Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 37 (2011) 1879–1887
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Scanning electron microscopy and micro-Raman spectroscopy of slip layers of Hellenistic ceramic wares from Dorylaion/Turkey

Ali İssi [a], Aleksandra Raškovska [b], Alpagut Kara [a,*], Orhideja Grupce [b], Biljana Minčeva-Šukarova [b], Fisun Okyar

[a] Department of Materials Science & Engineering, Faculty of Engineering & Architecture, Anadolu University, İki Eylül Campus, 26555, Eskişehir, Turkey
[b] Institute of Chemistry, Faculty of Natural Sciences and Mathematics, University Ss Cyril and Methodius, 1000 Skopje, PO Box 162, Republic of Macedonia

Received 15 December 2010; received in revised form 23 December 2010; accepted 11 February 2011
Available online 29 March 2011

Abstract

Anatolia (Asia Minor) was inhibitated by several civilizations during the history. Dorylaion at Eskişehir/Turkey, an ancient site, is on the crossroads of many ancient civilizations. Artifacts belonging to different historical periods and cultures have been uncovered during the excavations carried out there since 1989. One of the two important groups of ceramic findings uncovered in these excavation works is the moldmade bowls, familiarly known as the Megarian bowls and the other is the West Slope wares. Both types of wares were probably the fashion cups around the east Mediterranean basin of the Hellenistic period. In this study, an attempt was made to enlighten the technological parameters and production technology of selected Megarian bowls and West Slope wares by characterizing their slip layers. Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX) were performed for microstructural and microchemical characterization. Micro-Raman spectroscopy was further applied for assessing the mineralogical components. The slip layers of both wares have similar elemental diversity, apart from the fact that the West Slope wares have more iron content than the Megarian bowls. The iron rich composition of the slip layers in different colors showed that hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) are the principal coloring agents for the slip layers of the investigated Hellenistic ceramic wares. However, firing conditions affecting the formation and the abundance of these minerals were probably adjusted in order to obtain the desired color.

Keywords: Scanning electron microscopy; Micro-Raman spectroscopy; Hellenistic ceramics

1. Introduction

In different periods of history, Anatolia was inhabitated by many ancient civilizations, namely Hatti, Hittite, Urartu, Phrgyia, Hellenistic, Roman, and later, Seljuk and Ottoman. In order to unveil the life of these civilizations, there have been considerable number of archaeological excavations carried out in different sites in Turkey. Amongst these sites, ancient site of Dorylaion, located about 3 km to the north-east of Eskişehir/Turkey, is one of biggest mount in the west of the middle Anatolia (Fig. 1). It is known nowadays as ‘‘Şarhöyük’’. Many artifacts belonging to different historical periods have been found during the excavations in this mound since 1989 carried out by the Ministry of Tourism and Culture and Anadolu University of Turkey. Most of the findings are Megarian bowls and West Slope wares from the Hellenistic period.

Megarian bowls were probably the fashion cups around the Mediterranean basin during the Hellenistic period. They are the predecessors of today’s wine holding glasses which were produced as terracotta bowls. These wares were produced in a semi-spherical shape without pedestal. Outer surface of the wares was decorated in relieves either with floral or figurative decoration. The studies so far, have clearly demonstrated that these wares suddenly emerged in Athens as imitations of gold or silver vessels without a development process. The usage of these wares was greatly appreciated because they could be obtained easier and cheaper than the metal wares. The production procedure was easily imitated and quickly spread beyond the boundaries of Athens and local productions

* Corresponding author at: Anadolu University, Faculty of Engineering and Architecture, Materials Science & Engineering Department, Iki Eylul Campus, 26480 Eskisehir, Turkey. Tel.: +90 222 335 0580 (6584); fax: +90 222 323 9501.
E-mail address: akara@anadolu.edu.tr (A. Kara).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.02.013

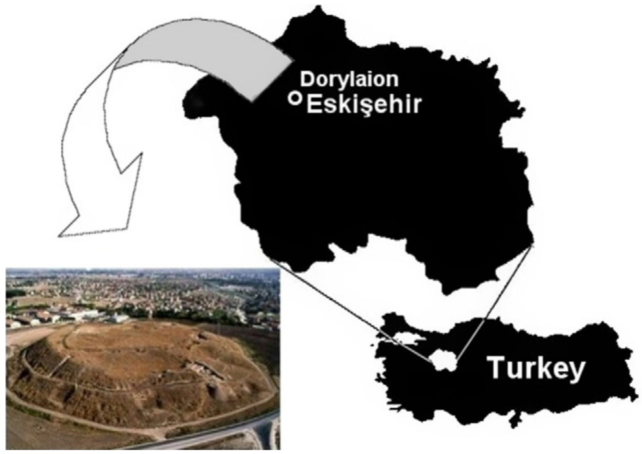


Fig. 1. The location and an aerial photo of Dorylaion.

emerged in the entire Mediterranean basin in the second century BC [1].

West Slope wares were named for the first time after the excavations performed in the Acropolis of Athens and entered the archaeological literature as ''Westabhang Keramik''. They also constitute an important familiar group of the Hellenistic period ceramic wares. West Slope wares may be characterized with laurel or ivy wreath of ornamental plants, white or orange-yellow in color complemented by the branches or various geometric ornaments with scraping technique on the slip layers. One of the most remarkable decorative features of them is the ground with basic black or dark slip and the light color of the decoration creating contrast with the background [2,3].

X-ray based techniques such as X-ray diffraction (XRD) and X-ray fluorescence (XRF), Fourier transform infrared (FTIR) and Raman spectroscopy, scanning electron microscopy (SEM) with energy or wavelength dispersive X-ray spectrometry (EDX/WDX) are conventional characterization techniques to enlighten constitutional characteristics of ancient ceramic slip layers and decorations [4–8]. This study presents a detailed investigation of the slip layers with different colors (orange, red, brownish and black) of representative Hellenistic findings from Dorylaion/Turkey. SEM and EDX were performed for microstructural and microchemical characterization, respectively. Micro-Raman spectroscopy was further performed for assessing the mineralogical components of slip layers and the identification of coloring agents used for decoration.

2. Materials and methods

2.1. Archaeological samples

Twenty shards of Megarian bowls and 23 shards of West Slope wares were selected for the study. Representative images of some selected Megarian bowls and West Slope wares are given in Fig. 2. As seen, they have the colors of orange, red, brown and black glossy slip layers. There are also some plants or figurative decorations. The body layers have a buff or light brown color with a homogeneous medium and fine-grained texture. Shard types are the handles and the rim of the wares.

2.2. Scanning electron microscopy

Backscattered electron images from polished cross sections and secondary electron images from freshly broken surfaces were obtained by Zeiss Evo 50EP SEM. Semi-quantitative chemical analyses of the slip layers were obtained by EDX detector (Oxford instruments) attached on the SEM column. Samples were sputtered with Au-Pd alloy in order to obtain conductivity to prevent charging under electron beam. Images were taken under the conditions of 20 kV accelerating voltage with a tungsten filament. The EDX spectra were gained from 10 mm working distance between 5 and 10 kcps at least 40 s. Semi-quantitative results were obtained with the processing the spectra with Bruker Quantax software. Quantification results were given in the form of oxides.

Fig. 2. Representative images of some selected Megarian bowls (coded as M) and West Slope wares (coded as B).

2.3. Raman spectroscopy

The Raman spectra were recorded in situ using Horiba Jobin-Yvon, LabRam 300 micro-Raman spectrometer, equipped with double-frequency Nd:YAG laser line operating at 532 nm with the excitation power of 6.7 mW at the sample. An Olympus MPlan microscope with magnification of the objective 100× and 50× was used to focus the laser. The backscattered light was dispersed by using a grating of 1800 lines/mm and was detected on a multi-channel air-cooled CCD detector. The exposure time was between 5 and 150 s with 5–10 scans. The instrumental resolution was around 2 cm^{-1}. LabSpec package [9] was used for spectra acquisition and GRAMS 32 [10] for spectra manipulation. All the spectra were baseline corrected with the LabSpec software in order to remove background fluorescence.

3. Results and discussion

3.1. Scanning electron microscopy

Elemental composition of the slip layers is important for the assumption of raw materials used for production. Both, the slip layers of the selected Megarian bowls and West Slope wares have similar elemental diversity but in different ratios (Tables 1 and 2).

According to these tables, iron seems to be the major colorant of the slip layers. Amount of Fe_2O_3 varies between 7.39 and 15.94 wt.% for the Megarian bowls and from 7.48 to 20.92 wt.% for the West Slope wares. It is believed that such high amounts of iron oxide could not be supplied from a typical clay batch. Additional iron or iron rich materials should have been needed for the enrichment of the clay batch. Some traditional approaches require selecting specific clay; rich in iron oxides of decanted clay or adjusting the composition of clay with specific compounds [11]. It is assumed that the enrichment processes of iron for the slip layer of the West Slope wares should have been more progressed than for the Megarian bowl slip layers. Total amount of iron in the raw material and redox conditions of firing were generally the main factors determining the color of potsherds [12]. In order to investigate how the amount of the iron present in the batch relates with the other elements inside the slip layers, correlation plots were obtained. The correlation coefficient (R) is related how the variation of one compound could be corresponded with the variation of the others. The highest correlation coefficients for iron oxide were obtained from Al_2O_3 and SiO_2 for the Megarian bowls and West Slope ware slip layers, respectively (Fig. 3). These results suggest that along with the iron enrichment processes of the clayey batches, the fraction of the other components, mainly siliceous materials, was decreased.

Na_2O and CaO contents are similar in both Megarian and West Slope wares. Na_2O changes in a narrow range from 0.41 to 1.91 wt.% for the Megarian bowls and differ in a range from 0.41 to 3.34 wt.% for the West Slope wares while CaO is in a range of 0.11–2.34 wt.% and 0.09–1.07 wt.% for the Megarian and West Slope slip layers, respectively. The presence of these oxides in such amounts suggests that the use of plagioclases or calcareous materials for the slip preparation were limited as possible raw materials. The correlation between CaO and Na_2O for the West Slope wares is stronger than the Megarian bowls (Fig. 3(c) and (d)). The use of Na_2O and CaO rich materials, probably plagioclases, was more common for the West Slope ware slips than the Megarian bowl slips. MgO content is also

Table 1
Semi-quantitative EDX results taken from the slip layers of the investigated Megarian bowl shards.

Code	Oxide (wt.%)							
	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	CaO	TiO_2
M1	50.03	31.66	11.17	1.32	0.98	4.01	0.36	0.46
M2	52.22	33.35	9.84	1.34	0.41	1.98	0.19	0.66
M3	51.71	31.55	10.75	1.21	0.43	3.13	0.55	0.67
M4	49.92	33.49	9.04	1.09	0.85	4.49	0.87	0.25
M5	51.97	31.93	10.44	1.00	0.66	2.85	0.36	0.79
M6	43.51	34.99	10.79	2.26	1.30	4.48	2.34	0.33
M7	45.74	34.51	9.04	3.05	1.68	4.77	0.83	0.37
M8	48.60	34.00	8.32	2.83	1.33	3.30	0.94	0.68
M9	44.36	35.23	9.16	3.13	1.47	5.38	0.66	0.60
M10	45.89	32.65	13.30	2.26	1.01	3.69	0.78	0.42
M11	48.14	37.03	7.39	2.01	0.85	4.10	0.16	0.33
M12	45.84	38.28	8.38	2.07	1.03	2.99	1.04	0.37
M13	45.44	36.41	11.65	1.79	0.82	2.89	0.22	0.77
M14	45.26	35.46	9.11	2.22	1.30	5.24	1.02	0.39
M15	46.29	36.04	9.62	2.42	1.01	2.06	2.04	0.52
M16	40.33	29.87	15.94	1.98	1.60	7.95	1.94	0.39
M17	44.60	35.73	11.39	1.82	1.28	3.25	1.15	0.77
M18	47.26	37.69	10.34	1.50	0.57	1.89	0.11	0.64
M19	45.77	34.99	8.65	1.62	1.91	5.61	0.89	0.55
M20	51.68	32.82	9.52	1.25	0.80	2.75	0.40	0.77

Table 2
Semi-quantitative EDX results taken from the slip layers of the investigated West Slope ware shards.

Code	Oxide (wt.%)							
	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	CaO	TiO_2
B1	50.59	26.72	13.08	3.00	0.90	4.31	0.57	0.85
B2	46.15	28.82	12.80	1.79	1.16	8.03	0.55	0.70
B3	49.04	33.70	11.02	1.24	1.12	3.02	0.21	0.66
B4	45.37	28.38	14.48	1.98	0.92	7.69	0.61	0.58
B5	45.47	27.73	15.94	2.41	1.86	4.78	1.07	0.74
B6	51.04	26.64	11.32	2.80	0.76	6.19	0.69	0.56
B7	48.07	27.58	11.44	1.80	1.40	8.76	0.69	0.26
B8	49.62	31.29	7.48	1.69	3.34	5.28	0.98	0.32
B9	55.51	24.43	8.76	4.20	1.58	4.79	0.67	0.07
B10	50.06	27.96	15.23	2.99	0.41	2.43	0.37	0.56
B11	52.79	29.79	8.88	1.84	1.30	3.81	0.61	0.97
B12	47.73	34.78	10.04	1.01	1.23	4.02	0.40	0.79
B13	48.23	29.38	13.63	2.64	0.90	4.02	0.63	0.57
B14	46.78	29.21	14.15	2.39	1.41	4.88	0.67	0.49
B15	47.05	29.78	16.78	2.19	0.60	2.96	0.15	0.48
B16	45.05	27.44	14.23	2.15	2.76	6.93	0.95	0.49
B17	43.45	28.42	16.26	1.72	2.06	6.62	0.88	0.60
B18	51.08	34.01	10.11	1.19	0.72	2.11	0.09	0.70
B20	45.75	28.57	11.38	1.45	1.15	10.26	0.88	0.57
B21	43.78	28.15	15.10	2.03	2.26	7.21	1.07	0.41
B22	43.89	30.88	18.09	2.30	0.63	3.38	0.31	0.51
B23	43.28	30.84	20.92	1.42	0.42	2.37	0.16	0.59

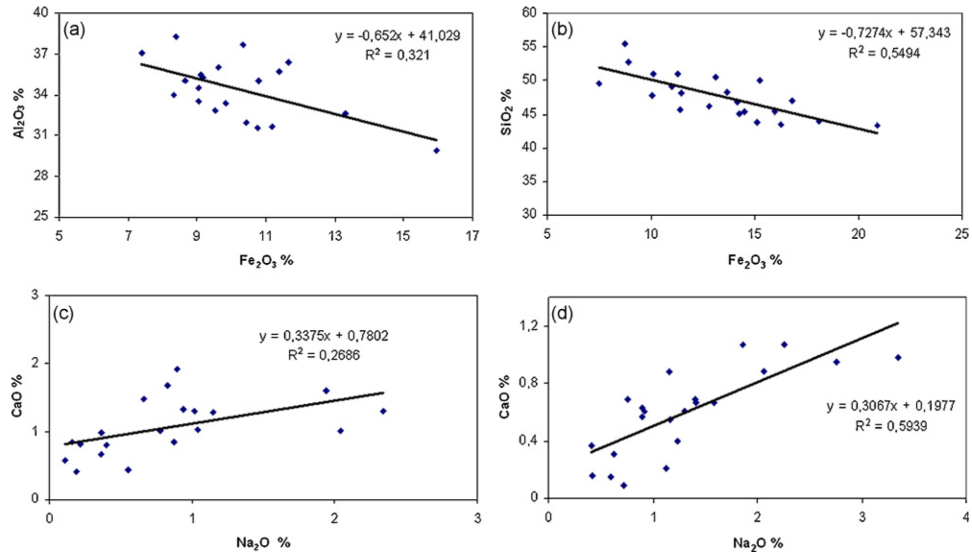


Fig. 3. The correlation between (a) Fe_2O_3 vs. Al_2O_3 for the Megarian bowl, (b) Fe_2O_3 vs. SiO_2 for the West Slope ware, (c) CaO vs. Na_2O for the Megarian bowl and (d) CaO vs. Na_2O for the West Slope ware slip layers.

nearly the same in both types of the shards and it is in a moderate range from 1.00 to 3.13 wt.% for the Megarian bowl and 1.01–4.20 wt.% for the West Slope ware slips. The fluctuation in the amount of K_2O, however, suggests the deliberate addition of K-feldspars or employment of naturally potassium rich micaceous clays, i.e. muscovite, phlogopite or sericite, as the principal inorganic source for the slip layers. This could be the explanation for the drastic change in amount of K_2O from 1.89 to 7.95 wt.% in the slip layers of Megarian bowls and from 2.11 to 10.26 wt.% in the slip layers of the West Slope wares. TiO_2 content of the slip layers changes from 0.25 to 0.79 wt.% for the Megarian bowls and 0.07–0.97 wt.% for the West Slope wares. If the source of TiO_2 was a mineral such as ilmenite ($FeTiO_3$), the change in iron content would have lead to a drastic change of TiO_2 content. However, it resembles that source for TiO_2 is a constituent of typical clays such as rutile or anatase, the later being confirmed by Raman spectroscopy.The variation of alkaline and earth alkaline oxides detected in all the investigated slip layers is given in Fig. 4. Non-synchronized changes of these oxides show diversity for the raw materials used in the slip batches. In case that the same materials had been used regularly, more synchronic variation of the oxides would have been observed for both types of wares.

Representative SEM images of body and slip layers in cross sections and the corresponding EDX spectra taken from the slip layers of selected shards, namely M8, M16, B8 and B23, with the lowest and the highest iron contents are given in Fig. 5.

As seen from the SEM images, the thickness of the slip layers changes from 5 to 30 μm with a dense structure having stable thickness tolerances. This suggests that the slips should have been applied to body surfaces in a form of suspension. Otherwise, it could have been difficult to obtain such a uniform slip layer. It is also noticed that the slip layers of the shards still stand even though they had been exposed to several principally climatic or hot–cold cycles through more than 2000 years. Producing such a durable coating layer should not be random. These slip layers should also have similar thermal expansion coefficients with the underlying bodies since almost all the slip layers have no cracks or spalling.

Megarian bowls and West Slope wares have iron rich slip layers with nearly similar elemental diversity but with different colors. Difference in mass ratio of the elements present in the slip layers and the redox conditions of firing were the most effective parameters to adjust to obtain the desired color [13–16]. It is also known that monochrome and bichrome coatings were produced through a single firing cycle consisting of a sequence of oxidizing and reducing steps obtained by varying the firing atmosphere for ancient Greek ceramic wares [14,17]. There is still a lack of comparative characteristics for these unique wares in the relevant literature but, the similar chemical and physical characteristics of the Megarian bowls and West slope wares from Dorylaion may be considered as a part of the continuity of this traditional approach for pottery production.

During the sample preparation, cross sections were obtained from the vacuum-impregnated samples to obtain the back-scattered electron images of body and slip layers. Carbon element is discarded from the EDX analyses since it originates from the mounting resin. On the other hand, using micro-Raman spectroscopy, amorphous carbon was identified in several black slip layers, including B20. Thus, a freshly broken sample of B20 was further analyzed with EDX. Representative secondary electron image and the corresponding EDX spectrum are given in Fig. 6.

The EDX spectrum shows relatively high amount of carbon in the slip layer. Natural organic or added carbonaceous material would fire black in color in a reducing atmosphere. Furthermore, ferruginous clays containing iron oxides and hydroxides could form spinel phases that were mainly black in color [18].

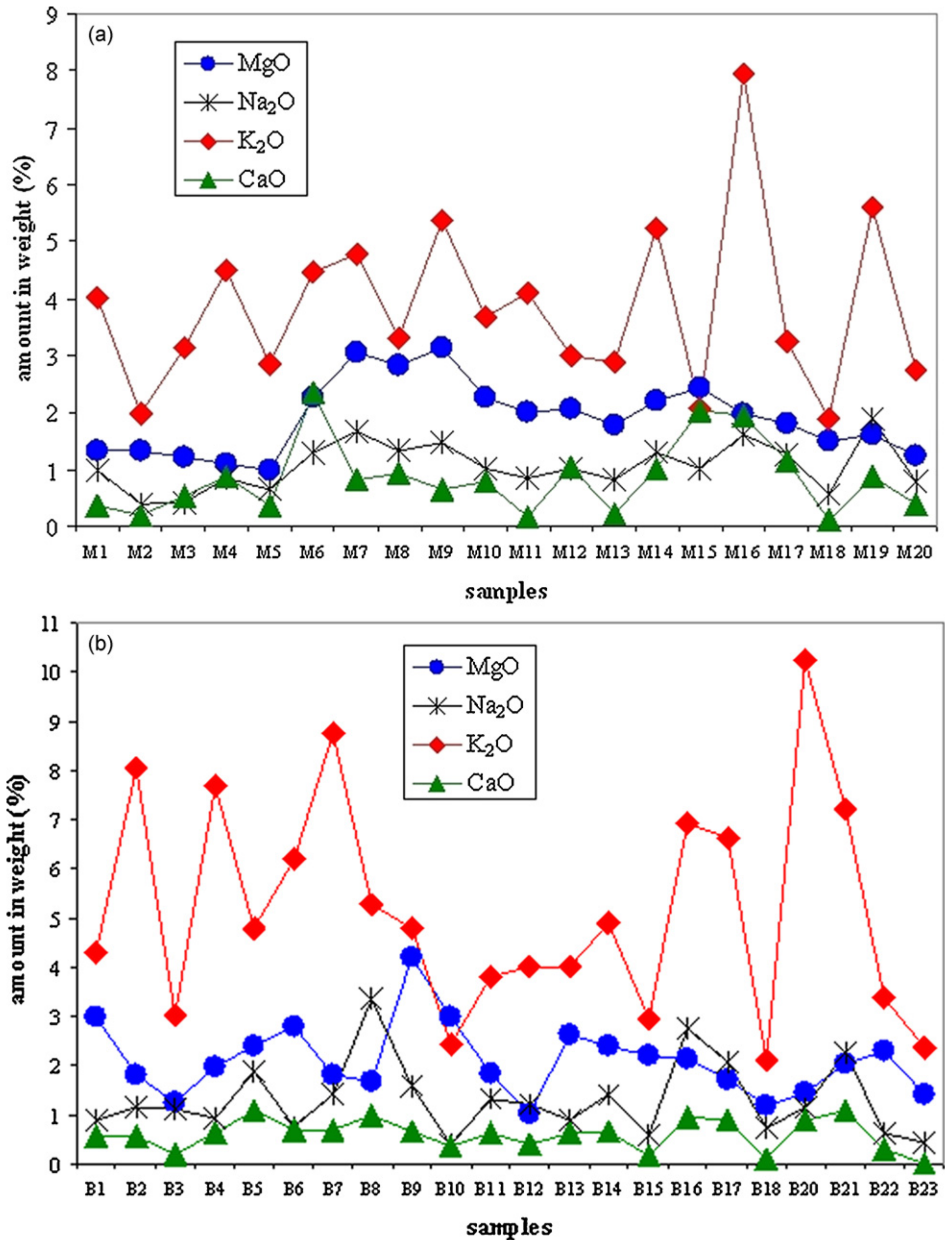


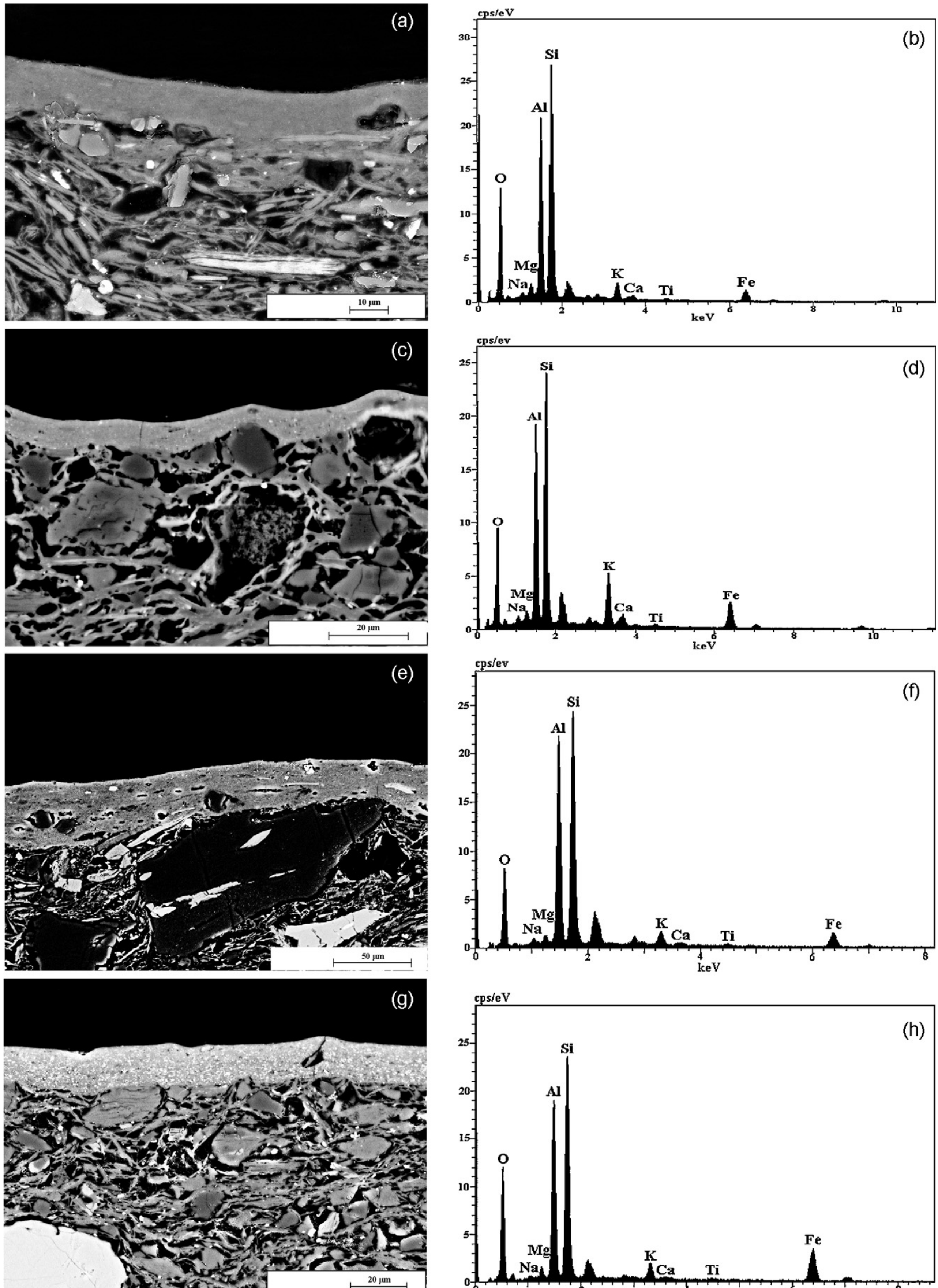
Fig. 4. The variation of alkaline and earth alkaline oxides in the slip layers for (a) Megarian bowls and (b) West Slope wares.

3.2. Micro-Raman spectroscopy

Micro-Raman spectroscopy is a well-established technique for characterization of archaeological artifacts. Many minerals of importance to pottery (iron oxides, quartz, feldspars, and carbonates) are good Raman scatters. Disordered or heterogeneous carbonaceous materials are also well characterized by their Raman spectra [18–22]. In the case of Megarian bowls and West Slope wares, micro-Raman spectroscopy was used for assessing the mineralogical composition of the slip as well as the coloring agents used for the decorations over the slip. In addition, based on the identified minerals, estimation for firing conditions of the wares could be made.

The Raman spectra of the slip layers were recorded for 11 Megarian bowls and 17 West Slope wares. Most of the analyzed samples were monochromatic with different shades of orange-red or brownish-gray-black. Only a couple of samples were ornate with decoration (B4 and B8) while one of samples was with patchy red-blackish surface (B19). The Raman spectra were recorded in situ by shining the laser beam (of a radius of 1–2 μm) on the surface of the slip, on several spots.

Iron rich composition of the slip layers of Megarian bowls and West Slope wares established by EDX spectra was also confirmed with Raman spectra. In all of the recorded spectra, bands belonging to some form of iron oxide, or a mixture of iron oxides were identified [18,19,23,24]. As shown in Fig. 7 and Fig. 8, independently of the color of the samples, hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) were detected, in some cases as individual mineral, in other cases as different iron oxide combinations (Table 3). The presence of magnetite and hematite provides interesting information about the firing atmosphere. Iron oxides are very influenced by the


(a)
10 µm
(b)
cps/eV
O
Mg
Na
Al
Si
K
Ca
Ti
Fe
keV
(c)
20 µm
(d)
cps/ev
O
Mg
Na
Al
Si
K
Ca
Ti
Fe
keV
(e)
50 µm
(f)
cps/ev
O
Mg
Na
Al
Si
K
Ca
Ti
Fe
keV
(g)
20 µm
(h)
cps/eV
O
Mg
Na
Al
Si
K
Ca
Ti
Fe
keV

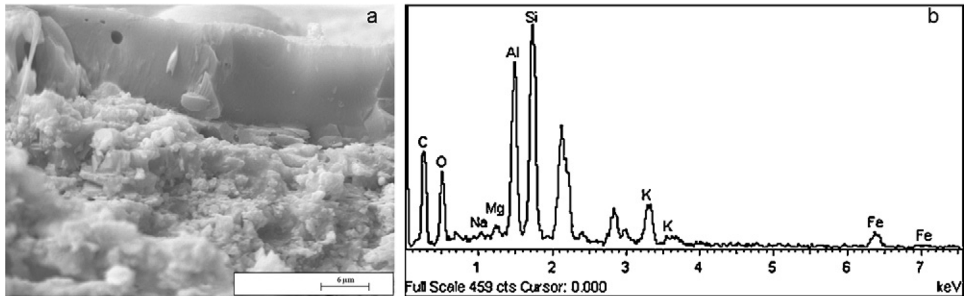


Fig. 6. (a) Representative SEM image of freshly broken B20 sample and (b) EDX spectrum of the slip layer.

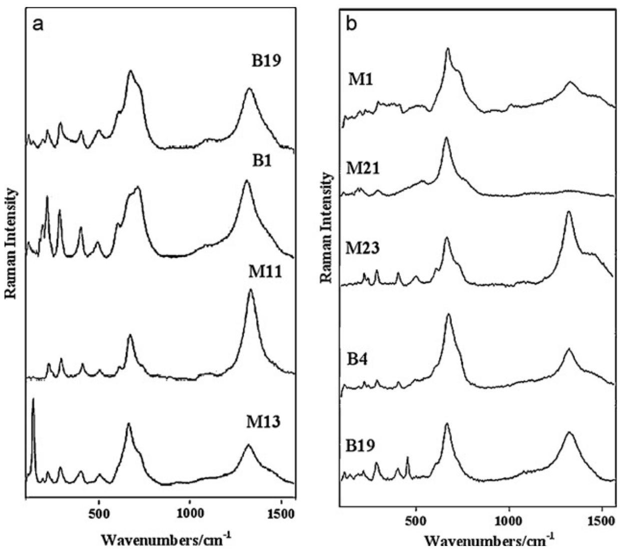


Fig. 7. Raman spectra of the identified iron oxides in the representative (a) red color slips, (b) black color slips of the analyzed wares.

firing atmosphere; in fact they differ in color according to firing conditions. When oxygen is almost absent in the kiln, i.e. under reducing conditions, reduced compounds as magnetite (black in color) form. On the contrary, under the influence of oxidizing conditions, the oxidized form as hematite (reddish) prevail. Although Raman signatures of different iron oxides appear in similar spectral region, it is possible to make differentiation between the different iron oxides [19,23,24]. In some of the samples, the change of the wave numbers, as well as the change of the shape and/or broadening of the Raman bands due to hematite was observed. This could be due to variation in crystallinity or grain size and/or to the partial Fe/M substitution in the hematite structure [19,25]. Although the presence of the maghemite in the raw materials cannot be excluded, since its existence in the natural ores is scanty, most probably it was obtained during firing [26]. Its presence affects the color of the applied slip, the higher content of maghemite the darker color, and suggests reduction atmosphere during firing [25,26]. It is not clear, though, if the conditions during firing were adjusted intentionally or simply by chance. But, in almost all the dark brown or black samples, carbon black was identified, suggesting reduction atmosphere of firing (Table 3). Carbon may be supplied from an organic material to the slip batches but, it is also a requirement that firing temperatures must be lower or reductive; otherwise, oxidation of carbon to carbon dioxide occurs [18].

Besides iron minerals and carbon black, the presence of others, constituents of the clay, was also recorded. These are quartz, gypsum, anatase, talk and diopside/augite. Since the

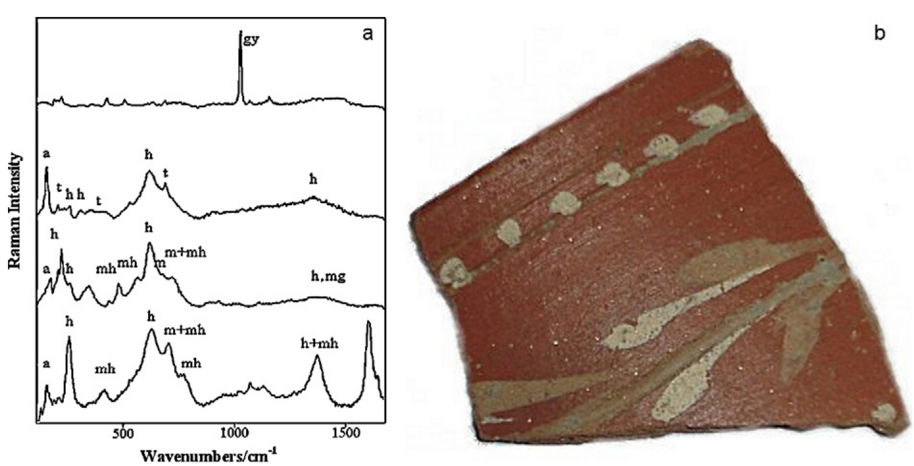


Fig. 8. (a) Raman spectra of the different color decorations on (b) B8 sample (gy - gypsum; h - hematite, m - magnetite, mh - maghemite, a - anatase, t - talc; gr - graphite).

Fig. 5. SEM images of the general view of the body and slip layers in cross sections and EDX spectra of the slip layers for sample of (a and b) M8, (c and d) M16, (e and f) B8 and (g and h) B23.

Table 3
Iron oxides and carbon identified in the slip layers of the investigated shards shown in Fig. 7(a) and (b).

Code	Minerals/phases			
	Hematite	Magnetite	Maghemite	Carbon black
Black samples				
M1		✓	✓	✓
M21		✓		
M23	✓	✓	✓	✓
B4	✓		✓	✓
B19	✓		✓	✓
Red samples				
B19	✓	✓	✓	
B1	✓		✓	
M11	✓	✓		
M13	✓	✓	✓	

presence of these minerals was especially noticeable in the ornament decoration, it appears that they were used intentionally, in order to obtain wider palette of color shades.

In the West Slope wares, black samples are more abundant than in the Megarian bowl samples. It may be the matter of aesthetics or fashion, but relates to the higher iron and potassium content in the wares, as well. During firing, potassium oxide acts as a fluxing agent. Then, a vitrification layer is formed on the surfaces of the wares, hindering the oxidation in the slip layer and leading to dark brown or black colors [25,26]. The potters were probably aware of the effect of firing conditions on the color of the pottery and were used it to their advantage, to obtain different shades of the ware [25,26]. Although the presence of titanium oxides detected by semi-quantitative EDX analysis is below 1 wt.%, the presence of anatase was also identified in several samples by micro-Raman spectroscopy (Fig. 8). This is not surprising since anatase is usually detected by Raman spectroscopy due to its high scattering effect [27]. On the other hand, the presence of rutile was not identified. The firing temperature for the slip layers should not exceed the anatase–rutile transition point (750–950 °C), which depends on various factors including the iron concentration [28].

4. Conclusions

There is a wide range of colors and shades ranging from orange-red to dark brown-black in the investigated slips of the Megarian bowls and West Slope wares. Iron minerals are the principal coloring agents for the slip layers. Being independent of the color of the samples, hematite, maghemite and magnetite were identified, in some cases, as individual mineral, in other cases as different iron oxide combinations. Abundance of these minerals or their ratio is believed to affect the observed color of the shards.

The variation of the iron rich clayey materials, variation of the potassium content, the presence of carbon in the black samples suggest that potters had knowledge and experience in achieving the right conditions for obtaining desired color. Finally, it may be concluded that the traditional approach for preparation and firing processes of these types of wares has unique characteristics which are compatible with a larger scale of ceramic production in Greek style in specific periods of history.

Acknowledgment

Financial support of this study by the Scientific and Technological Research Council of Turkey (TÜBİTAK) with the project number of 106M463 and Ministry of Education and Science, Republic of Macedonia is greatly acknowledged.

References

[1] S.I. Rotroff, Hellenistic Pottery: Athenian and Imported Moldmade Bowls: 22 (The Athenian Agora), American School of Classical Studies at Athens, New Jersey, 1982.
[2] F.F. Jones, The Hellenistic and Roman periods, in: H. Goldman (Ed.), Excavations at Gözlu Kule, Tarsus, Princeton University Press, Princeton, 1950, pp. 149–296.
[3] R.M. Cook, Greek Painted Pottery, Routledge, New York, 1997.
[4] J. Striova, C. Lofrumento, A. Zoppi, E.M. Castellucci, Prehistoric Anasazi ceramics studied by micro-Raman spectroscopy, J. Raman Spectrosc. 37 (2006) 1139–1145.
[5] J.M. Compana, L. Leon-Reina, M.A.G. Aranda, Archaeometric characterization of Terra Sigillata Hispanica from Granada workshops, Bol. Soc. Esp. Ceram. V 49 (2010) 113–119.
[6] P. Mirti, X-ray microanalysis discloses the secrets of ancient Greek and Roman potters, X-ray Spectrom. 29 (2000) 63–72.
[7] S.R. Bertolino, V.G. Josa, A.C. Carreras, A. Laguens, G. de la Fuente, J.A. Riveros, X-ray techniques applied to surface paintings of ceramic pottery pieces from Aguada Culture (Catamarca, Argentina), X-ray Spectrom. 38 (2009) 95–102.
[8] A. Mangone, L.C. Giannossa, G. Colafemmina, R. Laviano, A. Traini, Use of various spectroscopy techniques to investigate raw materials and define processes in the overpainting of Apulian red figured pottery (4th century BC) from southern Italy, Microchem. J. 92 (2009) 97–102.
[9] LabSpec version 5.25.15.
[10] GRAMS/32 Spectral Notebase, Version 4.10, Galactic Industries Corporation, 1996.
[11] A. Mangone, L.C. Giannossa, A. Cianicio, R. Laviano, A. Traini, Technological features of Apulian red figured pottery, J. Archaeol. Sci. 35 (2008) 1533–1541.
[12] L. Nodari, E. Marcuz, L. Maritan, C. Mazzoli, U. Russo, Hematite nucleation and growth in the firing of carbonate-rich clay for pottery production, J. Eur. Ceram. Soc. 27 (2007) 4665–4673.
[13] J. van der Weerd, G.D. Smith, S. Firth, R.J.H. Clark, Identification of black pigments on prehistoric Southwest American potsherds by infrared and Raman microscopy, J. Archaeol. Sci. 31 (2004) 1429–1437.
[14] C.C. Tang, E.J. MacLean, M.A. Roberts, D.T. Clarke, E. Pantos, A.J.N. Prag, The study of Attic black gloss sherds using synchrotron X-ray diffraction, J. Archaeol. Sci. 28 (2001) 1015–1024.
[15] C. Rathossi, Y. Pontikes, Effect of firing temperature and atmosphere on ceramics made of NW Peloponnese clay sediments. Part I. Reaction paths, crystalline phases, microstructure and colour, J. Eur. Ceram. Soc. 30 (2010) 1841–1851.
[16] P. Mirti, M. Gulmini, A. Perardi, P. Davit, D. Elia, Technology of production of red figure pottery from Attic and southern Italian workshops, Anal. Bioanal. Chem. 380 (2004) 712–718.
[17] P. Mirti, A. Perardi, M. Gulmini, M.C. Preacco, A scientific investigation on the provenance and technology of a black-figure amphora attributed to the Priam group, Archaeometry 48 (2006) 31–43.
[18] J.M. Perez, R. Esteve-Tebar, Pigment identification in Greek pottery by Raman microspectroscopy, Archaeometry 46 (2004) 607–614.
[19] F. Froment, A. Tournie, P. Colomban, Raman identification of natural red to yellow pigments: ochre and iron-containing ores, J. Raman Spectrosc. 39 (2008) 560–568.

[20] V. Tanevska, P. Colomban, B. Minceva-Sukarova, O. Grupce, Characterization of pottery from the Republic of Macedonia. I. Raman analyses of Byzantine glazed pottery excavated from Prilep and Skopje (12th–14th century), J. Raman Spectrosc. 40 (2009) 1240–1248.

[21] A. Raskovska, B. Minceva-Sukarova, O. Grupce, P. Colomban, Characterization of pottery from Republic of Macedonia. II. Raman and infrared analyses of glazed pottery finds from Skopsko Kale, J. Raman Spectrosc. 41 (2010) 431–439.

[22] O. Beyssac, B. Goffe, J.P. Petitet, E. Froigneux, M. Moreau, J.N. Rouzaud, On the characterization of disordered and heterogeneous carbonaceous materials by Raman spectroscopy, Spectrochim. Acta A 59 (2003) 2267–2276.

[23] http://www.dst.unisi.it/geofluids/raman/spectrum_frame.htm (14/10/2010).

[24] http://www.ens-lyon.fr/LST/Raman/index.php (14/10/2010).

[25] J. Capel, F. Huertas, A. Pozzuoli, J. Linares, Red ochre decorations in Spanish Neolithic ceramics: a mineralogical and technological study, J. Archaeol. Sci. 33 (2006) 1157–1166.

[26] P.R.S. Moorey, Ancient Mesopotamian Materials and Industries. The Archaeological Evidence, Oxford University Press, New York, 1994 , pp. 152–156.

[27] R.J.H. Clark, Q.Y. Wang, A. Correia, Can the Raman spectrum of anatase in artwork and archaeology be used for dating purposes? Identification by Raman microscopy of anatase in decorative coatings on Neolithic (Yangshao) pottery from Henan, China, J. Archaeol. Sci. 34 (2007) 1787–1793.

[28] M. Sendova, V. Zhelyaskov, M. Scalera, M. Ramsey, Micro-Raman spectroscopic study of pottery fragments from the Lapatsa Tomb, Cyprus, ca 2500 BC, J. Raman Spectrosc. 36 (2005) 829–833.