
**CHARACTERISATION OF A PAINTED
POTTERY VESSEL EXCAVATED AT
THE SITE OF TEPE SIALK, KASHAN,
CENTRAL IRAN**

Nasim Qanbari-Taheri¹ and Parviz Holakooei²

*¹Faculty of Conservation, Art University of Isfahan, Isfahan,
Iran*

*²Department of Objects Conservation, The Metropolitan
Museum of Art, New York, U.S.A*

Email: parvizholakooei@gmail.com

Introduction

The mound of Tepe Sialk, in the suburbs of the city of Kashan (Figure 1), is one of the major archaeological sites in central Iran and was occupied from the fifth millennium to the first millennium BC. It was excavated from 1933 (Ghirshman 1938-1939) until recently (e.g. see Shahmirzadi 2004). During the

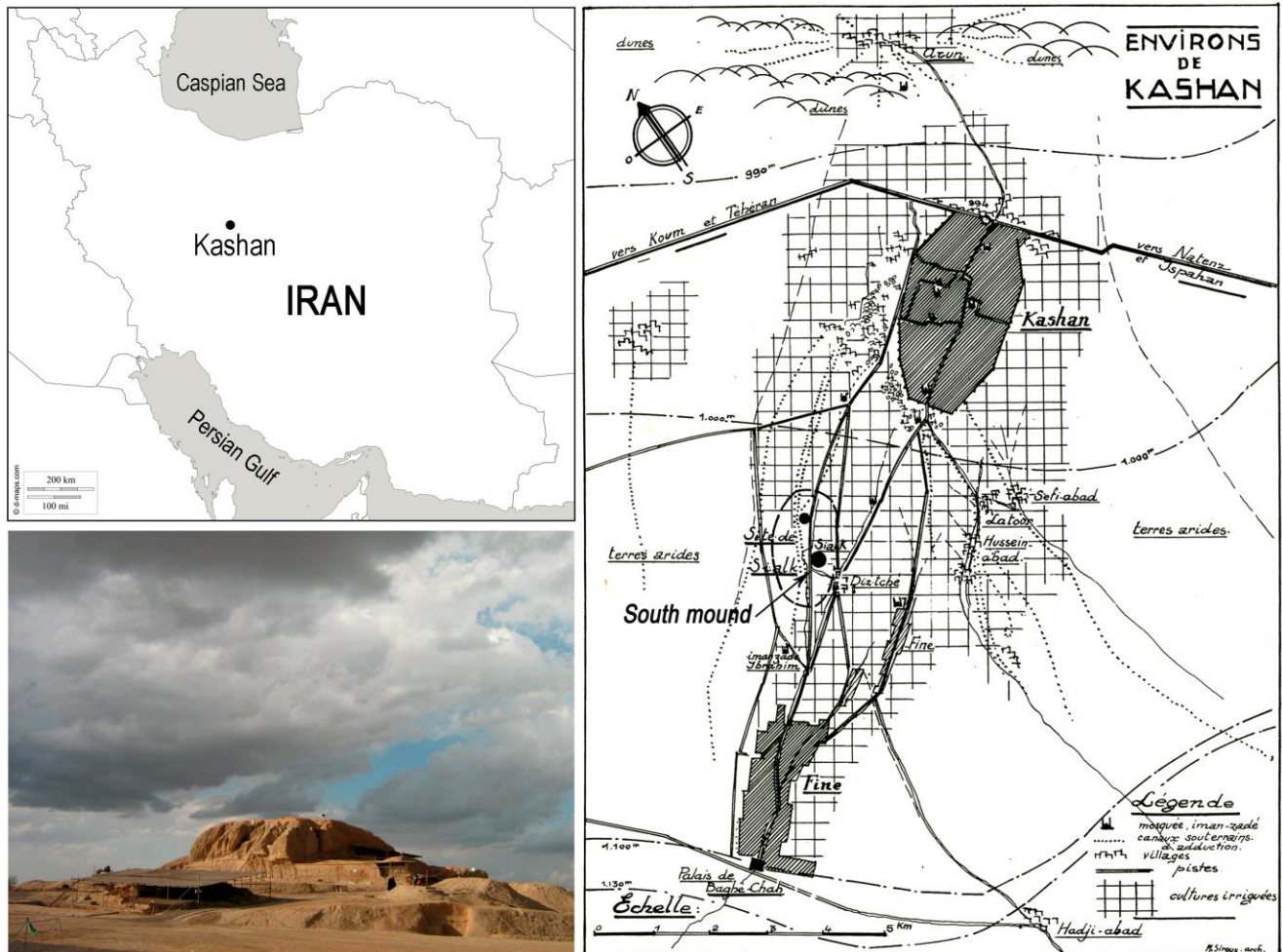


Figure 1. Tepe Sialk: (top left) Location of Kashan, (right) the archaeological site and its south mound (Ghirshman 1938-1939); (bottom left) view of the south mound.

excavations, a large collection of ceramic vessels has been unearthed from various locations of the site, yet it has received little attention in terms of scientific analysis (Kingery 1974; Nosrati 2012; Boulanger 2014).

A black-painted pottery vessel (*c.* 27 cm diameter) was excavated at the southern mound of Tepe Sialk and was of particular interest, as a part of the pot was deformed. This pot (Figure 2a, b) was found broken into 71 sherds. It has been recently reassembled with animal glue during conservation and is currently stored at the museum of the Bagh-e Fin-e Kashan. It is a wheel-made ceramic with a greenish-coloured body and is deformed below its neck by partially collapsing inwards (Figure 2a). The black-painted decoration around the neck depicts an animal (*Capra* or wild goat) and geometric patterns (cross or sun motifs and crosshatched areas) and lines (Figure 2b). These patterns are similar to those observed on the pottery found at Tall-e Bakun, Tepe Qabristan and Susa (Alizadeh 1992; Fazeli Nashli 2004; Shahmirzadi 2004; Alizadeh 2006), suggesting that the pot could

have been manufactured in the fourth millennium BC.

Traces of organic residues were identified in the pot, which show that the pot might have been used for storage or cooking.

The aim of the present study was to investigate the paint composition and the ceramic firing regime of this vessel. The paint was examined by micro-X-ray fluorescence spectrometry (μ -XRF) and micro-Raman spectroscopy (μ -Raman), while the firing was studied by measurements of porosity and specific gravity (SG) of the body, which were interpreted in the light of analytical data provided by XRF, X-ray diffractometry (XRD) and scanning electron microscopy (SEM).

Materials and methods

A small fragment of the pot's core body was removed to be used for SG measurements and pelleting for XRF and XRD Analysis. In addition, a

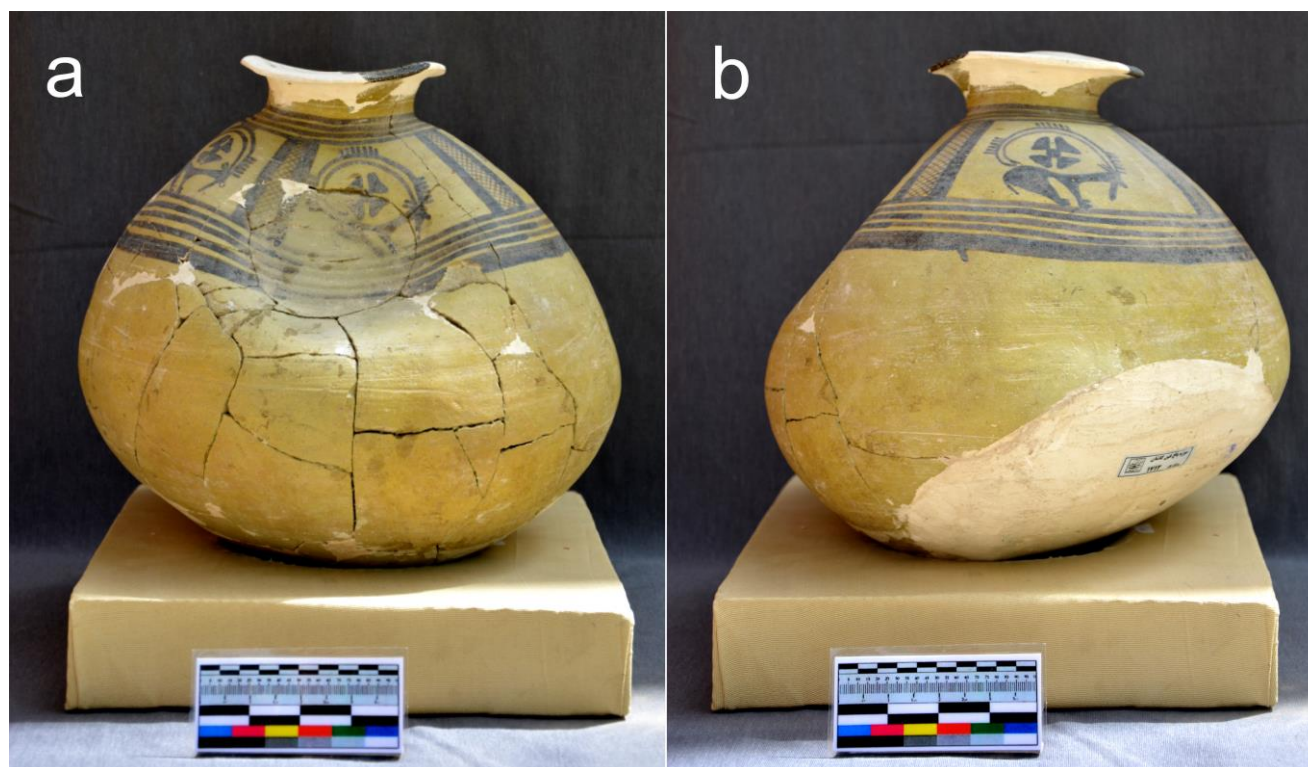


Figure 2. (a) The pot under study excavated at the south mound of Tepe Sialk with the partially collapsed body and (b) the animal and geometric patterns which are painted on.

fragment was taken to measure the porosity and water absorption of the pot, and to provide a fractured cross section of the body and slip for SEM examination.

An XMF-104 instrument from Unisantis® was used to perform XRF analyses on a powdered pellet from the ceramic body. A portable XRF micro-analyser, ARTAX™ 200 from Bruker AXS Microanalysis with a Mo target, and an SSD Peltier-cooled detector with a Be window and 1 mm collimator was used at 50 kV and 1000 μ A to analyse the black paint in air for 120s. A LabRam HR800 micro-Raman instrument from Horiba Scientific equipped with an air-cooled CCD detector at -70°C , an Olympus BXFM microscope, a 600 groove/mm grating and a 50x objective were used to collect the Raman scattering signals. The excitation source was a He-Ne laser (632.8 nm line) with a maximum laser power of 20 mW and the spectrometer was calibrated with silicon at 520 cm^{-1} .

XRD analysis was performed with an Inel EQUINOX 3000 powder X-ray diffractometer run at 50 kV and 30 mA working with Co-K α radiation ($\lambda = 1.78901\text{ \AA}$) and a step size of 0.032° . Crystalline phases were identified based on the International

Centre for Diffraction Data Powder Diffraction Files.

SEM observations of vitrification were carried out on a gold-coated fractured sample of the ceramic body using a Seron Technology Inc AIS2300C SEM at 15 kV, using secondary electron imaging.

Specific gravity (SG) was calculated for the bulk of a small powdered sample. To do so, a sample was dried in an oven at 100°C to a constant weight. Then it was immersed in water and the specific gravity of the sample was calculated with a pycnometer following equation (1) and weighing the mass of the sample (m_s), pycnometer and water (m_i) and pycnometer, sample and water (m_b).

$$(1) \text{ SG} = (d m_s) / (m_i + m_s - m_b)$$

where d was the density of water at the temperature which the measurements were performed.

Porosity (Φ) of the body was measured from a sherd sample dried at 100°C to a constant weight. It was calculated weighing the mass of the dried sherd (m), the water-saturated sherd (m_w) and the water-saturated sherd suspended in water ($m_{w\prime}$), following equation (2). Water absorption percent ($A_w\%$) of the sherd was then calculated through equation (3).

A. XRF analysis. Elemental composition of the pot body (normalised to 100%)									
K ₂ O	Na ₂ O	MgO	CaO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	Fe ₂ O ₃	MnO ₂	TiO ₂
2.04	2.22	4.76	3.60	12.35	64.05	0.46	9.38	0.16	0.98
B. XRD analysis. Mineralogical composition									
Quartz (SiO ₂)			Pyroxene (Ca(Mg,Fe)Si ₂ O ₆)			Anorthite (CaAl ₂ Si ₂ O ₈)			
++++			+			+			
C. Porosity (Φ) Water absorption A _w (%)			D. Specific gravity						
		m _w	d at 27°C	Bulk			Powder		
m	m _s			m _v	m _l	m _b	m _v	m _l	m _b
65.02	76.20	74.52	0.996345	0.2892	74.3316	74.5088	0.2788	75.5715	75.7452
A _w 17%		Φ 6.65%		2.57			2.64		

Table 1. The summary of analytical studies performed on the painted pottery vessel from Tepe Sialk.

$$(2) \quad \Phi = 100 (m_s - m) / (m_s - m_w)$$

$$(3) \quad A_w \% = 100 (m_s - m) / m$$

Results and discussion

The body

According to the XRF results (Table 1A), the chemical composition of the vessel is consistent with the composition of some pottery sherds from Tepe Sialk reported by Boulanger (2014). In fact, the CaO content (3.6%) of the body is much lower than the average value of CaO% reported by Nosrati (2012) and Boulanger (2014) for Sialk III's calcareous pottery. Following Maniatis and Tite (1981), the body of the studied vessel should be considered non-calcareous, as it contains less than 6% CaO (Table 1A).

XRD showed presence of quartz (SiO₂) as the major component, and traces of pyroxene (augite, Ca(Mg,Fe)Si₂O₆) and anorthite (CaAl₂Si₂O₈) (Table 1B). Pyroxene can form at about 950°C or at higher temperatures in calcareous bodies (Jordán *et al.* 1999). Although pyroxene might have naturally occurred in the clay of which the pot was made, the trace contribution of anorthite in the body may be evidence of an equivalent firing temperature of about 1000°C or above (Cultrone *et al.* 2001). Interestingly, the absence of gehlenite (Ca₂Al(AlSi)O₇), which is formed at about 850°C and is stable until 1050°C, when it starts to transform to anorthite (Cultrone *et al.* 2001; Moroni and Conti 2006), confirmed that the pottery was fired at a temperature exceeding 1050°C, which explains why the pottery was partially

deformed and collapsed (Figure 2a). The pot might have been overfired due to its position in the kiln, but no kiln evidence is available from the site.

As well as XRD evidence, porosimetry and specific gravity of the pottery's body showed interesting results (Table 1C-D). With increasing firing temperature, the clay matrix sinters and starts vitrifying gradually (Hein *et al.* 2008). The formation of the vitreous phase in clay bodies is usually accompanied by the formation of closed porosity in which air is trapped, consequently decreasing the specific gravity of the ceramic body. The porosity calculated for the pottery's body (6.65%) (Table 1C) is far from the values reported for porous archaeological pottery (Harry and Johnson 2004; Hein *et al.* 2008; Velraj *et al.* 2010) and is consistent with those reported for modern high-temperature porcelain (Lange 1997).

The presence of closed pores in the pottery body was accordingly confirmed by the difference of the values measured for the specific gravity of the bulk and the powdered sample of the body (Table 1D). In addition, the low specific gravity of the pottery (about 2.5) shows that minerals with high specific gravity like gehlenite (about 3.1; Mursky and Thompson, 1958) were not present in the body. The specific gravity of the powdered body was entirely consistent with alkali glasses (Lange, 1997), which may fit the extensive formation of a vitreous phase in the pottery's body as well. SEM observations (Figure 3a) also confirmed the extensive vitrification of the body and its slip (Figure 3b). As Maniatis and Tite (1981, p. 61) wrote, non-calcareous clay bodies start vitrifying at temperatures above 1000°C and forming

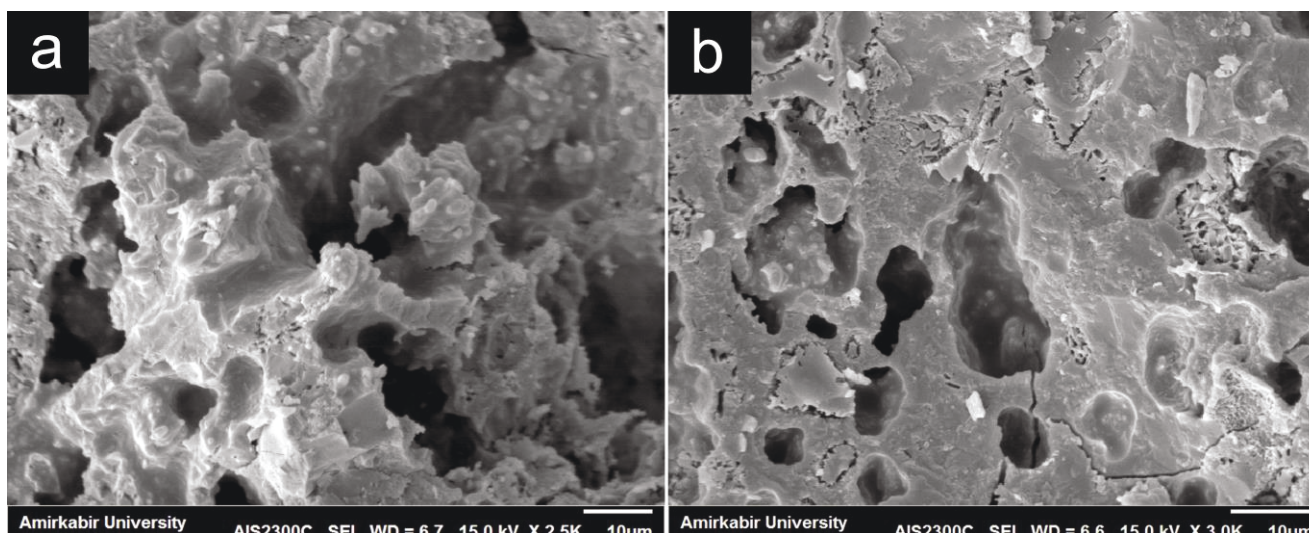


Figure 3. SEM secondary electron images of fractured surfaces showing extensive occurrence of the vitreous phase in (a) the body and (b) the slip on the pottery (approximately 60-70 microns thick).

closed pores, eventually evolving “bloating” pores, which may occur in a partially reducing firing atmosphere (see the following section). Thus, according to Maniatis and Tite’s (1981) SEM observations, it may be suggested that the vessel was fired at about 1050-1100°C or above.

The black paint

Qualitative micro-XRF analysis of the black paint showed the presence of Fe, Mn and Ca as major elements associated with lower levels of Ti, K, S and Si (μ -XRF was not sensitive for elements lighter than Si). Traces of Ni, Zn, Cu and Cr were detected, and these are usual transition metals which occur with Fe and Mn (Figure 4a).

More specifically, μ -Raman predominantly registered the Raman bands at 335, 460 and 616 cm^{-1} , which are most certainly attributable to jacobsonite, MnFe_2O_4 (Buzgar *et al.* 2013), and a shoulder at 670 cm^{-1} which can be assigned to magnetite (Shebanova and Lazor 2003) (Figure 4b). In addition, μ -Raman showed further details about the composition of the black paint in some spots (bands at 292, 331, 382, 523, 606, 670 cm^{-1} ; Figure 4c) assigned either to magnetite or jacobsonite, and the Raman bands at 758 and 972 cm^{-1} can be assigned to hercynite, $\text{Fe}^{2+}\text{Al}_2\text{O}_4$ (Leon *et al.* 2010), which is black in colour. As Leon *et al.* (2010) have shown, the presence of hercynite may suggest a high firing temperature. Moreover, the presence of magnetite suggests firing in a reducing atmosphere. The reducing atmosphere may also have been the reason for the extensive vitrification of the body (Tite and Maniatis 1975) and subsequent collapse of the body. Although the presence of magnetite and

hercynite as black paints on ancient pottery is fairly well-documented in literature (Noll *et al.* 1975), the presence of jacobsonite has only been reported occasionally for the decoration of archaeological pottery (Stos-Gale and Rook 1981; Centeno *et al.* 2012; Buzgar *et al.* 2013).

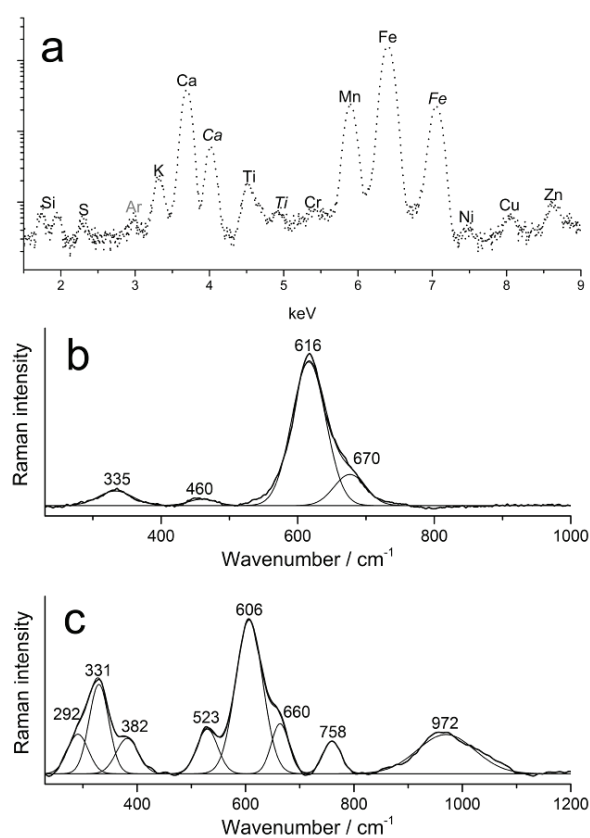


Figure 4. (a) Micro-XRF spectrum (logarithmic scale) of the black paint (note that Ar is introduced from air to the spectrum). Raman spectra of (b) jacobsonite and magnetite, and (c) magnetite, jacobsonite and hercynite in the black paint.

Conclusions

A combination of various analytical studies on a black-painted pot excavated at Tepe Sialk of Kashan showed that it was fired at a temperature of ca. 1050-1100°C. Micro-XRF and micro-Raman results showed that the black paint is a mixture of magnetite, jacobsite and hercynite formed in a relatively reducing atmosphere of the kiln. As this study showed, a combination of various analytical techniques gives a comprehensive picture of the thermal history of an archaeological vessel.

As cheap, easy-to-use and fast methods, porosimetry and specific gravity of ceramic bodies may be considered useful techniques for characterising aspects of archaeological ceramics and particularly their firing regime. However, if these are to be used without the complementary scientific techniques described above, then comprehensive preliminary data should be first provided on laboratory-made specimens prepared under controlled firing regimes to contextualise the physical properties of archaeological pottery. Therefore, future studies may investigate how porosity, specific gravity and water absorption of pottery specimens made of various clay types change under different firing regimes, in order to compare the manufacturing aspects of archaeological pottery with a suite of reference data obtained on the laboratory-made specimens.

Acknowledgments

This paper is a part of the B.A. thesis of the first author accomplished at the Art University of Isfahan, Iran, in 2014. We are grateful to Carmela Vaccaro at the University of Ferrara, Italy, for providing μ -Raman and μ -XRF analytical facilities. Somayeh Nosrati is especially thanked for providing her analytical data of the Sialk III pottery.

References

- Alizadeh, A. 1992. *Prehistoric Settlement Patterns and Cultures in Susiana, Southwestern Iran: The Analysis of the F.G.L. Gremliza Survey Collection*. University of Michigan, Museum of Anthropology.
- Alizadeh, A. 2006. *The Origins of State Organizations in Prehistoric Highland Fars, Southern Iran: Excavations at Tall-e Bakun*. University of Michigan. Oriental Institute of the University of Chicago.
- Boulanger, M. 2014. *Iranian Ceramics: Compositional and Descriptive Data*. Lawrence Berkeley National Laboratory. (tDAR id: 372490); doi: 10.6067/XCV83F4NGK.
- Buzgar, N., Apopei, A. I. and Buzatu, A. 2013. Characterization and source of Cucuteni black pigment (Romania): vibrational spectrometry and XRD study. *Journal of Archaeological Science* 40, 2128-2135.
- Centeno, S. A., Williams, V. I., Little, N. C. and Speakman, R. J. 2012. Characterization of surface decorations in Prehispanic archaeological ceramics by Raman spectroscopy, FTIR, XRD and XRF. *Vibrational Spectroscopy* 58, 119-124.
- Cultrone, G., Rodriguez-Navarro, C., Sebastian, E., Cazalla, O. and de La Torre, M. J. 2001. Carbonate and silicate phase reactions during ceramic firing. *European Journal of Mineralogy* 13, 621-634.
- Fazeli Nashli, H. 2004. *The Archaeology of the Qazvin Plain from the Sixth to the First Millennium BC*. Tehran, University of Tehran Press (in Persian).
- Ghirshman, R. 1938-1939. *Fouilles de Sialk près de Kashan 1933, 1934, 1937* (vols. I, II). Paris, Geuthner.
- Harry, K. G. and Johnson, A. 2004. A non-destructive technique for measuring ceramic porosity using liquid nitrogen. *Journal of Archaeological Science* 31, 1567-1575.
- Hein, A., Müller, N. S., Day, P. M. and Kilikoglou, V. 2008. Thermal conductivity of archaeological ceramics: The effect of inclusions, porosity and firing temperature. *Thermochimica Acta* 480, 35-42.
- Jordán, M. M., Boix, A., Sanfeliu, T. and de la Fuente, C. 1999. Firing transformations of cretaceous clays used in the manufacturing of ceramic tiles. *Applied Clay Science* 14, 225-234.
- Kingery, W. D. 1974. A note on the differential thermal analysis of archaeological ceramics. *Archaeometry* 16, 109-112.
- Lange, R. A. 1997. A revised model for the density and thermal expansivity of K₂O-Na₂O-CaO-

- MgO-Al₂O₃-SiO₂ liquids from 700 to 1900 K: extension to crustal magmatic temperatures. *Contributions to Mineralogy and Petrology* 130, 1-11.
- Leon, Y., Lofrumento, C., Zoppi, A., Carles, R., Castellucci, E. M. and Sciau, P. 2010. Micro-Raman investigation of terra sigillata slips: a comparative study of central Italian and southern Gaul productions. *Journal of Raman Spectroscopy* 41, 1550-1555.
- Maniatis, Y. and Tite, M. S. 1981. Technological examination of Neolithic-Bronze Age pottery from central and southeast Europe and from the Near East. *Journal of Archaeological Science* 8, 59-76.
- Moroni, B. and Conti, C. 2006. Technological features of Renaissance pottery from Deruta (Umbria, Italy): an experimental study. *Applied Clay Science* 33, 230-246.
- Mursky, G. A. and Thompson, R. M. 1958. A specific gravity index for minerals. *The Canadian Mineralogist* 6, 273-287.
- Noll, W., Holm, R. and Born, L. 1975. Painting of ancient ceramics. *Angewandte Chemie International Edition* 14, 602-613.
- Nosrati, S. 2012. *The Study of the Technology of Pottery in 4th Millennium BC by Using Laboratory Methods of XRD and XRF in North Centre of Iran (Case Study of Sialk III, Arisman I and Tepe Ghabristan II)*. M.A. Thesis for Archaeology, Art University of Isfahan, Iran (in Persian).
- Shahmirzadi, S. M. 2004. *The Potters of Sialk*. Tehran, Archaeological Research Centre, Iranian Cultural Heritage Organization (in Persian).
- Shebanova, O. N. and Lazor, P. 2003. Raman spectroscopic study of magnetite (FeFe₂O₄): a new assignment for the vibrational spectrum. *Journal of Solid State Chemistry* 174, 424-430.
- Stos-Gale, Z. and Rook, E. 1981. Analysis of pigments used for decoration of Neolithic pottery from Bilcze Zlote, Ukraine. In Hughes, M. J. (ed.), *Scientific Studies of Ancient Ceramics*, British Museum Occasional Papers, No. 19, 155-161.
- Tite, M. S. and Maniatis, Y. 1975. Examination of ancient pottery using the scanning electron microscope. *Nature* 257, 122-123.
- Velraj, G., Mohamed Musthafa, A., Janaki, K., Deenadayalan, K. and Basavaiah, N. 2010. Estimation of firing temperature and ancient geomagnetic field intensity of archaeological potteries recently excavated from Tamilnadu, India. *Applied Clay Science* 50, 148-153.
-