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AN INVESTIGATION OF POLYCHROME RELIEFS FROM PTOLEMAIC RUINS IN UPPER EGYPT

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Abstract

Multiple analytical techniques were applied to testing inorganic pigments and renders on the surviving ruins of the temple of Ptolemy XII (117–51 BC) at Tell Atrib, Upper Egypt. The samples were analyzed by handheld digital microscope, the visible reflectance spectroscopy (VRS), the environmental scanning electron together with the energy dispersive X-ray microanalysis unit (ESEM-EDXMA), and the attenuated total reflection Fourier-transform infrared spectroscopy (FTIR-ATR). The results showed that the blue pigment is a kind of Egyptian blue characterized with its semi-fined texture, while the green tonalities were produced using green earth pigments "dioctahedral mica group". The residues of the dark reddish-brown pigment were identified as red ochre. The underlying smoothed render layer consists mainly of gypsum and calcite. The detection of calcium oxalate films on the painted reliefs was also reported.

Keywords*:* *ptolemaic ruins; visible reflectance spectroscopy; egyptian blue; green earth; ca-oxalate.*

Introduction

Many of the surviving temples in Upper Egypt belong to the Ptolemaic era. The surviving ruins at the archaeological site of Tell Atrib near Sohag Governorate in Upper Egypt are dating back to the Late period to the Coptic period. Actually, considerable ruins were part of the temple of Ptolemy XII (117–51 BC). The site was re-excavated by the Egyptian Antiquities Organization between 1981 and 1985 [1], and by an expedition of the University of Tübingen [2]. It seems that the stone blocks used in the temple were workable enough and could be easily carved. Indeed, the Ptolemaic relief sculptures are of great quality and originality. The studied ruins are decorated with raised and sunken-raised reliefs, when the pictorial scenes are laying out high or below the stone surface. In most cases, the stone surface would be smoothed and plastered with a thin layer (render) in order to receive the pigment material usually suspended in a fluid of organic binder. The ancient Egyptians used mineral pigments derived from natural resources, and they also produced the first artificial pigments in history.

Objective of the study

Previous studies have been undertaken to characterize materials of Ptolemaic coffins, papyri, and stones [3-10]. The main objective of the present work was planned to study pigment samples collected from the ruins of the temple of Ptolemy XII (117–51 BC) at Tell Atrib, Sohag Governorate, Upper Egypt, by multi-analytical methods.

Instrumentation

The limited size of the pigment samples prompted the conducting of complementary analytical approach capable of provide sufficient information on the nature of the analyzed materials. The analysis of samples was started with the microscopic examination. Using an optical

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microscope, information about the thickness, stratigraphy of the successive layers, colour and particle size can be collected. The samples were examined using a USB digital microscope RoHS (the magnification range was 20 up to 200X). The chromatic characteristics were registered using the visible reflectance spectroscopy, which is rapid and accurate method to identify pigments. Pigment materials can be identified depending on shapes and peak positions of the reflectance spectrum curves. The reflectance values of the samples were registered (along a 400 to 700 nm wavelength range and every 10 nm) by the aid of Optimatch 3100® spectrophotometer (SDL Company). The colorimetric coordinates were calculated and expressed in the CIE $L^*a^*b^*$ colour system (1976). A Quanta FEG-250 environmental scanning electron microscope was used to determine the microstructure and microanalysis of the samples. The magnification applied to the studied samples ranged from 500 and up to 2000x. The microscope is equipped with an energy dispersive spectrometer (an Oxford Aztec system) which was applied for an elemental analysis on the samples. The molecular composition of the samples was determined using a BRUKER'S VERTEX 70- Attenuated total reflection infrared spectroscopy (ATR-FTIR spectrometer). The scans were collected in the mid-infrared (MIR) range with a resolution of 4 cm^{-1}.

Results and Discussion

Visual observations

Indeed, very useful aspects were obtained from the visual examination of the painted reliefs. Black layers were observed covering the blue areas (Fig.1a), this most probably due to dirt accumulations, formation of degradation products of gypsum, or the physio-chemical degradation of the organic binder [11]. The examined sample showed light blue colour with dark blue grains in the matrix (Fig.1b). The light blue grains may suggest that high amount of alkali was used to produce the pigment material. It was reported that light and diluted-light Egyptian blue pigment appeared during the 18th dynasty of the New Kingdom [12]. The surface of the green pigment sample shows a compacted surface with green-olive tonality (Fig. 1c). Residues of the reddish-brown particles were observed covering the underlying blue pigment, this layer was probably applied on purpose by the ancient artist to draw the outlines in some pictorial figures (Fig.1d). The thickness of the reddish-brown layer (70–100µm) was not surprisingly in comparison to the blue pigment layer (~300µm), as reported in the literature of the ancient Egyptian wall decorations. The microscopic observation of a bulk fragment showed clearly the cross-section stratigraphy of the layers, the slightly thick render layer (0.2–2mm) is clearly observed (Fig. 1e).

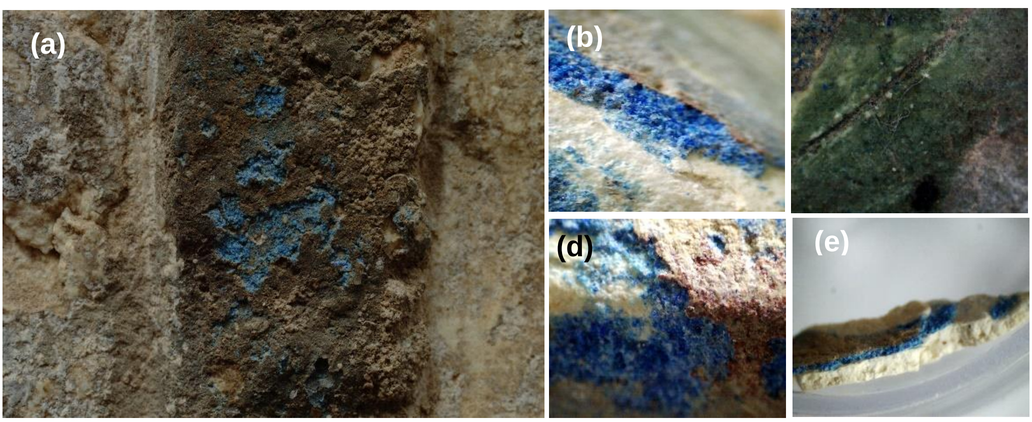

Fig. 1. a) The surviving blue pigment on the stone reliefs; b) cross-section on the blue paint layer; c) the surface of the green pigment sample; d) residues of the reddish-brown particles; e) stratigraphic view shows the thickness of the render layer.

The visible reflectance spectra

This method was reported as a useful tool to identify pigments and their chromatic alterations. The chromatic values of the samples were expressed according to the CIE 1974 colour system. The spectrum recorded on the Egyptian blue sample shows characteristic absorptions in the form of a slope at wavelengths higher than 650nm (Fig.2a). Size and particle shape may affect the chromatic characteristics of the pigments. The Egyptian blue pigment contains clusters of amorphous silica and glass phases which are not uniformly distributed in the matrix. After the grinding process of the pigment material, amounts of coarse grains and particles remain in a heterogeneous form. This may explain the poor covering power of this pigment. A sharp slope after wavelengths higher than 550 nm, in the yellow-green region, was detected in the green pigment spectrum, which is the characteristic absorption of the green earth pigment (Fig. 2b).

Microstructure and microanalysis (ESEM- EDXMA)

ESEM-EDXMA investigation applied on the rough surface of the blue pigment sample revealed the occurrence of semi fine-grained structure with dispersed angular coarse grains (their size ranges from 40-100μm) (Fig.3a). The EDXMA microanalysis obtained on the sample showed the detection of major elements and their atomic ratio as follows: silicon (16–25%), calcium (16.4–16.9%), sulfur (6–11%) and copper (6–7%) (Fig.3b).

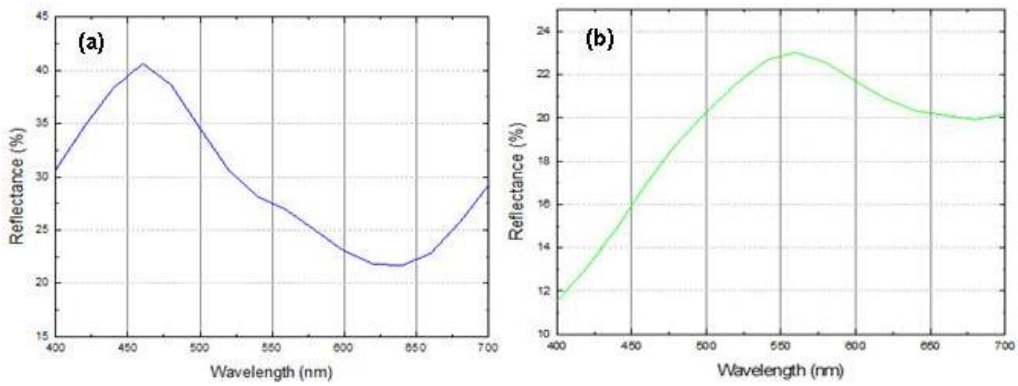

Fig. 2. The visible reflectance spectra recorded on the outer surface of some samples: a) the blue pigment sample; b) the green pigment sample.

Silicon, calcium and copper are correlated with the existence of the mineral "cuprorivaite" ($CaCuSi_4O_{10}$), which plays as the main colouring agent of the Egyptian blue pigment. The copper source for producing the Egyptian blue pigment probably derived from copper ore occurs in Sinai and in the Eastern Desert. Evidences on copper ore smelting from the Ptolemaic times have been reported in the Wadi Abu Gerida in the Eastern Desert [13]. Copper ores in Sinai are principally located at Wadi Magharah, Serabit el-Khadim and Gebel Um Rinna [14]. These deposits consist mainly of malachite ($Cu_2CO_3(OH)_2$) associated with other minerals of Azurite ($Cu_3(CO_3)_2(OH)_2$) and Chrysocolla ($Cu_2H_2Si_2O_5(OH)_4$) [15].

Moreover, the distribution of other ions of sodium and chlorine in the examined sample are probably related to the accumulations of soluble salts (halite, NaCl). Halite is one of the predominant salt types damage the archaeological monuments in Egypt. The ESEM micrograph recorded on the green pigment sample shows fine morphology with some coarse grains dispersed in the matrix (Fig. 4a). The EDXMA microanalysis showed that calcium (Ca), silicon (Si) and iron (Fe) are the main elements in the sample (Fig. 4b). Other amounts of aluminum (Al), potassium (K) and magnesium (Mg) were also recorded throughout the sample. These contents are probably related to the presence of clay-pigment of the green earth (dioctahedral mica group)

[16]. Green earth is identified by its color variations, such as pale green, bright green, bluish-green, olive-green, and black-green.

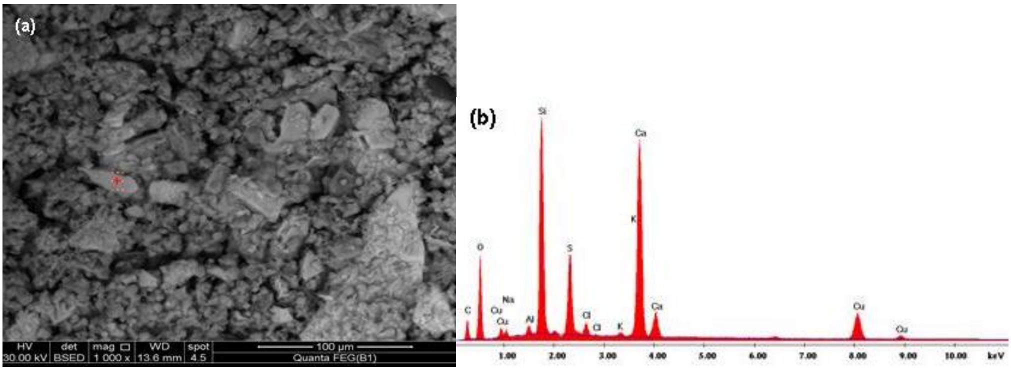

Fig. 3. ESEM image and EDX spectrum obtained on the blue pigment sample

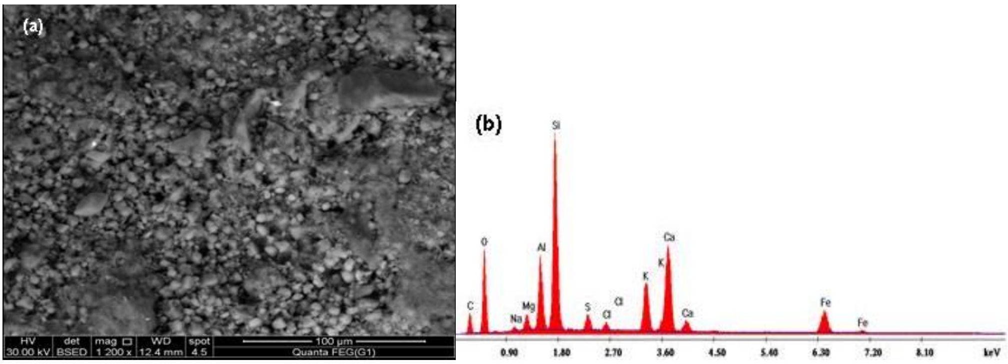

Fig. 4. ESEM image and EDX spectrum obtained on the green pigment sample

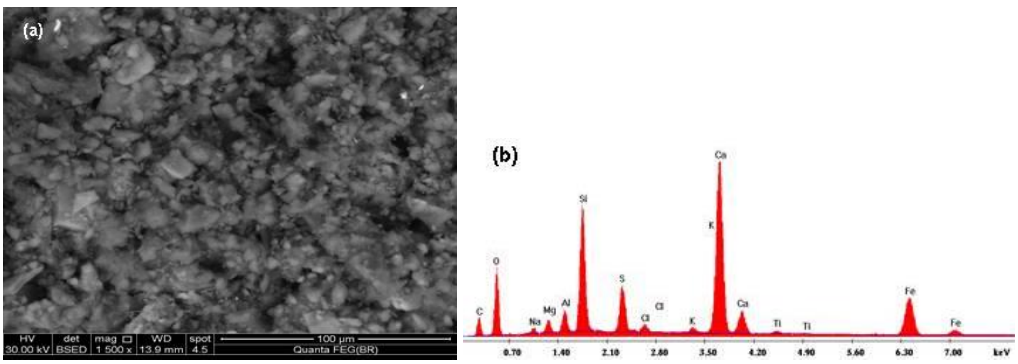

Fig. 5. ESEM image and EDX spectrum obtained on the reddish-brown pigment sample.

The deposits of green earth- mainly of glauconite minerals- are widely spread in the Western Desert of Egypt [17]. The investigation of the reddish-brown sample showed fine grains of the pigment with large grains of quartz (SiO_2) together with calcite ($CaCO_3$) (Fig. 5a). EDXMA microanalysis of the sample revealed calcium, silicon, sulfur and iron as the dominant elements in the sample. Considerable amounts of aluminum and potassium together with small ions of titanium, sodium, magnesium and chlorine were recorded all over the sample (Fig. 5b). This indicates that red ochre was used as the red colouring material [18]. The red ochre pigment owes its colour to iron oxides (hematite, αFe_2O_3). Accessory minerals of quartz, clay minerals, calcite are also associated with the pigment material [19, 20].

Hematite was mined in the Eastern Desert of Egypt during the Roman Period. The iron ore deposits in Egypt are existed in the Eastern Desert, in Sinai, near Aswan and in El-Bahariya oases [21]. EDXMA microanalysis of the render layer showed the presence of calcium and sulfur in remarkable amounts. This elemental composition can be interpreted as calcium sulfate dihydrate (gypsum, $CaSO_4{\cdot}2H_2O$), which was used as a preparation layer to rendering the temple walls. The deposits of gypsum in Egypt are spread in many locations, for example near Alexandria, Fayoum and also through the Red sea coasts [22].

Molecular structure (FTIR-ATR)

Figure 7 shows FTIR-ATR spectra recorded on the blue pigment and the render layer. The data recorded on the blue pigment sample (Fig. 6a) showed the most characteristic peaks at 1003, 1044 and 1154 cm^{-1}, are marked for Si−O−Si stretching vibrations in the structure of cuprorivaite [23, 24].

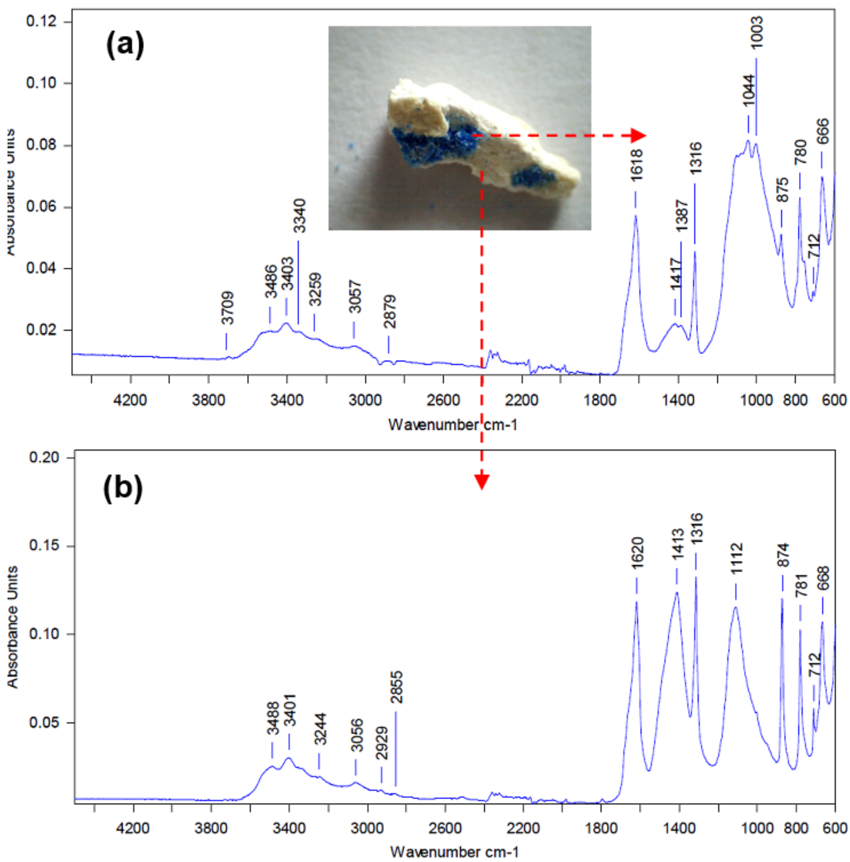

Fig. 6. FTIR-ATR spectra obtained on: (a) the blue pigment, (b) the render sample.

For the green pigment sample, characteristic bands of aluminosilicates materials (Si–O–Al) were recorded. The render layer gave typical absorption bands of gypsum at 3488, 3401, 1620 and 668 cm^{-1}. The bands at 1413, 874 and 712 cm^{-1} are due to the existence of calcium carbonate (calcite) (Fig. 6b). This suggests that a mixture of gypsum and calcite has been used to prepare a smooth layer for the decorations. Moreover, the contribution of quartz particles is probably corroborated for the appearance of the band at 781 cm^{-1}. Furthermore, the band at 1314 cm^{-1} is probably attributed to calcium oxalates (whewellite and weddellite). The formation of calcium oxalate films on the stone surface is commonly attributed to microbiological attacks [25], these processes work aggressively to dissolve the original compounds of the paint layers to form secondary degradation products.

Conclusion

An analytical investigation was performed on pigment and renders from the ruins of the temple of Ptolemy XII at Tell Atrib (Sohag Governorate, Upper Egypt). The results revealed the use of a semi-fined Egyptian blue pigment as the blue colouring material. Light Egyptian blue suggests the use of high amounts of alkali in the starting formula when producing the pigment. The chromatic characteristics of this pigment are highly affected by the coarse grained powder resulting from the grinding process of the material. The green pigment was identified as green earth and the reddish-brown pigment as red ochre. The pigments were applied on a smoothed preparation layer consists mainly of gypsum and calcite. Also, calcium oxalate films were observed on the reliefs, most probably derived from biodeterioration mechanisms. The results ascertain that visible reflectance spectroscopy can be used as a helpful tool for fast *in situ* identification of pigments. The obtained results are in agreement with the literature data concerning the ancient Egyptian pigments in polychrome monuments. Only the green earth pigments detected in the reliefs provide an exception, these pigments were never used before the Ptolemaic and Roman period in Egypt.

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