

Technical Studies in Ancient Greek Painting and Polychromy: From Scientific Investigation to Archaeological Interpretation

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Abstract

Technical studies in the field of ancient painting and polychromy aim at elucidating our understanding regarding composition and the various uses of colours in antiquity that served to produce either figural paintings or polychromy on a varied range of artifacts. The increasing number of newly excavated material, as well as the publication of old finds, has opened up new fields of investigation of both ancient Greek painting and polychromy from an art historical and a technical perspective, allowing us to retrace the history of painting traditions in ancient Greece, from prehistory to the Hellenistic times. This paper discusses the results of recent analytical investigations on ancient Greek painting materials and offers a brief historical overview of their uses. Problems regarding the discoloration of the original paint layers caused by the weathering and ageing of pigments and binders are also underlined.

Introduction

The increasing number of newly excavated material, as well as the publication of old finds, has opened up new fields of investigation of both ancient Greek painting and polychromy from an art historical and a technical perspective, allowing us to retrace the history of painting traditions in ancient Greece. Studies in Late Bronze Age wall paintings from Thera and the Greek mainland have produced new knowledge regarding the Aegean painters' materials, leading to a revision of old theories on *fresco* painting (Brecoulaki et al. 2012; Brecoulaki et al 2013 a; Brecoulaki et al 2013d) and to a recognition of a richer gamut of mineral and organic pigments (Dandrau 1999; Perdikatsis et al. 2000; Sotiropoulou 2004.; Jones and Photos-Jones 2004; Brysbaert 2008; Vlachopoulos and Sotiropoulou 2012). The recent examination of the wooden panels from Pitsa in Corinthia (Brecoulaki et al. 2008; Brecoulaki et al. 2013b) and the discovery of wall paintings from the Archaic temple at Abai/Kalapodi (Niemeier et al. 2012) have offered entirely new insights on painting that was realized during the seventh and sixth centuries BC. On the micrographic paintings of a unique painted marble sarcophagus, recently discovered in ancient Kition (Cyprus) and dated to the late Classical period, the varied palette and the effects of shadow and light reflect a mature application of colour that stands apart from the restricted and plain polychromy of white ground vases (Georgiou 2009; Georgiou 2010; Fluorentzos 2011). The large funerary corpus of paintings from ancient Macedonia has provided significant evidence for large scale figurative compositions, and for the use of sophisticated painting techniques during the late fourth and third century BC—techniques which had assimilated the tradition of Classical Greek painting (Brecoulaki 2006). The scientific examination of the polychromy attested on a number of luxurious artifacts from the Classical and Hellenistic periods, has allowed us to further reconstruct the various applications of painting materials and their combinations, and to document the use of unusual pigments, which also reflect a taste for imported and expensive materials (Brecoulaki forthcoming). This paper discusses the results of recent analytical investigations on ancient Greek painting materials and offers a brief historical overview of their uses. Problems regarding the discoloration of the original paint layers caused by the weathering and ageing of pigments and binders are also underlined.

The combination of analytical techniques: non-invasive and destructive methods of investigation

Technical studies in the field of ancient painting and polychromy aim at elucidating our understanding regarding composition and the various uses and meanings of colours in antiquity that served to produce either figural paintings or polychrome layers applied to a varied range of artifacts. The purpose of the technological investigation is not limited to the identification of the constituent materials of a painted surface, but extends to the reconstruction of the various pictorial stages and to an understanding of the sequences and combinations of the materials involved— materials that include a wide range of mineral and organic pigments and binders. With the development of new analytical methods of investigation for the study of paint layers (Janssens and Van Grieken 2004; Karydas et al. 2006; Salomon et al. 2008; Cotte et al. 2009; Sokaras et al. 2009; Janssens et al. 2010; Colombo et al. 2011; Kanngiesser et al. 2012; Alfred et al. 2013), and of sophisticated chemical analysis for complex organic materials (Colombini and Modugno 2009), the examination of painted archaeological documents becomes more comprehensive and accurate. Furthermore, the experience obtained during these last decades in laboratories dealing with the technology of ancient painting materials, has dramatically enhanced the reliable interpretation and evaluation of results.

Due to the rarity of preserved ancient painted documents and the restrictions imposed on sampling, the use of non-invasive in situ analytical methods of investigation (Karydas et al. 2006; Zarkadas and Karydas 2004; Anglos and Karydas 2009; Karydas et al. 2009) and of imaging techniques has become a necessary step in our examination of ancient polychromy, offering significant advantages in comparison to the use of destructive methods of analysis. These advantages emerge due to the possibility of analyzing an unlimited number of positions on a painted surface through the elemental mapping of the pigments' constituents; due to the spatial information on the distribution of specific pigments (such as Egyptian blue, Madder lake and Lapis Lazuli), and to the recovery of scantily preserved paint layers - not traceable through visual examination - with the use of imaging techniques (Rosi et al. 2009; Verri 2009a; Verri 2009b; Verri et al. 2010). However, non-invasive techniques do not allow for a comprehensive analytical assessment of every kind of material present in ancient paintings, and the need to perform sampling is still required in order both to study the stratigraphy of complex pictorial layers and to

detect the organic materials sealed within. A combination of techniques (Artioli 2010; Varella 2013) is therefore necessary in order to appreciate, in a holistic way, the variety and modes of application of ancient painting materials and to safely reconstruct ancient polychromies.

On pigments and their applications: a brief overview based on recent investigations

Current knowledge on the range and uses of pigments in Greek painting allows us to safely reconstruct the history of colour from the Late Bronze Age to the Hellenistic period. Of course, there are still probably pigments to identify, and there are certainly more applications to discover with the ongoing studies on ancient painting and polychromy, but what is readily available is a comprehensive background which shows us the diachronic use of a common range of pigments; pigment preferences related to the mineral resources of a region and to the workshop trends or artistic idiosyncrasies of a given historical context (Brecoulaki and Perdikatsis 2002); rare use of imported and precious materials for the decoration of luxurious artifacts (Brecoulaki forthcoming).

A basic common palette composed of iron oxides (red, brown and yellow ochres), carbon black and calcium carbonate white seems to have been used diachronically throughout antiquity. The artificial composition of the mineral cuprorivaite in Egypt offered ancient Greek painters, from as far back as the Late Bronze Age, the blue pigment that is the most stable and rich in hues, the Egyptian blue. Included in the palette of the Cretan (Dandrau 1999; Brysbaert 2008) and Thera painters (Perdikatsis et al. 2000), often mixed with the local mineral riebeckite (Vlachopoulos and Sotiropoulou 2012), Egyptian blue would go on to become the basic blue of Mycenaean painting and be used without interruption until late antiquity (**Fig. 1**). With the use, exceptionally, of the natural mineral azurite in Archaic sculptural polychromy and of lapis lazuli on a rare luxurious marble vase of the fifth century BC (Brecoulaki forthcoming), Egyptian blue has been identified up to now in almost all painted documents of the Classical and Hellenistic periods that have retained their blue hues. Its various applications have already been discussed in previous publications (Brecoulaki 2000; Brecoulaki 2006; Brysbaert 2008; Kakoulli 2009). In its pure form or mixed with other pigments to produce green and purple hues, Egyptian blue was often used in both painting and sculpture to produce vivid blue backgrounds, usually superimposed onto a layer of carbon black (Brecoulaki 2006). The uniform blue background of Egyptian blue represents a strong stylistic marker of ancient Greek painting and polychromy, with a long-lasting tradition from prehistory to Hellenistic times (**Fig. 2**). An interesting use of Egyptian blue to indicate the white area of the eyes, recently revealed by G. Verri on Greek and Roman sculpture (Verri 2009b; Verri et al. 2010) is also

attested in late Classical and Hellenistic figural painting. It seems to have represented a common pictorial technique to evoke the moistness and inner light of the glance (Brecoulaki 2012). The mixture of Egyptian blue with yellow ochre to produce green hues in late Bronze Age paintings represents a current practice, and until recently the absence of other copper based greens in Aegean painting was taken for granted (Brysbaert 2008; Peters 2008). With the exception of malachite identified on a Mycenaean wall painting fragment from Tiryns (Heaton 1912), no other natural greens had been reported as painting materials for this period. However, the recent technological investigation of the corpus of Mycenaean wall paintings from Pylos has confirmed the use of copper chlorides (atacamite and paratacamite) together with malachite and chrysocolla, a hydrous copper silicate (Brecoulaki et al. 2013d) (**Fig. 3**). Those minerals very often occur in association with each other in nature and their visual colour is closely associated. Copper chlorides may be derivatives of corrosion processes of other copper based pigments, such as malachite. The use of copper based natural pigments remains parsimonious in Greek painting and polychromy (Brecoulaki and Perdikatsis 2006; Brecoulaki et al. 2006). Malachite has been used in the context of the sculptural polychromy of the Archaic period together with other associated minerals, such as conicalcrite. Conicalcrite, a copper arsenate, was identified for the first time as a deliberately chosen pigment – and not as a random associated mineral – on the gold and ivory couch of the tomb of Philip II at Aegae (Brecoulaki and Perdikatsis 2002). Its use was further attested afterwards on other Macedonian paintings and on some grave stones from Demetrias, often associated with malachite (**Fig. 4**). During a very recent investigation on the hunting frieze of the tomb of Philip II at Aegae, a very interesting application of conicalcrite was revealed on the light pink bodies of the hunters: conicalcrite was mixed with carbon black to evoke the cool shadows of the flesh tones, in a gray-greenish tone (**Fig. 5**). The technique of using green pigments to produce cool hues on the bodies and faces of human figures, known as the historical *verdaccio* technique, represented in a rather naive manner on the illuminated Medieval manuscripts, was adapted and refined by early Italian and Flemish painters (Brecoulaki 2012). The use of the rare pigment conicalcrite in Macedonian paintings and artifacts must have been connected to the occurrence of local copper resources in the area of Chalcidice.

The use of cinnabar has a long history in Greek polychromy and painting (Trinquier 2013; Brecoulaki forthcoming). Although it was quite extensively used to decorate Cycladic marble figurines, cinnabar is completely absent from the Late Bronze Age palette, both in the islands and the Mycenaean mainland. It appears *ex novo* during the Archaic period on both sculpture and

panel painting and continues to be part of the gamut of precious pigments up to the late Hellenistic period. The technological examination of the four Archaic wooden panels from Pitsa in Corinthia has confirmed its use both for the bright red of the figures' garments (**Fig. 6**) and for the women's outlines on one of the panels (Brecoulaki forthcoming; Brecoulaki et al. 2013b). New evidence for the pictorial use of cinnabar during the fifth and early fourth century BC is available in the form of painting on marble. On a white marble pyxis from the collection of the National Archaeological Museum (Brecoulaki forthcoming) depicting battle scenes, cinnabar was mixed with red ochre to produce the red orange-brown colour of the horses; on a late Classical extraordinary marble sarcophagus found in tomb 128 at Kition (Cyprus), cinnabar was applied to both figural and ornamental motifs (Fluorentzos 2011). Extensive presence of high quality cinnabar (**Fig. 7**) has already been attested on the wall paintings of Macedonian funerary monuments of the late Classical and Hellenistic period (Brecoulaki 2006) and its selective use is also documented on painted grave stones from the 3rd and 2nd centuries BC (Von Greave 1987).

Other mineral pigments, rarely encountered in Greek painting, comprise realgar, orpiment and lapis lazuli. Realgar was identified on the Archaic panels from Pitsa and this is the first attested historical use of this pigment in Greek painting (Brecoulaki et al. 2013b). Orpiment, lapis lazuli, cinnabar and a purple colorant, were all employed for the micrographic paintings of the aforementioned marble pyxis. It is clear that the use of all those precious and rare pigments on a single painted document is related to its high value as a luxurious artifact within its material culture. The choice of lapis lazuli - a precious stone used as a gem in antiquity- for a pictorial application remains unique until now in Greek painting and represents the first attested use of this mineral as a painting material in the historical periods (Brecoulaki forthcoming). The use of such uncommon pigments on luxurious artifacts is often associated with the application of gold leaf, usually applied on top of a yellow ochre undercoat (such as the ivory and gold couch of tomb of Philip II at Aegae; Brecoulaki 2006), or directly onto a marble surface. The application of gold leaf on sculpture and terra cottas has been discussed thoroughly by B. Bourgeois and Ph. Jockey in previous publications (Bourgeois and Jockey 2005; 2007). Pigments of organic origin such as Murex purple, Madder lake or Rocella Tinctoria are also part of the ancient Greek painter's palette. The earliest occurrence of Murex purple in figural painting is on the wall paintings from Thera, applied with parsimony in order to depict details (Sotiropoulou 2005). Evidence of Murex purple in Aegean painting is rare, but the wall paintings from the Mycenaean palace at Pylos offer a unique case in which this pigment is used in large quantities, not only for garment details and other figurative

elements but also to fill ornamental zones and backgrounds (Brecoulaki et al. 2013d). A pictorial use of Murex purple in the Archaic and Classical periods has yet to be confirmed, but it was certainly applied on late fourth and third century wall paintings from Macedonia (Brecoulaki 2006; Lilimbaki-Akamati 2007) and pre-Roman Italy (Giachi et al. 2007) (**Fig. 8**). The use of Madder lake is much more common on painted documents and sculptural polychromy of the third and second century BC, and is in fact considered one of the most characteristic and “trendy” colours of this period (Jeammet et al. 2007; Jeammet et al. 2010). Rocella Tinctoria has up to now only been revealed on terracotta figurines (Pagès-Camagna 2010), but we still need to explore and further investigate the uses of this colorant, as well as that of other colorants of marine and plant origin, which we know from textual sources but for which we do not yet have the archaeological evidence.

The choice of various white and black pigments, other than the usual calcium carbonate and carbon black, usually depends on practical requirements rather than visual ones (Brecoulaki 2006). Although until recently the use of lead white was only attested on documents dated to the late fourth century BC onwards, we now know that this pigment had already, from the fifth century BC, assumed its function as an undercoat for paintings on marble and in mixtures with other pigments. Interestingly, although new research on raw materials and tools from Akrotiri (Thera) attested an extensive presence of lead pigments (Sotiropoulou et al. 2010), these pigments never seem to have been used as painting materials on the wall. Whether they were reserved for lost panel paintings or simply for cosmetics is an open question. Mineral black pigments, and particularly pyrolusite, were more often used in prehistory than in historical times. Early evidence from Late Bronze Age painting confirms the use of manganese and iron based minerals to produce blacks (Brysbaert 2008; Brecoulaki et al. 2013d). However, in Classical and Hellenistic painting the use of mineral blacks remains extremely rare.

Tempera and secco techniques in Greek painting: new evidence based on the identification of organic media

The systematic examination of paint layers through chromatographic analytical techniques (combination of GC-MS and PY-GC-MS) has yielded entirely new evidence on the practice of tempera and secco techniques in Greek painting, evidence dating back to the Late Bronze Age. A representative number of samples from the wall paintings of the Mycenaean Palace at Pylos

(Brecoulaki et al 2012) have confirmed the use of egg, animal glue and vegetable gums as binding media. Recent investigation on samples from the wall paintings of the West House at Mycenae further attested the use of tempera and secco techniques during the Late Bronze Age (Brecoulaki et al. 2013 a). It becomes clear from the above results that our previously held convictions on the extensive use of *fresco* technique in Late Bronze Age painting should be entirely reconsidered. More research on the wall paintings from the other palatial centers of the Greek mainland, but also on sites in Crete and Thera, is required in order to correctly evaluate the original painting techniques used during the second millennium BC and the transfer of technological knowledge from the East--mainly Egypt. Until very recently there was no research carried out on the binding media of Archaic painting. The new discovery of wall paintings from the Archaic temple at Abai/Kalapodi (Niemeier et al. 2011) allowed us to further document the practice of secco technique, and the examination of an Archaic painted sarcophagus from Chiliomodi in Corinthia attested the practice of tempera technique, with egg being identified as the binding medium (Korka et al. 2013). Egg as a binding medium was also detected in the paintings of the late Classical marble sarcophagus from Kition in Cyprus, while the use of egg and plant gums (fruit tree gums and tragacanth gum) has already been extensively documented on the funerary paintings from Macedonia (Colombini et al. 2002; Brecoulaki 2006). However, the use of arabic gum as a binder on the painted marble throne of the "tomb of Eurydice" at Aigai (Kakoulli 2009) needs to be reconsidered: a new ongoing technological examination of the throne and sample analysis with GC-MS and PY-GC-MS confirmed the use of egg inside the paint layer, excluding the presence of gums and wax (Brecoulaki et al. 2013c). It is probable though that a plant gum may have been used as a coating for the painted surface.

Issues of pigment and binder weathering and discoloration

The original colour of ancient paintings and painted artifacts is often altered as a result of environmental and burial conditions. The most common phenomenon is the accumulation of saline or/and soil encrustations on the original paint surface; this creates either a whitish veil or a grey-brown patina which affects the physical aspect of the paint layers. Changes in the chemical or physical structure of painting materials that result from ageing, bacterial attack or weathering by external factors, such as exposure to the high temperatures caused by fire, may affect the hue and saturation of the original colour (Kakoulli 2009). The interpretation of such changes in the original colour of ancient paint layers needs, however, to be treated with caution. In certain cases,

aesthetic preconceptions on how a painting of a given period should look have led to erroneous reconstructions. An interesting example is the case of the Mycenaean wall paintings of the “Palace of Nestor” at Pylos in Western Messenia (Lang 1969). Because of the destruction of the palace by fire during its final phase of occupation in the LH CII-III, the archaeologists who studied the wall paintings had taken for granted the fact that almost all pigments had undergone significant discolorations, and, thus, tried to reconstruct colours that looked unfamiliar to them - such as brown, purple and green - with what they considered to be the “Classical Mycenaean palette”, comprising the triad of bright blue, red and yellow. They did not realize that the pictorial style found on those wall paintings was simply expressing different aesthetic requirements and colour harmonies from what was already known from other Mycenaean paintings of the Greek mainland (Brecoulaki et al. 2013d). According to M. Lang (Lang 1969), the fire changed some white to blue, a large amount of blue to lavender-green, some tan to brown, and some yellow to gray or tan. She also considered certain dark, almost black, paint surfaces as an alteration product of a green pigment, she described the dark purple colour as the weathering product of a vivid blue hue, and she took for granted the transformation of red pigments to brown. This problem was not unique to Lang’s study at Pylos. In a study predating Lang’s, in the publication of the wall paintings of the Ramp House from Mycenae, W. Lamb had suggested that blue was burnt to violet and that fire had turned the blue to green and the red to brown (Lamb 1921-1923). Such erroneous assumptions significantly affected the way in which original polychromy was reconstructed. Indeed, with the exception of yellow ochre and natural green copper-based minerals, none of the inorganic pigments identified on the paintings of Pylos were likely to suffer significant discolorations when heated. But even in those cases, analytical and microscopical examination confirmed that no copper based pigment was present in black areas and that yellow ochre was not converted into red ochre. The role of purple in the Pylian wall paintings, identified through recent analytical investigations as Murex purple (Brecoulaki et al. 2013d), was also significantly underestimated, since it was either considered a discoloration of Egyptian blue, or was dismissed as gray in the areas where it had actually lost its original colour, most probably due to the effect of fire (**Fig. 9**).

Darkening of the original colours or changes of hue has also been attested on ancient paintings on wood, marble and stone (Twilley 2002; Perdikatsis et al. 2002). Such phenomena are usually the result of the degradation of organic binders sealed within the paint film or applied on

top of it, or of the chemical decomposition and photodegradation of mineral pigments such as lead white (Giovannoni et al. 1990; Kotulanova et al. 2009), cinnabar (Grout and Burnstock 2000; Keune and Boon 2005), Egyptian blue (Schiegl et al. 1992) copper based greens (Pollard et al. 1992), green earth (Kakoulli 2009) and realgar (Douglass et al. 1992; Corbail and Helwig 1995). Although lead white (cerussite) has been widely used in Classical and Hellenistic painting, both on lime plaster and stone or marble (Brecoulaki 2000; 2006), so far no darkening or staining of the pigment layer related to oxidation states has been attested. It is known that cinnabar is subject to darkening due to the formation of metacinnabar and that the blackening of cinnabar is often attested on Roman wall paintings (Cotte et al. 2006). However, despite its extensive use on Late Classical and Hellenistic wall paintings and other artifacts, we have very rarely observed evidence of discoloration. Recent investigation of cross-sections with paint layers composed of cinnabar from the marble throne of the “tomb of Eurydice” at Aigai, has attested the presence of random darkened particles of cinnabar inside the paint layer (Brecoulaki et al. 2013c). In general, when cinnabar is applied, even over extensive parts of plastered walls, it still preserves its original saturation and hue (the tomb of Aghios Athanassios in Thessaloniki offers the most significant example (Brecoulaki and Perdikatsis 2002; Brecoulaki 2006). Although recent literature has underlined issues of discoloration of Egyptian blue and other ancient copper based pigments, such as copper chlorides (Pollard et al. 1992), the identification of those pigments on Greek paintings has not revealed any notable alterations. Very often, thick layers of Egyptian blue have lost their cohesion, and have suffered a significant loss of pigment; as a consequence the painted surface looks pale and less saturated. This phenomenon is even more pronounced in cases where the Egyptian blue was originally used in coarse grain size. The decomposition of green earth and its transformation into limonite has been observed on late Hellenistic wall paintings from nea Paphos and Jericho (Kakoulli 2009). An interesting case of photodegradation of realgar has been documented on the Archaic painted panels from Pitsa, in Corinthia (Brecoulaki et al. 2013b). During the non-invasive examination of the panels at the National Museum in Athens using Raman spectroscopy (Brecoulaki et al. 2008), a change in the colour of the pendant beads on panel 16466 was observed. Indeed, while older photos and painted reconstructions of the panels shortly after their discovery document the colour of the beads as red and blue (Walter-Karydi 1986), in their actual state red beads have been transformed into bright yellow ones. This alteration is the result of the effect of light which breaks As-As bonds and leads to the formation of a new crystal structure; a behavior comparable to the photo-decomposition of orpiment (Douglass et al. 1992).

The case of the Pitsa panels shows the importance of taking into consideration, prior to our analytical investigation, all previous documentation on the ancient painted artefacts we are going to examine, in order to avoid false interpretations.

The degradation of organic binding media in ancient paintings is another issue that needs to be studied in more depth. The discoloration of a paint layer may be affected by the degradation of the original binders, such as gums, egg and animal glue (Brecoulaki 2006). The case study of the marble throne at the “tomb of Eurydice” at Aegae has revealed a thin layer of discolored varnish on top of the painting’s surface and inside the matrix of the paint layer (Kakoulli 2009). This discoloration (**Fig. 10**) has been considered as the result of a microbiological attack of gum arabic, identified as the medium of the paint layer. However, the recent analysis on the throne’s polychromy, suggesting the use of egg (Brecoulaki et al. 2013c), should now be taken into consideration in order to determine the exact nature of the binders and understand the mechanisms of their alteration.

Conclusion

The technological investigation of ancient painting materials offers many challenges, but also requires an awareness of a series of problems or questions that we need to keep in mind: How reliable is a certain analytical technique and how safe are our results? Did we cross check our results by combining the maximum number of available techniques? Did we consider all previous documentation on the artifacts we examined? Did we compare our results with existing literature? To what extent do our results allow us to safely reconstruct ancient polychromies? To what extent is our sampling representative of the painting or polychromy we are examining? How do we deal with contradictory or different analytical results on the same artifact? (an interesting case study is the *purpurissum* from Pompeii; Clarke et al. 2005). Various parameters should be taken into consideration in our effort to interpret scientific results and incorporate them in an intelligent manner into our archaeological or art historical perspectives, as for example: the state of preservation of the pictorial surface with possible discolorations or alterations of the painting materials; the historical context of the document we are examining; the artistic quality and function of the given artifact; the geological resources available to painters and the incorporation of local pigments into the painters’ palette; the different uses and modes of application of the same pigments according to the desired aesthetical effect (pigments used in their pure and

saturated form to attract the eye and create vivid polychromy or mixed to evoke more painterly effects); the frequency in which pigments appear; the possible reasons for the choice of a specific uncommon pigment. In certain cases, we are also confronted with the limits of modern analytical techniques with regard to the identification of ancient materials, as is the case with many purple colours that remain enigmatic and await identification. Ongoing research on ancient painting is likely to shed more light on all these interesting aspects of Greek painting and the secrets of ancient technology.

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