Analytical study of ancient pottery from the archaeological site of Aiani, northern Greece

A. Iordanidis[a,*], *J. Garcia-Guinea*[b], *G. Karamitrou-Mentessidi*[c]

[a]*Department of Geotechnology and Environmental Engineering, Technological Educational Institute (TEI) of Western Macedonia, Kila, 50100 Kozani, Greece*
[b]*Museo Nacional Ciencias Naturales, CSIC, C/José Gutierrez Abascal 2, Madrid 28006, Spain*
[c]*30th Ephorate of Prehistoric and Classical Antiquities, Archaeological Museum of Aiani, 500 04 Aiani, Kozani, Greece*

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ABSTRACT

The present study is a multi-analytical approach on the characterization of several potsherd samples, dated from prehistoric to hellenistic times, from Aiani, ancient Upper Macedonia, northern Greece. In particular, X-ray Diffraction (XRD), X-ray Fluorescence (XRF) and Environmental Scanning Electron Microscopy, coupled with Energy Dispersive X-ray system (ESEM-EDX) were used for the determination of the morphological, chemical and mineralogical characteristics of the potsherds. The preliminary results indicated a rather local provenance of the analyzed ancient pottery samples and a finer texture and thus better ceramic manufacture as getting to hellenistic era. The use of a silicious or calcerous raw material is probably related to the specific utilization of each ceramic vessel in ancient times. The presence of gehlenite or pyroxene minerals in the ceramic matrix indicated higher firing temperatures, while lower temperatures were deduced when finding phylosilicate minerals. The preliminary results of this study do not necessarily imply that all the pottery of this area, belonging to the same chronological type, have similar physicochemical characteristics.

1. Introduction

The employment of interdisciplinary chemical, geological and physical analytical techniques in the study archaeological artefacts (e.g. ceramics, mortars, slags, marbles etc.) is 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, 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 [1]. The chemical analysis of ancient pottery encompasses several analytical techniques, such as Inductively Coupled Plasma spectroscopy (ICP), X-ray Fluorescence (XRF), Neutron Activation Analysis (NAA) etc. [2–5]. 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.

Aiani is located approximately 20 km south of the city of Kozani, western Macedonia (Greece) (Fig. 1). 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

* *Corresponding author*. Tel.: +30 24610 68298; fax: +30 24610 39682.
E-mail address: aiordanidis@yahoo.co.uk (A. Iordanidis).

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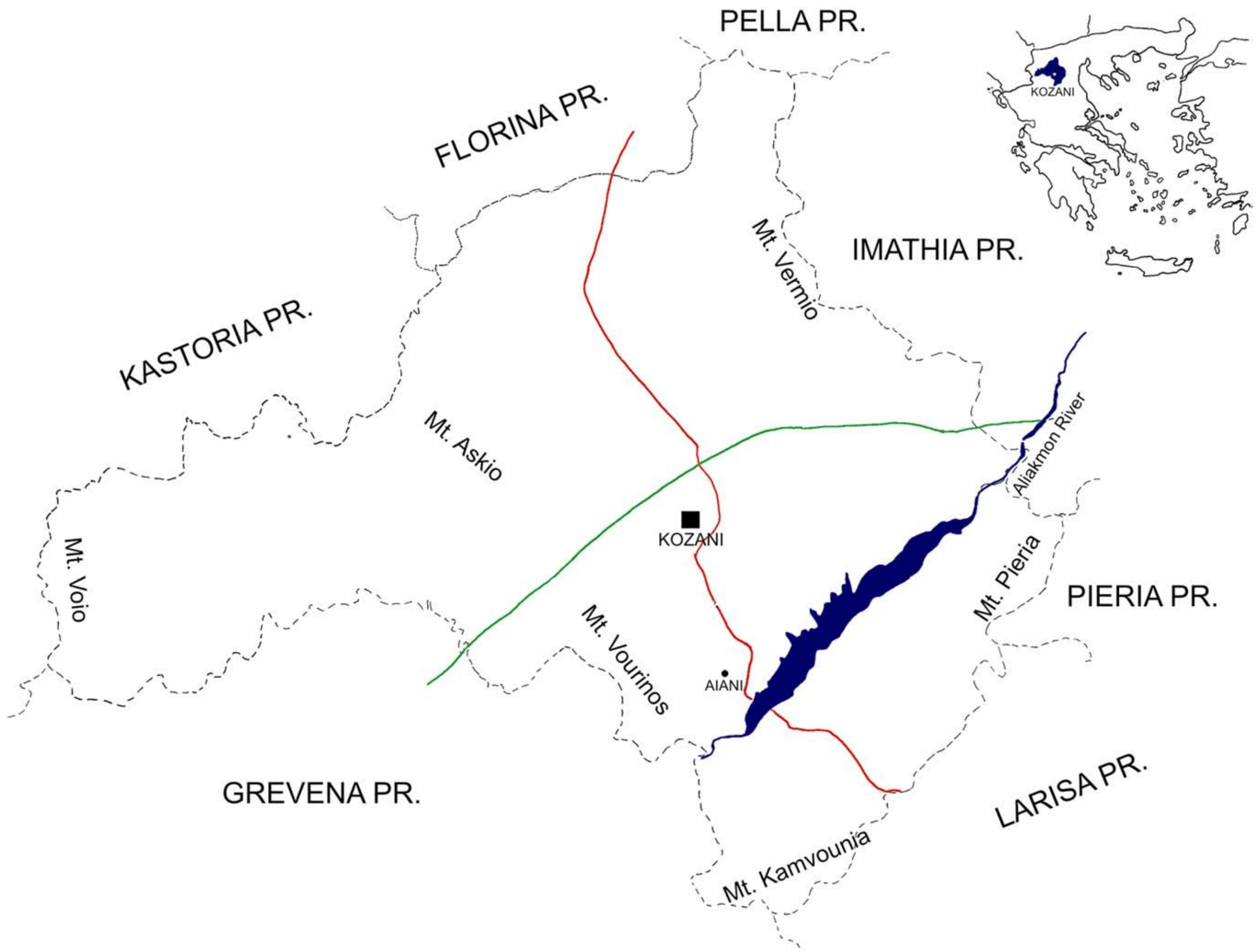


Fig. 1 – Map showing the location of Aiani, ancient city of Upper Macedonia, now situated at Kozani's prefecture, northern Greece.

(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 [6,7].

In the present study, ancient pottery from Aiani was obtained from the local archaeological authorities and subjected to several analytical methodologies. XRD was used for the mineralogical characterisation, XRF for the determination of the chemical elements concentrations and ESEM-EDX for morphological, structural and chemical assessment of ancient potsherds. The evolution of pottery manufacture in Aiani's area through time, based on the technological characteristics, was estimated.

2. Sampling and Analytical Methods

Approximately eighty potsherds were provided from the archaeological authorities covering a period from prehistoric to hellenistic times. The archaeological survey in Aiani's area affirmed five distinctive ceramic classes from the 15th to 3rd century BC: Mycenaean, matt-painted, monochromatic, archaic–classical and hellenistic pottery. Based on their macroscopic features (colour, fabric, glaze), sixteen sherds were selected for structural, morphological, mineralogical and chemical analysis. The characteristics of all the aforementioned potsherds are shown in Table 1. 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. 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 CuKα radiation was used. Patterns were obtained by step scanning from 3° to 63° 2θ, with a goniometer speed of 0.03°/s, 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 (4 kW) X-ray Fluorescence (XRF) instrument was used for the chemical analysis of major, minor and trace elements. While all the sixteen samples were analysed by

Table 1 – Description of potsherd samples from Aiani, ancient Upper Macedonia, Greece

Sample ID	Chronological type	Location	Analytical method employed	Colour (surface)	Colour (cross-section)	Texture
A2	Mycenaean (14th–12th c. BC)	Leivadia	ESEM-EDX, XRD,XRF	Red–black	Red	Medium grained
A4	Mycenaean (14th–12th c. BC)	Leivadia	ESEM-EDX	Red	Outer red–inner grey	Medium-coarse grained
M2	Matt-painted (15th–11th c. BC)	Leivadia	ESEM-EDX	Yellow to brown	Creamy	Fine-medium grained
M3	Matt-painted (15th–11th c. BC)	Leivadia	ESEM-EDX, XRD,XRF	Black	Creamy	Fine-medium grained
MAD3	Monochromatic (14th–11th c. BC)	Leivadia	ESEM-EDX	Red	Outer red–inner grey	Medium-coarse grained
MAD10	Monochromatic (14th–11th c. BC)	Ano Komi	ESEM-EDX, XRD,XRF	Red	Red	Medium-coarse grained
MAD17	Monochromatic (14th–11th c. BC)	Ano Komi	ESEM-EDX	Red	Red	Fine-medium grained
AKL8	Archaic–classical (6th–5th c. BC)	Leivadia	ESEM-EDX, XRD,XRF	Red	Red	Fine-coarse grained
AKL12	Archaic–classical (6th–5th c. BC)	Leivadia	ESEM-EDX	Black	Creamy	Fine-medium grained
AKL15	Archaic–classical (6th–5th c. BC)	Leivadia	ESEM-EDX	Red	Red	Fine-grained
AKL22	Archaic–classical (6th–5th c. BC)	Leivadia	ESEM-EDX	Yellow–brown	Brown	Fine-medium grained
AKL27	Archaic–classical (6th–5th c. BC)	Leivadia	ESEM-EDX, XRD,XRF	Yellow to brown	Red	Fine-grained
AKL34	Archaic–classical (6th–5th c. BC)	Leivadia	ESEM-EDX	Red	Red	Fine-grained
E4	Hellenistic (3rd–2nd c. BC)	Megali Rachi	ESEM-EDX, XRD,XRF	Red–brown	Brown	Fine-medium grained
E6	Hellenistic (3rd–2nd c. BC)	Megali Rachi	ESEM-EDX	Red	Red	Fine-grained
E12	Hellenistic (3rd–2nd c. BC)	Megali Rachi	ESEM-EDX	Grey	Creamy	Fine-grained

ESEM/EDX, only six samples were chosen for the application of XRF and XRD analytical methods. Table 1 summarises the details of each analysed sample.

3. Results and Discussion

3.1. *Macroscopic Description*

The macroscopic characteristics of fresh fragments of the analysed potsherds are shown in Fig. 2. There is no distinctive fabric, colour or glaze for each chronological type of pottery. The surface colour varies between creamy, red, brown and black with different hues. Similar variation in colours is shown in cross-section. For example, the pale creamy colour of the Mycenaean potsherd is typical of ceramics produced by firing calcareous clays at low temperatures [8], or may be a consequence of the maintenance of reducing conditions during the final firing step and during cooling [1]. Coarse, medium and fine-grained potsherds were observed in all ceramic types. The observation of the cross-section of some potsherds revealed a red margin and a dark-grey core. 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 [10]. All the macroscopic features of the analysed ceramic samples are included in Table 1.

3.2. *Mineralogical (XRD) Analysis*

The X-ray diffractograms of six selected potsherds (A2, M3, AKL27, AKL8, MAD10 and E4) are shown in Fig. 3. The semi-quantitative mineralogical results of the same samples are also shown in Table 2. The main identified minerals are quartz [SiO_2], feldspars [$(K,Na,Ca)AlSi_3O_8$], calcite [$CaCO_3$], dolomite [$CaMg(CO_3)_2$], gehlenite [$Ca_2Al_2SiO_7$], illite [$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$] and pyroxenic augite [$(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$].

The presence or absence of specific mineral assemblages is often used for the estimation of the firing temperature of pottery. Quartz and feldspars are abundant in all potsherd samples. The higher calcite content is observed in samples M3 and AKL8, the higher quartz contents in samples A2 and AKL27 and the higher feldspar concentration in MAD10 potsherd. The presence of quartz and feldspars may indicate a temperature of at least 900 °C [9]. These two minerals persist on firing up to 1000 °C [11], 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 [8]. The small percentages of dolomite and calcite in A2 sample may be attributed to

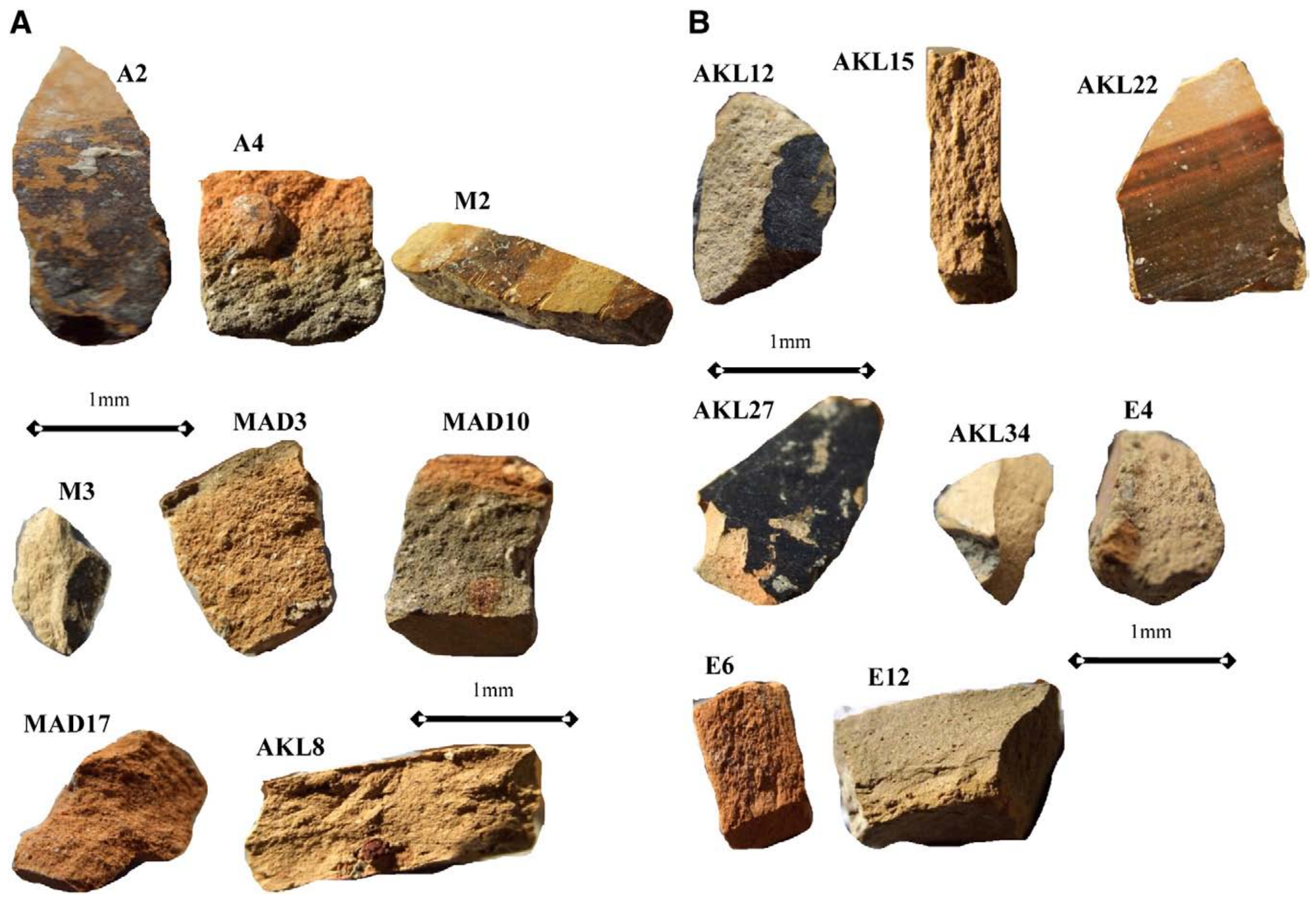


Fig. 2 – Macroscopic images of potsherds dated from prehistoric to hellenistic times from Aiani, ancient Upper Macedonia, Greece. (A = matt-painted, M = mycenaean, AKL = archaic–classic, MAD = monochromatic, E = hellenistic).

secondary carbonates. Secondary calcite may occur in ceramics due to post-burial depositional processes (recarbonation of lime) [8,12]. 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 [13,14].

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 or aluminocalcosilicates, such as gehlenite and pyroxenes. The presence of augite pyroxene and absence of calcite in the potsherds E4 and AKL27 might indicate that the primary calcite was completely decomposed upon firing at a temperature of at least 900 °C [8,15].

Illite undergo a decomposition process between 700 and 1000 °C. The well-preserved illite mineral phase in samples AKL8, MAD10 and M3 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 Cultrone et al. [15], illite disappears at 900 °C and gehlenite appears at 800 °C. Maritan et al. [10] 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. [12], 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 [9].

It should be noted however, that the redox conditions, heating rate and residence time all control the temperature of decomposition and recrystallisation reactions considerably [10]. 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 [8]. The quartz-rich raw clay or quartz-tempered potsherds (A2, AKL27, MAD10 and E4) of our study are less resistant to mechanical and thermal stresses during use, compared to calcite-rich or calcite-tempered M3 and AKL8 pottery. The matt-painted (A2) and monochromatic (MAD10) samples were probably hand-made pots, treated as coarse utensils with a short period of life, while others (M3, AKL8) were wheel-made pots, and therefore plastic calcite minerals were added so as not to be destroyed during manufacture. Papachristodoulou et al. [8] have noted that using calcareous clays or adding calcite temper to the clay paste may produce pots for storage and/or

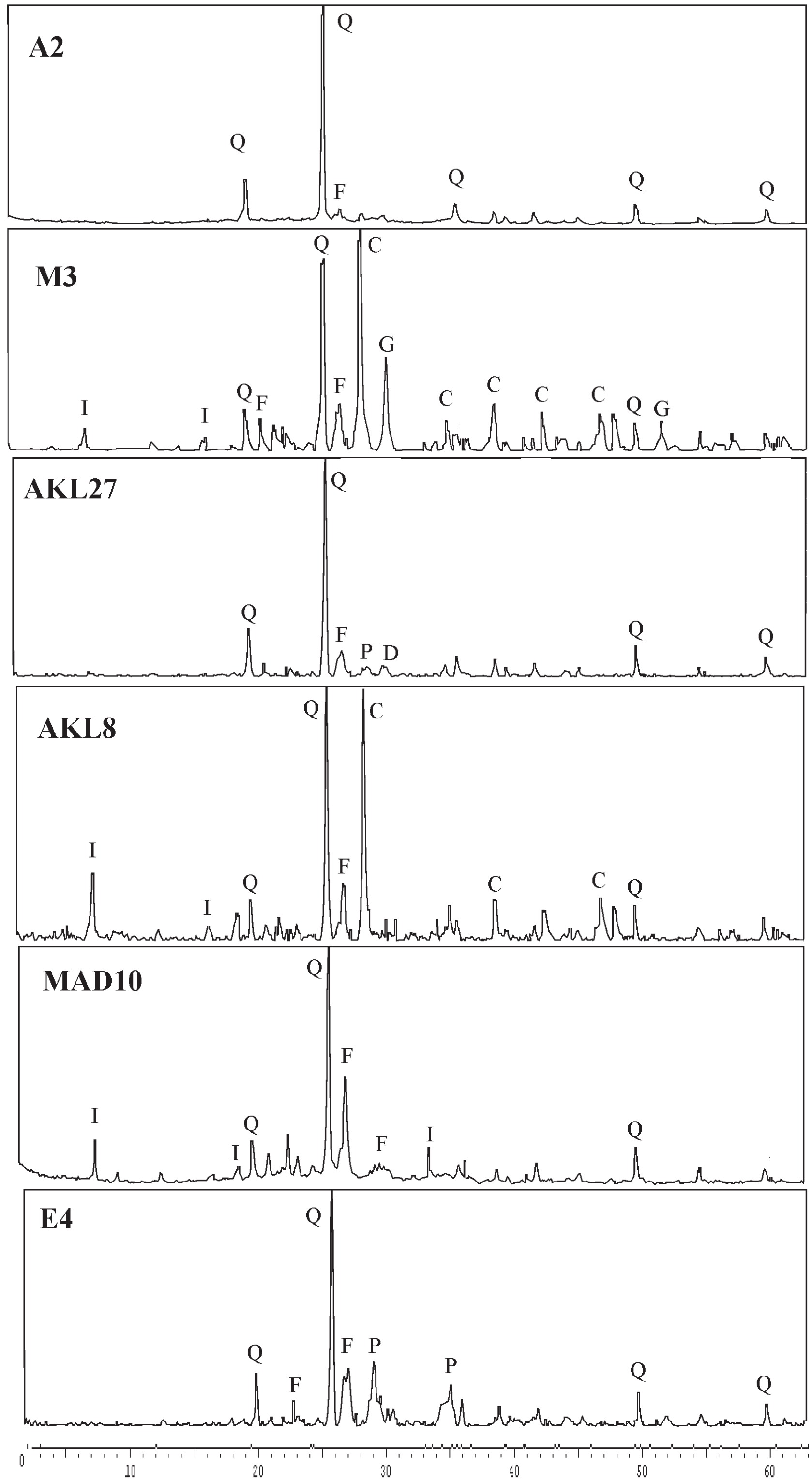


Fig. 3 – XRD patterns of matt-painted (A2), mycenaean (M3), monochromatic (MAD10), archaic–classic (AKL27 and AKL8) and hellenistic (E4) pottery from Aiani, ancient upper Macedonia, Greece. (Q = quartz, F = feldspar, C = calcite, G = gehlenite, I = illite, D = dolomite, P = pyroxene).

transport of foodstuff. The calcium deficiency in the above-mentioned pots may indicate that either the raw clays were extracted from a non-calcareous deposit or were not refined with calcite temper [8].

Table 2 – Mineral assemblages of characteristic potsherds from Aiani archaeological site, ancient Upper Macedonia, Greece

	A2	M3	AKL27	AKL8	MAD10	E4
Quartz (%) SiO_2	76	20	64	28	47	42
Calcite (%) $CaCO_3$	<5	42	–	44	–	–
Feldspars (%) $(K,Na,Ca)AlSi_3O_8$	11	12	18	12	41	24
Dolomite (%) $CaMg(CO_3)_2$	6	–	–	–	–	–
Gehlenite (%) $Ca_2Al_2SiO_7$	–	20	–	–	–	
Illite (%) $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)$	–	6	–	16	8	–
Pyroxenes (%) Augite$(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$	–	–	18	–	<3	34
Amorphus (%)	<2	–	–	–	<2	–

A2 = matt-painted, M2 = mycenaean, AKL8, AKL27 = archaic–classic, MAD10 = monochromatic, E4 = hellenistic.

Table 3 – Chemical analysis (XRF) of characteristic potsherds from Aiani archaeological site, ancient Upper Macedonia, Greece

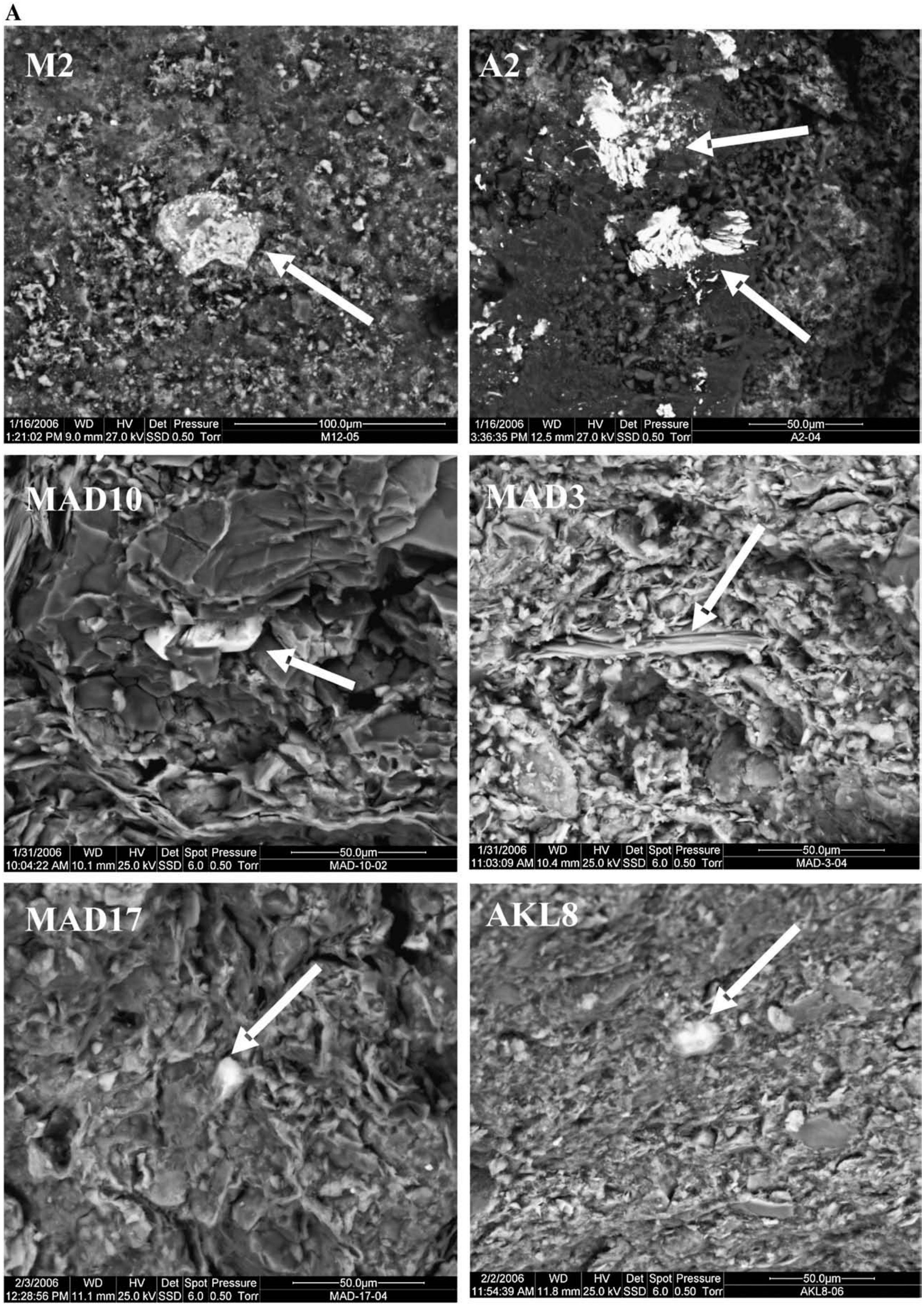
	A2	M3	AKL27	AKL8	MAD10	E4
SiO_2 (%)	62.03	34.68	50.53	41.12	55.23	42.73
Al_2O_3 (%)	15.47	12.05	16.5	9.26	18.26	9.62
Fe_2O_3 (%)	6.11	3.76	8.25	6.82	6.10	7.61
MnO (%)	0.06	0.05	0.12	0.10	0.40	0.14
MgO (%)	2.05	2.06	5.00	6.08	2.87	6.51
CaO (%)	2.54	23.52	5.07	15.37	1.85	14.05
Na_2O (%)	0.64	0.58	0.48	0.41	1.71	0.52
K_2O (%)	2.47	2.14	3.59	1.69	3.68	1.85
TiO_2 (%)	0.95	0.40	0.90	0.48	0.80	0.49
P_2O_5 (%)	0.08	0.10	0.10	0.13	0.13	0.21
LOI (%)	7.60	20.68	9.46	18.53	9.00	16.28
As (ppm)	5	4	35	4	4	5
Ba (ppm)	407	381	277	330	1211	481
Cd (ppm)	4	5	10	8	19	12
Ce (ppm)	75	58	76	44	102	60
Cl (ppm)	5	21	22	19	16	204
Co (ppm)	21	14	31	31	22	44
Cr (ppm)	242	122	364	533	124	1489
Cu (ppm)	21	18	50	22	20	25
F (ppm)	168	726	312	502	616	63
La (ppm)	53	29	36	20	49	35
Ni (ppm)	130	129	250	475	81	658
Pb (ppm)	25	16	27	16	27	12
Rb (ppm)	116	101	111	53	128	69
S (ppm)	–	163	–	82	–	37
Sb (ppm)	4	–	10	2	6	–
Sn (ppm)	10	4	20	8	29	1
Sr (ppm)	57	163	182	180	193	185
V (ppm)	138	52	163	83	121	94
Y (ppm)	28	19	21	17	32	23
Zn (ppm)	90	71	122	74	97	88
Zr (ppm)	243	98	105	93	190	115

A2 = matt-painted, M2 = Mycenaean, AKL8, AKL27 = archaic–classic, MAD10 = monochromatic, E4 = hellenistic, LOI = Loss on ignition.

3.3. *Chemical (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 [16,17]. The chemical analysis of six analysed potsherds (A2, M3, AKL27, AKL8, MAD10 and E4) is shown in Table 3. The high Loss On Ignition (LOI) values of M3, AKL8 and E4 samples is attributed to the higher amounts of calcite and clay minerals in its matrix. Therefore, higher concentrations of CaO are well documented for the latter samples, while higher SiO_2 amounts are revealed for A2, MAD10 and AKL27 samples, which is related to the high quartz and/or feldspar contents of these samples. Sample AKL27, though belonging to the same chronological type of pottery (i.e. archaic–classical) has reduced amounts of calcium. Iron (Fe_2O_3) and aluminum (Al_2O_3) concentrations range from 3.76% to 8.25% and from 9.26% to 18.26% respectively. Alkalis have moderate concentrations (0.41%–1.71% for Na_2O and 1.69%–3.68% for K_2O). The highest sodium and potassium contents are observed in MAD10 potsherd, a fact which is related to its high feldspar content. 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 [9]. MgO ranges between 2.05% and 6.51% (the highest value in E4 might be related to its Mg-rich pyroxene assemblages), while MnO contents vary between 0.05% and 0.40%. titanium (TiO_2) and phosphorous (P_2O_5) concentrations range from 0.40% to 0.95% and from 0.08% to 0.21% respectively, without significant variations amongst the analysed potsherds.

Trace elements like Mn, Cr, Zr, Ti could be used as geochemical ‘fingerprints’, as they are associated to specific petrological types [18]. The elemental profile of the trace elements is similar for almost all samples. Relatively high concentrations of Cr, Ni, Ti are attributed to the geochemical affinity of these elements with the ultramafic rocks in the surrounding of Aiani, Vourinos complex area [14,19,20]. The Ni content ranges between 81 and 658 ppm (E4 has the highest Ni content). Chromium concentrations range between 122 and 1489 ppm (again E4 has the highest Ni content). MAD10 sample has the lowest Ni and Cr contents comparing to all the other potsherds. The increased chromium content is probably related to the chromite ores, found in the vicinity of the Aiani town [21]. The zirconium content is also rather high (especially in A2 sample [243 ppm]), probably linked to the igneous phases, coming from the granite and pegmatite regional rocks [20]. The concentrations of the aforementioned trace elements allowed us to distinguish in one of our previous studies [22] between locally produced and imported pottery. There is also evident a substantial amount of Rare Earth Elements (REE), originating probably from the pegmatite veins situated southwards of Aiani or the hydrolised (mainly magnesites or to a lesser extend phosphates) sedimentary rocks which are abundant throughout the area [13,23]. The quite uniform chemical profile implies that Mycenaean and matt-painted pottery were probably 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 [8]. Thus, the abundance ratios of some


A
M2
1/16/2006 WD HV Det Pressure 100.0µm
1:21:02 PM 9.0 mm 27.0 kV SSD 0.50 Torr M12-05
A2
1/16/2006 WD HV Det Pressure 50.0µm
3:36:35 PM 12.5 mm 27.0 kV SSD 0.50 Torr A2-04
MAD10
1/31/2006 WD HV Det Spot Pressure 50.0µm
10:04:22 AM 10.1 mm 25.0 kV SSD 6.0 0.50 Torr MAD-10-02
MAD3
1/31/2006 WD HV Det Spot Pressure 50.0µm
11:03:09 AM 10.4 mm 25.0 kV SSD 6.0 0.50 Torr MAD-3-04
MAD17
2/3/2006 WD HV Det Spot Pressure 50.0µm
12:28:56 PM 11.1 mm 25.0 kV SSD 6.0 0.50 Torr MAD-17-04
AKL8
2/2/2006 WD HV Det Spot Pressure 50.0µm
11:54:39 AM 11.8 mm 25.0 kV SSD 6.0 0.50 Torr AKL8-06

elements may be altered as a result of mixing of several materials.

3.4. *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 [24]. Characteristic microphotographs of ESEM microscopy for all the sixteen potsherd samples are shown in Figs. 4 and 5. ESEM observation confirms the results found through the mineralogical (XRD) and chemical (XRF) analyses. The observation of the potsherds under the same magnification (for almost all samples with the exception of M2, Fig. 4) is helpful in order to roughly estimate the vitrification rank of these ceramics. It could generally be deduced that higher vitrification, and thus higher firing temperatures, is observed as we descend to the Hellenistic pottery. The preservation of the laminar habit of phyllosilicates (MAD3, AKL15, AKL34) may indicate a firing temperature between 700 and 800 °C [15]. Characteristic feldspar (E12), iron silicates (MAD10, E6), and carbonate (AKL22) minerals are also observed. Feldspars and quartz predominate as part of the temper of the potsherds, since they are resistant against chemical transformation and mechanical attrition [25]. The presence of zircon (MAD17), Ti-rich mineral inclusions (E4), as well as ilmenite ($FeTiO_3$) crystals (M2) were revealed under ESEM examination. 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 [17,25]. Such characteristic minerals have been observed in the surrounding area of Aiani by several authors [20,21,26].

Ni and Cr-rich assemblages have been revealed in Fig. 4 for A2 sample. Chromiferous and nickeliferous inclusions are also shown in Fig. 5, along with their EDX spectra. The latter are probably related to the ultramafic rocks of the Vourinos mountain in the west direction of Aiani [19,21,27].

4. Conclusions

Several chronological types of pottery from Aiani, ancient Upper Macedonia were analysed in this study. 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. A finer texture and thus better ceramic manufacture as getting to Hellenistic era was observed. The use of a silicious or calcerous raw material probably related to the different manufacture process applied and/or the differentiation in potential utilization. There is evidence of higher firing temperatures when finding gehlenite and/or pyroxenes and lower when finding phylosilicate minerals. The chemical composition of the trace elements revealed high concentrations of characteristic elements like Cr, Ni, Ti, Zr, 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 clay-beds could be drawn. The preliminary results of this study do not necessarily imply that all the pottery of this area belonging to the same chronological type have similar physicochemical characteristics. It should be noted that a large number of potsherds from Aiani region, dated from the Late Bronze Age down to the hellenistic era, are being analyzed by several Greek and foreign laboratories. This ongoing archaeometrical research of pottery is expected to provide useful information on pottery tradition, trade and cultural exchange through time.

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Fig. 4 – ESEM images of the analyzed potsherds. The arrows point to: M2) an ilmenite crystal ($FeTiO_3$), A2) Ni and Cr-rich assemblages, MAD10) an iron silicate mineral, MAD3) a phyllosilicate mineral, MAD17) and AKL8) a zircon ($ZrSiO_4$) crystal, AKL15) a phyllosilicate mineral flake, AKL22) an aggregate of calcium carbonates ($CaCO_3$), AKL34), a phyllosilicate mineral, E4) a Ti-rich inclusion, E12) a feldspar crystal, E6) an iron silicate mineral.

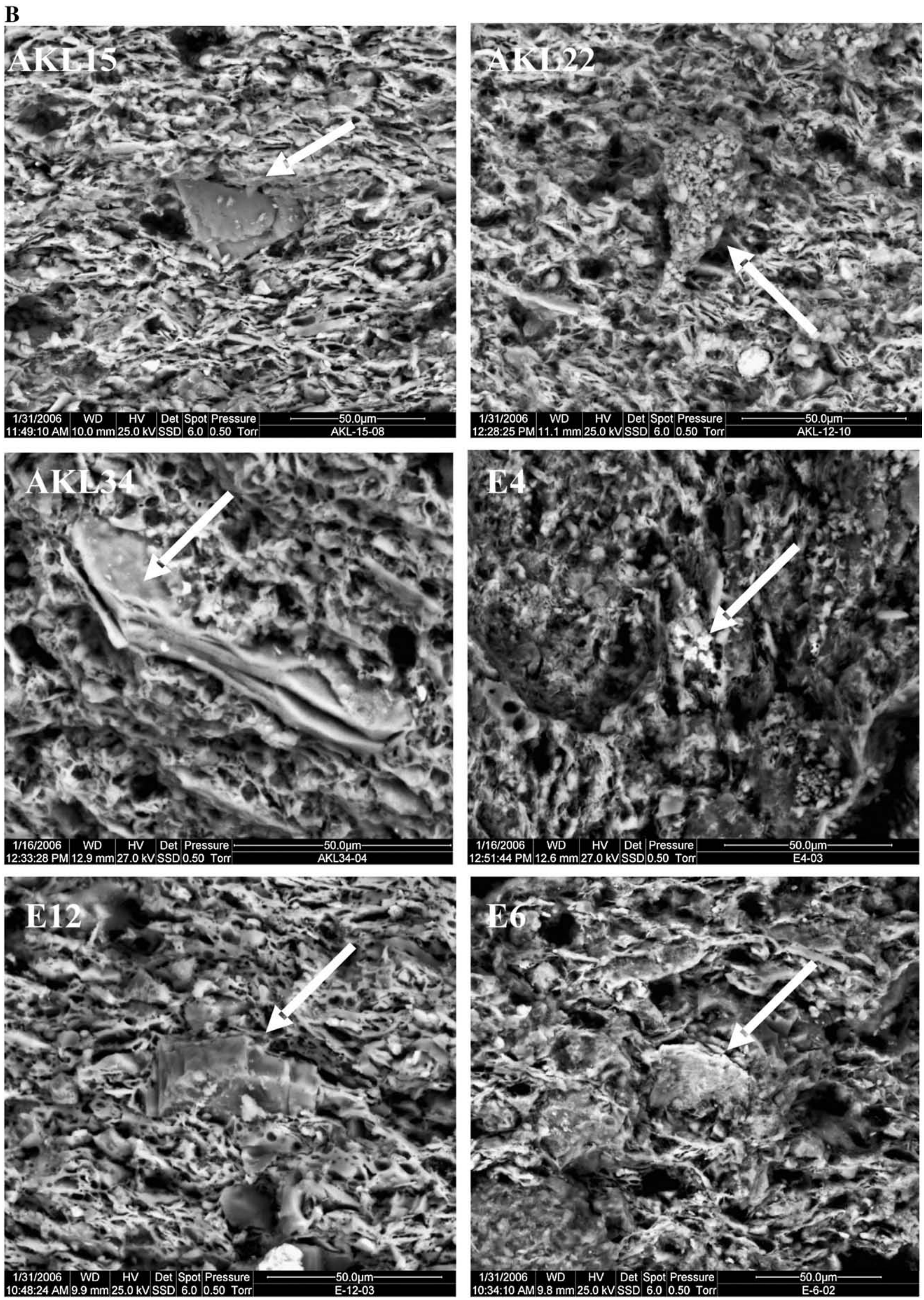

Fig. 4 (*continued*).

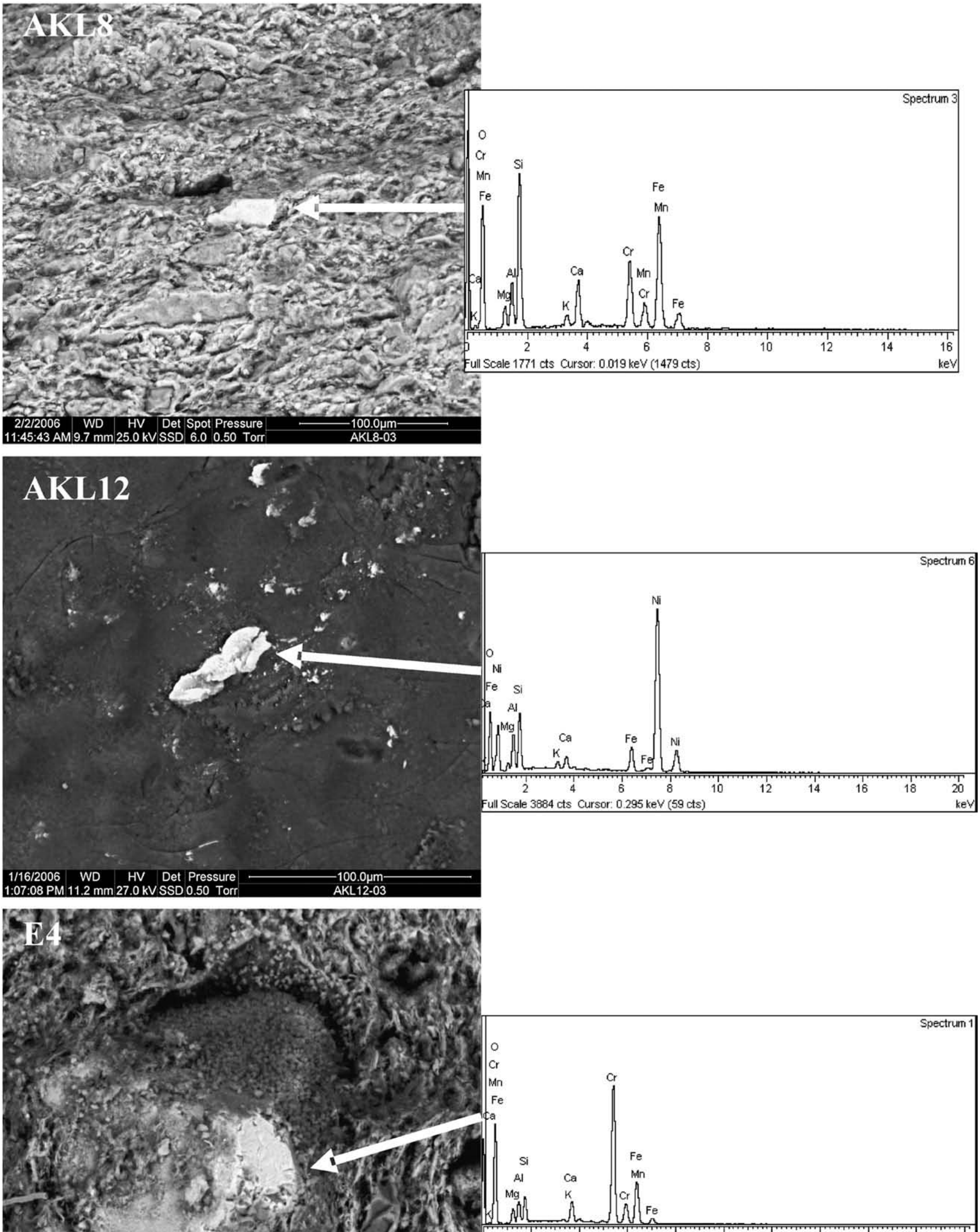

Fig. 5 – ESEM images and EDX spectra of three analyzed potsherds, with the arrows pointing at: AKL8) a chromiferrous mineral, AKL12) A Ni-rich inclusion, E4) a chromite mineral ($FeCr_2O_4$).

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