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A multi-analytical approach to gold in Ancient Egypt: Studies on provenance and corrosion

I. Tissot [a,b,*], L.G. Troalen [c], M. Manso [a,d], M. Ponting [e], M. Radtke [f], U. Reinholz [f], M.A. Barreiros [g], I. Shaw [e], M.L. Carvalho [a], M.F. Guerra [h]

[a] LIBPhys – UNL, Faculty of Science and Technology, 2829-516 Caparica, Portugal
[b] Department of Physics, Faculty of Sciences, University of Lisbon, Campo Grande, 1649-004 Lisbon, Portugal
[c] National Museums Scotland, Collections Services Department, 242 West Granton Road, Edinburgh EH5 1JA, UK
[d] Faculdade de Belas-Artes da Universidade de Lisboa, Largo da Academia Nacional de Belas-Artes, 1249-058 Lisbon, Portugal
[e] Archaeology, Classics and Egyptology, University of Liverpool, 12-14 Abercromby Square, Liverpool L69 7WZ, UK
[f] BAM Federal Institute for Materials Research and Testing, Richard-Willstaetter-Strasse 11, 12489 Berlin, Germany
[g] LNEG, I.P., Estrada do Paço do Lumiar, 22, 1649-038 Lisbon, Portugal
[h] ArchAm, UMR 8096 CNRS - Université Paris Sorbonne, MAE, 21 allée de l'Université, 92023 Nanterre, France

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ABSTRACT

Recent results from a three-year multi-disciplinary project on Ancient Egyptian gold jewellery revealed that items of jewellery from the Middle Kingdom to the New Kingdom were manufactured using a variety of alluvial gold alloys. These alloys cover a wide range of colours and the majority contain Platinum Group Elements inclusions. However, in all the gold foils analysed, these inclusions were found to be absent. In this work a selection of gilded wood and leather items and gold foil fragments, all from the excavations by John Garstang at Abydos (primarily from Middle Kingdom graves), were examined using Scanning Electron Microscopy-Energy Disperse Spectroscopy (SEM-EDS), X-Ray Fluorescence (μXRF), Particle Induced X-Ray Emission (μPIXE) and Double Dispersive X-Ray Fluorescence (D^2XRF). The work allowed us to characterise the composition of the base-alloys and also to reveal the presence of Pt at trace levels, confirming the use of alluvial gold deposits. Corrosion products were also investigated in the foils where surface tarnish was visually observed. Results showed that the differences in the colour of corrosion observed for the foils are related not only to the thickness of the corrosion layer but also to a multi-layer structure containing the various corrosion products.

1. Introduction

Goldwork from Ancient Egypt was made in a wide variety of colours. The few publications on the analytical study of gold and silver items show the use of a large range of gold base-alloys [1–7] and also the exploitation of gold and aurian silver sources [8,9]. One recent publication showed, however, that during the 2nd Intermediate Period (ca. 1650–1550 BC) a variety of gold colours may be observed within a single tomb and among items belonging to a single individual [5], as is also found in the New Kingdom (ca. 1550–1070 BC) [2]. This reflects the use of different alloying practices or the exploitation of gold from different origins [8].

A primary question is that of the origin of the gold. How could the Egyptian goldsmith achieve such a rich palette of gold shades? Before the introduction of parting in the metallurgical process of gold during the first millennium BC [1], diverse colours could only be achieved by the exploitation of different sources of gold.

In their publication on the excavations of Naqada and Ballas in 1896, Petrie and Quibell [10] were the first to report the presence of osmiridium inclusions in the 12th Dynasty scarab of Mu-en-ab. The presence of Platinum Group Elements (PGE) inclusions in gold is always related to the use of alluvial sources [11] and the characteristics of the PGE composition have been suggested as a possible indicator for a change of source [12].

Since the publication by Petrie and Quibell in 1896 [10], other authors have referred to the presence of PGE inclusions on the surface of Egyptian goldwork, mentioning their quite heterogeneous compositions [5,12,13]. In spite of the discovery of Os-rich and Os–Ir alloy minerals in the Eastern Desert [14], the PGE mineralogy of Egypt remains very poorly documented. Recent publications have remarked on the consistent presence of PGE inclusions on the surface of Egyptian gold jewellery [4,5,15]. With the exception of the recent analysis of gilded wood samples from the tomb of Tutankhamun, which characterised the Pt element in two regions of analysis [16], the presence of PGE inclusions in gold foils from Ancient Egypt has hitherto never been characterised.

Before the presence of PGE elements can be used to demonstrate that the foils were produced using gold from different sources (which may not be alluvial but mined), the experimental difficulties in the

* Corresponding author at: Department of Physics, Faculty of Sciences, University of Lisbon, Campo Grande, 1649-004 Lisbon, Portugal. Tel.: +351 939212005.
E-mail address: isabeltissot@gmail.com (I. Tissot).

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identification of PGE inclusions in gold must be considered. Firstly, depending on their size, these inclusions cannot always be recognised using a stereo microscope and raking light; smaller inclusions may only be detected by increasing the magnification using Scanning Electron Microscopy (SEM). Additionally, elemental scanning using Energy Dispersive Spectroscopy (EDS) on the region of interest may be necessary.

Harris and Cabri [17] separated the PGEs into two groups: the first, less soluble in gold and usually associated with chromites, contains Ir, Os, and Ru; and the second, more soluble in gold and usually associated with sulphides, contains Rh, Pd, and Pt. For this reason, the identification of PGEs in a gold alloy is usually identified by determining the trace elements of the gold alloys (for example [18–21]). Elemental analysis of the more soluble PGEs in gold alloys is difficult to carry out because of their atomic number, as Pt and Pd are very close to the major elements of the gold alloys, respectively Au and Ag. Attempts were made to solve this problem for X-ray Fluorescence (XRF) by various approaches, using different excitation energies and data processing strategies [18,19,21].

Other question is related to the corrosion of Egyptian gold objects, which is characterised by a rose to dark purple colouration of the surface. The very thin and iridescent tarnish layer, which may in certain cases attain for gold alloys a thickness as low as 100 nm [22], has an influence on the surface appearance, and it can be misread as an intentional surface colouration. The gold tarnish phenomenon, already reported in 1926 by Lucas [23], is always attributed to the formation of silver–gold sulphides [24]. However, the influence of the gold alloy composition on the corrosion mechanism, and the identification of different corrosion products, are still not clearly understood or fully described.

In this work, as part of the multi-disciplinary CNRS funded project PICS 5995 (French National Centre for Scientific Research International Programs for scientific cooperation), and by using several analytical techniques, a selection of gilded wood and leather items and gold foil fragments, all from the excavations by John Garstang at Abydos, were investigated. These gold foils were analysed to shed more light on the composition of the gold alloys and to determine the possible presence of PGE elements. Finally, a microscopic study combined with elemental mapping was undertaken in order to identify fully the corrosion products present in the areas of the foils that were visually tarnished.

2. Archaeological context of the gold foils

Between 1906 and 1909, John Garstang, Professor of Archaeology at the University of Liverpool, undertook extensive excavations in the cemeteries at Abydos, in Upper Egypt. A detailed corpus, based on Garstang's field notes and archival data, was created by Dr Steven Snape (1987) [25]. Many of the objects from Garstang's Abydos excavations are now in the Garstang Museum of Archaeology at the University of Liverpool.

During the 1907 and 1908 seasons respectively, Garstang excavated tombs 381 and 533 at the southern edge of the so-called 'North Cemetery' at Abydos that contained gilded objects (Fig. 1a). On the basis of the other contents of these two tombs, including such diagnostic items as a decorated wooden coffin fragment in tomb 381, and an anhydrite vessel in tomb 533, both are thought to have contained the burials of Middle Kingdom individuals (ca. 2055–1650 BC).

In addition to these gilded objects, we also analysed a quantity of gold foils in the Garstang Museum that had probably originally been attached to a wooden artefact destroyed by burning (Table 1). These foils almost certainly derive from Garstang's Abydos excavations in 1908, since they are stored in the museum alongside objects clearly labelled as deriving from that season at Abydos. There is, however, no longer any indication of the date or location of the specific grave in which the foils were found (Fig. 1b).

3. Methods and instrumentation

The gold foils were analysed by complementary techniques in order to obtain information on the composition of the base-alloy, on the presence of trace elements related to PGE inclusions, and on the composition and morphology of the corrosion products present on the surface of the majority of the foils.

The elemental composition of the gold alloys was determined by using X-ray based techniques with different detection limits and spatial resolution. The base-alloys were determined by conventional SEM–EDS, XRF and Particle Induced X-ray Emission (PIXE). In addition to these, Double Dispersive X-Ray Fluorescence (D^2XRF) at the BAMline [30] at synchrotronBerliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (BESSY) II was used for the determination of very low concentrations of Pt in the gold alloy. Finally, the morphology of the corrosion products was observed in a Field Emission Gun - Scanning Electron Microscopy (FEG-SEM), and comparison of the compositions between corroded surfaces and un-corroded surfaces was obtained by using XRF and the EDS set-up of the FEG-SEM.

3.1. XRF

μ-XRF was carried out at LIBPhys at the New University of Lisbon with a M4 Tornado, from Bruker, (50 kV, 300 μA) comprising a Rh X-ray source with a poly-capillary lens offering a spot size down to 25 μm, coupled to a SDD detector. Spectra deconvolution was made using Bruker M-Quant software with the provided detector response function. This response function contains contributions of shelf and tail and also the enhancement of peak FWHM due to detector and electronic noise. After deconvolution the peak intensities are directly available. The accuracy of quantitative results was validated by the analysis of a set of home-made gold standards certified by other techniques [26].

3.2. PIXE

μ-PIXE was carried out at the Accélérateur Grand Louvre d'analyse élémentaire (AGLAE) accelerator of the Centre for Research and Restoration of the Museums of France (C2RMF) with a proton beam of 3 MeV, analytical spot of 50 μm diameter and SDD detectors, one covered with a Cu filter of 75 μm, at the experimental conditions specified for gold alloys [18,27]. Quantitative processing of the spectra was

Fig. 1. a) Examples of some objects from tomb 381. On the left fragments of wood with gold leaf (Liv. E. 5727) and on the right wooden object with gold leaf and black painted figures (Liv. E. 5728); b) Fragments of gold foil from Garstang's Abydos excavations in 1908 (date and tomb unknown).