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Preliminary cross-correlated archaeometrical analysis on Iron Age representative pottery specimens from ancient Karkemish (Turkey)

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***Abstract* – Archaeometrical investigation on the ceramic assemblage from Karkamış Höyük, ancient Karkemish started in 2016, mainly focusing on Iron Age materials. Preliminary cross-correlated analytical investigations highlighted crystal structure and chemical composition of samples, selected to represent all technological ceramic classes. This work reports on the first step of a broader program of analyses on both sherds and raw clay, with the aim to connect the site and its ceramic production with the geological deposits in the surrounding region.**

I. KARKEMISH IN ITS CONTEXT

The site of Karkamış Höyük, ancient Karkemish is now located on the Turco-Syrian border, with about 65% of it lying in Turkey. Excavations on behalf of the British Museum were led, among others, by C.L. Woolley, together with T.E. Lawrence (later known as Lawrence of Arabia) at the beginning of the 20th century, and uncovered many monumental buildings dating from the Bronze and Iron Ages. Archaeological investigations were resumed in 2011 by the Turco-Italian Archaeological Expedition of the Universities of Bologna, Gaziantep and Istanbul (under the direction of prof. N. Marchetti, whom we thank for his support to our research) and are still ongoing [1].
Its position on the western bank of the river Euphrates makes Karkemish a pivotal site between Syria and northern Mesopotamia. Past and recent investigations focused on the so-called “Lower Palace Area,” located at the footstep of the Acropolis. Turco-Italian excavations have uncovered a large palatial area, which provided an outstanding quantity of stratigraphic and material data.
Fieldwork is integrated by a systematic analysis of the material, such as small finds, soil samples and pottery.

II. THE METHODOLOGICAL FRAMEWORK

Ceramic sherds from the Karkemish excavations are usually studied and filed during the excavation campaign: they are preliminarily divided in three technological groups, based on the macroscopical observation of fabrics’ colour and composition, then different open or closed shapes are distinguished [2]:
- Kitchen or Cooking Ware (hereafter KW): all vessels employed for the heated preparation of food, especially cooking pots, are part of this class. The fabric is coarse, porous and shapes often have burning traces from direct contact with fire. Firing temperatures are quite low (600°-800°C), which improve the fire-resistance of KW fabric to direct sources of heat.
- Preservation or Storage Ware (hereafter PW): this group includes large, mainly closed, shapes for storage and transport of solid and liquid foodstuffs. Fabrics are often very coarse, with many vegetal and mineral inclusions of medium and even large size. Firing is often incomplete: outer surfaces can be well-baked, while core remains poorly fired.
- Simple or Common Ware (hereafter SW): the term marks all remaining vessels which are used for food preparation without any source of heat. It is a big and heterogeneous group, which includes several different shapes, mainly tableware, for transformation or short-term preservation of solid and liquid foodstuff. Fabric is fine, with few or almost no inclusive materials, while the vessel’s surface is often treated or decorated in different ways.
Each functional class includes different shapes: PW is dominated by large closed shapes, such as storage jars, while SW and KW have in common both open and closed vessels. Anyway, some cross standard types have been detected: platters, bowls and kraters among open shapes, and jugs, jars, pithoi among closed ones. However, the lack of complete vessels forced the detection of these shapes through their diagnostic

fragments and comparisons with evidence from other sites.

Up to the 2017 campaign, the ceramic assemblage dating to the Iron Age includes 6569 selected and filed sherds. Among them, five representative samples have been chosen manly to confirm conclusions coming from macroscopical observation.

The work focused on samples belonging to Iron Age levels of areas G (KH.G..1) and S (KH.S.1-4). Each sample is labelled with the name of the site, the excavation area they come from and a sequential number. The selection was made with the aim to cover all ceramic classes, in technological and temporal terms. Two specimens of red-slipped sherds (KH.S.2-3) were analysed to obtain information on the possible different composition of their clay slips.

A wide array of cross-correlated archaeometrical methods has been employed: reflected and transmission polarized Optical Microscopy (OM) digitized with CCD high resolution colour camera, Scanning Electron Microscopy (SEM) with X-ray microanalysis (SDD-EDS) also sensitive to low atomic numbers (C, N, O, F) and X-ray Diffraction (XRD), which provided crystal structure composition of baked clay. A specific method based on resin impregnation was applied for the preparation of thin-sections for both OM and SEM-EDS analyses. This method allows porosity evaluation through image analysis. Their combination and cross-correlation on the same area resulted in a complete mineralogical overview on the analysed samples.

The first step of our work was the selection of ceramic samples and a preliminary analysis of their general, macroscopic features, such as fabric colour and texture and surface decorations. Then, for Optical Microscopy (OM) analysis, the material was prepared in thin-sections (about 30 ± 1 µm), polished at least with 0.5 µm grit, over areas 20 mm large. Observation focused on five areas of the samples, both core and edges (Fig. 1). In this paper, the focus will mainly be on core part, as less affected by external agents. Both stereo and mineralogic/petrographic microscopes were used, and with the latter views were made with parallel and crossed nicols in transmission mode. Scanning Electron Microscopy (SEM), integrated with Energy Dispersive Spectroscopy (EDS), allows a granulometric analysis of sample, giving information on the structure and distribution of clasts, with an average chemical composition. Different magnifications have been employed on thin-sections, but the most widespread are 40x, 60x and 400x. The largest range were used for KH.S.4 (20x-800x), as this specimen displayed a larger variety of clasts to be identified. Aliquots of powder for each sample were taken by "grinding" technique, with a diamond grinder (Mohs hardness of 10). Then, the resulting outcome has been ground with agate mortars.

X-ray diffraction (XRD) was carried out on the same powder used for EDS analysis. We want to stress on this reiteration in investigating the same pulverized portion of the sample (cross-correlation method). This process increases the accuracy on its identified mineralogical components. For XRD, powders are placed on zero background holders for data acquisition. For EDS spectra, we had to consider the correlation between size of grains, the degree of penetration of electrons and the resulting interaction volume. If this latter is comparable to the size of grains under analysis, it is possible the EDS spectra gives information from other next grains. In this situation, a specific chemistry is not assigned to a grain. Monte Carlo EDS X-ray analysis was performed to check out this effect.

The analysed parts of the samples are the core and the surface coating as indicated in Fig. 1, when present (KH.S.2-3).

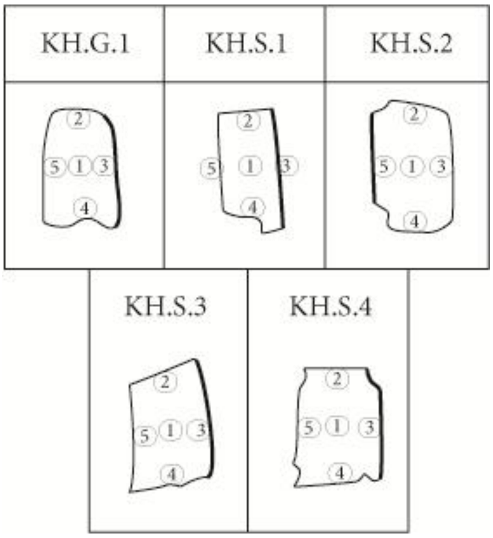

Fig. 1. Schematic overview of shape and numbering of investigated areas

III. ARCHAEOMETRICAL OUTCOMES

This overview is organized by technological classes, according to the aim of preliminary analyses. These confirmed an interesting array of data on mineralogical and chemical composition, which almost fits with previous macroscopical observation.

A. KH.G.1

Excavation context: K.H.13_F.2309

Macroscopical description: fragment of PW, greyish fabric (10YR 7/4), fine texture, small mineral and vegetal inclusions (< 0.5 mm – < 10%), white slip, no decoration attested.

OM: the thin-section displays a whitish/yellowish, uniform matrix with widespread clasts, which compose

about 57% of the overall volume. Type and distribution of clasts are varied. Most are quite large (< 300 μm) and oval or rectangular with smoothed angles in shape. Colours ranges from dark/light grey to brownish and dark green. The most widespread are irregular, greyish grains, about 200 μm large. Microporosity is mostly attested. See Fig. 2 for an example of reflection (upper left) and transmission (upper right) OM images.
SEM: magnifications show a low-cleaned clay, with several grains of irregular shape and about 10-20 μm large. Identified minerals includes quartz, augite and pseudobrookite in traces. No mica or illite are present in this sample. See the central left image of Fig. 2 for an example.
EDS: the core part has a high quantity of silica, together with aluminium and calcium in lower degree. Residual presence of iron, magnesium, potassium and sodium is attested. The outer surface displays a similar trend, with a lower presence of calcium and a higher presence of aluminium and iron. See the central right image of Fig. 2.
XRD: the main mineralogical phases include clinopyroxenes and gehlenite (which are almost absent in other samples), which mark higher firing temperatures (800-900°C). Moreover, amorphous material in the core part could stand for organic inclusions included in the clay. See the bottom image of Fig. 2.
Results. The typical Storage Ware features are displayed by this sample. The fabric is quite coarse, with even organic (probably vegetal) elements included. High-fired vessel brought to less porous surfaces, which are preferable for the storage function.

B. KH.S.1
Excavation context: K.H.16_F.6111
Macroscopical description: fragment of SW, orange fabric (5YR 7/6), fine texture, small mineral inclusions (< 0.5 mm – < 3%), white slip, no decoration attested.
OM: magnifications show a whitish/light greenish clay with several clasts of small size (10-100 μm), mainly rectangular or lamellar in shape, which compose up to 45% of the matrix volume. A high level of macroporosity is also recorded.
SEM: the fabric is quite homogeneous, with widespread clasts of different shape and limited size, which ranges from 20 to 100 μm. Quartz and calcite are the most common components. Illite, anorthite and diopside are attested too, as traces of hematite and pseudobrookite. The two latest minerals have been detected thanks to a 400x enlargement. The analysis of the outer surface uncovered a similar mineralogical framework, even if the texture is less coherent than in the core area.
EDS: almost no differences among values are recorded between core and outer surface of the sample: high concentration of silica, aluminium and calcium are followed by small quantities of magnesium, potassium, titanium and iron.
XRD: core and outer edge have similar mineralogical presence, with standard quartz, calcite and plagioclases phases, together with small illite/mica ones. However, unlike the previous PW type, clinopyroxenes are in low percentages, and only traces of gehlenite have been detected in the outer part.
Results. The typical features of Simple/Common Ware are displayed in this sample, with fine, homogeneous clay texture, while small clasts are widespread in the whole matrix.

C. KH.S.2
Excavation context: K.H.16_F.7423
Macroscopical observation: fragment of SW, buff fabric (5YR 6/4), fine texture, small mineral inclusions (< 0.5 mm – < 3%), red slip, no decoration attested.
OM: the light brownish/reddish fabric has a brighter band behind the outer surface coating. Different sizes of clasts are attested, but their quantity is the lowest recorded among all samples (32% of the volume). Their size mainly ranges from 20 μm to 1 mm: most of them are dark greyish (possibly pinkish and whitish), while their shape ranges from triangular and rectangular to lamellar. Microporosity is highly attested, while macroporosity is nearly absent. From OM analysis, red-slipped coat results to be about 20 μm thick, and brighter in shade than the fabric.
SEM: widespread clasts (about 30 μm large) of circular and rectangular shape are included in a fine cement. The coating is less homogeneous than the fabric of the vessel, with irregular clasts of 20-30 μm. Several minerals have been identified, as k-feldspar, calcite, quartz, plagioclases and anorthite, while for others XRD should be employed.
EDS: this analysis confirms the higher concentration of potassium, sulphur and iron in the outer part and in the slip of the vessel, which are almost not detected in the core part.
XRD: The core and peripheral areas shares similar mineralogical phases, with abundant presence of quartz, calcite and plagioclases, with K-feldspar and illite phases. Hematite and (pseudo)brookite are present in traces. The analysis carried on the clay coating undercovered different mineralogical components. A clay minerals phase with interplanar spacing of 7.2 Å is attested in average quantity, together with probably apatite. These components are instead totally absent in the analysed sample from the vessel.
Results. Differences between the fabric and the coating are clear, although both share the same basic mineral structure. Probably, the liquid clay used to cover the vessel was integrated with some minerals (still

unknown) to improve its technical features (adherence, viscosity, brightness).

D. KH.S.3

Excavation context: K.H.16_F.7423

Macroscopical description: fragment of SW, light brownish fabric (7.5YR 7/6), fine texture, small mineral and vegetal inclusions (< 0.5 mm – < 3%), red slip, no decoration attested (fire burning evidence).

OM: the greyish/greenish matrix presents a poorly homogeneous texture and mainly square or rectangular clasts (composing about 43% of overall volume). Their colour ranges from greyish to whitish. The clay-made coating is about 30 μm thick and displays a texture quite similar to the vessel fabric, probably because of a homogeneous, high-temperature firing.

SEM: The 100x view allowed to detect a large typology of clasts, whose shape ranges from rounded to rectangular, lamellar or irregular. Some of the largest clasts can reach even 100 μm in size. Cement is not fine but homogeneous. The analysis on the coating underlined its homogeneous texture with an average quantity of small calcite and plagioclases grains, integrated by some bigger quartz clasts.

EDS: the coating displays a lower presence of calcium in comparison with the core, but the presence of silica, aluminium, potassium and iron (with small quantity of sodium, magnesium and titanium) are constant for the whole sample.

XRD: the coating displays mineralogical phases similar to those of the vessel core, with abundant presence of quartz, calcite and plagioclases, with K-feldspar, illite phases and hematite in traces. As for the previous type, an unknown clay minerals phase with interplanar spacing of 7.2 Å is recorded, as traces of gehlenite.

Results. Trends in mineral composition of this sample are quite similar to the previous one, with an even more homogeneity between vessel and slip. Also in this sample, the slip shows an unknown mineral not attested in the core fabric.

E. KH.S.4

Excavation context: K.H.16_W.7440

Macroscopical description: fragment of KW, reddish fabric (2.5YR 6/6), coarse texture, medium/large mineral inclusions (1/2 mm – < 3/10 %), no surface treatment attested, no decoration attested.

OM: a reddish/dark brown cement with large percentages of clasts of similar or darker colour (from brownish to reddish). Most of them have squared or lamellar shape and can also reach considerable size (more than 1 mm). Texture is quite irregular, with inner large blank spaces, resulting on a general microporosity of the cement where fissures are not uncommon.

SEM: the brittle texture of this sample is evident from this analysis. Several clasts of different size and shape are present without any coherent distribution. Several minerals cannot be identified by SEM analysis, because of their small size and variety. The lack of homogeneity is even more evident in the outer edge, where amorphous parts and average mineral inclusions are common.

EDS: levels of silica, aluminium and calcium are similar to the previous examples. Only a lower presence of the latter element is recorded for the outer edge.

XRD: this Cooking Ware sample have an abundant phase of illite/mica, unlike previous samples, while clinopyroxenes, gehlenite and (pseudo)brookite phases have not been detected.

Results. The low firing temperature (with possible bad firing conditions) is evident for this sample, in particular on the surface, where mineral elements are not soldered, resulting in a brittle texture.

This archaeometrical overview on a small ceramic sample wishes to be a final completion of the previous work and a starting perspective for further, broadening researches. Despite the paucity of investigated samples, information obtained from them could only push for wider archaeometrical investigations. According to the analysed fragments, some macroscopical features are confirmed, while other hints have been uncovered.

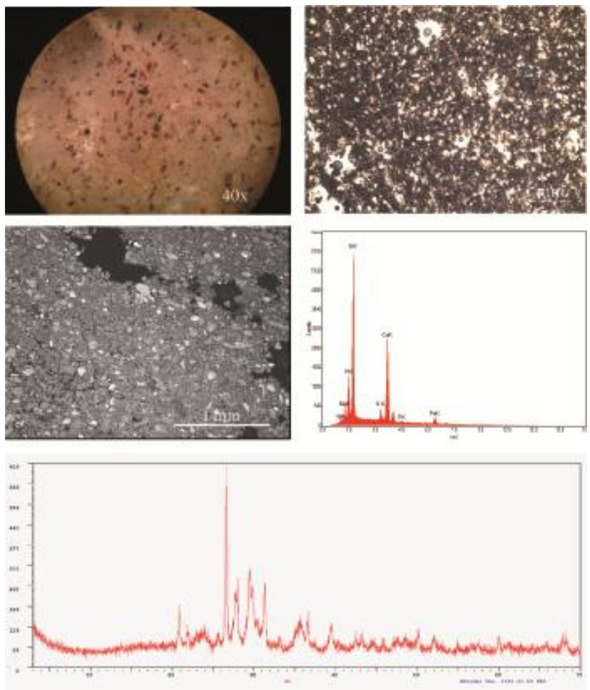

Fig. 2. OM (reflected and transmitted crossed polars), SEM with EDS, and XRD spectra of sample KH.G.1(1).

Bronze Age/Iron Age pottery in the Near East is usually fired less than 900/1000°C [1]. Common and Storage Ware are usually well-fired in comparison with Cooking Ware, whose average firing temperature is usually 500/600°C. This firing is the responsible for a wide presence of mineral inclusions, as the melting point and thermostructural transformation are higher than that value. This pattern deeply affects the general texture of the fabric, which results to be coarser and brittle [1]. Actually, firing atmosphere and temperature affect several properties of fired vessels, mainly colour and texture (porosity, hardness and shrinkage). In particular, storage vessels (KH.G..1) are well-fired not only for an aesthetic reason, but also for a functional purpose. The surface of a storage container (especially for liquids) must have a low degree of permeability, thus its porosity must be reduced as much as possible [3]. In contrast, cooking vessels (KH.S.4) are low-fired because an "increasing porosity may be a more appropriate strategy for dealing with thermal shock" and stresses [2]. The presence of gehlenite within Common Ware is another proof for higher firing temperatures for this class, as its mineralogical phase is attested only starting from 900°C [4], while is absent in Cooking Ware group.

Porosity also depends on the presence of distinct minerals in the fabric: for example, higher percentages of calcite guarantee a porous matrix [5]. This is confirmed by our sample, as KH.S.4 displays a very abundant presence of calcite, while storage vessel (KH.G..1) have the lowest record among all analysed samples.

Other interesting information comes from Red Slip analysis: we have already underlined how KH.S.2-3 samples present different macroscopical features (colour, thickness), confirmed by microscope-led analysis. X-ray diffraction provided a further framework on mineral composition. In fact, coatings share a basic clay composition similar to the vessel itself, while some minerals are also added in order to obtain technological improvements (viscosity, adherence, different colour of the slip). In particular, apatite (calcium phosphate) found in the coating of KH.S.3 deserves great attention, because of its possible origin.

IV. FUTURE PERSPECTIVES

This report on the Iron Age pottery from Karkemish must be considered as a preliminary step of a broader program of analyses. The plan is to exploit archaeometry by means of the presented cross-correlated analytico-structural method to solve several hanging questions, without solution by standard macroscopical study. For this reason, material from the site will be collected exponentially, with samples from all excavated areas, in order to detect fabrics' groups.

The first aim is to obtain a general framework on the local IA repertoire, focusing on the study of fabrics and surface treatments. Mineralogical and chemical composition, as transformations occurred following drying and firing processes, could be understood, matching them to texture and colours. Often only fabrics allow to define local production and imported vessels. A specific task will focus on clay slip composition, settling anomalies and relations between it and core fabric.

Then, resulting data should be correlated to historical and social contexts, detecting, among others, differences in pottery repertoires between sites or even contexts with distinctive functions (palatial, domestic, productive, funerary).

The research is not limited to the Karkemish assemblages only, but the plan is to tie local evidence to several researches carried out on other assemblages of the Northern Levant in a regional perspective. Above all, data from inland Syria (Tell Afis, Tell Mishrifeh) [6] and the ‘Amuq valley (Tell Tayinat, Taşlı Geçit Höyük) [7] must be considered, to build up a complete framework for the region. An intensive work on geomorphological maps, from the Turkish Geological Society (www.mta.gov.tr/eng/) is aimed at establishing a connection between ceramic production and geological deposits in the surrounding region of Karkemish (Gaziantep region), through surveys in the region around the site and the intensive collection and analysis of clay samples. A GIS will provide an ideal platform for handling these different data.

Actually, the Northern Levant does not display a large number of pioneering archaeometrical works on pottery repertoire, while for other Mediterranean regions the current "state of art" is in constant development, employing additional techniques and devices. Similar and innovative investigation approaches such as that of QEMSCAN and EBSD which generate compositional maps and mineralogical texture could be an additional supplement to the study of clay mixing surface treatments [8].

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