Journal of Archaeological Science: Reports xxx (2018) xxx-xxx

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: www.elsevier.com

Four shades of black: Non-invasive scientific studies on the painted potteries from Shahr-i Sokhta, eastern Iran

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ARTICLE INFO

Keywords:
Shahr-i Sokhta
Bronze age
Raman
XRF
Jacobsite
Painted pottery

ABSTRACT

Shahr-i Sokhta in east of Iran represents different stages of settlements from the fourth to the second millennium BC. A large assemblage of ceramics shards has been unearthed from Shahr-i Sokhta many of which are decorated with different shades of black, yellow and red colours. Micro X-ray fluorescence (μ-XRF) and micro-Raman spectroscopy (μ-Raman) on some seventy painted shards from Shahr-i Sokhta with polychrome, bi-chrome and monochrome decorations showed haematite and goethite as red and yellow decorations, respectively. Black decorations, however, consisted of four main groups including carbon black, magnetite, haematite and jacobsite. This paper represents a successful application of non-invasive spectroscopic methods for identifying pigments on archaeological ceramics.

1. Introduction

Shahr-i Sokhta is located at some sixty kilometres to the south of Zabol and considered as one of the largest Bronze Age archaeological sites in Iran (Fig. 1). Shahr-i Sokhta demonstrates a continuous line of settlement for at least two millennia. Economic development of this ancient city was due to its strategic location along the trade routes of Asian civilizations. There are many evidences which indicate the trade and cultural relations of Shahr-i Sokhta, Mesopotamia and other important prehistoric sites of the region (Biscione, 1974; Salvatori, 2006) (Fig. 1). As a result, excavations at Shahr-i Sokhta revealed wide range of archaeological findings including ceramic objects.

The 150-hectare area of Shahr-i Sokhta encompasses four periods of settlement spanning 3200 to 1800 BCE (namely the period I (ca. 3200–2800 BCE), the period II (ca. 2800–2500 BCE), the period III (ca. 2500–2200 BCE) and the period IV (ca. 2200–1800 BCE)) and consists of eleven structural layers. The main excavated parts of Shahr-i Sokhta are “residential area” (including “central quarters”, “oriental residential area”, “burnt building” and “monumental area”), “industrial zone” and “graveyard” (Tosi, 1976; Sajjadi, 2004) (Fig. 2). Amongst various interesting findings in this site, a large number of potshards testifies not only technical advances of the site, but also indicates trade and circulation of ceramics with neighbouring regions (Mugavero, 2008).

The large number of ceramics retrieved from Shahr-i Sokhta and the general durability of ceramic materials against weathering provide a unique chance for studying the archaeological findings unearthed from this archaeological site. Pigments and patterns on the potteries of Shahr-i Sokhra are from those important sources of information which can contribute to understanding of the less-known history of Shahr-i Sokhta. On the other hand, different types of ceramics unearthed from Shahr-i Sokhta have always prompted scholars to argue in favour of ceramic imports to the site as an aid for the local production (Salvatori, 2006, p. 32). All these make Shahr-i Sokhta and its pottery assemblage a particular case for study which characterises traditions of pottery-making during the Bronze Age.

Apart from ceramics with no decoration, ceramics from Shahr-i Sokhta include monochrome (black and different shades of brown) and polychrome decoration (white, red, black, yellow and green) over clay body (Mugavero, 2008, pp. 4–5). The polychrome ware, which is found at “graveyards”, is similar to the ceramics from Nal in Pakistan and often is considered as imported objects to Shahr-i Sokhta (Sajjadi, 2006, p. 178; Festuccia, 2015, p. 132). Moreover, there are ceramics on which two red and black colours are applied (the so-called bi-chrome ceramics). According to Mugavero (2008), the ceramics from the period I often have rich decorations while simpler decorations on ceramics appeared towards the end of the period III in Shahr-i Sokhta. In fact, the first two periods of the history of pottery-making in Shahr-i

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https://doi.org/10.1016/j.jasrep.2018.09.012
Received 26 June 2018; Received in revised form 14 September 2018; Accepted 14 September 2018
Available online xxx
2352-409/ © 2018.

Fig. 1. Location of Shahr-i Sokhta and some other important archaeological sites (1: Shahr-i Sokhta, 2: Altyn Tape, 3: Mundigak, 4: Tureng Tape, 5: Tape Hissar, 6: Tape Yahya, 7: Shahdad, 8: Susa, 9: Namazga, 10: Muhenju daro, 11: Bampur, 12: Nal and 13: Quatte).

Sokhta include almost exclusively painting on pottery while potteries from the period III encompass the shards which sometimes bear no pigment and painted pattern on the body (Festuccia, 2015).

While the buffware painted with black and brownish colours are found within the archaeological findings from all four periods of Shahr-i Sokhta, the greyware from Shahr-i Sokhta with red decoration is exclusively found in the potteries from the period I. Nonetheless, the greywares painted with black colour are popular in the potteries from the periods I and II. Almost all the greywares from Shahr-i Sokhta bear painted decoration on the body. On the other hand, the large occurrence of redware with black decoration is reported from the periods I and II of Shahr-i Sokhta. The redware began to be disappeared by the end of the period III (Festuccia, 2015). As far as the polychrome wares are concerned, they have been retrieved from the layers dated to the period I to period III. The polychrome ware with eleborated forms and graphics, however, belong to the period II (Mugavero and Vidale, 2006). Biscione (1974) believes that there are no remarkable decorated ceramics in the period IV, compared to the ceramics from previous periods, probably because of a sudden decline of the city.

In general, the most delicate iconographic designs are found on the ceramics with monochrome decorations on red- and greywares with natural motifs such as plants, rivers, lakes, fields, leaves, trees and animals. On the contrary, simpler and less refined decorations represent the iconographic designs of monochrome buffware, which is generally decorated with various geometric patterns such as lozenges, triangles and zigzag motifs. These patterns are also used to decorate the polychrome and bi-chrome potteries (Potts et al., 2001, pp. 270–271; Sajjadi, 2005). This essay is an attempt to characterise the colours used over the clay bodies of the ceramics from Shahr-i Sokhta using non-invasive analytical methods. The question of provenance of the painted shards is not however addressed here.

2. Materials and methods

2.1. Samples

Some seventy potshards including both excavated and surface-retrieved potshards (Fig. 3; Table 1) were studied to characterise the colours and pigments used on the ceramics from Shahr-i Sokhta. Painted decoration was found on clay-based bodies of the buff-, red- and greywares. Colours on the bodies included black, red (comprised of different shades of brown and red) and yellow decorations. While white and yellow decorations were only found on the polychrome ceramics, red, black and brownish/black colours were observed on almost all types of the ceramics. Although Mugavero (2008) mentions the use of green colour on the polychrome ceramics from Shahr-i Sokhta, no green decoration was found on the polychrome shards preserved in the on-site storage of the site. Table 1 provides further information about the shards, their place of excavation, pigments, the colour of the bodies and their painted decorations.

2.2. μ-XRF

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 25 kV and 1500 μA to analyse different colours on the potshards in air for 120 s. The surface area under the deconvoluted $K\alpha_1$ energy lines of Fe and Mn were used for comparison of energy counts of the elements.

2.3. μ-Raman

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 50× 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

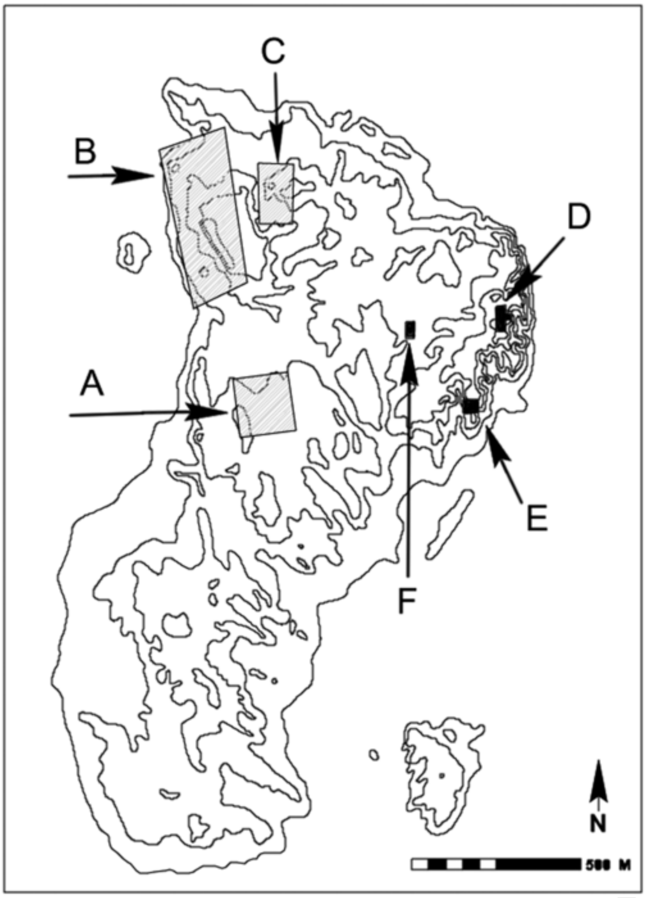

Fig. 2. The main excavated areas at Shahr-i Sokhta (A: Grave yard, B:Industrial Zone, C: Monumental Area, D: Oriental Residential Areas, E: Burnt Building and F: Central Residential Area) (reproduced from the topographic map of the Research Base Centre of Shahr-i Sokhta).

of 20 mW and the spectrometer was calibrated with silicon at 520 cm^{-1}.

3. Results and discussion

3.1. Red and yellow colours

As μ-XRF suggested, the red colours on all the potshards were rich in Fe. Also, Fe showed a high positive correlation with Mn ($R^2 = 0.72$) suggesting the manganese content of the colours has been driven from Fe (Fig. 4). μ-Raman accordingly showed red haematite is the main colouring agent of the red paints with the Raman bands at 224, 244, 290, 408, 498, 610 and 656 cm^{-1} (Hanesch, 2009) (Fig. 5a). On the other hand, the yellow colour, which was only observed on the polychrome shards, showed the Raman bands at 240, 293 and 385 cm^{-1} consistent with yellow goethite, FeOOH (Hanesch, 2009) (Fig. 5b).

The occurrence of haematite and yellow iron hydroxide as red and yellow colours was not surprising as red and yellow pigments on archaeological ceramics have always been reported to be linked with iron (hydr)oxides (Noll et al., 1975). It must be emphasised that several parameters affect the role of iron oxides in colouring clay-based decorations. For example, the yellow colour on the Attic pottery is mainly achieved by the potassium content and the thickness of the decoration. In fact, the black layers on the Attic pottery are thick and have high potassium content while the yellow decorations contain less potassium and are thinner (Noll et al., 1975). The yellow decorations on the potteries from Shahr-i Sokhta, however, seems to have no connection with the Attic yellow colour as the yellow goethite on the polychrome shards has not received firing after painting the pigment on the ceramics. In other words, the yellow decorations represent the colour of the original raw material used for decorating the potteries (see also 3.2.1 Carbon-black decorations).

3.2. Black and brownish/black colours

Scientific investigation revealed four groups of black colour within the painted potshards as follows.

3.2.1. Carbon black decorations

The first group, comprised of the black colours on the polychrome shards, showed no significant Fe and Mn content (filled circles in Fig. 6). μ-Raman study on this group of black colours exhibited two broad Raman bands at about 1320 and 1570 cm^{-1} attributable to carbon black (Jawhari et al., 1995) (Fig. 5c). The fact that carbon black and yellow iron hydroxide are not stable pigments under oxidising firing condition of historical kilns suggests that polychromy on the polychrome ceramics from Shahr-i Sokhta has been achieved by painting carbon black, yellow goethite and red haematite on pre-fired clay-based ceramic bodies.

The carbon black on the shards from Shahr-i Sokhta showed negligible P content which excludes the use of ivory/bone black in the black decorations. Also, the absence of V and Ni in the composition of the black decoration in this group ruled out the use of crude oils, bitumen and asphalt materials as possible black pigments (Filby, 1994).

3.2.2. Iron-reduced blacks

The second group of the black pigments on Shahr-i Sokhta shards consists of the black colours with high Fe content but low Mn quantity (void squares in Fig. 6). μ-Raman study on the this group of black pigments demonstrated a broad and strong Raman band at ca. 680 cm^{-1} consistent with black magnetite (Hanesch, 2009) (Fig. 7b). This is interesting to mention that magnetite was only identified on the greyware which are fired in a reducing atmosphere of kiln. The reducing atmosphere has been in favour of the formation magnetite.

This type of black decoration on pottery, according to Noll et al. (1975), is probably the oldest of all ceramic-decoration processes. Black colour is produced by firing and reducing ferruginous clay and, consequently, the formation of a spinel. This spinel is black in colour and if associated with haematite, a dark- to pale-brown colour would be formed according to the haematite content. An incomplete reduction or to partial re-oxidation during cooling can lead to the formation of haematite. The dark black colour of this group of black decorations on the shards from Shahr-i Sokhta is consistent with the low to negligible haematite content discerned by μ-Raman.

3.2.3. Iron-manganese blacks

The third group of black decorations on the Shahr-i Sokhta shards showed higher Mn content with appreciable amounts of Fe (void triangular in Fig. 6). Raman bands at 345, 615 and 680 cm^{-1} subsequently suggested jacobsite, $MnFe_2O_4$, as the black component of these decorations (Buzgar et al., 2013) (Fig. 7a). Buzgar et al. (2013) show that the most intense Raman band of jacobsite is centred at ca. 620 cm^{-1}. However, at temperatures higher than 600 °C and when sufficient Mg is present Mg-jacobsite is formed resulting in a shift in the Raman band to lower wavenumbers (ca. 600 cm^{-1}). Also, according to Buzgar et al. (2013), a reducing atmosphere or agent is necessary to this reaction happens. Thus, since the most intense Raman band of jacobsite in the shards under study is centred at 615 cm^{-1}, it can be suggested that the Mg content of the black colours is relatively low. The shoulder at 680 cm^{-1} in the Raman spectrum of the black decoration of this group is driven from the Fe^{2+} content of jacobsite.

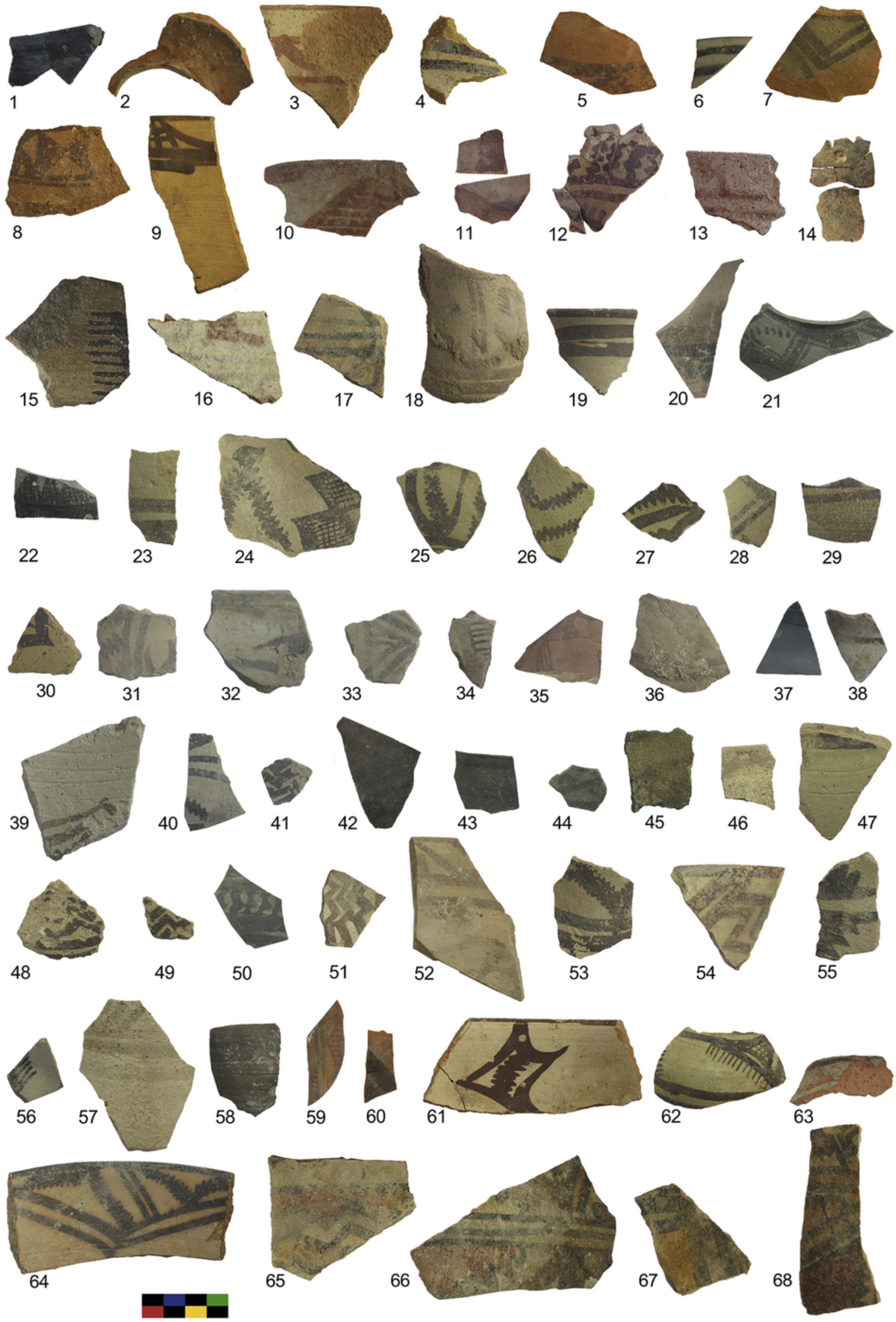

Fig. 3. The studied painted potshards from Shahr-i Sokhta.

Jacobsite has been reported as black colouration within the archaeological painted potteries (Noll et al., 1972) and documented to occur as black decoration on a fourth millennium BC painted pottery from Tepe Sialk (Qanbari-Taheri and Holakooei, 2016) and also on the potteries from Tall-i Bakun and Cheshmeh Ali in Iran (Noll et al., 1975). The manganese black decoration is not as widespread as the iron-reduced blacks in the ancient world. The oldest evidences are reported

Table 1
Shards and their decoration.

No.	Location	Inventory number	Period	Body colour	Decoration		
					Type	Colour	Pigments
1	Storage[a]	4-5812-84 ش س	II–III	Grey	Monochrome	Black	Magnetite
2	Storage	–	II–III	Red	Monochrome	Red	Haematite
3	Storage	4-4410-82 ش س	II–III	Red	Monochrome	Brown	Haematite
4	Storage	87-MJO-8321	II–III	Buff	Monochrome	Black	Haematite
5	Storage	10 -5202 -83 ش س	II–III	Red	Monochrome	Black	Haematite
6	Storage	م: A- 3سطحی -85 ش س- MJN	Surface[b]	Grey	Monochrome	Black	Magnetite
7	Storage	–	II–III	Red	Monochrome	Black	Jacobsite
8	Storage	4 -3311 -81 ش س	II–III	Red	Monochrome	Black	Haematite
9	Storage	5 لایه 1-کارگاه -86 ش س - OYE- روی کف	II	Buff	Monochrome	Brown	Haematite
10	Storage	9 -3909 -81 ش س	I	Grey	Monochrome	Brown	Haematite
11	Storage	3 -5202 -82 ش س	II–III	Buff	Monochrome	Brown	Haematite
12	Storage	2 -5806 -84 ش س	II–III	Buff	Monochrome	Brown	Haematite
13	Storage	11 -8309 -86 ش س	II–III	Buff	Monochrome	Brown	Haematite
14	Storage	3000- 13 -HDY-89 س ش	II–III	Buff	Monochrome	Black	Jacobsite
15	Storage	–	II–III	Grey	Monochrome	Black	Magnetite
16	Graveyard	–	II–III	Buff	Polychrome	Black, Red	Carbon, Haematite
17	Graveyard	3ب -41ف -1ک	II–III	Buff	Polychrome	Black, Red	Carbon, Haematite
18	Central Quarters	–	Surface	Buff	Monochrome	Black	Haematite
19	Central Quarters	–	Surface	Buff	Monochrome	Black	Magnetite
20	Central Quarters	–	Surface	Grey	Monochrome	Black	Magnetite
21	The Monumental Area	–	Surface	Grey	Monochrome	Black	Magnetite
22	The Monumental Area	–	Surface	Grey	Monochrome	Black	Magnetite
23	The Monumental Area	–	Surface	Buff	Monochrome	Black	Jacobsite
24	The Monumental Area	–	Surface	Buff	Monochrome	Black	Haematite
25	The Monumental Area	–	Surface	Buff	Monochrome	Black	Haematite
26	The Monumental Area	–	Surface	Buff	Monochrome	Black	Haematite
27	The Monumental Area	–	Surface	Buff	Monochrome	Black	Haematite
28	The Monumental Area	–	Surface	Buff	Monochrome	Black	Haematite
29	East of the Burnt Building	–	Surface	Buff	Monochrome	Black	Haematite
30	East of the Burnt Building	–	Surface	Buff	Monochrome	Black	Haematite
31	East of the Burnt Building	–	Surface	Buff	Monochrome	Black	Magnetite
32	East of the Burnt Building	–	Surface	Buff	Monochrome	Black	Magnetite
33	East of the Burnt Building	–	Surface	Buff	Monochrome	Black	Magnetite
34	East of the Burnt Building	–	Surface	Buff	Monochrome	Black	Haematite
35	East of the Burnt Building	–	Surface	Red	Monochrome	Brown	Haematite
36	The trench in north of the Burnt Building	–	Surface	Buff	Monochrome	Black	Haematite
37	South of the Monumental Area	–	Surface	Grey	Monochrome	Black	Magnetite
38	South of the Monumental Area	–	Surface	Buff	Monochrome	Brown	Haematite
39	Industrial Zone	–	Surface	Buff	Monochrome	Black	Magnetite
40	Industrial Zone	–	Surface	Buff	Monochrome	Black	Magnetite
41	Industrial Zone	–	Surface	Buff	Monochrome	Black	Haematite
42	Oriental Residential Area	–	Surface	Grey	Monochrome	Black	Jacobsite
43	Oriental Residential Area	–	Surface	Grey	Monochrome	Black	Magnetite
44	Oriental Residential Area	–	Surface	Grey	Monochrome	Black	Magnetite
45	Oriental Residential Area	–	Surface	Grey	Monochrome	Black	Magnetite
46	Oriental Residential Area	–	Surface	Buff	Monochrome	Brown	Haematite
47	Central Quarters	–	Surface	Buff	Monochrome	Black	Haematite
48	Central Quarters	–	Surface	Buff	Monochrome	Black	Haematite
49	Central Quarters	–	Surface	Buff	Monochrome	Black	Haematite
50	Central Quarters	–	Surface	Grey	Monochrome	Black	Magnetite
51	East of the Burnt Building	–	Surface	Buff	Monochrome	Brown	Haematite
52	The Monumental Area	–	Surface	Buff	Monochrome	Brown	Haematite
53	Central Quarters	–	Surface	Buff	Monochrome	Black	Haematite
54	Oriental Residential Area	–	Surface	Buff	Monochrome	Brown	Haematite
55	Industrial Zone	–	Surface	Buff	Monochrome	Black	Haematite
56	Oriental Residential Area	–	Surface	Grey	Monochrome	Black	Magnetite
57	Oriental Residential Area	–	Surface	Buff	Monochrome	Brown	Haematite
58	Oriental Residential Area	–	Surface	Grey	Monochrome	Black	Magnetite
59	The trench in north of the Burnt Building	–	Surface	Red	Bi-chrome	Red, Brown	Haematite
60	Storage	2- 80 ش س- hy53	II–III	Red	Monochrome	Black	Jacobsite
61	Storage	–	II–III	Red	Monochrome	Brown	Haematite
62	Storage	3 لایه 1- کارگاه -86 ش س- OYE شمالی	III	Buff	Monochrome	Black	Haematite
63	Storage	–	II–III	Red	Monochrome	Black	Jacobsite
64	Storage	11097 -1376 ش سIRS-	II–III	Buff	Monochrome	Brown	Haematite
65	Graveyard	79- 38ف 1 ک	II–III	Buff	Polychrome	Black, Red, Yellow	Carbon, Haematite, Goethite

Table 1 (*Continued*)

No.	Location	Inventory number	Period	Body colour	Decoration		
					Type	Colour	Pigments
66	Graveyard	ف 8 ب 3 ش ک 70 78	II–III	Buff	Polychrome	Black, Red, Yellow	Carbon, Haematite, Goethite
67	Graveyard	ف 4 ک 1 ب4 ف 31	II–III	Buff	Polychrome	Black, Yellow	Carbon, Goethite
68	Graveyard	ش س 79- ب6 ف29- 41	II–III	Buff	Polychrome	Black, Red, Yellow	Carbon, Haematite, Goethite

[a] Most of the shards kept at the storage are excavated from the graveyard. The exact location of excavation for these shards is not reported in the published documents.
[b] Shards with no certain dating. These shards are retrieved from surface survey on the site. They also do not bear accession number.

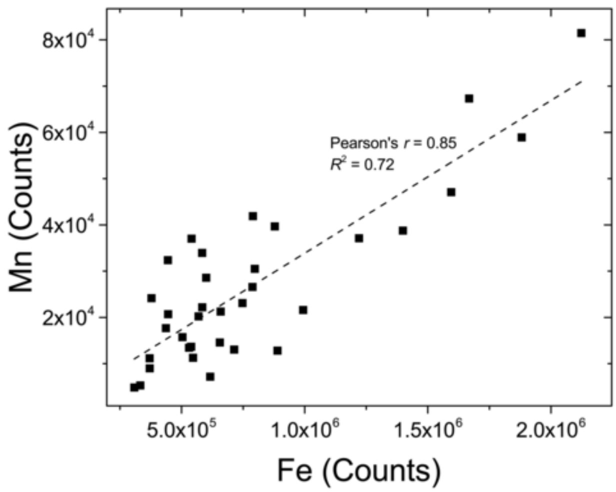

Fig. 4. Fe vs. Mn scatter plot based on the energy counts acquired from the red colours. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

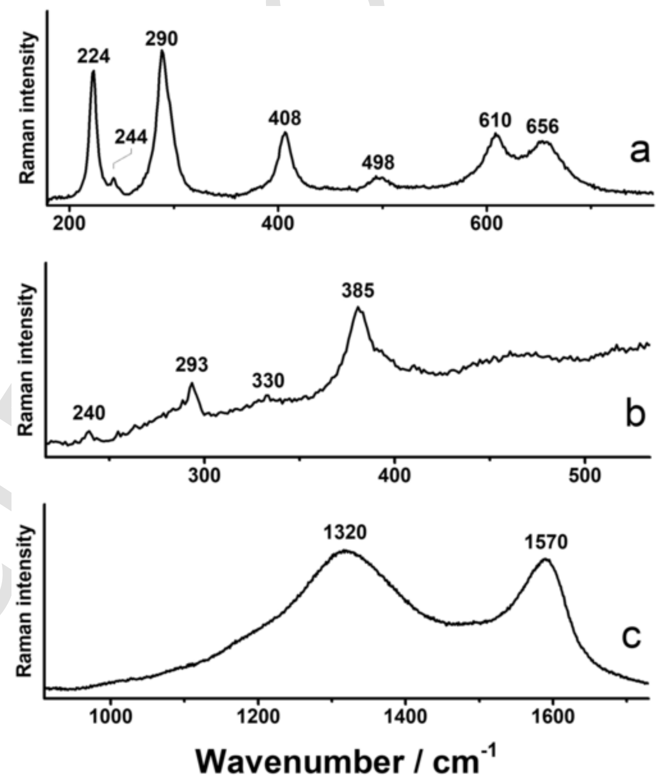

Fig. 5. Raman spectra of (a) haematite on shard #61, (b) goethite on shard #65 and (c) carbon black on shard #66.

from Catal Huyuk and Mersin in southeast Anatolia and date from the 6th–5th millennium BC. Also these decorations have been documented from the 4th–3rd millennium in Thrace, Thessaly, and Attica, as well as in the Danube-Moldau region and in Cyprus. The iron-manganese blacks seem to be survived until the 7th century BC (Noll et al., 1975).

3.2.4. *Haematite blacks*

The last group of black colours showed a fairly linear correlation between Fe and Mn (filled squares in Fig. 6). μ-Raman showed haematite used as black decoration on a relatively large set of shards. It must be mentioned that no significant Fe^{2+} contribution was observed in these black decorations as the Raman band at 680 cm^{-1} was weakly observed in this group of black decorations. In other words, it can be said that the black decoration in this group of painted shard is driven from almost pure haematite. Noll et al. (1975), nonetheless, do not mention pure haematite as possible black decoration in ancient pottery. It is worth-mentioning that no traces of hercynite, $Fe^{2+}Al_2O_4$, were either detected in the black decorations of painted shards from Shahr-i Sokhta. As the formation of hercynite requires a high firing temperature (above 1200 °C) (Leon et al., 2010), one may suggest that the shards painted with Fe- and Mn-bearing colours have not been fired at high temperatures.

3.3. *A new approach for discriminating different types of black decorations*

As discussed, the Raman band at 615 cm^{-1} is driven from Mn content and the Raman band at 680 cm^{-1} is the strongest Raman scattering band from magnetite. A further study on the surface area of the most intense Raman bands of magnetite at 680 cm^{-1} (A_{680}) and jacobsite at 615 cm^{-1} (A_{615}) and their relation with the Fe and Mn content discriminated very well the shards decorated with black magnetite, haematite and jacobsite (Fig. 8). The spectra were deconvoluted through Gausian/Lorenzian approach and the surface area under the 615 and 680 cm^{-1} Raman bands were calculated. As Fig. 8 demonstrates, magnetite black decorations show high Fe/Mn ratio while their intense Raman band at 680 cm^{-1} has resulted in a low A_{615}/A_{680} (nearly zero). On the other hand, jacobsite containing black decorations revealed to have higher Mn content (lower Fe/Mn ratio) and higher intensity of the Raman band at 615 cm^{-1} (i.e. A_{615}/A_{680} ratio higher than 1). Finally, black/brown haematite painted decorations showed an A_{615}/A_{680} near to 1 and relatively high Fe/Mn ratio. It is interesting to see that the Fe/Mn and A_{615}/A_{680} ratios demonstrate a high correlation (Fig. 8) suggesting that the intensity of Raman bands at 615 and 680 cm^{-1} is proportional to the concentration of Mn and Fe in the black decorations.

3.4. *Pigments on the wares from Shahr-i Sokhta*

Some general technological and archaeological facts can be inferred from the scientific findings of this research. First, all the greyware are only decorated with a single colour (either black or red). While a single red painted greyware (i.e. the shard #10) bears haematite as red

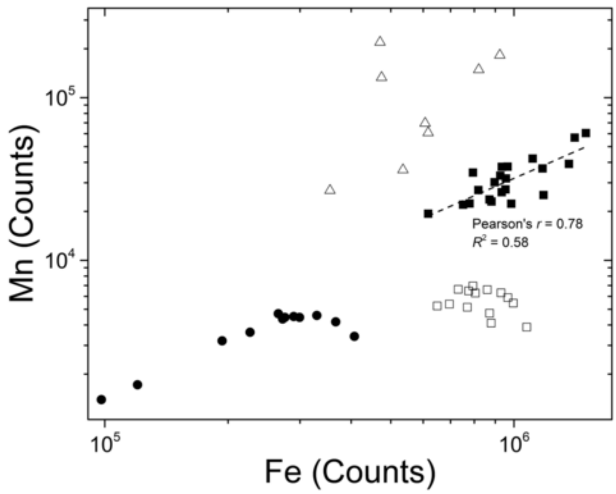

Fig. 6. Fe vs. Mn scatter plot based on the energy counts acquired from the black colours (the filled circles include the black colours achieved by painting carbon black, the void squares represent magnetite black colours, the filled squares mainly comprised of the black/brown colours rich in haematite and the void triangular consists of the black paints rich in jacobsite). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

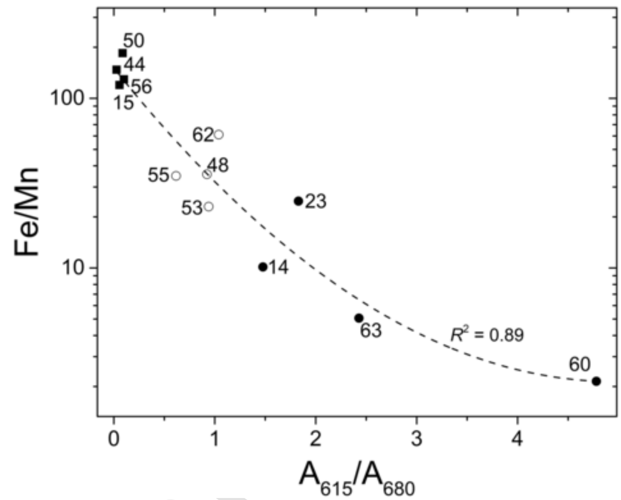

Fig. 8. Scatter plot based on the surface area under the most intense band of jacobsite (A_{615}) and magnetite (A_{680}) versus the ratio of energy counts for Fe and Mn in black decoration of twelve shards contained jacobsite (filled circles), haematite (void circles) and magnetite (filled squares).

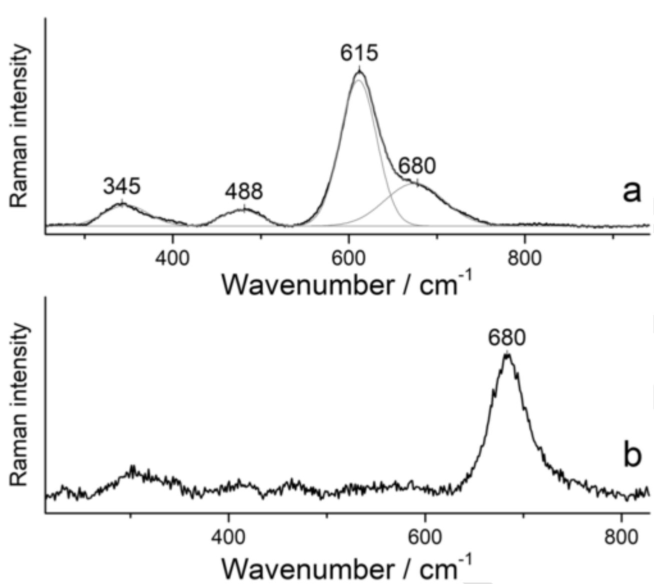

Fig. 7. Raman spectra of (a) jacobsite on shard #14 and (b) magnetite on shard #50.

colour, magnetite is the only black pigment found on the greyware from Shahr-i Sokhta. It is believed that the greyware painted with red are from the period I (Sajjadi, 2016). Thus, the grey red-painted pottery (i.e. the shard #10) decorated with haematite must be from the earliest ceramics from Shahr-i Sokhta.

All the redware are monochrome except for the shard #59 which is bi-chrome. The red and brown colours on this body include two shades of red iron oxide. The rest of the redware bear either red colour obtained by haematite (i.e. the shards #2, #3, #35 and #61) or black decoration achieved by jacobsite (i.e. the shards #7, #60 and #63) or haematite. The jacobsite-bearing decorations are on redware covered with greyish slip. Jacobsite was also found on the shards #14 and #23 with a buff colour of body. It is interesting to mention that magnetite was never seen on the redware from Shahr-i Sokhta.

4. Conclusion

Potteries retrieved from Shahr-i Sokhta have different shades of black, yellow, and red on three major classes of clay bodies namely "buffware", "greyware" and "redware". While red and yellow pigments on the potteries of Shahr-i Sokhta are obtained from Fe-based pigments, black decorations showed to be varied in composition. Although most of the decorated potteries have monochrome black, red or black/brown decorations, polychrome decorated potteries have also been excavated at Shahr-i Sothta. The fact that the polychrome decorated potteries have been unearthed from "graveyards" (see Fig. 2) may indicate that these ceramics have been manufactured/imported for a certain purpose.

Non-invasive scientific studies proved to be reliable in characterising colouring agents of archaeological painted pottery. Spectral and compositional non-invasive data, when treated appropriately, can provide useful information about pigments used on objects of art and archaeology. Although it was not the aim of this research to suggest a provenance for the studied shards by means of pigment identification, working on larger spectral and compositional datasets with multivariate statistical methods of data handling might end up further insights about the provenance and origin of colourants on ancient pottery.

Uncited references

Centeno et al., 2012
Salvatori, 1978

Acknowledgments

NE is grateful to The Ministry of Foreign Affairs and International Cooperation (MAECI) for awarding a post-doctoral fellowship to pursue a research on the colourants of the ceramics from Shahr-i Sokhta. We wish to thank the offices of Cultural Heritage, Handicrafts and Tourism Organization of Iran in Sistan and Baluchestan Province and the Research Base Centre of Shahr-i Sokhta for providing the samples. Also, the authors are very grateful to an anonymous reviewer for his/her useful comments.

References

Biscione, R., 1974. Relative chronology and pottery connections between Shahr-i Sokhta and Mundigak, Eastern Iran. Studi di Paletnologia, Paleoantropologia, Paleontologia e Geologia de Quaternaria 2, 131–145.

Buzgar, N., Apopei, A.I., Buzatu, A., 2013. Characterization and source of Cucuteni black pigment (Romania): vibrational spectrometry and XRD study. J. Archaeol. Sci. 40, 2128–2135.

Centeno, S.A., Williams, V.I., Little, N.C., Speakman, R.J., 2012. Characterization of surface decorations in Prehispanic archaeological ceramics by Raman spectroscopy, FTIR, XRD and XRF. Vib. Spectrosc. 58, 119–124.

Festuccia, S., 2015. La Ricerca Archeologica nel Vicino Oriente: Siria, Anatolia e Iran. Con Prefazione di Paolo Matthiae. Gangemi Editore spa. Roma, 130–132.

Filby, R.H., 1994. Origin and nature of trace element species in crude oils, bitumens and kerogens: implications for correlation and other geochemical studies. Special Publications 78, 203–219.

Hanesch, M., 2009. Raman spectroscopy of iron oxides and (oxy)hydroxides at low laser power and possible applications in environmental magnetic studies. Geophys. J. Int. 177, 941–948.

Jawhari, T., Roid, A., Casado, J., 1995. Raman spectroscopic characterization of some commercially available carbon black materials. Carbon 33, 1561–1565.

Leon, Y., Lofrumento, C., Zoppi, A., Carles, R., Castellucci, E.M., Sciau, P., 2010. Micro-Raman investigation of terra sigillata slips: a comparative study of central Italian and southern Gaul productions. J. Raman Spectrosc. 41, 1550–1555.

Mugavero, L., 2008. Polychrome Ware From Shahr-i Sokhta, (Translated by S.M. Sajjadi, ICHHTO, Zabol).

Mugavero, L., Vidale, M., 2006. The Helmand polychrome wares as skeuomorphs: interlacing pottery making, painting and basketry. East and West 56 (4), 433–437.

Noll, W., Holm, R., Born, L., 1972. Manganoxyd-Phasen als Pigmente antiker Vasenmalerei. Naturwissenschaften 59, 511–512.

Noll, W., Holm, R., Born, L., 1975. Painting of ancient ceramics. Angew. Chem. Int. Ed. 14, 602–613.

Potts, D.T., Lamberg-Karlovsky, C.C., Pittman, H., Kohl, Ph.L., 2001. Excavation at Tepe Yahya, Iran: 1967–1975. The Third Millennium, Bulletin of American School of Prehistoric Research, no. 45. Peabody Museum of Archaeology and Ethnology, Harvard University, Cambridge, Mass..

Qanbari-Taheri, N., Holakooei, P., 2016. Characterisation of a painted pottery vessel excavated at the site of Tepe Sialk, Kashan, central Iran. The Old Potter's Almanack 21, 12–18.

Sajjadi, S.M., 2004. The beginning of urbanization in the eastern half of the Iranian plateau (Aghaze shahr neshini dar nimeye sharghi falat Iran). Nameye Ensan Shenasi 6, 63–96, (in Farsi).

Sajjadi, S.M., 2005. The First Cities on Iran Plateau (Nokhostin Shahrh-Ye Falat-e Iran). Samt, Tehran.

Sajjadi, S.M., 2016. Shahr-i Sokhta and impacts on and from its neighbouring lands. Journal of the Society for Iranian Archaeology 1 (1), 1–30.

Salvatori, S., 1978. Problemi di protostoria iranica: note ulteriori su di una ricognizione di superficie a Shahdad (Kerman, Iran). Rivista di Archeologia 2, 5–15.

Salvatori, S., 2006. Il panorama storico. In: Tucci, G. (Ed.), La Città Brucita del Deserto Salato. Erizzo Editrice, Venice, pp. 23–40.

Tosi, M., 1976. A topographical and stratigraphical periplus of Shahr-i Sokhta. In: Proceedings of the 4th Symposium of Archaeological Research in Iran: Tehran, 3rd - 8th November 1974. Iranian Centre for Archaeological Research, Tehran Vol. 3, pp. 130–158.