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# Multi-technique characterization of various artefacts and raw materials from Old Nisa (Turkmenistan): A preliminary study

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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.



## 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 (Fig. 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.

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 and 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 analysed materials were excavated during the recent Italian–Turkmen archaeological expedition (Centro Scavi di Torino and Ministry

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**Fig. 1.** Map of the Old Nisa archaeological site.

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 and 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 (Fig. 2, left) and on wall plasters.

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-α 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 (Fig. 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 ($CaSO_4$) that easily alters to the much more common hydrated form, gypsum ($CaSO_4 \cdot 2H_2O$). 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 antrophic 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