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AN ARCHAOMETRIC STUDY OF PROVENANCE AND FIRING TECHNOLOGY OF HALAF POTTERY FROM TILKITEPE (EASTERN TURKEY)

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ABSTRACT

The approximation of the raw material source as well as the minimum and maximum firing temperatures in the pottery production technology can be determined depending on the mineralogical and chemical changes in the ceramic components. For the determination various analytical techniques are used such as X-ray diffraction (XRD), thermal analysis (TGA-DT), Scanning electron microscope (SEM), X-ray fluorescence spectrometry (XRF) and inductively coupled plasma (ICP). In this paper the possible clay resources of Halaf pottery from Tilkitepe is required to determine. The analyzed pottery fragment and the clay samples were collected around the mound. Experimental studies were carried out at temperatures of 600 °C, 700 °C, 800 °C and 900 °C. The results show that the Halaf type ceramic piece from the mound is most probably made using local clay sources in the region and fired at temperatures below 800 °C under oxidation conditions.

KEYWORDS: Tilkitepe, Halaf, provenance studies, firing technology, clay mineralogy, chemical analysis.

1. INTRODUCTION

Archaeometry studies of clay paste and ceramic products are essential for classification and characterization that provide data on the provenance of the raw material, ancient technologies for pottery production and possible function and social meaning of the products (Meloni *et al.*, 2000; Zeinab 2018). Clays are hydrous aluminosilicates generally defined as minerals that are the colloidal fraction ($<2\mu\text{m}$) of soils, sediments, rocks and water, and may consist of mixtures of fine grained clay minerals and non-clay minerals such as quartz, calcite and metal oxides (Rafatullah *et al.*, 2010). All these minerals are deposited in different environments by various transport methods. Minerals undergo change as a result of different operative conditions the firing process. For example, hematite is formed only in the oxidation conditions, or the sanidine is found only in ceramics containing initially low amount of CaO in the matrix (De Benedetto *et al.*, 2002). Thus determining the conditions of the firing process in ceramic production, i.e. firing time, temperature and atmospheric conditions play a fundamental role in contributing to the final properties of the products (Santos *et al.*, 2009). The archaeometric characterization of pottery mainly focuses on defining the petrological, mineralogical, chemical and textural composition of the vessels. The approximate firing temperature can be determined by various techniques like XRD, FTIR and TG-DTA which depends on mineralogical and structural characteristic changes within clayey material (Cogswell *et al.*, 1996; Singh and Sharma, 2016).

The provenance studies on clay sources make possible to define the raw material like a fingerprint. These data can be compared with results of analysis on archaeological ceramic artifacts (Meloni *et al.*, 2000). It is important to identify the presence and quantity of trace elements, which are usually specific in a raw material from a particular geological origin. The common techniques used for this purpose are ICP and XRF (Adriaens, 2005). In addition, SEM is used to identify unknown minerals and provides complementary information about these minerals which have very small or indefinite optical properties (Adriaens, 2005).

The purpose of this work is to: (1) identify possible sources of raw material for the earliest ceramic in Van Lake Basin; (2) discuss whether Halaf ceramic from Tilkitepe is a local production product or come from another place; (3) obtain information about the production process and firing technology of Halaf pottery (Bertolino and Fabra, 2003). In order to answer these and other questions one Halaf type ceramic piece from Tilkitepe was selected for analysis. Also, clayey samples were collected from very close

vicinity around Tilkitepe archaeological site situated at the eastern shore of Lake Van in Eastern Turkey.

The changes in mineral structure during firing process were evaluated at different temperatures. XRD and SEM techniques were used to determine mineralogical composition of the Halaf type ceramic and thermal treatment clayey samples. In addition, thermal analysis (TG-DTA) was used to determine the different steps of weight loss due to release of adsorbed water (dehydration reactions), OH (dehydroxylation reactions) and CO₂ (decarbonation reactions) for the selected clayey sample (Ayari *et al.*, 2005). Minor and major elements were studied by ICP and XRF spectrometry.

2. SITE LOCATION AND SIGNIFICANCE

Tilkitepe, one of the most important archaeological places, lets to generate concrete information for the prehistory of the Near East. The mound is located 7 km southwest of the city center of Van, about 6 km south of former Urartian capital Tushpa of the early 1st millennium B.C.E. and about 1 km away from the coastline of the Lake Van (Fig. 1). Korfmann speculated (1982) whether Tilkitepe was a kind of trade and manufacturing center in the northeast corner of the region in which the Halaf settlements spread in 6th millennium B.C.E. It was suggested that those settlements in a diffusion area extended in eastern Turkey as well as northern Syria and Iraq, are mostly small sized and short-lived sites. But also a few quite big and continuously sedentary villages are known (Akkermans, 1993; Frangipane, 1996).

The results of geological investigations and the archaeological surveys in the Lake Van basin were evaluated together then it was attempted to reconstruct the environmental conditions, which indicate that the region is a seasonal hunting and raw material processing center (Kılıç, 2013). Accordingly it was stated that Tilkitepe and other few Chalcolithic settlements in the vicinity discovered during a survey in 2004 (Marro and Özfırat, 2005) are described not to be permanent and long-term settlements as it generally suggested for Halafian ones (Kılıç, 2013). This opinion can be also applied to two other Halaf sites discovered in the Muş Plain, which is the western extension of the Lake basin (Rothman, 1992, 1994).

The mound Tilkitepe is heavily damaged in the present day, despite the fact that it is located within the area of constantly guarded city's airport. The northern part of the round hill, 55 m in diameter, was completely flattened by bulldozer and the original 6 m height measured earlier fell considerable down (Kılıç 2006).

The first excavations conducted in 1899 by Belck, who considered the mound a tumulus because of many skeletal remains; Reilly reached 1937 the bad

rock 2 m below the present surface, and determined three archaeological phases; lastly Mr. and Mrs. Lake worked at Tilkitepe for several weeks during their archaeological researches in the region in 1939 (Korfmann, 1982).

Tilkitepe is a significant archaeological site in terms of cultural sequence from Halaf period extending until the Iron Age. Although the stratification started with Phase I from top to down (earlier stratigraphy), the Urartian ceramic pieces collected from

the surface belong to a new level named as Phase 0, in which there are no features of architectural remain (Korfmann, 1982). On the surface also some examples of polychrome painted wares were identified including wheel-made pottery dated to the end of the 3rd Millennium or to the beginning of the 2nd Millennium B.C.E. compared with the similar ones found in Keban area at the river Euphrates and further west (Korfmann, 1982).



Figure 1. The map of the Lake Van basin (eastern Turkey) with location of the prehistoric site of Tilkitepe

The most prominent type of pottery from the surface to 1.4 m deep, Phase I, is reddish beige in color, slightly smoothed and burnished, handmade and with pink-red core, beige-white or red-pink slip and straw and sand temper. %15 of these ceramic examples were defined locally and named as "Tilkitepe Ware", which have red painted decoration with wavy or straight parallel lines on the outer surface from mouth to down (Korfmann, 1982). In addition, there are examples of black burnished, handmade and mineral tempered pottery, which belongs to the Early Bronze Age culture of "Kura-Araxes" or "Karaz" (Korfmann, 1982). It is reported that this material was concentrated in the upper part of the Phase I, so this phase seems to be separated into two levels, IA and IB (Kılıç, 2006).

Mr. and Mrs. Lake reviewed the details of the earlier excavations and discovered a thick ash layer, which was 4 m below the surface and divided the

Phase II into two different levels, IIA and IIB (Korfmann, 1982; Kılıç, 2006). In the Level IIA above the ash layer "Tilkitepe Ware" with red painted decoration is still available and below disappeared totally. As it goes deeper, a pottery type was dominant which was hand-made, brown or matte red in color, slipped and well burnished, thick sand and straw tempered. The forms of this pottery consisted cups and glasses, e.g. "Coba bowls", which are dated to Late Obeid period. Reilly records only one piece of Halaf ceramic at 2.75 m depth (Korfmann, 1982).

Phase III bearing the traces of Halaf culture, which is separated from the previous phase by a hiatus, is defined as the main settlement among the phases found at Tilkitepe in terms of the area covered by the settlement. Most of the potsherds collected from this phase are described as having thin clayey and being pink or yellowish gray in color, cream or white slipped. On the outer surface or both surfaces of the

vessels is decorated by black color with geometric motifs. This type of pottery is emphasized as having many similarities with the ceramic found in northern Syria and Iraq which is the homeland of the Halaf culture.

Tilkitepe is located in the extreme northeast direction of the extending area of the Halaf culture (Frangipane 1996; Palumbi 2011), and the Phase III was intended to be placed in its later stages (Korfmann, 1982; Akkermans, 1997). While earlier an origin was sought between the regions of the Lake Van and northern Iraq (Mallowan, 1936), today a Mesopotamia-oriented approach has still dominated (Akkermans, 1997). However, the studies carried out in the region of Jezirah in Syria revealed the transition period from pre-Halaf to Halaf period (Akkermans, 1997). Accordingly, it is argued today that the Halafian groups has not used this wide geography at same time, and spread out gradually towards the different directions from the Jezira region where the culture emerged (Frangipane, 2007).

Recently researchers generally agree that Halaf culture actually emerges in the Late Neolithic period at the end of the 7th millennium B.C.E. and the Halafian painted pottery was spread between 6000-5900 B.C.E. in northeastern Syria and northern Iraq (Akkermans and Schwartz, 2003; Cruells and Nieuwenhuys, 2004; Campbell 2007; Nieuwenhuys 2007; Özbal 2011). This pottery is considered to be the most striking evidence of the close ties between the Halafian communities (Frangipane, 2007), and described before as "luxury" and high quality pottery that might be exchanged as prestigious substance among the local elites (Leblanc and Watson, 1973), and this view was supported with the Neutron Activation Analysis (NAA) (Davidson and McKerrel, 1976). Accordingly it was determined that painted Halaf pottery was imported from Tell Arpachiyah to Tepe Gawra in northern Iraq (Davidson and McKerrel, 1980; Davidson, 1981). This determination may be valid also for Halaf settlements in southeastern Turkey.

Another study, conducted by Electron Microscopy in the 1980s, showed that the Halaf pottery from settlements in Northern Iraq was not imported, and that regional clay reserves were being used (Steinberg and Kamilli, 1984). What interesting in this study is that the material and application technique of paint is standard, while the clay component is vary. The new data from Tell Sabi Abyad level 6 (Burnt Village) caused the interpretation that the Halaf pottery is a regional production and produced in household levels by families, and there are no evidences about an "elite" group who support and/or control this production activity (Nieuwenhuys, 2010).

3. MATERIAL AND METHOD

For the analytical progress of this study, one Halaf type ceramic piece was taken from the surface of the mound (Figure 2). This sample was mechanically cleaned using emery paper and was washed with distilled water to remove the impurities before being powdered in a mortar. In order to fix the possible source of raw material clayey samples were collected from a drilling, which was about 70 m east of the mound of Tilkitepe, in three different depths (0-2 m, 2-6 m and 6-12 m). Samples taken from each depth were labeled and stored in polyethylene bags.

It is known that the levels of Halaf culture reach to 2 m depth from the present surface (Korfmann, 1982; Kılıç, 2006). Therefore the clayey sample from the depth of 2-6 m was selected for the determination of the firing temperature of ceramic piece. Each a mass of 10 g clayey samples were heated from 600 °C to 900 °C in 100 °C intervals with a rate of 10 K/min, and were thermally treated by keeping at each temperature for 2 hours (h) in an electrical kiln under oxidizing conditions. Thermal treatment time of clayey samples was selected as 2 h because specific surface area did not change significantly after this time.

Thermally untreated clayey sample was marked as T_R , and Halaf type ceramic piece as T_{HC} . Clayey samples taken from each depth were specified as 0-2 m, 2-6 m and 6-12 m and thermal treated samples were labeled as T_{600} , T_{700} , T_{800} and T_{900} .

The samples including possible raw material, thermally processed samples and ceramic piece were chemically characterized (Eiland and Williams, 2001). The weight losses were determined by Thermo-Gravimetric (TG) and Differential Thermal Analyses (DTA) with an instrument of Rigaku 2.22E1 Thermal Analyzer by heating from 10 to 1099 °C at a rate of 20 °C min⁻¹ in atmospheric air. Quantitative chemical analysis was determined by X-ray fluorescence (XRF) spectroscopy using a Philips PW 2400 spectrometer, and minor elemental analysis was performed by ICP instrument. Mineralogical analysis of raw materials, thermally treated samples and ceramic piece were determined by X-ray diffraction (XRD) analysis on a Philips PW 1830-40 X-ray diffractometer with a Cu-K radiation (Maritan *et al.* 2006).

4. RESULTS AND DISCUSSION

The dimensions of the ceramic part are 4.5 x 3 cm and the thickness is 8 mm. The color of outer surface is beige, there are brown stains on the beige interior surface, and the section is pink colored and less porous. Powdered ceramic clay is brown (Munsell: 7.5YR 5/4), fine and sand tempered (Figure 2). The

colors of raw and fired clay samples are given in the Table 1 according to Munsell Soil Color Charts (Edition 1975).

The ceramic colors give an idea about the minerals in the clayey material. Red color corresponds to iron oxide while white is a rich titanium oxide, yellow is related to FeOOH goethite, and brown color corresponds to a difference in surface oxidation during firing (Uda, 2005). In particular, the amount of iron in raw material and the redox conditions of firing determine the color of the ceramic. The amount of carbonate in raw material also determines the color;

the pottery produced by using carbonate-free clays become reddish brown when it fired in an oxidizing atmosphere, and dark grey or black when it fired in a reductive atmosphere. Conversely, when carbonate-rich clays used the ceramic color becomes creamy in an oxidizing atmosphere and brownish in a reductive atmosphere. Hematite occurs at an appropriate temperature of the oxidation firing conditions. Hematite is the mineral phase in the ceramic that gives the main pigmentation (Nodari et al., 2007).

Table 1. The colors of raw and thermally treatment clay samples according to the MSCC (1975).

Sample	Munsell Color System		
	0-2 m	2-6 m	6-12 m
T _R	2.5Y6/2 (light br. gray)	5Y7/2 (light gray)	10YR8/2 (light gray)
T ₆₀₀	7.5YR6/4 (light brown)	7.5YR6/4 (light brown)	7.5YR7/4 (pink)
T ₇₀₀	7.5YR6/4 (light brown)	7.5YR6/4 (light brown)	7.5YR7/4 (pink)
T ₈₀₀	7.5YR6/6 (red. yellow)	7.5YR6/4 (light brown)	7.5YR7/4 (pink)
T ₉₀₀	7.5YR6/6 (red. yellow)	10YR6/4 (light yel. brown)	10YR7/4 (very pale brown)



Figure 2. Halaf type ceramic piece taken from the surface of the mound of Tilkitepe.

4.1. Thermal Analysis

The thermal curves of the raw clayey material taken from 2-6 m depth are given in Figure 3. The DTA curves show the effect of energy changes (endothermic or exothermic reactions) in a sample. The TG curves ideally indicate only weight changes during heating (Guggenheim et al., 2001). Some mineral phases were detected in the DTA and TG patterns and were evaluated as follows.

In particular, the thermal diagram probably shows endothermic peak at 133 °C, which is 2.9% weight loss due to the removal of hygroscopic water in the illite. The TG curve shows a gradual decrease in the range of 180- 540 °C and is due to the release

of adsorbed water from clay minerals. As the temperature increases, an endothermic band occurs at 579°C for sample was due to the dehydroxylation of the clay minerals (Mahmoudi et al., 2008; Çelik, 2010) Moreover, the DTA diagram shows decarbonation of calcite at 852 °C, where a weight loss of 9% is observed (Maritan et al., 2006). After about 900 °C appears weak various exothermic effects, belong to crystallization of high temperature phases (Trindade et al., 2009).

4.2. XRD Analysis

The X-ray powder diffraction results of T_{HC} and thermally treatment clayey materials (600-900 °C) are shown in Fig. 4a and b.

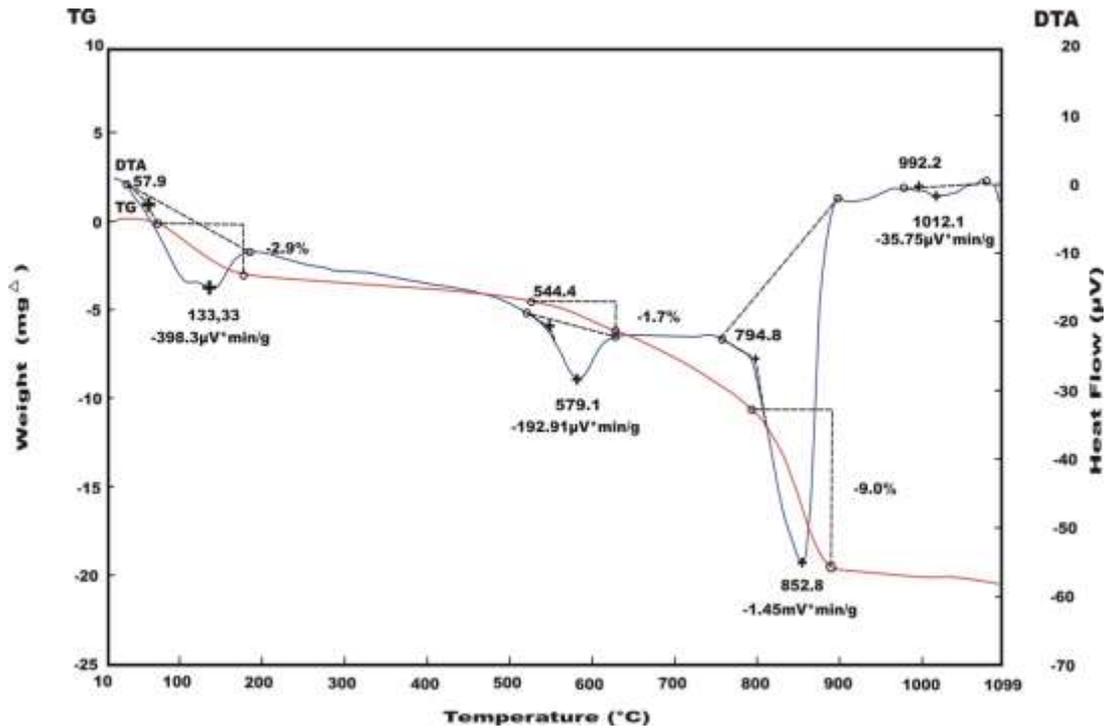


Figure 3. The thermal curves of the raw clayey material taken from 2-6 m depth around the mound of Tilkitepe.

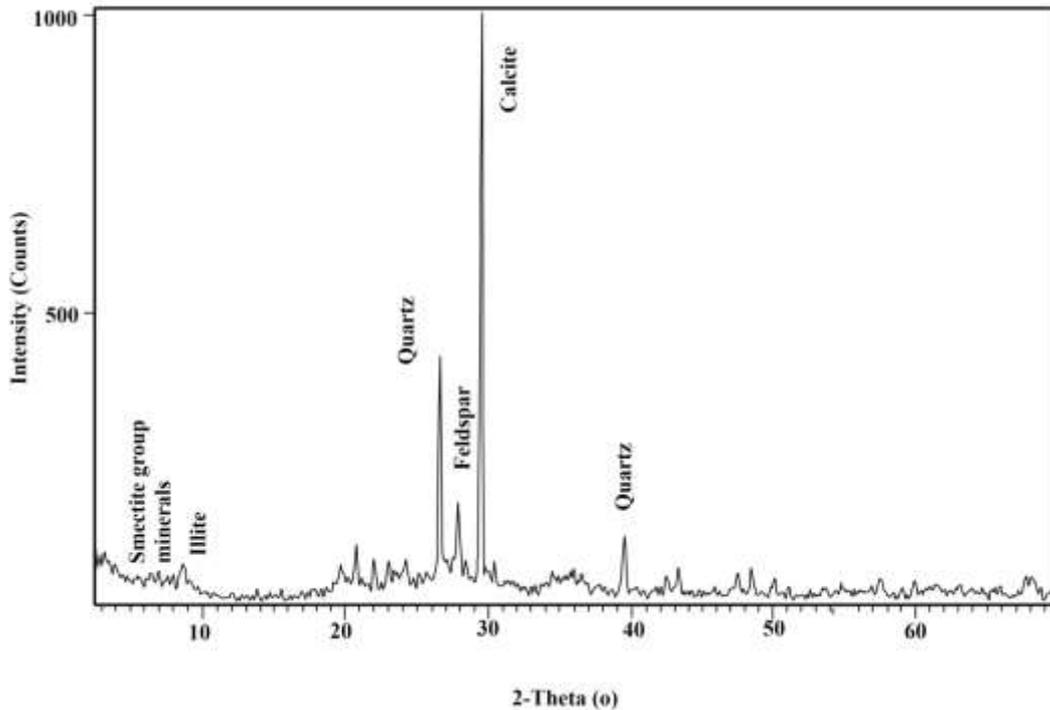


Figure 4a. XRD pattern of Halaf type ceramic from obtained Tilkitepe.

The analyzed ceramic piece is composed of clay minerals and non-clay minerals such as smectite group minerals, calcite (CaCO₃), quartz (SiO₂), feldspar group minerals (KAlSi₃O₈ - NaAlSi₃O₈ - CaAl₂Si₂O₈), illite / mica group minerals ((Si_{8-x}Al_x)(Al₄, Fe₄, Mg₄, Mg₆)O₂₀(OH)₄K_x), mixed layer clays, kaolinite group mineral, amorphous materials, magnetite (Fe²⁺Fe³⁺₂O₄), chlorite group minerals

(Mg,Fe,Li)₆AlSi₃O₁₀(OH)₈, zeolite group minerals and talc group mineral. Smectite group minerals are dioctahedral smectites such as montmorillonite ((Na,Ca)_{0,33}(Al_{1,67}Mg_{0,33})Si₄O₁₀(OH)₂.nH₂O), nontronite and beidellite and trioctahedral smectites such as hectorite (Na_{0,33}(Mg_{2,67}Li_{0,33})Si₄O₁₀(OH)₂.nH₂O) and saponite (Na_{0,33}(Mg_{2,67}R_{0,333})(Si_{3,34}Al_{0,66})O₁₀(OH)₂.nH₂O).

(Grim, 1968; Pinnavaia, 1983). Illite group minerals include the clay-micas. The difference from the smectite group is the presence of potassium (K^+). Illite is the only common mineral and its chemical formula is given as $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$ (Wentworth, 1970; Eberl and Hower, 1976). Kaolin group includes the minerals kaolinite, dickite, halloysite, and nacrite (polymorphs of $Al_2Si_2O_5(OH)_4$). The zeolite and feldspar groups are in the tectosilicates sub-

division of the silicates group. Zeolites are hydrous aluminum silicates containing sodium or calcium and can replace one another. These minerals are generally located in igneous rocks. Mixed-layer clay minerals are two or more layer types (i.e. mica, smectite, chlorite etc) are intermixed in vertical stacking sequence within a single crystal. Chlorite group clay minerals can be described as hydrated aluminum silicate with magnesium.

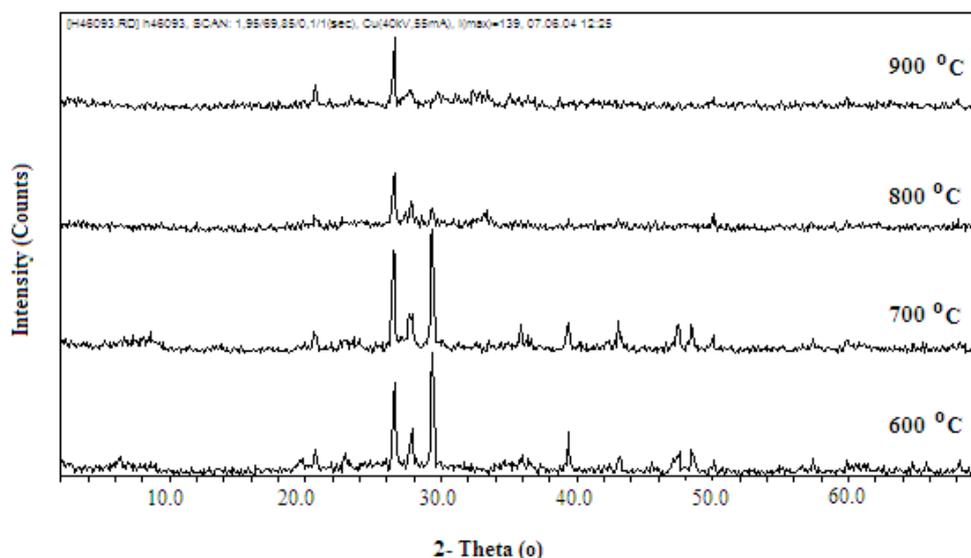


Figure 4b. XRD patterns of heated clay taken around the mound of Tilkitepe in depth of 2-6 m.

From Fig. 4a, the XRD diffraction peaks of quartz and calcite are high and narrow, which means that the original firing temperature was not high (Zhu et al., 2014). Low-fired ceramics are characteristically complex mixtures of clays, carbonates, SiO_2 and locally varying silicates (Eiland and Williams, 2001). In particular, the presence of clay group minerals and calcite allows us to assume that the parts are subject to a firing temperature of less than $800^\circ C$. Calcite, of which microfossils are composed, actually decomposes at a temperature higher than $800^\circ C$ and leaves only the so-called traces (Barone et al., 2003). Also, the chlorite begins to decompose between $500-600^\circ C$ and disappeared $650^\circ C$ (Maritan et al., 2006).

It is known that kaolinite and calcite minerals do not change at low temperatures, ie $300-400^\circ C$. Kaolinite decreases at higher temperatures, ie $400^\circ C$ and $500^\circ C$, and disappears completely at $600^\circ C$, although metakaolinite is still present (Eiland and Williams, 2001). From Fig. 4b, the maximum diffraction at 10° corresponds to dehydroxylated mica-like phase (illite / mica group minerals). The mineralogical crystalline phases found in ceramics depend on the regional geology, production habits and experience of potters (Iordanidis et al., 2009). Therefore,

differences in the intensity of the peaks can be observed between the data of the experimentally obtained laboratory products and the data of the archaeological samples. In Fig. 4a, there are many criteria that are effective for changes in the intensity of mineral groups up to $10^\circ 2\theta$, such as temper, heating rate and the time of exposure to temperatures (Gosselain, 1992). According to Sarıkaya et al (2000), the peak of clay mineral (Ca-montmorillonite) decreases in intensity while maintaining its position after thermal treatment between $100-300^\circ C$. As the temperature increases it decreases further and changes the position of the peak. Also, 2 hours is sufficient for firing time. The increase in the firing time does not have a significant effect on the clay minerals (Sarıkaya et al., 2000). However, mineralogical changes to new secondary phases could take place during the burial period (Bugoi et al., 2008). The peak density of this phase disappeared with increasing firing temperature from $700^\circ C$ to $800^\circ C$ and hematite formation occurs at about $800^\circ C$ (Nodari et al., 2007; Trindade et al., 2009). At $700^\circ C$ $CaCO_3$ begins to decompose yielding CaO $800^\circ C$ (lime) with release of CO_2 from the fired body. This process is often very effective at about and the re-

maining calcite is almost lost due to increased firing temperature (Trindade *et al.*, 2009). The shape and density of the feldspar reflections change with increasing temperature as a result of the compositional changes (Riccardi *et al.*, 1999). Quartz remains as the

most abundant phase at any temperature in all thermally treatment samples. The detailed clay analyses of the thermally treatment materials and ceramic piece are given in Table 2.

Table 2. Results of analyses of the raw and thermally treatment clay materials from different depths from the immediate vicinity of Tilkitepe.

Sample	Mineralogic analysis data (XRD)		
	0-2 m	2-6 m	6-12 m
T _R	quartz, calcite, feldspar, smectite (montmorillonite), amorphous material, mica (biotite), illite, kaolinit-serpentine group minerals, mixed layered clay mineral	calcite, quartz, feldspar, amorphous material, smectite (montmorillonite), chlorite group, clay minerals, amphibole group mineral, serpentine group minerals, mixed-layer clay mineral kaolinite, illite	calcite, amorphous material, feldspar, quartz, kaolin-serpentine group minerals, smectite clay mineral group, mixed layer clay minerals, illite
T ₆₀₀	calcite, quartz, feldspar, amorphous material, smectite group clay mineral, illite	calcite, quartz, feldspar, amorphous material, smectite group clay mineral, illite, periclase	calcite, feldspar, quartz, amorphous material, mix layer, periclase
T ₇₀₀	quartz, feldspar, calcite, amorphous material, smectite group clay mineral	calcite, quartz, feldspar, illite, smectite group clay mineral, amorphous material, periclase	quartz, calcite, amorphous material, feldspar, smectite group clay mineral, illite
T ₈₀₀		quartz, feldspar, low calcite, amorphous material, hematite, smectite group clay mineral	
T ₉₀₀		quartz, amorphous material, feldspar, basanite, opal CT	

4.3. XRF Analysis

The nature of the clay minerals can be determined from the calcium oxide (CaO) percentage as calcareous or non-calcareous clay. The calcareous nature of clay minerals can be understood from the percentage of calcium oxide (CaO). Clay containing more than 6% of CaO is defined as calcareous clay whereas less than 6% of CaO is known as non-calcareous clay. The ratio of iron oxides (Magnetite-Fe₃O₄ and Hematite-Fe₂O₃) in the sample shows the atmospheric condition of the sample fired during manufacturing. If the amount of magnetite in the sample is large, it indicates that the firing process is performed in a reducing atmosphere and when the amount of hematite in the sample is high, it is made in an oxidizing atmosphere (Mohamed Musthafa *et al.*, 2010). The quantitative chemical analysis of raw material and ceramic samples obtained by X-ray fluorescence

spectrometry technique is given in Table 3. The content of CaO is higher than 6 % in ceramic and all raw clayey the samples. Therefore, the examined ceramic and possible raw materials are of calcareous nature (Barone *et al.*, 2003). Also, the XRD pattern indicates that the reddish brown pigment is composed mainly of hematite (α Fe₂O₃) (Uda, 2005).

The clayey materials have high SiO₂ and Na₂O, moderate Al₂O₃ and very high CaO and MgO content. The high content of CaO and MgO is related to the high abundance of carbonates. Besides, low K₂O/Na₂O ratios indicate a low illite content and the high SiO₂/Al₂O₃ ratios suggest the predominance of quartz over clay minerals (Trindade *et al.*, 2009).

In addition, the trace elements in raw material and ceramic samples are given in Table 4. Eleven elements were determined by using inductively coupled plasma source.

Table 3. Results of XRF analysis (%)

oxides	T _{HC}	T _R (0-2 m)	T _R (2-6 m)	T _R (6-12 m)
Na ₂ O	2.0	2.0	1.3	1.7
MgO	3.7	6.2	3.4	4.8
Al ₂ O ₃	12.1	5.6	5.2	6.1
SiO ₂	49.2	37.5	34.1	39.8
P ₂ O ₅	0.1	0.1	0.1	0.1
K ₂ O	2.6	1.3	1.2	1.4
CaO	11.2	20.5	24.5	20.7
TiO ₂	0.7	0.6	0.5	0.6
MnO	0.1	0.1	0.1	0.1
Fe ₂ O ₃	7.2	5.4	4.5	5.7
SO ₃	0.44			
BaO	0.03			

Table 4. Results of ICP analysis (ppm or mg kg⁻¹)

Sample	As	Cu	Cr	Pb	Rb	Sr	V	Th	U	Zn	Y
T _{HC}	<15	25	174	<20	95	490	172	<20	<20	102	22
T _R (0-2 m)		<30	440	<20	38	669	89	<15	<15	58	20
T _R (2-6 m)		<30	559	29	27	258	93	<15	<15	46	20
T _R (6-12 m)		<30	459	26	47	508	95	<15	<15	63	25

It is known that the elemental analysis is a priority in order to assess the origin of archaeological pottery (Cariati et al., 2003). Results of the raw clayey materials from different depths of a drilling at the mound of Tilkitepe are showed in Tab. 4. The amounts of Thorium (Th) and Uranium (U) are less than 15 ppm in both the ceramic sample and possible clay material. Strontium (Sr) is geochemically similar to Ca and is found in lime-containing materials (such as sea shell, limestone). More than 400 ppm of Sr indicates that the raw material used to make the ceramics is completely marine effect. However, the amount of Sr is usually less than 150 ppm in terrestrial raw material containing limestone (Akyol and Aydın, 2016). The Sr values of the ceramic piece and raw material samples which are collected from 0-2 to 6-12 meters depth are above 400 ppm. From XRD analysis, the presence of serpentine indicates an ultramafic or mafic source rock, which probably is also the reason for the relatively high Cr concentration in these clays (Hein et al., 2004). The amount of Cr in all clay samples is high level. It is also similar to the high Cr value in the ceramic part. In sedimentary rocks, Rb is mainly found in K-feldspar, mica and clay minerals. Due to the strong association with K, high Rb values may show the presence of felsic rocks, mainly kaolinized intrusives (McLennan and Murray, 1999). Vanadium is largely stationary during metamorphism (Huang et al., 2015). The V content of sedimentary rocks primarily reflects detrital Fe oxides, clay minerals, Fe and Mn aqueous oxides, and organic matter. The average V content of quartzite sandstone and pure carbonate sediments is low (<15 mg kg⁻¹), with higher values in greywacke (40–150 mg kg⁻¹), shale (90– 260 mg kg⁻¹), and clay (ca. 200 mg kg⁻¹). Yttrium (Y) is a lithophile metallic element with various minerals such as xenotime YPO₄ and yttrialite (Y, Th) ₂Si₂O₇. But is also an auxiliary ele-

ment in biotite, feldspar, pyroxene, garnet and apatite minerals. The amount of Y of all samples examined is between 20 and 25 mg kg⁻¹. Yttrium exhibits very low mobility under all environmental conditions (Van Middlesworth and Wood, 1998). It can be said that the samples are similar to the local formation due to the rock structure and the raw materials are provided from the same region.

4.4. SEM Analysis

Ceramic morphology investigation through SEM analysis and the comparison of a ceramic piece and the clay samples fired in different temperatures make possible to predict the original firing temperature. The composition of a mineral depends on the temperature and pressure at which it is formed, its rate of formation and the composition of the bedrock. Therefore, the composition of a mineral can provide useful information about the type of rock and geological environment in which it is originate (Freestone and Middleton, 1987). According to Welton (2003) the minerals determined through XRD analysis, such as calcite is a rhombohedral-structured mineral; magnetite are usually octahedral crystals and/or very well-formed; hematite occur in thin plate forms, clusters of small micaceous plates and thin splinters; chlorite is generally tabular and pseudo-hexagonal and/or prismatic. Furthermore, the same minerals can also occur in thick flakes, lamellar and scaly forms. Quartz is very complex in a transition between alpha and beta quartz. Such crystals form as hexagonal prisms with modified faces. Montmorillonite, found in sandstones, is mostly seen in stratified aggregates and displays a coarse honeycomb cellular arrangement. Kaolinite has hexagonal morphology, smooth basal surfaces and plenty of pores in the form of slits and wedges.

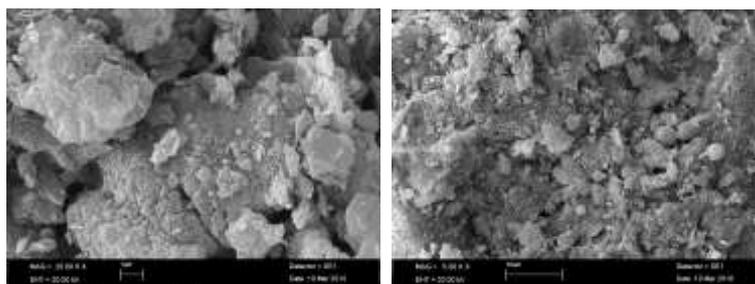


Figure 5a. The SEM image of Tilkitepe ceramic piece.

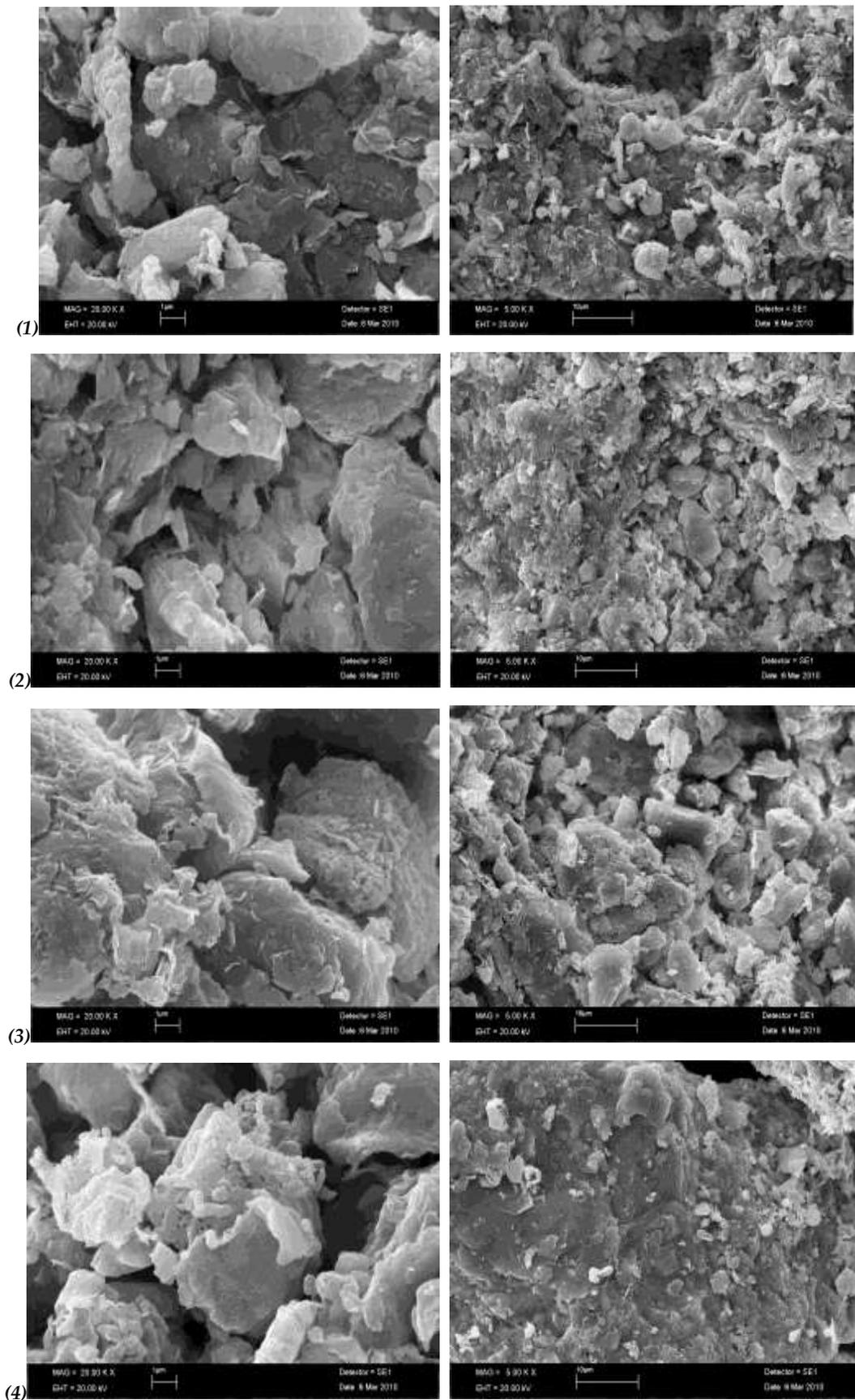


Figure 5b. SEM images of raw clay samples taken from 2-6 m depth and heat treated at 600-900 °C temperature range, 600 °C (1), 700 °C (2), 800 °C (3) and 900 °C (4).

Thin and lath-like crystals represent the earliest stages of illite formation. As it develops, the particle size increases and the morphology of the irregular plateau turns into well-built hexagonal forms (Inoue and Kitigawa, 1994).

The SEM images of ceramic part show the crystals of calcite and clay minerals (Fig. 5a), and the SEM images of thermally treated clay samples indicate clusters formed with increasing temperature (Fig. 5b). Especially at 900 °C, it is observed a different structure of clay samples. Due to the presence of clay minerals and calcite the firing temperature should be definitely below 800 °C, although higher temperature have been speculated in earlier studies (Frankel, 1979).

It is also possible to say that local clay was used for the pottery production due to the similarity of mineral structure. This result is consistent with the data of other analyses. Pottery analyses from Tell Aqap (North Syria) show that most of the unpainted Halaf pottery was produced with regional clay material, but some of painted pottery is imported from different sites (Davidson, 1981).

5. CONCLUSION

At the end of the 6th millennium B.C.E., Tilkitepe is the most extreme point in the northeast corner of the Halaf culture area, which is located in North Iraq, North Syria and Southeast Turkey. The chemical and mineralogical analysis of the Halaf ceramic piece from Tilkitepe was the result of the fact that this was probably produced using local clay sources. From the XRD analyses the mineralogical structure of the ceramic and possible clay material shows great similarity. This result is also supported when the data obtained from XRF major and ICP minor element analyses of ceramics and possible clay sources are compared. Mineralogical changes in the structure were observed with different temperatures

applied on the clay material, and it was understood that the firing of ceramic must be below 800 °C in the oxidizing conditions.

The development of firing techniques is important in the regional or imported Halaf pottery. It is great advance for its period that the reduction and increase of the heat and oxygen level in a close firing system, such as a kiln. Thanks to this new technique, it should be said that the painted pottery production of dark color on light color ground has been successful.

It is generally stated that the painted Halaf pottery has been traded. Nevertheless, only bitumen may have been imported as a raw material of dye (Connan et al., 2004). In this context, it is determined that the unpainted ceramic piece from Tilkitepe was produced with clay from the immediate vicinity of the mound. Although there is no trace of paint on this ceramic piece, this can be an unpainted part of a painted Halaf vessel, because of its size. This possibility lets to suggest that the ceramic production may have been made with local clay, and only dye raw material may be a commodity of commerce.

The Halaf potters seem to have used different clay sources from their environment and achieved superior quality products with superior design and elegance. Some of the finest painted ceramics were produced towards the end of the Halaf period. Clay analysis indicates the presence of production centers and regional replication, but it is still discussible how and why it spread so broadly. The facts, that the Halaf pottery is a regional products manufactured in the household level and the painted ones are evidences of short and/or long distance exchange system, can be described as presence of an economic system in which distinguished goods were offered by family producers in Late Neolithic and Early Chalcolithic in the Near East.

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