Complementary techniques for pigment analysis from the festival hall of Thutmosis III, the Karnak temples complex (Luxor, Egypt)

by Hussein H. Marey Mahmoud

The present paper aims at analyzing some ancient pigments from the festival hall of Thutmosis III, the Karnak temples complex (Luxor, Egypt). The analytical techniques utilized in this study were optical microscopy (OM), environmental scanning electron microscopy (ESEM) coupled with an energy dispersive X-ray analysis system (EDX), μ-X-ray fluorescence spectrometry and colorimetry.

Tuthmosis III (*c.*1504–1450 BC, the 18th Dynasty) was the creator of a vast Egyptian empire and one of the great Pharaohs of ancient Egypt, and his festival temple (hall) is located beyond the central court of the Karnak Temples complex, a complete temple built at the eastern end of Karnak, wholly enclosed by its own girdle walls [1]. Iit is a spacious and elegant temple, 44 meters wide and 10 deep. The roof is supported by 20 columns in two rows and 32 square pillars on the sides [2]. Karnak temples complex is considered to be among the greatest of ancient Egyptian monuments, it is located about 2.5 km in the north of Luxor (about 670 km south of Cairo). Figure 1 illustrates some painted reliefs from the festival hall of Thutmosis III. Even though the Karnak temples complex enjoys an archaeological and touristic value, few published data are available for the wall decorations at Karnak. For this, the present research was devoted to study pigment samples collected from the festival hall of Thutmosis III, the Karnak temples complex (Luxor, Egypt). Different analytical techniques were used in this work such as optical microscopy (OM), environmental scanning electron microscopy (ESEM) coupled with an energy dispersive X-ray analysis system (EDX), μ-X-ray fluorescence spectrometry and colorimetry. The results of this study supplied information on the constituent materials and execution techniques of the wall decoration in the Karnak temples complex.

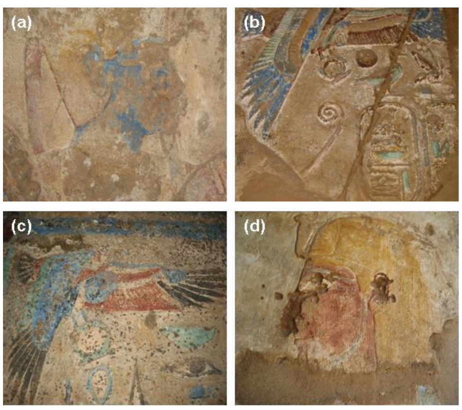

Fig. 1 - Painted reliefs of the festival hall of Thutmosis III, the Karnak temples complex (Luxor, Egypt).

EXPERIMENTAL

Sampling

Tiny pigmented samples (a few milligrams) were carefully scraped off the painted walls with a metallic scalpel.

Optical Investigation

Preliminary observations on the samples were performed using an Olympus SZ-40 stereomicroscope (10 and 20x objectives) equipped with an Olympus DP10 digital camera.

ESEM and X-ray microanalysis

Samples were directly analyzed without any preparation by environmental scanning electron microscope model Quanta FEG 250 (FEI, Netherlands). The FEI Quanta 250 is equipped with an energy-dispersive spectrometer (EDS) (an Oxford Aztec system) for elemental analysis on a microscopic scale. The accelerating voltage was 20 kV and pressure of 2.0 Torr.

μ-X-ray fluorescence spectrometry (μ-XRF)

The μ-XRF spectra were recorded by μ-XRF spectrometer (SPECTRO, COPRA model) which includes a side-window X-ray tube with Mo anode (Oxford Instruments, Series 5011 XTF), potential acceleration 35 kV, lamp stream 0.9mA, and analysis time 300s. A long-distance optical microscope located on the detector and X-ray tube plane is used in order to select the points of interest over the surface of the sample.

Colorimetry

The chromatic characteristics of the different samples were obtained by a Miniscan® XE Plus spectrophotometer (HunterLab). The reflectance spectra were registered in the visible range over several points for each one of the different sample colours. Chromatic values are expressed as colour coordinates in the CIE *L*a*b** colour system (1976) and illuminant D65/10°. We then obtained the diffuse reflectance factor of the paint according to the visible wavelengths domain (from 400 to 700 nm).

RESULTS AND DISCUSSIONS

Visual observations

In Figure 2, a microscopic image obtained on the blue pigmented surface is presented. Microscopically, the sample showed an heterogeneous texture, both coarse and fine, showing dark and light blue colours. Diluted blue is used to describe the colour of fine-textured Egyptian blue that has

Fig. 2 - Optical photomicrograph of the blue pigment sample (microscope objective 10x)

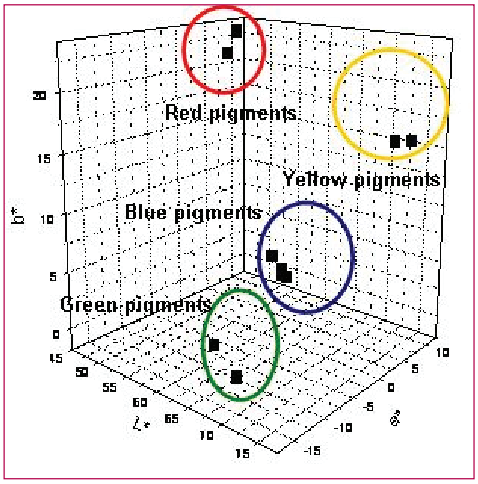

Fig. 3 - 3D graphic chart of the chromatic parameters measured for the studied pigment samples in the L* a* b* (CIE 1976) colour system.

a large amount of glass formed in its composition, which masks the blue colour and gives it a diluted appearance.

Chromatic characterization

Figure 3 represents a 3D scatter chart of the chromatic parameters measured for the studied pigment samples in the L*a* b* (CIE 1976) colour system. One of the most common numeric systems for expressing colour or colour difference is CIELAB notation which utilizes the principle of opposing colours. Lightness is defined as L*(L* = 0 indicates black and L* = 100 indicates white), and hue is expressed in terms of a* and b*., as well as its position between red and green (negative values of a* indicate green, and positive ones indicates red) and between yellow and blue (negative values of b* correspond to blue, and positive ones to yellow). The studied samples exhibit four main colours including blue, green, yellow and red hues. The composition of the pigments can be hypothesized on the base of the shapes and of the peak positions in the reflectance spectra , here the peaks including both the characteristic reflectance and first derivative peaks [6, 7]. The blue samples gave average values of L* = 65.06, a* = 5. 76 and b* = –7.65. The reflectance spectra picked on the sample showed a slope at wavelength higher than 650 nm. The green samples gave average values of L* = 66.54, a* = –4.76 and b* =3.43. The green pigments tend to give a sharp slope at wavelength higher than 630 nm and return to increase after this wavelength. For dark pigments such as haematite, which naturally have low reflectance, the presence of a sub layer has a different impact; in general, dark pigments usually consist of bigger grains and are much denser than other pigments [8]. The red pigments gave average values of L* = 48.34, a* = 5.22 and b* =21.76 and the yellow pigments gave average values of L* = 66.12, a* = 9.47 and b* =15.25. The spectra of the ochre show the characteristic features, especially the sharp positive slope at wavelengths higher than 600 nm for the haematite and red ochre, and lower than 600 nm for the goethite and the yellow ochre.

ESEM-EDX results

Figure 4 shows ESEM image and EDX spectrum on polished cross-section of the blue paint layer. The ESEM image shows that the small crystals of the Egyptian blue are embedded in the plaster matrix. The EDX spot microanalysis on individual crystals in the sample allows to reveal the peaks of Si, Ca and Cu, giving the chemical formula of cuprorivaite ($CaCuSi_4O_{10}$). Other elements, such as S, Al, and Cl were also detected. This synthetic pigment was produced by mixing a calcium salt (carbonate, sulphate or hydroxide), a copper compound (oxide or malachite), sand (silica) and an alkali flux (sources of alkali flux could either have been natron from areas such as Wadi Natrun and El-Kab, or soda-rich plant ashes) [9]. The analysis on the green pigment sample showed chemical composition similar to that of the blue sample with an higher content of Si. This results suggests that the green pigment was the widely used Egyptian green, a multi-component pigment consisting of green wollastonite as major phase, a blue copper-compound, sodium-and chlorine-bearing glass phase, sporadic cuprorivaite, silica minerals and the tin compounds cassiterite and malayaite [10]. The investigation on the red pictorial layer shows the presence of fine granular aggregate particles made of red ochre with large

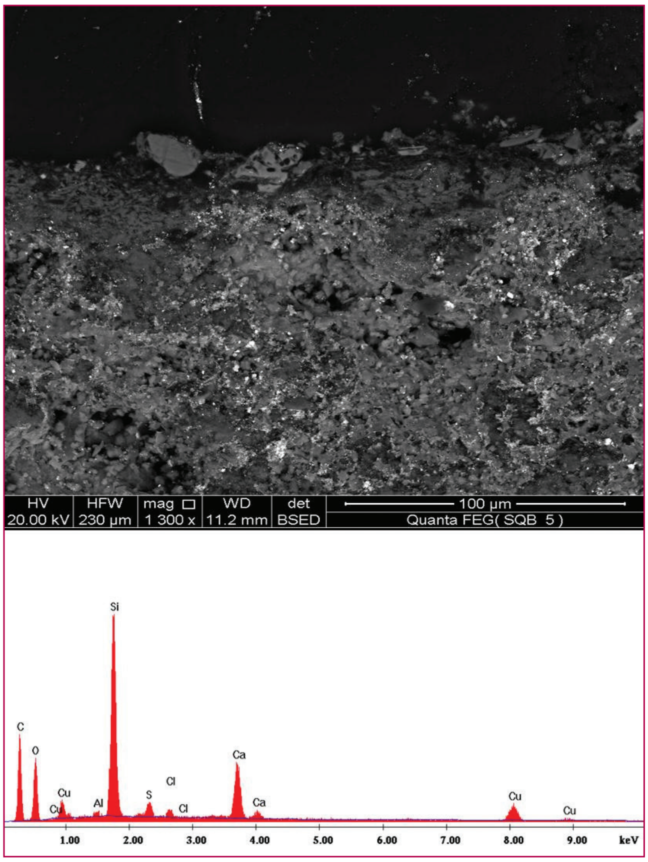

Fig. 4 - ESEM image (1300x, bar 100µm) and EDX spectrum obtained on polished cross-section of the blue paint layer.

grains of calcium sulphate phases. The EDX microanalysis of the sample showed high concentration of Fe, suggesting the presence of iron oxide (haematite, α-Fe_2O_3) as possible colouring material. The other detected elements, S and Ca, are probably present in the underlying ground layer (gypsum, $CaSO_4 \cdot 2H_2O$). The strong contribution of Al and Si indicates a possible existence of an aluminosilicate material [11]. The investigation on the yellow pigment sample shows the slightly small grains of the yellow ochre scattered on the surface. The EDX microanalysis of the sample showed the presence of the peak of Fe indicating the possible use of goethite (α-FeOOH), while the strong contribution of Al and Si suggests the presence of an aluminosilicate material (probably clay minerals); this gives indication that yellow ochre was used to obtain the colour. Ochre is typically composed of two common forms of iron oxide (Fe_2O_3 and FeO), mixed with clays, silicates, and other minerals and they range in colour from deep purple to light yellow [12].

μ-XRF analysis

The μ-XRF spectrum obtained on a dark blue sample is shown in Fig. 5. Significant ratios of Pb, P, Ni, Cl, Mn and Cr were measured by μ-XRF in the blue pigment sample which are highly correlated to Cu. The presence of Ni and Cr suggests an ultrabasic geochemical origin for the copper ore. Such origin also rules out the use of malachite, which is highly depleted in the weakly mobile Cr, whereas Ni preferentially forms hydrous silicates on its own in ophiolites, such as garnierite. Such outcrops suggest that some hydrothermally remobilized ophiolites must have been the geochemical settings of this association [13].

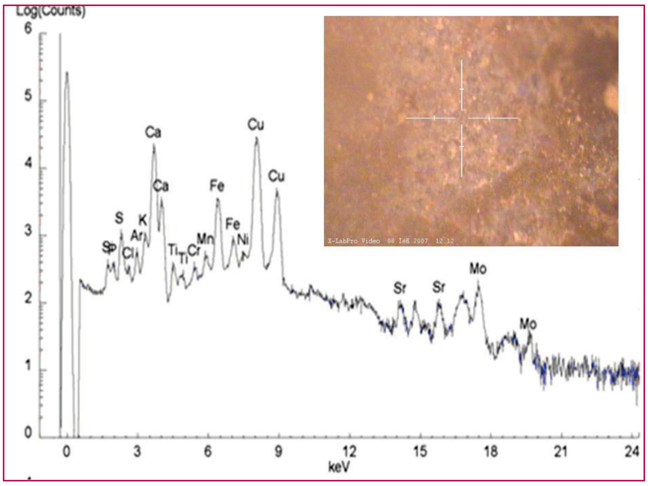

Fig. 5 - μ-XRF spectrum recorded on the blue pigment sample.

CONCLUDING REMARKS

A multi-analytical approach was applied to study the microstructure, morphology and chemical composition of some pigment samples collected from the festival hall of Thutmosis III, the Karnak temples complex (Luxor, Egypt). The analytical techniques used in this work were optical microscopy (OM), ESEM–EDX, μ-XRF and colorimetry. The chromatic palette used in the temple was identified as Egyptian blue (cuprorivaite, $CaCuSi_4O_{10}$) for the blue colour, Egyptian green (Cu-wollastonite) for green, red ochre (haematite, α-Fe_2O_3) for the red and yellow ochre (goethite, α-FeOOH) for the yellow hue. In conclusion, this paper illustrates preliminary results of the first group of samples collected from the wall decorations of the temple. An integrated study aimed to a complete description of the chromatic palette used to decorate the whole temple, is currently in progress.

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Abstract

The present paper aims at analyzing some ancient pigments from the festival hall of Thutmosis III, the Karnak temples complex (Luxor, Egypt). The wall decorations of the festival hall are carved with raised and sunken reliefs and painted with religious scenes and hieroglyphs texts. The analytical techniques utilized in this study were optical microscopy (OM), environmental scanning electron microscopy (ESEM) coupled with an energy dispersive X-ray analysis system (EDX), μ-X-ray fluorescence spectrometry and colorimetry. Based on the results of these analyses, the microscopic features, microstructure and the chemical composition of the studied pigments were identified. The results revealed the blue pigment as Egyptian blue (cuprorivaite, CaCuSi4O10), the green pigment as Egyptian green (Cu-wollastonite), the yellow pigment as yellow ochre, and the red pigment as red ochre.

Keywords

Pigments; the Karnak temples complex; Egyptian blue; ESEM–EDX; m-XRF

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