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RESEARCH

Investigating polychromy on the Parthenon's west metopes

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Abstract

The Parthenon's west metopes depict scenes of combat between Greeks and Amazons. The ten metopes that remain in situ have suffered extensive destruction and decay but they still retain traces of colored paint layers. In the present study, these metopes are investigated by means of imaging techniques (Portable Digital Microscopy and Visible-induced Infrared Luminescence-VIL) and laboratory techniques (Stereomicroscopy, μ-Raman Spectroscopy, ATR-FTIR, SEM/EDX). The obtained results revealed that the taenia that crowns the metopes was painted blue, by using Egyptian blue. No other blue pigment has been found at this point of the research. The background of the metopes was painted with red pigment consisting of hematite-Fe_2O_3 (associated with red ochre) and litharge (PbO). The concurrent presence of Fe- and Pb- compounds can be attributed to the use of either a Pb-containing natural source for red earth or an artificial red pigment (sandyx or syricum), derived by mixing and perhaps calcinating red ochre with a lead-based pigment, in order to achieve a certain hue. Carving marks (mainly made by a tooth chisel) are observed on the metopes' flat areas (background and taenia), as a preparation stage before the application of the polychromy. The rough surface enhanced the adhesion of the applied paint layers adding to the durability of the polychromy. Additionally, a red pigment residue found inside an ancient kylix that was discovered inside the architraves of the Parthenon was also investigated. μ-Raman spectroscopy was used in the Acropolis museum where the kylix is now exhibited. Hematite (red ochre) was the main compound identified. Litharge was also identified, but only in a single grain. This could indicate a red paint similar to the one found on the metopes' background, but still needs further investigation. The red and blue colors identified by the current research are, in most cases, in accordance with the literature and drawings of nineteenth century scholars who studied the Parthenon, thus allowing modern science to provide more concrete insight regarding the polychromy of the Athenian Temple.

Keywords Parthenon · Metopes · Polychromy · VIL · μ-Raman spectroscopy · Red ochre · Litharge · Egyptian blue · Sandyx · Syricum · Ancient kylix · Carving marks

Introduction

The fact that ancient temples and sculptures were decorated with color is today undisputable. On ancient temples, the pediments and the frieze, situated over 10 m above ground level and narrating mythological battles and religious rituals, required the use of color, in order to appear more natural, plastic, and clear to the pilgrim's eye.

The frieze of the Parthenon's external entablature consists of carved pictorial panels (metopes), separated by formal architectural triglyphs typical of the Doric order. The ninety-two metopes of the Parthenon are characterized by high-relief compositions depicting mythological battles, communicating the public character of the temple: the Fall of Troy on the north, the Gigantomachy on the east and the Battle between the Centaurs and the Lapiths on the south metopes (Michaelis 1871; Brommer 1967; Orlandos 1977; Korres and Bouras 1983).

The metopes on the west side represent battle scenes between Greeks and Amazons, a mythical tribe of all-female warriors. When the local Athenian hero, Theseus, abducted one of them, Antiope or Hippolyta, the Amazons invaded

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Attica, only to be defeated by the Athenians soon afterwards (Titi 2023).

The west metopes of the Parthenon suffered violent destruction by intentional hammering, perhaps during the conversion of the Parthenon into a Christian church not later than the sixth century C.E. (Korres 1994). The bombardment of the Parthenon by Francesco Morosini in 1687 did not affect the west metopes. In 2012, four of the fourteen west metopes that decorate the NW (WMO-1, WMO-2) and SW corners (WMO-13, WMO-14) were removed from the monument in order to protect them from further environmental impact; they are now exhibited in the Acropolis Museum. The remaining ten metopes remain in their original positions on the Parthenon.

Despite the extremely poor preservation state of the west metopes, in most cases it is possible to recognize their subject and composition. They depict scenes of combat between Greeks and adversaries in oriental garments identified as Amazons. The fourteen west metopes each depict two figures per panel, except for the first (from north to south) (WMO-1). The rest of the metopes (WMO-2 to WMO-14) each depict two figures, with alternating compositions. On even metopes, where the composition is discernable, a Greek and an Amazon can be distinguished, both on foot (WMO-2, 4, 10, 12, 14). On odd metopes, an Amazon on horseback and a Greek on foot seem to be depicted, with the Greek almost always on the ground (WMO-3, 5, 9, 11, 13) (Ebersole 1899; Praschniker 1954; Yeroulanou 1998).

Several scholars of the nineteenth century who studied the Acropolis monuments refer to the polychromy then still visible on the Parthenon's metopes. These references provide important information to scholars today, even though their descriptions vary. This literature refers either to the total ensemble of the Parthnenon's metopes (Michaelis 1871; Brommer 1967; Berger 1986; Yeroulanou 1998), or to groups such as the west metopes (Ebersole 1899; Praschniker 1954) or the east and the north metopes (Praschniker 1928). Regarding the west metopes, a description of their subject and composition was attempted, while some studies provide drawings (Praschniker 1954; Brommer 1967) or even photographs (Ebersole 1899; Brommer 1967; Berger 1986) of their state of conservation. Praschniker (1954) even produced reconstruction drawings of the west metopes, depicting them as he believed they must have appeared in ancient times.

Although the west metopes have suffered extensive destruction and decay, they still retain traces of colored paint layers. In the current study, the ten west metopes that remain in situ were investigated regarding their polychromy by applying an integrated methodology. The aim of this research is to reveal how the Parthenon's metopes were depicted at the time of their construction and to obtain new information regarding architectural polychromy of the classical period.

Materials and techniques

Thanks to the scaffolding installed for the needs of the current and the past restoration programs on the west entablature of the Parthenon, the visual inspection of the west metopes from a close distance was deemed possible. The remaining paint layers usually appear under –or together with– decay crusts and patina layers and, in most cases, they can hardly be distinguished with a naked eye.

The first step of the applied methodology was the detailed documentation of the polychromy remains, in macro- and micro- scale. By using imaging techniques (portable digital microscopy and Visible-induced Infrared Luminescence (VIL)), traces of color were detected under decay crusts and patina layers. Following the documentation, microsamples of paint layers were obtained and laboratory techniques were applied, such as:

- Portable digital microscopy (I-SCOPE-USB2, Moritex Corporations, magnification: $\times 30, \times 50, \times 120$)
- Visible-induced Infrared Luminescence-VIL (White light source: PAR CAN 36×3W LEDs (R: 12, G: 12, B:12), DMX controllable DSLR CANON EOS50E camera, from which the inner IR cut-off filter has been removed, Filter: B + W, 093IR, 52 mm), with the aim of detecting and mapping the Egyptian blue. This technique is based on the ability of EB to absorb visible light and luminesce in the near-infrared region (Verri et al. 2010; Kakoulli et al. 2017).
- Stereomicroscopy (MZ6 Leica Stereomicroscope) with magnifications from $12\times$ to 64x. The exterior and the interior (that was in contact with the marble) side of the microsamples were observed.
- μ-Raman spectroscopy (Renishaw inVia reflex μ-Raman microscope, magnifications: 5x, 20x, $50\times$ και 100x (SWD), laser wavelength: 785 nm (Diode: 300 mW), Spectra in the area of 100–2000 cm^{-1}, spectral resolution: ~2 cm^{-1}). μ-Raman spectroscopy was carried out with a microscope system (in Via, Renishaw) that enables users to study samples with uneven, curved, or rough surfaces. The system is coupled with an optical confocal microscope with transmitted and reflected light, notch filters, and a thermoelectrically cooled charged-coupled device (CCD) detector. The laser beam was focused on different areas of the samples. The spot size of the laser beam was ~2 μm, as focused with the objective lens $20\times$ and 50x. Density filters were used to set the laser power usually at 1% and in some cases lower, in the range of 0.01–1%) for an exposure time of 10 s. A 1200 lines/

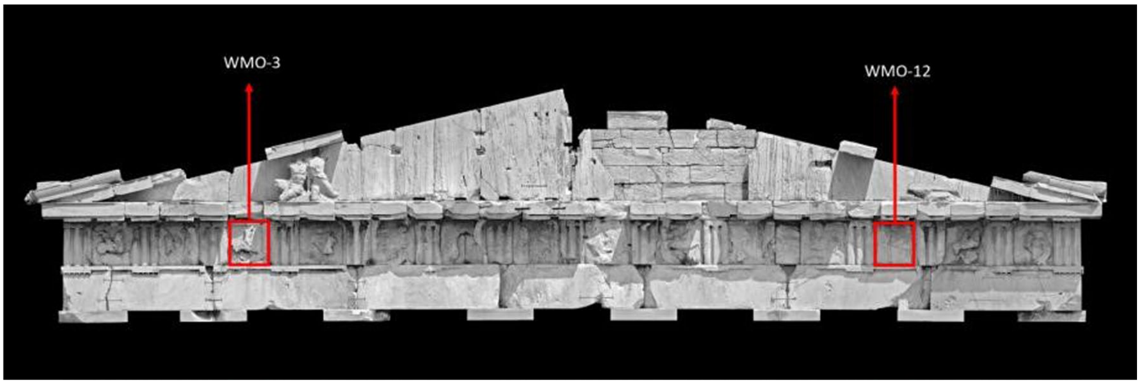

Fig. 1 West side of the Parthenon. Orthophotomosaic (D. Mavromati. YSMA archive). Red frame: The west metopes investigated via laboratory techniques

mm grating was used, and in each spot, 3–10 scans were acquired for each measurement, depending on the investigated sample.

- Fourier transform infrared spectroscopy (FT-IR) (Alpha II, Bruker) measurements, with a single reflection ATR module and a diamond crystal, were performed on selected samples. The spectrum was obtained in the mid-IR spectral range: 4000 cm^{-1}—400 cm^{-1} and collected 16 scans with a spectral resolution of 4 cm^{-1}. All spectra are presented after baseline correction and normalization.
- Scanning electron microscopy was employed with energy dispersive X-ray examination (SEM/EDX, SEM FEI Quanta 200) and secondary electron imaging (Analytical conditions: accelerating voltage 20 kV; filament current 2.00 A; emission current 25 μA; working distance 10–12 mm). Samples were placed without preparation in the instrument in order to preserve them as much as possible.

The microsamples were placed bottom-up during the spectroscopic investigation and SEM/EDX measurements. In that way, the cleaner surface that was in contact with the marble was examined and not the exterior one that was in contact with the environment.

The west metopes are numbered from north to south (Korres and Bouras 1983) (Fig. 1). The 1st metope (WMO-1) corresponds to the first from the north ending with the 14th metope (WMO-14) that is placed on the south side of the entablature (Fig. 1). The Parthenon's metopes are composed of the sculptural decoration which stands on the metope's background, a taenia and an astragal on the top of the metopes, as shown in Fig. 2.

In the present study, the entire surfaces of the ten west metopes that remain in situ are investigated. Unfortunately, due to their poor conservation state and the defacement of the sculpted figures, not much information remains, especially on the sculptures. Traces of paint layers were documented in the case of the third (WMO-3) and the twelfth west metope (WMO-12) of the Parthenon, whence microsamples were obtained and examined in lab (Fig. 1).

In addition to the investigation of the metopes' polychromy, it was also decided to examine a red pigment residue found at the site, inside a kylix. The aim of this supplementary investigation was to examine if the red pigment used for the metopes' decoration was the same as the one found inside the ancient kylix

This ancient copper kylix (500–480 BC) (Fig. 3) was discovered in 1994during the restoration works that were carried out at the opisthonaos of the Parthenon (Vlassopoulou 2017). The object was found during the dismantling of the opisthonaos' entablature, at the junction of the west and south wall, in the gap between the architraves and the inner frieze blocks, under a layer of marble flakes used for filling the gap. The kylix contained red pigment residues

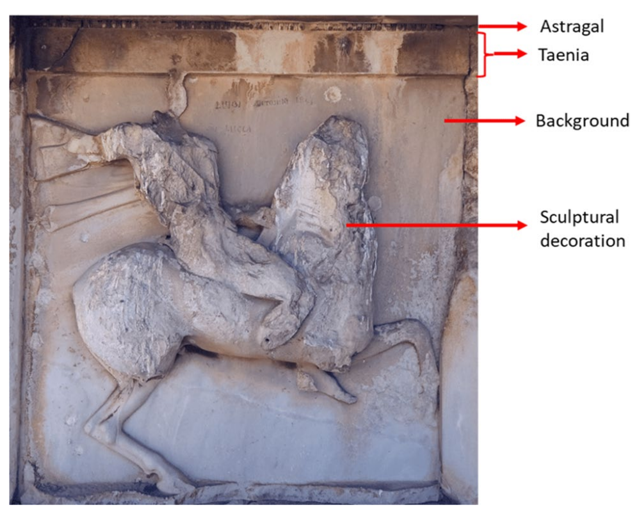

Fig. 2 The first west metope (WMO-1) where the different parts are indicated

Fig. 3 Ancient kylix of the Parthenon. Macroscopic image as it is exhibited in the Acropolis Museum

mixed with marble dust. The Parthenon's ancient kylix is now exhibited at the Acropolis Museum in Athens (Inventory no: Ακρ. 20,392), which provided permission for the in-situ examination of the red pigment residue, by means of μ-Raman measurements (portable B&W Tek i-Raman EX device). The device used was equipped with a laser excitation source operating at 1064 nm and spectra were recorded in the spectral range of (100–2000) cm^{-1} with a spectral resolution of 9.5 cm^{-1} at 1296 nm. The probe was attached to a camera. The spot size of the laser beam was 100 μm or 40 μm, when focused with the objective lens at 20× or 50x, respectively.

Results

Previous scholarship

Alexis Paccard (1813–1867) (Paccard 1982) holds a significant place in the study of the Parthenon's ancient polychromy since his descriptions were based on his own observations. Regarding the colors that were selected for the decoration of the metopes, Paccard states that the sculptures of the pediments, metopes and frieze stand out uniformly against a red background. He also states that he did not manage to detect any traces of color on the metopes that were still in place due to their existing condition, despite his efforts (Paccard 1982).

William Stahl Ebersole (1899), who studied the west metopes, comments on their coloring. He mentions that the upper left field of west metope 14 shows certain remains of red. He also states that some traces of red were observed on west metopes 1, 3, 8, 10 and 12, but he was not precise regarding the specific area of the metope where this color was observed (Ebersole 1899).

Adolf Michaelis (1835–1910) in his "Der Parthenon" claims that the high reliefs of the metopes project against a red background. He also mentions the literature of that time referring to south metope 12. (Michaelis 1871). Frank Brommer (1911–1993) in his Die Metopen de Parthenon (1967) devotes a small chapter to the metopes' polychromy. In a few pages he gathered all of the literature available regarding the colors applied and the published results from analyses of paint samples taken in 1926 and 1950. Moreover, he compares the previous scholarship with the observations that he made himself and he mentions the presence of red paint on the west metopes. Brommer also made his own observations regarding west metope 12: "…At the bottom of the west metope 12, I observed dark red on the ground, between the remains of the legs of the right figure, about 3 cm high with a horizontal upper edge. Perhaps this is the color that Ebersole was referring to. Prashniker said nothing about it. If this color is ancient, then the ground of the metope would have been red."[1] Thus, he concludes that according to his observations regarding west metope 12 and the observations of other scholars regarding south metopes 10 and 12, the background was probably red (Brommer 1967).

According to Anastasios Orlandos (1887–1979) traces of red color were preserved on the taenia (or fillet) of two metopes of the east side. He also states that color must have been used for the depiction of the vestments of the figures, while the background of the metopes was probably painted red (Orlandos 1977).

At this point it is worth mentioning the work of Herbert Koch (1880–1962) who studied the so-called Theseus temple, whose construction probably began as early as 449 BC, alongside the Parthenon. Koch observed bright red ("carmine red") as the background color in most relief metopes and blue for the decoration of the taenia at the top of the metopes (Koch 1955). Bruno Sauer (1861–1919) who also studied the Theseus temple, agrees with Koch, referring to the metopes' red background alternating with blue triglyphs (Sauer 1899).

Yet alongside references to the use of red on the metopes' background (Fig. 4a), different opinions regarding the color of the metopes' background are also found in the literature. William B. Dinsmoor (1886 – 1973) believed that the metopes of classical temples were always white, while the sculptured figures and weapons may have demanded colored details (Dinsmoor 1950). Dinsmoor did not explain the basis for his very confident statement and

[1] "West 12. Am unteren Rand der Metope sah ich zwischen den Fußresten der rechten Figur auf dem Grund dunkelrote Farbe etwa 3 cm hoch mit waagrechtem oberen Rand. Es könnte sein, daß dies die Farbe ist, die Ebersole erwähnte. Praschniker sagte nichts davon. Wenn diese Farbe antik ist, dann wäre der Metopengrund rot gewesen. Vgl. zu Ostmetope 9".

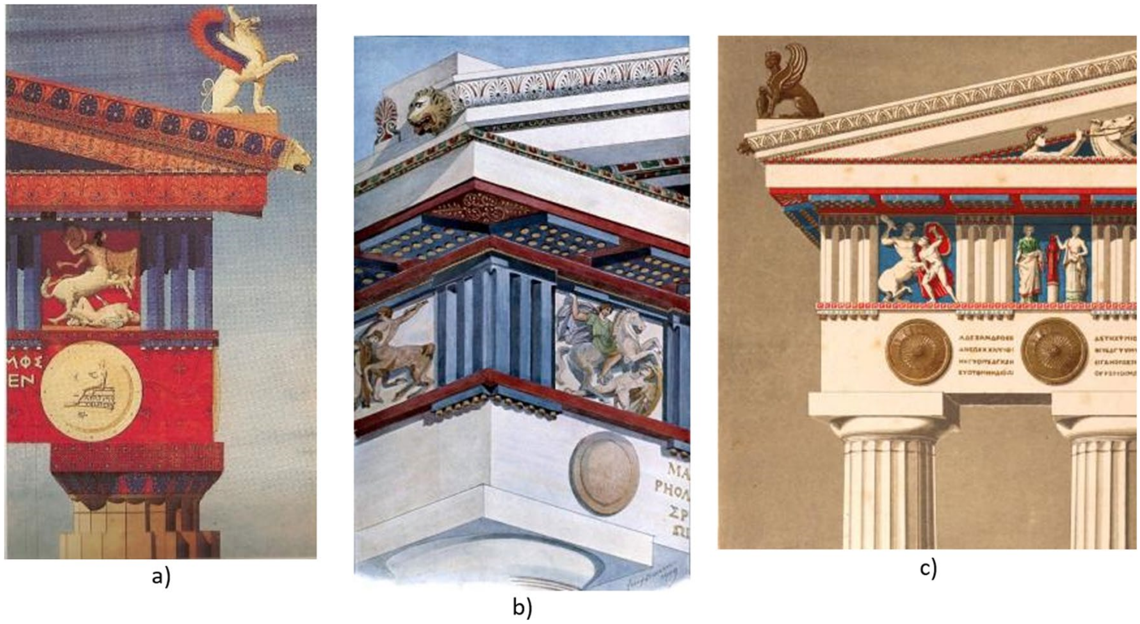

Fig. 4 Polychromatic reconstructions of the Parthenon. Use of red, white or blue color for the depiction of the metopes' background. **a**) Loviot, B. Restauration di Parthenon. 1879–80. Paris, Ecole Nationale Supériere des Beaux-Arts, evn. 79–01, **b**) Durm, J. W.(1837–1919) 1881. Die Baukunst der Griechen (Taf.IV, p.231), c) Kugler F., 1835. Uber die Polycromie der griechischen Architektur und Skulptur und ihre Grenzen, Berlin

his opinion obviously contradicts the accumulated testimony of many earlier observers. However, at this point, it is worth mentioning that the metopes that decorate the façade of the ancient Macedonian tomb of Judgement in Lefkadia (built in the beginning of the third century BC) exhibit a white background, while 'colored details' are present on the figures, thus aligning with Dinsmoor's theory. These metopes contain scenes of single combat between Lapiths and Centaurs and although they are not sculpted, they were painted in a technique intended to simulate metopes with carved reliefs such as those of the Parthenon (Bruno 1981). In the literature, there are also several reconstructions that use white for the background of metopes, such as the reconstruction of Josef W. Durm (1837–1919) (Durm 1881) and Anton H. Springer, (1825 – 1891) (Springer et al. 1923) (Fig. 4b).

There are other scholars who stated that the background was painted blue, such as Franz Kugler (1808–1858) (Kugler 1835) (Fig. 4c). Adolf Michaelis (1835–1910) also referred to the tendency of that time to think that the background of the metopes was painted blue andexpressed his doubts on that opinion: he says that he did not find blue anywhere in the background and stated that blue was definitely the color of the triglyphs, it seemed paradoxical to him that it was used on the metopes' background as well (Michaelis 1871).

Finally, there is even one theory, presented by Patrick Reuterswärd (1922–2000) (Reuterswaird 1958), that the background of the metopes alternated red and blue around the four sides of the building, the system that is supposed to have been employed at the temple of Zeus at Olympia.

Regarding the color of the taenia above the metopes and the triglyphs, in the literature it is mentioned that it must have been blue (Vlassopoulou 2010, 2014).

Regarding the investigation of pigments used for the decortation of the metopes that previously occurred in the lab, minimal references exist in the bibliography. Both Reuterswärd (Reuterswaird 1958) and Brommer (Brommer 1967) refer to the work of Cesare Brandi (Brandi 1951), who mentions that in south metope 10, which is located in the Louvre, red-brown was found at the bottom of the metope. This red paint layer was subjected to chemical analysis in 1950–1951 and the results revealed that this sample was comprised of red ochre with calcium carbonate.

In the mid-1980s, during the restoration program carried out on the East side of the Parthenon, scholars observed the existence of blue paint decorating the taenia of the east metopes and triglyphs. A sample of the blue paint taken from the taenia of the 14th east metope was characterized by means of SEM/EDX and XRD analysis as Egyptian blue (Kouzeli et al. 1989).

Moreover, in 2006–2007 during the conservation and laser cleaning of the fourteen east metopes, traces of paint were revealed in various areas of eight of the metopes (East 3, 4, 9–14), among patinas. Traces of blue pigments, varying in shade from azure to gray-green, were also discovered on the taenia and the astragal, as well as scattered on the background. Red pigment was located on the taenia and the background (Vlassopoulou 2014).

Current investigation – imaging and laboratory techniques

In the ten metopes under investigation here, no color was detected on the sculpted figures, since in most cases the original surface of the carved areas does not survive due to extensive defacement. Moreover, no paint layer was documented on the astragals. Traces of paint layers were documented only in the area of the taenia and the background of the metopes and mainly on the third (WMO-3) and the twelfth west metopes (WMO-12). These two metopes are presented thoroughly below.

West metope 3

The current conservation state of west metope 3 (WMO-3) is presented in Fig. 5a along with the investigated and sampling areas. According to the literature, WMO-3 depicts an Amazon on a horse on the right and a wounded man fallen below them on the left (Fig. 5b). The Amazon wears a short chiton and her left-hand rests on the horse's mane, possibly holding the reins. Her right hand was evidently raised and perhaps held a spear. The figure on the right rides a prancing horse, whose tail, slightly extended and then falling, is gradually flattened into the background. The wounded warrior on the left, probably a Greek, is depicted nude and is falling forward to the right, resting on the left hip and hand (Ebersole 1899; Praschniker 1954). Both figures and the horse are damaged and the horse is missing its two right legs. The original surface of the relief is visible only at the left back leg and the lower part of the horse's stomach and at the background of the metope (Fig. 5c).

WMO-3 currently exhibits a poor state of conservation. Patina layers and decay crusts are present mainly on the north part of the metope, while the marble surface of the south part has significantly eroded. The back left leg of the horse, however, preserves its original surface. The detail in the relief and the smooth final surface, probably elaborated with abrasives such as emery and pumice (Palagia 2006), can still be admired. Carving marks are observed on the background of the metope (Fig. 5a) and on the taenia. The observed marks were mostly made with a tooth chisel. Although the carving marks seem to have been made in a certain direction for each area, the marks intertwine when the direction is altered between areas, thus creating a connection between the carved surfaces. This pattern is also observed in other west metopes and cornice blocks. The current finding enhances the theory that the surfaces were prepared to enhance adhesion of the paint layers to the marble substrate. Traces of different carving tools were also observed on the Parthenon sculptures examined at the British Museum. In that case, however, the different carving tools were used mainly in order to represent different textures (e.g. skin, wool, linen) for the vestments depicted (Verri et al. 2023).

VIL investigation revealed no information on the background of the remaining sculptures. However, Egyptian blue was recorded in certain parts at the top of the taenia (Fig. 6a). VIL was also applied to the other nine west metopes that remain in situ, but no information was recorded in the background of the remaining sculptures. To the contrary, strong luminescence was recorded on the continuous taenia that runs along the upper part of the metopes and triglyphs, not only in the case of the 3rd metope, but also at the taenia of the 4th, 5th, 10th, 11th, and 12th west metopes. This luminescence is related to the presence of Egyptian blue and in some cases (i.e. borders of the taenia) it is more intense, whereas in other areas a faint presence is documented. Most probably, it was entirely depicted with Egyptian blue and in some cases the pigment has washed out. In the case of the 3rd metope, after the detection of Egyptian blue by means of VIL, digital portable microscopy was applied and the blue paint layer was recorded behind the brown-orange patina layers (Fig. 6b).

A blue paint layer microsample (WMO3_T) taken from the taenia area was investigated in lab aiming to confirm the presence of Egyptian blue. ATR-FTIR spectroscopy (Fig. 6c) was applied on the microsample and Egyptian Blue was identified through the characteristic triplet at 1006, 1057 and 1162 cm^{-1} (Mazzocchin et al. 2004; Mahmoud and Papadopoulou 2013). Moreover, the FTIR-ATR spectra recorded typical absorption bands of gypsum with peaks at 3529, 3401, 1620, 1104 and 668 cm^{-1} (La Russa et al. 2009) and calcium oxalates (1637, 1321 and 779 cm^{-1}) (Calia et al. 2011; La Russa et al. 2017).

Another area that preserved traces of polychromy is the background, in contact with the horse's tail, where a line of dark red–black is discerned (Fig. 7a). This line could either be the remains of an outline used to emphasize the tail's relief or the conserved color of the background, on account of this area being more protected. Digital portable microscopy could not be applied in this area due to the geometry of the existing relief. However, a microsample of the red–black paint layer (WMO3_B) was taken (Fig. 7b) and examined by μ-Raman spectroscopy (Fig. 7c). Plattnerite (b-PbO_2) was detected through the peaks at 515 and 225 cm^{-1} present in the Raman spectra (Ruff.info/Plattnerite/R080019 2024) and is related to the degradation of the red lead pigment (minium, Pb_3O_4) that will be discussed further in the Discussion section of this paper. The spectra also showed Raman bands centered at 1345 and 1577 cm^{-1}. These bands were assigned to carbon (1325(br), 1580(br), most probably originating from pollution, attached through

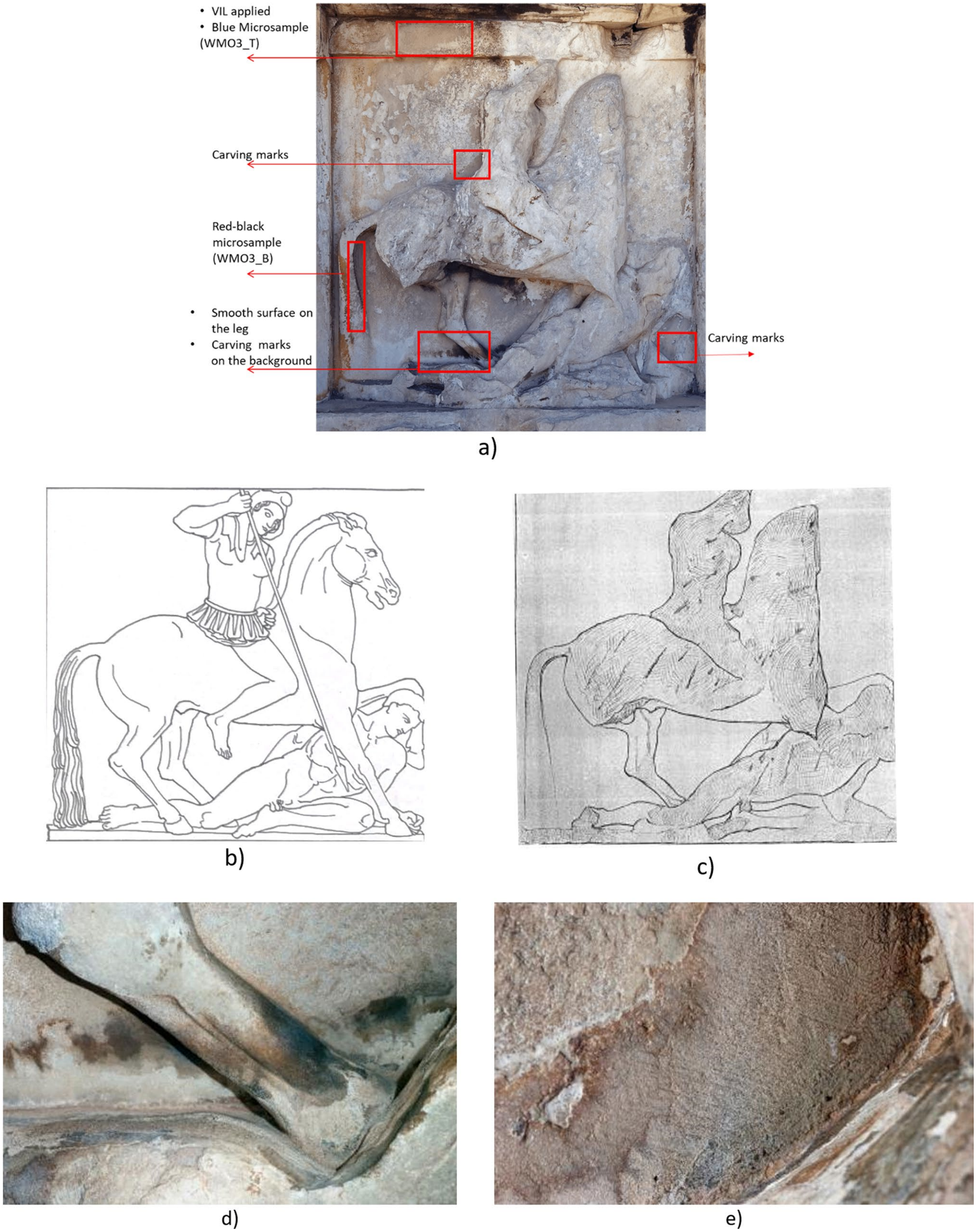

Fig. 5 The third west metope of the Parthenon (WMO-3). a) Current image. Investigated and sampling areas are indicated, b) Representation (Praschniker 1954-pl.6), c) Mapping of the original and the defaced areas (Praschniker 1954-pl.5), d) Detail of the left back leg of the horse, e) Carving marks on the background area (seen in Fig. 5a)

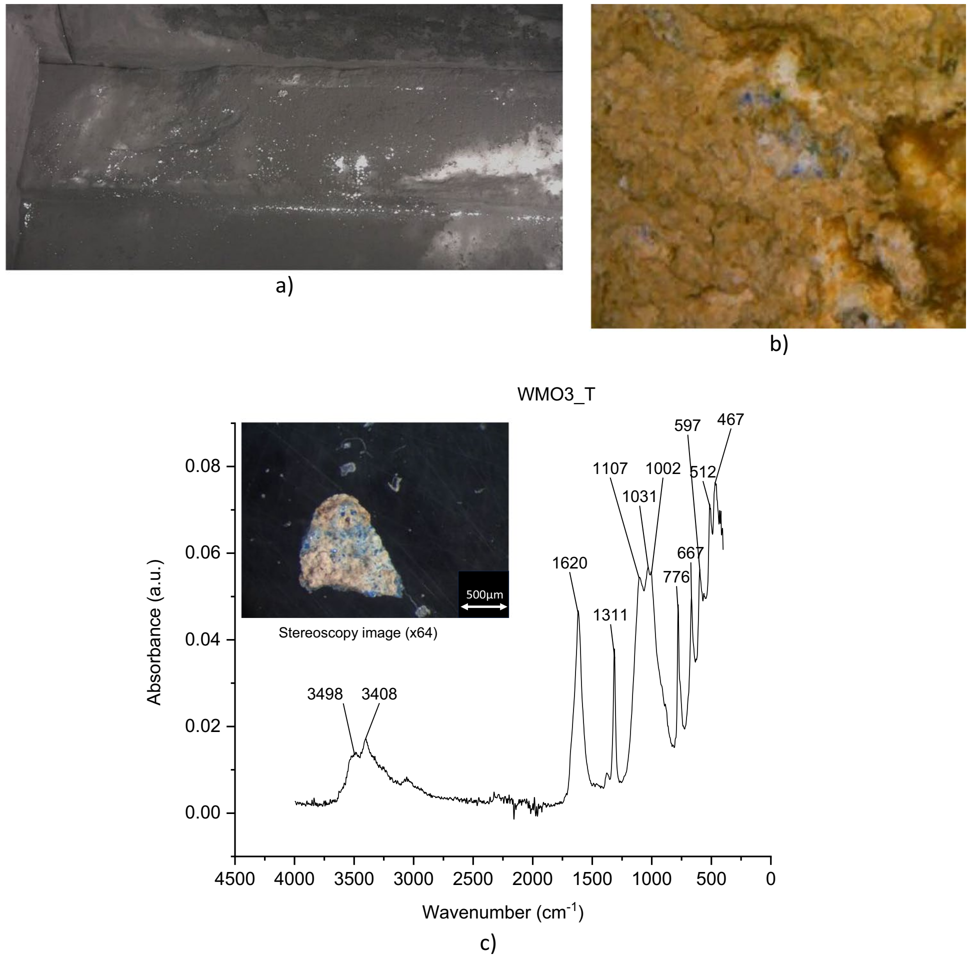

Fig. 6 Taenia of the WMO-3. a) VIL image (area seen in Fig. 5a). Luminescence related to the Egyptian blue presence, b) Digital portable microscopy image (×50). Blue paint layer behind the patina layer, c) ATR-FTIR spectra of the blue paint layer microsample (WMO3_T). Egyptian blue, gypsum, and oxalates

dry deposition (soot particles) (Marszałek 2016; Martınez-Arkarazo et al. 2007).

West metope 12

According to the literature, the twelfth west metope depicts two standing warriors (Fig. 8a-b). The figure on the left probably depicts a Greek carrying a round shield on his left arm. His right arm is raised upwards and his left foot is advanced. The figure moves to the right towards an enemy who seems to be on the defense, retreating to the right. The figure on the right, probably an Amazon, has almost vanished.

Despite the poor conservation state of west metope 12 (WMO-12), two extensively damaged figures can still be distinguished (Fig. 8a). On the right part of the metope, the relief has been carved to a depth of 3 cm and only the lower half of the slab is preserved in good condition (Ebersole 1899; Praschniker 1954). Patina layers and decay crusts are present mainly on the upper half part of the metope, while the marble surface on the lower part has been significantly eroded.

VIL was applied to WMO-12 and no information was recorded as to the background coloration of the remaining sculptures. However, Egyptian blue was recorded in certain parts at the taenia on the top of the metope (Fig. 8c).

Regarding the remaining polychromy, traces of red paint survive on the background of the metope. More specifically, a relatively large area (Height: ~ 3.5 cm, Length: ~ 7 cm), depicted with a rather dark red color, is present at the bottom of the metope between the remains of the legs of the right figure with a horizontal upper edge (Fig. 9a). This is probably the area that Brommer referred to in his work "Die Metopen Des Parthenon" and it seems that the red color has survived decades after Brommer' s observations. Other spots of dark or brighter red color are present on the left part of the metope, in the middle area. In order to identify the pigments present in the observed red paint layer three microsamples were obtained, as shown in Fig. 8a. The microsamples correspond to varying tones of red, from dark to bright.

The microsample obtained from the bottom right area of the metope (WMO12_B1, Fig. 9b), which preserves a significant amount of red, was examined via µ-Raman spectroscopy. The spectra (Fig. 9d) revealed the presence of

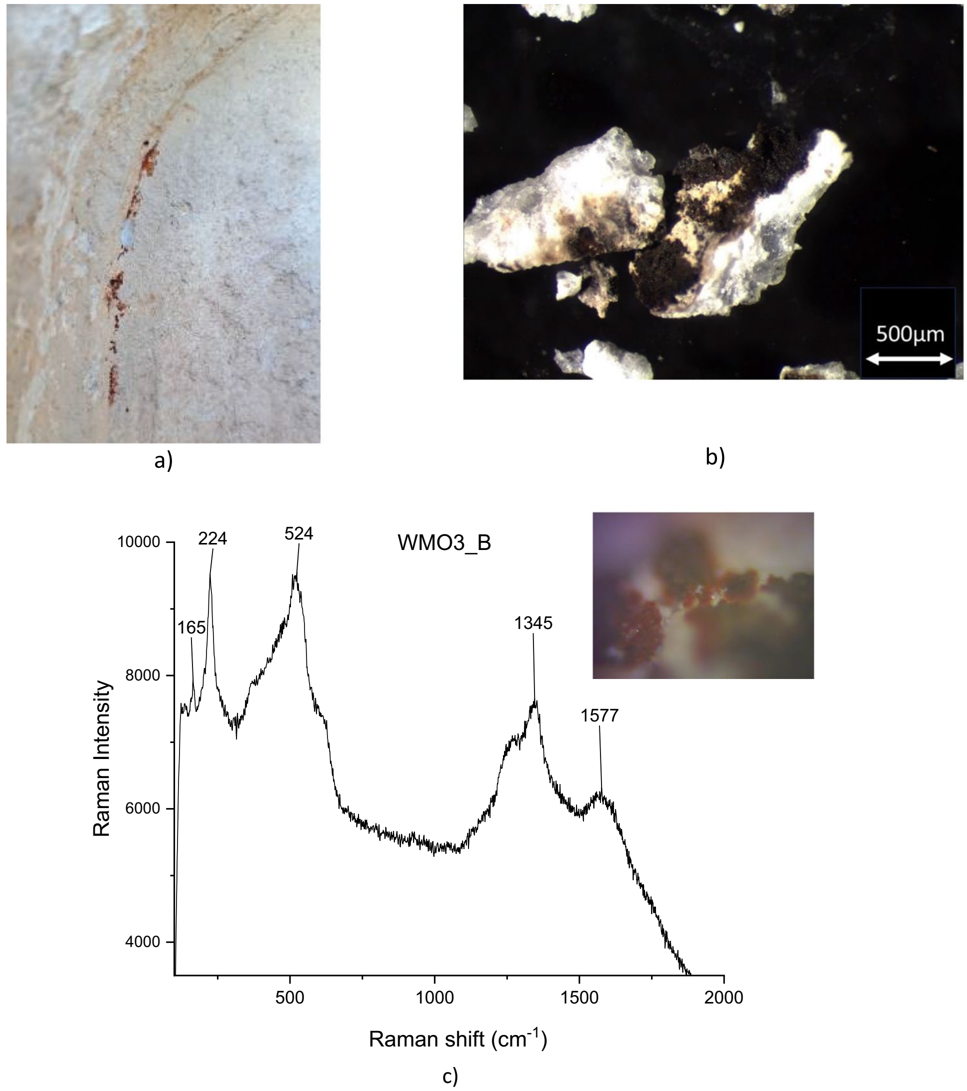

Fig. 7 Horse's tail area of the WMO-3. a) Red–black painted line next to the horse's tail (area seen in Fig. 5a), (b) Stereomicroscopic image (×64) of the microsample (WMO3_B) c) μ-Raman spectra and microscopic image. Plattnerite and carbon black are identified

hematite (iron(III) oxide, hematite (α-Fe_2O_3)), as the characteristic peaks of 220, 295, 410 and 611 cm^{-1} occur (Bell et al. 1997; Bouchard and Smith 2003). In this microsample, calcium oxalates of the more stable monoclinic monohydrate ($CaC_2O_4 \cdot H_2O$, whewellite) are also present, as identified through the Raman peaks 1462, 1490, 894 cm^{-1} (Ruff.info/Whewellite/R050240 2024)**.** Oxalates may be associated with biodecay (Rampazzi, L., 2019) and this may be evidence for the existence of primitive life forms, such as lichens and fungi, on top of the paint layers (Krajanová, 2023; Frost 2004; Chisholm et al. 1987).

SEM/EDX analysis applied on microsample WMO12_B1 (Fig. 9c) confirmed the presence of the iron-based pigment (red ochre). Fine grains of hematite were detected with an average diameter of ~ 2-10 μm. Spot analysis revealed a high concentration of iron (Fe: 17.09%), silicon (Si: 3.16%), and aluminum (Al: 0.46%) elements, strongly related to red ochre. It is interesting that high concentrations of lead (Pb: 10.82%) were detected in almost all examined spots, indicating that a lead compound is present in the paint layer, even though no lead compound was found through the μ-Raman investigation.

Phosphorus in relevant high percentage (P: 3.37%) was also detected in all investigated spots. In prior research works, phosphorus was also identified in orange-brown patinas of the Acropolis monuments (Maravelaki-Kalaitzaki 2005; Polikreti & Maniatis 2003). In these cases, the presence of phosphorus (in the form of hydroxyapatite) was associated with the decomposition by-products of organic matter from ancient treatments/practices used for the marble's protection and/or toning.

During this stage of the research the presence of a Ph-compound pigment, such as bone white or bone black, which was used for color mixing, cannot be excluded. Additionally, in some spots, arsenic (As: 1.08%) was detected. The existence of this compound can be attributed to the presence of

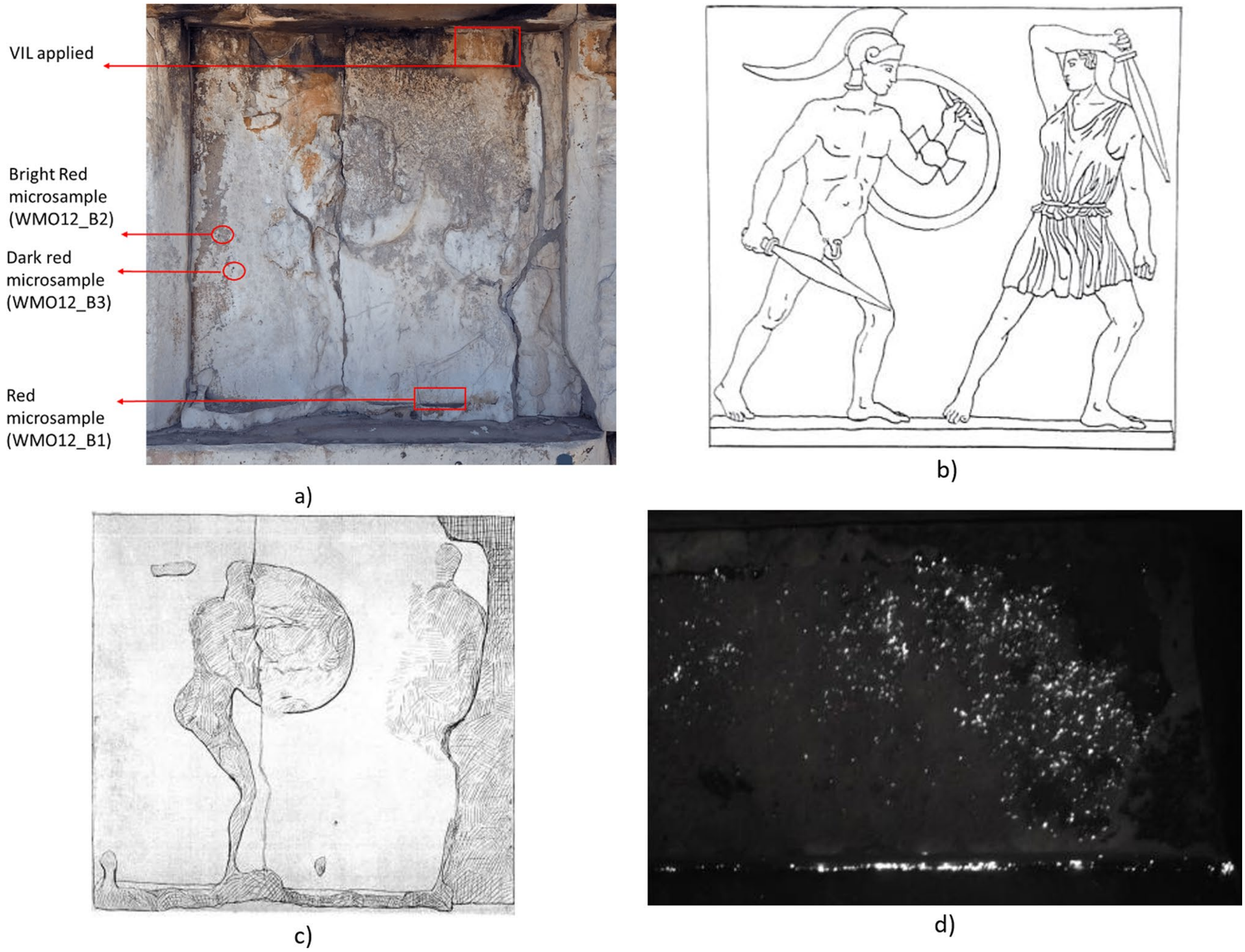

Fig. 8 The twelfth west metope of the Parthenon (WMO-12). **a**) Current image. Investigated and sampling areas, **b**) Representation by Praschniker 1954-pl.22, **c**) Mapping of the original and the defaced areas (Praschniker 1954-pl.21). **d**) VIL image (area indicated in Fig. 8a). Luminescence related to the presence of Egyptian blue

red ochre, as a naturally occurring impurity. Lavrion ore, located at the outskirts of Athens, presents a high percentage of the arsenic mineral and deposits of red ochre, as well. Moreover, in the literature, red ochres containing arsenic are also referred (Secco et al. 2021). In any case the presence of these elements requires further investigation.

The investigated microsample with the bright red color (WMO12_B2, Fig. 10a) obtained from the middle of the metope revealed, by means of the μ-Raman spectroscopy, the presence of litharge (tetragonal lead (II) oxide, α-PbO) with the characteristic μ-Raman peak at 147 cm^{-1} (Aze et al. 2008; Burgio and Clark 2001). The presence of gypsum ($CaSO_4 \cdot 2H_2O$) was also identified, mainly from its main Raman peak at 1008 cm^{-1}, present in the spectra (Kramar et al. 2010). Taking into account that the paint layers were applied directly to the marble substrate without a preparatory layer (Aggelakopoulou and Bakolas 2022), the presence of gypsum can be associated with the decay of the marble layer due to SO_2 pollution. Quartz was also identified through the characteristic peaks of 464, 355, 129 cm^{-1}, associated with the presence of red ochre (https://rruff.info/quartz/R100134 2024; Saikia et al. 2016).

Finally, the microsample with the dark red color (WMO12_B3, Fig. 10b) obtained from the middle of the metope revealed, by means of μ-Raman spectroscopy, the presence of hematite, litharge, and quartz. In this microsample, calcium oxalates ($CaC_2O_4 \cdot H_2O$, whewellite) are also present.

Ancient *kylix* of the Parthenon

After its discovery in 1994, the ancient kylix (500–480 BC) was sent to the National Archaeological Museum for the characterization of the pigment and its conservation. Atomic absorption analysis was applied to study the pigment and revealed the elemental chemical composition of the red

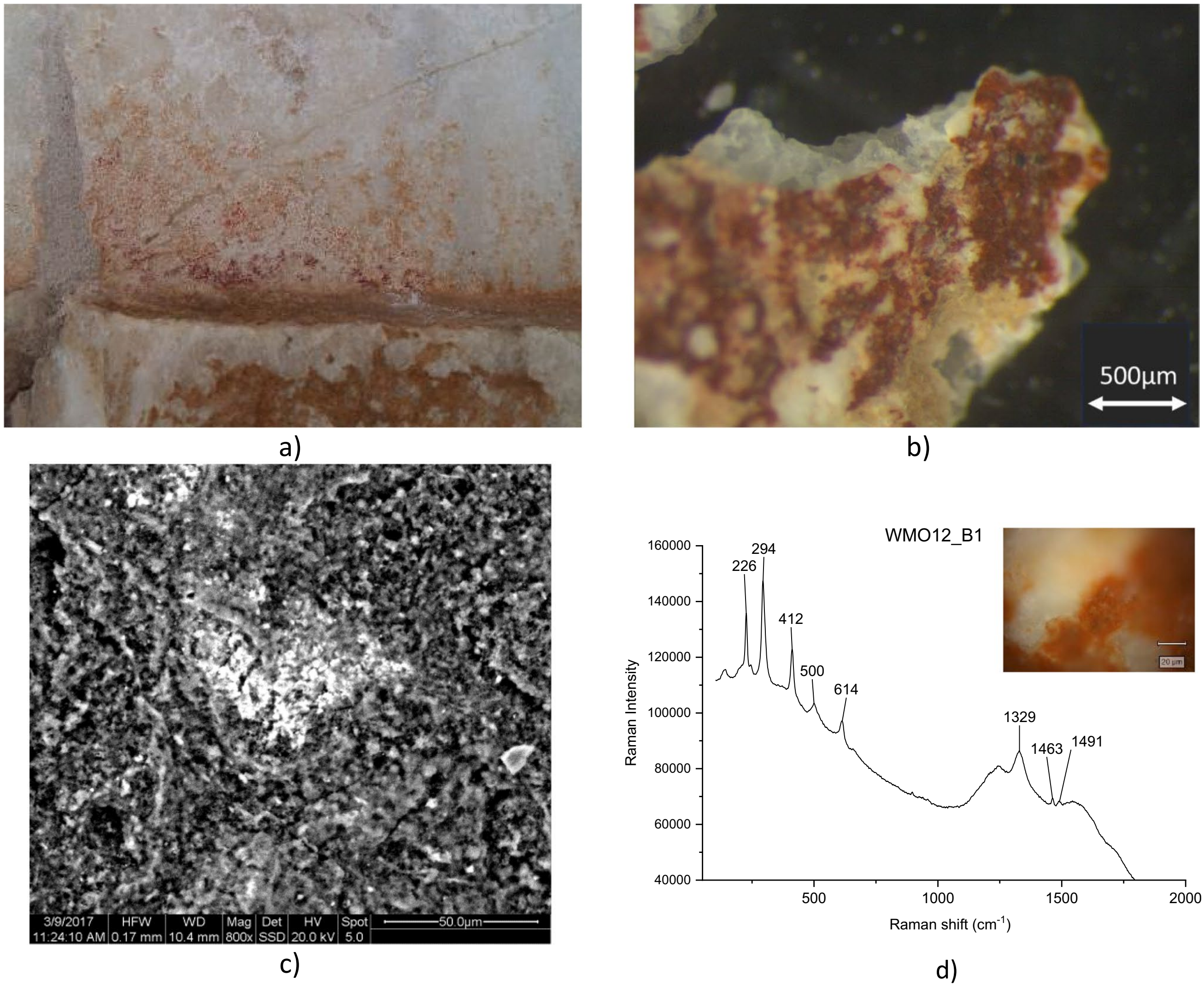

Fig. 9 Bottom right area of the WMO-12, which preserves a significant portion of red. **a**) Macroscopic image **b**) Stereoscopic image (×64) of the microsample (WMO12_B1), **c**) SEM Image (×800). Presence of hematite grains, **d**) μ-Raman spectra. Presence of hematite and whewellite

pigment as follows: Ca: 61.95%, Pb: 6.10%, Fe: 6.90%, Zn: 0.58%, Mg: 0.72%, K: 0.14%, Na: 0.07%.

In the present study, different spots were investigated on the pigment residue via μ-Raman technique, in situ. Most of them revealed a spectra characteristic of hematite (red ochre with peaks at 220, 290, 410, 610 cm^{-1}). A specific grain, though, demonstrated a spectra typical to litharge (characteristic peak at 145 cm^{-1}), as seen in Fig. 11. This finding is in accordance with the atomic absorption analysis data of 1994, which indicated a high percentage of lead inside the pigment, up to 6.10%.

Therefore, according to the current results, hematite (red ochre) was the main compound found inside the ancient kylix. The red pigment perhaps includes a lead-containing compound along with the hematite, but this requires further investigation.

4. Discussion

Concerning the taenia at the top of the metopes, a blue paint layer was recorded on the third west metope of the Parthenon with a portable digital microscope, while by means of VIL the presence of Egyptian blue was revealed on the taenia of most of the west metopes. The presence of Egyptian Blue was also identified with ATR-FTIR spectroscopy in a microsample taken from the taenia of the third west metope. This finding is in accordance with the study of the mid-1980s where a sample of the blue paint obtained from the filet of the 14th east metope was characterized as Egyptian blue (Kouzeli et al. 1989). The blue taenia that was found through the current research is in line with certain literature regarding the Parthenon's polychromy (Vlassopoulou 2010, 2014). This finding is also in accordance with the work of

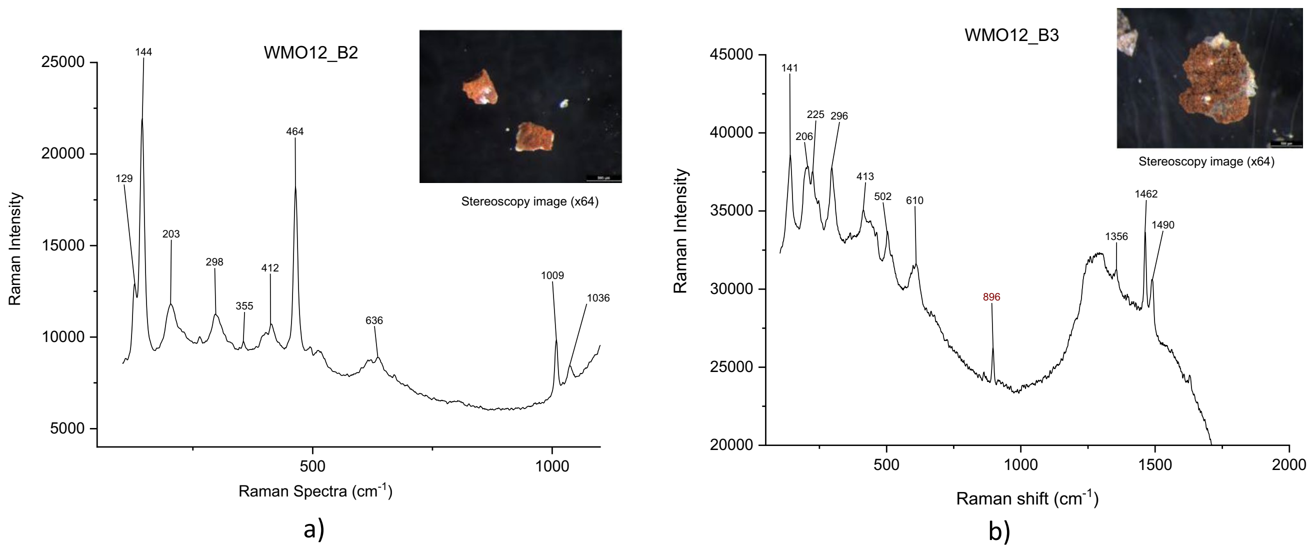

Fig. 10 µ-Raman spectra and stereoscopic image (×64) of microsamples taken from the middle of the background area. **a**) WMO12_B2. Presence of litharge, gypsum and quartz, **b**) WMO12_B3. Presence of litharge, hematite and whewellite

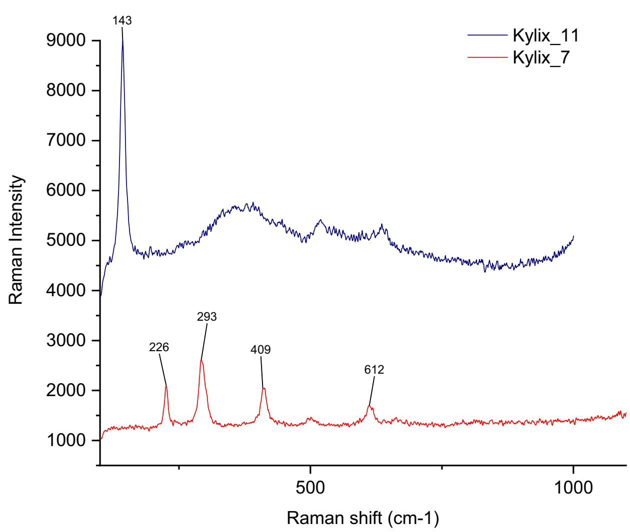

Fig. 11 µ-Raman spectra of the red pigment residue of the ancient kylix of the Parthenon. Presence of litharge and hematite

Koch who studied the Theseus temple (Koch 1955) and describes the blue color that was applied to the decoration of the taenia at the top of the metopes. Egyptian blue was also used in other architectural members of the Parthenon (Aggelakopoulou and Bakolas 2022) and on the Parthenon sculptures at the British Museum (Verri et al. 2023).

As it concerns the red paint layers on the metopes' background, the results from the microsamples obtained from west metope 12, revealed different mixture percentages of hematite (related to red ochre) and litharge (a-PbO, tetragonal) in the three investigated microsamples (the first characterized as red ochre, the second as litharge, and the third as a mixture of litharge with red ochre). Red ochre is a pigment that was identified in many other investigated architectural areas of the Parthenon (cornice blocks—viae, bottom side of the guttae, background of the taenia at the base, impost block of the south-west anta) and the Propylaea (Impost block of the north-west anta) (Aggelakopoulou and Bakolas 2022; Aggelakopoulou et al. 2022).

The investigated red pigment residue found in the ancient bronze kylix (500–480 BC) of the Parthenon revealed the presence of hematite (red ochre) as the main compound. Litharge was also identified in a single grain of the red pigment residue. Therefore, the red pigment perhaps contains a Pb-compound along with the hematite and it could indicate a red paint similar to the one found on the metopes' background. This hypothesis requires further investigation. In any case, the discovery of red pigments inside the kylix strengthens the theory that the ancient kylix was used as a painting vessel and was perhaps thrown or dropped from a painter's hands in the fifth century BC.

At this point, the statement that arises and needs further discussion is the simultaneous presence of a lead compound (litharge) together with an iron compound (hematite derived from red ochre) in the red paint layer of the metopes' background and perhaps in the red pigment residue found in the ancient kylix. Two possible interpretations might explain the presence of lead in these pigments.

The first interpretation is related to a Pb-containing natural source of red earth. According to certain scholars the prominent red pigment from Kea, known as the best-quality red earth, was found to contain hematite and lead oxide (Katsaros and Bassiakos 2002). Other scholars have not found lead oxide in investigated samples of Kean earth

(Photos-Jones et al. 1997, 2018), although such variations can be expected from materials of natural origin.

The second interpretation is related to the use of an artificial red pigment for the background of the Parthenon's metopes. According to this interpretation, the identified lead and iron compounds derived from a mixing process and even a calcinating process in order to produce an artificial red pigment of a certain hue. Such artificial red pigments were well-known in ancient times and were named sandyx or syricum.

Regarding the use of a mixture of red pigments, relevant references can be found in ancient texts. Pliny the Elder, in book 35 "An account of paintings and colors" of his "Natural History", refers to the use of more than one red pigments, one imposed over the other, or to the mixture of two red pigments, aiming to produce a specific chromatic result. More specifically, he states that "… It is with this material (earth from Lemnos, sphragis) that they provide the undercoating to minium, in the adulteration of which it is also extensively employed" – a clear reference to a red pigment produced by a mixture of different red pigments (Pliny, *NH* 35.14). He also writes that "Among the artificial colors, too, is syricum, which is used as an under-coating for minium, as already stated. It is prepared from a combination of sinopis with sandyx" (Pliny, *NH* 35.24). According to Pliny, sinopis is a red earth of Sinope (Pliny, *NH* 35.13), and Sandyx (Pliny, *NH* 35.23) derives from a calcined mixture of equal proportion of rubrica (red earth) and sandarach (prepared by calcining ceruse in the furnace and therefore it correlates to the contemporary red lead-minium) (Levidis 1994). Moreover, it should be borne in mind that often, when the ancients spoke of minium, they in some cases meant cinnabar (HgS) (Levidis 1994, Bearat 1995). Regardless, Pliny made a clear reference to the imposition or the mixing of various red pigments, in order to succeed a certain aesthetic effect.

Moreover, in the color catalogue of Pompeii, under colors deposited at the Naples National Museum, in inventory no. 112246, there is a red pigment referred to in antiquity as sandyx or syricum, which is cerussa usta + ocra rossa, lead minium associated with hematite (Augusti 1967).

Red pigments containing both iron and red lead (minium) have been identified in several studies: in Roman wall paintings (Bearat 1995; Fermo et al. 2013), in polychromy traces on Trajan's column (Del Monte et al. 1998), and polychrome sculptures (Antonelli et al. 2017; Kopczynski et al. 2017). Hematite with lead tetroxide (Pb_3O_4, minium) was also found as pigments lumps at a Hellenistic pigment production site in the ancient agora of Kos (Kostomitsopoulou-Marketou et al. 2019).

As we can see in the literature, the use of an artificial red pigment composed of red lead and hematite is often referred to, though in our case litharge and hematite were identified. The presence of litharge instead of red lead can be justified if we take into consideration the production process of red lead and the alteration products of red lead under specific conditions. Litharge or massicot may be present in the red lead pigment, depending on the production process of the red lead and possible incomplete reactions (Ciomartan et al. 1996; Gliozzo and Ionescu 2022; Risold et al. 1998). Monoxide contents, in the form of litharge, up to 92% were detected in traditional Chinese red lead pigments (Yamasaki 1959).

The discovery of the Pb- and Fe-containing paint layers on the Parthenon reinforces the hypothesis that such pigments were produced and widely used in antiquity.

Moreover, in the microsample of the background of metope WMO-3 (associated with a red–black line observed next to the horse's tail), plattnerite (β-PbO_2), and carbon black were identified. Carbon black most probably originated from pollution processes since it is attached through dry depositions (soot particles). Regarding the presence of plattnerite in the microsample, according to the literature it can be produced by red lead pigment (minium, Pb_3O_4) in high humidity conditions, which favor the ability to support microbial development, according to the following chemical reaction (Qingping et al. 1999; Aze et al. 2008):

$$Pb_3O_4(\text{minium}) + 4H^+ \rightarrow PbO_2(\text{Plattnerite}) + 2Pb^{2+} + 2H_2O$$

The transformation of red lead into black lead dioxide is generally stated as the main cause of red lead darkening. Plattnerite has been identified in numerous artworks (Gliozzo and Ionescu 2022), such as polychrome sculptures (Doménech-Carbó et al. 2000) and wall paintings (Bøllingtoft and Christensen 1993; Brill et al. 1997; Bikiaris et al. 2000).

This is the second case where plattnerite has been detected in a Parthenon microsample. Plattnerite was also found (together with litharge) in a brown–red paint layer derived from a line border on the ceiling's background at the north-west corner cornice block (Aggelakopoulou and Bakolas 2022) and its presence was associated with the presence of red lead. In both cases, plattnerite (associated with red lead) is found at line borders (as an outline) and thus perhaps red lead was used only in order to highlight some lines. Or maybe it was used as an admixture to the red ochre. This is something that will be clarified when further polychromy data is obtained in the future.

In any case, the use of red for the decoration of the metopes' background is in accordance with various references and representations of the nineteenth and twentieth centuries (Paccard 1982; Michaelis A., 1871, Ebersole 1899; Brommer 1967; Orlandos 1977; Koch 1955).

Another result which is quite surprising is that in the investigated microsamples taken from the metopes no beeswax is identified, although beeswax is present in many

Fig. 12 Color representation of the Parthenon according to current scientific data (representation (Penrose 1852) that is digitally processed)

of microsamples taken from the area of the west cornice (Aggelakopoulou and Bakolas 2022). This can be explained by the area of the metopes being much more damaged than the protected area of the cornice blocks. Moreover, the metopes are much more exposed to environmental loads and UV radiation, which can harm the binder of beeswax, present in the original paint layers. The above also explain why only minimal traces of paint layers are still present on the Parthenon' s west metopes.

Finally, if one imagines the metopes at the time of their construction, with the blue taenia at the crown, the profound red for their background, and the high relief of horses and warriors with blue and green cloaks (as mentioned in the bibliography), we can assume that the result would have been extremely impressive. A digital color representation of the new findings is attempted in Fig. 12, taking into account the scientific data of previous (Aggelakopoulou and Bakolas 2022) and current research, and thus completing the findings regarding the polychromy of the cornice blocks.

Conclusions

The applied imaging techniques in situ along with the laboratory investigation applied to paint layer microsamples, allow for the following results to be drawn, regarding the Parthenon's metopes' polychromy:

- The taenia that crowns the metopes was blue, using Egyptian blue. No other blue pigment was found.
- The background of the metopes was red, as stated and/or hypothesized in most nineteenth century literature and drawings.
- The red paint layer microsamples obtained from the metopes' background consist of hematite-Fe_2O_3 (associated with red ochre) and litharge (PbO). The concurrent presence of Fe- and Pb- compounds can be attributed to the use of either a Pb-containing natural source of red earth or an artificial red pigment (sandyx or syricum), derived through mixing and perhaps calcinating red ochre with lead compounds.
- On the third west metope, plattnerite was discovered as the main compound of a dark red–black line in contact with the horse's tail. Plattnerite is the decay product of red lead and thus perhaps red lead was used for highlighting line borders of the figural relief sculptures.
- The red pigment residue found inside an ancient kylix (500–480 BC) discovered inside the entablature of the Parthenon was also investigated. The pigment consists of hematite while litharge was also identified, if only in a single grain. Therefore, this could indicate a red paint similar to the one found on the metopes' background, however this hypothesis requires further investigation.

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Declarations

Competing interests The authors declare no competing interests.

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