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A PRELIMINARY INVESTIGATION OF BLACK, BROWN AND RED COLOURED POTSHERDS FROM ANCIENT UPPER MACEDONIA, NORTHERN GREECE

A. Iordanidis[1] & J. Garcia-Guinea[2]

[1] *Department of Geotechnology and Environmental Engineering, Technological Educational Institute (TEI) of Western Macedonia, Kila, 50100 Kozani, Greece*

[2] *Museo Nacional Ciencias Naturales, CSIC, C/ José Gutierrez Abascal 2, Madrid 28006, Spain*

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Corresponding author: aiordanidis@yahoo.co.uk

ABSTRACT

Black, red and brown coloured surfaces of several ancient potsherds from an archaeological site of northern Greece, dated from the prehistoric (16th c. BC) to the Hellenistic (3rd c. BC) era were analysed by Raman microspectroscopy, non-destructive X-Ray Diffraction (XRD), Environmental Scanning Electron Microscopy coupled to Energy Dispersive system (ESEM-EDX) and Thermogravimetry (TG). Black colour comprises of amorphous carbonaceous material and iron oxides (hematite and/or magnetite), red colour is due to hematite (the raw material being iron oxides and hydroxides either from an ochre deposit or an iron-rich clay deposit) and brown from a mixture of hematite and calcite. The decoration seems to have been applied before firing, and the colours were obtained of mixtures of specific proportions of the main constituents and by controlling the kiln atmosphere (combined reducing and oxidizing). The possibility of post-firing decoration on the prehistoric sample is also discussed.

KEYWORDS: pigments, Raman, XRD, ESEM-EDX, TG/DTG

INTRODUCTION

Pigment identification on archaeological artefacts such as wall paintings, sculptures, pottery etc. is crucial for the understanding of the raw material applied and the technology used for decoration and furthermore for resolving conservation and restoration problems. The employment of interdisciplinary analytical techniques is a common practice nowadays, with both destructive and non-destructive analytical methods being widely used for colour determination. Amongst them, a well established analytical technique used for pigment identification of art objects through a non destructive approach is Raman spectroscopy, which has been widely used in the last decade (Colomban et al., 2004; Smith and Clark, 2004; Clark, 2007). Information on the chemical and mineralogical nature of the different pigments used by ancient potters to decorate ceramic vessels can also be obtained with the help of X-Ray Diffraction, Thermogravimetry, Scanning Electron Microscope, X-Ray Fluorescence, Neutron Activation Analysis (NAA) etc. (Kallithrakas-Kontos and Maravelaki-Kalaitzaki, 2004; Drebushchak et al., 2007; Welter et al., 2007; Mastrotheodoros et al., 2010).

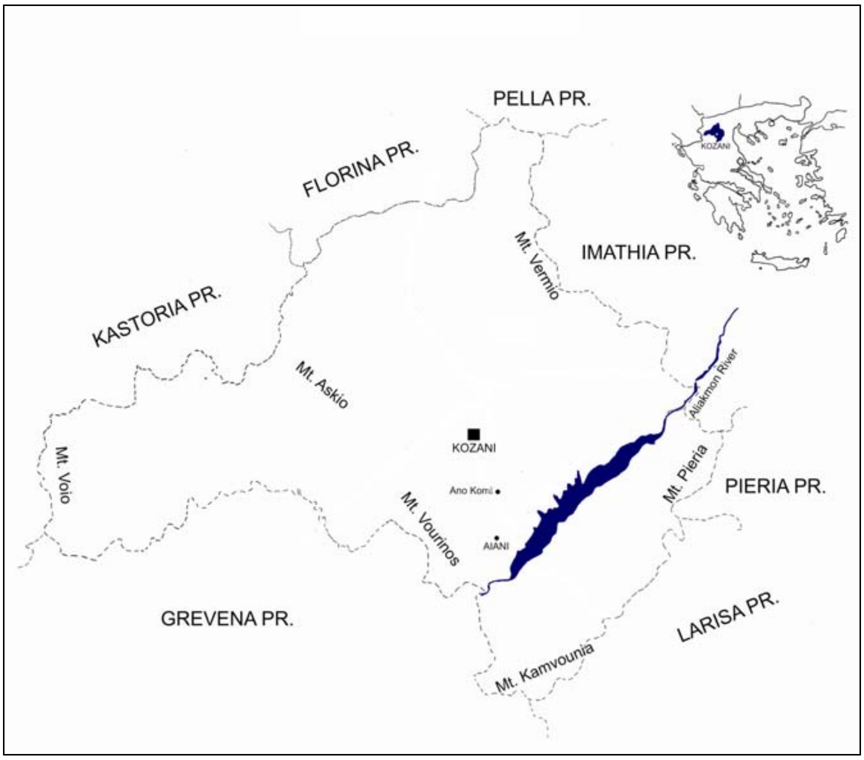

Figure 1. Map showing the location of Aiani, ancient city of Upper Macedonia, now situated at Kozani's prefecture, northern Greece.

The analytical characterization of bulk potsherd samples from Aiani, ancient Upper Macedonia, northern Greece was previously studied (Iordanidis et al., 2009). In the present study, we focus on the three characteristic colours (black, brown and red) that predominate in the ancient pottery found on the archaeological site of Aiani. Black, brown and red colours are those more often observed on ceramic slips around the world and the application of the decoration could have taken place after or before firing. Micro-chemical techniques, such as X-Ray Diffraction (XRD), Environmental Scanning Electron Microscopy (ESEM) coupled with Energy Dispersive System (EDX), Thermogravimetry (TG) and Raman microspectroscopy are employed in order to investigate the raw materials used and the technology applied for these pigments, and moreover to demonstrate how consistent the utilization of these pigments was through time (16th to 3rd century BC).

ARCHAEOLOGICAL CONTEXT

Aiani is located approximately 20 km south of the city of Kozani, western Macedonia, Greece. In historical times, Aiani was situated within the region of the ancient kingdom of Elimeia which, together with the kingdoms Tymphaia, Orestis, Lyncestis, Eordaia and Pelagonia constituted, since the Archaic period, ancient Upper (i.e. mountainous) Macedonia. Systematic excavation and research have revealed the architectural remains of both large and small buildings, rich in small finds, and groups of graves and organized cemeteries dating from the prehistoric to the Late Hellenistic period. The quality of the painted decoration and the variety of colours and motifs on ceramics suggest that the area of ancient Aiani was a notable production centre for pottery, making its appearance from the 16th century BC (Karamitrou-Mentessidi, 1993 and 1999). The pottery includes a large number of vases of the so-called Macedonian matt-painted ware. According to Horejs (2007), a distinct stylistic group of late Bronze matt-painted pottery originated from Aliakmon (Aiani's surrounding area) occurs. Local pottery workshops seems to have operated continuously from the Archaic-Classical up to the Roman period (Karamitrou-Mentessidi, 1989).

EXPERIMENTAL

Sampling

Approximately seventy potsherds were provided by the archaeological authorities covering a period from prehistoric to Hellenistic times. Based on the prevailing black, brown (including orange and yellow) and red colours of their surfaces, five representative potsherd samples, belonging to three distinctive chronological types, which were precisely determined in our previous study (Iordanidis et al., 2009), were selected for the analysis: one matt-painted (16th -11th c. BC) potsherd, named as M2; three Archaic-Classical (7th - 5th c. BC) samples, named as AKL29, AKL27 and AKL22; and finally one Hellenistic (4th – 3nd c. BC) sherd, named as E6. The successful analytical characterization of this small number of samples, will stimulate relevant research in the region, using a larger set of samples. It should be mentioned that all sherds were carefully examined macroscopically, stereoscopically and, for a few of them, under Raman microscope, before selecting the representative ones. All samples are illustrated in Figure 2. Brown, orange and yellow colours predominate on the surface of the prehistoric (M2) sample. A characteristic metallic-black colour, along with a red paint is revealed on all Archaic-Classical pots, while the red-coloured E6 Hellenistic sample was as a non-decorated potsherd.

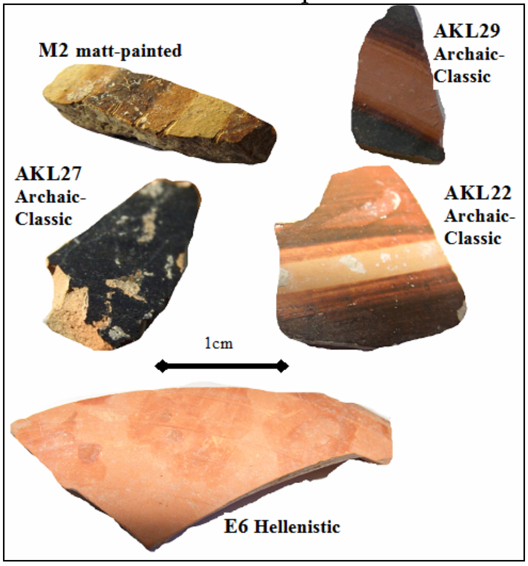

Figure 2. Macroscopic images of potsherds dated from prehistoric to Hellenistic times from Aiani, ancient Upper Macedonia, Greece. (M2= matt-painted, AKL22, AKL27 and AKL29=Archaic-Classic, E6=Hellenistic)

Analytical methods

Freshly fractured samples of the potsherd samples were used for the ESEM-EDX analysis. A Philips QUANTA 200 Environmental Scanning Electron Microscope (ESEM), coupled with an Oxford INCA Energy 200 Energy Dispersive System (EDS) was used. The X-Ray Diffraction (XRD) was employed for the semi-quantitative mineral identification of the coloured surfaces of the pottery slips. Samples were carefully placed horizontally on a special holder, so as to analyse the pigmented surfaces of the sherds non-destructively. A Philips PW-1710 powder diffractometer with CuKα radiation was used. Patterns were obtained by step scanning from 3° to 63° 2θ, with a goniometer speed of 0.03°/sec, operating at 30kV and 10 mA. The XPOWDER analytical software was used for the semi-quantitative determination of the mineral phases. A Perkin Elmer STA6000 device was used for the thermogravimetrical analysis (TG/DTG). Approximately 2-10 mg of pigments was scratched off the pottery slips and placed in aluminum crucibles. The temperature programme ranged from 50°C to 1000°C, at a heating rate of 10°C min^{-1} under nitrogen atmosphere. The Raman spectroscopic study was performed with a Thermo Scientific DXR Raman Microscope. The average spectral resolution in the Raman shift range of 100-3000 cm^{-1} was 5 cm^{-1} (grating 400 lines/mm, spot size 2μm). Raman images were obtained using the 20X objective of the con-focal microscope. A 780 nm laser beam was used, and the power value of the sample irradiation was 12 mW. Other analytical parameters were as follows: 30sec bleaching time; 5 exposures of 10 sec exposure time. Under the microscope the pigmented surfaces could be clearly seen and the area of their definite spectra could be precisely determined.

Table 1. Raman peaks assignment of the coloured surfaces of selected potsherds from Aiani, ancient Upper Macedonia, Greece (M2=matt-painted, AKL29, AKL27, AKL22=Archaic-Classic, E6=Hellenistic).

SAMPLE ID	Peaks (cm^{-1})	Mineral assignment
M2 BROWN	286, 1087	Calcite
	672	Magnetite?
	1395,1468,1666,1757	Carbon black
M2 ORANGE	144	Rutile
	283, 713, 1088	Calcite
	490	Hematite
	1271, 1394, 1549, 1739, 1924	Carbon black
M2 YELLOW	149	Anatase
	412, 614	Hematite
	1087	Calcite
	1119, 1222, 1333, 1415, 1480,	Carbon black
	1674, 1764, 1985, 2110, 2531	Carbon black
AKL29 BLACK	1397	Carbon black
AKL29 RED	147	Anatase
	229, 297, 609	Hematite
	467	Quartz
	1392, 1505, 1725, 1907	Carbon black
AKL27 BLACK	189, 480	Hematite
	705	Calcite
	1319, 1567	Carbon black
AKL22 BLACK	142	Rutile
	295, 492, (683)	Hematite
	704	Calcite
	1335, 1409, 1606, 1725, 1845, 2017	Carbon black
AKL22 DARK RED	146	Anatase
	229, 299, 418, 618	Hematite
	466	Quartz
	1142, 1394, 1461, 1505,	Carbon black
	1585, 1692, 1908, 2020	Carbon black
AKL22 LIGHT RED	146	Anatase
	230, 414, 620	Hematite
	466	Quartz
	1119, 1409, 1461, 1684, 1770,	Carbon black
	1997, 2112, 2138, 2536	Carbon black
E6 RED	146	Anatase
	229, 298, 418, 614	Hematite
	674	Magnetite
	463	Quartz
	1421, 1508, 1581, 1905	Carbon black

RESULTS AND DISCUSSION

Raman microspectroscopy

The Raman spectra of all the analysed samples along with characteristic micrographs of the coloured surfaces using the Raman microscope are shown in Figures 3 and 4. The identified mineral phases are also presented in Table 1, indicating the characteristic Raman peaks of each mineral.

The prehistoric M2 potsherd, having the typical brown, orange and yellow colours seems to be composed of different proportions of the following mineral phases: black carbon, hematite, magnetite, rutile / anatase and calcite. Amorphous carbon is evident from many Raman peaks (1119, 1222, 1271, 1333, 1394, 1395, 1415, 1468, 1480, 1549, 1666, 1739, 1757, 1924 cm^{-1}).

It is likely that various plants served as sources of amorphous carbon, having been converted to carbon after firing under reducing conditions. These easily accessible carbonaceous materials often employed in the decorations of ancient ceramics (Striova et al., 2006; Hernanz et al, 2008; Goodall et al., 2009).

Based on the database of the software (Omnic) used in our Spectrometer and moreover, due to the lack of relevant published results, it is extremely difficult to assign all these peaks to specific organic functional groups, e.g. aromatic, ketones, aliphatic etc. and thus to provenance the type of vegetation and/or animal origin. An indirect proof for the carbonaceous character of the decoration has been furnished by XRD and ESEM/EDX, as described below.

Hematite shows the characteristic peaks at 412, 490 and 614 cm^{-1}, magnetite is probably related to 672 cm^{-1} peak and rutile and anatase with the 144 and 149 cm^{-1} peaks respectively. The oxidation state of iron is strongly dependent on the atmosphere under which the ceramic body was fired.

The oxidizing or reducing atmosphere implies the formation of characteristic minerals, especially hematite Fe_2O_3, which is responsible for the reddish colour, and magnetite Fe_3O_4, which confers a dark shade on the ceramic material (Smith and Clark, 2004; Kallithrakas-Kontos and Maravelaki-Kalaitzaki, 2004; Striova et al., 2006 and 2009). The orange colour has been assigned to iron oxyhydroxides by other scholars (Hernanz et al., 2008), and this could be also our case, suggesting either the application of a post firing decoration on M2 sample or the firing under combined reducing and oxidizing atmospheres. In order to get a brighter colour, i.e. orange in our samples, hematite might have been mixed with calcite before decorating the pottery.

The very intense Raman band at around 144-149 cm^{-1} can be attributed to the vibrational modes of the Ti-oxides (rutile or anatase), which could be present as an ancillary component of silicates (Ospitali et al., 2006). It has been reported by other researchers that the Raman bands of clay minerals (i.e. silicates) are often masked in presence of anatase (Striova et al., 2006). This is due to the fact that the strongly covalent Ti–O bonds give intense Raman bands, while silicates are poor Raman scatterers.

Therefore the presence of clay (phyllosilicate) minerals in our samples could be implied. Anatase converts to rutile between 800°C and 1000 °C, and hence the fact that these two Ti-oxide phases co-exist in our potsherds could be used as an indicator of the firing temperature of the pottery (Smith and Clark, 2004).

In fact, firing temperatures around 850 °C have been suggested in our previous study regarding similar pottery from Aiani's archaeological site (Iordanidis et al., 2009). Nevertheless, according to Striova et al. (2006) this could be ambiguous since under the presence of SiO_2 the anatase/rutile transformation might be inhibited.

Calcite is evident from its peaks at 283 (or 286), 713 and 1087 cm^{-1}. Since the surface colour hues (brown, orange and yellow) show the same mineral composition, it could be assumed that the different colours are attributed to different percentages of the same minerals, e.g. well defined calcite proportions. The Raman spectroscopy could not give quantitative information, so the above speculation is to be ascertained by further analytical methods (ESEM-EDX and XRD).

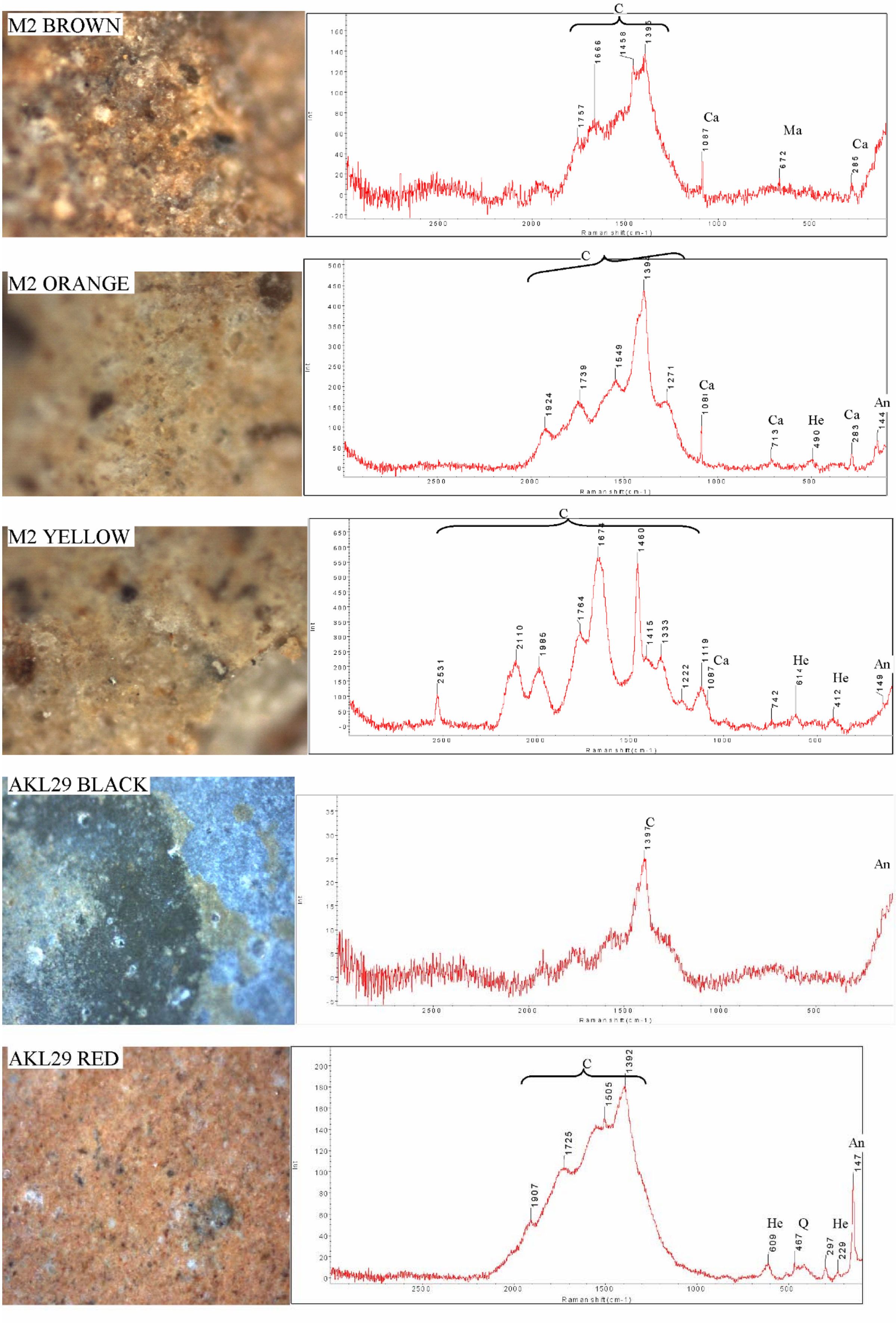

Figure 3. Raman spectra and microphotographs of brown, orange and yellow colours of M2 sample and black and red colours of AKL29 sample. (Laser wavelength 780 nm, objective 20X). Labels: He=hematite, Ma=magnetite, Q=quartz, Ca=calcite, An= anatase, C=black carbon.

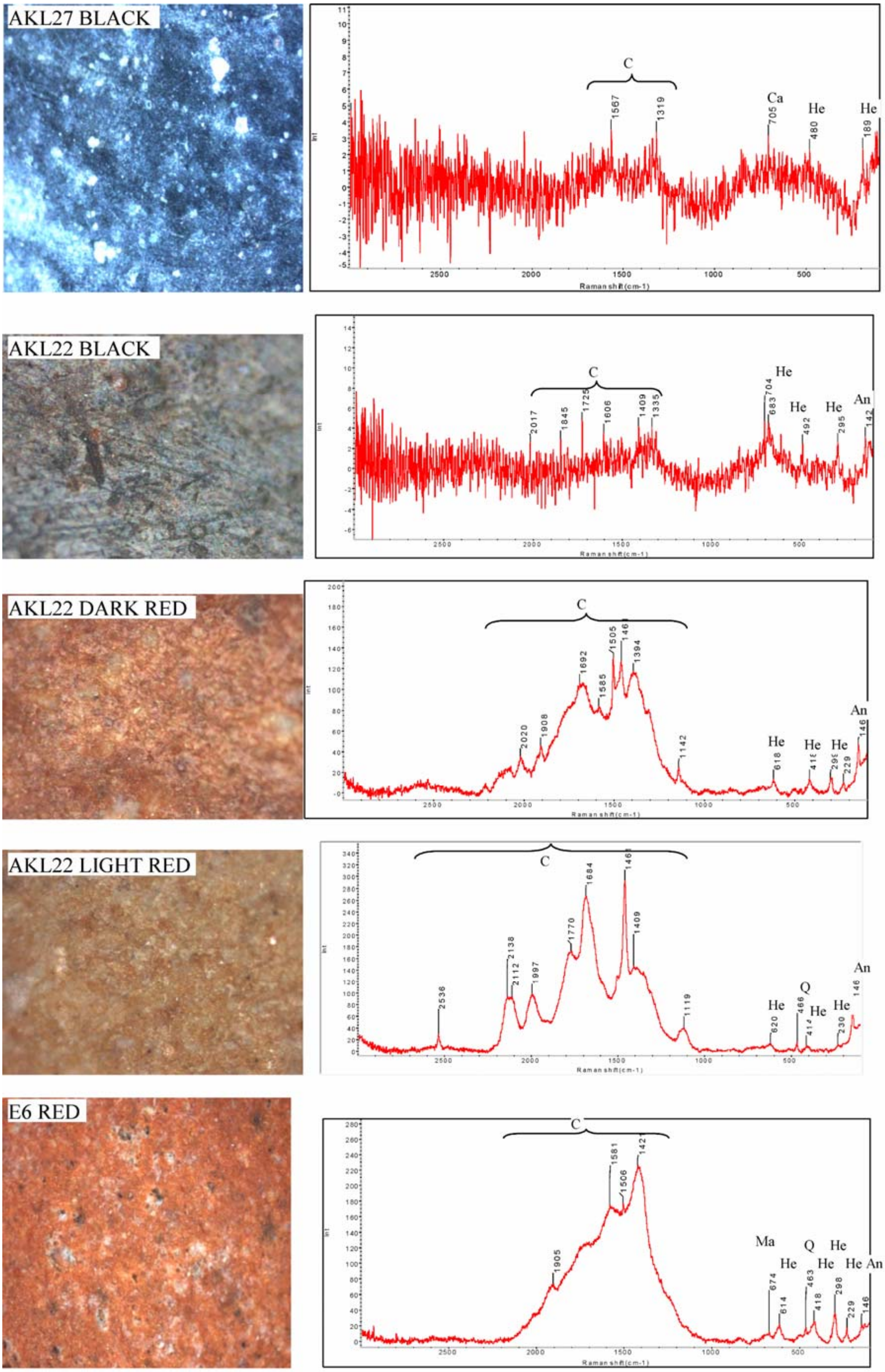

Figure 4. Raman spectra and microphotographs of black colour of AKL27 and AKL22 samples and red colours of AKL22 and E6 samples. (Laser wavelength 780 nm, objective 20X). Labels: He=hematite, Ma=magnetite, Q=quartz, Ca=calcite, An= anatase, C=black carbon.

The black pigmented surfaces of the Archaic-Classical pottery (samples AKL29, AKL27 and AKL22) contain amorphous carbon (black carbon), hematite, titanium oxides (anatase or rutile) and calcite. The black pigment of sample AKL29 seems to be composed almost exclusively of black carbon, while the other two black coloured surfaces (AKL27 and AKL22) show a composition of all the above mentioned minerals. The amorphous carbon shows a characteristic peak at 1397 cm^{-1} (the so-called D-band of black carbon) in sample AKL29, characteristic peaks at 1319 cm^{-1} (this peak could also be attributed to hematite) and 1567 cm^{-1} (the so-called G-band of black carbon) for sample AKL27 and numerous peaks for sample AKL22 (1335, 1409, 1606, 1725, 1845, 2017 cm^{-1}). Anatase (or rutile) shows characteristic peaks at 147 cm^{-1} (or 142 cm^{-1} respectively), hematite reveals its main peaks at 189, 295, 480, 492, 683 cm^{-1}, while calcite is inferred from the 704-705 cm^{-1} Raman peak. The lack of a Raman band at 960 cm^{-1} , related to phosphates from charred bones indicated that the carbon used is derived originally from charred plant material (Goodall et al., 2009).

The red pigmented surfaces of the AKL29, AKL22 and E6 samples revealed the following mineralogical composition by means of Raman spectroscopy: hematite, magnetite, quartz, anatase (or rutile) and carbon black. Hematite shows the characteristic peaks at 229-230, 297-299), 414-418, 609-620 cm^{-1} band ranges; magnetite shows a peak at 674 cm^{-1}; a strong Raman band at 463-467 cm^{-1} appears in many spectra, and can be assigned to the O–Si–O stretching vibration of quartz; amorphous carbon is evident from a number of peaks at 1119, 1392, 1505, 1725, 1907, 1142, 1394, 1409, 1421, 1461, 1505, 1508, 1581, 1585, 1684, 1692, 1770, 1905, 1908, 1997, 2020, 2112, 2138, 2536 cm^{-1}, being difficult to differentiate between different organic moieties. The desirable red colour of the pottery slips could be obtained by firing an iron-rich clay in an oxidizing atmosphere, which could cause the oxidation of iron (Striova et al., 2006). The higher intensity of the 297-299 cm^{-1} Raman band of hematite on sample E6 could be due to the use of a more crystalline phase of hematite (specular), when comparing to the Raman peaks assigned to hematite on all other potsherds (Goodall et al., 2009). The shifts in peak position as well as the changes in their intensities could be due to the material being subjected to phase transformation or due to the coexistence of various phases giving rise to not well-defined spectra (Striova et al., 2006). Under reducing conditions hematite is converted to magnetite between 650 °C and 900 °C and magnetite would remain stable and produce a black pigment (Goodall et al., 2009). Furthermore, according to Colomban et al. (2004), magnetite might suggest reducing conditions and higher temperatures (~950 °C) compared to hematite (~800 °C). The fact that magnetite is not always evident on all the black surfaces of the studied potsherds might be due to the high fluorescence background observed, which tends to mask the magnetite bands (Goodall et al., 2009). In summary, the presence or absence of magnetite on the black and red coloured surfaces of the potsherds does not necessarily suggest different raw material used for pigments, but rather a single component (ochre/hematite) applied to coat the pots and different sintering temperatures and/or kiln atmospheres used to achieve the final colour (Smith and Clark, 2004; Colomban et al., 2004).

The attribution of black carbon of plant origin to the black pigment of ancient pottery was often related to post-firing decoration, since this could facilitate the task for artisans, who were not able to use strictly controlled firing conditions (Maravelaki-Kalaitzaki and Kallithrakas-Kontos, 2003). This could be the case for the prehistoric M2 potsherd. However, the metallic-black colour of the Archaic-Classical potsherds (AKL22, AKL27 and AKL29) attests a pre-firing decoration; most probably, red clays rich in iron oxide and hydroxides were carefully mixed with a proper amount of calcium (and occasionally Mg) rich carbonates and organic carbon (most probably of plant origin) and the outer surface of pots were coated with that clay mixture before firing. By controlling and changing the firing atmosphere within the kiln (oxidizing or reducing) the desired colour could be obtained.

Table 2. Semi-quantitative mineralogical composition of the coloured surfaces of selected potsherds from Aiani, ancient Upper Macedonia, Greece, as revealed by non-destructive X-Ray Diffraction. (M2=matt-painted, AKL29, AKL27, AKL22=Archaic-Classic, E6=Hellenistic)

	M2	AKL29	AKL27	AKL22	E6
Quartz (%) SiO_2	35.3	33.5	9.7	25.3	71.8
Calcite (%) $CaCO_3$	15.6	6.6	-	-	-
Feldspars (%)$(K,Na,Ca)AlSi_3O_8$	45.9	24.0	-	26.2	-
Dolomite (%) $CaMg(CO_3)_2$	-	-	-	10.2	-
Gehlenite (%) $Ca_2Al_2SiO_7$	-	-	-	-	11.2
Hematite (%) Fe_2O_3	-	-	-	-	12.7
Mica (%) $KAl_3Si_3O_{10}(OH,F)_2$	-	33.6	66.8	35.0	
Amorphous (%)	3.2	2.2	23.6	3.4	4.2

X-Ray Diffraction

The mineralogical (XRD) composition of the analysed potsherds is shown in Table 2. It should be noted that the X-Ray Diffraction technique was applied non-destructively on the horizontally oriented surfaces of the bulk potsherd samples. According to Welter et al. (2007), a non-destructive XRD methodology requires limited sample sizes, homogenous composition and flat surface for a good focus of the X-Rays, and these prerequisites are met with our samples. It should be noted however that the mineralogical composition of every different colour of some samples are not particularly determined. Moreover, some minor mineral phases might not have been identified and the XRD results could not directly be correlated with the results of the other analytical methodologies, since different surface areas were sometimes analysed. Quartz is a common mineral found in all samples, with concentrations ranging from 9.7-71.8 %, while feldspars are also present in high amounts in three samples (M2, AKL29 and AKL22). Calcite is only apparent in M2 and AKL29 samples. The high percentage of the amorphous phase along with the absence of calcite in sample AKL27 is a clear indication that black carbon is the main constituent of this sample, as also attested by Raman spectroscopy. The Hellenistic sample contains gehlenite (a Ca-aluminosilicate, characteristic of the high firing temperature in the kiln) and hematite. The absence of hematite on the XRD results from the other red-coloured pot samples does not necessarily imply that it does not exist, since hematite in low quantities (<1%) is adequate to attain a red hue on the ceramics. Phyllosilicate minerals [mainly micas (e.g. muscovite)] are also present in the Archaic-Classical (AKL) ceramics and might be related to local clays used for pigments (Eliopoulos and Economou-Eliopoulos, 2000; Rassios, 2004; Skarpelis, 2006). The presence of Mg-rich dolomite minerals is also found in one sample (AKL22) and could be related to the local Mg-rich deposits found in the surrounding area (Rassios, 2004; Iordanidis et al., 2009).

Table 3. Chemical composition (major elements oxides in wt %, as determined by EDX-ESEM) of various coloured surfaces of selected potsherds from Aiani, ancient Upper Macedonia, Greece (M2=matt-painted, AKL29, AKL27, AKL22=Archaic-Classic, E6=Hellenistic).

	M2 BROWN	M2 ORANGE	M2 YELLOW	AKL29 BLACK	AKL29 RED	AKL27 BLACK	AKL22 BLACK	AKL22 DARK RED	AKL22 LIGHT RED	E6 RED
SiO_2	26.34	29.45	35.98	30.27	41.84	28.02	20.33	29.47	35.18	35.84
Al_2O_3	14.62	14.87	9.54	28.45	16.48	20.85	25.49	15.18	11.67	15.65
Fe_2O_3	10.83	9.80	7.93	18.52	12.01	13.79	20.82	14.11	10.78	8.55
MgO	3.68	4.14	4.93	3.10	5.12	1.50	2.65	5.01	6.50	1.99
CaO	10.51	7.05	14.92	1.31	5.00	-	1.77	6.19	10.56	4.30
K_2O	1.36	1.21	1.46	3.16	2.48	2.86	2.15	1.52	1.34	3.03
TiO_2	0.74	0.84	0.61	0.75	0.81	0.37	-	-	0.54	0.72
CO_2	31.92	32.63	24.63	14.44	16.25	32.62	26.79	28.52	23.44	29.93

ESEM-EDX

The chemical analyses (EDX) of the studied sherds are shown in Table 3. The different colours of the surfaces were clearly observed under Environmental Scanning Electron Microscope and the elementary composition of every different coloured area is clearly defined. Fe_2O_3 concentrations range between 7.93 and 20.82%, while aluminum and silicon contents are similar and are probably connected to the aluminosilicate (phyllosilicate) phases present in the raw clay material. The absence of manganese in the black colours is in accordance with the results of the afore-mentioned analyses (Raman, XRD) and thus strengthens the hypothesis of using organic carbon material for receiving black coloured surfaces. The high concentration of CO_2 in the black pigment of sample AKL27 along with the absence of CaO contents confirms the use of amorphous carbon. TiO_2 contents are always present in our samples in low quantities (0.37-0.84 %), probably as a minor constituent of local red clays (Christidis et al., 1998). The prehistoric M2 sample shows a similar chemical composition for all brown, orange and yellow colours. The variation in the colour is apparently due to different proportions of CaO, Fe_2O_3 and CO_2. It is possible that these colours were obtained using a mixture of local iron-rich clay with calcite and carbonaceous (plant) material on different percentages. It is also obvious from all samples that Na_2O, MnO and P_2O_3 are not contributing to the pigments of our potsherds. Phosphor could have indicated the use of charred bones as a black pigment, a common practice in ancient times (Ospitali et al., 2006). The black colour was also attributable to manganese in antiquity. It is also indicated that black colours have higher contents of Fe_2O_3 when compared to red tones. In the samples AKL29 and AKL22, lighter tones seems to be obtained by adding more CaO to the pigment's mixture. The presence of titanium in minor quantities is probably related to the clay deposits used for the pigment's raw material. Titanium is a common auxiliary mineral found within Fe-rich clays and is probably related to the Ti-rich primary rock formations and their secondary (sendimentary) erosion products found in the region (Christidis et al., 1998; Eliopoulos and Economou-Eliopoulos, 2000).

The absence of Na and presence of K could be due to the presence of mica [muscovite, $KAl_3Si_3O_{10}(OH,F)_2$], which was also found using the XRD technique, and its alteration product, illite, thus strengthening the hypothesis for utilization of local clay deposits. Moreover, the high contents of Al and Si in the red pigment on all samples indicate that the material used for the paint was either a mixture of iron oxides and clay to facilitate coverage and bonding or natural ochre was used directly (Goodall et al., 2009).

Thermal analysis (TG/DTG)

The Derivative Thermogravimetric (DTG) curves obtained by the thermal analyses of the studied samples are shown in Figure 5.

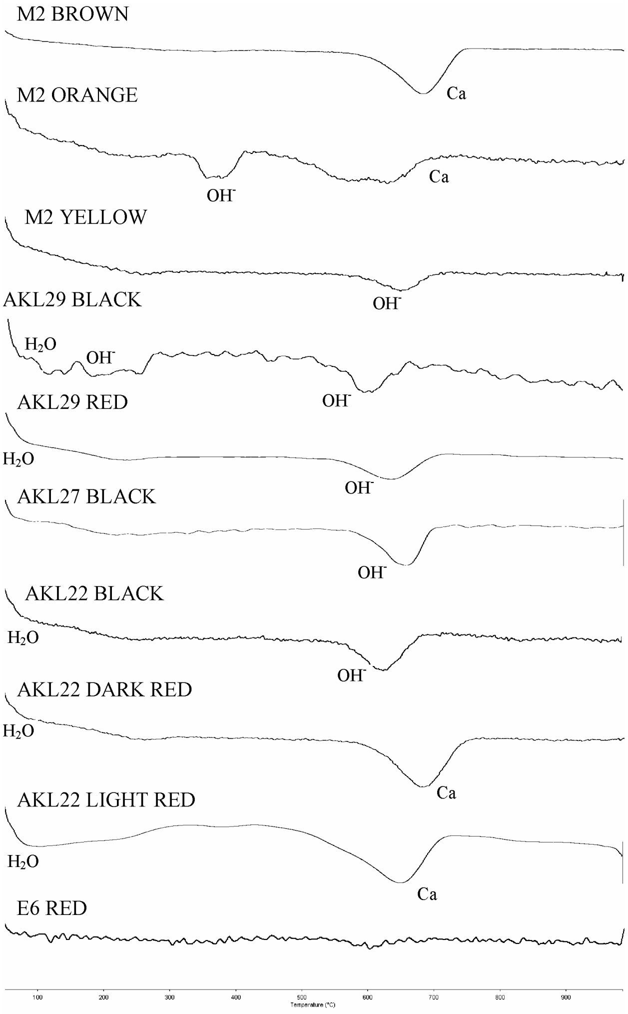

Figure 5. Derivative Thermogravimetric (DTG) curves of all the potsherds of this study. Label assignments: H_2O=water loss, OH^-=phyllosilicates, Ca=Calcite

The summary of the TG analytical results (mass loss during thermal treatment and peak assignment) are also shown in Table 4. The peaks below 100°C are related to the elimination of the adsorbed water, while the peaks from 120°C to 650°C are mainly attributed to the dehydroxylation of structural OH^- in micas (phyllosilicates). The peaks observed between 648°C and 769°C are probably associated with the decarboxylation of calcite.

Despite the fact that calcite usually decomposes at 750-850°C, the decrease in the decomposition temperature has been frequently observed in ceramic thermoanalysis, especially when we have mixtures of calcite with other impurities (salts, organics etc.) (Papadopoulou et al, 2006; Drebushchak et al, 2007). The high mass loss of sample M2 (up to 19.1%) is probably related to its higher calcite content, as was also revealed by the previous techniques. The presence of a peak at 948°C in sample E6 is associated with the gehlenite mineral phase, which was also evident in the XRD analysis. The presence of micas (phyllosilicates) in the red pigmented surfaces of the potsherds is evident in the characteristic DTG peaks within the region of 120 to 640°C. There is an obvious prevalence of higher LOI values in the brown and orange colours of M2 sample when compared to the yellow one. This could be attributed to either a higher calcite content of the darker tones or a higher carbon content of the brown and orange colours.

Table 4. Derivative Thermogravimetric (DTG) results and main peaks (cf. Fig.5) assigned to specific minerals from various coloured surfaces of selected potsherds from Aiani, ancient Upper Macedonia, Greece (M2=matt-painted, AKL29, AKL27, AKL22=Archaic-Classic, E6=Hellenistic).

SAMPLE ID	LOI (%)	Peaks (°C)	Mineral assignment
M2 BROWN	14.6	679	Calcite
M2 ORANGE	19.1	115	Phyllosilicates $(OH)^-$
		369	Phyllosilicates $(OH)^-$
		612	Phyllosilicates $(OH)^-$
		769	Calcite
M2 YELLOW	1.2	624	Phyllosilicates $(OH)^-$
AKL29 BLACK	0.9	75	Loss of H_2O
		184	Phyllosilicates $(OH)^-$
		448	Phyllosilicates $(OH)^-$
		592	Phyllosilicates $(OH)^-$
AKL29 RED	8.6	88	Loss of H_2O
		235	Phyllosilicates $(OH)^-$
		630	Phyllosilicates $(OH)^-$
AKL27 BLACK	2.7	86	H_2O
AKL22 BLACK	7.4	622	Phyllosilicates $(OH)^-$
AKL22 DARK RED	8.4	648	Calcite
AKL22 LIGHT RED	8.9	82	Loss of H_2O
		654	Calcite
E6 RED	8.4	122	Phyllosilicates $(OH)^-$
		390	Phyllosilicates $(OH)^-$
		432	Phyllosilicates $(OH)^-$
		672	Calcite
		928	Gehlenite

Based on the above, an alternative hypothesis is proposed: one could assume that the pottery was fired until the surface obtained a yellow colour and the brown and orange pigments were post-firing decorations, using carbonaceous, calcite and red clay raw materials. This hypothesis was also addressed above, based on the results of Raman spectroscopy. The low LOI values of the black coloured surfaces might indicate high firing temperatures.

CONCLUSIONS

Black, red and brown (with all the intermediate hues) coloured potsherds were analysed by interdisciplinary analytical techniques for the pigment identification. The black colours are associated with carbonaceous material of an amorphous character and iron oxides (hematite and occasionally magnetite). The Raman spectra of all the red pigments revealed hematite as the main constituent. The raw material for the painting derives probably from iron oxides and hydroxides either from a local ochre deposit or an iron-rich clay deposit. The presence of micaceous minerals, as determined by XRD corroborates the assumption that local Fe-rich clays were the raw material used. The decoration seems to have been applied before firing, and the colours were obtained by applying specific proportions of the above main constituents of the mixtures and by controlling the kiln atmosphere (combined reducing and oxidizing). There is also a possibility that a post-firing decoration was applied on the prehistoric sample. Manganese and phosphor are clearly absent, as shown by ESEM-EDX, Raman spectroscopy and X-Ray Diffraction. The similarities in the pigments and technologies used to produce them suggest that there might have been a formal relationship and continuity in the tradition of pot-manufacturing among the producers of this area. It should be noted that these are only some preliminary results and a larger set of samples is needed to strengthen our findings.

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