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(Article begins on next page)



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Archaeometric investigation on pottery from funerary gifts in Kal-e Chendar,

Shami (Khuzestan, Iran)

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ABSTRACT

30 fragments of red slip, glazed, common and cooking ware from Hellenistic and Parthian tombs at Kal-e Chendar, Shami (Iran) were investigated. Petrographic assemblage and chemometric evaluation on chemical data collect most samples in a large cluster, suggesting a common provenance, even in a quite wide area that includes the Izeh plain and the lowland Susiana, and underline the presence of smaller very distinguishing groupings. Surface finishing layers (both glazes and red slips) show a high degree of alteration of their morphological features. Blue glazes are typical plant-ash, with copper as colouring agent.

Keywords: Shami, Hellenistic and Parthian pottery, 3rd century BC-3rd century AD, glazed ware, red slip ware, SEM-EDX

1. INTRODUCTION

The Iranian Italian Joint Expedition in Khuzestan started excavation at Kal-e Chendar (valley of Shami), in the province of Khuzestan, about 30 km north of modern Izeh (Figure 1 - Supplementary Materials), on October 2013.

This project falls within a Memorandum of Understanding between the Research Institute for Cultural Heritage and Tourism of the Islamic Republic of Iran, Iranian Center for Archaeological Research (ICAR) and the *Centro Ricerche Archeologiche e Scavi di Torino per il Medio Oriente e l'Asia* (CRAST). Other involved partners are the *Dipartimento di Studi Storici*, the *Dipartimento di Chimica* and the *Dipartimento di Scienze della Terra* of the *Università di Torino* (Italy). The expedition is co-directed by Vito Messina (*Dipartimento di Studi Storici* – CRAST) and Jafar Mehr Kian (ICAR). The site was investigated in 1936 by Sir Aurel Stein, who excavated only for few days but was able to identify the site as an ancient sanctuary, considered in the subsequent literature as one of the most reputed religious places of Hellenistic and Parthian Elymais even if its historical identification is a matter of debate (Messina 2015). Important sanctuaries characterized by monumental cult terraces were also located on the ground and excavated at Masjid-e Sulayman and Bard-e Nechandeh (Ghirshman 1976) about 40 km north-west of Shami.

Shami site revealed clear traces of monumental terraces built in undressed stones and placed at different elevations, following the natural slope of the valley. The wide extension of these structures leads to suppose that they must have supported large buildings, or even building complexes, made in undressed stones and/or baked bricks.

Four excavation seasons (2013-2016) were conducted up to now (Baqherian et al. 2016; Bucci et al. 2017, Bucci et al. 2018), and it can be deemed that the religious complex at Kal-e Chendar was of a particular type: a wide cemetery including monumental tombs built in undressed stones extended over the area surrounding the monumental terraces, implying that the religious and funerary functions were strictly interrelated. Up to now, 32 tombs were identified, but basing on the extension of the cemetery area it may be supposed that their number is considerably higher. They

are underground saddle- or flat-roofed chambers. Some of them are monumental family tombs that seem to have been part of more articulated funerary complexes, in which corridors were used as walkways to other buried or semi-buried structures. This type of family tombs, with large chambers accessed by stairways and containing funerary benches, finds comparison with examples known at Susa, Babylon, Kish and Seleucia on the Tigris, and provides interesting information on the high social milieu of the people who decided to be buried there. This seems confirmed by what remains of the rich funerary goods dated to the Hellenistic and Parthian periods (3rd century BC-first quarter of the 3rd century AD).

Vessels and potsherds can be rarely found in archaeological layers because of the compressed and disturbed stratigraphy at the site; however, they occur in large number, as funerary gifts, in family tombs. The pottery found at the site was classified according to ware and surface treatment, allowing distinguishing four classes: red slip, glazed, common and cooking ware.

In Parthian Iran, like in preceding periods, the pottery production was highly regionalised (Haerinck 1983). In this context, the high occurrence of glazed vessels particularly points to the Mesopotamian tradition, also echoed in the production of lowland Khuzestan and Susiana (Hannestad 1983). The making of Hellenistic and Parthian glazes perpetuates the Mesopotamian long lasting tradition of alkaline glazing, particularly frequent since the Neo-Assyrian and Neo-Babylonian periods (Nunn 1988, 142-156; Moorey 1994, 159-162; Hausleiter 2010, 261-264).

If yellow, green and white glazes seem frequent in the 3rd-2nd century BC, blue and turquoise appear to be rather attested in the 1st-2nd century AD. At Shami blue, turquoise and green glazed vessels seem to prevail, often iridescent, opaque, or flaked.

Also vessels covered by a red slip were placed in the tombs together with glazed samples. These belong to a regional ceramic tradition still influenced by the production of the late Iron Age, and were also found at Susa, in layers dated to the 3rd-2nd century BC (Haerinck 1983; Boucharlat 1987). Here, in the major centre of lowland Elymais, red-slip pottery seems to disappear at the beginning of the Parthian period, having been replaced by monochrome glazed pottery, which

became very popular (Boucharlat 1987). Common ware is rarely attested. Buff, dark buff and orange are frequent ware's colours and the texture ranges from fine to coarse. Only few sherds can be classified as cooking ware. They are characterized by a particularly coarse ware with well visible mineral granules.

Therefore, the pottery assemblage of Shami shows clear influences of, and finds comparison with, the contemporary ceramic production of Elam and Mesopotamia dated from the beginning of the Hellenistic to the late Parthian period (Hannestad 1983, 97-112).

Given that the presence of pottery kilns was not evidenced by fieldwork, it can be proposed that the excavated vessels were not produced at the site. In any case, the pottery found in the tombs appears as the high-standardized production of specialized workshops. The archaeometric evaluation of the ceramic materials excavated in Shami offers the opportunity to understand the archaeological context of the site and the culture of the members of a wealthy plutocracy buried there, highlighting possible relationships between manufacturing centres and allowing important considerations on the technology of production, particularly for two most representative classes (red slip and glazed ware).

2. MATERIALS AND METHODS

Almost all the sampled potsherds come from Tomb 23 (27 samples out of 30) (Bucci et al. 2017, 17-21). The choice of this particular tomb is due to the high quality and good state of preservation of the vessels, and to the great variety of pottery forms. Two samples come from Tomb 20 and one from Tomb 7. The sampling was carried out taking into account the relative abundance of each typology in the ceramic *corpus* (Figure 2 – Supplementary Materials).

The four ceramic classes (red slipped, glazed, common and cooking), identified on the basis of ware

and manufacture, are represented by the selected samples.

Table 1

The petrographic characterization was carried out by Scanning Electron Microscopy coupled with Energy-Dispersive X-ray (SEM-EDX) analyses and by Optical Microscopy (OM). The determination of the average composition of fabrics, clay matrix (by scanning areas without evident inclusions or pores (Tite 1982)) and non-plastic inclusions (the fraction of rock fragments coarser than 15 μm , Damjanovic 2014 and reference therein) was performed by EDX. Samples were cut from the archaeological fragments with a diamond disk and encompassed in an acrylic resin. The impregnated sections were subjected to an abrasive treatment on silicon carbide papers with 500 and 1000 grit size and subsequently to a polishing step with a 1 μm diamond paste. The polished sections were covered with graphite by a SCD 050 Sputter Coater (Bal Tec, Scotia, NY, USA). The graphitized sections were analysed with a Cambridge S-360 SEM equipped with a X-Act3 SDD-EDX detector. The SEM-EDX calibration was performed using the polished and carbon-coated 53 Mineral Standard (Structure Probe, Inc., West Chester, PA) and quantification was performed using Oxford Instruments XPP correction on 11 elements, namely Na, Mg, Al, Si, P, S, K, Ca, Ti, Fe and Cu. The accelerating voltage was 15 kV, the probe current 2 nA and the working distance 10 mm. Semiquantitative parameters as inclusion/matrix ratio, inclusion mineralogy, inclusion grain size and porosity based on a backscattered (BS) electron image analysis, were taken into account.

Analyses on matrices were obtained by scanning four areas (20x20 μm^2 ca.) without evident inclusions or pores at 400X magnification; simultaneously spot spectra were acquired on all the mineral inclusions observed in the selected area. The fabric composition was detected by scanning four areas (comprising both matrix and mineral inclusions) at 50 magnifications (1x1.35 mm^2 ca.). The morphological and compositional characterization of glazes and vitrified clayey slips was performed by acquiring images at different magnifications and spot or small raster spectra, respectively. OM investigations were performed with a polarized microscope with transmitted light (type Olympus BX41) coupled with Jenoptick ProGres C5 digital camera, on thin sections.

X-Ray Powder Diffraction (XRPD) patterns were collected in order to propose some considerations on the firing temperature, by using an Analytical X'Pert Pro (PANalytical B.V., Almelo, The Netherlands) equipped with a X'Celerator detector powder diffractometer using Cu K α radiation generated at 40 kV and 40 mA. The 2 θ range was from 5 to 90°.

Principal Component Analysis (PCA) and Agglomerative Hierarchical Cluster Analysis (HCA) were performed on EDX data by the XLSTAT Addinsoft software, using Ward's method for building up dendrograms, after an autoscaling pre-processing procedure.

3. RESULTS AND DISCUSSION

3.1 Petrographic evaluation

Petrographic evaluation obtained combining SEM-EDX and OM observations and based on the systematic description proposed by Whitbread (1989) (Figure 3 - Supplementary Materials) revealed the presence of different minero-petrographic assemblage, allowing a classification of the samples in 7 main groups with some sub-groups, as reported in Table 1 and described in Table 2.

Group 1a – Granitic sands

Samples assigned to Group 1a are characterized by the presence of numerous Ca-rich oriented lamellar aggregates and large calcite inclusions. The limited primary porosity is more abundant near the surface where large inclusions are absent. Round but angular sandy inclusions mainly constituted by quartz and minor K-feldspar and calcite, quite uniform in size (about 20 μ m), are homogeneously dispersed in a carbonatic matrix. In few cases, small white mica oriented flakes also

occur. Sporadic inclusions of plagioclase, biotite, rutile and accessory minerals typical of magmatic rocks as iron oxides, titanite, apatite, tourmaline and ilmenite are observed. These features suggest raw materials deriving from granitic sands except for the large calcitic inclusions, not compatible with a geological source from granites, which might be added as temper or derive from the calcination product of original fossil remains.

In some cases, (i.e. sample 12R) a medium-low macroporosity, revealing the presence of both rounded and elongated pores occur, while the microporosity is definitely higher (Figure 1).

Figure 1

Group 1b – Granitic sands with high T neoformation phase

Group 1b is analogous to group 1a, but it is characterized by the presence of a high temperature Ca-containing phase, and reaction rims are diffusely exhibited by most clasts.

This group is characterized by a fine grain size and limited porosity with few round large inclusions ($<100\text{ }\mu\text{m}$), mainly plagioclase and neoformation Ca-rich phases, the same phases constituting the abundant finer grain clasts ($<50\text{ }\mu\text{m}$, very homogenous), together with quartz.

Minor inclusions of titanite, albite, biotite, white mica, diopside, epidote, iron oxides and ilmenite are also present. Calcite clasts are absent but the matrix is Ca-rich. Large fossil relicts (about 2 mm) were observed, reflecting a marine or lacustrine origin of the sediment.

Locally, large inclusions of microgranite and K-feldspar with a dimension up to few mm can be observed. Also for this group an origin of raw material from the dismantling of granitoid rocks can be supposed.

Sample 06G was assigned to this petrographic group but shows somewhat different characteristics, revealing a much more heterogeneous and coarse grain size distribution, suggesting the use of a common sediment but with a lower degree of refinement and purification. Within the clasts titanite, barite, Cr-spinel and the neo-formation Ca-rich phase were observed, together with distinguishing glass inclusions and glassy rims around many quartz grains. The matrix is highly carbonatic.

Group 2 – Low grade metamorphic

This group is characterized by the presence of several lamellae of kaolin/pyrophyllite/fengitic mica at different steps of transformation, uniformly dispersed in the matrix and heterogeneous in size (from less than 50 up to 400 μm).

The same features are exhibited by the numerous inclusions of a Fe-rich aluminosilicate (presumably chamosite). The finer grain size inclusions are mostly pyrophyllite, which also seems the main matrix component, while quartz and chlorite are less abundant. These characteristics seem to suggest the use of a sediment with distinguishing composition as a deposit of primary kaolin. The samples are characterized by high compositional homogeneity, with very scarce quartz inclusion and no carbonatic occurrence (Figure 1).

Group 3a – Metamorphic (phengite)

The only sample of this group (14R) is marked by oriented voids and a 50 μm thick layer near the surface with the same petrographic composition of the rest of the body but with different porosity. The sample exhibits few large inclusions, while the other clasts have a smaller grain size ($< 50 \mu\text{m}$). The most frequent phase is calcite; albite, quartz and phengite are quite abundant, while iron oxides and biotite are only sporadic. This assemblage suggests the use of a raw material deriving from the dismantlement of metamorphic rocks equilibrated under high-pressure conditions (i.e. the occurrence of phengitic mica). The matrix is rather Ca-rich.

Group 3b – Granitic sands + Metamorphic (phengite)

The samples attributed to group 3b show petrographic features intermediate between Groups 1a/b and 3a (Figure 1). They are marked by quartz and feldspar inclusions and by the presence of phengitic mica. This composition suggests a mixed (granitic and metamorphic) origin. The inclusions show a round shape, homogeneous grain size and no orientation of components occur.

The voids show sub-spheric shape with heterogeneous grain size (10 – 100 µm) and homogeneous distribution. The micromass is optically inactive.

Group 4 – Mixed sands

This group shows a complete absence of large inclusions. Finer grains (around 50 µm), homogeneous in dimensions and with round shapes, are mainly quartz, calcite and marly limestone. K-feldspar, apatite, titanite, chlorite, biotite, albite, iron and titanium oxides are present in lower abundance. The porosity is moderate and coarse and reaction rims are frequently present. The body matrix is marly, quite irregular and microporous. The source of these samples probably comprises both silicate and carbonate components.

Group 5 – Heterogeneous

Group 5 exhibits coarse texture, broad pores and several heterogeneous and large fragments of pure calcite with sharp edges, clearly deriving from spathic calcite of crushed vein (Figure 1). Plurimillimetric clasts of fossiliferous limestone with veins of pure calcite also occur, whose origin is undoubtedly different from the temper observed in Group 1a/b samples. Other large composite fragments contain Fe-poor clay (almost kaolin), muscovite, K-feldspar and very low calcite. The most abundant phase in the finer (20-50 µm) grain size fraction is calcite while quartz, albite, phyllosilicates, chlorite and iron oxides are less frequent.

Group 6 – Quartz (+ fluxes)

Sample 30G exhibits the presence of a very limited amount of small rounded quartz clasts (<50 µm), without reaction rims. The sample also shows a distinguishing matrix chemical composition (see below) with very high P₂O₅ and FeO contents. Also sample 05G reveals the presence of very few inclusions, mainly constituted by quartz and glassy clasts.

Group 7 – Volcanic

In this group the inclusions (up to 100 μm) are abundant and homogeneous. Besides quartz, albite, biotite, mica, chlorite, iron oxides and pyroxenes, several clasts of anorthoclase were observed, which was not detected in the other groups, and few hornblende grains, suggesting a volcanic origin of the sediment. The matrix is microporous and very few reaction rims were observed (Figure 1).

The petrographic grouping (Table 1) adds new information to the archaeological evaluation. First of all, the grouping does not match the class partition: Group 2 includes only red slip ware, sample 14R is classified separately from all the other samples, the cooking ware are grouped together (Group 5) and petrographic groups 6 and 7 gather two petrographically different subgroups of glazed ware. On the other hand, the majority of the samples are classified under Groups 1a and 1b, which mainly contain glazed ware, Group 3b, which mostly includes red slip and Group 4, which contains both red slip and glazed pottery. Furthermore, all the analysed sherds are characterized by abundant silicate inclusions, despite the archaeological site is located along a side valley of the Karun river, which flows entirely in the Cretaceous and Cenozoic carbonate formations of present-day southwestern Iran. Indeed, according with archaeological premises, it is consistent that the analysed manufactures were possibly “imported” from different places, presumably as grave goods. At this moment no definitive proofs can be produced on the specific provenance of the different groups, since the comparison with analyses performed on sherds from documented production where the objects could come from (i.e. Susa or other Iranian sites) would be necessary. On the other hand, a consistent hypothesis is that these centres were located in the Khuzestan Plain, downline of the confluence of the Karun river and the other Tigris tributaries, which originate from the Zagros mountains, where the distinctive minerals could eventually arrive due to the river flow action. Indeed, the Zagros mountain chain is characterized by: 1) the presence of metamorphic basement rocks that would account for the phengitic mica, 2) the occurrence of basic rocks that

would originate minerals of mafic origin and 3) granitic bodies from which the K-feldspar would derive (Garzanti 2016). The only petrographic group for which a local origin can be hypothesized is Group 5, which is composed by two cooking ware sherds, and is characterized by coarse inclusions of fossiliferous carbonates, compatible with the sedimentary formation of the archaeological site.

3.2 EDX chemical composition and technological considerations

EDX chemical composition of the matrix, expressed as oxide wt% and normalized to 100 is reported in Table 1 – Supplementary Materials. The highest Na₂O values are observed for petrographic Group 1a and 1b samples. Al₂O₃ values are below 20.0 wt% in all the groups except for Group 2 and Group 3a. MgO content is below 2.0 wt% for Group 2, Group 6 and samples 24G (Group 1b), 14R (3a) and 26 G/C (Group 7) but it is generally rather higher for all the other samples, up to 7.3 wt% for sample 25G (Group 1b). SiO₂ is below 50 wt% for 18 out of 30 samples and it exceeds 60 wt% only for Group 7 and for sample 21Ck (Group 5). Phosphorous content is generally below 1.5 (P₂O₅ wt%), but it shows abnormally high values for sample 24G (Group 1b, 5.0 P₂O₅ wt%) and, in particular, for the two Group 6 samples (13.3 and 15.8 P₂O₅ wt%), where the presence of phosphorous might be considered as a contamination effect from the burial environment. For this reason, P was excluded from the chemical data statistical treatment. On the other hand, neither the petrographic evaluation nor the XRD analysis showed crystalline P-containing phases. K₂O is generally below 2.5 wt%, with few exceptions, but it reaches up to 6.2 wt% for sample 22R (Group 2). CaO content is higher than 25 wt% for half of the samples and it falls below 10 wt% only for Groups 2 and 5 and for sample 30G (Group 6). These very high CaO contents find a good correspondence with literature observations on Mesopotamian clays characteristics (Van As and Jacobs 2014). Group 2 exhibits the lowest CaO values and the highest

aluminium contents. These values match with the petrographic evaluation, suggesting that the matrices of these samples are mainly constituted by pure clay. TiO_2 and FeO values range from 0.3 to 1.7 wt% and from 3.9 to 15.7 wt%, respectively. Finally, the chemical composition of sample 3a and of Group 3b sherds, which were slightly distinguished for their petrographic assemblage, confirms their differentiation, particularly due to their MgO , Al_2O_3 , K_2O and CaO contents. This observation agrees with the petrographic features themselves, as sample 3a is marked by the occurrence of phengite, an Al and K-rich phyllosilicate mineral. The CaO (and SO_3) enrichment for Group 3b could suggest the presence of gypsum in the matrix even if gypsum was not observed as inclusion.

The PCA diagram (Figure 2 top) highlights the distinguishing composition of Groups 2, 3a, 5, 6 and 7, which split up from one another and from the rest of the samples (Groups 1a, 1b, 3b, 4 and 4+7). These form a wide cloud along PC2, with two subgroups characterized by different relative Si and Ca contents. As a more general consideration, Si and Ca represent the two elements of discrimination between the bigger subgroup of Groups 1a, 1b, 3b, 4 and 4+7, which gathers the samples mainly characterised by the presence of granitic sands (with the exception of a metamorphic component in Group 3b and a volcanic component in Group 4+7 sample) and whose matrices are CaO richer, and all the other samples, whose matrices are SiO_2 richer. As for the SiO_2 -richer materials, Groups 2, 3a and 7 samples, which correspond to objects manufactured by using raw materials of metamorphic or volcanic origin, are then distinguished from Group 5 and 6 based on their relative Al_2O_3 , K_2O , FeO and TiO_2 contents. Finally, Group 3a only sherd separates from Group 3b samples.

Figure 2

The considerations from PCA are perfectly mirrored by a clustering method (HCA), which identifies two large clusters (Figure 2 bottom), the first containing most of the samples of petrographic Groups 1a and 1b, 3b, 4 and 4+7, and the other gathering all the other samples, splitted in two subclusters. No specific correlations between the chemical classification and the typological

class of the ceramics emerged, either from PCA or from HCA, except for petrographic Groups 2, 5 and 6, which are chemically well distinguished and exclusively contain red slip, glazed and cooking ware, respectively.

In order to extrapolate the influence of specific elements on the classification, an evaluation of bivariate diagrams was carried out.

By plotting FeO vs CaO matrix contents (wt%, normalized to 100; Figure 3) the distinguishing composition of Groups 2, 5, 6 and 7 (and partially of the only 3a Group sample) emerges, while a negative correlation is generally observable for the remaining mostly Ca-richer samples (Groups 1a, 1b, 3b, 4 and 4+7). The linear spreading observed for this bigger cluster would suggest a rather common source of raw materials for these sherds, even in view of a continuous temporal and/or geographic variability leading to hypothesize the use of similar raw materials either in different more or less localized ceramic manufacturing centres or in different workshops from a same centre. Due to the absence of pottery kilns or wastes on the site, the archaeological hypothesis proposed that the most of the vessels were not locally manufactured. Indeed, even if in the present conditions and in absence of specific reference ceramic materials it is not possible to put forward archaeometric conjectures on the sherds provenance, the Ca-richer samples can be with good confidence connected with the Khuzestan alluvial plain. From an archaeological point of view, the glazed vessels from the cemetery of Shami are clearly influenced by shapes of western Hellenistic origin, while the red-slip pottery perpetuates a regional ceramic tradition still reproducing forms of the late Iron Age and Achaemenid period. On the other hand, the coexistence of glazed and red slip ware (and common pottery) in the Ca-richer cluster would suggest an unexpected common origin (even if on a relatively large geographic scale). For the glazed pottery, similarities can be made out with scientific data on similar materials (from Veh Ardasir, Pace 2008, and from Susa, Lahlil 2008) and the sherds from Shami find typological and technological comparisons with material coming from the Izeh plain, extending about 30 km south of the Shami valley. Indeed, H. Eqbal, who studied part of the pottery collected during the survey of the Izeh/Mal-e Mir plain conducted in

1976 by the ICAR and University of Michigan, noticed that glazed pottery and red slipped pottery, often polished, are characteristic of the Seleucid and Parthian periods in the area (Eqbal 1979).

Figure 3

As for the rest of the samples (i.e. Groups 2, 3a, 5, 6 and 7) the relatively lower CaO contents in the matrix composition and the clearly different petrographic profile suggest a different provenance. On the other hand, as reported in the scientific literature (Erb-Satullo 2011), the Mesopotamian geological variability, due to the presence of Tigris and Euphrates, which cross the alluvial plain, and of the Tigris tributaries descending from Zagros Mountains, suggests an intrinsic difficulty in distinguishing different production sites and limits the possibility to make accurate evaluations on the origin of the raw materials. Indeed, in the cited paper Erb-Satullo (2011) affirms that “the identification of “local” production can only be as specific as the size of the smallest geologically distinct region”. As for Group 5, a distinguishing situation is observed with matrices showing very low CaO values together with the presence of abundant and large calcitic inclusions. Since both Group 5 samples are cooking ware fragments, it could be hypothesized that their manufacturing occurred following different routes with respect to the other ceramic classes, presumably on a more limited local scale, as commented above.

As for the relative FeO vs CaO content of the two main ceramic classes (glazed and red slip ware), no defined trend can be inferred from the sample distribution. On the other hand, a general slightly higher Fe content with respect to the red slip samples (which generally show a bright red paste) can be observed, notwithstanding the paste colour of the glazed sherds is light pink/buff in most cases. Therefore macroscopic difference in the paste colours for the two ceramic classes can presumably be ascribed to a different technological procedure, that is the adoption of higher firing temperatures for the glazed pottery with respect to the red slip ware. Indeed, the hematite development in calcareous paste ceramics is limited by the formation of new Ca-silicate phases, which incorporate iron in their structure between 900 and 1000°C (De Bonis 2017 and references therein). At lower temperatures the scarce development of these phases leads to higher iron availability for oxides

formation (e.g. hematite) and to more reddish paste shades (Molera 1998).

XRPD results evidenced the systematic presence of calcite, quartz and hematite in all the red slip ware samples (Table 2 – Supplementary Materials), allowing to estimate a maximum original firing temperature around 750-800°C (De Bonis 2017 and references therein). In fact, calcite, which decomposes and reacts with clay minerals to form new Ca-silicates from 850°C, is still abundant and hematite, which begins to form at 700°C, is already present. As for the glazed pottery (Table 2 – Supplementary Materials), the diffractometric analysis revealed the presence of high-temperature neo-formation phases like gehlenite (which forms from 800°C following Cultrone 2001 or 900°C following Trindade 2010) and Fe-containing silicates (i.e fassaite, Rathossi 2010, or augite) which limit hematite formation by incorporating Fe in their framework around 900-1000°C.

3.3 Surface treatments

Glazed pottery

The original blue-turquoise colour of the glazes is hardly visible in most of the glazed sherds, which show quite deteriorated and altered surfaces. In particular, a bright patina (with macroscopic characteristics similar to those observed by Gulmini 2009) is frequently observed on the coloured glazes and in few cases the whole glaze is completely discoloured and it seems to be completely converted into the patina. Also in the samples where the colored glaze is still observable, it is not evenly distributed the surface, which shows a mottled aspect. SEM observation confirmed the macroscopic evaluation, evidencing the presence of preserved areas of the original glaze, together with the occurrence of weathering products either only on the exterior surface of the glaze or also penetrating into its thickness.

The surface morphology prevented to obtain a quantitative chemical composition in many cases. In

the sherds with the best preserved glazed surfaces (08G, 24G, 29G and 30G), EDX analyses gave the following mean chemical composition (expressed as wt%, normalized to 100): Na₂O 9.4, MgO 2.7, Al₂O₃ 2.0, SiO₂ 68.9, SO₃ 0.4, Cl 0.3, K₂O 6.1, CaO 6.7, TiO₂ 0.2, FeO 1.1, CuO 2.2. These values quite well resemble those reported in the literature for Sasanian glazed pottery (Pace 2008, Hill 2004) and for Sasanian glass (Brill 1999, Mirti 2008, Mirti 2009) except for slightly lower Na, Mg, Al and Ca and slightly higher K contents and suggest a similarity to High Magnesium Glass (HMG), rich in Mg and K, produced by using plant ash as flux instead of Na-rich evaporitic mineral sources. On the other hand, K₂O content is rather higher with respect to the values generally suggested for this class of materials (Purowski 2018 and reference therein), which are generally characterized by K₂O values up to 4% and MgO contents from 2 to 6%. Moreover, in these conditions, due the alteration of the original glaze (or glass) we should even expect a selective depletion of some elements (i.e. Si, Na, K, Ca and Mg) and an enrichment of Al, Ti and Fe contents (Gulmini 2009 and reference therein). Given that the present data can not be considered representative of a specific production (also due to their semi-quantitative nature), the systematically high K₂O contents would rather suggest the preferential use of a specific plant. The Chenopodiaceae family is found world-wide and includes many halophytes, which are known to accumulate alkaline ions (Na⁺ and K⁺) in ratios that are specific to each families or species. Usually the accumulation capability is higher for Na⁺ than for K⁺, but in the literature is reported that, for example, in the *Salsola kali* ash the ratio Na₂O/K₂O is lower than 1 indicating a K⁺ preferential accumulation (Tite 2006 and reference therein). In the present case the ratio values Na₂O/K₂O (1.6 ca.) and (CaO+MgO)/(Na₂O/K₂O) (0.6 ca.) find a rather good correspondence with those reported in the literature by Tite (Tite 2006 and reference therein) for this kind of plants.

The use of halophyte ashes as a flux for the studied materials is consistent with the panorama illustrated in the literature (Mirti 2009 and reference therein). The first excavated vitreous materials were typical silica-soda lime glass, with relatively high Mg and K, deriving from the use of desertic plant ashes. From the first millennium, in the Mediterranean area and in continental Europe, the

employment of sodic evaporites begun to replace plant ash glass and these materials prevailed during the Roman and Byzantine period. On the other hand, this transition towards a mineral sodic flux did not occur east of Euphrates where the tradition of plant-ash glass is continued from the third to the seventh century during the Sasanian epoch and from the seventh to the tenth century AD for the early Islamic glass in Iraq and Iran.

Copper is the main colouring agent in all the examined glazes (mean CuO value of 2.2 wt%). On the other hand, all the glazes contain also iron (mean FeO value of 1.1 wt%); such amount suggests either the use of impure sand or an intentional addition of iron as a second colouring agent.

There seems to be no correlation between the petrographic group and/or the chemical composition of both fabrics and matrices and the conservation conditions of the glazes.

The observed morphologies of the unaltered glazed areas and of the alteration layers, as well as the characteristics of their interaction, are quite heterogeneous (Figure 4). Some of the glazes (i.e. samples 24G, not showed, and 30G) show quite compact areas, but they also reveal the presence of large inclusions, bubbles and fractures. Sample 30G also exhibits round alteration with an inner concentric lamellar structure protruding in the glaze.

Figure 4

The glassy structure is almost completely absent in sample 07G glaze, with the exception of a very thin layer at the glaze/body interface and of few relict areas in the glaze thickness. The rest of the layer is composed by concentric lamellar structures, generally developing around a globular fulcrum.

A similar situation is observed for sample 28G glaze, but in this case a thicker glassy layer is present at the interface between the glaze and the body, the lamellar structure is less geometrically defined and is developed only in the glaze outer layer.

Sample 10G glaze is characterized by a thick compact glassy layer, characterized by the presence of acicular structures and separated from the body by a thinner layer rich in quartz inclusions. A thin layer (patina) brighter in the BS image can be observed on the glaze exterior surface.

Red slip ware

Also in the case of the red slip ware, the surface of the samples is quite deteriorated in many cases (preventing, in the case of sample 12 R, to obtain EDX data) and the EDX chemical composition (expressed as oxide wt%, normalized to 100) is to be considered semi-quantitative.

Data in Table 3 – Supplementary Materials show that the sample distinction in different petrographic groups is also paralleled by the slip mean chemical composition. Group 2 revealed the highest P_2O_5 and the lowest CaO contents. Groups 3a and 3b decisively differ for their overall composition. Group 3b showed the highest FeO content and relatively high CaO and MgO values, while Group 4 exhibited the highest CaO and MgO and the lowest Al_2O_3 . On the other hand, by comparing these results with data reported in the literature for other red slip ware productions (e.g. Terra Sigillata, Mirti 1999; Coral Red Slip on Greek Attic pottery, Walton 2009), rather high CaO and MgO contents and relatively low Na_2O , K_2O and FeO values can be observed. Moreover, the comparison with the body compositions (not showed) lead to observe a lack of a systematic increment in the contents of elements with a flux function in the slips, as usually observed for this ceramic class, with respect to the corresponding body pastes. In particular, Na_2O and K_2O values are rather similar for both slips and bodies and FeO contents are slightly higher for Groups 2 and 3b slips but lower in the case of Group 4. On the other hand, alkaline-earth elements data are systematically lower in the slips (except for Group 3a MgO content), especially for CaO. To summarize, the overall slip composition shows rather a marked depletion of alkaline-earth elements than a substantial contribution of flux elements. This observation, which can be either due to the original composition or, at least in part, to a selective depletion during burial, together with a relatively low firing temperature, would explain both the limited degree of vitrification and the poor state of conservation of most of the sherds. In fact, as far as the morphology is concerned, most of the slips showed no sign of vitrification but only a certain degree of orientation of the clay particles parallel to the external surface (Figure 4, sample 18R). Only in few cases a vitrified slip was

observed, even if the coating showed an irregular surface and the presence of inclusions and holes (Figure 4, sample 13R).

4. CONCLUSIONS

30 ceramic fragments of different ceramic classes (red slip, glazed, common and cooking ware) from the Hellenistic and Parthian Kal-e Chendar (Iran) were investigated. SEM-EDX and OM petrographic analyses revealed the presence of different minero-petrographic assemblages, allowing a classification of the samples in several petrographic groups. Chemometric treatments on the EDX matrix chemical composition partially confirmed the petrographic classification, marking the differentiation of several Si-richer PCA clusters and evidencing a lower variability in a bigger Ca-richer cluster, suggesting different supply areas in the first cases and either a common source, presumably on a quite large geographic scale, or multiple sources with a similar Ca content, in the second case. As for the Ca-richer samples, this could suggest the existence of different workshops producing objects with comparable typological characteristics, with similar but not identical raw materials, or, eventually the presence of a single workshop using raw materials from different sources. On the other hand, the observed spreading in the Ca-richer cluster could also be ascribable to a natural variability of one or more clay outcrops. Given that the presence of pottery kilns or waste were not evidenced by fieldwork and due to the small amount of potsherds in stratigraphic context, it can be proposed that most of the found vessels were not produced at the site. At this moment no specific proofs can be given on the provenance of the different groups, due to the current lack of reference data on materials from possible coeval sites. On the other hand, based on the petrographic composition, the most probable hypothesis could be that the origin of the Ca-richer samples was located in the Khuzestan alluvial plain and more specifically in the area of the

confluence of the Karun river and the other Tigris tributaries, originating from the Zagros mountains. Bearing in mind the importance of the Shami sanctuary, one of most reputed religious place of Hellenistic and Parthian Elymais and probably a prestigious burial place, the hypothesis that the dead and their grave goods could come not only from the neighbouring Izeh plain but from even distant places, such as Susa, cannot be excluded.

From an archaeological point of view, the red-slip pottery excavated in the Shami tombs follows a regional ceramic tradition still reproducing forms of the late Iron Age and Achaemenid period, while the glazed vessels are a local production clearly influenced by shapes of western Hellenistic origin. Thus, local pottery traditions, elaborated since the Iron Age III, continued to be followed during the first centuries of the Seleucid-Parthian period in the highlands of Khuzestan but the red slip ware tends to decrease and to be replaced by a new repertoire of shapes elaborated in central and lower Mesopotamia and in low-land Susiana in consequence of long-lasting political and cultural contacts.

It is quite remarkable that the big Ca-rich cluster gathers different ceramic class (glazed, red slip and common ware). However, a slight chemical differentiation between the different productions within this cluster can be pointed out, presumably suggesting a different technological choice in function of the desired aesthetical objective. Notwithstanding the higher Fe amount for the glazed sherds, with Ca contents comparable to the red slip samples, the resulting paste is buff-coloured due to higher firing temperatures adopted for the glazed ware manufacture.

As far as the surface treatments are concerned, the glazes were obtained by using plant ash fluxes (particularly K-rich), following a tradition that will last until the Sasanian epoch and in the early Islamic glass in Iraq and Iran, and copper as colouring agent. Both glazes and red slips appear very deteriorated, revealing typical alteration morphologies. In the case of the red slips a lack of enrichment of fluxes (both alkaline elements and iron) in the slip with respect to the body could account for a scarce vitrification and the consequent deterioration.

Credits

Introduction and Material description by A. Cellerino, Methods and Results and Discussion by P. Davit, F. Turco, L. Operti and A. Borghi, Conclusions by all the authors.

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Figure captions

Figure 1: BS SEM images (at different magnifications) of samples 12R (Group 1a, top left), 22R (Group 2, top right), 16R (Group 3b, middle left), 21Ck (Group 5, middle right), 05G (Group 6, bottom left), 28G (Group 7, bottom right).

Figure 2: top) PCA (red = red slip ware; blue = glazed ware; yellow = common ware; green = glazed/common ware; black = cooking ware) and bottom) HCA diagrams obtained from the matrix EDX chemical composition data.

Figure 3: FeO vs CaO matrix contents (wt%, normalized to 100) bivariate diagram.

Figure 4: BS SEM images (at different magnifications) of samples 30G (top left), 07G (top right), 28G (middle left), 10G (middle right), 13R (bottom left), 18R (bottom right).

Table captions

Table 1: Archaeological description of the samples. In the sample name, G = glazed ware, R = red slip ware, C = common ware, Ck = cooking ware. Last two columns: minero-petrographic classification from SEM-EDX and OM evaluation .

Table 2: Systematic description of thin sections for all the identified petrographic groups, following Whitbread (1989).

Supplementary Materials – Figure and table captions

Figure 1 – Supplementary Materials: Map of the Iraq-Iran border area with the position of the main archaeological site (Shami location in the inset).

Figure 2 – Supplementary Materials: Overview of the sample *corpus*.

Figure 3 – Supplementary Materials: Representative selection of thin section microphotographs of the analyzed sherds. Top left: Quartz (light) and k-feldspar (brown) inclusions surrounded by a fine-grain carbonatic matrix (sample 23G, group 1a), crossed pol.; top right: large fossil relicts (about 2 mm) reflecting a marine or lacustrine origin of the sediment employed as raw material for the

manufact (sample 04G, group 1b), crossed pol.; bottom left: fine-grained matrix composed by pyrofillite with major chamosite inclusions (Sample 18 R, group 2), crossed pol.; bottom right: large limestone inclusion showing bioclastic content (Sample 19 Ck, group 5), crossed pol.

Table 1 – Supplementary Materials: EDX matrix chemical composition results (oxides wt%, normalized to 100) for all the samples.

Table 2 – Supplementary Materials: XRPD mineralogical pattern for 8 out of the 30 studied samples. Qz: quartz, Ca: calcite, Di: diopside, He: hematite, An: anorthoclase, Ge: gehlenite, Fe-Si: Fe-silicates (fassaite or augite).

Table 3 – Supplementary Materials: Mean chemical (EDX) composition (wt%) for the slips of petrographic groups 2, 3a, 3b and 4.