Mediterranean Archaeology and Archaeometry, Vol. 11, No. 1, pp. 99-106

A PRELIMINARY INVESTIGATION OF ANCIENT PIGMENTS FROM THE MORTUARY TEMPLE OF SETI I, EL-QURNA (LUXOR, EGYPT)

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Received: 20/05/2010
Accepted: 30/10/2010

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ABSTRACT

The present paper aims to apply different analytical techniques to characterize some ancient pigments from the first group of samples collected on the wall paintings of the mortuary temple of Seti I (c.1291–1278 BC), El-Qurna (Luxor, Egypt). The analytical characterization has been carried out by means of optical microscopy (OM), scanning electron microscopy (SEM) equipped with an energy dispersive X-ray detector (EDS), μ-Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR). The results allowed the identification of different pigments used in the polychromatic decorations of the temple and to establish a preliminary analytical database of the chromatic palette used in this period of the Egyptian history.

KEYWORDS: El-Qurna, Mortuary temple of Seti I, Pigments, SEM–EDS, μ-Raman, FTIR

INTRODUCTION

In ancient Egypt, the mortuary temples (or memorial temples) were built to honour a deceased pharaoh and often worship them as a god. The mortuary temple of Seti I (the 19th Dynasty, c.1314–1304 BC) is located about 670 km south of Cairo in the Theban necropolis, Upper Egypt. The construction was begun in the 13th century BC by Pharaoh Seti I and was completed by his son, the famous Ramesses II. During the Roman period; it was transformed into a work area for artisans. After Christianity came to Egypt, the northern courtyard became a church. Of the original length of some 158 meters, only about 47 meters of the temple remain, mostly the area containing the sanctuary, its halls and ante-chambers (Kamil, 1976). The walls, columns and ceilings of the temples are decorated with raised and sunken reliefs with different figures and hieroglyphs texts usually decorated with a chromatic palette widely used in ancient Egypt (Fig. 1).

Fig. 1: Wall decorations of the mortuary temple of Seti I, El-Qurna.

In general, many papers have been devoted to study ancient Egyptian pigments (Riederer, 1974; Jaksch et al., 1983; El Goresy et al., 1986; Uda et al., 1993; El Goresy, 2000; Uda et al., 2000; Colinart; 2001; Marey Mahmoud, 2009). Saleh (1987) in his study of pigments from the tomb of Nefertari, Valley of Queens, Luxor, mentioned that the blue pigment was of Egyptian blue mixed with wollastonite, quartz and tridymite with other impurities. Pagès-Camagna et al. (1999) studied seven cakes of raw Egyptian pigments were found in excavations in the village of the craftsmen who built and painted royal graves near Karnak, and are now conserved in the Louvre Museum (Paris).

The aim of this work was to characterize some of the painting materials used to decorate the walls of the mortuary temple of Seti I, El Qurna (Luxor, Egypt). For this purpose, different optical and analytical techniques were used such as optical microscopy (OM), scanning electron microscopy (SEM) equipped with an energy dispersive X-ray detector (EDS), μ-Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR). The results will provide information about the chemical composition and crystal structure in addition to the stratigraphy of the paint layers. Furthermore, the obtained results will be used in the conservation-restoration interventions of these murals.

EXPERIMENTAL

1. Samples

Appropriate representative samples including different visible colours (blue, red, yellow, and white) were collected to provide stratigraphic information of the paint layers.

2. Analytical techniques

In order to identify the stratigraphy of the paint layers, polished cross-sections were investigated under the reflected light by a polarized light microscope. Cross sectional areas of the studied samples were investigated in the back-scattered electrons mode (BSE) to determine their micro structural characteristics. EDS mapping analysis of the same areas were performed to determine the elemental distribution across each area.

On the other hand, vibrational spectroscopy represents a powerful method to study and characterize art objects. Thanks to its sensitivity to chromophores, Raman spectroscopy is particularly suitable for the identification of pigments in complex matrixes and inorganic pigments in artworks (Edwards et al., 2004; Castro et al., 2006; Marano et al., 2006).

Moreover, Raman technique is more suitable for the non-destructive analysis of binding me-

dia in very small samples (Vandenabeele, 2004). In micro-Raman spectroscopy, the laser beam is focused by means of a microscope objective, employing a backscattering configuration; thus, the Raman scattered light is collected within the cone defined by the same objective (Perardi et al., 2000). Fourier transform infrared spectroscopy (FTIR) is an efficacious tool able to yield quantitative information to identify the substances present in samples. The FTIR technique offers a quick analysis of micro samples (less than 0.5 mg) (Bruni et al., 1999).

2.1. Optical microscopy

In order to analyze the stratigraphy of the mural paintings, some samples were embedded in Epoxy resin (EpoFix), cross-sectioned using variable speed silicon carbide papers and DP-lubricant blue for fine and cool polishing, and mounted on glass slides. The polished cross sections were examined under the reflected light by a Leitz orthoplan (binocular polarized) microscope with a Nikon Cooplix 990 camera.

2.2. Scanning electron microscopy with an EDS microanalysis detector (SEM–EDS)

The morphology and microstructure of pigment crystals was investigated using a JEOL JSM-840A scanning electron microscope and the microanalysis was carried out using an energy dispersive X-ray (EDS) Oxford ISIS 300 micro analytical system. Polished cross-sections were investigated in the backscattered electrons mode (BSE) for the purpose of pigment identification in each colour layer, the elemental composition was determined using the prepared carbon coated cross- sections.

2.3. μ-Raman spectroscopy

μ-Raman spectra were recorded using a triple grating spectrometer (Dilor XY) equipped with a Charge Coupled Device (CCD) liquid-nitrogen cooled detector system. The red line (632.8 nm) spectra were excited from a 35 mW air-cooled He–Ne laser (Spectra Physics, mod.127). The spectral resolution of the system was ~3 cm^{-1}. The laser was focused on the sample through the system's microscope equipped with a standard objective lens 100x. In order to avoid damaging of samples, the laser power was kept at 0.1–0.3mW.

2.4. Infrared spectroscopy

Some samples were selected and studied by infrared spectroscopy using a Perkin Elmer Spectrum One FTIR Spectrometer, in transmittance mode, over a wave number range of 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} on KBr pellets (IR, Merck).

RESULTS AND DISCUSSIONS

Table 1 shows the results of EDS microanalysis carried out on the studied pigment samples.

1. Blue pigments

Optical microscopic investigation on the prepared polished cross-section of the blue paint layer shows that the pictorial layer is slightly thick with different chromatic hues range from pale green to dark blue. It is observed that the paint layer was applied directly on the stone substrate below (Fig. 2a). The back scattered electrons investigation (BSE) performed on a polished cross-section of the blue paint layer shows the heterogeneity of *cuprorivaite* crystals dispersed within the preparation layer (Fig. 2b). The microanalysis of the blue pigment, performed with EDS, shows that the peaks of Si (54.25%), Ca (22.04%) and Cu (14.54%) are present, and their atomic percentage ratios are in agreement with the formula of *cuprorivaite*.

Egyptian blue is a multi-component synthetic pigment appeared in Egypt since the Old Kingdom and its principal components are calcium-copper tetra silicate crystals (i.e. $CaCuSi_4O_{10}$, cuprorivaite), which produce the blue colour (Hatton et al., 2008). According to Jaksch et al. (1983), this pigment is consisting of cuprorivaite with variable amounts of wollastonite ($CaSiO_3$), Cu-rich glass and cuprite (Cu_2O) or tenorite (CuO) was prepared by melting the copper-rich ingredient with lime and desert sand.

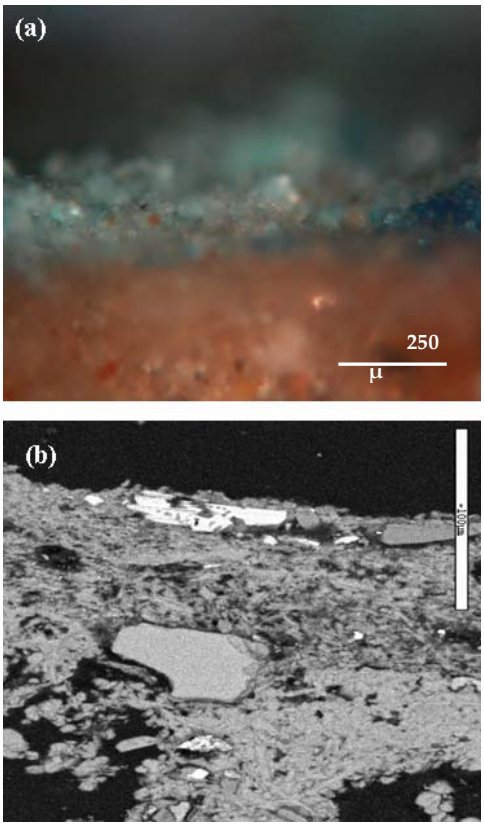

Fig. 2: a) Optical micrograph of a polished cross-section of the blue paint layer (under reflected light), b) BSE micrograph of the same paint layer.

The Egyptian blue pigment with light blue colours is usually known as diluted light Egyptian blue (Green, 2001), and it contains a high percentage of alkali materials with significant amounts of glass phases. The use of this kind has been spread frequently since the period of the 18th Dynasty (c.1540–1292 BC). Micro-Raman analysis was employed to study a dark blue crystal in the sample, the spectrum is weak with the red laser (Baraldi et al., 2007), but Egyptian blue is identifiable through the characteristic bands at ~1086, 985, 574, 470, 432, 382, 229 cm^{-1} (Fig. 4a). The band at 1086 cm^{-1} (symmetric stretching, ν1) (Hernanz et al., 2008), is attributed to calcite ($CaCO_3$). Few spectra at 200 and 400 cm^{-1} are probably due to the presence of quartz and amorphous silica.

2. Red pigments

The optical investigation of a polished cross section of the red pigment sample shows that the paint layer is applied directly on the underlying substrate which is rich in voids, fossils, gypsum and quartz particles (Fig. 3a). BSE micrograph obtained on the sample shows the granular aggregate particles of the red ochre; large grains of gypsum are notable in comparison with the small ones of calcite (Fig. 3b). EDS microanalysis shows that the peak of iron (14.25%) is present, indicating the existence of iron oxide of hematite (Fe_2O_3) as possible colouring material.

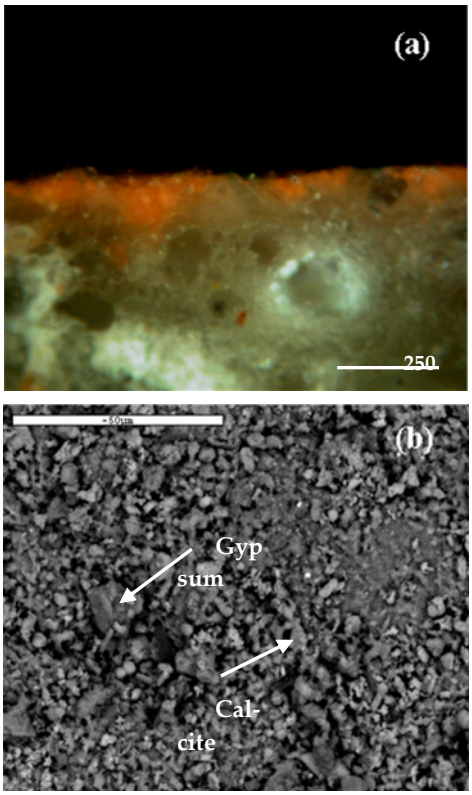

Fig. 3: a) Optical micrograph of a polished cross-section of the red paint layer (under reflected light), b) BSE micrograph of the same paint layer.

Elements of sulphur and calcium detected in sample refer to the existence of calcium sulphates. Aluminium (6.58%) and silicon (19.06%) indicate possible existence of an aluminosilicate material (Zorba et al., 2007). The principal red pigments in Egypt are of two main types, red iron oxide (hematite) and red ochre (hydrated iron oxide, perhaps partially dehydrated goethite) (Calza et al., 2007). Ochre pigments were used since prehistory in caves; all ochre pigments are natural and contain iron oxide (III) (Fe_2O_3) as their main component. Natural ochre pigments present a wide range of colours, from yellow to orange, red and violet (Ramos et al., 2008).

Hematite is relatively abundant in sedimentary rocks among geological formations in the

Nile valley (El Goresy, 2000). Subtle differences in colour of the red ochre may be accounted for by differences in mineralogy, e.g. the presence of carbonate minerals such as dolomite or substitution by other metals at low concentrations (Marshall et al., 2005). The detection of titanium in the studied samples could be a result of the presence of ilmenite ($FeTiO_3$) which is found in the Egyptian sand or possibly forming intergrowths with hematite (Berry, 1999).

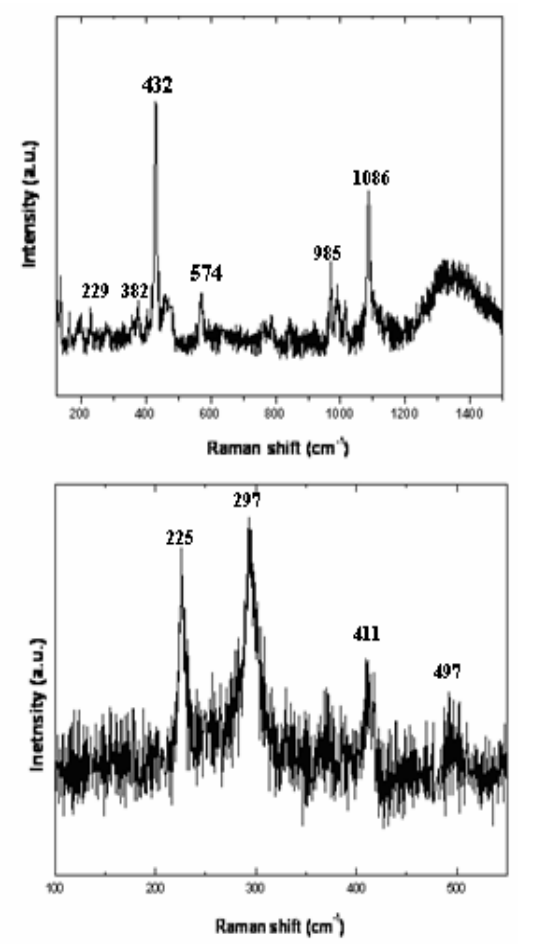

Fig. 4: μ-Raman spectra of: a) the blue pigment, b) the red pigment.

The micro Raman spectrum obtained on a red spot in the sample (Fig. 4b) shows the main characteristic strong bands at ~225, 297 cm^{-1} with the weaker ones at 411 and 497 cm^{-1}. In accordance to Helwig (2007), the main peaks for hematite are present at 224, 291, 407, 494, 610, 630, also 247, 412, 226, 246 cm^{-1}.

3. Yellow pigments

The optical investigation of a polished cross section with yellow pigment sample shows that the thick paint layer of the yellow colouring material is applied directly on the underlying stone support (Fig. 5a). BSE micrograph obtained on the sample shows the slightly small grains of ochre and calcite with large grains of gypsum scattered on the surface (Fig. 5b).

The microanalysis of the sample -performed with EDS- shows the presence of iron (3.26-6.32%) indicating possible existence of goethite. Moreover, a strong contribution of Al (27.64%) and Si (46.03%) indicate the existence of an aluminosilicate material; this gives indication that yellow ochre was used to obtain the yellow colour.

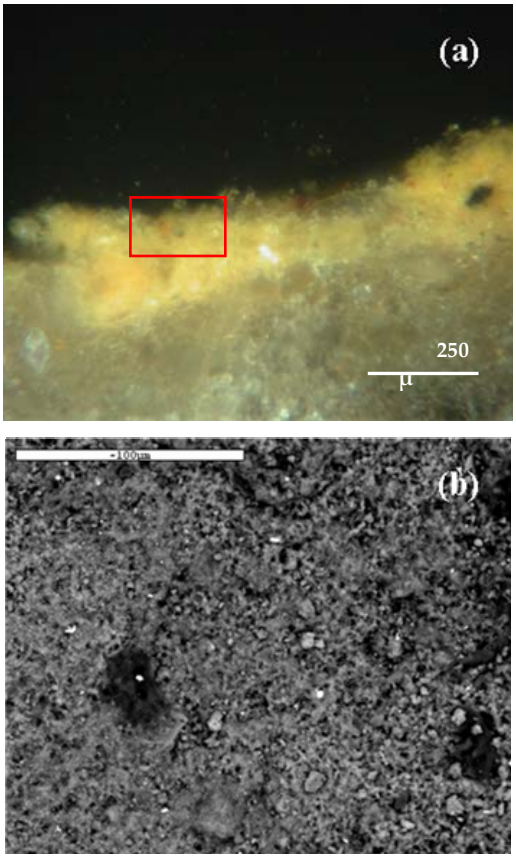

Fig. 5: a) Optical micrograph of a polished cross-section of the yellow paint layer (under reflected light), b) BSE micrograph of the same paint layer.

3.4. White pigments

For white pigments, some representative samples were employed for FTIR analysis. FTIR spectrum obtained on the white pigment sample is shown in Figure 6. The characteristic bands of calcite are present, the sharp one at ~875 cm^{-1}, is due to its asymmetric bending.

Table 1: The EDS microanalysis carried out on the studied pigment samples.

Atomic (%)	Blue pigment	Red pigment	Yellow pigment	White pigment
Na	1.32	11.83	2.21	1.12
Mg	1.14	2.06	1.06	2.43
Al	–	6.58	27.64	2.24
Si	54.25	19.06	46.03	12.20
S	3.72	20.15	4.13	7.43
Cl	1.43	–	0.52	3.51
K	–	–	3.04	5.66
Ca	22.04	24.21	10.64	64.65
Ti	1.1	0.62	1.43	0.76
Fe	0.46	14.25	3.26	–
Cu	14.54	–	–	–

Calcite FTIR spectrum shows beaks at 1428, 875 and 712 cm^{-1} due to the C–O stretching of carbonate, and the weak peaks at 1792 and 2505 cm^{-1}, which are combination and overtone bands (Baraldi et al., 2006).

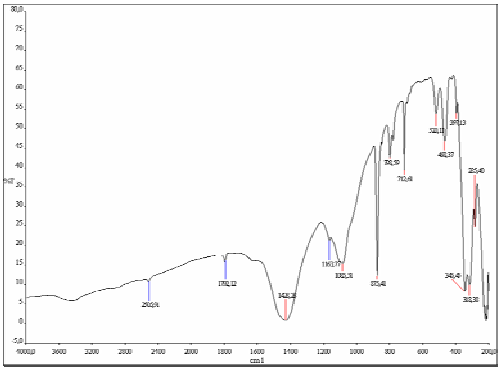

Fig. 6. Transmittance FTIR (KBr) spectrum of the white pigment.

The bands at 468, 1083 and 1163 cm^{-1} are attributed to which are attributed to SiO_4 group vibrations. Calcium carbonate and calcium sulphate have been reported as white pigments in ancient Egypt. From geological point of view, calcite and dolomite are by far the most important carbonate minerals in ancient sedimentary rocks.

CONCLUSIONS

Many of the surviving texts from ancient Egypt were created in order to complement and annotate the paintings and reliefs decorating the surfaces of the walls and ceilings of temples and tombs (Shaw, 2004). The application of different analytical techniques namely optical microscopy (OM), SEM–EDS, μ-Raman, and FTIR methods helped to provide a preliminary image on the composition of some ancient pigments collected on the mortuary temple of Seti I, El Qurna, Luxor, Upper Egypt. The results revealed the characterization of a part of the chromatic palette used for decorating. The results have shown that the attested pigments used in the temple are the common ones used in ancient Egypt based mainly on natural minerals, in addition to synthetic pigments such as the Egyptian blue. The blue pigment was identified as Egyptian blue, the red pigment as red ochre, the yellow pigment as yellow ochre and the white pigment as calcite. Moreover, an extensive study to characterize additional samples of the painting materials is now in progress. Furthermore, the obtained results will help in establishing a conservation plan for the wall painting of the temple.

ACKNOWLEDGEMENTS

The author is grateful to Mr. S. Oikonomidis and to Mr. G. Mechailidis, School of Geology, Aristotle University for SEM study and the embedding of the cross-sections.

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