Investigation of Neolithic pottery from Ebrahimabad in the central plateau of Iran, utilising chemical–mineralogical and microstructural analyses

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ABSTRACT

Prehistoric sherds recovered from Ebrahimabad, in the Central Plateau of Iran, were investigated using X-ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electron microscope (SEM)/energy dispersive X-ray (EDX) analyses. The results showed a gradual evolution in production from Sialk I-type pottery to Sialk II-type pottery, eventually leading to the production of bulk red pottery. The relative similarity of composition, homogeneous microstructures and the presence of high-temperature phases demonstrated a high degree of specialisation in the selection of raw materials and control of firing temperature and atmosphere by the potters of Ebrahimabad in the late fifth to early sixth millennia BC, peaking in the final phase associated with Sialk II.

1. Introduction

In 2003 an international project was launched in order to study the socio-economic transformation of the Neolithic and Chalcolithic settlements within the Central Plateau of Iran. One of the main objectives was to study the evolution of craft specialisation and settlement patterns of pre-urban societies in the region (Coningham et al., 2004; Fazeli et al., 2007a). Multidisciplinary work was carried out to provide stratigraphic information and absolute dating, as well as to characterise the pottery excavated from three sample sites on the Central Plateau, namely Pardis, Ebrahimabad and Sialk, located on the Tehran, Qazvin and Kashan plains, respectively.

In this paper, the stratigraphic information and absolute dating, as well as characteristics of the pottery excavated from the Ebrahimabad site in 2006 (Fazeli et al., 2007b), will be discussed. Tepe Ebrahimabad is located on the Qazvin Plain in the Central Plateau of Iran, 20 km southeast of the city of Qazvin (Fig. 1).

The main geographical features of the Central Plateau of Iran include mountains, deserts and plains. According to geological studies, a great tectonic line separates the Central Plateau from the geological deposits to the south (Dewan and Famouri, 1968). Along this line eruptive rocks, such as andesite, and numerous springs are present in different areas. These springs have caused the deposition of travertine, a form of limestone, and sediments from the Palaeozoic, Mesozoic and Tertiary are also present (Dewan and Famouri, 1968).

The plains are mostly covered by water-transported alluvial sediments, and encompass a number of inter-montane areas and small kavirs that can be divided into different micro-environmental zones (Fazeli, 2001, 14). Alluvial fans are the most extended sediments found across the plains. They are fan-shaped deposits formed where a fast-flowing stream flattens, slows down and spreads, for example at the exit of a valley onto a flatter plain. They are the main site of deposition in areas where mountains gradually wear away, over geological time spans, and basins are filled with sediment (Wilkinson, 2003, 76–78). Alluvial fans in the Central Plateau range in size from less than 1 km² to massive fans measuring more than 2500 km², for example Jajrud located on the Tehran Plain (Beaumont, 1972). The exact date of the appearance of alluvial fan sedimentation on the Central Plateau is not clear, but it has been suggested that optimum conditions for the formation of fans were initiated mainly during the glacial phases of the Pleistocene. Two major phases of alluvial deposition in Iran are recognised (Beaumont, 1972; Vita-Finzi, 1968): an earlier phase of deposition that probably began about 50,000 years ago and had ended by the fourth millennium BC; and a second phase that occurred during the Middle Ages. Because of the lack of data, it is impossible to estimate the thickness of the alluvial fans correctly. For example, in the Tehran Plain, which is a structural basin at the southern margin of the Alburz Mountains, formed by the down warping of Palaeozoic and Mesozoic sediments and Eocene volcanic materials (Beaumont, 1972), thick Miocene beds were laid down and, more recently, thick alluvial deposits from Jajrud (one of the main rivers in the region) flooding events have played a significant role in depositing large volumes of sediment over a short time period (Beaumont, 1972). These sediments consist mainly of fine-grained clays and silts, as well as coarse sands and...
granules. Limited excavations on the Jajrud fan have revealed the existence of a deposit 275 m deep, but greater thicknesses might occur elsewhere (Beaumont, 1972). The plain of Qazvin is another large alluvial basin comprising volcanic rock formations elsewhere (Beaumont, 1972). The plain of Qazvin is another large al-

existence of a deposit 275 m deep, but greater thicknesses might occur (Fazeli et al., 2007b, 2013) was carried out in order to investigate the Plateau (Marghussian et al., 2017). The excavation of Ebrahimabad there were cultural interactions between large areas of the Central Plateau (Fig. 2a,b). Ghirshman first reported the existence of these pottery types following his excavation at the site of Sialk in 1936–38 (Ghirshman, 1938). Sialk ware continues to be a key cultural and chronological marker for the interpretation of the late prehistoric chronology of the Central Plateau (Table 1). Sialk I ware (dated to c. 5600–5200 BCE) is characterised by handmade, buff, painted pottery, decorated with simple black geometric motifs. The succeeding stage, Sialk II ware (dated to c. 5200–4600 BCE), is characterised by thin handmade, red, painted pottery, typically decorated with black motifs that include simple or composite geometric designs.

The presence of Sialk I pottery, with its main distribution in regions such as Kashan and Tehran, shows that by early sixth millennium BC there were cultural interactions between large areas of the Central Plateau (Marghussian et al., 2017). The excavation of Ebrahimabad (Fazeli et al., 2007b, 2013) was carried out in order to investigate the possible presence of Sialk I pottery in the Qazvin Plain, another area located on the Central Plateau. These excavations have revealed for the first time the presence of pottery characteristic of Sialk I and II in the Qazvin Plain, and provided an absolute chronology for the Qazvin Plain’s Late Neolithic to Early Transitional Chalcolithic sequence (Fazeli et al., 2007b, 2010, 2013).

Since the start of archaeological studies in Iran, ceramics from the Central Plateau have been studied in a traditional manner, using descriptive and classification methodologies, based mainly on the colour and decoration of the pottery. Using more advanced techniques, such as chemical-mineralogical analyses and microstructural studies, to characterise the newly excavated pottery from Ebrahimabad, as well as stratigraphic information and absolute dating, should help us gain a better understanding of the evolution of the processes behind these pottery styles, including changes in techniques and the organisation of ceramic production from the Late Neolithic to the Transitional Chalcolithic (c. 5700–4800 BCE) in this region.

To the authors’ knowledge, the techniques used in the present study have not been used previously to characterise the prehistoric pottery of this region. By providing additional information on the evolution of the pottery process, the results of this study can help us address questions about the causes of the general chromatic change in pottery that occurred in the region from the Late Neolithic to the Transitional Chalcolithic, and reveal the relevance of this to the economic and cultural connections and interactions of the prehistoric communities living in the Central Plateau during that period.

2. Materials and methods

2.1. Sample selection

For the present study, 22 sherds from the Ebrahimabad site (Table 2), excavated in 2006 (Fazeli et al., 2009, 2013), were investigated. The sherds comprised two different assemblages of 14C-dated Sialk-type pottery, an assemblage of 12 Sialk I sherds and an assemblage of 10 Sialk II sherds (Table 2). The samples for each assemblage had been randomly selected from the excavated pottery on the basis of their appearance (colour and decoration). The Sialk I pottery samples were selected from the excavated buff pottery group decorated with black-painted simple geometric motifs, and Sialk II samples from the excavated red pottery group decorated with black-painted simple or composite geometric motifs.

2.2. Typology

The excavated pottery was divided into a number of broad categories: jars (form J), bowls (form B), beakers (form BE), trays (form T), bases (forms F and R) and dishes (form D). Each of these categories was further subdivided, generally along the lines of having open or closed mouths (e.g. B1 and B3). A further subdivision was then made depending on whether the sides were steep or shallow (e.g. J1a and J1b). Fig. 3 depicts the main forms of excavated pottery from Ebrahimabad.
Table 1
The chronology of the Qazvin Plain, in comparison with other sites located on the Central Plateau of Iran (after Fazeli et al., 2009).

<table>
<thead>
<tr>
<th>Period (BC)</th>
<th>Location</th>
<th>Qazvin Plain sites</th>
<th>Tehran Plain sites</th>
<th>Kashan Plain sites</th>
<th>Damghan/Shahrud sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early Bronze II (Kura-Araxes), 2900–2000</td>
<td>Shizar, Doranabad</td>
<td>Shizar</td>
<td>Arasto Tepe</td>
<td>?</td>
<td>Hisar III</td>
</tr>
<tr>
<td>Early Bronze I (Proto-Literate), 3400–2900</td>
<td>Shizar</td>
<td>Ghbristan III-IV, Tepe Sagz Abad, Ismail Abad, Shizar</td>
<td>Tepe Sofalin, Shogali</td>
<td>Arisman C, Sialk IV</td>
<td>Hisar IIB</td>
</tr>
<tr>
<td>Late Chalcolithic, 3700–3400</td>
<td>Ghabristan II, Shizar</td>
<td>Ghbristan II, Shizar</td>
<td>Cheshmeh-Ali, Tepe Pardis, Shogali</td>
<td>Arisman B, Sialk South 6–7</td>
<td>Hisar IIA</td>
</tr>
<tr>
<td>Middle Chalcolithic, 4000–3700</td>
<td>Ghabristan I</td>
<td>Ghbristan I</td>
<td>Cheshmeh-Ali, Tepe Pardis, Shogali</td>
<td>Sialk South 4–5</td>
<td>Hisar IC</td>
</tr>
<tr>
<td>Transitional Chalcolithic Late, 4600–4300</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>Shir Azhian, Aq Tappeh'</td>
</tr>
<tr>
<td>Neolithic Late, 5600–5200</td>
<td>Chahar Boneh, Ebrahim Abad</td>
<td>Cheshmeh-Ali, Tepe Pardis</td>
<td>Sialk North 4–5</td>
<td>Sang-i Chakhmaq</td>
<td>'Djeitun' phase</td>
</tr>
<tr>
<td>Early, 6000–5600</td>
<td>Chahar Boneh</td>
<td>?</td>
<td>Sialk North 1–3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Without C14 dates.
2.3. Chemical analysis

There are many different techniques that can and have been used for the chemical analysis of archaeological artefacts. In this study, we used X-ray fluorescence (XRF), on an Oxford ED2000 spectrometer. The XRF spectrometer is an X-ray instrument used for routine, relatively non-destructive, chemical analyses of rocks, minerals, sediments and fluids. XRF analysis is useful for investigating about 80 elements present in major quantities (Pollard, 2007, 101; Rice 1987, 394).

In order to prepare the bulk samples, the sherds were first broken up and the resulting fragments then crushed into a coarse gravel. This material was ground using a Tema Laboratory Disc Mill, with a tungsten carbide barrel. Grinding usually took 3–4 min until a very fine powder was obtained, then 5–7 drops of wax were added as a binding agent. Approximately 12 g of the powdered samples were then pressed into briquettes using a Specac’s Atlas series hydraulic (pressure between 5 and 10 tons).

The briquettes were dried in an oven at 110 °C for 1 h. The resulting discs were then placed in the sample holder of the XRF spectrometer. Before analysing the actual samples, a series of standards or known samples were analysed to confirm that the chosen procedure would result in accurate, reproducible data. All 22 archaeological samples were subjected to XRF analysis.

2.4. Mineralogical analysis

Study of the thermal behaviour of ancient pottery has always attracted attention within the archaeological sciences because it yields

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**Table 2**
The chronology of the pottery from the site of Ebrahimabad.

<table>
<thead>
<tr>
<th>Pottery ID</th>
<th>Context</th>
<th>Trench</th>
<th>Period</th>
<th>Calibrated date with 95% probability (BC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1t</td>
<td>266</td>
<td>II</td>
<td>Late Neolithic II (Late)</td>
<td>5518–5372</td>
</tr>
<tr>
<td>E1r</td>
<td>260</td>
<td>II</td>
<td>Late Neolithic II (Late)</td>
<td>5518–5372</td>
</tr>
<tr>
<td>E1k</td>
<td>248</td>
<td>II</td>
<td>Late Neolithic II (Late)</td>
<td>5378–5218</td>
</tr>
<tr>
<td>E1i</td>
<td>248</td>
<td>II</td>
<td>Late Neolithic II (Late)</td>
<td>5378–5218</td>
</tr>
<tr>
<td>E1n</td>
<td>247</td>
<td>II</td>
<td>Late Neolithic II (Late)</td>
<td>5378–5218</td>
</tr>
<tr>
<td>E1p</td>
<td>246</td>
<td>II</td>
<td>Late Neolithic II (Late)</td>
<td>5378–5218</td>
</tr>
<tr>
<td>E1o</td>
<td>244</td>
<td>II</td>
<td>Late Neolithic II (Late)</td>
<td>5378–5218</td>
</tr>
<tr>
<td>E1f</td>
<td>157</td>
<td>I</td>
<td>Late Neolithic II (Late)</td>
<td>5356–5216</td>
</tr>
<tr>
<td>E1e</td>
<td>361</td>
<td>III</td>
<td>Late Neolithic II (Late)</td>
<td>5230–5051</td>
</tr>
<tr>
<td>E1g</td>
<td>361</td>
<td>III</td>
<td>Late Neolithic II (Late)</td>
<td>5230–5051</td>
</tr>
<tr>
<td>E1s</td>
<td>349</td>
<td>III</td>
<td>Late Neolithic II (Late)</td>
<td>5228–5032</td>
</tr>
<tr>
<td>E1u</td>
<td>330</td>
<td>III</td>
<td>Late Neolithic II (Late)</td>
<td>5220–5011</td>
</tr>
<tr>
<td>E2f</td>
<td>214</td>
<td>II</td>
<td>Transitional Chalcolithic (Early)</td>
<td>5320–5206</td>
</tr>
<tr>
<td>E2i</td>
<td>214</td>
<td>II</td>
<td>Transitional Chalcolithic (Early)</td>
<td>5320–5206</td>
</tr>
<tr>
<td>E2b</td>
<td>355</td>
<td>III</td>
<td>Transitional Chalcolithic (Early)</td>
<td>5230–5051</td>
</tr>
<tr>
<td>E2d</td>
<td>355</td>
<td>III</td>
<td>Transitional Chalcolithic (Early)</td>
<td>5230–5051</td>
</tr>
<tr>
<td>E2n</td>
<td>355</td>
<td>III</td>
<td>Transitional Chalcolithic (Early)</td>
<td>5230–5051</td>
</tr>
<tr>
<td>E2c</td>
<td>349</td>
<td>III</td>
<td>Transitional Chalcolithic (Early)</td>
<td>5228–5032</td>
</tr>
<tr>
<td>E2a</td>
<td>346</td>
<td>III</td>
<td>Transitional Chalcolithic (Early)</td>
<td>5228–5032</td>
</tr>
<tr>
<td>E2e</td>
<td>342</td>
<td>III</td>
<td>Transitional Chalcolithic (Early)</td>
<td>5228–5032</td>
</tr>
<tr>
<td>E2h</td>
<td>342</td>
<td>III</td>
<td>Transitional Chalcolithic (Early)</td>
<td>5060–4882</td>
</tr>
<tr>
<td>E2j</td>
<td>342</td>
<td>III</td>
<td>Transitional Chalcolithic (Early)</td>
<td>5060–4882</td>
</tr>
</tbody>
</table>

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**Fig. 3.** The distribution of pottery forms at Ebrahimabad.
useful information about the technology used to make and fire ancient pottery. X-ray diffraction (XRD) is one of the most popular techniques used to identify the minerals present in ceramics (Pollard, 2007; Rice, 1987, 382–386). Determining and determining the nature of the minerals present in ceramics can provide an indication of the firing history of the ceramics. An estimation of firing temperature made using XRD is based on the fact that the mineralogical composition of clays changes during firing. These changes normally include the loss of water from the clay minerals and other hydroxides, the decomposition of carbonates with a loss of carbon dioxide, and the formation of various new phases and crystalline minerals. These changes occurring during the firing of clay bodies can be monitored by XRD. Therefore, as a direct method, XRD is of continual interest in determining the firing temperature of ancient ceramics (Holakoei et al., 2014).

For this study, 13 sherds from Ebrahimabad (five and eight samples of the Sialk I and II types, respectively) were selected randomly and analysed by powder XRD (PXRD) (using a PANalytical Xpert Multi-Purpose Diffractometer), with Cu Kα1 radiation and a PIxcel solid-state detector in a 2θ range of 5–120°. The step-scan size was approximately 0.013° in 2θ and the total acquisition time per pattern was 40 min. Identification of the crystalline phases by XRD was carried out using the International Centre for Diffraction Data Powder Diffraction Files (ICDD PDF). JCPDS (Joint Committee on Powder Diffraction Standards) reference cards were used to interpret the patterns.

2.5. Microstructural examinations

Scanning electron microscopy (SEM) analyses the surface of materials and provides detailed high-resolution images of samples by rastering a focused electron beam across the surface and detecting the secondary or backscattered electron signal. An energy-dispersive X-ray analyser (EDX or EDA) can also be used to provide element identification and quantitative compositional information (Pollard, 2007, 109). For this study, X-ray mapping of some samples was also carried out. In this way the whole surface area was analysed and systematically mapped in terms of mineralogy or element composition, and the resulting data provided a false-colour mineralogical/compositional map of the sample. In addition, the compositional data were reported as modal mineralogy in area%, along with the size of each discrete mineralogical component. Sometimes the nature and extent of the changes that occurred during the firing process can also be observed and determined by SEM, such as an estimation of the degree of vitrification within the clay matrix of ceramics.

For this study, some typical samples (E1c, E1r, E1t, E2i, E2h, and E2d) were subjected to SEM (using a Hitachi TM-3000) and phase compositions of certain zones in the microstructures were determined by EDX (using a Swift ED) attached to the SEM. For this kind of SEM analysis, no preparation of samples was needed.

3. Results and discussion

3.1. Typological studies

Fig. 3 shows the assemblages from Ebrahimabad for the Transitional Chalcolithic and Late Neolithic time periods. As can be seen, vessel form types B1a, B3b and B4b were exclusive to the Late Neolithic (Sialk I), while J1c, B3d, B6, R1, R2 and F3 were exclusive to the Transitional Chalcolithic (Sialk II). Other forms were more or less common between the two pottery types. The forms were classified as follows.

B1a is a closed bowl with a curved body and a low shoulder (at an angle of 45–75°).

B3b is an open bowl with a rounded and flared rim and a straight or slightly concave neck.

B4b is an open bowl with a steep, inwardly sloped (75° to near vertical) gently curving body.

J1c is a jar with a steep shoulder (75°–90°) and an everted rim.

B3d is an open bowl with a steep shoulder and vertical straight shoulder (75° to near vertical).

B6 is a closed bowl with a steep shoulder and globular body leading to a narrow pedestal base.

R1 is a ring-footed base leading to a steep (< 45°) body.

R2 is a ring-footed base leading to a shallow (45–60°) body.

F3 is a flat-bottomed base leading to a shallow (> 45°) inwardly curving body.

The following forms were present equally in both Sialk assemblages.

B2b is a closed bowl with a steep shoulder (< 45°) and a flattened rim.

B3a is an open bowl with a shallow inwardly sloped (45–75°) straight-sided body.

B3c is an open bowl with a shallow inwardly sloped (45–75°) gently curving body.

B5 is an open bowl with a steep inwardly sloped (75° to near vertical) straight-sided body.

D1 is a shallow dish with a very shallow inwardly sloped (< 45°) straight-sided body.

BE1 is a beaker with a steep and vertical straight shoulder (75° to near vertical) leading to a flat-bottomed base.

3.2. XRF studies

Table 3 lists the chemical composition of the Sialk I and II samples. Obviously, the Sialk I samples exhibited quite homogeneous compositions. The relatively high value for the standard deviation shown by calcium oxide (CaO) is common and can be attributed to the variation of its content in the original clay deposits. It has been shown that, comparing six element oxides, the greatest variation within a single clay deposit occurs with CaO (Buko, 1984). In the burial environment, a variety of processes can also alter the chemical composition of pottery. Two of these processes are cation leaching (Bieber et al., 1976) and exchange (Hedges and McLellan, 1976). Calcium is one of the elements that are susceptible to all of these processes. Leaching and ion-exchange processes can also affect the alkali elements, such as Na and K, whereas Si, Al and Fe are more resistant. On the basis of these results, it can be deduced that the pottery had been made using a single source of clay as the raw material, or clay from very similar sources, and the relatively high content of CaO in many samples indicates the use of a calcareous clay as the raw material for most of the pottery represented.

On the other hand, the chemical composition of the Sialk II samples indicated the existence of two different types of pottery, Ca-rich and relatively Ca-poor, each group exhibiting quite homogeneous compositions. The Ca-rich samples had a similar composition to the Sialk I samples, and therefore had apparently been made using the same clay as the raw material as the Sialk I pottery. These vessels were distinguished by a strong red colour for the surface and a buff colour for the core, while the samples from the second group, which had a red colour for both the surface and the core (as shown in Table 3), were the product of different raw materials. Although iron oxide (Fe2O3) minerals may be present in clays used as the raw material in the production of pottery, these minerals can also appear during the firing of pottery as a product of the destruction of Fe-containing minerals present in the raw material and recrystallisation of secondary crystals. In an oxidising atmosphere, haematite crystals can be formed, which is responsible for the red colour of the pottery. However, it must be borne in mind that calcareous lumps in Ca-rich clay can prevent the formation of haematite crystals by fixation of Fe in the network of newly formed calcareous silicate and aluminosilicate minerals, consequently inhibiting the generation of a red colour in the fired pottery (Rice, 1987, 336).

A principal component analysis (PCA) was also carried out on the XRF chemical composition data, using the statistical package SPSS V21. For the statistical analysis, silicon oxide (SiO2), aluminium oxide
(Al$_2$O$_3$), Fe$_2$O$_3$, magnesium oxide (MgO), CaO, potassium oxide (K$_2$O) and titanium oxide (TiO$_2$) were used. A correlation matrix was used for the PCA analysis and a plot was drawn representing the variation in the second principal component (PC) against the first component.

The PCA plot is shown in Fig. 5. The cumulative variance for the first two PCs was 74.94 and 70.33%, respectively. From Fig. 5 it can be deduced that a group of pottery samples from the Ebrahimabad I period, as well as Ca-rich samples from Ebrahimabad II, exhibited considerable clustering of pottery composition, whereas the Ca-poor samples from Ebrahimabad II showed discreet clustering that was effectively separated from the first group of samples. These results conform with the above discussion concerning the homogeneity of the chemical composition within both Ebrahimabad I and II pottery, and the similarity and differences in composition between the Ebrahimabad I pottery and Ca-rich and Ca-poor Ebrahimabad II pottery, respectively.

### 3.3. PXRF

Fig. 6 shows the XRD traces of some typical samples, and Table 4 summarises the mineralogical analyses of Sialk I and II samples. It can be seen that quartz and esseneite (Ca(Fe$_{1.4}$Al$_{0.6}$)SiO$_6$) were the major crystalline phases of Sialk I samples. On the other hand, for the Sialk II samples, while the Ca-rich samples contained similar mineral phases as Sialk I (quartz and esseneite), the Ca-poor Sialk II samples were composed mainly of quartz, hematite and augite (Ca(Mg,Al,Fe)Si$_2$O$_6$) phases [also gehlenite (Al$_2$Ca$_2$SiO$_7$) in some samples].
It is well known that within any single pottery type there is an acceptable range of variability, consisting of > 10 oxides and differences in firing techniques, hence it can be very labour-intensive to identify the mineral phases shown in XRD traces. In this study, for example, for identification of esseneite we compared each sample with the reference card for seven 22 values, located in the 27.59–35.29 range. Obviously, exact matches were never observed, but with some variation in the height and position of peaks a number of acceptable matches were obtained; the resulting matches were not observed in other similar minerals.

Given the fact that the plain of Qazvin is an alluvial basin made of volcanic rock formations filled by deep sedimentary layers (see the Introduction), and the XRD results, which showed traces of calcium carbonate (CaCO₃) and illite phases (which were more pronounced in older samples of Sialk I pottery, e.g. samples E1r and E1t), it can be postulated that the raw materials used for the production of Sialk I-type pottery and the Ca-rich samples had been calcareous illite clays. It should also be noted that illite is one of the most common clay minerals in calcareous sediments (Rice, 1987, 50). The Ca-poor Sialk II samples, on the other hand, had been made using a non-calcareous clay source.

3.4. Microstructural analysis of ceramics

The relatively uniform microstructures and the absence of large and angular particles indicated that the raw materials used were probably sedimentary (secondary) clays, and that no inorganic tempers (including carbonates) had been deliberately added to the original raw material. However, traces of organic tempers, such as fine chaff or dung, could be seen on the microstructures and element maps depicting the cross-sections of some Sialk I and II samples (Fig. 7 and 8). The element maps showed that these remnants were mainly composed of C.

Fig. 9 shows the SEM micrograph of a typical Ca-rich Sialk II-type sherd exhibiting a quite dense and vitrified microstructure that could not only have been achieved with the presence of a liquid phase, in a sufficient quantity and with a relatively low viscosity, at the maximum firing temperature of the pottery. Fig. 10a, b depicts the SEM micrographs of the E1t and E1c Sialk I-type sherds. It can be seen that, despite the difference of c. 300 years in the dates of these two samples, they exhibited very similar microstructures.

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3.4. Microstructural analysis of ceramics

The relatively uniform microstructures and the absence of large and angular particles indicated that the raw materials used were probably sedimentary (secondary) clays, and that no inorganic tempers (including carbonates) had been deliberately added to the original raw material. However, traces of organic tempers, such as fine chaff or dung, could be seen on the microstructures and element maps depicting the cross-sections of some Sialk I and II samples (Fig. 7 and 8). The element maps showed that these remnants were mainly composed of C.

Fig. 9 shows the SEM micrograph of a typical Ca-rich Sialk II-type sherd exhibiting a quite dense and vitrified microstructure that could only have been achieved with the presence of a liquid phase, in a sufficient quantity and with a relatively low viscosity, at the maximum firing temperature of the pottery. Fig. 10a, b depicts the SEM micrographs of the E1t and E1c Sialk I-type sherds. It can be seen that, despite the difference of c. 300 years in the dates of these two samples, they exhibited very similar microstructures.
and Mg can act as fluxes (Segnit and Anderson, 1972). That is why ancient potters might have explored these types of clay, in order to use less energy when using their pots.

It has also been reported that gehlenite appears at 800 °C (Dondi et al., 1998) and new Ca compounds, such as diopside, wollastonite and calcium ferro-silicates, are mainly formed at high temperatures of 900–1100 °C (Tite and Maniatis, 1975b). El-Didamony et al. (1998) have shown that, during the firing of a calcareous clay, the content of the mineral diopside, which first appears at 850 °C, gradually increases up to 1150 °C. However, Eftekhar Yekta and Alizadeh (2001) have detected the formation of diopside at a temperature range of 930–1080 °C, during the firing of a calcareous clay with a similar composition to the latter clay.

On the basis of PXRD analysis and microstructural studies, it can be claimed that, apart from a very few CaO particles present in some samples, which are the remnants of large particles that did not have enough time to react during the firing of the pottery, there is no evidence for the presence of CaO particles in the samples. On the other hand, there are clear signs of the formation of Ca–Fe–Al–silicate minerals such as esseneite in the Sialk I-type pottery, produced mainly as the result of reactions between the destructed illite clays and CaO resulting from the decomposition of CaCO3, as discussed above. Moreover, it can be deduced that the Fe2O3 liberated from the decomposition of some clay minerals, such as illite, has possibly been incorporated into the silicate lattice structures at temperatures lower than those reported above. Considering the fact that the main silicate mineral present in the Sialk I samples is an esseneite-like mineral, and that no hematite crystals were detected in the samples, it can be deduced that Fe had largely been incorporated into the esseneite crystal structure, which could accommodate high amounts of Fe (43.3 wt%). Hence, when considering the decomposition and distraction temperatures of CaCO3 and clay minerals, the sintering and vitrification processes and the formation temperatures of silicate and alumino-silicate phases, it can be suggested that Sialk I as well as the Ca-rich Sialk II pottery at Ebrahimabad, which had similar chemical and mineralogical compositions, could have been fired at 900–950 °C, while the older pottery (samples E1r and E1t; Table 4) had been fired at lower temperatures, c. 800–850 °C.

However, in the case of the red-coloured Sialk II samples, the EDX element map showed no differences between the content of Fe on the interior and exterior of the samples (Fig. 11a, b). Therefore the presence of a red Fe-rich coating on the outer surface of these samples should be ruled out. As a result, it can be suggested that the main factor responsible for the change from the apparently buff-coloured Sialk I ware to the distinctively red-coloured Sialk II ware is a more efficient and ingenious control of the firing process: in an oxidising atmosphere, hematite crystals can be formed that are responsible for the red colour of the pottery.

It should be noted that half of the Sialk II red pottery samples from Ebrahimabad were distinguished by the strong red colour of their surface and buff colour of their core, whereas the other half had a red colour on both the surface and the core (Table 3). As discussed above, while the Ca-rich samples of Sialk II ware had similar chemical and mineralogical compositions to the Sialk I samples, the pottery sherds possessing a relatively lower content of CaO contained a different Ca–Al–Fe–Mg–silicate mineral, augite, as their major crystalline phase. Augite mineral accommodates much lower amounts of Fe2O3 (10.62 wt %) in its structure and, because of the lower content of Ca in the original clay, the volume of augite would also be lower in comparison with the esseneite mineral in Sialk I pottery. Hence, a great proportion of Fe2O3 present in the raw materials of this group has appeared as the Fe2O3 mineral (hematite) in the fired bodies.

On the other hand, the Ca-rich Sialk II sherds exhibited quite dense and vitrified microstructures (Fig. 9). This could only have been achieved by the presence of a liquid phase, in a sufficient quantity and with a relatively low viscosity, at the maximum firing temperature for these ceramics. Considering the higher refraction of the raw materials
used in the production of Sialk II ware (because of its higher content of SiO$_2$ and Al$_2$O$_3$ and lower content of CaO), a higher firing temperature should be anticipated for this pottery in comparison with Sialk I. On the basis of the above facts and observations, a temperature range of 1000–1050 °C can be assigned to the firing of the Ca-poor Sialk II-type pottery. It should be noted that, in non-industrial firing, there can be considerable fluctuations in firing temperatures. Even in kiln firing, temperature differences of as much as 100 °C can exist between different sections of the kiln (Mayes, 1961, 1962) and, under these conditions, determining the exact firing temperatures is impossible.

3.6. The evolution of pottery production in Ebrahimabad

As mentioned above, all the Sialk I-type sherds from Ebrahimabad had a similar chemical composition and almost all of them were composed of minerals such as quartz and esseneite. These pottery sherds also exhibited a very similar microstructure. For example, samples E1t (Fig. 10a) and E1c (Fig. 10b), despite a difference of c. 300 years in their dating, determined using the $^{14}$C–dated sequence and chronology of Ebrahimabad (Table 2), exhibited similar microstructures.

However, as shown in the chemical composition (XRF) results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral phases (JCPDS card no.)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1c</td>
<td>Calcite (01-0837) Ilite (09-0343) Quartz (01-0649) Hematite (01-1053) Augite SiO$_2$ (24-0202) Esseneite CaO (25-0143) Gehlenite Al$_2$Ca$_2$O$_7$Si</td>
</tr>
<tr>
<td>E1p</td>
<td>+ + + + + + + + + + + + + + + + + + + +</td>
</tr>
<tr>
<td>E1s</td>
<td>+ + + + + + + + + + + + + + + + + + + +</td>
</tr>
<tr>
<td>E1t</td>
<td>+ + + + + + + + + + + + + + + + + + + +</td>
</tr>
<tr>
<td>E1r</td>
<td>+ + + + + + + + + + + + + + + + + + + +</td>
</tr>
<tr>
<td>Ca-rich</td>
<td>E2d</td>
</tr>
<tr>
<td>E2a</td>
<td>+ + + + + + + + + + + + + + + + + + + +</td>
</tr>
<tr>
<td>E2b</td>
<td>+ + + + + + + + + + + + + + + + + + + +</td>
</tr>
<tr>
<td>Ca-poor</td>
<td>E2i</td>
</tr>
<tr>
<td>E2h</td>
<td>+ + + + + + + + + + + + + + + + + + + +</td>
</tr>
</tbody>
</table>

$^a$ 1 and 2 denote the corresponding Sialk period (I and II).

$^b$ +, trace; ++, minor; +++, abundant.

Fig. 7. SEM microstructure and EDX element map of the exterior surface of sample E1r, showing the remains of organic particles added as temper. Mixed map: Ca, Ka1(red); Si, Ka1(green); C, Ka1_2 (blue); 400 × 400 μm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 8. SEM microstructure and EDX element map of the exterior surface of sample E2i, showing the remains of an organic fibre added as temper. Mixed map: Ca, Ka1(red); Si, Ka1(green); C, Ka1_2 (blue); 200 × 200 μm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
(Table 3), the Sialk II-type sherds from Ebrahimabad indicated the existence of two different types of pottery, Ca-rich and Ca-poor, each group having a homogeneous composition. These two types of pottery also possessed different major mineral phases. The Ca-rich pottery showed similar mineral phases as Sialk I (quartz and esseneite), whereas the Ca-poor pottery possessed mainly augite and quartz plus a hematite phase, as discussed above. The SEM element map also showed no difference between the Fe content on the interior and exterior of either group of Sialk II samples. Hence, there was no red Fe-rich coating present on the outer surface of the Sialk II-type pottery from Ebrahimabad. Therefore, it can be suggested that the main factor responsible for the change from buff-coloured ware to red-coloured ware, from the Late Neolithic II to the Transitional Chalcolithic (Early), was a more efficient control of the firing process. In an oxidising atmosphere, hematite crystals can be formed, which are responsible for the red colour of pottery. Without mastering the appropriate firing techniques, such as the accurate control of firing temperature and atmosphere, the production of the red pottery could not have been achieved at Ebrahimabad.

Moreover, it should be stated that efficient control of temperature and time, i.e. maintaining the required degree of oxidising atmosphere and observing the appropriate time–temperature schedule during the firing of pottery, can result in an elevation of firing temperature and more efficient sintering and vitrification processes. This would give rise to denser and stronger red pottery (Fig. 9), hence the production of bulk red pottery, which is red in colour on both the core and surface, in addition to possible aesthetic considerations, would be of prime importance in producing denser, impermeable and strong pottery.

On the basis of the above findings an apparent gradual development in pottery production at the site of Ebrahimabad from the Late Neolithic...
to the Transitional Chalcolithic (from c. 5500 to c. 5000 BCE) is proposed. Development of the pottery industry was slow at first, in fact it seems that there is no substantial difference between the pottery quality and structure (as shown by the mineralogical composition and microstructural studies) between the beginning of the Sialk I-type period and the beginning of the production of bulk red Sialk II-type pottery (which was red-coloured both on the surface and in the core). During this period, no distinct change occurred in the process of making pottery, concerning the resources and firing technology. However, the pottery industry then witnessed a very distinct change between Sialk I and Sialk II, with the production of bulk red pottery.

The production of the new pottery involved a radical change in the resources used as well as the firing techniques. The changes in technique involved elevation of the firing temperature (as the change in the raw materials resulted in more refractoriness of the pottery material, necessitating a much higher firing temperature) and more precise control of the firing atmosphere (using a more oxidising atmosphere to produce completely red pottery), as well as more precise control of the time–temperature relationship during the firing process. This would result in products of much higher quality, which would be denser, less porous, stronger, less fragile and less permeable to liquids. Producing such pottery indicates the existence of quite a high degree of specialisation in the selection of materials and mastery of firing techniques by the potters of Ebrahimabad during this time period. It is interesting to note that, however, while the typography of the produced pottery was not subjected to radical changes during the transition period, some novel types of pottery did appear during the period of transition (Fig. 3).

Although no kilns were discovered during the excavations at Ebrahimabad (perhaps because of the limited extent of the excavations carried out at the site), as discussed the strict control needed for the firing atmosphere and temperature as well as precise time–temperature monitoring required during the firing process, production of this pottery would have been impossible without the use of relatively sophisticated kilns during this specific period. Therefore, it is proposed that a long-term, permanent ceramic production, from the first half to the end of the sixth millennium BC, existed in Ebrahimabad, during which time the pottery industry witnessed a gradual specialisation in the selection of materials and mastery of techniques, that towards the end of the period approached its culmination in the production of bulk red pottery. Other evidence of mass production and the specialisation of ceramic production is provided by the use of kilns in the firing process and the standardisation of craft production concerning the quality, composition and style of pottery, as discussed above. Hence, most of the conditions usually accompanying the Late Neolithic to Transitional Chalcolithic period within the communities of the Iranian Central Plateau, such as the establishment of specialised craft areas, standardisation of craft production and use of kilns for ceramic production (Fazeli et al., 2007a), had obviously been realised at Ebrahimabad by the time production of the high-quality pottery had commenced, which could be considered to coincide with the critical period entering into the Transitional Chalcolithic era.

4. Conclusion and suggestions for further work

Chemical and mineralogical analyses along with microstructural studies of Sialk I and II-type pottery sherds from the site of Ebrahimabad have revealed a quite homogeneous nature of the sherds within each group, both chemically and mineralogically, and the occurrence of a gradual evolution and development in pottery production at the site. However, they have also demonstrated that the pottery industry witnessed a very distinct change between Sialk I and Sialk II ware with the production of bulk red pottery. The production of the high-quality bulk red pottery can be considered as a breakthrough in the evolution of pottery production at Ebrahimabad, occurring at a critical time at the beginning of the Transitional Chalcolithic era.
It has also been shown that the chemical compounds present in the sherds were the products of reactions occurring at temperatures of 900–950 °C and 1000–1050 °C for Sialk I and II wares, respectively. Taken together, these results have revealed the existence of a high degree of skill and experience displayed by the potters producing Sialk II, concerning both raw material selection and mastery of firing techniques, i.e. precise control of the firing temperature and atmosphere. Without the existence of this high degree of specialisation in Sialk II pottery production, developed over several centuries in this region, the fine, well-made, dense red pottery could not have been produced. In the future, these results could be complemented with petrographic analysis of thin sections, which would allow visualisation of the minerals and organics in the fabric.

Unfortunately, there are no data from chemical and mineralogical analyses of Sialk pottery from other sites, as a comparison of the pottery from different sites displaying the same traditions could be revealing, especially for assessing the similarity of sources of raw materials and the techniques of shaping and firing the pottery. This would provide valuable information about the economic and cultural connections and interactions of the prehistoric communities living in this region in the sixth millennium BC.

References