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News from the Pilina Research Project: Identifying a Lime Painting Technique on Greek Terracotta Figurines (4th–3rd cent. B.C.)

Brigitte Bourgeois – Yannick Vandenberghe – Violaine Jeammet

Abstract

As scientific research advances, we are gaining a deeper understanding of the arts and crafts of colouration in ancient Greek coroplastic production. The intricate quality of the polychrome decorations found on numerous figurines highlights the refined skill and expertise of ancient painters. Despite these advancements, our knowledge of ancient techniques pertaining to binding agents remains somewhat restricted. While it is widely believed that organic compounds such as egg, animal glue, and gums were used in a tempera-like technique, precise scientific identification is often lacking due to the weathering or dissolution of these substances over time.

New findings from the Pilina research project, focused on investigating Greek polychrome terracotta figurines, have identified a painting technique utilizing lime as a mineral binder on a dozen pieces produced by Attic and Boeotian workshops from the 4th–3rd cent. B.C. This paper presents the scientific evidence collected through a comprehensive multi-technique approach, including multi-spectral imaging, microscopy, XRF, XRD, SEM-FEG, FORS, Raman, and cathodoluminescence. The findings reveal that ancient craftsmen employed the lime technique either for the entire polychrome decoration of a statuette using various pigments, or selectively in specific areas, often in association with a purple organic colourant. Finally, the historical context of this painting technè will be discussed.

Keywords: Polychromy, coroplastic studies, Attica, Boeotia, imaging, analysis, cathodoluminescence, binder, purple, organic colourant.

The Pilina Project

Launched in 2014 through a partnership between the Louvre-C2RMF, in collaboration with the French School of Athens (Efa), the Pilina project is an interdisciplinary research initiative dedicated to studying polychromy in Greek terracotta figurines. By integrating archaeological, scientific, and art-historical data, the project aims to enhance our understanding of ancient materials and techniques, characterize specific workshop recipes where possible, and highlight the evolution of polychrome patterns and styles over a long period of time. Beyond the technical approach, the project seeks to unveil fresh insights into the interplay among craftsmen who may have been involved in various stages of the manufacturing process, traditionally categorized into separate roles such as potters, sculptors, coroplasts/moulders, painters, and gilders. A further aim is to better understand the role of patrons – whenever the archaeological context is known – and ultimately the values of colour and status of the object.

Our research corpus takes into account some 250 pieces in order to grasp general trends and particularities over a large historical context, from the Archaic down to the Late Hellenistic-Early Roman periods. The selection of objects includes pieces from diverse production areas, with a focus on those originating from Mainland Greece (Attica, Boeotia, Corinth, etc.), Eastern Greece (Myrina, Smyrna,

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Tarsus), and to a lesser extent South Italy, Cyrenaica and Alexandria. The artefacts are housed in the collections of the Louvre Museum (Department of Greek, Etruscan and Roman Antiquities) as well as in Greece. A sub-branch of the project, conducted in collaboration with G. Verri, is underway in Greece, supported by the French School, focusing on objects kept in the National Archaeological Museum of Athens and in the Archaeological Museum of Thebes, Boeotia[1].

Our understanding of ancient Greek terracotta production relies entirely on material studies since ancient written sources, whether literary or epigraphic, are notably silent on this subject. With limited physical evidence at our disposal, it becomes imperative to investigate the artefact's structure through scientific methods, employing an integrated multi-technique and multi-scale methodology. A preliminary study has been conducted on a large part of the corpus utilizing multi-spectral imaging (visible, raking light, UV, IR, VIL), detailed surface examination with digital microscopy, and non-invasive analyses (XRF, XRD, Raman spectroscopy, FORS, FTIR, ion beam analysis [Aglae], tailored to specific cases). In a subsequent phase, an in-depth analysis involving sub-millimetric surface layer samples has been conducted on approximately 80 objects from the Louvre collection and eleven objects kept in Greek museums, using SEM-FEG, Raman spectroscopy, XRD, and cathodoluminescence on cross-sections[2]. The results have been integrated into a database on ancient inorganic materials and painting techniques, with future plans to include chromatography analyses for organic material identification (colourants and binders).

Among the array of findings, a previously unreported lime-based painting technique has been identified. This article will present the analytical evidence and addresses some of the historical inquiries associated with the utilization of this newfound technique.

Identifying a New Painting Technique with a Lime Binder

Painted Terracotta Figurines: the Mystery of the Binders

Greek craftsmen responsible for the polychrome decoration of terracotta objects are commonly believed to have utilized a tempera-like technique involving water-soluble binders to apply layers onto the fired clay body, encompassing the white ground (or preparation), paint layers, and in some cases metallic highlights of gold or tin leaves[3]. Identifying these binding media on sub-millimetric samples is challenging. Due to enduring millennia of heavy erosion in the soil, the organic substances have undergone mineralization or dissolution, rendering them undetectable even by highly sensitive analytical methods[4]. Faced with this limitation, one can only suggest that in coroplastic polychromy, binders such as egg, animal glue, casein, or plant-gums were likely employed, either individually or in various combinations, similar to their application recently evidenced on Greek mural painting and diverse polychrome objects[5]. Adding to our current knowledge, we can now add a new piece of information indicating the potential use of mineral binders.

Visual Observation and Imaging

It all began with the observation of an unusually smooth surface on some 4th cent. B.C. ‹Pre-Tanagrean› and Tanagrean statuettes depicting draped women in sculptural poses. These statuettes were found in Attica and Boeotia and are housed in the Louvre. The term ‹Tanagrean› is less ambiguous than the tradi-

1 Bourgeois – Jeammet 2020. For the first results on objects kept in Athens, see Bourgeois et al. 2019.

2 XRF: Equipment Niton XLT3 900, conditions: 40 KeV, Al/Fe filter. XRD: XENOCS – GENIX 3D Cu High Flux source, detector Rigaku R-AXIS IV++. Raman: confocal microspectrometre Horiba – Infinity, laser 532 nm. SEM-FEG : JEOL 7800F, detector SDD Bruker AXS 6/30. Cathodoluminescence: CITL cathodoluminescence Mk5-2, 0,5 µA, 14 KeV.

3 See for instance Higgins 1970; Jones 1987, 813 f.

4 Within the framework of the Pilina project, GC-MS (gas chromatography – mass spectrometry) analysis has been carried out on the preparation and paint layers of the ‹Lady in Blue› (Tanagra, 330–300 B.C., Louvre inv. MNB 907), but the organic binder could not be identified. On the ‹Lady in Blue›, see Jeammet 2010, 122 cat. 91.

5 Colombini et al. 2004; Brecoulaki et al. 2006; Kakoulli 2009, 35 f.; Brecoulaki et al. 2012. For an hypothesis on terracotta figurines from Pherai (Thessalia), see Asderaki-Tzoumerkioti et al. 2019.

tional ‹Tanagra›, which has been associated with these figurines since the end of the 19th century, when thousands were unearthed in the necropolis of this Boeotian site. The so-called Tanagrean style actually originated in Athenian workshops around the mid-4th cent. B.C.[6]. Among the Louvre series, four particularly high-quality pieces stand out which will be briefly introduced here.

The first represents a standing veiled woman (inv. MNB 495) wearing a whitish mantle framed by a purple border, with remnants of intense purple-coloured paint still preserved on the left wrist and on the vertical fold under the left arm (Fig. 1). Technical and stylistic features point to a Boeotian production (at Thebes) around 380–340 B.C.[7]. Another noteworthy piece is a small figurine of a standing veiled woman (inv. MNB 584) painted in a remarkable and quite well preserved purple colour, possibly from Thebes around 330 B.C. (Fig. 2 a)[8]. Her tunic features a white central part adorned with vertical bands of pure purple on the right and left sides. Similarly, the white mantle showcases lateral bands and a thin belt tied on the chest in subtle shades of purple and blue (Fig. 3 a–c). VIL imaging conducted by A. Maigret confirms the use of Egyptian blue solely on the mantle (Fig. 2 b). Such tonal variations are extremely rare on ancient terracotta figurines and add considerable value to this exceptional ‹Purple Lady›, who was painted with the same purple colourant as found recently on the large-size marble statue of a goddess from the Parthenon East pediment (figure M, ‹Aphrodite›, London, inv. BM 1816,0610.97). The comparison of FORS analyses performed on the Parthenon sculptures and the delicate Boeotian clay statuette shows that painters used the same organic colourant materials in both ‹high› and ‹low› types of creation (see further Verri et al. in this volume). The third noteworthy instance showcases a standing veiled woman wearing a pointed hat or tholia (inv. MNB 572). This figurine is of Boeotian production, possibly from Thebes, and dates back to 330–300 B.C.[9]. Traces of purple are still visible on her chiton running down the legs. Additionally, the polychromy of her mantle, white at the centre and pale blue at the sides, is evocative of the pattern of the ‹Purple Lady› (inv. MNB 584). A similar colour pattern is observed on another contemporaneous Boeotian statuette of a standing veiled woman holding a fan (inv. MNB 581) (Fig. 9 a)[10]. This recurring series suggests a prevalent use of a chromatic scheme combining purple and blue in women's attire in Boeotian workshops during that period.

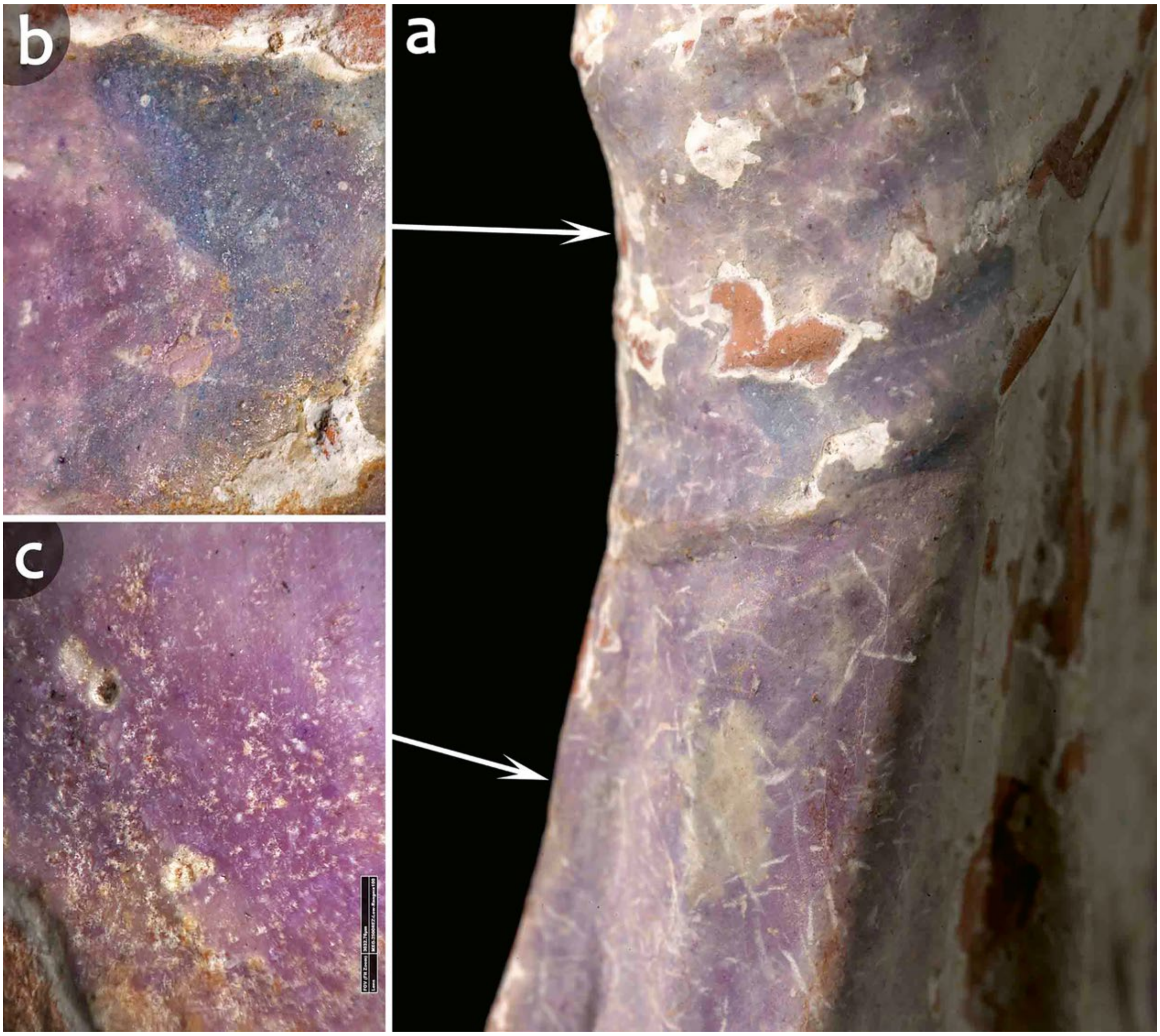
1 Standing veiled woman, c. 380–340 B.C., Boeotian production (Thebes). Height 24 cm, inv. MNB 495

All these pieces share similar optical properties. The smooth painted surface displays a glossy, sometimes nearly ‹glazed› quality. Particularly remarkable is the face of the veiled woman MNB 495 (Fig. 1).

6 Burr Thompson 1966; Jeammet 2010, 62–69; Jeammet 2014.
7 Jeammet 2010, 252 cat. 204. Due to a lack of space the question of workshop attribution – an important part of the Pilina project – cannot be addressed in detail in this article. Suggested attributions are based on the study of various parameters: archaeological data, whenever available; technical characteristics (clay analysis, white ground analysis, size of the object, thickness of the walls, shape of vent hole etc.); typology and style. See Jeammet et al. forthcoming.
8 Jeammet 2010, 99 cat. 72.
9 Besques 1972, 24 D 117; pl. 26a.
10 Jeammet 2010, 116 cat. 87.

2 Standing veiled woman or ‹Purple Lady›, c. 330 B.C., Theban (?) production. Height 16.5 cm, inv. MNB 584. a) Visible light; b) VIL imaging

Its intense hue, semi-translucent quality, and lack of visible grain under the microscope, suggest that the purple paint may come from an organic colourant, akin to those found on some objects in Greek museums that also exhibit no discernible UV-induced luminescence (see Verri et al.).

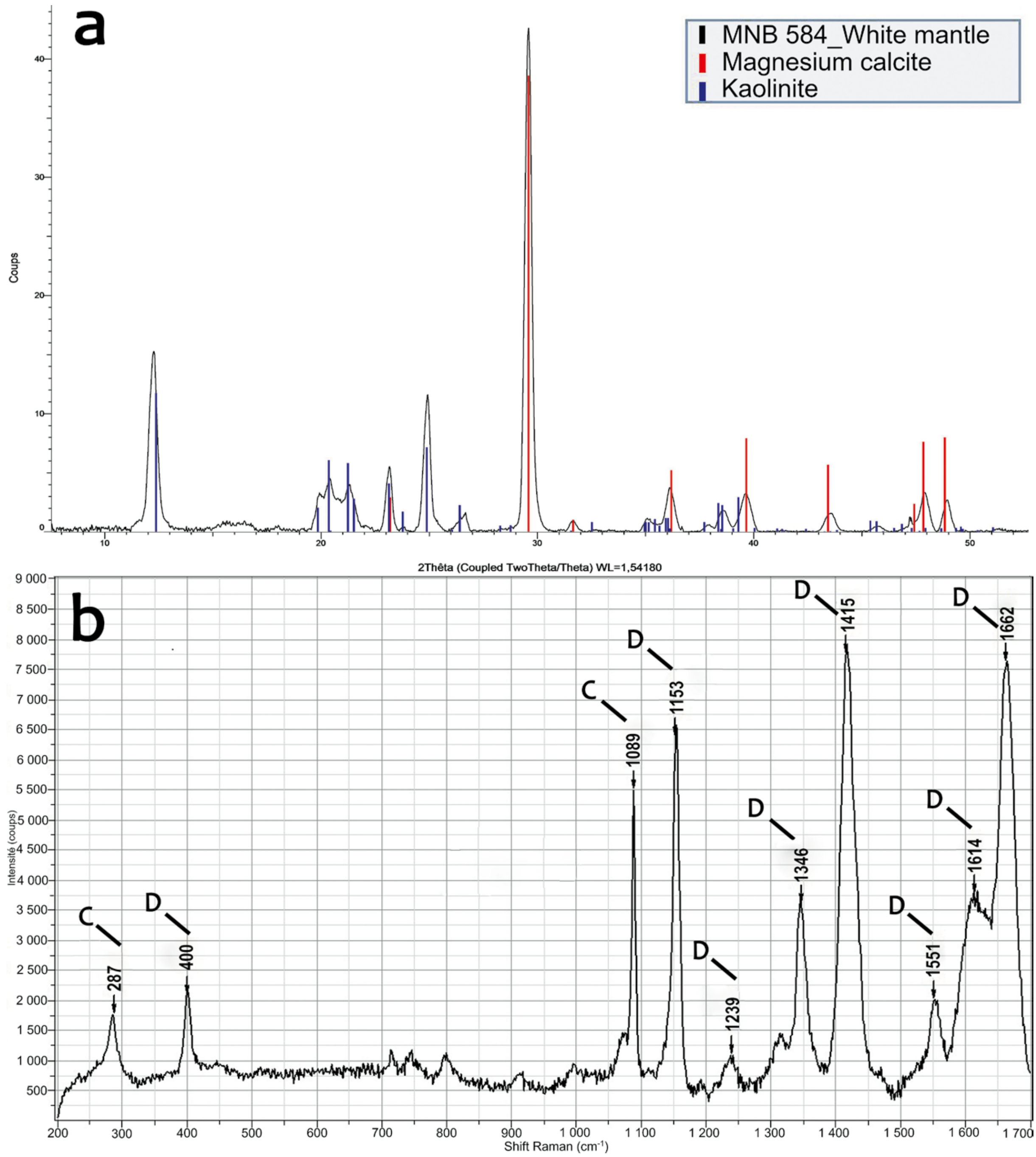


3 Tonal variations on the ‹Purple Lady› inv. MNB 584. a) Detail of the right side; b) Macrophotograph of the blue-purple paint on the mantle; c) Microphotograph of the purple paint on the tunic

In Situ Analysis and Sampling: Characterization of Neoformed Calcite

To gain a better understanding of the technical expertise involved, initial non-invasive analyses were conducted. Examination on the ‹Purple Lady› (inv. MNB 584) involved point-XRF and macro-scanning XRF analysis by Eric Laval, revealing a significant presence of calcium across the surface, including the purple, blue and purple, and white painted areas. XRD analysis of a white area on the mantle confirmed the presence of calcite and kaolinite (Fig. 4 a). In a second step, micro-flakes were sampled and prepared in cross-sections to investigate the morphology and stratigraphy of the purple paint layer. While no pigment was detected in SEM analysis, the use of an organic colourant – currently still unidentified – was confirmed. Previously, S. Pagès-Camagna had suggested «orceine, a colouring molecule contained in orchella weed (*rocella tinctoria*)» as a possible source[11]. However, recent FORS and Raman analyses on this figurine and others indicate that the spectra do not perfectly align with any known standard dyes such as shellfish, orchil, kermes, cochineal, alkanet, madder, among others. Notably, the FORS spectrum of MNB 584 is identical to the purple found on the

11 S. Pagès-Camagna, in: Jeammet 2010, 250.

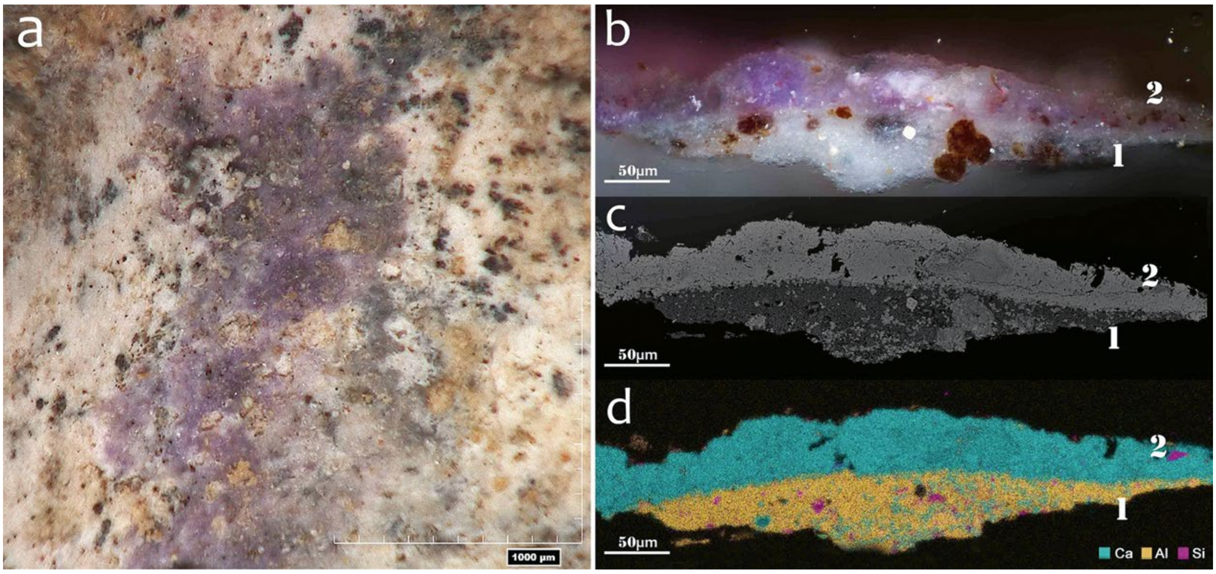


4 Analysis of the white and purple paint layers on the ‹Purple Lady› inv. MNB 584. a) Diffractogram of the white paint layer on the tunic, showing the presence of calcite and kaolinite; b) Raman spectrum of the purple layer. The peak at 1088 nm corresponds to calcite (C) and the others to an unknown purple dye (D).

Parthenon sculpture and another statuette of a standing woman draped in red and purple (inv. 35418), now in the museum of Thebes (see Verri et al. in this volume). Unearthed in 2000 during Greek excavations at Thebes, Tomb B 158, this elegant figure likely originated from a Boeotian workshop and dates back to approximately 340–250 B.C.[12].

Raman spectroscopy, performed on the cross-section of MNB 584, showed that the omnipresent calcium carbonate in the paint layer, is, indeed, calcite

12 Harami – Jeammet 2015, 320 f. 329 fig. 4.



5 Calcitic binder (neoformed calcite) on the standing veiled woman inv. MNB 495. a) Microphotograph of purple paint on the mantle, left wrist; b) Cross section of the corresponding sample in optical microscopy showing the ground layer (1) and the purple paint layer (2); c) The same in SEM-FEG imaging; d) Elemental mapping of calcium (blue), aluminium (orange) and silicium (pink), showing the calcite of the paint layer and the kaolinite of the ground layer

(Fig. 4 b). Additionally, SEM analysis revealed a very specific morphology characterized by a compact, homogenous mass with an extremely fine grained structure, situated on top of the white ground preparation composed of kaolinite. The same configuration was observed on the veiled women MNB 572 and MNB 495: SEM chemical mapping shows how the purple dye is effectively ‹cemented› by calcium carbonate throughout the paint layer (Fig. 5).

Calcite, far from being exclusively associated with a purple dye, was also present with the same morphology and distribution in red and blue-painted layers on some other figurines. One example among several is the statuette of a standing woman wearing a cecryphale, a head-handkerchief (inv. MNB 486; Fig. 6), manufactured around 330–300 B.C. in the Tanagra workshop known for producing the ‹Sophoclean Lady›[13]. The blue paint layer on the mantle comprises a mixture of Egyptian blue, kaolinite (also used in the white preparation), and calcite, creating a comprehensive coating across all elements (Fig. 7).

Out of the 80 figurines analysed on cross-sections in SEM, a dozen cases from Attic and Boeotian workshops show the same configuration: the paint layer is made of a homogeneous, solid block of cryptocrystalline grains of calcite forming a compact mass when a dye is used (Fig. 8 a) or embedding other components such as kaolinite when pigments are employed (Fig. 8 b. c). In some cases, a clear stratigraphy is evident, with the calcium carbonate compound strictly limited to the paint layer, although in most cases calcite is also present in the upper part of the ground layer. Such features point to the presence of neoformed calcite. Furthermore, the distribution of calcite on the figurines appears uniform and related to an intentional application. This contrasts with the random deposits or impregnations typically associated with burial contexts.

An Intentional Lime Binder Characterized through Cathodoluminescence

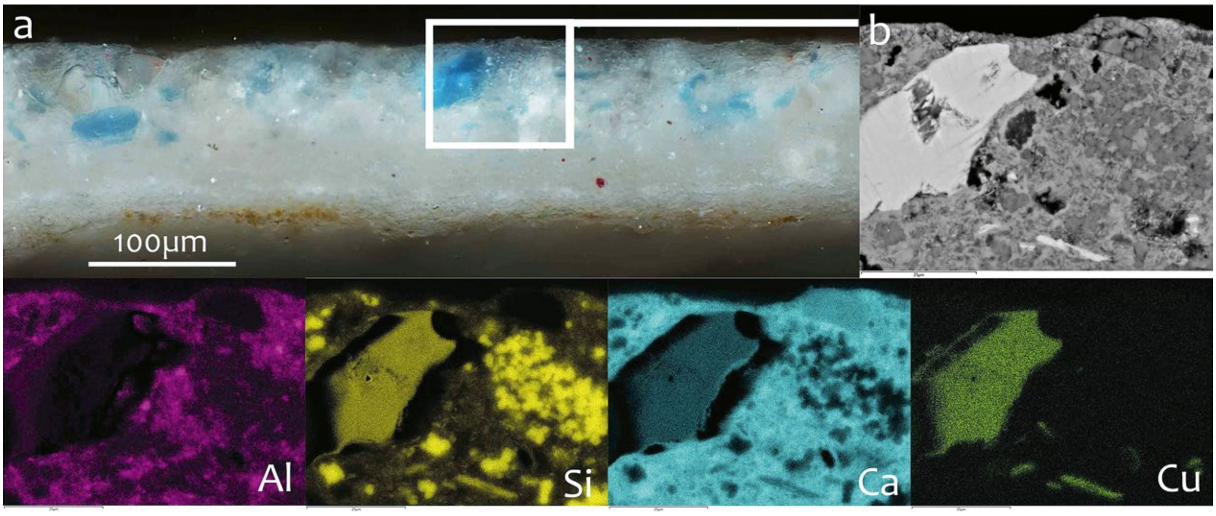
Further investigation into the formation process of this neoformed calcite involved cross-sections in cathodoluminescence under optical microscopy, with results compared against published data from recent archaeometric studies[14]. The cathodoluminescence technique, increasingly used in polychrome studies, elucidates a compound's formation mechanism, en-

13 Attribution based on stylistic and scientific data (clay and white ground analysis). Inv. MNB 486: Jeammet 2010, 115 cat. 85. On the ‹Sophoclean Lady› (inv. MNB 585) Jeammet 2010, 112 f. cat. 83.

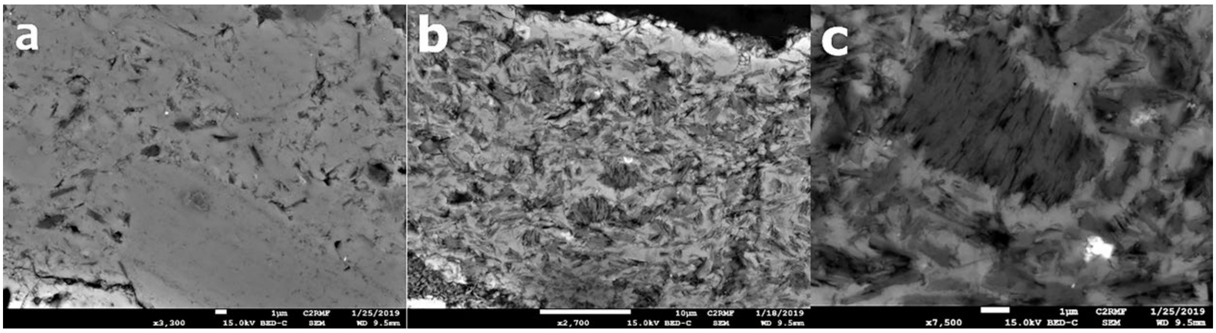
14 Murakami et al. 2013 and Toffolo et al. 2019 deal in detail with the technique and experimental conditions.

6 a) Standing woman wearing a cecryphale (inv. MNB 486), around 330–300 B.C., Tanagra production, group of the ‹Sophoclean Lady›. Height 27.5 cm; b) Detail of head and bust in visible light; c) VIL imaging

vironment, and crystalline structure by the emission of a specific luminescence. The hypothesis of a calcitic impregnation linked to secondary deposit during the burial phase was first examined and disproven. Although soil accretions may indeed be present on the painted surface, for instance on the white and blue mantle of the veiled woman holding a fan MNB 581 (Fig. 9 a), the sedimentary calcite that cements them emits a strong orange-coloured hue under cathodoluminescence (Fig. 10 a. b).



7 Calcitic binder (neoformed calcite) on the standing woman wearing a cecryphale (inv. MNB 486). a) Optical microscopy imaging of a cross section of the blue mantle; b) Detail of the paint layer in SEM-FEG imaging; lower row: in the selected area, elemental mapping of aluminium (purple), silicium (yellow), calcium (blue), copper (green), showing respectively kaolinite, quartz, calcite and Egyptian blue



8 SEM-FEG imaging of paint layers with the lime binder. a) Detail of the purple paint layer, standing veiled woman with a tholia, MNB 572; b) Detail of the white paint layer showing the kaolinite embedded by calcite, ‹Purple Lady› (inv. MNB 584); c) Detail of grains of kaolinite embedded by calcite, standing veiled woman with a fan (inv. MNB 586)

A similar observation was made regarding the use of sedimentary calcite as a paint component; specifically, finely ground calcium carbonate was added to other elements of the white ground preparation or paint layers before being applied to the figurine. Such is the case with the magnificent ‹Lady in Blue›, one of the masterpieces of the Louvre collection, produced by a Tanagra workshop in the years 330–300 B.C. (inv. MNB 907)[15]. Although her mantle, featuring an exceptionally large gilded border, was originally painted with Egyptian blue, it has since worn out (Fig. 9 b). A cross-section analysis reveals the blue pigment overlaying a carbon-black underlayer (Fig. 10 c)[16]. The careful craftsmanship also involved the application of two different preparation layers: a lower beige layer composed of dolomite and calcite mixed with some aluminosilicates, as well as an upper white layer of kaolinite containing some alunite. In cathodoluminescence, the dolomite-calcite mixture is clearly characterized by its bright orange emission (Fig. 10 d).

When examining the woman with a cecryphale (inv. MNB 486), the blue-paint layer containing the calcitic binder reacted in a different way and did not show any clear orange luminescence (Fig. 10 e. f). This result, in accordance with geochemical studies, indicates the presence of neoformed calcite originating from the carbonation of lime within the paint

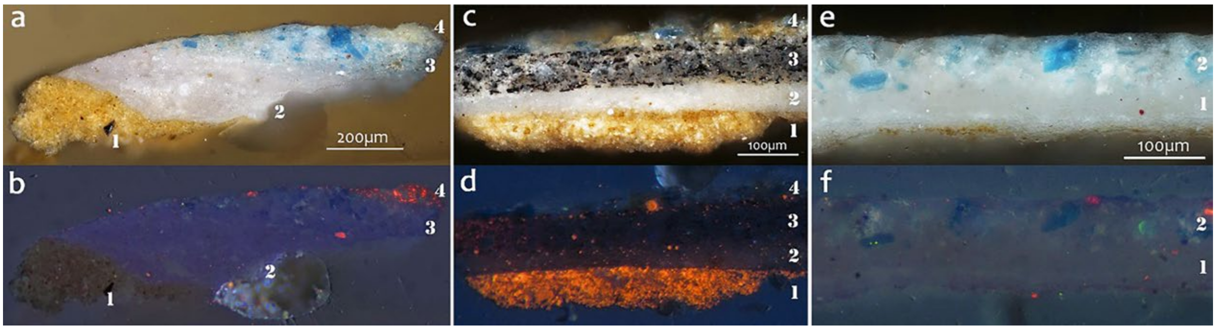
15 Cf. Jeammet 2010, 118 f. 122 f. cat. 91.

16 In both layers, pigments are mixed with kaolinite containing some alunite and calcite.

9 a) Standing veiled woman holding a fan, c. 330–300 B.C., Theban production (inv. MNB 581). Height 26 cm; b) ‹Lady in Blue›, c. 330–300 B.C., Tanagra production (inv. MNB 907). Height 32.5 cm

layer. The painting technique on these figurines thus made use of a limewater solution coloured by pigments or organic materials.

At first sight, the similarities with wall painting seem evident, as the technique entails a similar chemical reaction where calcium hydroxide transforms into calcium carbonate due to the presence of carbon dioxide in the air. However, on terracotta figurines, calcium hydroxide does not stem from a freshly prepared lime substrate, as seen in the buon fresco technique. Rather, it is exclusively found in the surface polychrome layers applied onto a dry support (white clay ground over the fired clay body of the figurine). Lime, blended with pigments, dyes, and other additives prior to application, acts as a binding agent in the paint layer. This ‹intermediate› painting technique aligns more closely to a tempera or a secco technique rather than a fresco.



10 Neoformed calcite (lime-based technique) vs. secondary calcite in cathodoluminescence. Optical microscopy imaging of cross sections under visible light (upper row) and cathodoluminescence (lower row). a. b) Blue of the mantle on the standing veiled woman holding a fan (inv. MNB 581): 1. terracotta; 2. ground layer of kaolinite containing quartz; 3. blue paint layer of kaolinite containing quartz, Egyptian blue; 4. soil accretions of calcite (bright orange luminescence) and some aluminosilicates. c. d) Blue of the mantle on the ‹Lady in Blue› (inv. MNB 907): 1. lower beige ground layer of dolomite and calcite (with a bright orange luminescence) mixed with some aluminosilicates; 2. upper white ground layer of kaolinite (containing some alunite); 3. black underlayer of kaolinite (containing some alunite and calcite) and carbon black; 4. blue paint layer of kaolinite (containing some alunite and calcite) and Egyptian blue. e. f) Blue of the mantle on the standing woman wearing a cecryphale (inv. MNB 486): 1. ground layer of kaolinite and neoformed calcite (without orange luminescence); 2. blue paint layer of neoformed calcite (without orange luminescence), kaolinite and Egyptian blue

The Use of the Technique: Colour Materials, Overall or Selective Application, Paint or ‹Glaze› Layers

In the current stage of research, the new findings already shed light on the specific use of the technique in the Late Classical and Early Hellenistic terracotta production of Attic and Boeotian workshops.

A Variety of Colour Materials: Organic Colourants and Pigments

To our current knowledge, lime was systematically associated with the still unidentified violet-purple colourant, while pure madder, a red colourant, was prepared with a tempera-like technique[17]. A number of Tanagrean statuettes from the late 4th to early 3rd cent. B.C., predominantly of Boeotian production (including the ‹Lady in Blue›), feature this bright colourant, which became the hallmark of Hellenistic polychromy.

When it comes to mineral pigments, the lime technique has been associated with Egyptian blue and cinnabar[18]. Egyptian blue is showcased in pieces like the woman wearing a cecryphale (inv. MNB 486), and a small figurine of a seated woman draped in a blue-painted mantle from Tanagra production around 330–300 B.C. (inv. MNB 480). Cinnabar, on the other hand, has been detected on the statuette of a boy holding a theatre mask, produced in Tanagra and traditionally dated to 330–200 B.C. (inv. MNB 1321). In this case, the red cinnabar paint layer on the drapery is cemented with lime, which has also permeated the white kaolinite preparation underneath[19]. In another instance, the ‹Lady in red and purple› from Thebes, Tomb B 158, features a magnificent red mantle painted with cinnabar and framed by a large purple band (Fig. 11). The organic colourant employed for the semi-translucent purple layer is identical with the Parthenon purple and the ‹Purple Lady› (inv. MNB 594) at the Louvre.

Finally, an in-depth analysis carried out on the ‹Purple Lady› (inv. MNB 584) to study the full spectrum of colours revealed the use of lime as the medium for all paint layers. Lime was identified in the purple of the tunic (organic colourant), the purple-blue of the mantle (organic colourant and Egyptian blue), the white of the mantle (kaolinite), and the black of the base (carbon black) (Fig. 12).

17 This point is currently undergoing further investigation.
18 We keep the common term of ‹cinnabar›, referring to mercury sulphide, although the analysis could not prove whether the painter used the natural form of the pigment (proper cinnabar) or a synthetic form (vermilion).
19 SEM analysis on cross-section.

11 Standing woman in red and purple, 340–250 B.C., Theban(?) production (Thebes Archaeological Museum, inv. 35418). Height 20 cm (preserved fragments). a) Front view; b) Microphotographs of red paint (cinnabar) and (c) purple paint (unknown dye), both lime-based technique

A Binder Used for the Paint, not for the Ground

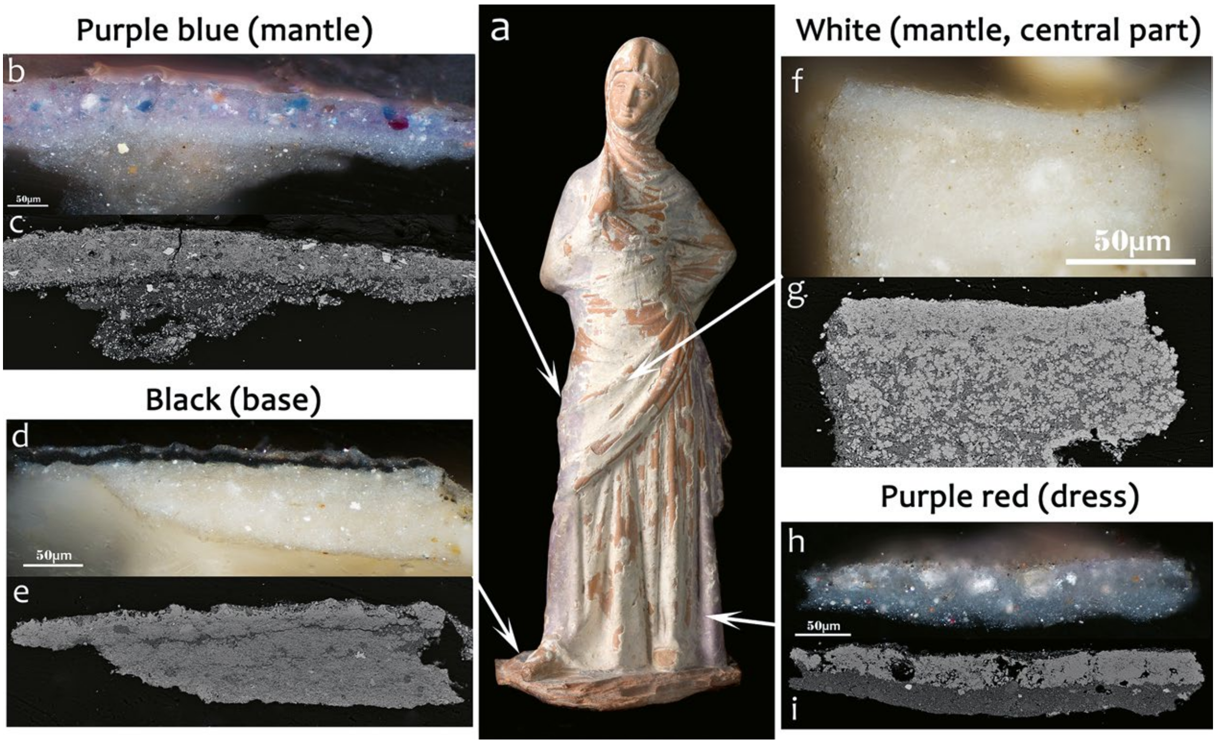
By the same token, the analysis of the ‹Purple Lady› (inv. MNB 584) shows that calcium carbonate has permeated the underlying ground to different depths (Fig. 12). This phenomenon is absent on the cross-section of the purple dress, it is limited in the case of the purple-blue mantle, and it goes much deeper in the case of the central white area of the himation. In the sample taken from the black painted base, full impregnation results in the complete cementation of the white preparation by the calcitic medium. This suggests the potential migration of the mineral binder from the paint layer into the ground, influenced by factors such as lime percentage in the water solution, paint viscosity, and degree of carbonation during the application on the clay support.

Overall or Selective Application

Ancient painters employed the lime-based technique in varying ways, applying it either to the entire polychromy of an object or selectively to specific paint layers.

In the case of the ‹Purple Lady› (inv. MNB 584), as just noted, an overall application of the lime technique was identified. Conversely, the woman with a fan (inv. MNB 581) exemplifies a selective use of the technique: the purple-coloured paint of the chiton (using a colourant identical to MNB 584) contains a lime medium, while the blue paint of the mantle was executed in a tempera manner.

Some cases demonstrate an even more remarkable level of precision and selectivity in employing multiple painting techniques on a single object, as will be discussed next.



12 ‹Purple Lady› (inv. MNB 584), front view. Optical microscopy and SEM-FEG imaging of cross sections, showing how the limewater binder cementing the paint layers infiltrated, to varying degrees, the preparation underneath; b. c) Partial penetration for the blue-purple and d. e) Total impregnation for the black of the base; f. g) White of the mantle; h. i) No penetration for the purple of the dress.

Paint and ‹Glaze› Layers

In our examination so far, we have come across the use of a lime binder in paint layers of various colouration and thicknesses (ranging from 30–100 µm). A notable discovery was made on an Attic plastic lekythos representing Leda and the swan (inv. CA 1131), where a ‹glaze› layer[20] bound with lime was found applied on top of a paint layer executed a tempera (Fig. 13).

Originating from Athens between 375 and 350 B.C., produced in the workshop of the Berlin Group according to Trumpf-Lyritzaki, this figurine-vase stands out for its remarkable polychromy, originally full of colour and lustrous[21]. Extensive investigation[22] revealed the use of precious colour materials such as Egyptian blue, malachite, cinnabar, and gold leaf gilding as an additional sign of luxury. Several sample analyses indicated a tempera technique employing an (undetermined) organic binder, with these pigments and for the gilded highlights. Interestingly, a detail has been added with the lime technique: a subtle and superficial mauve ‹glaze› layer on the now pink border of the green himation, visible only upon close inspection (Fig. 14 a). The cross-section of a mauve sample confirmed that the ‹glaze› layer (about 30 µm) was coloured with an organic dye[23] and contained a lime binder (Fig. 14 b. c). Surprisingly, the thick pink layer underneath (around 300 µm) was prepared differently, without lime; it consists of a dye – of the same family as the glaze over it – and kaolinite, bound by an unknown organic substance.

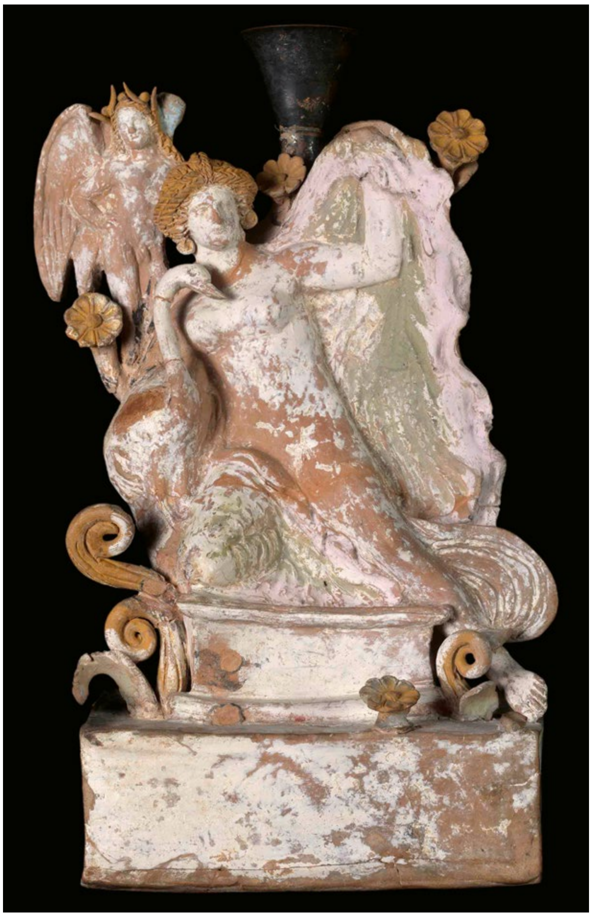
A parallel case characterized by the use of the same materials, stratigraphy, and combination of lime-based and tempera-painting techniques was evidenced in another Attic plastic lekythos representing a winged daimon seizing a young woman (Athens,

20 In the terminology of painting techniques, glaze usually refers to a transparent layer of a mostly organic nature, coloured or not. We keep here this term in quotation marks, as the composition is different (mineral, not organic) and so are parts of the visual properties.

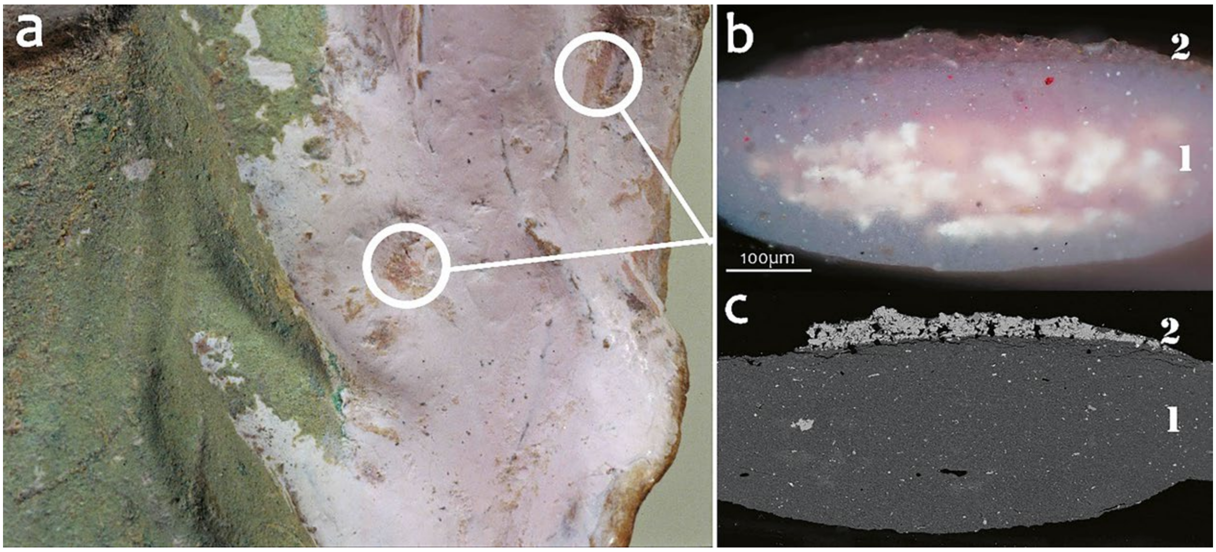
21 Trumpf – Lyritzaki 1969; Jeammet 2010, 78 f. cat. 43; Bourgeois 2010. See further Bourgeois et al. forthcoming.

22 Multi-spectral imaging, digital microscopy, in situ and sample analyses (XRF, XRD, FORS, Raman, SEM-FEG).

23 So far unidentified; Raman spectrum identical to the ‹Purple Lady› MNB 584.



13 Plastic lekythos representing Leda and the swan, c. 375–350 B.C., Athens (inv. CA 1131). Height 24 cm



14 Selective application of the lime-based technique on Leda and the swan. a) Detail of border of the green himation, showing the remains of a purple ‹glaze› layer on a pale pink layer; b) Cross section of a corresponding sample under optical microscopy imaging; c) SEM-FEG imaging: 1. pale pink paint layer of kaolinite and an unknown dye; 2. purple ‹glaze› layer of neoformed calcite and an unknown dye

inv. EAM 2059; cf. Verri et al. in this volume). Found in a tomb at Tanagra and dated to the period 400–350 B.C.[24], it has probably been produced in the same workshop as the Louvre lekythos, evident in the chromatic scheme and technical features. Notably, both demonstrate a special green-yellow hue reminiscent of the ancient Greek term *chlôros*[25], in addition to a similar treatment of the purple border.

These premium lekythoi underscore the meticulous craftsmanship, showcasing sophisticated painting skills and a high level of execution on clay objects in Athens during that era.

Discussion and Conclusion

Scientific results confirm that, during the 4th to early 3rd cent. B.C., some painters in coroplastic workshops of Mainland Greece used a limewater solution as a binder for painting terracotta figurines with mineral pigments and organic colourants.

To date, the technique has been identified on 13 objects. These include figurine-vases, such as the Attic Daimon lekythos and Leda lekythos, as well as figurines from the early Tanagrean series, which often depict elegant ladies draped in elaborate costumes highlighted with a vibrant purple colour. The spread of a ‹purple fashion for the *demos*› during the 4th cent. B.C. (see Verri et al. in this volume) certainly accounts for the frequent occurrence of such violet-purple dye, which was prepared with the lime binder. This systematic association might indicate that lime was used in the manufacture of the dye.

Various scholars[26] have previously established that lime was used in early times as a mordant for various purple dyes in the production of highly renowned textiles, and ancient texts contain recipes for obtaining a beautiful purple dye with cochineal and lime. However, in the present study, SEM-FEG analysis of cross-sections showing how the polychrome layers have been prepared and built up proves that, in this context, lime serves not only as a fixative for the colourant but also as a binder homogeneously distributed within the paint layer, cementing all other components. Additionally, the limewater solution was used with other organic colourants (such as carbon black) and mineral pigments (such as kaolinite, cinnabar, Egyptian blue). Therefore, this painting technique was deliberately chosen in some cases, not (only) as a technical requirement linked to the use of a specific colour.

This result presents a new chapter in our understanding of the history of ancient Greek painting techniques. However, further research is necessary to better understand the implementation of the technique. What about the concentration of lime and the pH of the binding solution? Were some organic additives (such as caseine) also used to improve the working properties of the solution? Lime and dyes are said to be incompatible, yet in this context, dyes have been used – and well preserved over millennia – in a lime-based medium. Is this due to the use of a secco – and not a fresco – technique? To answer these questions, experimental reproductions would be most helpful.

Another open question concerns the reasons for selecting such a technique instead of painting a tempera. Was it a matter of visual properties? Judging from the present state of conservation, it does bring a greater smoothness and gloss to the surface, not to mention the semi-translucency of the purple dye bound with neoformed calcite. Was it a matter of durability? If so, the ancient craftsmen succeeded, as the condition of these polychrome ladies is quite remarkable after millennia of burial in the ground. The significant resistance to weathering of this ‹mineral painting› calls for comparison with the field of fresco painting. However, as mentioned above, the implementation remains very different: there is no fresh lime substrate here, but a ‹dry› clay body and ground. There is also no migration of calcium hydroxide to the surface or any formation of calcin trapping the colouring substance – which might explain why the visual properties are different and why the colours do not appear duller and more opaque.

Beyond these questions directly linked to the role and properties of the lime binder, the nature of the purple organic colourant(s) remains to be identified through further analysis. The variety of hues – pink, mauve, or violet – present on the Louvre figurines matches the result of the investigation conducted in

24 Dug out by Stamatakis in 1881 (Stamatakis 1881, 13–15).
25 Bourgeois et al. 2022.
26 Brysbaert 2006, 260; Cardon 2014.

Greece (cf. further Verri et al. in this volume). Echoing the rich terminology of purple in ancient Greek texts[27], this variety confirms that the taste for purple could encompass an array of colour rendering – and probably materials. An important element to stress here is that the purple dye analysed on a number of high-quality terracotta statuettes is identical to the one used on the Parthenon marbles. Given that sampling is possible on the clay figurines – but obviously not on the rare traces kept on the precious Parthenon sculptures – the contribution of the coroplastic field might prove essential to the knowledge of the most famous monument of ancient Greek art.

Another important issue to explore further concerns the historical context of the lime technique: where did the practice originate, and what was the background of the craftsmen who mastered such multiple painting techniques? This high-quality coroplastic production has remained totally anonymous. No artist's name exists to dream about in this field of low-esteemed ‹minor objects›. However, examining a larger historical context may present some initial answers.

Within the studied corpus, the lime technique is attested as early as the 4th cent. B.C. in Athenian ceramic workshops, which specialized in the production of figurine-vases, before being adopted by Boeotian coroplastic workshops (Tanagra, Thebes) in the second half of the century and early Hellenistic period. It has not been found on Attic or Boeotian Late Archaic seated figures, nor on the traditional types of protomai and peplophoroi of the 5th cent. B.C.

What is also clear is that, during the middle and late Hellenistic period, the technique is not in use in major coroplastic centres of Eastern Greece such as Myrina or Smyrna. It thus appears to be characteristic of a certain time and place: Athens and Boeotia where the Tanagrean style was immediately adopted and produced on a large scale, mainly during the late 4th cent. B.C.

Outside the coroplastic field, very few cases of lime painting as a secco technique are known, and these are all dated to later times. Within the context of Macedonian funerary painting, the poros sarcophagus excavated in a tomb at Tragilos might have been painted with a lime binder, according to H. Brecoulaki and her co-authors[28]. Another probable occurrence is the painted décor of some metopes and architectural elements in the ‹Tombe de la balançoire› at Cyrene[29].

To summarize the question: was the lime technique a new practice developed by painters in ceramic workshops? Or should we think of craftsmen active in the field of mural painting who translated their technè to the ornamentation (kosmèsis) of offerings, specifically small-scale sculpture in clay? Does this technique bear any relationship to the growing influence of renowned painting centres such as Thebes in the 4th cent. B.C.[30]? Or did the initial input come from Athens, which plays such an essential role in the polychrome revolution of Late Classical art? In any case, it is a clear sign of an interesting diversification of painting techniques and the strong technical interconnection between fields of craftsmanship which are too often kept apart in modern taxonomies. It is hoped that further research, which is currently being conducted at C2RMF on Attic white-ground lekythoi and figurine-vases of the Late Classical period, will provide additional information on these questions.

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27 Bogensperger 2017; Brøns 2017.
28 Brecoulaki et al. 2006; Brecoulaki 2006, 388.
29 Rouveret – Walter 2004, 93–126. 149 f.
30 Reinach 1985, 268–280.

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