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Mineralogical Phase Transition on Sandwich-like Structure of Clinky Pottery from Parthian Period, Iran

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Abstract

Parthian period (250 B.C. - 224 A.C.) in the west of Iran is specified by appearance of Clinky pottery. In this study, Clinky pottery was investigated to evaluate the impact of raw materials and firing conditions (temperature and kiln atmosphere) due to the sandwich structure on this type of pottery. Samples were mineralogically and chemically characterized with petrography, semi-quantitative X-ray diffraction (XRD), X-ray fluorescence (XRF), and scanning electron microscopy (SEM) analysis. Hematite and magnetite in the matrix of these samples indicate that firing process carried out under oxidation- reduction condition. High temperature products such as gehlenite, secondary anorthite, pyroxenes and pseudomullite, denote on firing temperature approximately between 950 to 1000 °C. This study shows that kiln atmosphere has changed to reduction in a temperature of about 850 to 950 °C. In reduction conditions, vitrification occurs approximately in 50 °C less than oxidation condition. Consequently, amorphous phase develops in the matrix. Formation of this phase helps to internal reducing and poor diffusion of oxygen to the matrix and therefore, cause the appearance of magnetite in dark-gray core. In the final stage of firing (ca. 1000 °C), fast but controlled blowing of oxygen was happened. In this condition, iron ions in the vicinity of oxygen is changed to hematite and the color of surface became orange-brown. Accordingly, it seems that the vitrification and formation of Si-O-Si polymeric structure in final stage of firing and furthermore formation of secondary SiO_2, is the reason for formation of sandwich structure by preventing of oxygen penetration into the body. Due to this reason, iron ions near the surface were oxidized and magnetite remained in the core due to the lack of oxygen.

Key Words: archaeometry; sandwich structure; vitrification; Clinky pottery; Iran.

Introduction

Color, as an important feature in ancient pottery, is significant in two aspects: it provides information about the technology applied to manufacture of pottery furthermore aesthetic preferences of a specific culture given credit for the production (Nodari et al., 2004).

In the present study, Clinky pottery belonging to Parthian period (250 B.C. - 224 A.C.) were investigated. The importance of Clinky pottery is that the Parthian period in the west of Iran is specified by appearance of Clinky pottery (Niknami et al., 2006). The nomenclature of Clinky pottery is the clink sound of this kind of pottery when it is knocked. T.C. Young initially named these various ware items as Clinky Ware and then this term was quite well-known since D. Stronach used it when he reported the excavations at Tepe Nush-i Jan (Adachi, 2005). Clinky pottery is a fine ceramic with compact body and sandwich-like structure. Outer surfaces of Clinky potteries are orange-brown in color and the inner body is dark-gray. The section appears to have a sandwich-like shape (Figure 1).

Some researches in the field of ancient potteries with sandwich structure have been conducted. Some investigations have been carried out in this topic. Metallic ware in North-Mesopotamian Bronze Age pottery (Broekmans et al., 2006; 2008), black core structure in the production of Etruscan-Padan pottery (Nodari et al., 2004), potteries from the Carpathian Basin (Szakmány and Starnini, 2007) and also Molera et al., 1998; Bong et al., 2008; Palanivel and Kumar, 2011; etc.

Szakmány specified that the presence of dark cores indicates low firing temperature, an insufficient length of firing and a reducing atmosphere (Szakmány and Starnini, 2007). Broekmans and colleagues explained that their samples contain both hematite and magnetite, which is caused by the alternated use of oxidizing and reducing atmosphere, resulting in a combination of red and grey colors on this type of pottery (Broekmans et al., 2008). Nodari mentioned that the sandwich structure is occurred due to: 1) firing in reducing conditions with an

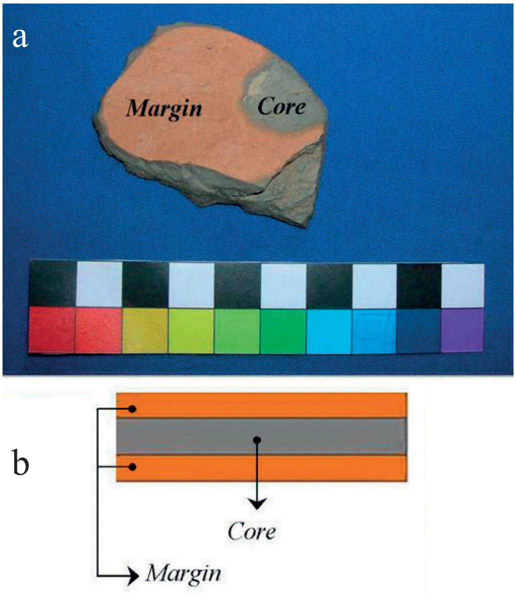


Figure 1. Typical sandwich structure of Clinky pottery (a) and the schematic form of margin and core layers (b).

oxidizing cooling stage, 2) firing organic bearing clays in oxidizing conditions, or 3) the presence of unburned carbon particles. In this research was pointed out that regarding the distribution of iron oxide, cores generally contain only magnetite-maghemite series and sometimes the appearance of hercynite in the samples indicate strong reducing firing conditions (Nodari et al., 2004) and/or as a result of local reducing condition (Maritan et al., 2006).

In this paper the mineralogical and chemical composition of Clinky pottery was studied in order to investigate about formation of sandwich like structure.

Materials and methods

Samples

This study was carried out on six pieces of Clinky pottery from surface surveying gathered from the Hegmataneh Hill and Bistun area (Figure 2). Three samples from Hegmataneh and three samples from Bistun were collected, Table 1. It should be notified that these samples were selected as a representative samples of this kind of pottery due to archaeological report (Mohammadifar, 2008).

Hegmataneh Hill is located in the center of modern city of Hamedan (in Hamedan Province, Iran) and its geographical coordinates are

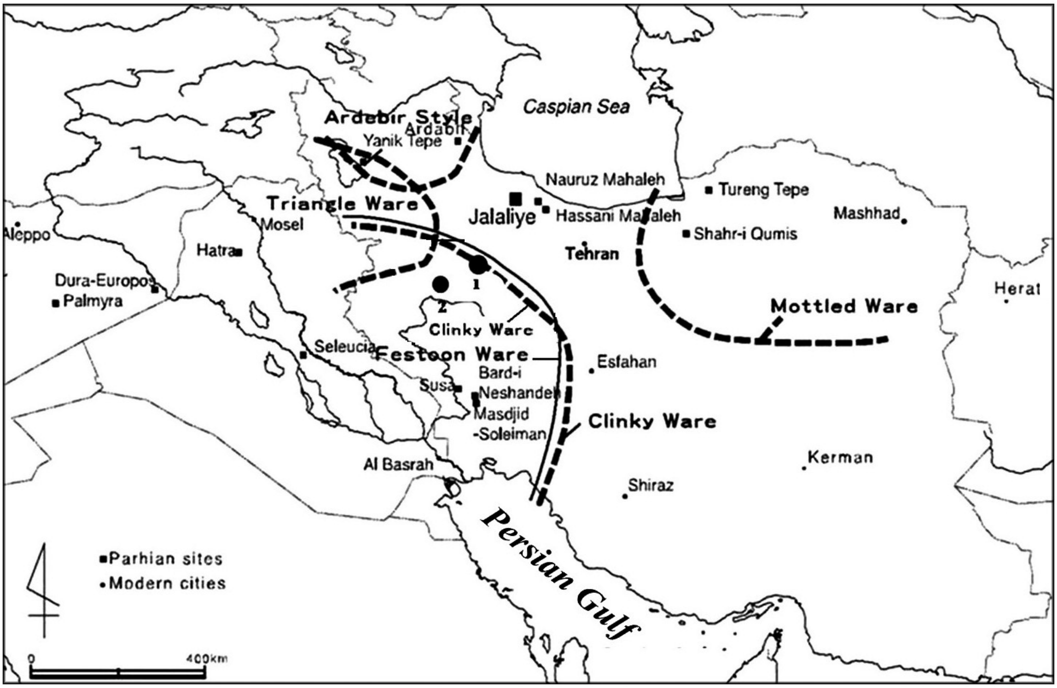
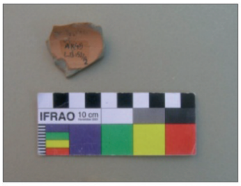


Figure 2. The Distribution of the Haerinck's Classification of the Parthian Fine Ceramics (Adachi, 2005). Point (1) Hegmataneh, point (2) Bistun. These points are located in the range of Clinky pottery distribution.

Table 1. Description of the representative samples.

Samples			
Sample Number	7080	7081	7082
Archaeological Site	Bistun Area	Bistun Area	Bistun Area
Color Code*	Margin:2.5YR 5/4 (reddish brown) Core: GLEY1 4	Margin: 2.5YR 5/6 (red) Core: GLEY2 5/1 (bluish gray)	Margin: 2.5YR 5/2 (weak red) Core: GLEY2 6/1 (bluish gray)
Thickness	0.40 cm	0.57 cm	0.45 cm
Samples			
Sample number	7083	7084	7085
Archaeological Site	Hegmataneh Hill	Hegmataneh Hill	Hegmataneh Hill
Color Code	Margin: 7.5YR 6/4 (light brown) Core: GLEY2 4/1 (dark bluish gray)	Margin:7.5YR 6/4 (light brown) Core: GLEY2 7/1 (light bluish gray)	Margin:7.5YR 7/4 (pink) Core: GLEY2 6/1 (bluish gray)
Thickness	0.55 cm	0.55 cm	0.40 cm

*According to Munsell Soil Color Chart. (Lynn and Pearson, 2000).

34°48′15″N 48°31′2″E. This archaeological site is one of the widest ancient hills in Iran with approximately 40 hectares area and has remains from Kassites, Medes, Achaemenid, Seleucid, Parthian, Sassanid and Islamic periods. Under the Persian kings, Ecbatana (Old Persian name of

Hegmataneh) was summer residence and later became the Capital of the Parthian kings.

Bistun (or Bisutun, Bagastana in Old Persian), meaning "the place or land of God", is famous for Inscription of Darius the great, one of the UNESCO World Heritage Site. It is located in the Kermanshah Province, in western Iran, along the ancient trade route linking the Iranian high plateau to Mesopotamia. Geographical coordinates of this ancient area are 34˚23′16″N 47˚26′7″E. Bistun area has features remains from the prehistoric times to the Median, Achaemenid, Sassanian, and Ilkhanid periods.

The samples from Bistun were found in Ilkhanid Caravanserai within the archaeological layer from Parthian and Sassanian period. The samples of Hegmataneh were found through the 16th excavation seasons of Hegmataneh Hill as well (Expedition director of archaeological excavations: Dr. Yaghoub Mohammadifar, summer and fall 2009).

Experimental methods

To study the structure of Clinky pottery for identification of chemical and mineralogical composition of raw materials, firing products, secondary products, firing condition, and explanation of the relation between firing process and formatioan of sandwich structure, these analytical methods were selected:

Thin section of samples was petrographically analyzed using the Pol. Microscopy (Olympus BX60, and PM-240 SA Iran) for identification of matrix and its compounds relation. Identification of crystalline phases by X-ray diffraction (XRD) analysis (PANalytical X-ray Diffraction 1000G, Cukα, 40 kV, 40 mA, measuring time 1 sec per step) was accomplished using X'pert high score software. Chemical composition of samples was determined by energy dispersive X-ray fluorescence (XRF) analysis (X-ray Fluorescence Analyzer, Bruker, S4 PIONEER, Germany). The maximum relative error for method was 1%. The major, minor and trace elements measured as oxides. Microstructural analysis and study on sintering process were done by scanning electron microscopy (SEM) (Philips XL30 with Scandium Software) in vacuum chamber. Samples were coated by graphite in 3 minutes.

Result and discussion

Petrographic analysis of six case studies show compact matrix. Crystalline phases are mainly fine grains in size and are distributed almost equally in the matrix (Figure 3). Pores are mostly isolate and close. The presence of isolated porosity is useful for insulation to fluid. The boundary between the orange-brown margins and the dark-grey core is not sharp. The trace of crack was not perceived in the thin section of samples.

Fine and angular grains are distributed in the matrix (Figure 3g) and sometimes rounded quartz can distinguish.The grain shape of quartz is depend on their origin (Riederer, 2004). Based on their production technology, crushed quartz with sharp and angular or sub-angular edges could be preferred as temper. Rounded quartz indicates mostly on sedimentary source and it could be as a part of raw materials. It seems that one technological feature of Clinky pottery is the

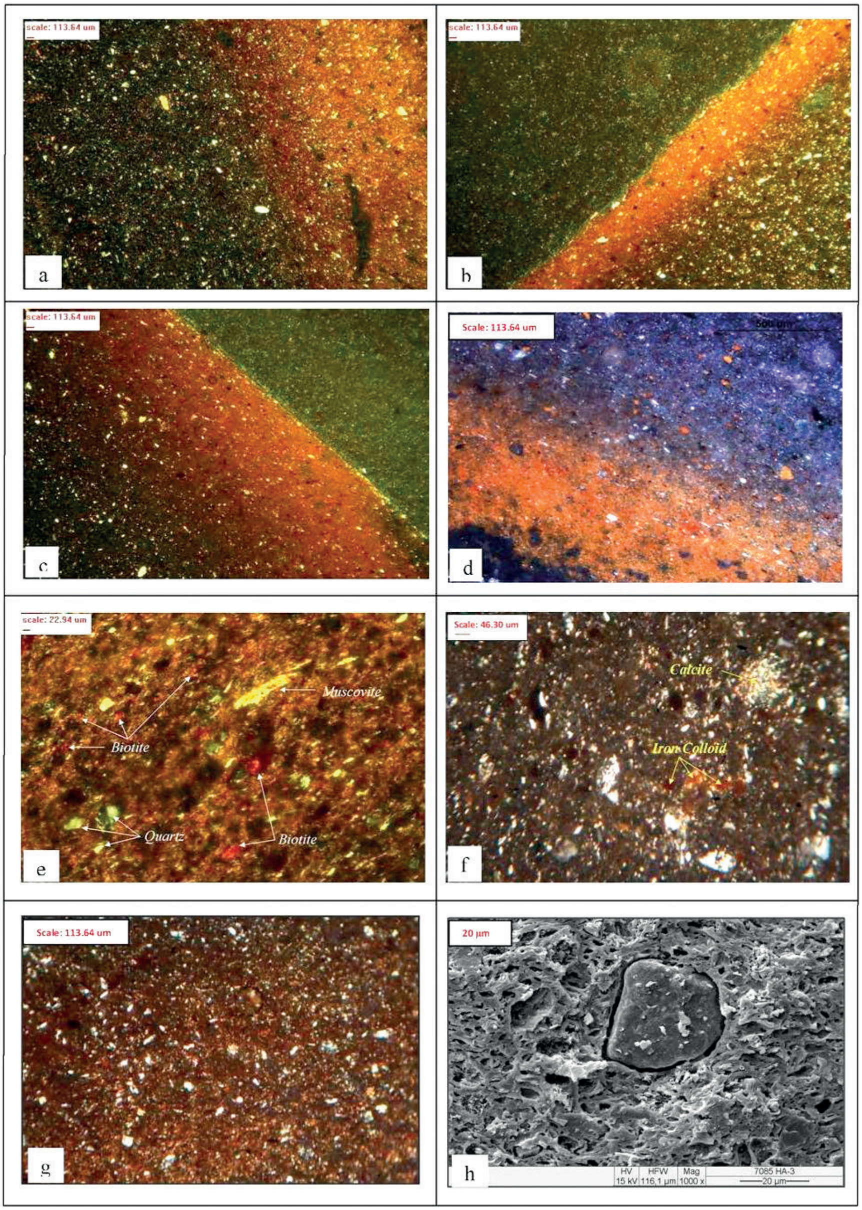


Figure 3. Petrographical characteristic of the matrix of representative samples. See text.

use of grinded and sieved quartz as an inorganic temper. The use of small angular quartz can improve the mechanical correlation between quartz grain and clay minerals, followed by interface increasing. Furthermore small size of these grains control tension effect which arise from polymorphic transition of quartz (α-quartz to β-quartz and vice versa) in 573 °C (Figure 3h). Volumetric changes in small size of quartz didn't cause tension and therefore microcracks. It should be notified that the mechanical behaviour of the quartz-calcareous caly system is very sensitive to the proportion of quartz inclusions. At low volume fraction of inclusions (less than about 10%) the system behaves as a normal brittle ceramic, but at higher quartz contents the material displays significant energy dissipation (toughening) during fracture (Kilikiglou et al., 1998).

Fine grain of micas (biotite and muscovite) are observed in all samples. Moreover fine grain calcite is scattered in the matrix (Figure 3 e,f). In the rim of some pores, secondary calcite which formed during the burial stage was also observed. Indeed, pores are not filled by secondary products and it indicates a low amount of phases such as feldspars, calcite, phosphates and sulfates in the matrix of these samples and/or these phases are surrounded by matrix via sintering process which are inactivated.

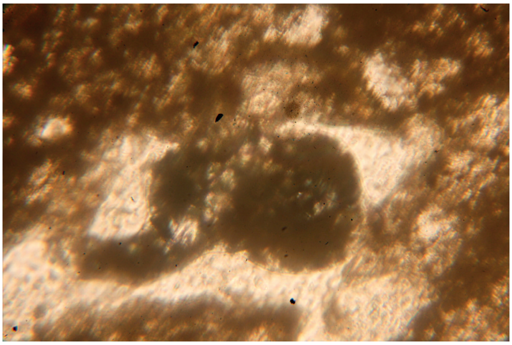


Figure 4. Petrographic image of sample No. 7082: accumulation of Carbon in one pore (25x).

In some pores, accumulation of opticaly isotropic carbon which originated from the fuel was also detected (Figure 4). Furthermore isotropic iron oxide accumulation was characterized by their reddish-brownish rims (Figure 3f). The iron ions can be derived from clay impurities and/or inorganic iron oxides.

The XRF result of chemical composition of samples is presented in Table 2 and Figure 5. The high amount of silica and alumina demonstrates the application of clay minerals and silica-rich matrix in these samples.

The amount of CaO is different in the samples from ca. 7% to 12.5% and these samples cannot be classified as calcareous ware (CaO > 15%) (Broekmans et al., 2008). This compound could be added as flux or as an inclusion which is existed in the raw materials. It is necessary to pay attention that carbonates are mostly present in the soil of local position of production of samples in the Central Zagros formation. With regard to the presence of carbonate grains and carbon colloids in the matrix, the atmosphere of firing conditions can be estimated. Decomposition of carbonate phases during firing depends on their grain size, temperature, and the partial pressure of carbon dioxide (f_{CO_2}) in the kiln. In these samples, calcite grains are not coarse and inclusion of calcareous stone such as marble was not observed. It seems that the change of atmospheric condition in the kiln from oxidation to reduction at about 800 °C and also increasing of the partial pressure of carbon dioxide caused decreasing of calcite breakdown. In addition, Trindade stated that a few

Table 2. Chemical composition of samples by XRF analysis. Results given as wt% oxides normalized to 100%. Trace elements were reported as ppm.

	SiO_2*	Al_2O_3	Fe_2O_3**	CaO	K_2O	TiO_2	MgO	Na_2O	P_2O_5	H_2O	Cl	SO_3
7080	49.96	25.05	9.11	7.20	2.66	1.26	1.04	0.43	0.19	0.00	0.00	970
7081	48.89	24.46	9.03	8.35	2.58	1.24	1.10	0.41	0.22	0.00	0.00	870
7082	49.80	23.92	9.59	9.23	2.58	1.29	1.26	0.45	0.16	0.00	0.00	680
7083	48.90	24.42	9.38	7.83	2.69	1.28	1.02	0.53	0.31	0.00	1500	590
7084	48.41	23.85	9.40	10.38	2.64	1.25	1.02	0.44	0.33	0.00	410	510
7085	48.20	22.78	8.84	12.23	2.74	1.22	1.03	0.43	0.22	1.80	400	950

	Mn	Sr	Cr	Zr	Cu	Zn	Rb	Ga	Y	Ni	LOI	Total
7080	750	460	310	270	200	180	160	100	50	0.00	2.63	99.87
7081	720	570	260	260	210	200	160	0.00	50	0.00	3.26	99.87
7082	870	570	330	250	270	220	160	0.00	0.00	90	1.25	99.87
7083	740	490	430	240	230	240	150	0.00	0.00	80	3.04	99.86
7084	780	660	270	230	250	240	170	0.00	0.00	120	1.80	99.88
7085	680	600	320	230	280	220	150	0.00	0.00	0.00	-	99.87

* Wt% total SiO_2 (quartz + other silicates)

**Wt% total iron oxide in matrix was calculated as Fe_2O_3

amount of calcite grains could remain in the matrix to 1000 ºC (Trindade et al., 2009).

Carbon accumulation in the matrix is one of the reasons for changing atmosphere from oxidation to reduction based on Boudouard equilibrium reaction. During the process of blowing of oxygen (fresh air in the end stage of firing) into the kiln, this reaction $2CO \leftrightarrow C + CO_2$ took place and carbon re-deposited in convenient location. On the other hand, some of these deposits can be result of local reducing in the matrix (Emami et al., 2009).

The classification of samples was presented in Figure 6 according to the result of XRF analysis and based on SiO_2-Al_2O_3-CaO+MgO system in Noll equilibrium diagram (Noll, 1991). Position of samples in this diagram indicates technical similarities in production of this kind of pottery in different location. The remarkable point here is the nearness of sample number 7082 from Bistun site to samples of Hegmataneh.

Based on Noll equilibrium diagram, samples are silica-rich potteries with high amount of clay minerals. Influence of cations Ca^{+2} and Mg^{+2} in the process of change and exchange took place in the phyllosilicates, depending on SiO_2/Al_2O_3 ratio and this change is developed to the nucleation and growth of new crystalline networks along the SiO_2-anorthite and anorthite - diopside lines (Figure 6). However, it is worth

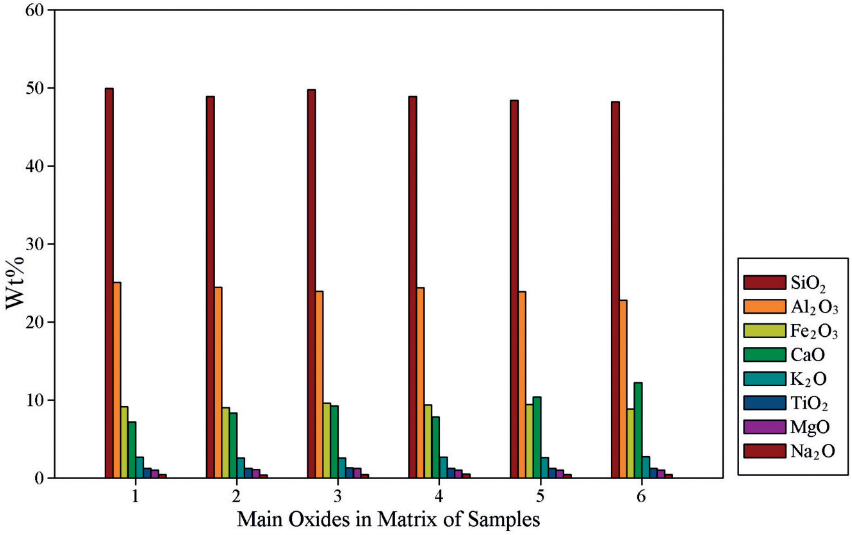


Figure 5. Chemical composition of samples according to XRF analysis.

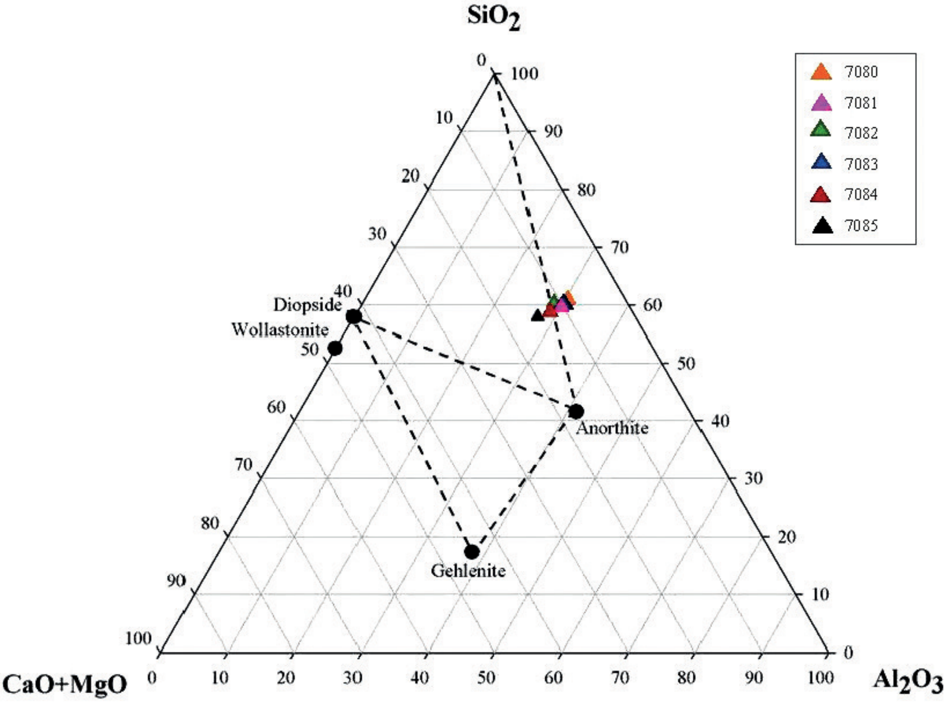


Figure 6. Ternary diagram of SiO_2-Al_2O_3-CaO+MgO (according to Noll, 1999).

mentioned that historic potteries have been produced in disequilibrium conditions and these kinds of diagrams express only chemical and mineralogical composition changes (because ancient potteries are polycrystalline compounds, and their firing products have changeable proportions; for example, not completely decomposed or recrystallized phases).

Investigation on crystalline structure of Clinky pottery (Semi quantitative XRD)

Mineralogical composition of samples. According to the result of XRD analysis, major detected minerals in these samples are quartz, anorthite, pyroxenes, hematite, magnetite, and gehlenite. Quartz has the most intensive peak in all samples, as it was observed in petrography of thin sections. Quartz was probably used as inorganic temper in production of Clinky pottery. High asymmetry of measuered structure in the prefered orientation about 2θ = 26.6° was mentioned as a result of partial sintering and destruction of the corner of quartz by means of phase-interface reaction of this phase with other adjacent phases.

Moreover, quartz peak in this area can be overlaped with other phases like mullite. Indeed mullite was not observed as a significant phase in the matrix of samples, but its basic form as pseudomullite (Figure 7), indicates a temperature of about 950 to 1000 ° C. (Noll, 1991, p. 105) pointed out that 2/1mullite forms in T > 1000 °C and 3/2 mullite forms in T > 1200 °C and Reedy (2008) stated that this phase can form in a temperature ca. 950 - 1000 °C in reduction atmosphere (Reedy, 2008, p. 118).

The major detected feldspar in the matrix of sample is anorthite that can form as primary within raw materials and secondary (formation in firing process in CaO rich raw materials) products. Formation of anorthite as firing products can occur in interface of phyllosilicates by calcium carbonates and silica in a temperature about 900 °C (Cultrone et al., 2001). Pyroxenes were also detected in 2θ ~ 28°.

Gehlenite ($Ca_2Al_2SiO_7$) was detected in all samples with different intensity. This phase forms about 800 °C in the adjacent calcite or quartz with phyllosilicates (Cultrone et al., 2001; Grifa et al., 2009). Solubility of gehlenite in the presence of acetic or humic acids causes the

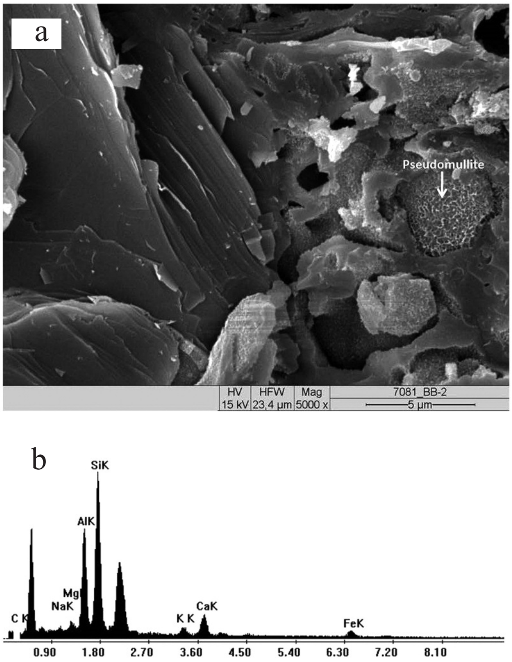


Figure 7. Formation of pseudomullite in samples by decomposition of kaolinite. (a) Sem image (5000x) and EDS spectrum (b).

formation of secondary calcite in many historical potteries (Heimann and Maggetti, 1981).

In all samples, calcite has low intensity due to its early decomposition of this phase. The presence of carbonates in texture of ancient potteries is important not only as a technical property, but also because of carbonate sensitiveness in acidic condition as conservation and restoration point of view. Also decomposited carbonate in the matrix and its sensitivity to acidic condition as a result of formation of CaO and $Ca(OH)_2$, can establish mechanical tension in the pottery.

Adding CaO to melting process reduces the surface tension of amorphous phase (Hara et al., 1991) and makes it easy to diffuse in pores.The effect of the presence of calcium oxide on increasing the activity of FeO, and furthermore its reducing has also been investigated by scientists (Meegoda et al., 2007). It seems that CaO has the same role in texture of pottery (as a flux and its important role in vitrification process) and reduction of adjacent iron ions due to penetrating into spinel network and release FeO (Meegoda et al., 2007). In addition, calcium oxide will be effective for coloring of pottery.

Presence of iron ions in the structure of Clinky pottery

Based on the color of Clinky pottery, it seems that one of the reasons for this color exchange is iron ions as a chromophore and it infers that iron ions exist in the structure of this kind of pottery with different oxidation state.The origin of iron ions in fabric of Clinky pottery are: as an impurity with kaolinite, within biotite as a carrier of iron ions in matrix, or inorganic hematite in the local clay.

Both hematite and magnetite was detected by XRD analysis in all samples. Ferric iron (hematite) makes red-brown color, but ferrous iron (such as iron sulfides, carbonate, and silicate) and ferrous - ferric iron (or magnetite) make gray or bluish-black colors. These colors can be observed in margin and core of samples (Table 1, color code according to Munsell Soil Color Chart).

Considering the color of core layer of samples (dark/bluish-gray), it seems that ferrous iron ions (iron silicates, iron carbonates and also magnetite) exist in this layer. The existence of magnetite suggests poor oxygen diffusion in the potsherds during firing (Nodari et al., 2004; Maritan et al., 2006).

Two reasons for poor diffusion of oxygen to pottery matrix during firing are: (1) providing general reducing conditions in the kiln, and (2) formation of amorphous phase and prevention of oxygen penetration. By dominating CO in the atmosphere of kiln, Fe ions are reduced indirectly. Although it is possible that in the interface between iron and carbon, direct reduction occurs in the matrix. On the other hand, based on the formation of amorphous phase and its vitrifying as a result of destruction of phyllosilicates, pores were filled by the viscous product of sintering and it can be one of the reasons for poor diffusion of oxygen to matrix of pottery during firing. Note that as the reducing condition sintering process occurs in a temperature about 950 °C (Broekmans et al., 2008). Therefore, Fe released ions, in suitable condition, enter silicates structure such as pyroxenes, or crystallized in form of magnetite.

It seems that iron ions in matrix of Clinky pottery was encountered to reduction condition about 850 - 950 °C. Inorganic iron oxides have changed to magnetite-maghemite series gradually and are effective in dark-gray color of core layer in this sandwich structure.

At least, during a fast and controlled oxidation, that was probably blowing fresh air to the kiln, ferrous irons transformed to ferric irons and hematite was formed in a temperature about 950 °C (Molera et al., 1998) and the final stage of firing. The oxygen diffusion to the structure of Clinky pottery had limited depth and firing stopped probably with respect to technical reasons according to time duration for firing that potter considered. Therefore, the sharp boundary of color change from dark-gray in core to orange-brown in margin cannot be observed (Figure 3 a, b and c). It should be noted that the complete crystallization of hematite takes place in temperature above 900 °C (Trindade et al., 2009) and this condition was provided for clinky pottery.

Sandwich-like structure of this kind of pottery is a result of actually conscious usage of iron ions bearing raw materials by potters and the control of firing condition. In addition, iron oxide has a flux role and can help to vitrification.

Formation of amorphous phase

SEM images confirm amorphous phase arising from sintering process in the matrix of Clinky pottery (Figure 8). By destruction of phyllosilicates from temperature about 550 °C to 950 °C, amorphous phase forms (Reedy, 2008, p.118). In reducing environment, this temperature is 50 °C less than oxidation condition (Broekmans et al., 2008). The formation of amorphous phase probably caused a reduction in porosity (Nodari et al., 2004). As it mentioned before, the presence of Fe_2O_3 and CaO as a flux, can help to this process. Then the formation of amorphous phase in matrix of Clinky pottery happened in reduction conditions and compounds such as magnetite could be stable.

Based on Boudouard reaction ($C/CO/CO_2$) and the decomposition of SiO_2 to SiO in reduction condition in a given temperature (Emami et al., 2009), the crystalline structure of SiO_2 will be damaged. Due to this damaging, it seems that formation of Si-O-Si polymeric network as an amorphous phase can be the reason of formation of sandwich structure. This vitrified network prevented to diffusion of oxygen and intensified inside reduction. Although this phase is very reactive and tend to be oxide, but the presence of $C/CO/CO_2$ prevented oxidation of SiO to SiO_2. SiO can be stable in wide range in form of ½ SiO_2. At the final stage of producing Clinky pottery and by flowing oxygen in the kiln, SiO oxidized to SiO_2 and secondary SiO_2 formed. Accordingly secondary SiO_2 made a passive layer which prevented further oxidation and this appeared as vitrified phase that has remained in the core. It seems that this phase is one of the main factor for clinking sound in Clinky pottery. Moreover, this phase surround all components in the structure of pottery by providing a dense and compact matrix that help to stability of this kind of pottery during the time.

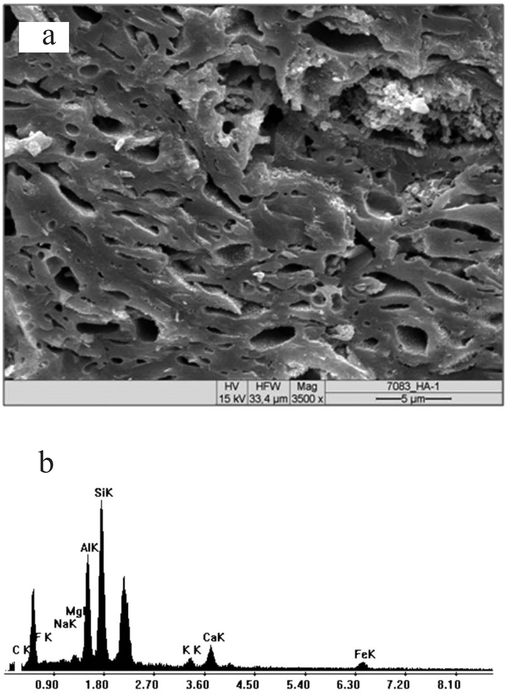


Figure 8. Formations of amorphous phase in sintering process, sample number 7083. (a) SEM image (3500x) and EDS spectrum (b).

Conclusion

With respect to SEM analysis, it is not observed phase differences between layer structure of samples and the matrix was formed with similar composition. This indicates that firing atmosphere and condition had the main role in formation of sandwich structures in Clinky pottery. Another result of this study is the approach of production process of this type of pottery in Parthian period (around 2000 years ago). Clinky type potteries were made in similar process, method, and certain formulation. Little differences (that can be observed in non-conformity between analysis result of all samples) is due to differences between raw materials or even local clay inclusions, firing time, lack of exact control on production process, different kiln or even different potters.

Firing temperature in samples is estimated between 950 - 1000 °C according to the presence of gehlenite, secondary anorthite and pyroxenes.This study shows kiln atmosphere has changed from oxidation to reduction in a temperature of about 850 to 950 °C. In terms of changing the atmosphere to reduction, the process of decomposition of carbonates has stopped (according to Le Chatelier's Principle), iron ions in matrix have reduced and magnetite has formed. In reduction conditions, vitrification occurs and amorphous phase develops in the matrix. Formation of this phase helps to internal reducing and poor diffusion of oxygen to the matrix and therefore, good situation provides for stability of magnetite in dark-gray core. Vitrification causes increasing the dense sintered product.

After applying the maximum temperature (average 1000 °C) in the final stage of firing, fast blowing of oxygen has happened and iron ions in the vicinity of oxygen has changed to hematite (orange-brown color of surface). As a result of fast diffusion of oxygen to the matrix in this stage, secondary SiO_2 has formed and this new formed oxide, like passive layer, has prevented to continuing the oxidation process of Si-O. Therefore, amorphous phase of Si-O polymers has remained in the matrix. Also due to the relative blowing control and rapid diffusion of oxygen into the matrix, the sharp boundary between core and margin is not seen in thin section. Dark red-brown color observed in the confluence of two layers is due to the presence of both hematite and magnetite at this borderline.

The remarkable thing in the production of Clinky pottery, in addition to fixed guidelines and formula for production, is the form and shape of this kind of pottery. More containers introduced with such a structure (sandwich or layer structure) have open shape and low thickness (samples in this study have a thickness less than 0.6 cm). These features have significant roles to contact outer surfaces to oxygen and also rapid diffusion of oxygen into the structure.

It must be considered that the results achieved by this first structural and mineralogical study on Parhian Clinky pottery referes to a limited number of samples. It is necessary to further investigate on new hypothesis propounded about formation of secondary SiO_2 and its effect on the formation of sandwich structure.

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