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# UNIVERSITÀ DEGLI STUDI DI TORINO

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# **MULTI-TECHNIQUE CHARACTERIZATION OF VARIOUS ARTEFACTS AND RAW**

## **MATERIALS FROM OLD NISA (TURKMENISTAN): A PRELIMINARY STUDY**

F. TURCO<sup>\*1</sup>, P. DAVIT<sup>1,2</sup>, A. BORGHI<sup>3</sup>, J. BRUNO<sup>4</sup>, C. LIPPOLIS<sup>4,5</sup>, L. OPERTI<sup>1,2</sup>

<sup>1</sup> Department of Chemistry, University of Turin, Via Pietro Giuria 7, 10125, Turin, Italy.

<sup>2</sup> NIS Centre of Excellence, Via Pietro Giuria 7, 10125, Turin, Italy.

<sup>3</sup> Department of Earth Science, University of Turin, Via Valperga Caluso 35, 10125, Turin, Italy

<sup>4</sup> Department of Historical Studies, University of Turin, Via Sant'Ottavio 20, 10124, Turin, Italy,

<sup>5</sup> Centro Ricerche Archeologiche e Scavi di Torino per il Medio Oriente e l'Asia, Piazza Statuto 10,  
10122, Turin, Italy

\*Corresponding author. Tel.: +39 011 6707583; fax: +39 011 2367583; *E-mail address*:

[francesca.turco@unito.it](mailto:francesca.turco@unito.it).

### **ABSTRACT:**

A multitechnique (SEM-EDX, XRD, TGA) characterization was performed on several materials and artefacts from Old Nisa excavated during the recent Italian-Turkmen archaeological expedition, which involved a large building in the SW corner of the citadel, formed by rooms utilized as warehouses and workshops. Polygenic conglomerates archaeologically classified as anhydrites were examined and proved to be highly compatible with all the studied architectural artefacts (a plaster, a mortar, and a mould), making strongly plausible their identification as raw materials. Besides, several pigments at different stages of the manufacturing process were examined. A very complex situation emerged, suggesting the existence of different productive processes. At last, a black cylindrical object, identified as a seal, but almost completely devoid of engravings, turned out to be made of graphite and obtained by turning.

The results of the analyses on these materials shed a new light on the complexity of the manufacturing processes carried out in Old Nisa in connection with the production of decorative elements for the monumental complex located inside the citadel.

**KEYWORDS:** plaster, mortars, stuccoes, gypsum, pigments, SEM-EDX, XRD, TGA, Old Nisa, seal, graphite

## 1. INTRODUCTION

Old Nisa is known as one of the main and most ancient sites of the Parthian culture, in the territories (nowadays southern Turkmenistan) that formed the original core of the Arsacids' kingdom. Although it was extensively excavated by Turkmen, Soviet and Italian expeditions, there are still many open questions about the precise nature of this important settlement. Today, Old Nisa is generally interpreted as a great ceremonial centre dedicated to the glorification and celebration of the first Arsacids, the Parthian rulers (Figure 1). Mud-clay fortification walls enclose a series of ceremonial buildings (temples, mausolea, reception halls, open courtyards) surrounded by functional edifices, mainly interpreted as warehouses for the storage of foodstuffs (wine, wheat, flour, oil etc.). Likely founded in the II century BCE, the main buildings were apparently abruptly abandoned after the first half of the I century CE.

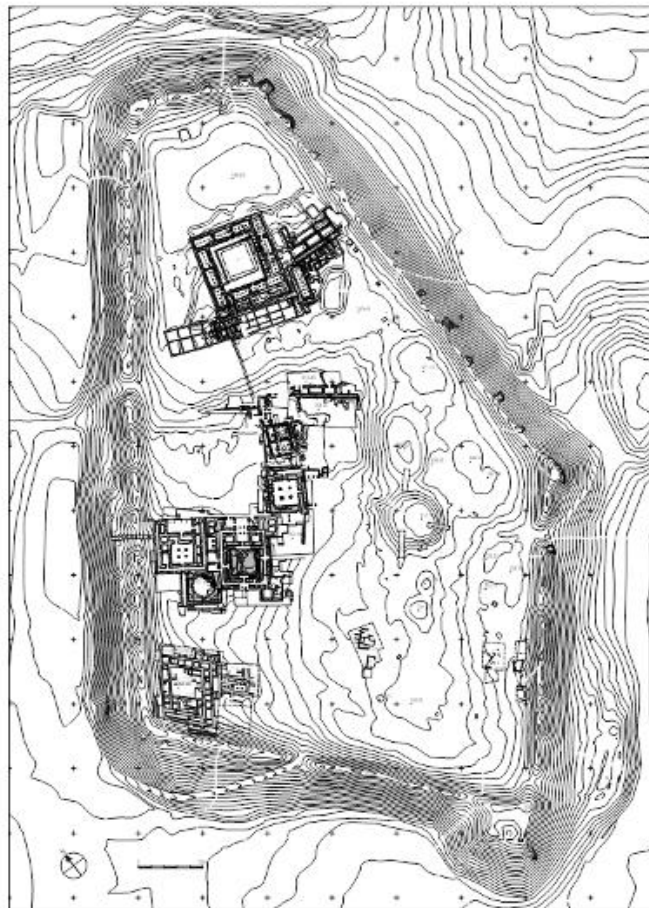


Figure 1: Map of the Old Nisa archaeological site.

Despite the site was widely studied from an archaeological point of view (for the Soviet and Russian excavations see Pilipko, 2001; for the Italian excavation see Invernizzi & Lippolis, 2008),

it is largely unknown from the archaeometric viewpoint. Therefore, in the present study a multitechnique investigation on various artefacts was carried out, with the aim of identifying their chemical and mineralogical composition and of drawing information on their technology of production. Besides, samples of polygenic conglomerates found on the site during the last excavation and suspected to be raw materials or semi-finished products, were examined in order to verify their compatibility with the presumable respective final artefacts. For these purposes, a morphological examination together with the determination of the chemical composition was carried out by Scanning Electron Microscopy coupled with an Energy Dispersive X-Ray microanalysis (SEM-EDX), while the mineralogical composition was determined by X-Ray Powder Diffractometry (XRPD) and the thermal behaviour was tested by means of a ThermoGravimetric Analysis (TGA). Petrographic examination was performed by means of optical microscopy.

### 1.1 Materials and archaeological context

All the analyzed materials were excavated during the recent Italian-Turkmen archaeological expedition (*Centro Scavi di Torino and Ministry of Culture of Turkmenistan - National Department for Protection, Research and Restoration of Historical and Cultural Sites of Turkmenistan*) in the Old Nisa SW area. From 2007 a large quadrangular building consisting of various rooms utilized as warehouses and workshops arranged around a central courtyard was investigated (Lippolis, 2013, 2010).

First of all, a mortar, a plaster and part of a mould were examined. From a technical point of view all these materials could be considered comparable, the choice of one term compared to another is generally relative to their functional purpose, respectively to bind bricks/stones, or to cover architectural elements, exterior walls or for decorative aims (Weiner, 2010). All these materials are composed of a binder and of added materials (aggregates) as carbonates, quartz or shells, increasing volume and improving mechanical properties. The utilized binders were gypsum and/or lime, with a marked prevalence, during the prehistoric period, of one material over the other, in most areas (Gourdin & Kingery, 1975; Kingery et al., 1988; Philokyprou, 2012a, 2012b). In particular, in the Levant, Anatolia and Greece lime was almost exclusively the material of choice, while gypsum was the material of choice in the area of the Tigris and Euphrates and further to the East (Philokyprou, 2012a).

In Old Nisa the use of plaster is attested for very simple wall cornices or panels, for smoothing sculptures surfaces and for the final finishing of wooden beams, brick columns and pillars. Mortar was widely used for fixing architectural details on the mud-brick masonries. As

attested also by the recent Italian excavations in the SW area of the citadel, plasters were widely used in the modelling and production of moulds for terracotta architectural details or for statues (this latter sculptural production technique is to be considered as imported from the West (Lippolis, 2011)): about 30 fragments of double-moulds have been discovered only in this area. The recurrence of colours, mostly red (ranging from pink to purple) and black, but also yellow-ochre and light blue, is largely attested on several architectural elements (Figure 2, left) and on wall plasters.



Figure 2: Coloured stone slab-frieze from the facade of the "Red Building" (left) and mould from Old Nisa SW area (right).

Although in the archaeological literature the use of gypsum for the production of these artefacts is assumed (Pilipko, 2001, p.263-264), an archaeometric evaluation has never been conducted, with the exception of some preliminary on-the-field PIXE- $\alpha$  investigations on some moulds, (Lippolis, 2011). The three samples (a mortar, a wall plaster and a mould) taken into consideration in the present study come from the excavation (2007-2015) from Parthian period (II century BCE-I century CE) levels of a storage building in the SW corner of Old Nisa citadel (Figure 1). Moreover, large polygenic conglomerates, usually defined as "anhydrite" from the Russian expedition and quite widespread at Nisa (Lippolis, 2013), were found in this area. From a mineralogic point of view, anhydrite is anhydrous calcium sulphate ( $\text{CaSO}_4$ ) that easily alters to the much more common hydrated form, gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). These two related minerals usually have evaporitic origin and form during episodes of highly saline water evaporation. In the present work one of the polygenic conglomerates was also analysed in order to ascertain their natural or anthropic origin and their possible use as raw materials for the artefacts production.

Secondly, materials suspected to be related to the manufacture of pigments were examined.

Red and pink mineral lumps and red, yellow-brown and pink clasts resembling fairly finished pigments were quite common findings during the excavations and they were sampled for the present study. Moreover, a deep-pink/purple powder on a ceramic bowl fragment was taken into consideration. The fragment was excavated from the fill layers inside a ditches system in the SW corner of the courtyard of a building excavated by the Italian Mission in the last years. Several fragments of bowls retaining traces of pink, red, black, yellow and light blue pigments on the inner surfaces were also discovered in some of the rooms of the *Red Building* and in the stockpile of the restoration materials of the *Tower Building* and of the *Square Hall* (Cellerino, 2008, p. 273; Pilipko, 2001, p. 305). These bowls should have been used by the ancient craftsmen for pigments and binders mixing and as palette for colouring statues, paintings, etc. All the sampled materials were examined in the present work in order to check their compatibility with the pigments previously identified on plasters and *terracotta* by Appolonia et al. (2008), and eventually to obtain information on the production technology.

At last, a black seal was examined (Lippolis, 2010, p.41, fig.7). Several fragments of black sticks, with very well finished and smooth surfaces and apparently without any significant decoration or engraving, were discovered during the excavation of the SW building. Although their extremity is unfortunately broken in all the excavated objects/pieces, their size and form suggest that they were used to produce the hollow impressions on the clay clumps (*bullae*) that sealed the big storage-jars originally stocked in the building.

## 2. ANALYTICAL TECHNIQUES

Morphological examinations (Scanning Electron Microscopy, SEM) and elemental composition (Energy Dispersive X-ray, EDX) analyses were carried out with a SEM-VP EVO50 (Carl Zeiss AG, Deutschland) microscope coupled with INCA x-sight model 7636 (Oxford Instruments, Concorde, MA, USA) microprobe at the following operating conditions: working distance = 8-12 mm, probe current = 200 pA, accelerating potential = 20 kV, counting time = 120 s.

Petrographic analyses were carried out by optical microscopy (OM) and integrated by SEM-EDX. 30 µm-thick sections were prepared and observed under polarized transmitted light with an Olympus BX-41 optical microscope, equipped with a digital Jenoptic camera. Images were acquired with a ProGres capture pro 2.6. Polished sections were examined by a Cambridge S360 Scanning Electron Microscope connected to an Oxford Instruments Inca Energy 200 EDS equipped with an Oxford SATW Pentafet Si(Li) detector. The analyses were conducted in the following conditions: working distance = 25 mm, probe current = 200 pA, accelerating potential = 15 kV, counting time =

60 s. Natural oxides and silicates (Astimex Scientific Limited; Ontario, Canada) were acquired as standards. A cobalt standard was used for instrumental calibration and the relative abundance of the elements was calculated by the instrument software, using the ZAF correction.

The morphological examination was carried out in the secondary electrons (SE) mode on fresh fracture samples. The polished sections for the chemical analyses were obtained by encompassing the appropriate amount of samples in an epoxidic resin. The obtained sections were subjected to an abrasive treatment on silicon carbide papers with a 500 and 1000 grit size and polished with a 1  $\mu\text{m}$  granulometry diamond paste on special clothes. The fresh fractures and the polished sections were then mounted on aluminium stubs using carbon tape and were covered with a coating of Au–Pd and graphite, respectively. The Au-Pd layer of approximately 20 nm thick was deposited using a SCD 050 Sputter Coater (Bal-Tec, Scotia, NY, USA) coating unit and the graphitization was performed by carbon rod evaporator under high vacuum ( $10^{-4}$  torr) conditions using a IMETEC K 950 coating unit equipped with a turbo-molecular pump (Balzer inc, Minnesota, USA). The thickness of the C layer was about 300 nm.

EDX semiquantitative analyses were carried out in the backscattered electrons (BS) mode on polished sections at 200X magnification, by scanning 5 rectangular areas of 1.72x1.16 mm, i.e. areas of 2.0  $\text{mm}^2$  and by raster or spot analyses on smaller aggregates.

X-Ray Powder Diffraction (XRPD) patterns were collected using an Analytical X'Pert Pro (PANalytical B.V., Almelo, The Netherlands) powder diffractometer equipped with an X'Celerator detector using Cu  $K\alpha$  radiation generated at 40 kV and 40 mA. The  $2\theta$  range was from 5 to 90°. For the measurement, the appropriate amount of sample ground in an agate mortar was placed in a quartz sample holder and compressed with a glass slide. The X'Pert HighScore software was used for the evaluation of the diffraction patterns and the identification of the mineralogical phases.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were simultaneously conducted by a SDTQ600 Thermal Analyzer (TA Instruments, New Castle, DE, USA) using a standard of aluminium oxide, following the procedure reported by Moropoulou et al. (1995).

Raman measurements were carried out with a Renishaw InVia Raman microscope with a 20X ULWD objective. Raman spectra were recorded with a 422 nm excitation wavelength and they corresponded to the sum of 20 acquisition, with acquisition time of 20 s. The laser power never exceeded 1 mW at the sample.

### 3. RESULTS AND DISCUSSION

#### 3.1 “Anhydrites”, plaster, mortar and mould



The SEM morphological evaluation carried out on polished sections evidenced that all the “anhydrite” samples consisted in large crystals (with dimensions up to several mm) embedded in a finer matrix (Figure 3, left). The specific morphology of the crystals is illustrated by the SEM image obtained on a fresh fracture of an “anhydrite” sample (Figure 3, right).

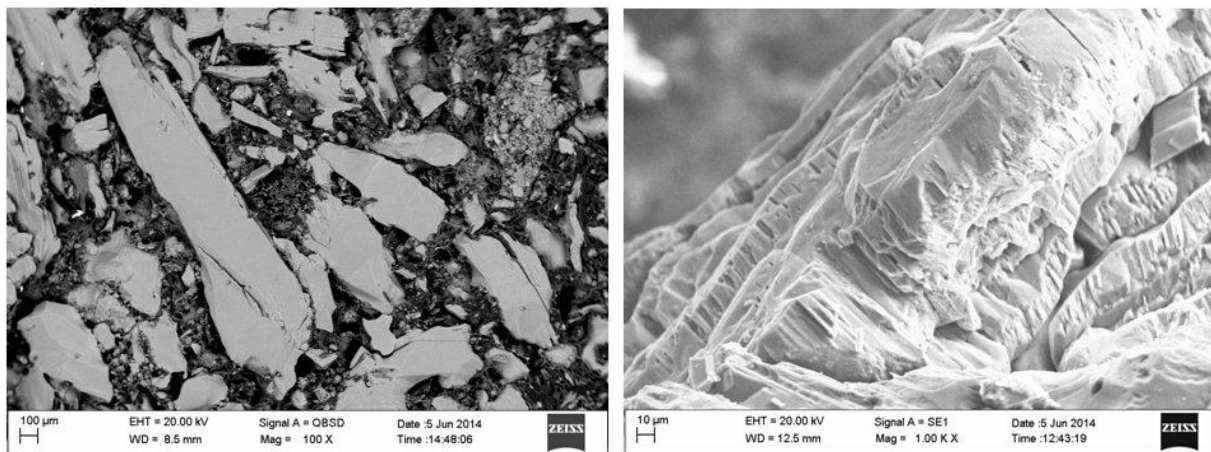


Figure 3: SEM images of an “anhydrite” sample (BS mode, 100X magnification, left) and of one of the crystals embedded in the “anhydrite” sample matrix (SE mode, 1000X magnification, right).

Notwithstanding the original archaeological attribution, the XRPD analysis underlined the total absence of the mineral anhydrite in the “anhydrite” samples, instead evidencing the prevalent presence of gypsum with much smaller amounts of calcite and quartz. The identification of gypsum over anhydrite was confirmed by the thermogravimetric results that showed a 20% weight loss between 35 and 200 °C related to an endothermic process revealing a two water molecules loss. These overall results evidenced that all the analysed “anhydrite” samples are actually composed by crystals of gypsum incorporated in a fine sediment of carbonates, quartz and traces of phyllosilicates.

Sulphur, calcium, silicon, aluminum, magnesium, sodium, chlorine, iron and potassium were detected by EDX; the relative elemental composition, expressed as weight % of the corresponding oxide (normalized to 100%), is reported in Table 1 for all the samples. Considering the relatively high standard deviation values, the composition of the artefacts is quite homogeneous, except for the higher  $\text{SO}_3$  weight % content of the mortar and its lower CaO amount. Besides, the relatively higher value of  $\text{Na}_2\text{O}$  for the plaster could probably be related to the evaporitic nature of the rocks used as raw material, even if halite ( $\text{NaCl}$ ) was not detected by XRPD (see below). On the other hand, comparing the composition of the “anhydrite” sample with the artefacts few remarks can be proposed.  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  values are systematically lower in the artefacts while the  $\text{SO}_3$  amount is comparable with the plaster and the mould but lower than the mortar and the CaO value

in the “anhydrite” is similar to the mortar and lower than the plaster and the mould. On the other hand, standard deviations are generally considerable for the “anhydrite”, accounting for the high heterogeneity of the material (Figure 3a) and making the above commented variations less remarkable.

	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SO <sub>3</sub>	Cl	K <sub>2</sub> O	CaO	Fe <sub>2</sub> O <sub>3</sub>
Mortar	1.2	1.7	1.7	5.6	64.0	0.1	0.1	25.6	0.1
dev std	0.5	0.2	0.3	0.8	0.8	0.1	0.1	0.7	<0.1
Plaster	2.3	1.7	1.5	6.4	53.8	1.4	0.3	32.2	0.4
dev std	0.9	0.4	0.2	1.5	1.5	0.6	0.1	0.4	<0.1
Mould	0.6	1.3	1.5	6.2	54.0	0.4	0.4	35.0	0.5
dev std	0.1	0.1	0.1	0.4	0.1	0.2	<0.1	0.9	0.1
Anhydrite	1.0	2.4	2.9	11.3	54.7	-	0.3	26.9	0.5
dev std	0.2	0.7	0.6	3.9	4.2	-	0.1	1.6	0.3

Table 1: Mean elemental composition (oxides wt%) and standard deviation as resulting by EDX analyses.

Ultimately, the comparison between the composition of the “anhydrite” sample and the artefacts strongly suggests that the “anhydrite” was used as raw material, without specific preprocessing, eventually except for a slight depletion in the fraction containing quartz and phyllosilicates.

XRPD examination confirms that the mineralogical composition of the artefacts mirrors the composition of the raw material (see Table 2), which is mainly constituted by gypsum as main mineral constituent with quite small amounts of calcite and quartz.

<b>Sample</b>	<b>Detected mineral phases</b>
Mortar	Gypsum (+++), Quartz (+), Calcite (+)
Plaster	Gypsum (+++), Quartz (+), Calcite (+)
Mould	Gypsum (+++), Quartz (+), Calcite (+)
Anhydrite	Gypsum (+++), Quartz (+), Calcite (+)
Black lumps in ES_red	Goethite (++++)
Matrix of ES_red	Quartz (+++), Muscovite (++)
ES_pink	Calcite (+++), Quartz (+), (Muscovite)
FF_yellow	Quartz (++) , Calcite (++) , Albite (+) Muscovite (+), (Goethite)
FF_red	Calcite (++) , Quartz (++) , Hematite (+), Kaolinite (+)
FF_pink	Calcite (++) , Quartz (++) , Gypsum (+), Muscovite (+), (Hematite)
Seal	Graphite (++++)

Table 2: XRPD semi-quantitative compositions. (++++: unique phase detected; +++: very abundant; ++: abundant; +:present; (weakly detected)).

These results, together with the EDX data (Table 1) suggest that the aggregates were, in fact, composed by the same raw material used to obtain the binder which was presumably previously prepared. EDX analyses carried out separately on the binder and on the aggregates (not shown) confirmed that also the binder is substantially composed by gypsum with the presence of very low amounts of calcite and silica (which, in this case, do not represent the aggregates, but are simply minor components of the original rock) together with some aluminosilicates, in the finer matrix.

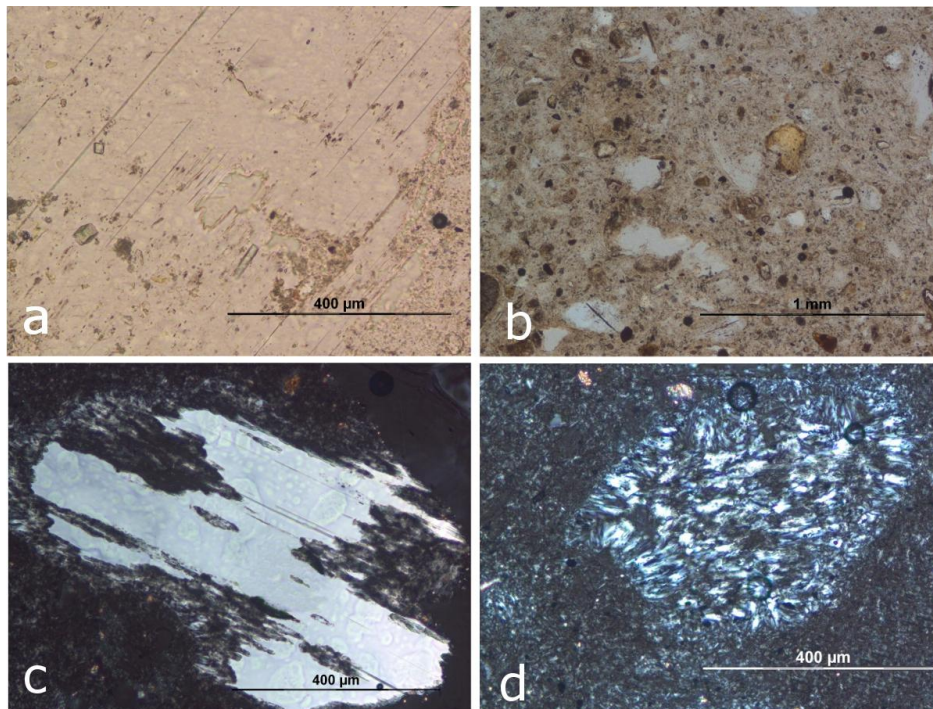


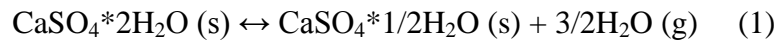
Figure 4: Optical microscope images of thin sections of the mortar sample (Figure 4a and 4b) and of the plaster sample (Figure 4c and 4d).

Petrographic analyses performed on the mortar sample highlighted a 40:60 aggregates:binder ratio. The aggregates are mostly constituted by gypsum and quartz clasts (together representing about 90% of the total (Figure 4a) with lower amounts of calcite and sporadic presence of biotite and *cocciopesto* (in such lower amounts not to modify the overall chemical composition, see Table 1). Classiation is very scarce (from 100 μm to more than 1 mm) but distribution is highly uniform. The binder does not show micro-fractures due to contraction and the overall porosity is lower than 10% (Figure 4b). On the other hand, the plaster sample exhibited a 40:40:20 aggregates:binder:pores relative %. The aggregates, of the same nature than those of the mortar, are instead well classated and rounded, but the gypsum clasts constituting the real aggregates (those added after the binder roasting and preprocessing) are probably a very low fraction while most of the gypsum clasts showed a partially (Figure 4c) or totally (Figure 4d) developed fibrous aspect due to the partial or total decomposition of the original mineral during the firing step and its

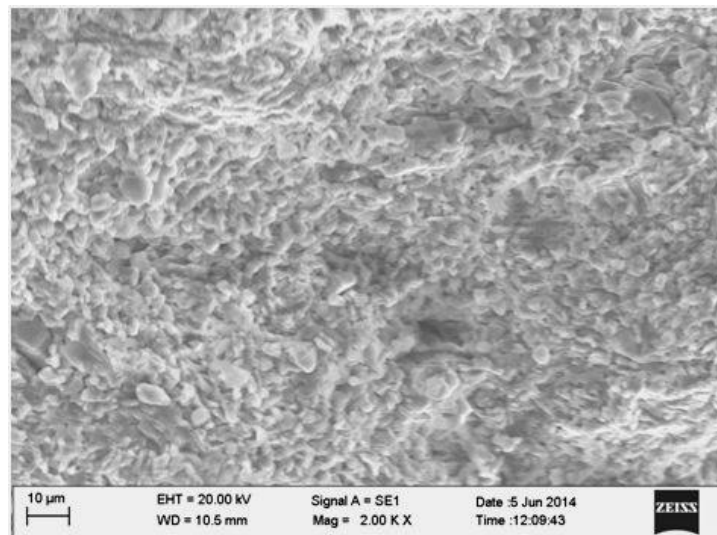
recrystallization during setting.

The observed differences either could be imputable to a scarce standardization of the production process or could be specifically searched for in order to modulate materials properties.

Gypsum-based mortars and plasters can be obtained by heating pure gypsum (calcium sulphate dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) at a temperature as low as 110-160° C. In these conditions gypsum forms the hemihydrate,  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ , bassanite or plaster of Paris, following the equilibrium:



Between 170° and 300° C, the dehydration is complete and anhydrous gypsum or soluble anhydrite ( $\text{CaSO}_4$ ) appears. Both processes are reversible and the obtained compounds can be easily rehydrated. At over 300° C the transformation of anhydrite into the insoluble form occurs, producing a stable and little hydratable material. At 500°C the reaction is completed. When mixed with water the hemihydrate reforms the dihydrate, by the reverse of the equilibrium (1) (Coppola et al., 2013). Gypsum rock and gypsum mortars and plasters have exactly the same chemical composition but show a different morphology. After heating and rehydration of the hemihydrate and of the soluble anhydrite, the reformed gypsum quite immediately composes a forest of microscopic interlocking needle-like crystals that cause the material cohesion. On the other hand, the anhydrous irreversible form takes a much longer time to set and harden and the microstructure of a rehydrated gypsum heated to a higher temperature shows larger and less needle-like crystals (Gourdin and Kingery, 1975; Kingery et al., 1988). It is documented in the literature that ancient Egyptian workers were aware of the correspondence between the production procedure and the quality of the raw material with the characteristics of the final product and they took into account these factors to obtain the most appropriate artefacts according to their function (Coppola et al., 2013).



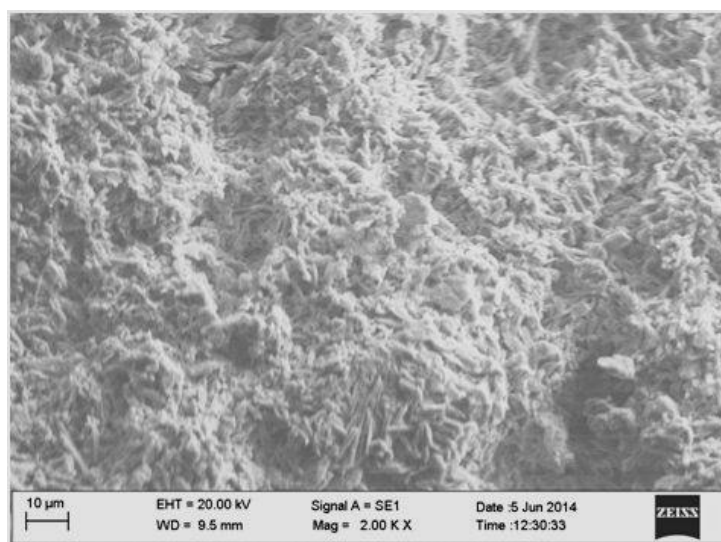


Figure 5: SEM images of the plaster (2000X magnification, top) and of the mortar (2000X magnification, bottom).

Assuming that both examined plaster and mortar are made from the same raw material (the examined ‘anhydrite’), as already discussed, the difference in morphology between the examined plaster (rounded particles, Figure 5, top) and the mortar (squared and elongated crystals, Figure 5, bottom) is clearly ascribable to differences in the production process. Due to the relatively low temperature involved in the firing process and to the very narrow temperature interval necessary to obtain only the hemihydrate form, multiphase plasters were definitely the resulting products and it is possible that the observed difference is accidental. But another possibility must be taken into account. As already mentioned, ancient artisans and workers widely knew the influence of the kind of raw material, of the time and temperature of the calcination and of the characteristics of the kilns on the features of the final products and they were able to modulate them in order to obtain specific properties. In the present case, notwithstanding the slight differences in the morphology of the samples, the technology of production of gypsum based materials seemed to be known also by Nisa artisans. Moreover, multiphase gypsum materials usually have a very quick initial setting time and a long final setting time, but it is well known (Wirsching, 2005) that the addition of the large gypsum crystals used as aggregates would have had an accelerating effect of the hardening reaction. For this reason, a relatively high calcination temperature (between 300°C and 500°C, since no anhydrite was detected by XRPD, see above) was allegedly used in order to obtain a material with a reasonable setting time. This could have led to the lacking formation of the needle-like crystals and to the development of different microstructures, such as the network of rounded particles in the plaster or the faceted gypsum grains observed in the mortar (Philokyrou, 2012a). The examination of a more conspicuous number of samples is undoubtedly needed to find a more definite solution on this topic.

### 3.2 Pigments

Analyses conducted by Appolonia (2008) on pigments applied on various architectural elements, clay sculptures and plasters from the *Round Hall*, evidenced a wide use of yellow and red ochres. Other hues as orange and pink were also occasionally observed and related to the presence of red ochre (Appolonia et al., 2008, pp. 203-206). In the present work two specimens of polygenic conglomerates found by the Italian expedition were characterized and the results were evaluated in order to check their compatibility with Appolonia determinations. The colours of the two samples are red and pink and they were archaeologically identified as possible raw materials or products of a pigment manufacture early stages (henceforth they will be referred as ES\_red and ES\_pink, respectively). Moreover, clasts of fairly finished red, yellow-ochre and pink pigments (FF\_red, FF\_yellow and FF\_pink) were examined. Besides, pink powder traces on a bowl used as palette and consequently at the definitive stage of production (Def\_pink) were analysed.

#### 3.2.1 Raw materials or products of the early stages of the manufacture

The ES\_red sample contains several globular inclusions, of a black colour at a macroscopic observation (Figure 6, left) and bright at the SEM image in BS mode (Figure 6, right), ranging from tenth of micron to about one mm. EDX analyses on the black inclusions show their Fe-rich composition (83.2 wt% of  $\text{Fe}_2\text{O}_3$ ) with moderate amounts of  $\text{Al}_2\text{O}_3$  (5.8 wt%) and  $\text{SiO}_2$  (7.7 wt%) (see Table 3). When grinded in a mortar, black inclusions give a yellow-brown powder according to the XRD identification of goethite as unique detectable mineralogical phase (Table 2).

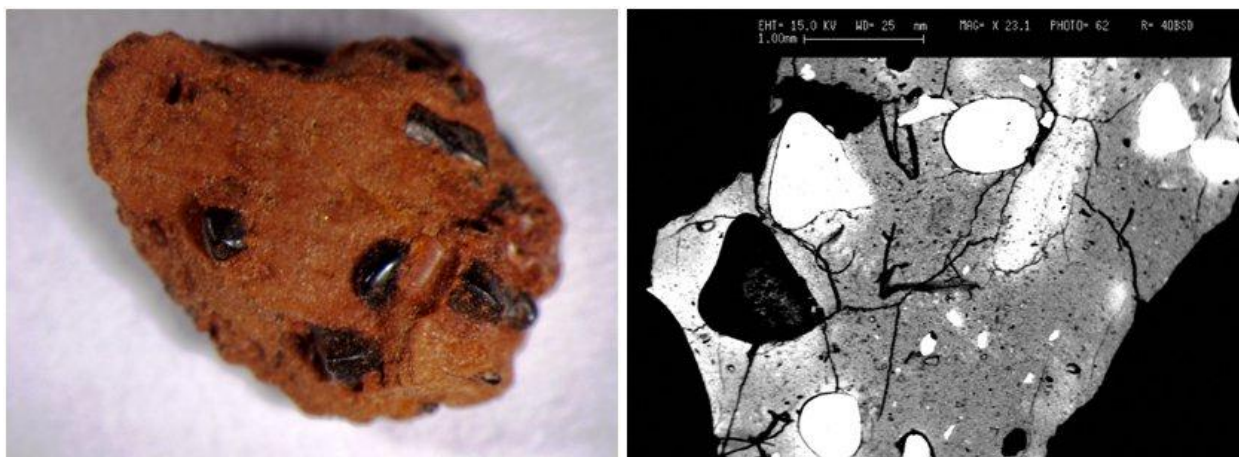


Figure 6: Left: ES\_red sample, supposed to be a raw material in the manufacturing process of pigments. Right: BS-SEM images (23 X) of the polished section of the sample. The white areas are the Fe-rich black inclusions embedded in the matrix (grey area).

Petrographic analysis performed on the matrix revealed an aggregate of grains with lamellar-

tended morphology, maximum size <10 microns and slightly preferred orientation. Fairly mixed minerals were identified: biotite, muscovite, fengite, rutile, albite, quartz, chlorite, ilmenite, zircon, xenotime, monazite and iron oxides, leading to the identification of the red sample as an immature sediment of restite fraction arising from the dismantling of continental crust units with both metamorphic and granitic source rocks (Boggs, 2009). Moreover, some metallic Pb lumps (10-20 micron length) were identified. In Old Nisa few metal artefacts were found, and the only items made of lead are wires used (together with wood and bone) inside the clay statues in order to strenghten the sculptures structure, often made by assembling various parts. This Pb finding matches with a previous discovery of red colour traces on these wires (Lippolis, 2010; Menegazzi, 2008, p. 320), connecting the ES\_red sample to the production of architectural ornaments. EDX analyses on the ES\_red matrix confirmed (Table 3) an aluminium-silicate rich composition, with 55.7 wt% of SiO<sub>2</sub>, 22.4 wt% of Al<sub>2</sub>O<sub>3</sub>, 10.5 wt% of Fe<sub>2</sub>O<sub>3</sub>, 4.3 wt% of MgO, 5.1 of K<sub>2</sub>O, 1.2% di Na<sub>2</sub>O and traces of CaO. Conversely, the matrix of the pink sample appears very rich in CaO (65.0 wt%), with minor amount of all other oxides. It may be noted that leaving out CaO and normalizing the values of the other 7 oxides, a very good agreement with the composition of the matrix of the red sample is obtained (see Table 3). Consequently, it can be inferred that ES\_pink were attained diluting the ES\_red with CaCO<sub>3</sub>. XRD determination agrees with this assumption, identifying various clay minerals and quartz as principal components of the matrix of the ES\_red specimen, while ES\_pink is principally constituted by calcium carbonate and quartz, with minor amounts of various aluminosilicates. Dilution was indubitably artificial and not natural. This is attested by the petrographic examination of the pink matrix, showing carbonates with inclusions of quartz, muscovite, apatite, iron oxides and zircon (this last mineral does not naturally occur in carbonate materials).

	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SO <sub>3</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>
Black lumps in ES_red	0.6	1.5	5.8	7.7	n.d.	0.9	0.3	n.d.	83.2
Matrix of ES_red	1.2	4.3	22.4	55.7	n.d.	5.1	0.4	0.5	10.5
ES_pink	0.4	1.5	6.5	20.3	0.6	2.1	65.0	0.2	3.4
ES_pink excluding CaO*	1.1	4.3	18.5	58.0	1.7	6.0		0.6	9.8
FF_yellow	1.7	3.9	14.8	57.5	2.0	2.8	7.9	0.6	8.8
FF_red	1.2	1.4	17.0	36.3	0.6	1.4	8.4	0.5	33.3
FF_pink	0.4	1.4	5.9	22.1	10.2	1.5	56.6	0.2	1.8

Table 3: Elemental composition, expressed as weight % of corresponding oxide, normalized to 100%, as resulting by EDX analyses. \*Composition calculated leaving out CaO and normalizing the values of the other 7 detected oxides to 100%.

These observations showed that the pink mixture was obtained by grinding together limestone and the red sediment. In order to grind it effortlessly, limestone was previously roasted as attested by TGA performed on the sample, that shows the decarbonation peak at a temperature lower than 800°C (Figure 7) This value, according to Fabbri (2014), indicates the secondary origin of calcite, resulting from the re-carbonation of previously fired materials. These overall observations well fit with Appolonia results and show indubitable evidence of artificial processing, confirming the archaeological interpretation ascribing the two samples to a pigments productive process.

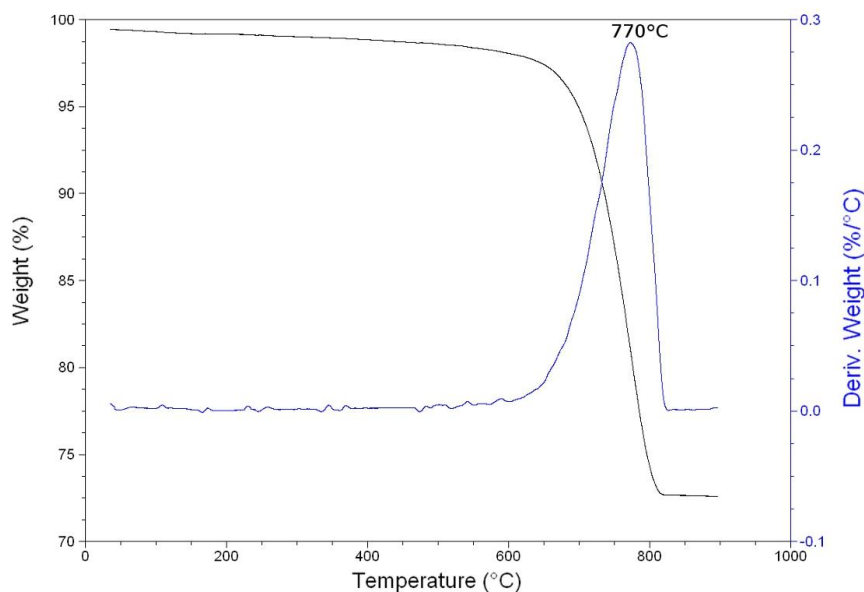


Figure 7: TGA of ES\_pink sample.

Calcination of yellow ochre containing goethite in order to produce the red pigment hematite is demonstrated since Palaeolithic (Gialanella et al., 2011; Pomiès & Menu, 1999; Salomon et al., 2015). Mixing red ochre with white gypsum or carbonate in order to obtain pink pigment was also a frequently observed procedure, widespread in time and space. For instance, in Egypt of Old and New Kingdoms pink pigments were obtained with ochre and gypsum mixtures (Scott et al., 2009) and Pallecchi (2009) reports the use of red ochre mixed with calcium carbonate in an Etruscan sepulchre (Italy, 4<sup>th</sup> century BC). Since extensive use of gypsum was made at Nisa, as showed above, the use of calcite is particularly curious, all the more since it requires much higher roasting temperatures (800-900 °C vs. 150-400 °C; see for instance Weiner, 2010, pp. 186–188) for its preparation. The use of this technology by artisans who perfectly mastered an effective alternative suggests the compliance to an imported recipe. At this purpose it might be interesting to observe that a pink pigment made up of red ochre and calcite was used in Bronze Age Thebes (Brysbaert, 2008).



### 3.2.2 Half-finished and finished pigments

While samples ES\_red and ES\_pink had to be carefully understood, there seemed to be little doubts about the interpretation of the FF samples as pigments. The samples are clearly anthropogenic for the intensity and homogeneity of the colour, moreover FF\_yellow and FF\_red are powdery (finger pressure is enough to pulverize them). XRPD analyses performed on the three samples indicated quartz, calcium carbonate and hematite as principal phases in FF\_red; quartz, calcium carbonate, aluminosilicates and goethite in FF\_yellow and calcium carbonate, quartz, gypsum, muscovite and hematite in FF\_pink (see Table 2). Therefore, also these samples correspond with the results of Appolonia (2008) on the coloured architectural elements, in relation to the colouring agents.

However, observing the elemental composition (Table 3) it is not possible to clearly identify a direct correspondence between the ES and the FF samples. Except for K<sub>2</sub>O, FF\_yellow quite well matches with ES\_red, but supposing the addition of both gypsum and carbonate. As for ES\_red, by calculating the composition that would be obtained by mixing the blacks lumps and the red matrix in a 30:70 ratio, a composition well fitting with the FF\_red sample would be achieved as for the most abundant elements (32.3 wt%, 17.4 wt% and 41.3 wt% would occur respectively for Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>) but there would not be correspondence for K<sub>2</sub>O (3.8 wt%) and MgO (3.5 wt%). The different contents of K<sub>2</sub>O could refer to a different mineral assemblage in the fine grained matrix. In particular, in the ES samples white mica and other phyllosilicates were detected in noticeable amount, while in the FF samples they occur in small quantities, a possible clue of different provenance of the raw materials. Another hypothesis for the lack of concurrence of the potassium content could be that a diagenetic process occurred presumably due to microclimatic conditions. This phenomenon could also account for the high friability of the FF\_red sample. The picture regarding the pinks is even more confusing. Some correspondence exists between ES\_pink and FF\_pink (also in this case, assuming addiction of gypsum), but Def\_pink composition is definitively different.

	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl	K <sub>2</sub> O	CaO	Fe <sub>2</sub> O <sub>3</sub>	CuO
spot 1	1.4	2.1	39.6	31.4	4.8	3.1	2.6	4.7	6.2	3.6	0.5
spot 2	1.9	1.4	48.9	28.3	5.5	3.2	2.7	2.3	3.9	1.4	0.5
spot 3	0.6	0.8	13.7	10.2	1.7	41.1	0.7	0.9	29.4	0.5	0.4
spot 4	1.8	1.5	39.5	35.6	5.1	4.6	2.4	2.5	5.7	0.9	0.4
spot 5	1.6	2	26.9	24.8	3.3	21.4	1.2	1.8	14.2	2.5	0.3
spot 6	1.1	1.4	26.1	22.7	3.1	17	1.8	3.6	20.3	2.4	0.5

Table 4: Elemental composition, expressed as weight % of the corresponding oxide, normalized to 100%, as resulting by EDX analyses on six different spots on the Def\_pink sample.

Def\_pink sample was far too little in order to perform quantitative measures on representative areas, six spot measures were then conducted with the aim of obtaining semiquantitative information. These analyses (Table 4) reveal a total lack of homogeneity, with some spots containing about 70 wt% of gypsum and others about 40 wt% of Al<sub>2</sub>O<sub>3</sub> making plausible the presence of kaolin, also identified by Appolonia (2008), in particular on clay statues. Also in this case the colouring agent is iron oxide, but a little amount of copper was also detected. The presence of copper could originate by traces of a previous use of the bowl as a palette for the application of a light blue pigment or could be an intentional addition in order to obtain a different hue by mixing up red and blue. In this regard it is noteworthy the detection of both Fe and Cu in a violet pigment by Appolonia (2008, p. 207, TV05 sample). Def\_pink is not violet, but rather deep pink/purple; anyway its hue is definitely different from all the other pink samples. Indeed, also observing the general composition of Def\_pink gypsum poor spots (spots 1, 2 and 4), it appears clearly different from ES\_pink and FF\_pink.

These overall compositional differences could presumably be ascribed to the different stages of the production (semi-processed, processed and finished products), but it looks like dilutions and enrichments necessary to account for all the differences would be too many. Therefore, it is much more likely to assume a low level of standardization in the productive process. This, in turn, could suggest the presence of several workshops (each with its own 'recipe'), as already proposed (Pappalardo, 2010) for the production of ivories that revealed a multitude of execution techniques. Another hypothesis could be the poor control of the details of the productive process or even different procedures for different artistic productions.

As for the comparison with other sites, very few literature exists about historically congruent sites. Evaluating our results with respect to observations reported by Kidd et al. (2004), a substantial compatibility with the palette in use in Chorasmia was observed.

In any case, the aim of the present work is to give a preliminary overview and the authors are perfectly aware that more samples would be required to draw definitive conclusions on the pigments technology of production in Old Nisa and on the eventual presence or absence of multiple workshops at the site.

### *3.3 The black seal*

The seal is a cylindrical black object that measures about 3 cm in length and 1 cm in diameter (Figure 8). One of its extremities shows a slight truncated cone narrowing and a small circular hole about 1-2 mm in diameter is present in the centre of the section. The external wall does not show

any figural engraving or decoration, except for four series of incised small points along the length.



Figure 8: Pictures of side and front of the cut seal (left) and of the seal signs on a clay block (right).

The SEM image at low magnification (Figure 9) revealed that the central hole (filled with a powdered material) is perfectly circular indicating that the seal was presumably obtained by turning.

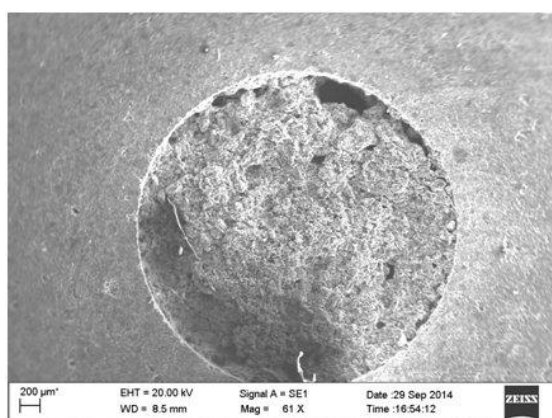


Figure 9: SEM microphotograph (60X) of the central hole of the seal.

XRPD results showed that the object is exclusively composed by a quite crystalline carbon phase that is confirmed by Raman spectroscopy (Figure 10) showing a relatively sharp signal (G band) around  $1600\text{ cm}^{-1}$  and a less intense peak with a maximum at  $1380\text{ cm}^{-1}$  (D band) (Goodall et al., 2009; Smith et al., 1999; van der Weerd et al., 2004). This finding is quite peculiar since there are no previous evidences of graphite seals in the Middle East area in the studied period in the scientific literature and it suggested the hypothesis, also supported by the lack of decoration on the seal external wall, that this object could have also had another function. In particular, the authors hypothesized that this graphite seal could have been used as a kind of charcoal pencil, especially to write the inscriptions on the *ostraka* (Morano, 2008). To test this hypothesis the inscription on a *ostrakon* found during the excavations was examined by Raman spectroscopy. The spectrum

obtained on the *ostrakon* inscription showed the shift of the G band towards higher wavenumbers and the broadening of the D band revealing the presence of a more amorphous carbon compound (Goodall et al., 2009; Smith et al., 1999; van der Weerd et al., 2004) and suggesting that the material used to write on the *ostrakon* was presumably an ink obtained by mixing carbon black with a binder.

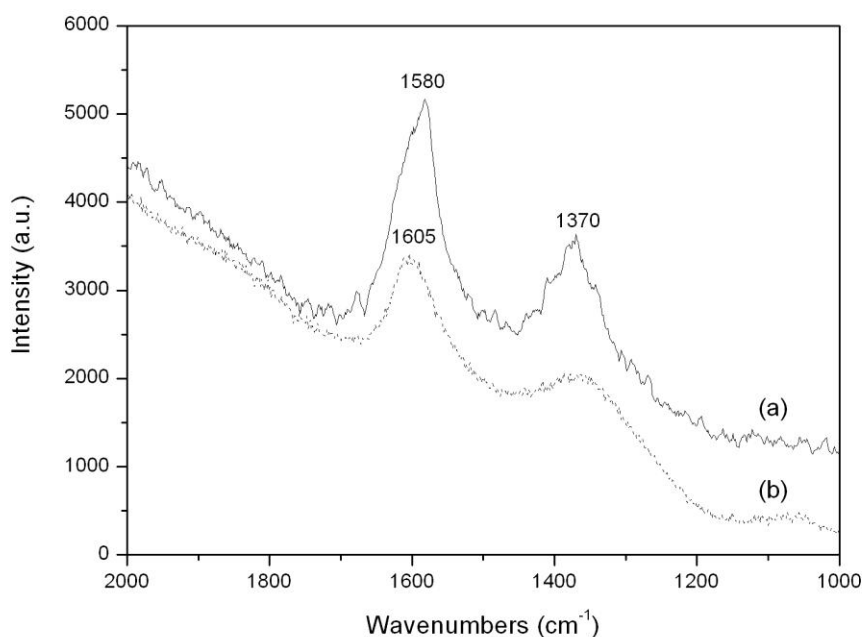


Figure 10: Raman spectra of the seal (a) and of the ostrakon inscription (b). For a better comparison the intensity of the seal spectrum was multiplied by 9.

#### 4. CONCLUSIONS

Notwithstanding widely archaeologically explored for its great relevance, the archaeometric literature about Old Nisa is virtually inexistent. The samples examined in the present work come from recent and abundant findings and this allowed to make sampling and to apply several invasive techniques with the aim to make some hypotheses on the productive processes in Old Nisa. Nevertheless, the authors are perfectly aware of the exploratory purpose of the present paper and of the necessity of increasing the number of samples in order to obtain more information about the technology of production of the various artefacts and to draw more definitive conclusions.

The multitechnique examination of a plaster, a mortar and a mould proved that they are essentially comparable both from a chemical and a mineralogical point of view with the samples classified as “anhydrites” by the first Soviet and Russian excavations (and revealed to be composed by gypsum with small amounts of calcite and quartz), allowing to conclude that these polygenic

conglomerates represent the raw material used for the production of the examined artefacts. From a technological point of view this simplicity is plausible due to the fact that the “anhydrites” are completely suitable for the production of mortar/plaster-like materials, without particular treatments or pre-processing. It can be observed that the pyrotechnological process of production of gypsum-based material is perfectly compatible with structures revealed in the excavation at Old Nisa. Inside the South-Western Building plastered basins were directly laying on the floor. In the corner of two of these basins, two heaps of powdered "anhydrite" were found. Immediately beside the basin, some raw blocks and minced stones of this same material were lying on the floor of the room, clearly in the two previous – intermediate - processing stages. All these findings are compatible with the gypsum-based materials manufacturing process and there are few doubts that we are facing installations meant to process and produce these artefacts.

Coloured lumps supposed to be raw materials or pigments at different stages of the productive process, were examined. All the analysed samples appear to be related to the pigment manufacture, as showed by the fact that the colouring agents are compatible with the painted architectural elements. However, the chemical composition showed remarkable difference between samples of the same colour, and this could be explained in several ways. A quite plausible explanation for a royal artistic centre is the presence of several workshops as already proposed for the production of ivories even if so far it was not possible to identify the single workshops or to prove the existence of different manufactures operating at the same time. It also must be taken into account that the period we are considering is culturally the same (Parthian), but spread over three centuries, therefore it is possible that some of the manufacturing processes evolved over time. Another hypothesis could be the simultaneous existence of different processes aimed at different artistic productions. Finally, it is also possible that these practises were merely poor standardized, even if the art of Old Nisa was of high aesthetic level. With regard to the comparison with other sites historically congruent, substantial compatibility with the palette in use in Chorasmia was ascertained.

At last, a very particular result was obtained from the examination of the black seal, that revealed to be obtained by turning a graphite block, a materials never observed before for these kind of objects, to our knowledge. An explanation of the use of this peculiar seal is still open since the hypothesis of its use as charcoal pencil to draw on *ostraka* was not confirmed by our results.

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