Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 2375–2380

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Estimation of ancient firing technique by the characterization of semi-fused Hellenistic potsherds from Harabebezikan/Turkey

Ali İssi *

Dumlupınar University, Department of Ceramic Engineering, Merkez Campus, 43100, Kütahya, Turkey

Received 28 April 2011; received in revised form 1 November 2011; accepted 2 November 2011
Available online 7 November 2011

Abstract

This study discusses the availability of different ancient firing techniques for some semi-fused potsherds which were recovered from an archeological excavation carried out for a Hellenistic workshop at Harabebezikan (Turkey). There are different ancient firing techniques such as open or surface firing (bonfire), pit firing and kiln firing. Each firing technique may create different effects on pottery. It sometimes may be possible to distinguish the firing technique used for a pottery if some evidential characteristics of firing could be defined. The potsherds were characterized with different analytical techniques in order to enlighten firing technique used for the production. Wavelength dispersive X-ray fluorescence (WDXRF) and X-ray diffraction (XRD) analysis were performed for chemical and mineralogical/phase contents, respectively. Scanning electron microscopy (SEM) in combination with energy dispersive X-ray spectrometry (EDX) was further performed for microstructural and micro-chemical characterization. Quartz (SiO_2), calcite ($CaCO_3$), plagioclase [$(Na,Ca)AlSi_3O_8$], hematite (α-Fe_2O_3), pyroxenes [$Ca(Mg,Al)(Si,Al)_2O_6$]/[$Ca(Mg,Fe)Si_2O_6$], akermanite ($Ca_2MgSi_2O_7$) and leucite ($KAlSi_2O_6$) were identified in the samples. Abundance of new mineral formations in the samples, related firing temperatures, microstructural and microchemical investigations suggested that kiln firing was the most probable technique for the production of the investigated potsherds.

Keywords: Archaeometrical characterization; Ancient firing technique; Hellenistic ceramics; Harabebezikan (Turkey)

1. Introduction

There are several ancient sites belonging to many civilizations lived in Anatolia in different periods of history. Archeological excavations are still being carried out to unearth the cultural heritage of the past civilizations. One of these ancient sites, Harabebezikan, is located 17 km south of Birecik in Şanlıurfa/Turkey (Fig. 1). It is left under water by the reservoir lake of Karkamış (Carchemish) dam today. The construction of the dam submerged Harabebezikan in an irrecoverable way. An archeological salvage project was carried out in 1999 shortly before the reservoir filling. It was understood that the main production of the workshop, probably active between the beginning and middle of the second century B.C., was narrow necked amphorae without handle. It seems possible that the workshop also produced jugs and bowls with incurved rim, called as ''fish plate''. One of the most important results of the excavations was to discover a ceramic workshop of the Hellenistic period. Clay storage and levigation pits, slags, lots of faulty produced ceramics were found in workshop area, but kiln or firing facility was not recovered [1]. Therefore, firing technique used for the pottery production is unknown. Among them, a few potsherds recovered from the Hellenistic workshop were interesting that some parts of the bodies were about to be fused during firing process. It was clear that they could verify the maximum temperatures and conditions of firing since they were over-fired.

There are different ancient firing techniques such as open or surface firing (bonfire), pit firing and kiln firing. The potteries were placed on the ground and surrounded with fuel for surface firing. A hole in the ground was used for pit firing. Potteries were placed in an open pit and covered by straw and wood. In order to preserve heat, it was covered with earth again. In both procedures, the pots were in direct contact with the fuel and the flames [2,3]. Kiln firing was more developed than the other techniques. Some permanent or partially permanent structures

* Tel.: +90 274 265 2031x4309; fax: +90 274 265 2066.
E-mail address: aliissi@hotmail.com.

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.11.002

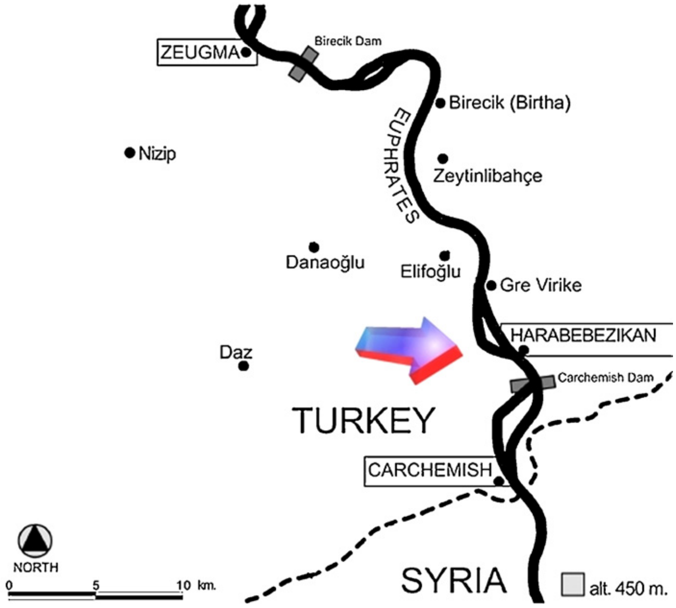

Fig. 1. Map showing the location of Harabebezikan with important ancient sites of southeastern Turkey.

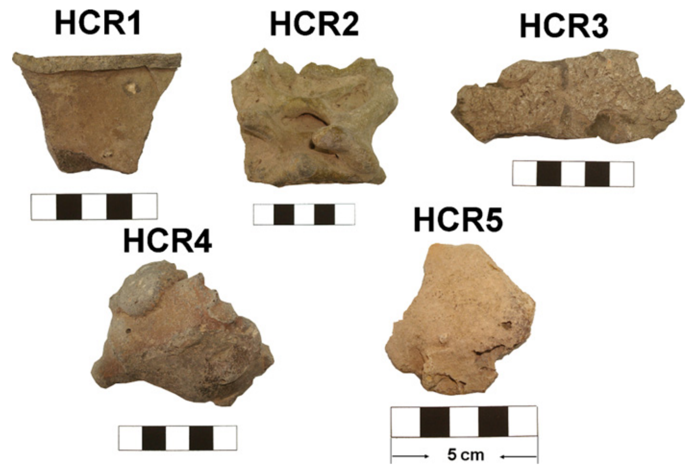

Fig. 2. Representative images of semi-fused potsherds.

were used. Moreover, the fire was separated from the potteries by a firing chamber. Pit firing has high heating rate, short residence time and reducing conditions. In kiln firing, the heating rate is generally low, residence time is long and redox conditions may vary depending on the type of kiln, although they are generally oxidizing [3]. The scope of this study is to discuss the availability of different ancient firing techniques for these materials, maximum temperatures reached during firing and enlightening the sophisticated firing procedure more. The characterization studies focus on these selected semi-fused potsherds. Wavelength dispersive X-ray fluorescence (WDXRF) and X-ray diffraction (XRD) analysis were performed for chemical and mineralogical/phase contents, respectively. Scanning electron microscopy (SEM) in combination with energy dispersive X-ray spectrometry (EDX) was further performed for microstructural and microchemical characterization.

2. Materials and methods

2.1. Archeological samples

Representative images of semi-fused potsherds investigated in this study are given in Fig. 2. It is not possible to classify the type of pieces as the bottom or the rim of the wares. The potsherds contain different textures together. Some parts of the potsherds exhibit melted texture as if they were about to be fused during firing. They have buff color without a glaze or slip layer.

2.2. Methods

Fine powders were prepared in an agate mortar in order to be analyzed by WDXRF and XRD techniques. Rigaku ZSX primus instrument was used for chemical analysis of major and minor elements. Glass tablets were prepared by fluxing for the measurement with a ratio of 1:10 powder:$Li_2B_4O_7$ (wt.%). Rigaku Rint 2200 powder diffractometer with Cu Kα radiation was used for the mineralogical analysis. XRD patterns were obtained by scanning 5–70° 2θ, with a goniometer speed of 2°/min, operating at 40 kV and 30 mA. Zeiss Supra 50VP SEM attached with Oxford instruments EDX was used for the characterization of vacuum impregnated bulk samples of the semi-fused potsherds. The samples were coarse and fine polished to obtain flat surfaces prior to SEM investigation.

3. Results

3.1. Chemical and mineralogical analysis

WDXRF results showed that all of the samples have high amounts of CaO. CaO quantities change between from 19.13 to 24.31 wt.% (Table 1).

There are rich calcareous raw material deposits around Harabebezikan which are still used for mining today [4,5]. This can be given as the explanation of high amount of CaO for chemical analysis results. Iron oxide (shown as Fe_2O_3 for the study) quantities change between from 7.23 to 7.61 wt.%. MgO quantities are in moderate range of 5.58–7.34 wt.%. Na_2O and K_2O quantities are also in moderate range of 1.57–1.95 and 2.27–4.73 wt.%, respectively. The WDXRF results of the semi-fused potsherds are similar to the results of calcium rich samples given for the Hellenistic potsherds in the previous study (Table 1) [6]. This may approve that these semi-fused potsherds were produced from the same raw materials used for the pottery production at Harabebezikan. Clays rich in calcareous materials should have been used for the body layers of the Hellenistic potsherds.

Quartz (SiO_2), plagioclase [(Na,Ca)$AlSi_3O_8$], pyroxenes: diopside [Ca(Mg,Al)(Si,Al)$_2O_6$] and augite [Ca(Mg,Fe)Si_2O_6], feldspathoid: leucite ($KAlSi_2O_6$), iron mineral: hematite (α-Fe_2O_3), carbonated mineral: calcite ($CaCO_3$) and a melilite: akermanite ($Ca_2MgSi_2O_7$) were identified from the XRD spectra of semi-fused potsherds (Fig. 3).

Table 1
WDXRF results of semi-fused potsherds (HCR1-5) and calcium rich Hellenistic potsherds (HB14 and HB18) investigated in previous study.

Oxide (wt.%)	Sample code						
	HCR1	HCR2	HCR3	HCR4	HCR5	HB14	HB18
SiO_2	45.29	45.89	43.45	44.04	48.22	44.99	44.66
Al_2O_3	11.84	11.45	11.37	11.39	10.77	11.78	10.49
Fe_2O_3	7.56	7.60	7.61	7.58	7.23	7.03	7.19
MgO	6.41	7.34	6.79	6.40	5.58	5.43	5.17
Na_2O	1.95	1.71	1.65	1.57	1.79	1.74	1.58
K_2O	2.53	2.27	2.82	4.42	4.73	2.63	3.28
CaO	22.80	21.55	24.31	22.29	19.13	24.22	25.43
TiO_2	0.84	0.96	1.05	0.98	0.78	0.86	0.92
P_2O_5	0.18	0.46	0.32	0.60	1.15	0.25	0.43
SO_3	0.19	0.12	0.15	0.10	0.13	0.29	0.39
Cl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.04
Cr_2O_3	0.11	0.17	0.13	0.15	0.12	0.13	0.10
MnO	0.13	0.23	0.14	0.26	0.15	0.13	0.15
NiO	0.05	0.05	0.04	0.04	0.04	0.05	0.04
CuO	n.d.	n.d.	0.02	n.d.	n.d.	0.02	n.d.
ZnO	n.d.	0.02	0.02	0.02	0.02	0.02	0.02
Rb_2O	0.01	0.01	0.01	0.01	0.01	0.05	n.d.
SrO	0.08	0.15	0.10	0.11	0.11	0.07	0.08
ZrO_2	0.02	0.03	0.03	0.03	0.02	0.02	0.02
BaO	n.d.	n.d.	n.d.	n.d.	n.d.	0.29	n.d.

n.d.: not detected or below the detection limits.

The presence and the absence of some mineralogical/phase contents of the semi-fused potsherds assisted to estimate firing temperature. Illite/muscovite was the only clay mineral identified in the previous study for the potsherds [6]. Illite/muscovite or mica structure breaks down in the range of 900–1000 °C [7–10]. These clay minerals were not found in the samples. For further stages of firing, from the destruction of illite, an intermediate phase between spinel ($MgO{\cdot}Al_2O_3$) and hercynite ($FeO{\cdot}Al_2O_3$) originates [11]. Calcite decomposition into CaO and CO_2 begins around 650 °C and it is completed up to temperature of 900 °C. Dolomite has the decomposition with two stages beginning at around 650 °C. After the decomposition of dolomite into calcite and magnesia, decarbonation of calcite again continues up to 900 °C [7,9,12]. It is concluded that the decarbonation of calcite may extend to 1100 °C for calcite rich systems [13]. However, secondary calcite may occur in ceramics as a result of post-burial deposition processes due to recarbonation of lime [7]. Pyroxenes like diopside and augite may be generated from dolomite and silica reactions at 800–900 °C. Gehlenite may be formed at 850 °C with the reaction of CaO and illite structure [14]. Akermanite occurs during firing as a product of solid-state reactions between clay minerals and carbonates in the temperature range of 900–1000 °C [15]. Quartz and feldspars can persist up to 1000 °C [16]. Crystallization of leucite from amorphous phase is possible with long heat treatment above 1000 °C for dental purposes [17]. Formation of leucite in porcelain from K-feldspar, however, requires higher temperatures around 1200 °C [18]. Moreover, these new mineral formation temperatures may be affected by firing type such as pit or kiln firing. For instance, calcite decomposition ends around 825 °C in kiln firing but it tends to 875 °C in pit firing conditions [3]. These reactions, of course, are related with peak firing temperature, soaking time, abundance and the type of minerals/phases present, firing atmosphere, pressure, specific surface area of components, etc.

Mineralogical/phase content of the investigated semi-fused potsherds is quite interesting that calcite, diopside/augite and leucite were found together in the samples, except HCR4. It suggests that these potsherds were exposed to partially firing. It may result with difference in temperature reached for a pottery due to the thickness of the body even it was placed in a uniform flame of firing [2]. In this case, the body obtained from firing could exhibit homogenous texture. The investigated potsherds contain different textures together. Some parts of the potsherds were about to be fused. It suggests that some parts of these potsherds were over-fired in a fixed position somewhere near the flame source. Considering the obtained results of mineralogical and phase analysis, leucite formation on the samples were provided by over-fired parts of the potsherds at around 1200 °C. The other parts of the pottery could not complete calcite decomposition relatively at lower temperatures ranging from 1000 to 1100 °C. The absence of clay minerals such as illite/muscovite and the presence of pyroxenes such as diopside/augite indicate that the temperature reached during firing was not lower than 1000 °C for the potsherds. While the abundance of new mineral/phase formations was increasing at one part of the potsherd, the other part should not be exposed to higher temperature for decarbonization of calcite. If the potsherds were homogeneously fired, calcite decomposition would be completed or leucite formation could not be provided during firing depending on the firing temperature. Moreover, the abundant mineralogical and phase content also require prolonged times of firing. Surface or pit firing has high heating rates with short residence time. But, in kiln firing, the heating rate is generally low, residence time is long. It is also

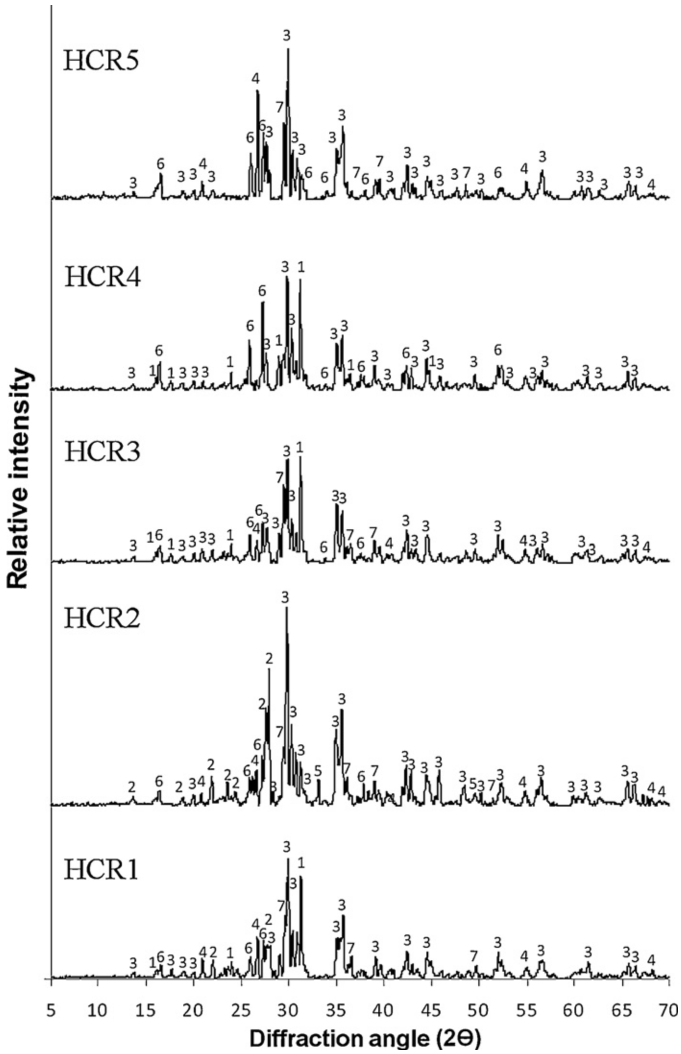

Fig. 3. Representative XRD spectra of semi-fused potsherds (1: akermanite, 2: plagioclase, 3: diopside/augite, 4: quartz, 5: hematite, 6: leucite and 7: calcite).

worth to mention that during open or pit firing, flame distribution can be supplied on potteries more homogenously than kiln firing since potteries were piled up and covered with fuel. Once the firing chamber is separated from the potteries in kiln firing technique, distribution of flame homogeneously in the kiln structure requires particular design. The most probable firing technique to obtain such kind of mineralogical or phase content together requires using a kiln rather than the others. Archeological excavations performed at Harabezikan could not approve a kiln or firing facility in the ceramic workshop. But, abundant new minerals especially leucite formation requires prolonged firing at around 1200 °C. However, semi-fused potsherds also have buff color. Firing in reductive atmosphere provides darker color for pottery [19,20]. Considering the presence of hematite in HCR2 sample, they should be fired in oxidative conditions.

3.2. Microstructural analysis

Some changes with increasing temperature in clay based ceramics can be described as (i) interactions between clay matrix and grains, (ii) shape changes of grains, (iii) increase of the aggregation rate within the clay matrix with the formation of secondary porosity and (iv) formation of intergranular bridges. These changes become more evident in calcareous clays than the siliceous materials including clays [21]. Since all the samples contain high amounts of calcium, SEM images exhibited predominantly arrangements of calcium rich new mineral formations in the microstructure of the samples (Fig. 4). Considering XRD results Ca, Mg rich aluminum silicate assemblages given in Fig. 4 should be the formation of pyroxenes and melilite such as diopside/augite and akermanite, respectively.

Quartz is one of the primary components of clay based ceramics with high melting temperature. It is considered that quartz is relatively insoluble below 1250 °C and above 1250 °C, dissolution of quartz forms silica-rich amorphous solution rims around quartz grains [18]. Quartz grain dissolution into vitrified clay matrix of the sample may easily be distinguished by the atomic contrast difference in BSE images of sample HCR1 and HCR2 (Fig. 5). The absence of quartz and the abundance of leucite for HCR4 sample suggest that it was exposed to the firing at around 1200 °C.

Feldspar is believed to melt around 1100 °C in the contact zone between feldspar crystals and clay relicts and potash

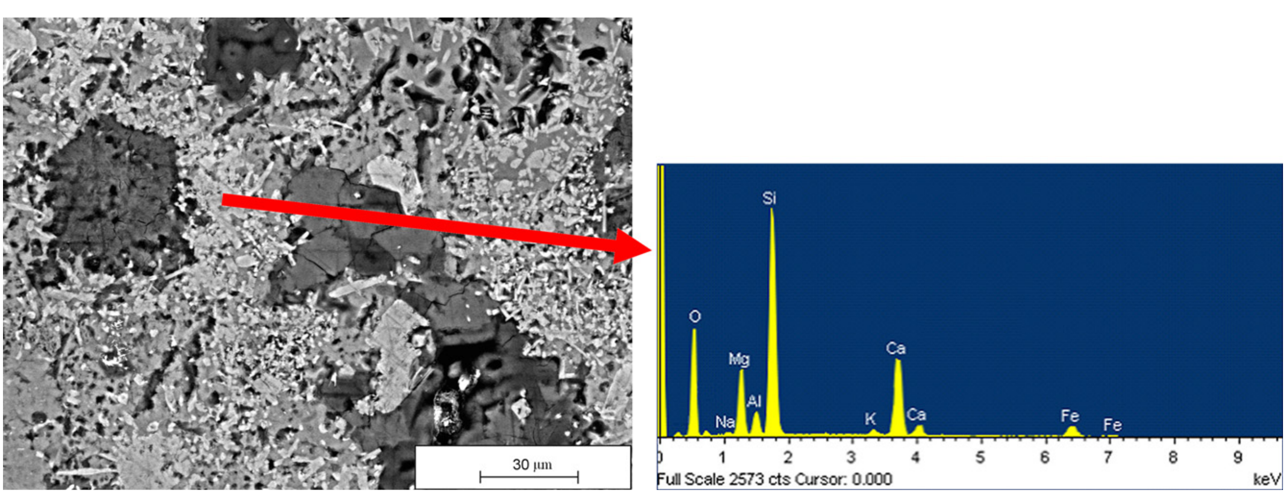

Fig. 4. BSE image of Ca, Mg rich aluminum silicate assemblages in HCR2 sample.

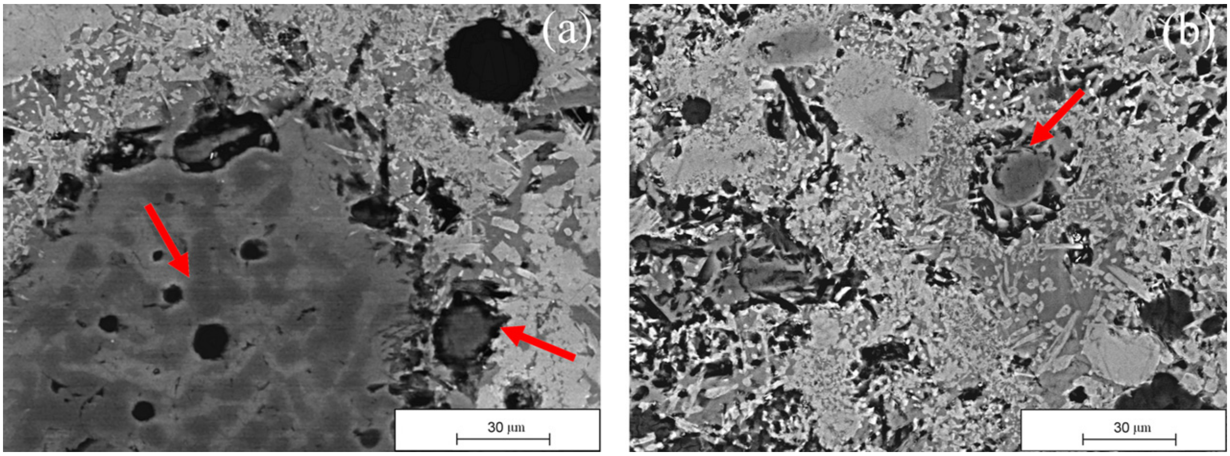

Fig. 5. Quartz grain dissolution into vitrified clay matrix of the samples of (a) HCR1 and (b) HCR2.

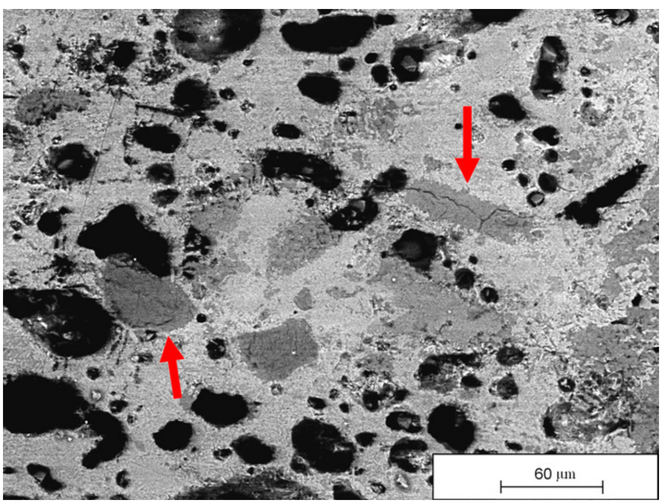

Fig. 6. BSE image of semi-dissolved potassium rich aluminum silicate grains in sample HCR5.

feldspar never crystallizes from its own melt and is known to dissociate into glass and leucite around 1170 °C [18]. The presence of abundant calcium in the samples hinders potassium rich rearrangements to be confirmed exactly by EDX analysis due to the gaining calcium peaks but, semi-dissolved potassium rich aluminum silicate grain shown in Fig. 6 may belong to K-feldspar leading to formation of leucite in the vitrified body.

It also should be noticed that the shape of almost all the pore structures are rounded and found in calcium rich locations. These are secondary porosity formations which were formed during decarbonization and densification of the bodies.

4. Conclusions

Chemical analysis results lead to suggest that semi-fused potsherds investigated in this study were produced from the same raw materials used for pottery production at Harabebezikan. Mineralogical/phase analysis showed interesting results in which calcite, diopside/augite and and leucite were found together, except one sample. It indicated that they were partially fired. The formation of leucite and dissolution of silica grains into vitrified matrix require high temperature around 1200 °C. Abundant new mineral formations in the samples also need prolonged firing. The investigated samples also have buff color which indicates oxidative firing condition. Therefore, the most probable firing technique to obtain such kind of potsherds is kiln firing. The absence of kiln in the Hellenistic workshop suggests that it should be destroyed in the past.

Acknowledgments

I gratefully thank to Dr. A. Oğuz Alp from Anadolu University (Turkey) for providing the samples and contributions to introduction of this study.

References

[1] A.O. Alp, M. Tekinalp, in: N. Tuna, et al. (Eds.), Harabebezikan Excavation: 1999 Season, Salvage Project of the archaeological Heritage of the Ilısu and Carchemish dam Reservoirs Activities in 1999, Middle East Technical University, Ankara, 2001, pp. 381–400.

[2] M. Maggetti, Ch. Neururer, D. Ramseyer, Temperature evolution inside a pot during experimental surface (bonfire) firing, Appl. Clay Sci. 53 (2011) 500–508.

[3] L. Maritan, L. Nodari, C. Mazzoli, A. Milano, U. Russo, Influence of firing conditions on ceramic products: experimental study on clay rich in organic matter, Appl. Clay Sci. 31 (2006) 1–15.

[4] http://www.mta.gov.tr/v1.0/turkiye_maden/il_maden/pdf_2010/sanliurfa.pdf (13/09/2011).

[5] http://www.mta.gov.tr/v1.0/turkiye_maden/il_maden/pdf_2010/gaziantep.pdf (13/09/2011).

[6] A. İssi, A. Kara, A.O. Alp, An investigation of Hellenistic period pottery production technology from Harabebezikan/Turkey, Ceram. Int. 37 (2010) 2575–2582.

[7] C. Papachristodoulou, A. Oikonomou, K. Ioannides, K. Gravani, A study of ancient pottery by means of X-ray fluorescence spectroscopy, multivariate statistics and mineralogical analysis, Anal. Chim. Acta 573 (2006) 347–353.

[8] R.W. Grimshaw, Reactions at high temperatures, in: The Chemistry and Physics of Clays, Techbooks, India, 1971, p. 727.

[9] L. Maritan, C. Mazzoli, L. Nodari, U. Russo, Second iron age grey pottery from Este (northeastern Italy): study of provenance and technology, Appl. Clay Sci. 29 (2005) 31–44.

[10] J.M. Bhatnagar, R.K. Goel, Thermal changes in clay products from alluvial deposits of the Indo-Gangetic plains, Constr. Build. Mater. 16 (2002) 113–122.

[11] M.M. Jordan, A. Boix, T. Sanfeliu, C. de la Fuente, Firing transformations of cretaceous clays used in the manufacturing of ceramic tiles, Appl. Clay Sci. 14 (1999) 225–234.
[12] S. Shoval, Using FT-TR spectroscopy for study of calcareous ancient ceramics, Opt. Mater. 24 (2003) 117–122.
[13] M.J. Trindade, M.I. Dias, J. Coroado, F. Rocha, Mineralogical transformations of calcareous rich clays with firing: a comparative study between calcite and dolomite rich clays from Algarve, Portugal, Appl. Clay Sci. 42 (2009) 345–355.
[14] G. Cultrone, C. Rodriguez-Navarro, E. Sebastian, O. Cazalla, M.J. De La Torre, Carbonate and silicate phase reactions during ceramic firing, Eur. J. Miner. 13 (2001) 621–634.
[15] M. Dondi, G. Ercolani, B. Fabbri, M. Marsigli, Chemical composition of melilite formed during the firing of carbonate-rich and iron-containing ceramic bodies, J. Am. Ceram. Soc. 82 (1999) 465–468.
[16] A. Iordanidis, J. Garcia-Guinea, G. Karamitrou-Mentessidi, Analytical study of ancient pottery from the archaeological site of Aiani, northern Greece, Mater. Charact. 60 (2009) 292–302.
[17] M. Novotna, J. Maixner, X-ray powder diffraction study of leucite crystallisation, Z. Kristallogr. (2006) 455–459.
[18] Y. Iqbal, W.E. Lee, Microstructural evolution in triaxial porcelain, J. Am. Ceram. Soc. 83 (2000) 3121–3127.
[19] 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.
[20] 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.
[21] M.P. Riccardi, B. Messiga, P. Duminuco, An approach to the dynamics of clay firing, Appl. Clay Sci. 15 (1999) 393–409.