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### Characterisation of Mycenaean and matt-painted pottery from Alani, ancient upper Macedonia, Greece

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## CHARACTERISATION OF MYCENAEAN AND MATT-PAINTED POTTERY FROM AIANI, ANCIENT UPPER MACEDONIA, GREECE

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### Abstract

Several analytical methods were applied for the study of ancient pottery from Aiani, ancient upper Macedonia, northern Greece. Mycenaean and matt-painted pottery sherds, dated from Late Bronze age, were analysed with the help of X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF) and Environmental Scanning Electron Microscopy, coupled with Energy Dispersive X-ray system (ESEM-EDX). Morphological, chemical and mineralogical characteristics of both types of ancient pottery indicated a rather local provenance, thus strengthening the hypothesis of the co-existence of Mycenaean and Dorian pottery workshops in the region, during Late Bronze period.

**Key words:** prehistoric ceramics, SEM/EDX, XRD, XRF.

### Περίληψη

Διάφορες αναλυτικές μέθοδοι εφαρμόστηκαν για τη μελέτη αρχαίων κεραμικών από την Αιανή, αρχαία Άνω Μακεδονία. Οστρακα μυκηναϊκής και αμαυρόχρωμης κεραμικής ηλικίας Ύστερης Εποχής Χαλκού συλλέχθηκαν και αναλύθηκαν με τη βοήθεια της περιθλασιμετρίας ακτίνων X (XRD), της φασματοσκοπίας φθορισμού ακτίνων X (XRF) και του «περιβαλλοντικού» ηλεκτρονικού μικροσκοπίου σάρωσης (ESEM). Τα μορφολογικά χαρακτηριστικά, η χημική και η ορυκτολογική σύσταση των αναλυθέντων οστράκων υποδηλώνουν την κατασκευή των κεραμικών αυτών σε τοπικά εργαστήρια της αρχαίας Αιανής, ενώ υποστηρίζουν και την υπόθεση των αρχαιολόγων για την συνύπαρξη μυκηναϊκών και δωρικών εργαστηρίων κεραμικής στην περιοχή αυτή, κατά τη διάρκεια της Ύστερης Εποχής Χαλκού.

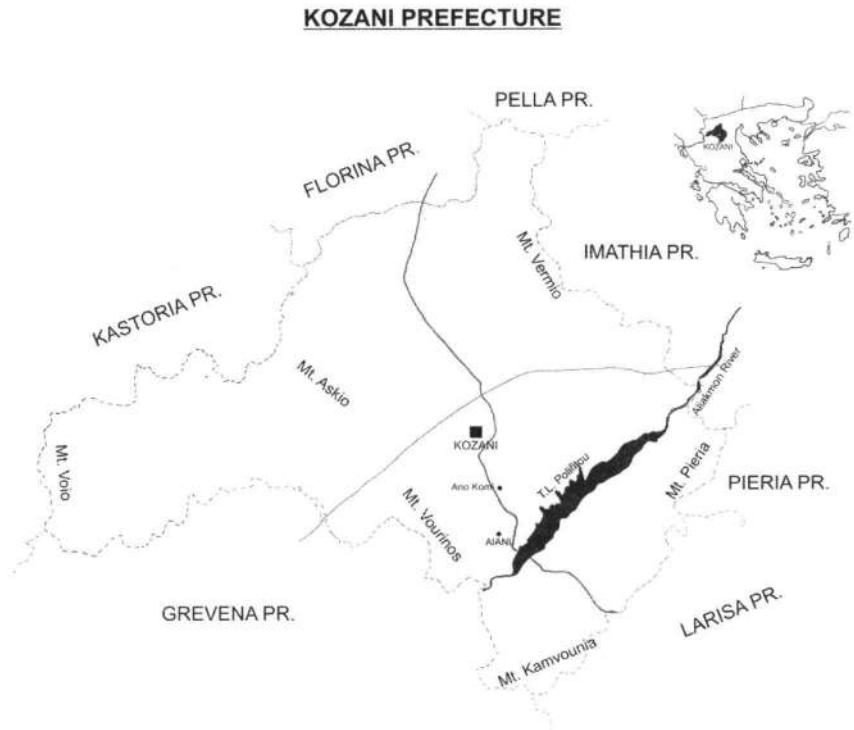
**Λέξεις κλειδιά:** προϊστορικά κεραμικά, SEM/EDX, XRD, XRF.

## 1. Introduction

The application of interdisciplinary analytical methods to archaeology is well established to date. The employment of various chemical, geological and physical analytical techniques in order to study archaeological artefacts (e.g. ceramics, mortars, slags, marbles etc.) is also a common

practice nowadays. The chemical, mineralogical and structural characterisation of ancient pottery can shed light to the provenance of raw materials for ceramic production and determine the technological processes related to pottery manufacture. The identification of specific chemical elements in high concentration could be related to the geological profile of the study region and thus imply local potters and differentiate from the imported ones. The mineralogical composition indicates the raw material and the firing temperatures and the firing conditions in the kiln (oxidising or reducing). Mineralogical analysis using X-Ray Diffraction (XRD) or Scanning Electron Microscopy (SEM) has been reported (Sofianopoulou *et al.* 2004). The chemical analysis of ancient pottery encompasses several analytical techniques, like Inductively Coupled Plasma spectroscopy (ICP), X-Ray Fluorescence (XRF), Neutron Activation Analysis (NAA) etc. (Maniatis and Tsirtsoni 2002, Mommsen *et al.* 2002, Sanchez-Ramos *et al.* 2002, Polvorinos *et al.* 2005). The variation in the chemical composition may imply pottery from different production sites or reflect the natural inhomogeneity of local clay deposits and the application of different manufacture processes in local workshops.

In the present study, ancient pottery from Aiani, Kozani area, ancient upper Macedonia, northern Greece was obtained from the local archaeological authorities and subjected to several analytical methodologies. XRD was used for the mineralogical characterisation, XRF for the chemical element concentrations and ESEM-EDX for morphological, structural and chemical assessment of ancient potsherds.



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

**2. Archaeological context**

Aiani is located approximately 20 km south of the city of Kozani, western Macedonia. Aiani was within the region of the ancient kingdom of Elimeia which, together with the rest of the Greek kingdoms (Tymphaia, Orestis, Lyncestis, Eordaia, Pelagonia) constituted the ancient Upper (i.e.

mountainous) Macedonia. The systematic excavational research, which began in 1983, has 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 Late Bronze Age in Upper Macedonia is marked by the appearance of Mycenaean finds, together with the appearance and spread of matt-painted pottery.

## 2.1. Mycenaean finds

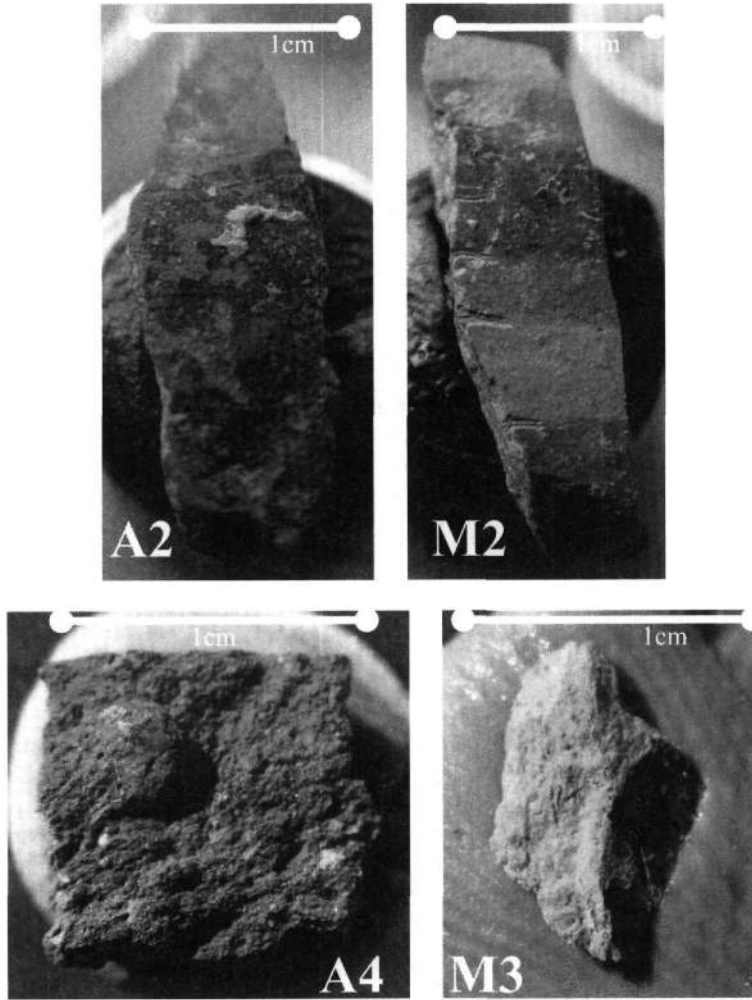
Mycenaean finds have been unearthed on twenty-six sites near nineteen villages in Kozani's prefecture. Eleven of the sites yielded graves and the rest pottery, which in eleven cases came from habitation layers. Examples are: the mouth of a pithos with linear painted decoration, and a cemetery with Mycenaean grave goods at Aiani; a Mycenaean figurine at Ano Komi; and similar cemeteries at Ano Komi, Rymnio, and Sparto, in the riverine and lacustrine area around the middle reaches of the Aliakmon river and at Trigoniko. The excavations of recent years have produced growing evidence of Mycenaean presence all over Macedonia. The numerous Mycenaean finds indicate that Mycenaeans established settlements of some kind in this area, though the question will be the subject of future investigations and studies. The view may be upheld with regard to the area around Aiani and the middle reaches of the Aliakmon in particular, which is very close to Thessaly and would naturally have developed a network of mutual contacts and influences, as was the case in earlier periods from the Neolithic onwards (the prehistoric finds from Servia, for instance, known since 1909, and from Pondokomi slightly farther away, produced by recent investigations), as also in later periods until the historical era. 'Mycenaean presence' is a complex phenomenon and it is difficult to conclude that the prevalence of Mycenaean elements in an area is necessarily due to Mycenaean presence (Karamitrou-Mentessidi 1999b).

## 2.2. Matt-painted pottery

Known as Macedonian matt-painted ware, north-western matt-painted ware, Doric ware, or Boubousti ware (after the excavation site, now Platania near Voio, where Heurtley discovered it in 1927), pottery with matt-painted decoration is widespread in the Late Bronze Age and Early Iron Age. Most of the find-spots are concentrated in Western Macedonia (45 in Kozani prefecture alone), especially along the river Aliakmon, spreading into Epiros and Albania as far as Korçë and sporadically into south-western Albania (the tumuli in the Drin valley), Pelagonia, Central Macedonia as far as the river Strymon, and south into Thessaly, Elasson, and Marmariani - a spread which is presumably due to the constant movement of pastoral populations. Scholars both earlier and modern believe it was manufactured by the northwestern Greek tribes, Herodotus's 'widely roaming nation' (1.56). He includes among these the Macedonians and the Dorians, who, he says, traveled from the south northwards and also settled in the Pindos. The Sperhios valley is believed to have been a major halting-place in the migrations of the Macedonians and the other north-western Greek tribes; matt-painted ware of the Middle Helladic period has been found at Lianokladi near Lamia.

The earliest date for the appearance of this type of pottery is put at the end of Late Helladic [LH IIIA] (late 15<sup>th</sup> c. BC). The latest finds from the archaeological site at Livadia not only confirm the early appearance of Late Bronze Age matt-painted ware (in the 15<sup>th</sup> c. BC) in Upper Macedonia contemporaneously with that of Central Macedonia, but they also probably provide reliable evidence for an even earlier dating. The most widely accepted theory today is that this pottery evolved from the Middle Helladic matt-painted ware of southern Greece (19<sup>th</sup>-16<sup>th</sup> cc. BC), probably with the influence of some Mycenaean motifs, rather than that it developed out of local imitations of Mycenaean wares. The Aiani's finds attest the existence of a pioneering workshop producing large quantities of wares of outstanding quality, some of which have already been located in neighboring areas. Dozens of large and small items are decorated in a distinctive manner, which lends support to the argument that this pottery is directly connected with similar ware of the Middle Helladic period. It has two-color decoration on a smoothed lustrous surface of brownish-red and brownish-black tin glaze applied before firing, and may be regarded as a

survival of a similar type of Middle Helladic pottery. Owing to the contemporary Mycenaean pottery, this specific category of matt-painted ware from Aiani is probably earlier than that which has been found in Macedonia to date, and supports the view that its origins should be sought in Upper Macedonia and that it spread from there. This theory is further strengthened by the density of the finds throughout Western Macedonia, as well as by the fact that they continue during the subsequent period, in contrast to Central Macedonia, where data so far show that there was not a great deal of matt-painted ware in the Early Iron Age.



**Figure 2 - Macroscopic images of sherds of Mycenaean (M2 and M3) and matt-painted (A2 and A4) pottery samples. A2 and A4 reveal the surface structure, while A4 and M3 are the cross sections of fresh fragments**

The Aiani's finds leave no further room for doubt that the north-western matt-painted ware was brought from the south by people returning to the north and north-west (to Aiani in the 15<sup>th</sup> c. BC) after having moved south at a much earlier date or having moved back and forth owing to their pastoral economy and their nomadic lifestyle. These people were none other than the Macedonians of the historical period, whom the literary tradition directly associates with the Dorians. So the Aiani's finds provide one more argument against the (anyway untenable) old theory of a massive Dorian invasion at the end of the second millennium (Karamitrou-Mentessidi 1999a).

### 3. Sampling and Analytical Methods

Several mycenaean and matt-painted potsherds were provided by the archaeological authorities. Based on their macroscopic characteristics, two representative sherds from both Mycenaean (M2 and M3) and matt-painted (A2 and A4) pottery were chosen for structural, morphological, mineralogical and chemical analysis. Freshly fractured samples of the aforementioned 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. Another part of each potsherd was finely ground in order to be analysed by X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) techniques. The X-Ray Diffraction (XRD) was employed for the semi-quantitative mineral identification. A Philips PW-1710 powder diffractometer with  $\text{CuK}\alpha$  radiation was used. Patterns were obtained by step scanning from  $3^\circ$  to  $63^\circ$   $2\theta$ , with a goniometer speed of  $0.03^\circ/\text{sec}$ , operating at 30 kV and 10 mA. The XPOWDER analytical software was used for the semi-quantitative determination of the mineral phases. A Philips Magic-pro (4Kw) X-Ray Fluorescence (XRF) instrument was used for the chemical analysis of major, minor and trace elements.

### 4. Results and Discussion

#### 4.1. Macroscopic description

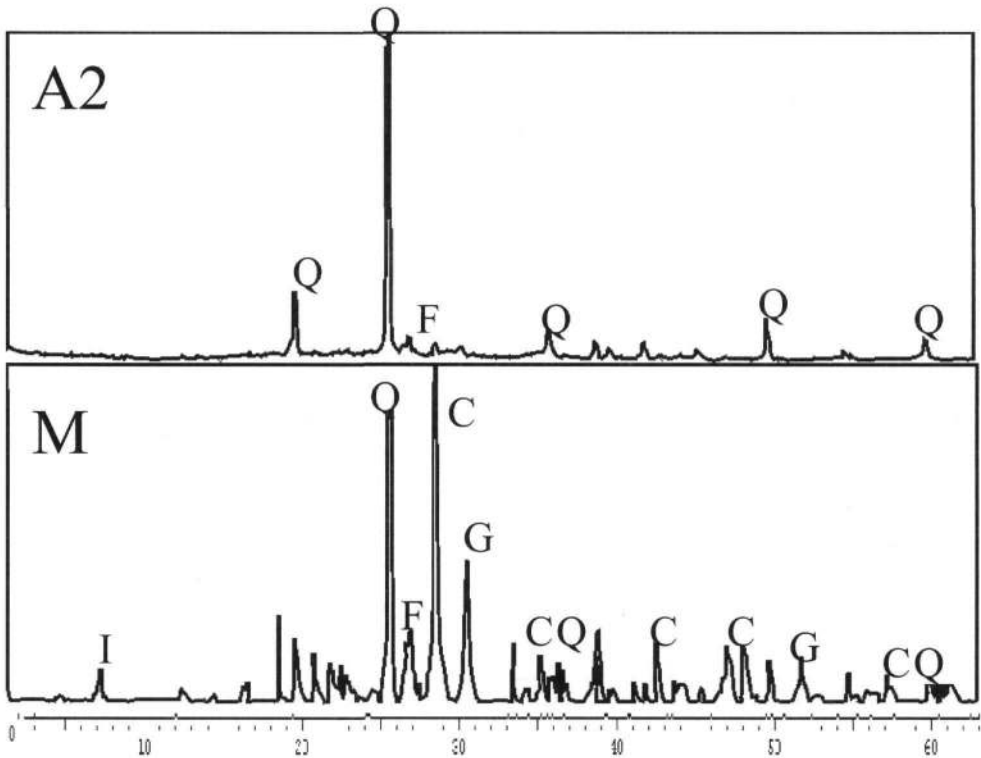
The macroscopic characteristics of fresh fragments of potsherds are shown in Figure 2. The Mycenaean potsherds have a characteristic creamy colour and are rather fine-grained, while the matt-painted pottery have a red margin and a dark-grey core with coarse mineral inclusions. The pale creamy colour of the mycenaean potsherd is typical of ceramics produced by firing calcareous clays at low temperatures (Papachristodoulou *et al.* 2006), or may be a consequence of the maintenance of reducing conditions during the final firing step and during cooling (Mirti and Davit 2001). The black reduced core and the reddish oxidised margin of the matt-painted pottery may imply an oxidising atmosphere, low heating rate and long residence time. This sandwich structure is characteristic of products fired in kilns (Maritan *et al.* 2006).

#### 4.2. Mineralogical analysis

The X-Ray diffractograms of one matt-painted potsherd (A2) and one mycenaean potsherd (M3) are shown in Figure 3. The identified minerals in A2 sample are Quartz [ $\text{SiO}_2$ ], Feldspars [ $(\text{K},\text{Na},\text{Ca})\text{AlSi}_3\text{O}_8$ ], Dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ] and Calcite [ $\text{CaCO}_3$ ], while in M3 sample, the main mineral phases are Calcite, Gehlenite [ $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ], Quartz, Feldspars and Illite [ $(\text{K},\text{H}_3\text{O})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2(\text{H}_2\text{O})]$ ]. The semi-quantitative assessment revealed the following percentages: for A2 sample Quartz (76 %), Feldspars (11 %), Dolomite+Calcite (10 %) and for M3 sample Calcite (41 %), Gehlenite (20 %), Quartz (19 %), Feldspars (13 %) and Illite (6 %).

The presence or absence of specific mineral assemblages is often used for the estimation of the firing temperature in pottery. In the case of A2 sample, the presence of quartz and feldspars may indicate a temperature of at least  $900^\circ\text{C}$  (Mirti and Davit 2001). These two minerals persist on firing up to  $1000^\circ\text{C}$  (Shimada *et al.* 2003), and thus they are obviously constituents of a silica-rich raw clay material. Quartz may be an indigenous mineral of natural clays or may be an intentionally added temper (Papachristodoulou *et al.* 2006). The small percentages of dolomite and calcite in A2 sample may be attributed to secondary carbonates. Secondary calcite may occur in ceramics due to post-burial depositional processes (recarbonation of lime) (Hein *et al.* 2002, Papachristodoulou *et al.* 2006). During post-burial period, Mg-rich waters should have replaced Ca and produced dolomite along with calcite. The presence of white colour magnesite deposits in the surrounding area of Aiani is a clear evidence for the magnesium abundance (Stamatakis 2004, Skarpelis 2006).

In the case of M3 sample, the simultaneous presence of gehlenite, calcite and illite helps us to determine the firing temperature. Thermal decomposition of calcite starts at approx. 600 °C and is completed around 800-850 °C, giving rise to the high temperature calcium silicates like gehlenite. Illite undergo a decomposition process between 700 and 1000 °C. The well-preserved illite mineral phase indicates low firing temperature, i.e. <850 °C. Several authors have argued on the exact determination of the temperature of illite decomposition and the gehlenite formation. According to



**Figure 3 – XRD patterns of matt-painted (A2) and mycenaean pottery (M3) form Aiani, ancient upper Macedonia, Greece. (Q=quartz, F=feldspar, C=calcite, G=gehlenite, I=illite)**

Cultrone *et al.* (2001), illite disappears at 900 °C and gehlenite appears at 800 °C. Maritan *et al.* (2006) state that the decarbonation of calcite and the crystallisation of gehlenite occur between 850 °C and 900 °C, while illite decomposes at 800 °C. According to Hein *et al.* (2002), gehlenite indicates a firing temperature of over 850 °C. Other scholars demonstrated that the presence of illite suggests that the temperature of 900 °C has not been exceeded, while calcium silicates, feldspars and quartz may indicate a temperature of at least 900 °C (Mirti and Davit 2001). Overall, a firing temperature between 800 and 850 °C should be recommended in the case of M3 potsherd. It should be noted however, that the redox conditions, heating rate and residence time all control the temperature of decomposition and recrystallisation reactions considerably (Maritan *et al.* 2006). The mineralogical composition depends on the regional geology and the potters' habits and experience. Adding non-plastic materials, known as temper the raw clay improve its workability and allows water to evaporate more smoothly, minimizing shrinkage and preventing cracking. Potters have used a variety of tempers including quartz, limestone, shells, volcanic ash and even crushed potsherds (Papachristodoulou *et al.* 2006). The quartz-rich raw clay or quartz-tempered matt-painted pottery of our study is less resistant to mechanical and thermal stresses during use, compared to calcite-rich or calcite-tempered mycenaean pottery. The first were probably hand-made pots, treated as coarse utensils with a short period of life, while the latter were wheel-made pots, and therefore plastic calcite minerals were added so as not to be destroyed during manufacture. Papachristodoulou *et al.* (2006) have noted that using calcareous clays or adding

calcite temper to the clay paste may produce pots for storage and/or transport of foodstuff. The calcium deficiency of matt-painted pots may indicate that either the raw clays were extracted from a non-calcareous deposit or were not refined with calcite temper (Papachristodoulou *et al.* 2006).

### 4.3. XRF analysis

The chemical composition of the ceramic fabric is strongly related to the source of clay and other materials used for its elaboration. Moreover, the variations in the trace element concentrations reflect geological diversity (Hein *et al.* 2004, Padilla *et al.* 2006). The chemical analysis of the two analysed potsherds (A2 and M3) is shown in Table 1. The high Loss On Ignition (LOI) values of mycenaean sample is attributed to the higher amounts of calcite and clay minerals in its matrix. Therefore, higher concentrations of CaO are well documented for M3 sample, while higher SiO<sub>2</sub> amounts are revealed for A2 sample, which is related to the high quartz contents of this sample.

**Table 1 - Chemical analysis of characteristic matt-painted (A2) and Mycenaean (M3) pottery from Aiani, ancient upper Macedonia, Greece. (LOI=Loss on ignition)**

	A2	M3		A2	M3
SiO <sub>2</sub> (%)	62.03	34.68	Zr (ppm)	243	98
Al <sub>2</sub> O <sub>3</sub> (%)	15.47	12.05	Sr (ppm)	57	163
Fe <sub>2</sub> O <sub>3</sub> (%)	6.11	3.76	Cu (ppm)	21	18
MnO (%)	0.06	0.05	Ni (ppm)	130	129
MgO (%)	2.05	2.06	Co (ppm)	21	14
CaO (%)	2.54	23.52	Zn (ppm)	90	71
Na <sub>2</sub> O (%)	0.64	0.58	Cr (ppm)	242	122
K <sub>2</sub> O (%)	2.47	2.14	V (ppm)	138	52
TiO <sub>2</sub> (%)	0.95	0.4	Sn (ppm)	10	4
P <sub>2</sub> O <sub>5</sub> (%)	0.08	0.1	Cd (ppm)	4	5
LOI (%)	7.6	20.68	Ce (ppm)	75	58
S (ppm)	-	123	F (ppm)	168	726
Y (ppm)	28	19	As (ppm)	5	4
Rb (ppm)	116	101	La (ppm)	53	29
Pb (ppm)	25	16	Ba (ppm)	407	381

Trace elements like Mn, Cr, Zr, Ti could be used as geochemical 'fingerprints', as they are associated to specific petrological types (Padilla *et al.* 2006). The elemental profile of the trace elements is similar for both samples. Relatively high concentrations of Cr, Ni, Ti (McLennan 1992) are attributed to the geochemical affinity of these elements with the ultramafic rocks in the surrounding of Aiani, Vourinos complex area (Dabitzias and Rassios 2000, Rassios 2004, Skarpelis 2006). The increased chromium content is probably related to the chromite ores, found in the vicinity of the Aiani town (Savvidis and Horkova 1997). The zirconium content is also rather high, a fact that might be related to the igneous phases, like granites and pegmatites situated in the area (Rassios 2004). The concentrations of the aforementioned trace elements allow us to distinguish between locally produced and imported pottery. The quite uniform chemical profile implies that these pots were produced locally. It should be noted, however, that the pottery



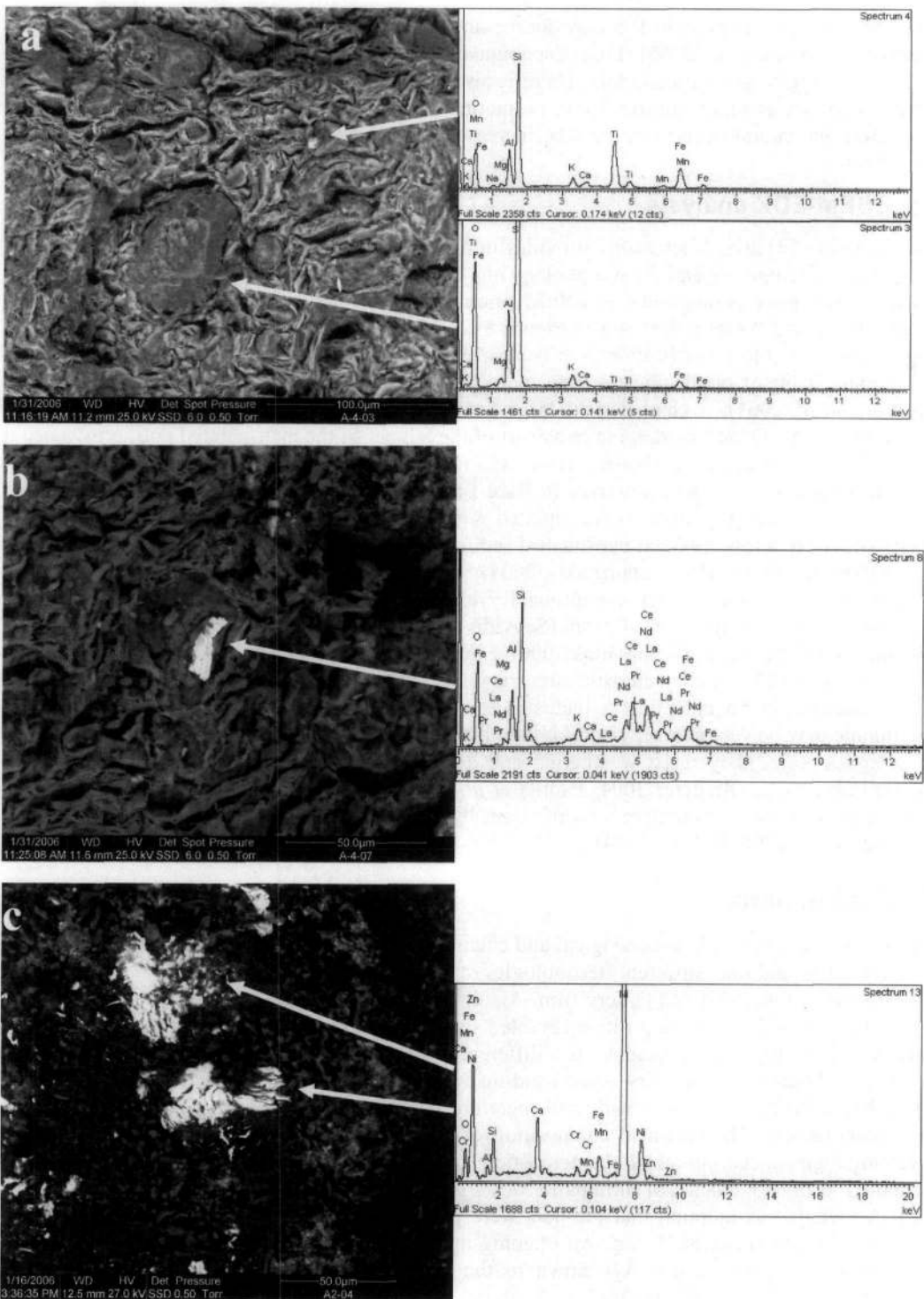
composition depends both in the clay source and in the recipe used to prepare the clay paste (Papachristodoulou *et al.* 2006). Thus, the abundance ratios of some elements may be altered as a result of mixing of several materials. There is also a rather high concentration of alkalis (Na, K). Alkalis may act as fluxes during firing, promoting sintering and vitrification. Potassium content apart from its natural occurrence may be increased through the addition of wood ash (Mirti and Davit 2001).

#### 4.4. ESEM-EDX analysis

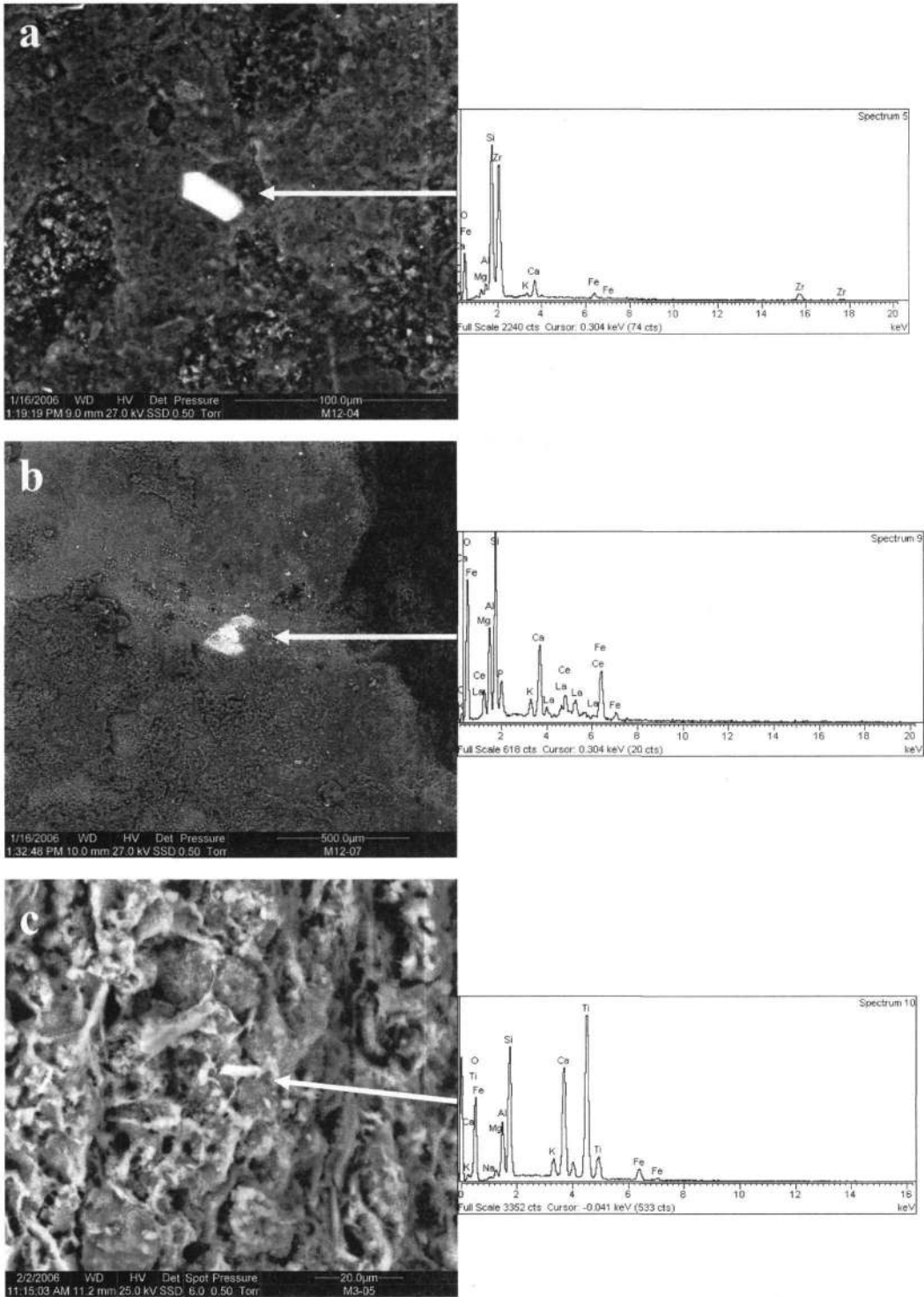
The Scanning Electron Microscopy provides information on the type of clay used, its degree of refinement or tempering and the morphology and chemistry of the final product (Day *et al.* 2006). Characteristic microphotographs of ESEM microscopy are shown in Figure 4 for matt-painted potsherd (A2 and A4 samples) and in Figure 5 for Mycenaean potsherds (M2 and M3 samples). High porosity and low vitrification rank is clearly observed, which along with the preservation of the laminar habit of phyllosilicates may indicate a firing temperature between 700 and 800 °C (Cultrone *et al.* 2001). A characteristic large quartz grain along with a titanium-rich inclusion is shown in Fig. 4a. Quartz predominates as part of the temper of the matt-painted potsherds, since it is resistant against chemical transformation and mechanical attrition (Riederer 2004). The bright spots in Figure 4b are inclusions rich in Rare Earth Elements (REE) [monazite(?)], originating probably from the pegmatite veins situated southwards of Aiani or the hydrolised (mainly magnesites or to a lesser extent phosphates) sedimentary rocks which are abundant throughout the area (Morteani *et al.* 1982, Stamatakis 2004). In Fig. 4c, nickel and chromium-rich mineral assemblages are shown which are probably related to the ultramafic rocks of the Vourinos mountain in the west direction of Aiani (Savvidis and Horkova 1997, Dabitzias and Rassios 2000, Eliopoulos and Economou-Eliopoulos 2000). Similar characteristics are observed for Mycenaean pottery under ESEM. A characteristic zircon crystal is shown in Figure 5a, inclusions rich in REE are revealed in Fig. 5b and a titanite inclusion is observed in Figure 5c. Heavy minerals like zircon and titanite may be very characteristic for their place of origin and hence determine the provenance of ceramics, since they resist weathering and are distinctive for certain types of magmatic or metamorphic rocks (Riederer 2004, Padilla *et al.* 2006). Such characteristic minerals have been demonstrated in the surrounding area of Aiani by several authors (Savvidis and Horkova 1997, Christidis *et al.* 1998, Rassios 2004)

### 5. Conclusions

Variations in the textural, mineralogical and chemical characteristics of ceramics reflect source of the raw clay and the different technologies applied for the production of these ceramics. Mycenaean and matt-painted pottery from Aiani, ancient Upper Macedonia were analysed in this study. The mineralogical composition revealed significant differences between these two types of pottery which might be related to the different manufacture process applied and/or potential utilization. Matt-painted pottery were hand-made, thus the abundance of quartz and feldspars, while Mycenaean were wheel-made and therefore it needs more plastic material like calcite for their manufacture. The chemical composition of the trace elements for both types was similar, revealing high concentrations of characteristic elements like Cr, Ni, Ti, Zr and REE, a fact that is attributed to the abundance of ultramafic rocks, gneisses and pegmatite veins in the surrounding area. A tentative assumption that the pots were prepared at different local workshop exploiting different claybed could be drawn. An ongoing analytical research of pottery from Aiani region dated from the Late Bronze Age down to the Hellenistic era is expected to provide useful information on pottery tradition, trade and cultural exchange through time.



**Figure 4 - ESEM images and EDX spectra of matt-painted pottery: a) a large quartz crystal and a tiny Ti-rich grain [A4 sample], b) a REE-rich (bright spots) inclusion [A4 sample], c) Ni and Cr rich mineral assemblages [A2 sample]**



**Figure 5 - ESEM images and EDX spectra of Mycenaean pottery: a) a zircon ( $ZrSiO_4$ ) crystal [M2 sample], b) a REE-rich (bright spots) inclusion [M2 sample], c) a titanite ( $CaTiSiO_5$ ) inclusion [M3 sample]**

## 6. Acknowledgments

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## 7. References

- Christidis, G.E., Economou-Eliopoulos, M., Marcopoulos, T., and Laskou, M., 1998. An unusual assemblage of high-Ti oxides and ferroan clinocllore along zones of brittle deformation in the Vourinos (Rodiani) ophiolite complex, Greece, *Canadian Mineralogist*, 36(5), 1327-1338.
- Cultrone, G., Rodriguez-Navarro, C., Sebastian, E., Cazalla, O., and De La Torre, M.J., 2001. Carbonate and silicate phase reactions during ceramic firing, *European Journal of Mineralogy*, 13, 621-634.
- Dabitizas, S., and Rassios, A., 2000. Hartburgites/Dunites for high quality olivine products in the Vourinos and Pindos ophiolite complexes. *Proc. of the 1st Conference on Mineral Wealth and Environment of Western Macedonia, Kozani, Greece, 12-13 February 2000*, 330-340. (in Greek with English abstract)
- Day, P.M., Joyner, L., Kilikoglou, V., and Gesell, G.C., 2006. Goddesses, Snake Tubes, and Plaques: Analysis of Ceramic Ritual Objects from the LM IIIC Shrine at Kavousi, *Hesperia*, 75(2), 137-75.
- Eliopoulos, D.G., and Economou-Eliopoulos, M., 2000. Geochemical and mineralogical characteristics of Fe-Ni- and bauxitic-laterite deposits of Greece, *Ore Geology Reviews*, 16, 41-58.
- Hein, A., Day, P.M., Quinn, P.S., and Kilikoglou, V., 2004. The geochemical diversity of Neogene clay deposits in Crete and its implications for provenance studies of Minoan pottery, *Archaeometry*, 46(3), 7-384.
- Hein, A., Tsolakidou, A., and Mommsen, H., 2002. Mycenaean pottery from the Argolid and Achaia—a mineralogical approach where chemistry leaves unanswered questions, *Archaeometry*, 44(2), 177-186.
- Karamitrou-Mentessidi, G., 1999a. *Voion, Notia Orestis, Archeologiki erevna kai historiki topographia*, Thessaloniki, 419 pp.
- Karamitrou-Mentessidi, G., 1999b. Mikinaika Aianis-Elimioidas kai Ano Makedonias, *2nd International Symposium Periphery of Mycenaean World (B' Διεθνές Συμπόσιο Η Περιφέρεια του Μυκηναϊκού Κόσμου)*, Lamia, Greece, 26-29 September, 167-190.
- Maniatis, Y., and Tsirtsoni, Z., 2002. Characterization of a black residue in a decorated Neolithic pot from Dikili Tash, Greece: an unexpected result, *Archaeometry*, 44(2), 229-239.
- Maritan, L., Nodari, L., Mazzoli, C., Milano, A., and Russo, U., 2006. Influence of firing conditions on ceramic products: Experimental study on clay rich in organic matter, *Applied Clay Science*, 31, 1-15.
- McLennan, S.M., 1992. Continental Crust. In W.A. Nierenberg (ed.), *Encyclopedia of Earth Sciences*, vol. 1, 581-592pp, Dordrecht, Kluwer.
- Mirti, P., and Davit, P., 2001. Technological Characterization of Campanian Pottery of Type A, B and C and of Regional Products from Ancient Calabria (Southern Italy), *Archaeometry*, 43(1), 19-33.

- Mommsen, H., Beier, Th., and Hein, A., 2002. A Complete Chemical Grouping of the Berkeley Neutron Activation Analysis Data on Mycenaean Pottery, *Journal of Archaeological Science*, 29, 613–637.
- Morteani, G., Moller, P., and Schley, F., 1982. The rare-earth element contents and the origin of the sparry magnesite mineralizations of Tux-Lanersbach, Entachen Alm, Spiessnagel, and Hochfilzen, Austria, and the lacustrine magnesite deposits of Aiani-Kozani, Greece, and Bela Stena, Yugoslavia, *Economic Geology*, 77 (3), 617–631.
- Padilla, R., Van Espen, P., and Godo Torres, P.P., 2006. The suitability of XRF analysis for compositional classification of archaeological ceramic fabric: A comparison with a previous NAA study, *Analytica Chimica Acta*, 558, 283–289.
- Papachristodoulou, C., Oikonomou, A., Ioannides, K., and Gravani, K., 2006. A study of ancient pottery by means of X-ray fluorescence spectroscopy, multivariate statistics and mineralogical analysis, *Analytica Chimica Acta*, 573–574, 347–353
- Polvorinos del Río, A., Sanjuán, L.G., Pérez, V.H., and Hernández Arnedo, M.J., 2005. Bronze Age Ceramics in Southwest Spain: An Exploratory Archaeometric Study of Technology and Function, *Geoarchaeology: An International Journal*, 20(3), 263–284.
- Rassios, A.E., 2004. *A Geologist's guide to West Macedonia, Greece. Grevena, Greece*, The Grevena Development agency, 119 pp.
- Riederer, J., 2004. Thin section microscopy applied to the study of archaeological ceramics, *Hyperfine Interactions*, 154, 143–158.
- Sanchez Ramos, S., Bosch Reig, F., Gimeno Adelantado, J.V., Yusa Marco, D.J., and Domenech Carboa, A., 2002. Study and dating of medieval ceramic tiles by analysis of enamels with atomic absorption spectroscopy, X-ray fluorescence and electron probe microanalysis, *Spectrochimica Acta Part B*, 57, 689–700.
- Savvidis, S., and Hovorka, D., 1997. Vourinos complex (Greece)- An example of Eastern Mediterranean ophiolite, *Geologica Carpathica*, 48 (1), 11–18.
- Shimada, I., Häusler, W., Hutzelmann, T., and Wagner, U., 2003. Early Pottery Making in Northern Coastal Peru. Part I: Mössbauer Study of Clays, *Hyperfine Interactions*, 150, 73–89.
- Skarpelis, N., 2006. Lateritization processes of ultramafic rocks in Cretaceous times: The fossil weathering crusts of mainland Greece, *Journal of Geochemical Exploration*, 88 (1-3), 325–328.
- Sofianopoulou, A., Labropoulos, B., and Kantiranis, N., 2004. Study of technology of glazed pottery from an excavation in Thessaloniki, Greece, *Bulletin of the Geological Society of Greece* vol. XXXVI, 2004, *Proceedings of the 10th International Congress, Thessaloniki, April 2004*, 1120–1128.
- Stamatakis, M.G., 2004. Phosphate deposits of Neogene age in Greece. Mineralogy, geochemistry and genetic implications, *Chemie Der Erde-Geochemistry*, 64 (4), 329–357.