

DECORATED ARCHAIC POTTERY FROM THE HERACLES SANCTUARY AT THEBES: A MATERIALS, TECHNOLOGY AND PROVENANCE STUDY*

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Forty-seven decorated samples of Archaic pottery excavated at a Heracles sanctuary (Thebes, Boeotia) were studied through a combined surface and body approach, using non-destructive techniques. Most of the samples were archaeologically classified as Theban/Boeotian, others as Corinthian and a few as possibly Euboean. The techniques employed were optical microscopy and SEM–EDAX (micromorphology and compositional analysis of the surfaces) and XRF for the analysis of the ceramic body. The results provided information on the technological level of the collected pottery as well as on the relation of the chemistry and micro-morphology of the pigments, aimed at assisting provenance studies.

KEYWORDS: ARCHAIC POTTERY, PIGMENTS, PROVENANCE, SLIP, THEBES, XRF, SEM–EDAX

INTRODUCTION

Macroscopic examination of pottery, with an emphasis placed upon surface features, served archaeology well for a substantial part of the 20th century and continues to be used alone as a source of valuable conclusions; archaeologists usually examine surface decoration in order to assess issues such as production/technology capacity and trends, evolution of sites, provenance and trade patterns. Elaborate versions of the approach have led to impressive results; for example, Boardman has relied substantially on his decorated Greek pottery expertise amassed from macroscopic studies for his key work on Greek colonization (Boardman 1999). Microscopic examination of pottery makes use of physics and chemistry methods appropriate for the chemical and microstructural study of materials, and eventually attempts to address almost the same questions as macroscopic examination, preferably in a complementary manner. For the microscopic approach, tiny fragments can turn out to be at least as useful as sizable fragments or intact objects; for example, a tiny pottery fragment properly oriented in a SEM–EDS holder constitutes a cross-section made available non-destructively and can be studied with regard to composition, layering and so on.

In the south-east Balkans and the Aegean, decoration techniques have been applied since the very beginning of pottery production, mainly in the form of engraved and simply coloured motifs.

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The engraved motifs were in most cases produced prior to firing, while a variety of coloured earths (usually calcium- or magnesium-rich clays for white colouring, iron-rich clays for red colouring etc.) were also applied to the surface. Following firing, the vases were further decorated using natural pigments, possibly combined with organic adhesives.

As early as the fifth millennium BC, an elaborate technique that led to permanent results evolved. The so-called 'iron reduction technique' (IRT) allowed ancient potters simultaneously to develop red and black motifs using a single firing (Noll *et al.* 1975). The IR technique proved to be extremely effective and continued to be used for thousands of years; pottery of the archaic period, as well as the well-known high-quality Attic gloss pottery of classic times, was produced using this method (Noble 1960; Hofmann 1962; Tite *et al.* 1982; Aloupi 1993; Maniatis *et al.* 1993).

According to the IRT, a high-iron and low-calcium, usually illitic, clay is selected and then subjected to extensive elutriation, leading to a fine final product (to be applied for decoration purposes) exhibiting an increased $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio and an enhanced iron content.

The firing begins in an oxidizing atmosphere, which is retained until the temperature approximates the 800–850°C range; at this point the furnace atmosphere is changed to a reducing one, possibly by introducing wet or resin-rich fuel and by sealing the air pipes. The CO and H_2O generated by the fuel act as reducing agents, and thus the iron present in the clay is converted from Fe(III) (hematite contained in the clay) to Fe(II). Black spinels such as magnetite ($\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4$), hercynite (FeAl_2O_4) and, at relatively high temperatures, wustite (FeO) are formed (Tite *et al.* 1982; Tang *et al.* 2001). As a result, the clay develops a dark-black colour. At the same time, the decoration layer sinters and vitrifies; the latter alteration is promoted by the presence of alkali ions that act as flux (mainly potassium in illitic clays); in addition, the smaller the clay particle size, the easier the sintering becomes (Hofmann 1962; Noll *et al.* 1975; Tite *et al.* 1982; Ingo *et al.* 2000; Mirti *et al.* 2006).

At the final stage of the firing, the atmosphere is changed back into an oxidizing one, while the temperature begins to fall below 850°C. Thus all exposed parts of the object (including the body of the object) reoxidize readily and gain light-red hues (the exact colour depends on the clay composition), while the vitrified decoration layer is unable to reoxidize and thus retains its black colour.

For white decoration, clays rich in calcium or/and magnesium were widely in use (Swann *et al.* 2000; Ferrence *et al.* 2002), while kaolin was an accessible alternative and was routinely encountered in the decoration of white *lekythoi* during the classical period (Noll *et al.* 1975). In addition, red hues could be simply achieved by the use of ferruginous clay for the body, in which case the non-covered (by the decorative clay-black) areas served as red patterns; iron ochres were also in use for the same purpose (Noll *et al.* 1975). Further, it was possible for a different grade of the raw material used for the black decoration to serve as a source of a final red colour: the potters simply had to collect a portion during the elutriation and before its completion. This quantity, less refined and thus coarser, would create a layer with a structure that was more open and less susceptible to complete vitrification during the reduction step; consequently, the latter layer would be able to turn red during the reoxidation step.

Purple is a colour encountered less frequently in the decoration of pottery. It has been proposed that this colour could be achieved by mixing iron ochre and a portion of refined (used for the black motifs) clay (Noble 1960; Mirti *et al.* 2006). The unusual purple colour might then result from the incomplete reoxidation of the iron particles (at the final oxidative stage of the firing), leading to the coexistence of a certain appropriate balance of Fe(II) and Fe(III) (Mirti *et al.* 2006).

The assemblage considered in this work was recovered from a small excavation plot of about 350 m² near a famous Theban *temenos*, the temple of Ismenian Apollo in the centre of Thebes, central Greece. Ancient Thebes is usually mentioned as the birthplace of the hero Heracles. The excavation resulted in the collection of hundreds of artefacts, which clearly indicates that an ancient sanctuary dedicated to Heracles was located at this site (Aravantinos 2009). The core cult area was an open-air monumental *eschara* (ash altar), measuring at least 9 × (9–10) m² (the structure continues to the east, beneath the modern road). It was carefully built of stones neatly squared on their outer faces. Courses of small bricks and quantities of small fieldstones on the inside of the structure perhaps indicate attempts to demarcate the layers of ash with a pyramid-shaped construction.

The altar was found to be full of pottery, ash, animal bones, metal objects, sculptural vases and even some faience, and was used probably from the Late Geometric II (late eighth century BC) to the Early Archaic period (seventh century BC). The vast bulk of the votive offerings consists of painted wheel-made pottery (drinking, mixing and serving vases, cosmetics containers and lamps) and unpainted hand-shaped pottery (kettles) (Aravantinos 2010). The local pottery has an eclectic character, depending on the neighbouring schools (Attic, Protocorinthian and Euboeo-Cycladic). The figured scenes are second only to those of Attica in the variety of their repertoire, including hunting, dancing and mythological scenes, and so on. A peculiar local group ('bird cups'; upper part of Fig. 1) is decorated with painted birds and, later, with linear motifs. The presence of Proto-Corinthian pottery is very strong in the ash altar (Fig. 1, bottom right), along with vases of the 'Thapsos' type. Probably because of the increasing height of the offerings, at some point after the middle of the seventh century it became necessary to seal the site and



Figure 1 Upper left and right: two Theban, 'bird cup' samples. Bottom left: characteristic, homogeneous 'high-quality' black slip ('Boeotian' sample). Bottom right: a representative Corinthian sample with black and purple-coloured motifs.

relocate the ritual centre a few metres north. The significance of this discovery is further underlined by the fact that Pindar (15th. 66–77) and Pausanias in his *Boeotika* (Paus. IX, 11, 1–7) describe such a sanctuary in detail.

From the vast number of pottery fragments, 47 were selected for the present study to provide a representative picture of the pottery findings and by following typology and decoration. Most of the fragments belong to the Early Archaic to Archaic (seventh to sixth centuries BC), the period during which the sanctuary was in full activity.

More specifically, the selection included only decorated samples that, according to the archaeological classification, were assigned as ‘local Theban’, ‘Corinthian’ and ‘possibly Euboean’, and one sample characterized as ‘possibly Attic’.

The scope of the study may be summarized as follows:

- (1) An experimental investigation of the techniques and pigments used for the decorations.
- (2) A possible connection between the technological features of the decorative pigments and the provenance of the samples.
- (3) A comparison of locally produced with other, contemporary, products.

EXPERIMENTAL

The samples were subjected to examination in the as-received state, although all samples had been cleaned in the conservation laboratory of Thebes Museum. The methods used in the examination are as follows:

- (a) Optical microscopy (OM): prior to further investigation, the samples were observed under a Zeiss (47 50 22-9022) stereoscope at 1× to 4× magnifications. Thus proper selection of the samples for further examination by means of electron microscopy was achieved.
- (b) Scanning electron microscopy combined with energy-dispersive X-ray analysis (SEM–EDAX): a FEI SEM–EDAX was used (model Inspect, with a Super Ultra Thin Window) for the micromorphological and quantitative investigations. The samples were observed alternately in the secondary (SE) and backscattered (BSE) electron modes. The voltage applied on the filament was 25 kV and every spectrum was collected for 150 live seconds (total counts \approx 50 000).
- (c) X-ray fluorescence (XRF): a milli-XRF unit with a Rh target and a Si-Pin detector (XR-100CR, Amptek Inc.), described at length elsewhere (Zacharias *et al.* 2009), was employed. Every sample underwent two sets of measurements, the first at 15 kV and 100 μ A for major and minor elements and the second at 40 kV and 300 μ A for the trace elements. Each spectrum was collected for 1000 s at a relatively stable counting rate ranging between 370 and 480 cps.
- (d) X-ray diffraction (XRD): for identification of the crystal structure of specific pigments, a Siemens XRD 500 diffractometer with a Cu–K $_{\alpha}$ anticathode was used. The voltage was 40 kV and the current 35 mA, while all the diffraction spectra were collected in the range between 2 and 85° (2 θ) with a step of 0.04°/2 s.

RESULTS AND DISCUSSION

Black decoration

The observation of the dark-brown to black-coloured decorations revealed that the samples are highly differentiated in terms of their colour/texture, micromorphology and chemical composition. At the same time, it is obvious from the microstructure and chemical composition of all samples that versions of the IRT methods were employed in all cases. With regard to composition,

the relevant fingerprints are as follows: moderate to high Al_2O_3/SiO_2 ratio, high iron content, low Ca and Mg content, and a strong presence of alkalis (K and Na). A characteristic plot of the Al_2O_3/SiO_2 ratio and the total alkaline earth content of the pigments compared with the body clays is presented in Figure 2. The considerable differences are an indication that in most specimens a distinct raw material, selected especially for this purpose, has been used as a pigment.

The CaO content versus Al_2O_3/SiO_2 the ratio of the pigments is presented in Figure 3. In order to compare the samples under investigation with previously published data, five samples discussed in another paper have been introduced in the chart (indicated by crosses in Fig. 3; data from Maniatis *et al.* 1993). These five samples are classical Attic and are regarded as high-quality. On the right-hand side of the chart appear the ‘high-quality’ samples (high Al_2O_3/SiO_2 ratio and low CaO content, similar to the Attic ones), while the ‘low-quality’ samples (less elaborate raw material selection and processing) are shown on the left. Yet, at least on the basis of the compositional parameters employed in Figure 3, one might assume that samples of intermediate quality exist as well.

On the basis of microscopic examination, all specimens under investigation present the same general micromorphology, characterized by a sintered layer attached to the porous clay body; this is largely a reflection of the employment of IRT decoration approaches. Microscopic differentiation of the various samples under consideration is possible on the basis of the thickness and texture of the sintered layer. More specifically, although some samples present a well-vitrified uniform layer, in many others this layer is not only uneven but also spotted with open (bloating) pores (Fig. 4).

These characteristic pores are caused by the presence of carbonates such as $CaCO_3$ and $MgCO_3$ (which decompose with CO_2 evolution) and also by the strong reductive conditions, which lead

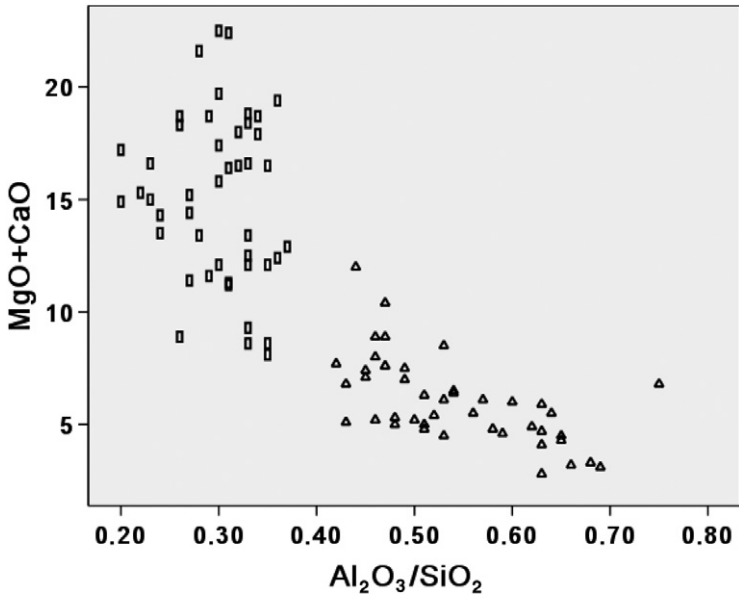


Figure 2 The MgO + CaO content versus the Al_2O_3/SiO_2 ratio: rectangles represent body clay, and triangles represent black pigments.

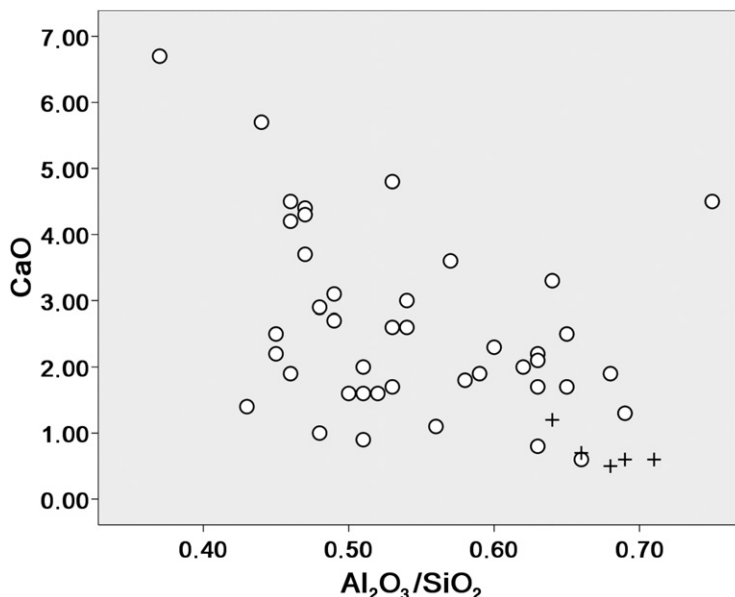


Figure 3 The CaO content versus the Al₂O₃/SiO₂ ratio for the dark-brown to black pigments. Circles indicate the samples under consideration, while the plus signs ('+') indicate five samples from Maniatis et al. (1993).

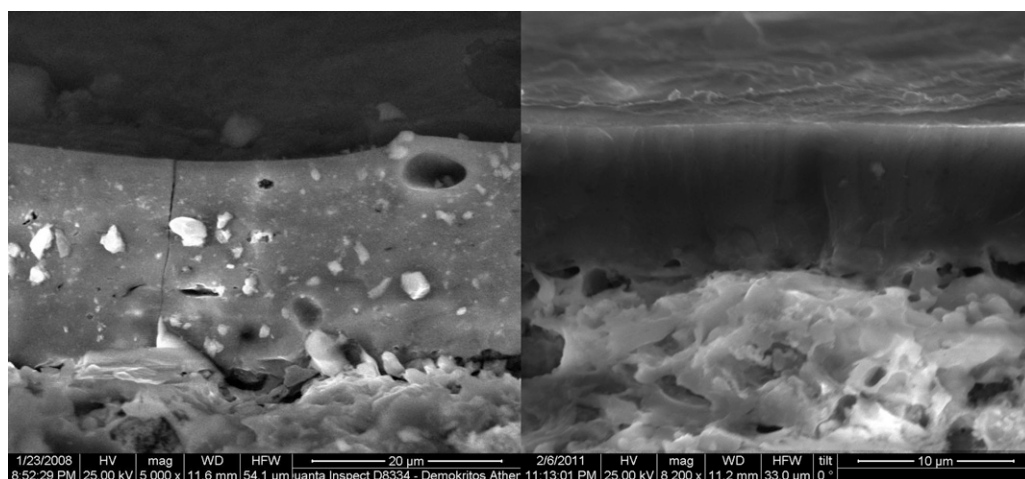


Figure 4 Left: a black layer with bloating pores (backscattered electron detector, 5000 \times). Right: a well-vitrified, homogeneous black layer (secondary electron detector, 8200 \times).

to the removal of oxygen from the Fe(III) oxides ($\text{Fe}_2\text{O}_3 \rightarrow 2\text{FeO} + 0.5\text{O}_2$) of the applied layer. The evolved gases penetrate the quasi-melted mass of the pigments and leave imprints in the form of characteristic pores. As the latter pores affect the surface morphology and thus the optical properties of the pigments (reduction of glossiness etc.), they are regarded as defects and their detection is an indication of an unsuccessful process (in terms of the raw material selection, the

treatment and/or firing conditions, and the duration and extent of the reducing stage). Moreover, it is well known that such pores are absent in high-quality samples (Tite *et al.* 1982; Maniatis *et al.* 1993; Mirti *et al.* 1996, 2006).

Consequently, it was noticed that the 'high-quality' (in terms of composition) samples appeared to be homogenous in terms of micromorphology and usually they do not exhibit bloating pores – or only exhibit them to a limited extent. With regard to the archaeologically estimated provenance of samples, it is noted that all the 'Corinthian' samples are included in the high-quality group. On the other hand, although the most of the 'Theban' samples appeared to fall into the low-quality group, some of them present high-quality characteristics (high $\text{Al}_2\text{O}_3/\text{SiO}_2$, low CaO and a well-vitrified, homogeneous microstructure). Two characteristic examples are presented in Figure 1: the upper left sample exhibits low quality and dull black decoration, while the bottom left sample has been decorated with a high-quality, shiny black pigment.

Red decoration

By visual examination, red decorations on the samples could be divided into two groups: the samples of the first group bear coloured areas that appear dull and have a rough surface, while in the samples of the second group the coloured areas exhibit a characteristic glossy surface. This separation into two groups is also evident in terms of composition. In Figure 5, where the Fe_2O_3 content versus the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio of the red pigments is presented, two distinct groups are present; the first appears on the right-hand side of the chart and is characterized by an $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio below 0.4 and an Fe_2O_3 content above 15%, while the second exhibits an $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio above 0.5 and an Fe_2O_3 content below 15%.

The fact that the compositionally differentiated pigments were also micromorphologically distinct was not surprising. The high- Fe_2O_3 /low- $\text{Al}_2\text{O}_3/\text{SiO}_2$ group presents a more or less open

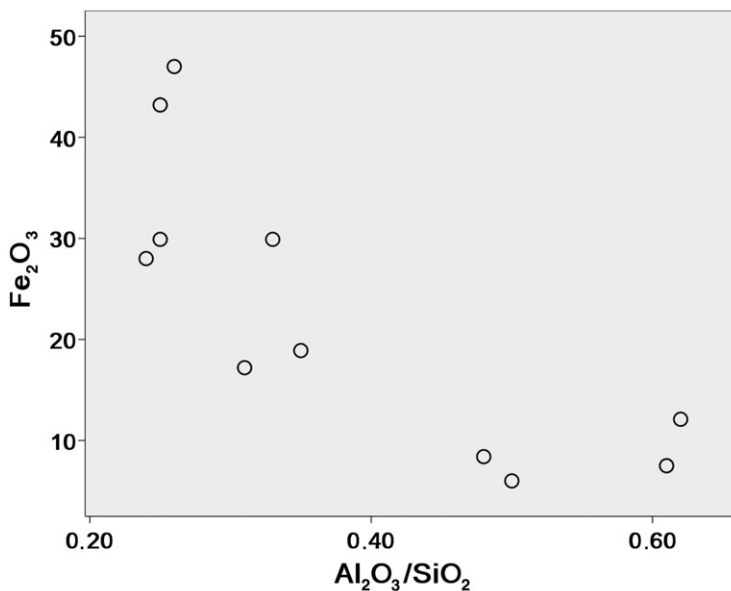


Figure 5 The Fe_2O_3 content versus $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio of the red decorative pigments (wt% oxides).

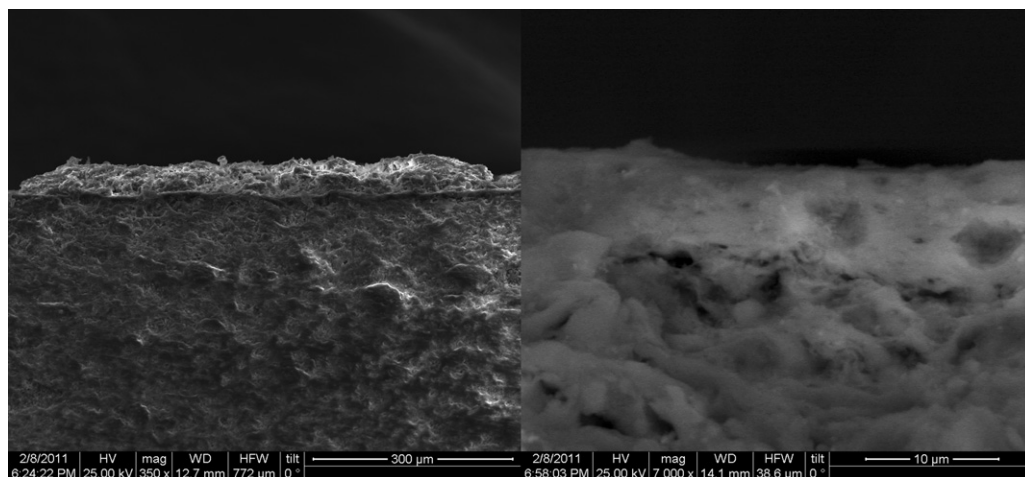


Figure 6 Two morphologically differentiated samples: on the left, a rough, grainy, non-vitrified layer of red pigment (secondary electron detector, 350 \times); and on the right, a quasi-vitrified sample similar to, though less vitrified than, that of the black pigments (backscattered electron detector, 7000 \times).

structure (Fig. 6), while the high- $\text{Al}_2\text{O}_3/\text{SiO}_2$ samples are similar to the well-vitrified black layers (Fig. 7). It must be also noted that in all the red-decorated samples, red pigments have been applied to the surface prior to firing. This is evident from the micromorphological features of the pigments, which in all cases exhibit a more or less vitrified structure.

In view of the overall composition and known decoration practices for pottery of the type considered herein, red pigments with an iron content exceeding 25% (w/w Fe_2O_3) can be classified as iron ochres that have been applied on the surface. This is the case for 4 out of 11 samples: all of them also present the characteristic grainy, open structure of fired ochres (Fig. 6, left), which is easily differentiated from burnt clays (Noll *et al.* 1975).

The two pigments with a relatively high iron content (15–20%) and a low $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio may be identified as high-iron clays. In fact, they are differentiated from fired ochres not only by their iron content, but also by their structure: while the ochres are grainy, the high-iron clays under consideration are much more even and vitrified to a greater extent (Fig. 6, right). However, both of these pigments retain enough porosity, a fact that makes them ideal for IRT use, as they are easily reoxidized after the end of the reducing stage of the firing, thus permitting the simultaneous production of red and black shades.

On the other hand, four pigments form a separate, third group with a relatively low iron content but a high $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio. Their chemical characteristics are almost identical with those of the black pigments. Furthermore, they present the characteristic, well-vitrified structure of the high-quality black pigments (Fig. 7).

These four samples come from pots on which there are no black-coloured motifs. However, the red-coloured pigments exhibit morphological and chemical characteristics that are identical with those of the typical—for the IR technique—black pigments. Thus it can be concluded that the raw materials used for the specific red pigment are similar to those commonly used for the production of black motifs; however, the final colour is red because the pots had been fired in a single oxidizing step.

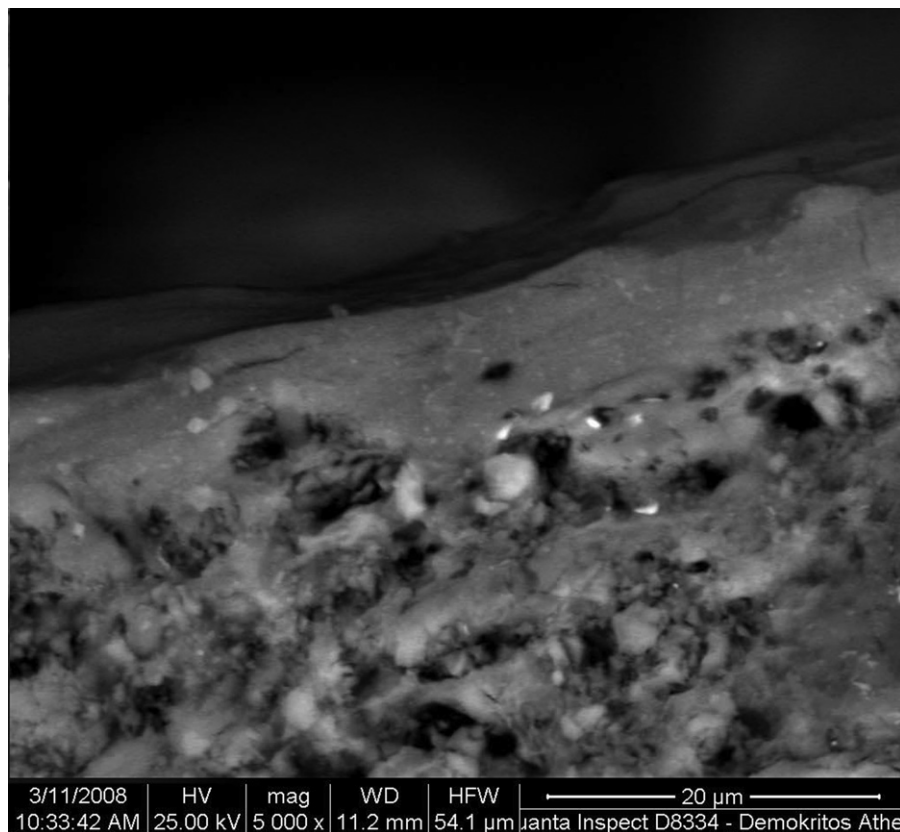


Figure 7 A well-vitrified red pigment (backscattered electron detector, 5000 \times).

In conclusion, the red decorations had been created by using three distinct raw materials: iron ochres, iron-rich clays (which are open-structured and reoxidize readily) and finely processed clay (identical, or at least very similar, to those used for black pigments) burned in a single oxidizing stage.

Purple decoration

Purple-coloured motifs are found on the surface of all the 'Corinthian' (5) and two 'Theban' samples (Fig. 1, bottom right). It must be noted that purple was used freely on Proto-Corinthian and Corinthian vases (Payne 1971). From a macroscopic point of view, there was no significant differentiation among the seven samples with regard to the hue of the colour. Furthermore, all of the samples exhibit similar rough and uneven surface micromorphology (Fig. 8), but they differ considerably with regard to the thickness of the pigment layer (which varies between 5 and 25 μm).

Observation of the pigment at a magnification above 10 000 \times revealed an unexpected morphology; that is, particles with dimensions ranging between 0.3 and 1.2 μm (Fig. 8, right).

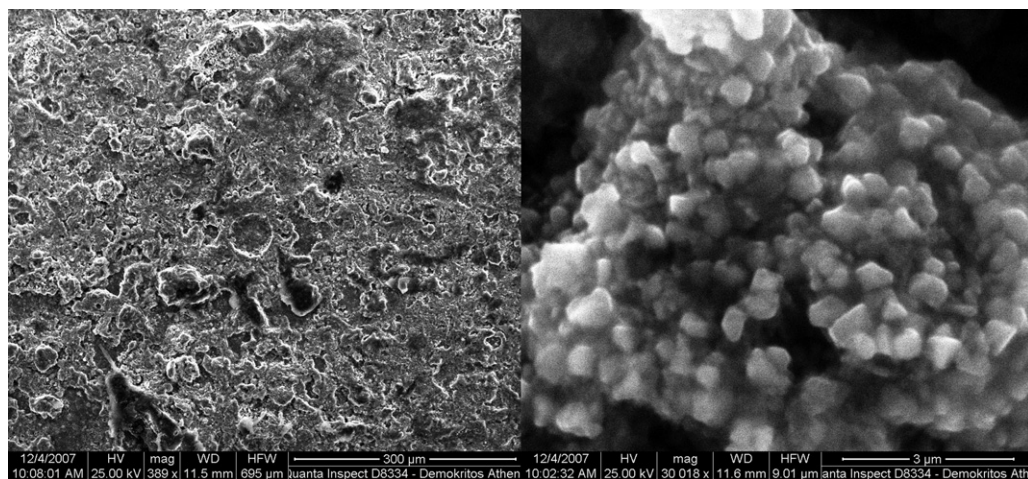


Figure 8 Left: the rough surface of the purple pigment (backscattered electron detector, 390 \times). Right: the grainy texture of the purple pigment (backscattered electron detector, 30 000 \times).

With regard to chemical composition, the main characteristic is the high iron content, which in all cases exceeds 30 wt% Fe_2O_3 . Another characteristic is the relatively low $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio (0.30–0.37), which indicates the presence of coarse clay.

On the other hand, spectra collected on areas with high concentrations of tiny particles exhibited an even higher iron content, which in some areas reached 80%; this fact, combined with the morphological characteristics (see below), led to the conclusion that the particles are pure iron oxide. In order to identify the crystal structure of the iron particles, an XRD spectrum was collected from the surface of a sample. XRD revealed that iron in the purple pigment is in the form of hematite.

These iron pigments had been applied on to the pottery surface prior to firing, a fact that was made evident by micromorphological observations, which revealed that the pigment is sintered (Fig. 8, left and right). Also, in cases where purple had been applied over black pigment, a diffusion zone has been created between the two layers by the diffusion of iron particles in the black gloss.

It has been stated elsewhere (Mirti *et al.* 2006) that this unusual colour may be attributed to the alternation of oxidizing–reducing–oxidizing conditions during firing: during the reducing stage, Fe(III) is converted to FeO oxide, which—due to partial sintering—may not be fully reoxidized upon the final reoxidation stage. The combination of Fe(II) (black-coloured) and Fe(III) (red) oxides leads to the purple colour (Mirti *et al.* 2006). However, the XRD examination in the present study showed that the iron in the purple pigment is in the Fe_2O_3 state. Furthermore, previous publications give no explanation for this peculiar iron particle morphology. An extended research approach on ancient iron pigments (Mastrotheodoros *et al.* 2010) revealed that high-iron (>90%) raw materials present a colour shift from red to purple upon firing at gradually rising temperature in oxidizing conditions. More specifically, a purple colour may develop at a temperature of 900 $^\circ\text{C}$ or higher, and the colour change observed is explained by the gradual shift of the iron particle dimensions. The purple hue is achieved when the iron particles exceed 0.4 μm in diameter. Thus although it is possible that a purple tint can be

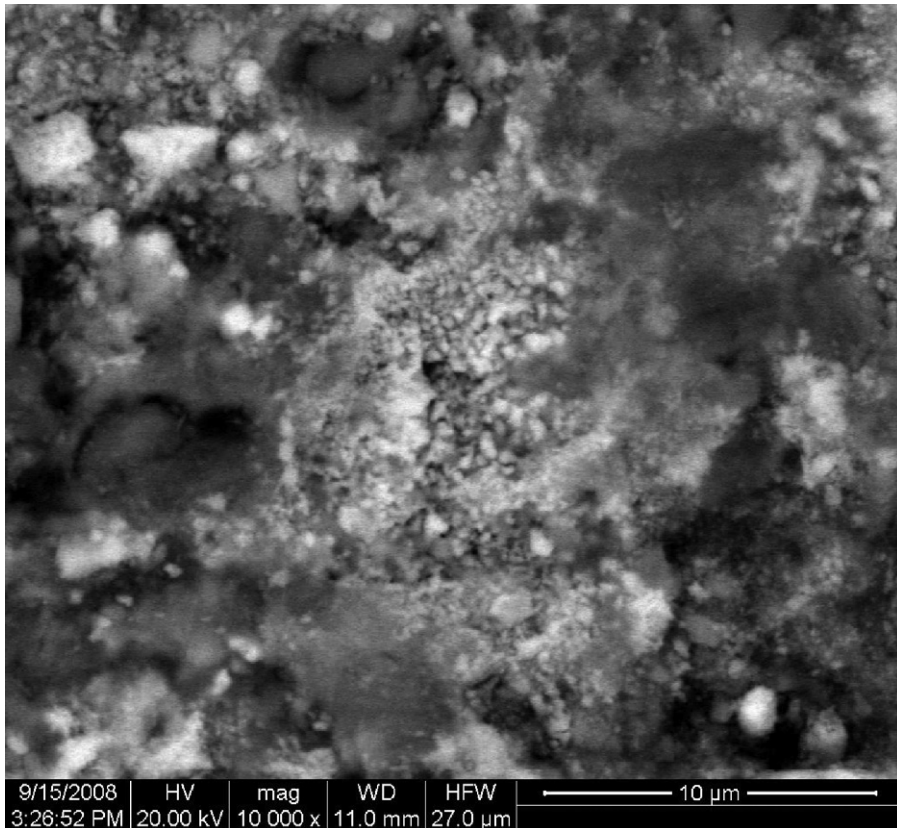


Figure 9 A high iron content at the centre (white particles), surrounded by areas with a high clay content (grey) (backscattered electron detector, 10 000 \times).

obtained by partial reoxidation of the Fe(II) oxides (Mirti *et al.* 2006), such a tint may also be obtained by firing iron-rich raw material at 900°C (or even higher), with a reducing stage not being necessary.

Also, in the samples under examination, the iron content is relatively low (30–47 wt% Fe₂O₃). Observation of the purple pigments with the BSE detector revealed the presence of areas that are rich in iron as well as areas rich in clay particles (Fig. 9). Thus the proposal for the use of a mixture of clay with a high-iron raw material (Noble 1960; Mirti *et al.* 2006) is also supported by the present study.

White–pale decorations

White–pale decorations are found on the surfaces of 16 samples. These samples exhibit similar macroscopic characteristics: a yellow tone combined with a dull and rough surface. The SEM observations revealed that their morphology is also similar: a characteristic open, mildly sintered, structure.

However, there are considerable differences with regard to the thickness of the white pigments and also the method of application, as there are samples where white pigment overlaps black and vice versa (Fig. 10).

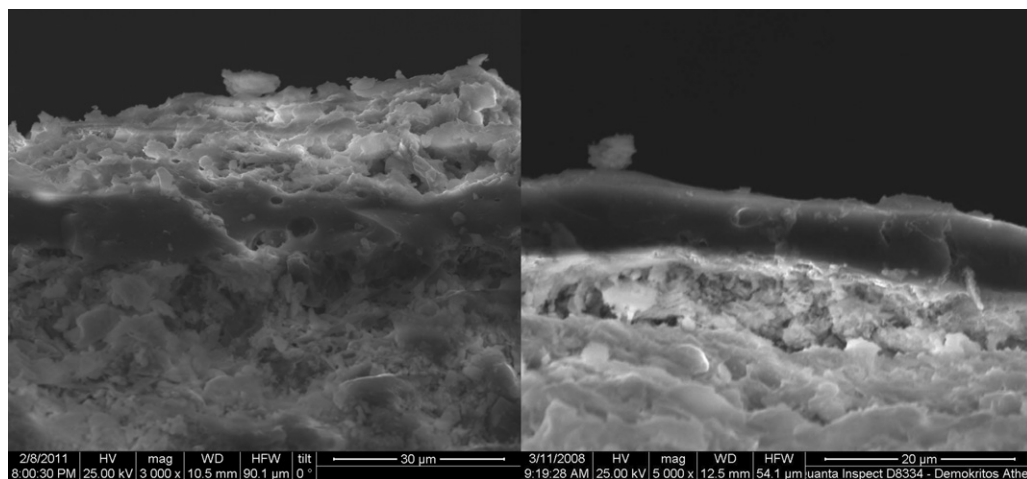


Figure 10 Left: a white pigment lies over a black layer, in which bloating pores are evident (secondary electron detector, 3000 \times). Right: a black, sintered layer overlaps a white pigment (secondary electron detector, 5000 \times).

On the other hand, micromorphological observations indicate that in all the samples, white pigments have been applied prior to firing: with the exception of the samples where the white pigments are covered by black and thus firing is evident, in all the other cases white appears to be more or less sintered (Fig. 11).

With regard to the chemical composition, all of the white pigments present a low $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio, which is indicative of the use of coarse raw material. However, they exhibit considerable variation with regard to the CaO and MgO content (Fig. 12).

Furthermore, the white pigments may be divided into three groups in terms of their CaO/MgO ratio: samples in which magnesium prevails ($\text{Ca}/\text{Mg} < 1$), samples with equal amounts of alkaline earths ($\text{Ca}/\text{Mg} \approx 1$) and samples with prevailing Ca ($\text{Ca}/\text{Mg} > 1$) (Fig. 13).

Further investigation in terms of XRD revealed that Ca or Mg clays have been used as white pigments. In addition, the detection of diopside, anorthite and other Ca–Al–Si phases is further proof of the simultaneous firing of pigments and vases.

The combination of technological and archaeological data regarding the samples with white–pale decorations did not reveal a clear correlation of the different ‘chemical’ groups with specific archaeological groups.

Provenance issues

As is evident from the experimental data, the samples under consideration exhibit a substantial variation in terms of pigment characteristics (chemical composition and micromorphology). This is the case not only for samples belonging in different provenance groups, but also for many others that are thought to have been produced in the same workshop (estimations based on archaeological–stylistic criteria). This fact led to the following question: Is it possible that samples that, according to archaeological criteria, were produced at different sites but reveal similar technological characteristics have been produced in the same workshop? Furthermore, is it possible to evaluate the provenance of samples from their pigments’ technological features?

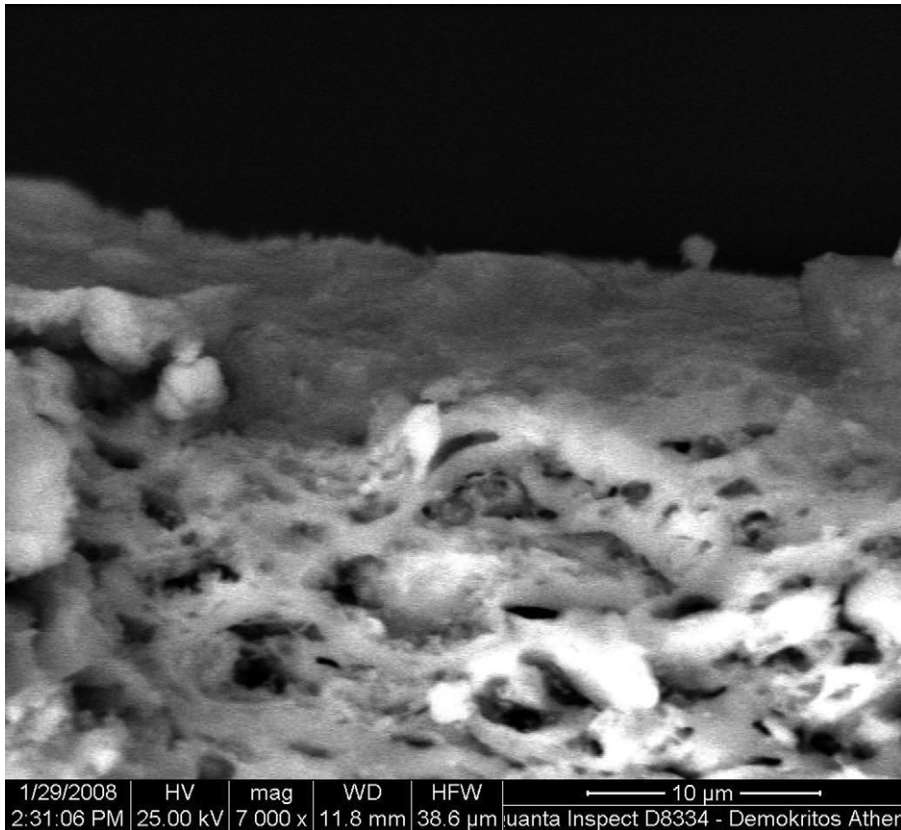


Figure 11 Sintered white pigment (backscattered electron detector, 7000 \times).

In order to deal with those questions, further investigations of the body clay by means of XRF were undertaken. The data collected in this way were evaluated in combination with the technological characteristics of the pigments in order to estimate the provenance of the samples.

The concentration of clays in trace elements is quite often used for the investigation of the possible origin (Hein *et al.* 2002; Schwedt *et al.* 2006); within these studies, samples of known origin are usually incorporated as internal standards. In the present study, we have used as standards only those of the samples considered to be archaeologically safe with regard to provenance; the latter samples are several Corinthian and local (Theban) ones. These samples present unique decorative features as well as an easily identifiable body clay texture.

XRF spectra were collected as described previously (see the 'Experimental' section). The grouping of the samples was achieved using maximum-intensity (counts) of several trace-element peaks, as it was soon observed that there were repeated differentiations among the internal-standard samples. For example, there is an obvious differentiation on the relative intensity of Sr peaks among the Corinthian and Theban samples (Fig. 14).

In order to assist the grouping of trends and normalize the experimental data, as well as to minimize the implications of the measurement conditions, sample preparation and so on, internal ratios of peak maxima (Papadopoulou *et al.* 2007; Liritzis and Zacharias 2010) were used.

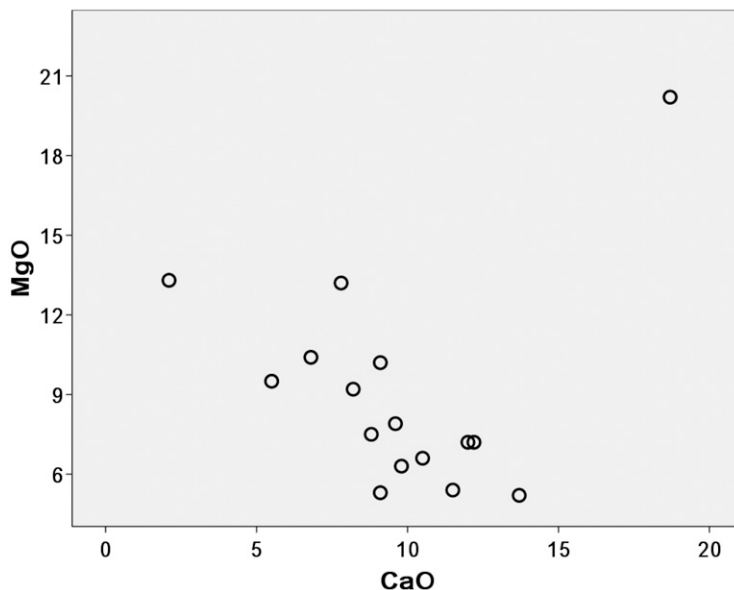


Figure 12 SEM-EDAX results showing the MgO content versus the CaO content (wt% oxides) in the white pigments.

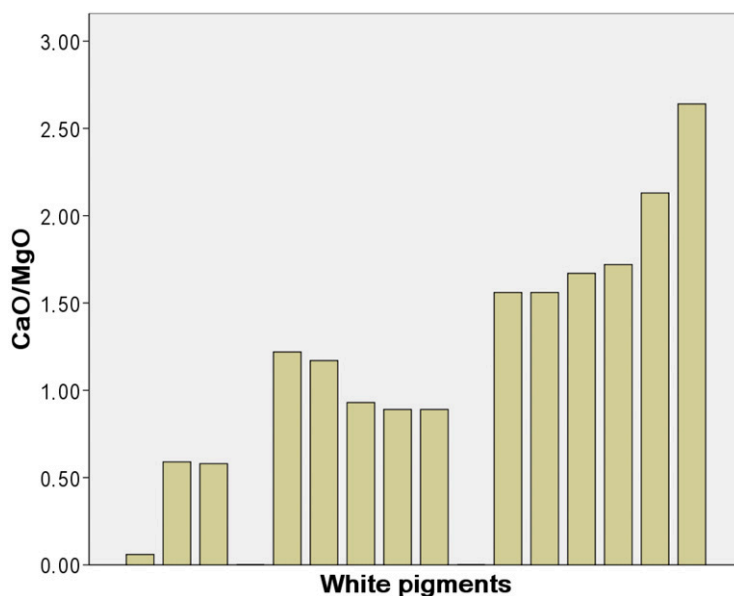


Figure 13 The CaO/MgO ratio of the white pigments.

On the basis of an empirically developed approach, several sets of peak maxima ratios were examined; by employing the ratio of Ti/(Cr + Ni) versus Rb/Sr (these five elements are those that exhibit the most pronounced differentiations among the samples), the samples under investigation could be divided into four groups (Fig. 15).

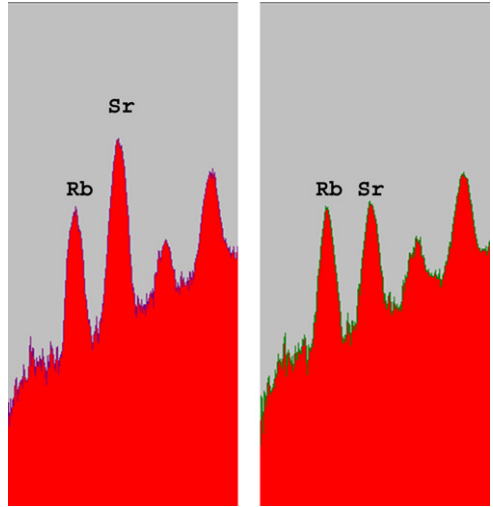


Figure 14 The Rb/Sr ratio allows for clear differentiation between samples of Corinthian origin (left) and Theban origin (right).

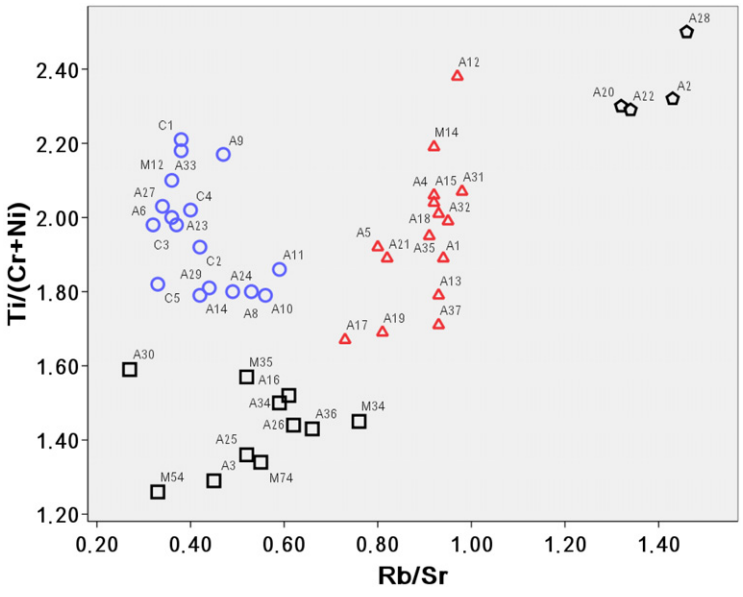


Figure 15 A plot of $Ti/(Cr + Ni)$ versus Rb/Sr , by means of XRF (peak maximum intensities): groups are distinguished by different symbols.

However, the attribution of these groups to different provenances can only be achieved by using the safely archeologically investigated samples; that is, the seven ‘Corinthian’ and several ‘Theban’ ones.

With regard to the ‘Corinthian’ samples, they all fall into the same part of the graph (circles in the upper left part of Fig. 15); the latter part includes 12 more artefacts. The black slip

on their surface presents high-quality characteristics (see the 'Black decoration' section). Interestingly, most of the other 10 samples of the same XRF group (according to Fig. 15) present similarly to the safely Corinthian black pigment technological characteristics: a high $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio, a low CaO content and micromorphological features similar to those of high-quality black pigments. The combination of these two facts, the similar chemical (XRF) pattern and the characteristics of the black slips, leads to the conclusion that most if not all of the additional 12 artefacts may also be attributed to a Corinthian provenance.

On the other hand, most of the samples that could be safely attributed to local Theban–Boeotian workshops (≈ 25 samples) form two groups on the graph (triangles and squares in Fig. 15). Once more, the black pigments on the surface of the samples of these two groups present similar characteristics (which differ from those of the Corinthian samples). In fact, these slips may be characterized as 'low-quality', since they exhibit a low $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio, a relatively high CaO content and usually a low Fe_2O_3 content. Additionally, many of them present non-homogeneous micromorphology with many bloating pores, as well as uneven colour (on many samples there is a wide, and apparently unintentional, range of hues, from brown to black); both of the latter features constitute signs of a poorly controlled firing process. These two groups may be attributed to local (Theban) or nearby workshops. The fact that they all exhibit identical technological characteristics is proof that they were produced by potters who shared a common technological background. In addition, their separation into two XRF groups is in accordance with the well-known lack of uniformity of the Theban clays (Jones 1986) and may reflect the use of different body clay raw materials (different local workshops).

Finally, four samples form a fourth group in the upper right region of the graph (Fig. 15). Unfortunately, none of these samples may be safely attributed to a specific provenance. However, they also exhibit common technological characteristics of pigments: they all present white-coloured slips with $\text{CaO}/\text{MgO} > 1$ as well as the highest $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio among all the white-decorated samples. Thus they may be attributed to a common provenance, possibly eastern Boeotian or Euboean—at least, if we assume a nearby origin.

Further investigation under XRF allowed the quantification of several trace element concentrations (Ba, Cr, Mn, Ni, Cu, Zn, Pb, Rb, Sr and Zr). From each of the four groups (a maximum peak intensity approach; see Fig. 15), two representative samples were selected and subjected to quantitative analysis. The results verified the above-mentioned grouping of the samples: Corinthian samples exhibit the highest Sr concentrations (> 200 ppm), while the Theban samples are separated into two main groups ($120 \text{ ppm} < \text{Rb} < 130 \text{ ppm}$ and $60 \text{ ppm} < \text{Rb} < 80 \text{ ppm}$) (Fig. 16). The 'possibly eastern Boeotian–Euboean' samples are characterized by the lowest Sr ($\text{Sr} < 100 \text{ ppm}$) and the highest Rb concentrations ($\text{Rb} > 150 \text{ ppm}$; Fig. 16).

Although the XRF data provided are considered of semi-quantitative character, a further attempt was made to relate these data with previously published data on pottery provenance. The high-Sr samples of Figure 16 (attributed to Corinth) exhibit relatively low Cr concentrations ($\leq 330 \text{ ppm}$), which is one of the characteristics of Corinthian pottery (Grimanis *et al.* 1980; Jones 1986, and chemical data therein). Further comparison of the XRF results with the data of Schwedt *et al.* (2006) revealed a correlation of our 'Theban' samples (triangles and squares in Figs 15 and 16) with the pattern of central Boeotia (Thebes) (and in a lesser extent with the eastern Boeotia – Tanagra pattern). In addition, the 'Theban' samples exhibit high Cr and Ni concentrations, which are also associated with Boeotia (Mommsen *et al.* 2002). With regard to the fourth group (the upper right region of Fig. 15), although it could not be clearly related to any of the groups presented by Schwedt *et al.* (2006), the relatively low Cr and Ni,

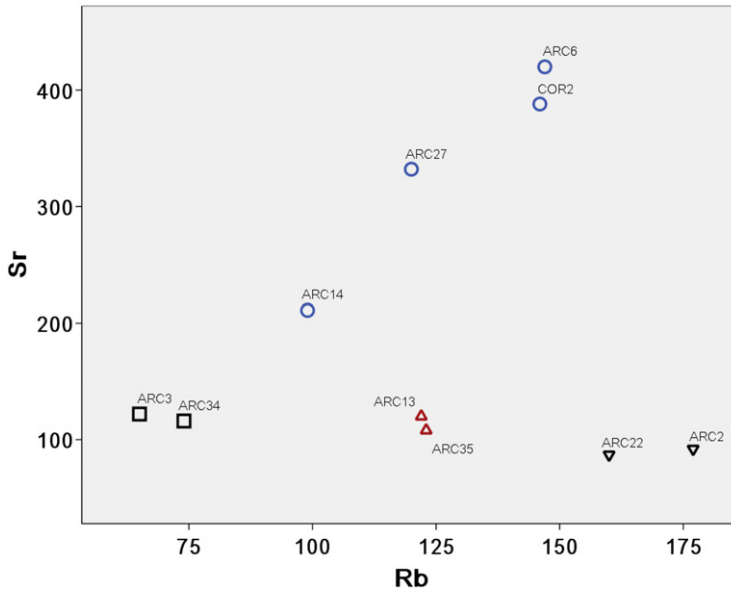


Figure 16 A plot of the Sr versus Rb concentrations (ppm) of representative samples from Figure 15, based on quantitative XRF analysis.

as well as the moderate Ti concentrations, indicate a possible correlation with the pattern of Euboean pottery (Jones 1986).

CONCLUSIONS

The examination, by means of optical microscopy and SEM–EDAX, of the decorative pigments on 47 samples excavated in an archaic sanctuary in Thebes revealed their technological characteristics. For the production of black motifs, the so-called ‘iron-reducing’ technique has been used exclusively. The samples exhibit considerable differences with regard to their optical characteristics (hue, glossiness and so on), their chemical compositions and the micromorphology of the pigments; these features are correlated with the technological characteristics of the production process (raw material selection and processing, firing conditions and so on). In order to produce red shades, ancient potters used a variety of raw materials, which included iron ochres as well as iron-rich clays, the latter being similar to those used for the production of black pigments but fired in a single, oxidizing stage. White–pale hues were mainly produced using Ca- or Mg-rich clays.

Of particular interest is the case of purple decorative pigments. SEM–EDAX analysis and micromorphological investigations, combined with an extended experimental approach to the thermal treatment modification of iron pigments (Mastrotheodoros *et al.* 2010), led to the conclusion that in order to produce purple hues, ancient potters had possibly used a mixture of clay and an iron-rich raw material. The crucial factor in the production of the purple hue is the iron particle-size distribution, which is affected by firing: at temperatures as high as 900°C, iron particles with diameters above 0.4 µm are formed, which exhibit the characteristic deep red–purple hue.

An in-depth interpretation of the technological characteristics of the pigments, along with further examination of the samples' body clay trace elements concentration pattern, led to the establishment of a correlation between decorative pigments and sample provenance. The chemical composition as well as micromorphology of the black pigments may be correlated with the provenance of the samples: Corinthian samples are characterized by high-quality black slips made using finely manipulated, high-quality raw materials and using a well-controlled procedure (furnace temperature and atmosphere). On the other hand, Theban samples generally exhibit low-quality black pigments: large compositional variations among different samples and medium-quality raw material processing, as well as poorly controlled firing (bloating pores, uneven final colour). Finally, it is also possible that a specific type of white–pale pigment may also be characteristic of the provenance.

Our understanding of the relation between pigment technology and provenance, as well as the pottery circulation issues pertinent to the Heracles sanctuary during the archaic period, might be enhanced via additional quantitative investigation of the minor and trace element concentrations.

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