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ANALYTICAL INVESTIGATION OF PIGMENTS, GROUND LAYER AND MEDIA OF CARTONNAGE FRAGMENTS FROM GREEK ROMAN PERIOD

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ABSTRACT

Some cartonnage fragments from Hawara, Fayoum Excavation were examined to identify pigments, media and grounds. It belonged to the Greek-Roman period. They were studied by X-ray diffraction (XRD), Energy dispersive X ray analysis (EDS) equipped with Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). These techniques were used to identify the composition and morphology of grounds, nature of pigments and media used in cartonnage fragments. The coarse ground layer was composed of calcite and traces of quartz. The fine ground layer used under the pigments directly was composed of calcite only. Carbon black was used as black pigment while lead oxide as red pigment, showing the influence of Roman and Greek pigments on Egyptian art in these later periods. Blue colorant was identified as cuprorivaite and yellow pigment was goethite. Animal glue was used in the four pigments as medium colored.

KEYWORDS: Fayoum , Hawara, Cartonnage, Pigments, FTIR

1. INTRODUCTION

Analytical investigations of archaeological objects bring us much information on the development and propagation of technologies on cultures. To conserve and restore these valuable and scarce objects, it is indispensable to understand their chemical constituents and crystal structures.

The Egyptian-Polish archaeological Excavation to Hawarra pyramid area, Fayoum (Fig.1A) covered many archaeological materials such as, many pieces of human bones, various skulls, two skeletons of sacred crocodiles, terracotta, and one gilded mask with many fragments of colored cartonnage. These fragments decorated with religious gods. Hawarra Labyrinth site is a unique combination of buildings and artefacts from two different eras and cultures: an Egyptian pyramid complex, and Roman period cemeteries (Shaw, 2000; Verner, 2001; Vila, 1976).

During late Pharonic times, cartonnage was used to make the inner coffins for mummies. It was molded to the shape of the body, forming a one- piece shell. It was often highly decorated with various geometric designs, an assortment of deities and inscriptions, which included verses from the Book of the Dead (Picton, *et al.*, 2007) colored with different pigments. Ancient Egyptian pigments have been analyzed extensively in laboratory studies (Barbieri *et al*. 1974; Riederer 1974; Jaksch *et al*. 1983; Goresy *et al*. 1986; Saleh 1987; Riederer 1988; Lucas and Harris 1989).

It is self-evident that non-destructive and non-contact analysis in the field is indispensable for investigating ancient remains. The process, of creating an entire mummiform coffin out of cartonnage, was a time consuming and expensive process.

During Ptolemaic times, a new, simpler method of mummy decoration was adopted. Instead of encasing the mummy in a one-piece mummiform shell, it would be covered with four to six separate pieces of decorated cartonnage. These would be attached to the outer mummy wrappings and could easily be mass produced. These separate sections of cartonnage consisted of a mask covering the head and shoulders, a pectoral, an apron for the legs and a foot casing.

Sometimes, two additional pieces were added to cover the ribcage and stomach. The cartonnage pieces which covered the ribcage and stomach often depicted the winged *ba* bird. These sections would often be cut to the shape of the figure. Sometimes, the image of a winged scarab was also depicted. On some of these pieces, a small, generally square section of the cartonnage would be left undecorated or painted a neutral color (Stewart, 1986).

This work analyzed some fragments from the painted cartonnage of a mummy that was discovered in Hawara pyramid excavation Fig. 1 (B) to establish its elemental composition and to verify if the pigments used in the decorative paintings are in accordance with those used by Egyptian craftsmen in the Roman period (Liritzis et *al*., 1997). These cartonnage fragments consist of two ground layers; coarse ground layer and fine or painting ground layer Fig. 1(C).

Fig.1(A) Hawara Pyramid and the area of excavation work, Fayoum, Egypt. (B) Studied excavated cartonnage fragments. (C) Two painting ground layers of cartonnage fragment.

Fig.2 (A),(B),(C) Three of Hawara cartonnage fragments represented the examined pigments

2. METHODS OF ANALYSIS AND INVESTIGATIONS

Different analytical techniques have been performed to characterize pigments, grounds, and binding media employed in a number of very small cartonnage fragments Fig 2 (A, B, C).

2.1 Optical microscopy

Samples were observed by a Wild M8 stereomicroscope, a Olympus BX51 optical microscope and recorded with a photocamera. The cross sections were prepared by embedding the sample in a polyester resin, cold polymer sable with the addition of a catalyst, and then polished with a Struers DAP-V machine by using Si–C paper discs with a decreasing granulometry (600, 1200, 2400 and 4000 grit size), until the cross-section surface became smooth and specular (Liritzis and Polychroniadou, 2007). These preparation processes were applied in the Geology Department, Faculty of Science, Cairo University).

2.2 Scanning electron microscope equipped with energy dispersive x-ray analysis

Samples were investigated by Philips (XL30) microscopy, equipped with EDS micro-analytical system to obtain the total element content qualitatively and quantitatively by EDX unit in the samples. It was useful for semi-quantitative elemental analysis to make up for the deficiencies of XRD (Hanlan, 1975). In some cases, doubt arose about specific minerals that could not be readily identified by XRD (Perdikatsis, *et al* ., 2000).

2.3 X-ray diffraction analysis

X-ray diffraction analysis carried out with Phillips X-ray diffraction equipment model pw/1840 with Ni filter, Cu radiation 1.54056 A° at 40 KV, 25mA, 0.05 /sec. High-resolution graphite monochromator, rotating sample holder and a proportional detector. Measurements were carried out on powders of the samples, in the range $0° < 2\theta < 70°$ with a step of 0.02°.

2.4 Fourier transform infrared spectroscopy

Samples were analysed as KBr pellets by JASCO FT\IR – 460 plus spectrometer, in the transmission mode (Bikiaris, *et al.,* 1999, Grigar, 2003). The powdered sample was examined between (400–4000cm^{-1}, 4cm^{-1} resolution).

3. RESULTS

To conserve and restore, it is indispensable to understand the chemical constituents and crystal structures. The technology of the materials used in the fabrication of ancient Egyptian cartonnage is still not fully investigated. (Daniels, 2007; Scott *et al.,* 2003; Scott *et al.,* 2009).

Among archaeological objects, pigments are most attractive targets for scientific study because their colors are yardsticks of a sense of beauty, and they provide a means for estimating ancient technologies' ability to prepare pigments artificially (Green 1995; Nagashima *et al*. 1996; Goresy 1997; Uda 1999, Uda *et al*. 2000a; Uda *et al*. 2000b; Yoshimura *et al*. 2002; Goresy et., al 1986).

3.1. Ground layers

From visual inspection and analysis of samples by X ray diffraction (XRD), energy dispersive X-ray analysis equipped with scanning electron microscope analysis (SEM) are characterized by two preparation layers or ground painting layers. The preparation technique used seems to have been to pour the first layer of a coarse ground layer directly on the linen mummy bandages. This coarse layer covered with another smooth layer prepared for painting process. These two-layered structures of plaster were observed on all fragments. Based on experimental results obtained, XRD analysis revealed that the inner coarse ground layer is composed of calcite $CaCO_3$ as a major with small amounts of quartz (SiO_2) (Fig. 3A). The material composition of the fine ground layer used under the pigments directly was composed of calcite, $CaCO_3$ only Fig. 3 B). This result agreed with (UDA, 1999). EDX data of ground layers (Fig. 3 C, D) respectively, showed the fine ground layer that composed of Ca that exhibited the highest concentrations 80.86% and 11.14% of C. This result indicates that the layer is consists of calcite. The coarse ground layer is composed of Ca, C, Si, agreed with the result of XRD data that is composed of calcite and quartz.

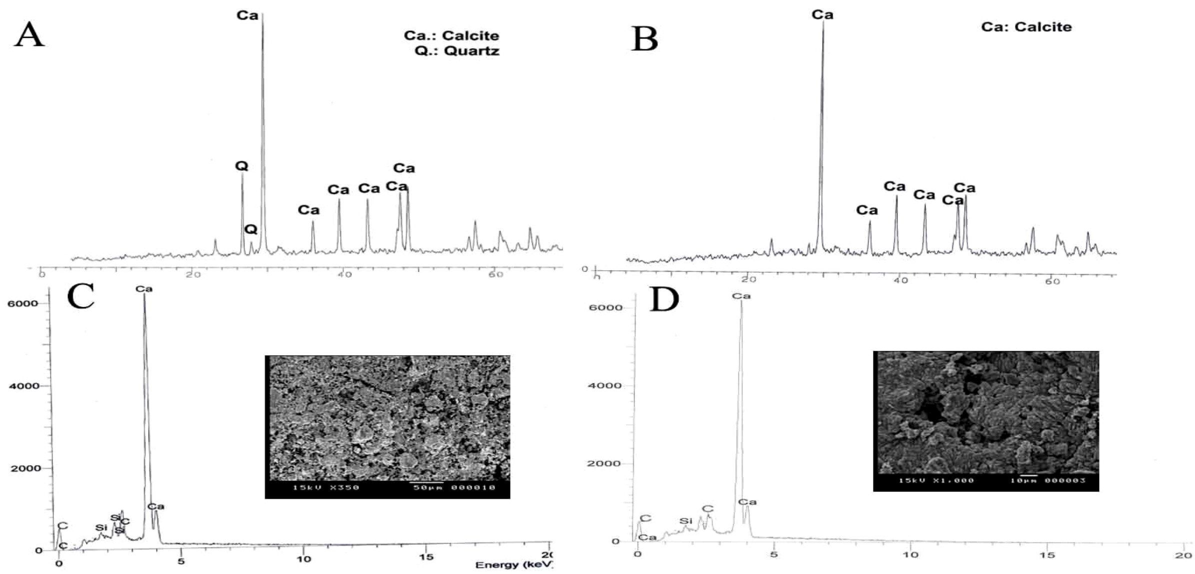

Fig.3 (A,B,C,D) XRD, EDX patterns of the internal and external ground layers of the cartonnage fragments. (A) XRD data of internal ground layer that consisted of calcite and quartz. (B) XRD data of external ground layer that contained calcite only. (C) EDX pattern of internal ground layer. (D) EDX data of external ground layer

3.2. Pigments

3.2.1 Red pigment

The majority of red pigments used in ancient Egypt were earthen based colors containing iron oxide. Hematite (αFe_2O_3) was very common (Green 2001, M. Uda, et al 2000). This Fe-based colors are longer lasting and light faster than others, and are sometimes of astonishing brilliance. Two further red pigments have been imported to Egypt by the Romans: Red lead (Pb_3O_4) and Vermillion (HgS). If these pigments are found on ancient objects, it can be assumed to be produced not earlier than the first century B.C. Mineralogical analysis conducted by XRD showed in the Fig. (4A). It presented calcite as a painting ground layer, lead oxide Pb_3O_4 as red pigment with carbon as black. This result agreed with (Burgio et al., 2007; Rocco Mazzeo, et al., 2004). Calcite and lead oxide were determined by SEM-EDS. Pb, Ca, with minor component of Si (Fig. 4 B).

3.2.2 Blue pigment

In 3000 BC, Egyptian craftsmen created the first synthetic pigment produced by man, Egyptian blue, which was widely used during antiquity, spreading all around the Mediterranean basin until the 7th century AD. The Egyptian green pigment, also called green frit, appeared shortly after, presenting the same chemical elements and a turquoise color. These two pigments have been confused for a long time (Mazzochin, 2004; Page`s 2003; Daniels, 2007). In many cases, Egyptian blue was added in small amounts to enhance the brilliance of other colors. It was reported by (Mazzochin 2003; Mazzochin ,et al., 2003). XRD data of blue pigment in Fig. 3C, which identified cuprorivaite, $CaCuSi_4O_{10}$, the major constituent in Egyptian blue. Cu, Ca, Si were identified by EDX pattern as showed in Fig 4D. The result verified the XRD data (see e.g. Katsaros et al., 2011).

3.2.3 Yellow pigment

In the Fig 4E, the yellow pigment is confirmed by XRD pattern as a goethite $Fe_2O_3.H_2O$ (Fig 4F). This was confirmed by EDX data. Ca is the main component of ground layer, Si, as quartz and Fe represent goethite as yellow pigment this result agreed with (Perdikatsis et al 2000; Brecoulaki, et. al., 2006).

3.2.4 Black pigment

The only black pigment identified is carbon black. It is the principal black attested and used from ancient Egyptian periods. Its use is very frequent both as an homogeneous paint layer and mixed with other pigments to produce darker tones (Mazzochin ,et al., 2003). SEM observation revealed the chemical composition that was characterized by a great amount of carbon.

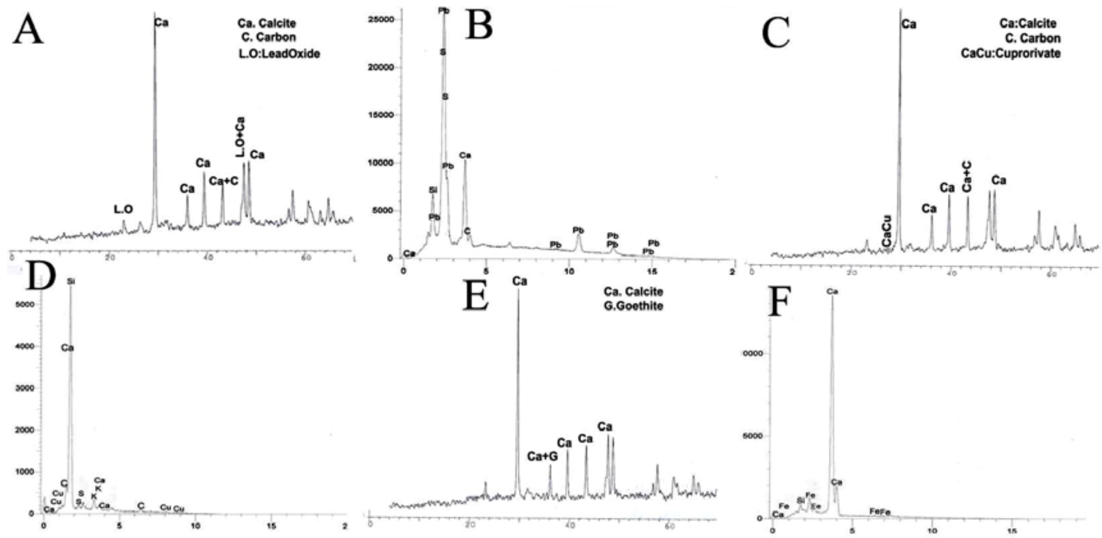

Fig 4 (A, B, C, D, E, F) XRD and EDX of pigment samples. Fig 3(A) XRD data of red and black pigments showed that red pigment consisted of lead oxide PbO_3 and black as carbon. Fig3(B) EDX data of the red and black pigments. Fig3(C) XRD of blue and black pigments data explained the cuprorivaite, $CaCuSi_4O_{10}$ as blue and black was carbon. Fig3 (D) EDX data of the blue and black pigments. Fig 3(E) XRD data showed that goethite $Fe_2O_3.H_2O$ was yellow pigment used on the cartonnage fragments. Fig 3(F) EDX data of yellow pigment

3.3. Binding media

The spectroscopic study was essentially addressed to characterize the colouring medium used in the cartonnage fragments. In all the analysed samples, the stretching vibrations of calcium carbonate, $CaCO_3$, peaked at 1409, 705 and 611 cm^{-1} were identified since the substrate was just a calcarenite (Griffith 1987). In particular, we evidenced the typical hydroxyl bands centred at 3694, 3669, 3652 and at 3620 cm^{-1}, the Si–O–Si band peaked at 1032 cm^{-1}, the Si–O–Al at 1009 cm^{-1} and finally the Al–O–H bands at 938 and 914 cm^{-1}. The use of animal glue is also shown in this IR spectrum by the presence of a band at 1540 cm^{-1} associated with the deformation vibration of the N-H link in the protein (Carbo,1997). In the four pigments, the same medium and working technique were found. (Schiegl et al., 1989; Mazurek et al. 2008; Scott et al., 1996; Hodgins and Hedges, 2000; Schilling et al., 2000).

4. CONCLUSION

The present study has shown the characterization of painted cartonnage fragments from Hawara excavation in Fayoum that belonged to the Greek Roman period, Egypt.

The technology of cartonnage making, ground layers composition, pigments constituents and color medium were identified by using different analytical methods as XRD, EDX, SEM and FTIR.

Two preparation or ground painting layers are applied; the inner coarse ground layer is composed of calcite $CaCO_3$ as a major with small amounts of quartz (SiO_2). The fine ground layer used under the pigments directly was composed of only calcite $CaCO_3$. Read pigment that used is red lead (Pb_3O_4). Blue pigment is cuprorivaite, $CaCuSi_4O_{10}$. Goethite $Fe_2O_3.H_2O$ used as yellow pigment. The only black pigment identified is carbon black. In the four pigments animal glue is found as the same medium in the working technique. The well preserved state of the pigments on the cartonnage fragments is attributed to the fact that they buried and therefore were not exposed to the open environment; soon after being excavated the fragments were packed in crates and kept in the conservation lab of the excavation until this study was undertaken. The results of the pigment analysis shed important light on the pigments that applied on the cartonnage fragments.

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