed by means of biomineralization. Interestingly, filament-like purple structures can be seen in the cross section (Fig. 14). These may correspond to the purple colourant which accumulated as a result of the procedure used for its preparation. Nonetheless, these considerations are at this stage of the research speculative and further investigations are required to fully characterize the purple compound.

39 Rafaëlly et al. 2008.

40 Sabatini et al. 2016, fig. 4.

Purple particles discovered on the drapery of East Pediment M (Aphrodite?)[41] on the Parthenon share the same apparent absorption spectrum as purple Type III, suggesting that the same organic colourant was used on coroplastic production and state-sponsored, large-scale sculptural production[42]. In addition, the same Raman spectrum was found on the Cypro-classical sarcophagi A and B in Kition, Cyprus[43]. In these examples, purple, also in a carbonate matrix, was used for the representation of textiles as well as various elements of the Doric frieze and floral patterns. Finally, an unidentified purple colour from the 13th cent. B.C. site of Gla in Boeotia showed a Raman spectrum very similar to purple Type III, found in association with calcite and aragonite[44].

Madder

Perhaps better described as pink rather than purple, a strong taste for madder developed in sculptural polychromy during the Hellenistic period, especially for the representation of textiles. Starting in the Hellenistic period, madder appears to have been privileged over the unknown purple colourant(s) to represent textiles. A sample of an Aphrodite leaning on an archaizing statuette (EAM 4999; Fig. 2), most probably from Myrina and dated to 200–100 B.C., shows clear traces of pink paint, characterized by bright-pink particles with aluminosilicates (kaolinite?) and otherwise unidentified particles containing Al, Si, Cl, P, Ca and S. The pink layer is applied over a white preparation of kaolinite, cristobalite, and gypsum. The white preparation is in turn applied above a greyish preparation composed of potassium-rich aluminosilicates, possibly illite, and grains of quartz[45]. The apparent absorbance spectrum is typical of an anthraquinone obtained from plants with absorptions maxima at c. 515 nm and 540 nm[46]. When exposed to ultraviolet radiation, the colourant emits a distinctive orange-pink light centred at c. 600 nm, confirming the presence of a pseudopurpurin-rich dye, likely madder extracted from the Rubia family[47].

Discussion and Conclusions

Diverse Sources and Shades of Purple

In the coroplastic figurines examined in this study, purple was found on the representation of textiles[48]; it thus seems reasonable to speculate that the same colourant might have also been used to dye textiles. However, the examples from Gla, Kition, and the marble pyxides indicate that the same purple was also used in other contexts (e. g., backgrounds, scrolls, etc.). Unfortunately, the scarce archaeological textile record up to the Hellenistic period in Greece only confirms the use of shellfish purple as a purple dye. The survival of shellfish purple on textiles, and not that of other purple colours, is possibly due to its durability compared to other dyes. Literary sources confirm the use of other dyestuffs, most of which are fugitive. Despite the inevitable complexities and inaccuracies in identifying natural specimens mentioned in ancient texts, works such as the Leyden Papyrus X and the Stockholm Papyrus discuss the use of many sources, including alkanet (and its imitation with beet juice, pine cones, peaches, etc.[49]), orchil[50], ‹a cer-

41 Purple particles were observed at the intersection between East Pediment M's himation and the drapery on which she is reclining, making it impossible to determine to which carved textile it originally belonged. For purple on bed coverings, see Hom. Od. 4, 298–300.

42 Verri et al. 2023.

43 See S. Pages-Camagna's analysis in Flourentzos 2011, 108 fig. 21.

44 Brysbaert 2006 and personal communication including Raman spectrum.

45 This greyish, lower preparation layer corresponds to the ‹grey underlayer› described by S. Pagès-Camagna in previous publications: see Jeammet et al. 2010, 247 for the bust of Aphrodite previously mentioned (Louvre, inv. Myrina 661).

46 Bisulca et al. 2008; Fonseca et al. 2019.

47 Daniels et al. 2014.

48 Possibly, and based on the FORS spectrum, purple Type I was also used for the skin tones of EAM 4163. However, this result needs to be further investigated.

49 E. g. Leyden 91–93.

50 E. g. Stockholm 96.

tain acanthus›[51], wine lees/grape skins[52], mulberry[53], laurel berries[54], amaranth petals (?)[55], calves' blood[56], red ochre, and vinegar[57], while Vitruvius mentions hysginum (?) and bilberry (?)[58]. Some recipes promise indelible purples[59]. In addition, literary sources refer to different shades of purple and not necessarily in diminutive or comparative terms. Purple is defined as *rodinoporphyros* (rose-coloured purple)[60] and a distinction is made between Sardian, Sicilian, Phoenician and Tyrian purples[61], suggesting the existence of well-developed local traditions, as well as demand for them even outside their main place of production. Shades of purple are clearly recognized, for example that of ‹bright red purple› which is obtained by mixing krimnos (?) and orchil[62]. A purple including unknown plant (?) material (hyacinthe) was used to produce a «very beautiful foreign appearance[63]». The term *porphyras aletheines* (genuine purple) is even used for orchil[64], while *porphyras alethos* denotes a mixture of woad, alkanet with an insect (?) red dye – promising a purple of a beauty «beyond all description[65]». Orchil and alkanet were also used for preparing Tyrian purple[66], possibly betraying different levels of flexibility (or understanding) related to what was considered true purple or simply a beautiful colour, appreciated in its own right, for which even a secret was worth keeping[67].

A Fashion for Purple in Late Classical Coroplastic Polychromy

In addition to a very early example of a mural painting from the Bronze Age site Gla in Boeotia, the unknown organic purples were already employed in the archaic period (EAM 32064-7), alongside optical purples, created by layering red and blue pigments (EAM 3972). However, the Classical and Late Classical periods appear to have favoured this type of colour, with multiple examples found in coroplastic productions and other contexts. Starting with the Parthenon, the most prominent and luxurious symbol of Periclean Athens, and perhaps spearheaded by this monument, a purple colour – currently not considered true purple – was found on East Pediment M. If future investigations confirm the presence of non-shellfish purple on the Parthenon, its significance cannot be underestimated. As a highly influential monument visible to the public, the Parthenon inspired generations of artists. The use of purple on this monument might have been emulated in other forms of art, such as coroplastic and fashion[68], possibly fostering interest in varied shades of purple.

The same purple colours are found on luxury objects, such as clay plastic lekythoi (e. g. EAM 2059 and EAM 2060), marble pyxides, and sarcophagi, as well as on more modest coroplastic production (e. g. EAM 19367 and 4163). By the end of the Late Classical period and the beginning of the Hellenistic period, madder begins to be used for the same type of coroplastic production, apparently marking the end of use of the hitherto unidentified non-shellfish purples.

The use of the non-shellfish purple in Gla testifies to a long tradition of employing this colour in various contexts, a tradition that will hopefully be further elucidated as more examples are studied and discovered. The apparent use of a non-shellfish purple on the Parthenon does not exclude the possibility that shellfish itself might have been used elsewhere on the monument. It also does not prove that the unidentified purple was more or even equally valuable as shellfish purple. It simply indicates that the cultural significance of this choice of purple – the collective values associated to it – may have been more nuanced than previously thought. It can be speculated that the values associated with this purple ranged from the most utilitarian (e. g. stability to degradation, availability, ease of preparation) to the most symbolic (e. g. sacred or cultural connotations). Further information on the chemical nature of this purple colour may shed additional light on these aspects. A further direction for research involves investigating samples from other sites that show the presence of similar purple pigments. It is hoped that analysing larger samples using HPLC-MS will yield conclusive results. Additionally, an XRD assessment of the relationship

51 Leyden 97.
52 Leyden 98 and Stockholm 86.
53 Stockholm 100.
54 Stockholm 98.
55 Stockholm 96, 98 and 128.
56 Stockholm 127.
57 Stockholm 126.
58 Vitr. 7, 14, 1–2.
59 E. g. Stockholm 124 and 125.
60 Bogensperger 2017.
61 Stockholm 93, 94, 109, 148 and 151.
62 Stockholm 110, 111 and 123.
63 Stockholm 97.
64 Stockholm 95.
65 Stockholm 101.
66 Stockholm 148 and 151.
67 Stockholm 101.
68 See, for example, the interest in purple borders that is clearly visible in white-ground lekythoi.

between aragonite and the purple pigment may provide insights into the origin of the purple colour.

«Keep this a secret matter, because the purple has an extremely beautiful luster», advised the ancient alchemist in Stockholm 101. His wisdom has been well heeded, as the purple shades of a beauty ‹beyond all description› retain their mystery to this day.

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Methodologies

Digital Microscopy

A portable digital microscope Hirox VCR-800, connected to a tripod or a stand, was used for the in situ examination of the objects. Equipped with a 2,1 Mega pixel video CCD and a 20–160 magnification zoom lens with LED axial and co-axial lighting, this compact, light-weight equipment allowed for the capture of 2D images under raking light.

Multi-Band Imaging

Visible- and ultraviolet-induced luminescence (VIL and UIL, respectively in the infrared and visible range) imaging was undertaken using the equipment and procedures described in Verri – Saunders 2014.

Fourier Transform Infrared Spectroscopy (FTIR)

A Bruker Alpha spectrometer with a reflectance interface was used (4 cm^{-1}, 256 scans).

Fiber-Optic Reflectance Spectroscopy (FORS)

FORS in the 400–900 nm range was performed using an Ocean Optics Jaz spectrometer, equipped with a LS-1 tungsten-halogen radiation source. Spectra are presented in apparent absorbance (log[1/R], where R is reflectance).

X-ray Fluorescence Spectroscopy (XRF)

X-ray fluorescence spectroscopy was undertaken using an XGLab Elio (Rh source, 50 kV, 40 µA, 200 s).

X-ray Diffraction Spectroscopy (XRD)

A Xenocs – GeniX3D Cu High Flux (50 kV, 600 µA) with a Rigaku R Axis IV++ detector and a Bruker D8 Advance using Cu Kα radiation (40 kV, 40 mA) with a Göbel mirror, a 1 mm UBC collimator, and with a Eiger2 R 500K Hybrid Photon Counting detector working in 2D mode were used.

Raman Spectroscopy

A confocal microspectrometer Horiba – Infinity was used, with a 532 nm laser diode Nd-YAG (×50 – spot size 7 µm).

Surface-Enhanced Raman Spectroscopy (SERS)

Analysis was carried out by means of a Bruker Senterra Raman spectrometer equipped with a CCD detector and an Olympus 20× long working distance microscope objective. Each sample was initially analysed as it was, after being covered with a 2-µL droplet of silver colloid and 0.5 µL of 0.5 M potassium nitrate. Three hydrolysis steps were also tested upon rinsing with ultrapure water, based on the use of hydrofluoric acid (vapor-phase, polyethylene microchamber, 5 or 15 min) and 1% nitric acid (1 µL, deposited onto the sample). Silver colloids were prepared following a previously published synthesis. Excitation at 488 nm and 633 nm was respectively provided by a Spectra Physics Cyan solid state laser and a Melles Griot He-Ne laser. An output laser power of 4 mW was employed for the analysis, with two integrations of 30 s[69].

Scanning Electron Microscopy (SEM)

A scanning electron microscope with a field-emitting gun – JEOL 7800F, equipped with two SDD Bruker AXS 6/30 detectors and a FE-SEM Zeiss Σigma HD, equipped with an Oxford Instrument X-MaxN 80 SDD detector – was used.

Laser Desorption-Ionization Mass Spectrometry (LDI-MS)

A Bruker MicroFlex matrix-assisted LDI time-of-flight (MALDI-TOF) mass spectrometer, equipped with a 337 nm pulsed nitrogen ultraviolet (UV) laser (20 Hz), was used in this study. The sample was adsorbed on the surface of the microScout MALDI target plate by depositing the micro-sample with a droplet of dimethyl sulfoxide (DMSO) (0.5 µL), with subsequent evaporation of the solvent. Mass spectra were obtained in the reflectron configuration with an accelerating voltage of -19 kV (negative-ion mode) or +19 kV (positive-ion mode). The laser intensity was set just above the ion-generation threshold to obtain peaks with the highest possible signal-to-noise ratio without significant peak broadening. The mass spectrometer was calibrated by the so-called «close external» method, using dithranol (DIT, 1,8-dihydroxy-10H-anthracen-9-one, molecular weight: 226.2274 g/mol) in the negative mode and polyethylenglycol (PEG300) in DIT matrix in the positive mode. The spectra were obtained by pointing the laser at different areas of the sample target to ensure that the results were consistent and representative[70].

The behaviour of the ancient sample and some reference materials (Kremer 37202 Madder lake genuine – Madder root extract, precipitated with aluminium hydroxide; Zecchi 2200E Rose Madder genuine) were compared.

HPLC-DA and -MS

The samples were treated with a sequence of mild extraction methods followed by stronger one. After each mild extraction, the supernatant was collected and immediately injected in the chromatographic system to avoid any possible photo-degradation of the extracted molecules. After the strong extraction, the solution was dried and the sample redissolved prior to injection, as detailed below.

50 µL of DMSO (dimethyl sulfoxide) were used for the extraction of dibromoindigoids, typical of purple, which took place for 10 minutes at 60 °C in an ultrasonic bath. The solid sample did not discolour after this treatment; the residue of step 1 was added with 50 µL of EDTA-DMF (0.1% Na_2EDTA in H_2O/DMF (1 : 1, v/v)) to extract pigment lakes; the treatment was performed at 60 °C for 60 minutes in an ultrasonic bath. The solid sample did not discolour after this treatment; the residue of step 2 was added with 50 µL of MeOH/HCl (30 : 1) and subjected to extraction in an ultrasonic bath at 60 °C for 60 minutes. The solid was eventually dissolved and the final solution was dried and reconstituted in 40 µL of DMSO.

All extracts were injected in both the HPLC systems. Blanks were run for all the extraction protocols. Further details on the instrumentation can be found in Sabatini et al. 2020 and Deyjoo et al. 2021.

69 Leona 2009.

70 Maier et al. 2004; Wyplosz 2003; Ribechini et al. 2013; Sabatini et al. 2016.

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