ORIGINAL PAPER

CHARACTERIZING THE PAINTED WALL RELIEFS FROM THE ANCIENT EGYPTIAN ROCK TOMBS OF MEIR AT ASSIUT, EGYPT

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Abstract.*The present research was designed to characterize the main components of ancient Egyptian wall reliefs of Meir rock tombs at Assiut of Egypt using severalμ-destructive analytical methods. The microscopic characterization included optical examination on painted surfaces and petrographic examination on thin sections of rock fractions. The morphology of pigments and their chemical structure were investigated by scanning electron microscopy and energy dispersive X-ray spectrometry (SEM-EDX). Fourier transform infrared spectroscopy (FTIR) was used for the investigation of the molecular composition of the render layer and the blue pigment. The mineralogical composition by X-ray diffractometry (XRD) helped to study the stone, underlying preparation layer, and some pigments. The results showed that the petrographic features of the rock samples are based mainly on fine calcite grains. The identified pigments were Egyptian blue (synthetic cuprorivaite), red ochre (iron oxides and clay minerals), and carbon black. While for the green colour, a mixture of Egyptian blue and yellow ochre was created. Since the materials used in the abovementioned tombs were never been previously analyzed, this research will be a valuable start for a future complex study related to painting materials used in the Meir necropolis of ancient Egypt.*

Keywords: *Meir rock tombs; wall relief; pigments; OM; SEM-EDX; FTIR; XRD.*

1. INTRODUCTION

The archaeological necropolis of Meir is located at a high point on the Western bank of the River Nile, about 15 km to the North-West of the city of Assiut. The area is located between (27°12′30″--27°27′30″ N) latitude and (30°40′--30°55′ E) longitude (Fig. 1). The studied area belongs to the Nile Valley depression including Quaternary deposits (e.g., gravels, sand, silts, and clay) and Eocene limestone formations, which are affected by a number of geological faults.

The necropolis was devoted to Old Kingdom (c. 2613–2181 BCE) and Middle Kingdom (c. 2040–1782 BCE) governors and noblemen of the 14th Nome of Upper Egypt [1, 2]. The site has been early excavated by many archaeologists, (e.g., E.G. Chassinat, 1890; G.E. J. Daressy, 1900; Ahmed Bey Kamal, 1910–1914). But, the British Egyptologist A. Blackman (during the period 1912–1950) had a notable fingerprint in these efforts as he ordered the tombs into groups taking the alphabetical labels ‘A, B, C, D and E’. The tombs have the letters B and C are from the Middle Kingdom, while A is for many tombs from the Old Kingdom, although some tombs are dated to the Middle Kingdom (Fig. 2). The tombs

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labeled D and E are from the Old Kingdom too. The necropolis comprises about seventy-five tombs that are characterized by featured colorful reliefs. The wall reliefs express a development in applying the gridlines system to perform rituals, offerings, and daily life scenes [3] (Fig. 3).

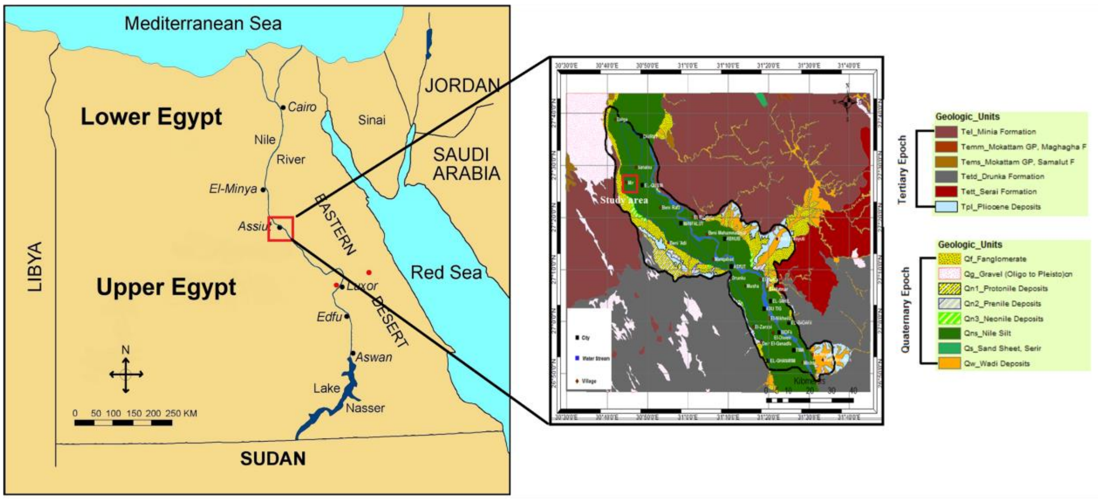

Figure 1. Map of Egypt and the location of Meir tombs (left), and the geological structure of the studied area (right) (after El Tahlawi et al.[4]).

The ancient Egyptian painting materials were a target for many analytical approaches. El Goresy et al. [5] presented one of the most important studies concerning ancient pigments and their chemical composition. The efforts of Ali [6–8] in studying the ancient painting materials, especially the Egyptian blue and green pigments, provided important data through analytical characterization of samples from the Old Kingdom to the Graeco-Roman period in Egypt.

Figure 2. A general view of the rock tombs of Meir and examples of some tombs.

As is well known, ochre and iron oxide-based pigments were the earliest pigments used by man for painting. The red pigments are based on anhydrous ferric oxide as the main coloring agent, such as hematite (α-Fe_2O_3). Further, their color hue is mostly influenced by the presence of clays and different impurities or other mineral oxides, e.g. MnO_2. While the yellow pigments contain hydrous ferric oxides, such as limonite ($FeO(OH) \cdot nH_2O$) or goethite (α-FeOOH) [9–13]. More, there is another yellow pigment called jarosite is based on potassium ferric sulfate hydroxide ($KFe_3(SO_4)_2(OH)_6$) [14]. This pigment was found in the wall paintings of Mereruka's tomb in Saqqara necropolis (the 6th Dynasty, ca. 2323–2150 BCE). But, there is no acceptable evidence for its application on purpose in the ancient Egyptian paintings.

In his fruitful study, Colinart [15] analyzed inorganic yellow pigments from the Old Kingdom till the Ptolemaic era. The study revealed minerals of gold, yellow ochre, jarosite-natrojarosite, and orpiment (As_2S_3). Also, FT-Raman and Raman microscopy were applied as non-destructive methods for pigment analysis from Tell el Amarna and the results gave important data about the painting materials of the Akhenaton period [16].

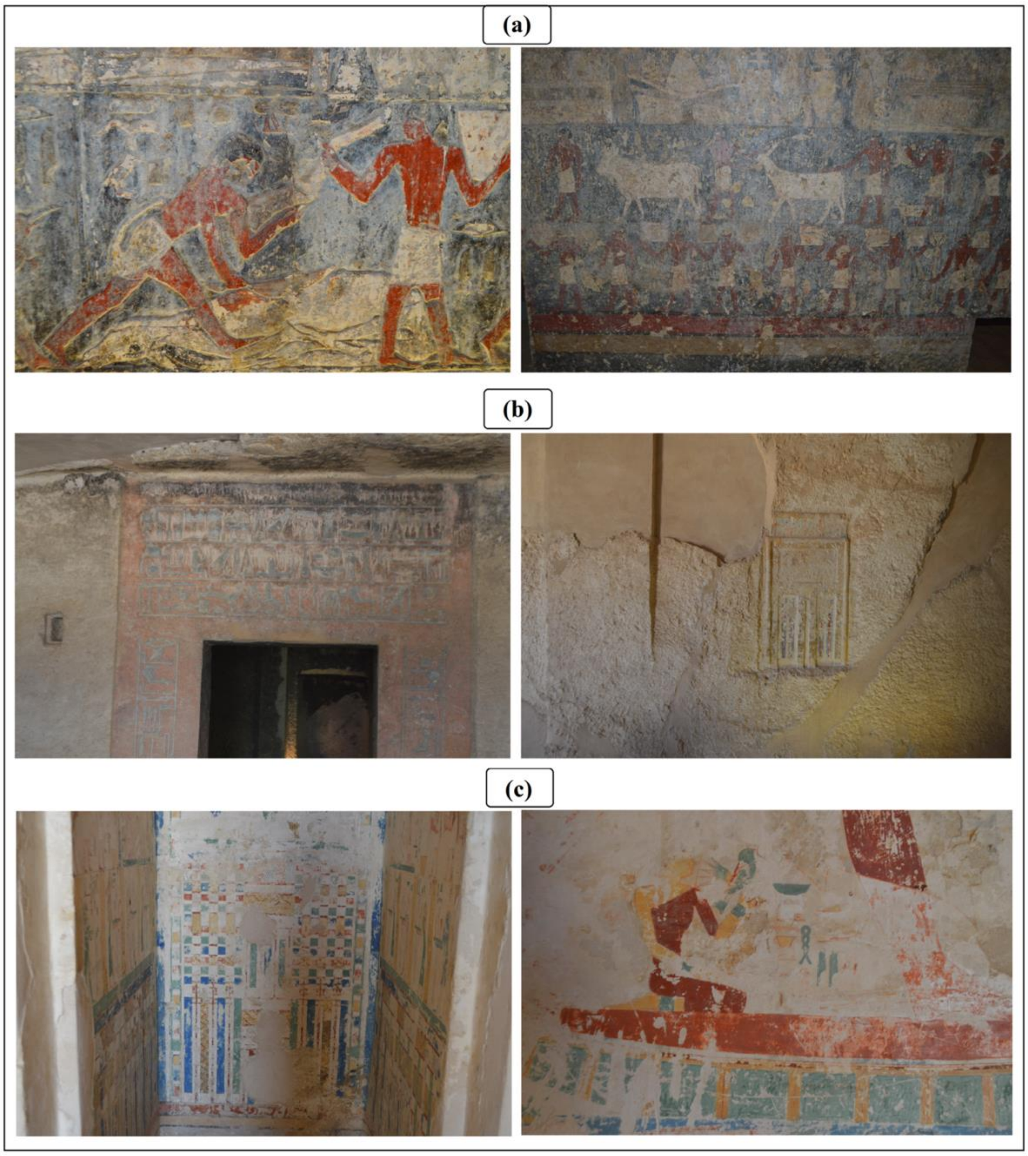

Figure 3. Examples of the painted wall reliefs of Meir tombs: a) Tomb of *Pepi-ankh* the youngest (A, No. 2), b) Tomb of *Senbi* II (B, No. 3), c) Tomb of *Ukhhotep* (C, No. 1).

On the other hand, a portable energy dispersive X-ray diffraction and fluorescence (ED-XRDF) spectrometry was developed for in situ analysis for the wall paintings of the tomb of Amenhotep III (c. 1386–1353 BCE) at Luxor. The results revealed pigments of huntite ($Mg_3Ca(CO_3)_4$, orpiment, Egyptian blue and goethite [17]. In addition, X-ray absorption fine structure (XAFS) analysis was applied successfully to study archaeological and modern produced Egyptian blue and green pigments [18].

The present research aims to add to the knowledge some data about painting materials used in the wall reliefs of Meir rock tombs at Assiut, Egypt. The samples were analyzed using some analytical methods including optical and polarized light microscopy, scanning electron microscopy, X-ray diffraction analysis, and FTIR spectroscopy.

2. MATERIALS AND METHODS

2.1 SAMPLES

Samples representing the used pigments and the rock painting support were collected and studied. The pigment samples included blue, green, red-orange, and black hues. The samples were collected mainly from the tombs (A, No. 2 and C, No. 1) using nondestructive methods.

2.2 METHODS

The samples' surfaces were first examined using a DigiMicro Mobilednt-USB microscope (dnt GmbH, Dietzenbach, Germany) at magnifications between 50x and 100x. Stone samples of the bed rock structure were prepared as thin-sections to study their petrographic characteristics.

The sections were examined with a Nikon Eclipse-E600 polarized microscope (Nikon Instruments Inc, Japan). The images were collected by a PixeLINK PL-A623 digital camera. Samples' morphology and their chemical investigation were performed using a field emission scanning electron microscope ZEISS Gemini Sigma 300 VP (ZEISS International, Germany). The samples were coated with gold and the instrument power was kept at 30.00 kV.

The FTIR spectra were recorded using a JASCO FTIR–460 plus spectrometer (JASCO, Easton, MD, U.S.), on the prepared KBr disks of the samples. A scanning range in the region 4000–400 cm^{-1} at spectral resolution of 4 cm^{-1} was applied during the analysis.

The mineralogical content of the studied samples was measured by a Philips PW 1840 X-ray diffractometer (Philips Healthcare, Amsterdam, Netherlands). The instrument was worked using 45 kV power/30 mA, Cu(Kα) radiation and wavelength of 1.54060 Å.

3. RESULTS AND DISCUSSION

3.1. MICROSCOPIC EXAMINATIONS

Fig. 4 shows the microscopic examination of the studied samples. In Fig. 4a, the blue-colored sample under a microscope with a magnification of up to 150x shows the appearance of a slightly thick layer with coarse irregular granules, which suggests the use of an artificial blue pigment. Compared to natural oxides, artificial pigments are usually characterized by coarse big-size grains.

Fig. 4b shows a microscopic image recorded on the green-colored sample, hence, a green hue together with a few dark blue grains and yellow particles were observed together with dark glossy pacthes (on the detailed iamge on the right).

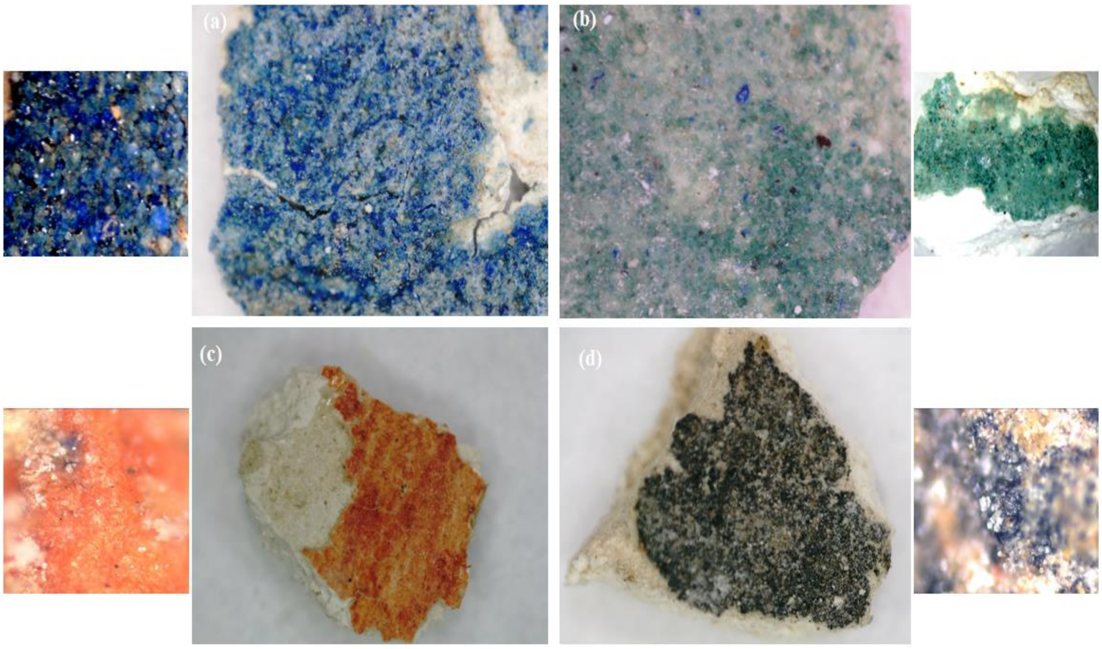

Figure 4. Microscopic photomicrographs obtained on a) blue paint layer from the tomb (C, No. 1), b) green paint layer from the tomb (C, No. 1), c) red-orange paint layer from the tomb (A, No. 2), d) black paint layer from the tomb (A, No. 2).

Well, this gives an indication that a pigment mixture was used to create the green color rather than using a single green pigment material. The microscopic image of the red-orange color is given in Fig. 4c. The image shows a glossy cracked surface with black grains scattered on the surface.

An exposed area on the surface clearly shows the underlying preparation layer (representing the whitewash coat). The surface of the black pigment sample shows multi-sized grains with salt deposits clearly noticed.

For the rock samples, some thin sections on the bedrock of the area were examined by a polarized light microscope. The photomicrographs of the sections, under the plane and cross-polarised light, show the wackestone/packstone microfacies with a fine-grained micritic matrix with considerable non-carbonates groundmass (Fig. 5, up). More, some recrystallized packstone grains and microquartz are observed in the sections (Fig. 5, down).

3.2. MORPHOLOGY AND MICROANALYSIS

Fig. 6 shows SEM-EDX analysis of the blue and green pigment samples. In Fig. 6a, the surface morphology of the blue pigment shows centered coarse crystals. EDX spectrum of the sample revealed the atomic concentrations of silicon (Si, 12.24%), calcium (Ca, 7.46%) and copper (Cu, 2.03%) are present as the main elements in the sample. The microscopic appearance of the blue pigment and the elements measured through the EDX chemical analysis suggest that the artificial Egyptian blue was used for painting in the studied tombs.

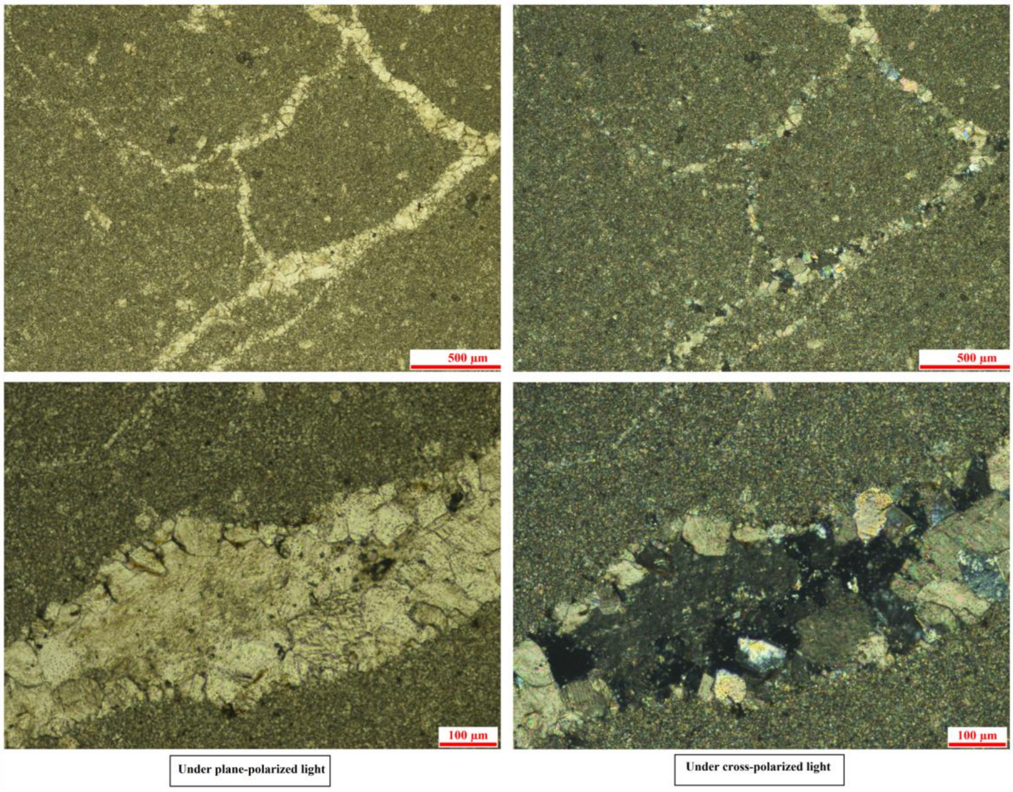

Figure 5. Photomicrographs, under plane and cross-polarized light, of thin-sections of the rock samples.

This pigment is based on a calcium copper tetra-silicate mineral named cuprorivaite, $CaCuSi_4O_{10}$. This pigment was appeared most probably about 2600 BC. The manufacturing process of the pigment material was performed *via* heating natural raw materials included desert sand, limestone blocks, copper ore and an alkali material of natron salt (hydrated Na_2CO_3) [19].

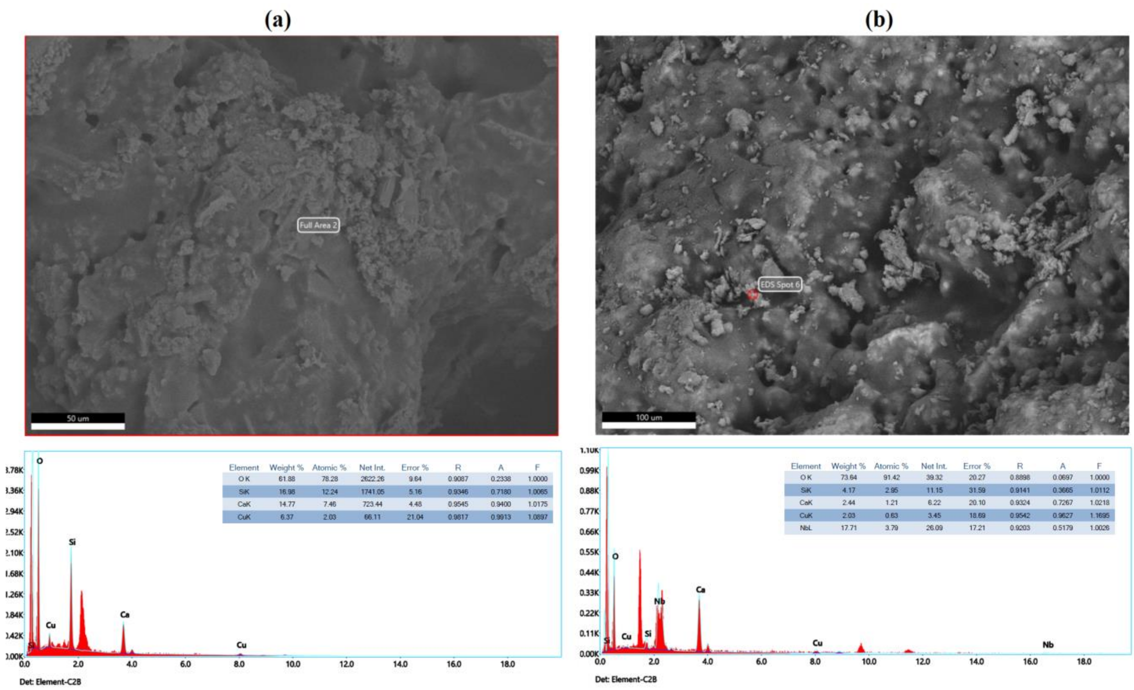

Figure 6. SEM images and EDX spectra obtained on: a) blue pigment sample, b) green paint layer.

Vitruvius referred that irregular balls of the abovementioned raw materials, which are usually ground into a fine powder and mixed with an organic binder, are heated in earthen jars at a temperature of about 950°C [20]. The study of Tite et al. [21] emphasized the relationship between the Egyptian blue color and its composition, they found that the size of the crystal aggregates plays a major factor in the produced hue. More, the stability of the Egyptian blue pigment can be explained by the stable silicate matrix which is the major content of the pigment [22, 23].

For the green paint sample (Fig. 6b), the pigment morphology appears as a glossy compacted surface. EDX microanalysis of the samples gave concentrations of silicon (Si, 2.95%), calcium (Ca, 1.21%), and copper (Cu, 0.63%). Since the optical microscopic examination revealed some blue and yellow particles along the green-painted surface, a mixture of Egyptian blue and yellow ochre (Fe-rich clay) was used to produce the green hue. Scott [24] stated that mixing amounts of pigments together was used in ancient Egypt to create different hues such as pink, grey, and green. Edwards et al. [25] reported that the green color can be achieved through an admixture of blue and yellow pigments (orpiment or ochre). Fig. 7 (a, b) shows SEM-EDX spectra obtained on different points on the red-orange pigment sample. In the images, the morphology of the pigment grains appears as fine aggregates together with large coarse grains of the underlying render layer.

The EDX analysis on several points on the sample revealed the main elements of silicon (Si), calcium (Ca), and sulfur (S) which reflect the components of the render layer. The variable concentrations measured of iron (Fe, 0.74–1.79%) are responsible for the red color. A scanning electron image of the black pigment (Fig.7c) describes large clusters of carbon that are clearly observed. It is probable that the pigment was obtained from plant origin (charcoal).

Typically through the chemical analysis, a high concentration of carbon was measured. The ancient Egyptians used carbon black from many sources such as soot, charcoal, charred bones, and in some cases, magnetite (Fe_3O_4). The latter was reported mainly in decorations from Graeco-Roman tombs in the Western Desert of Egypt [26].

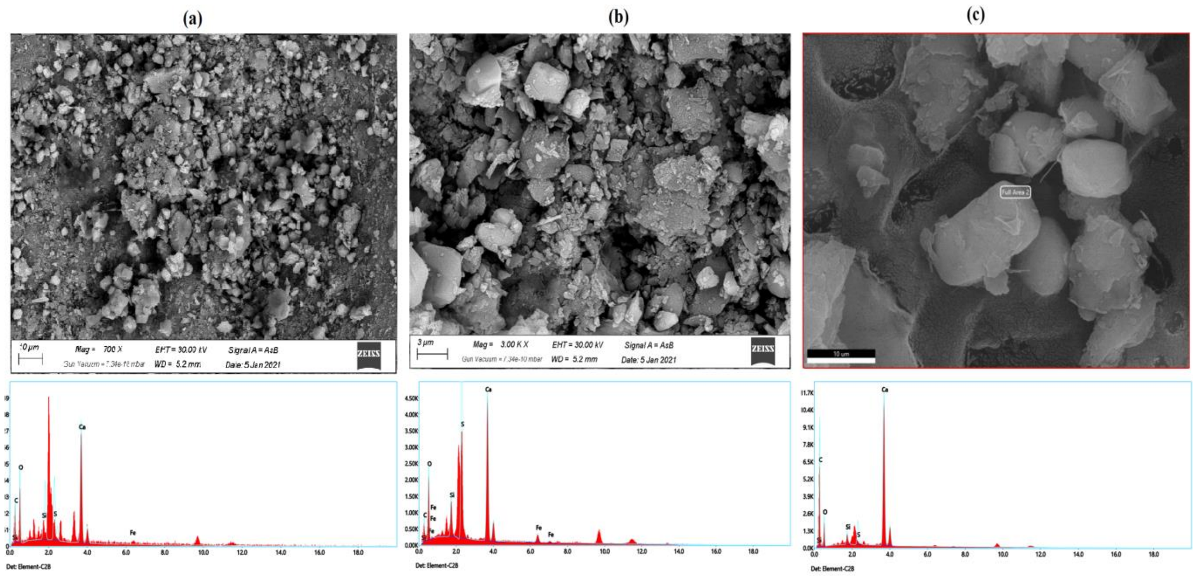

Figure 7. SEM images and EDX spectra obtained on: a, b) red-orange pigment sample, c) black paint layer.

3.3. MOLECULAR ANALYSIS

Fig. 8 shows FTIR spectra recorded on the blue pigment and the preparation layer sample. The spectra of the blue pigment sample (Fig. 8a) showed a number of featured peaks at 1425, 875, and 711 cm^{-1}, are for carbonate stretching vibrations that refer to calcium carbonate minerals (calcite, $CaCO_3$). The peaks around 1150−1180 cm^{-1} are for siliceous materials from the sand filler in the studied layer. The bands at 3400 and 1620 cm^{-1} are indications on the presence of gypsum (calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$) [27–30].

These findings suggest that a mixture of calcite and gypsum was used to refine the reliefs before applying the pigment materials. In the studied area, dense Eocene limestone formations which belong to the Drunka formation are occurred [31]. Gypsum and anhydrite occur together in many Miocene formations in Egypt and quarries are spread in many locations in Egypt, mainly along the Red sea coast [32].

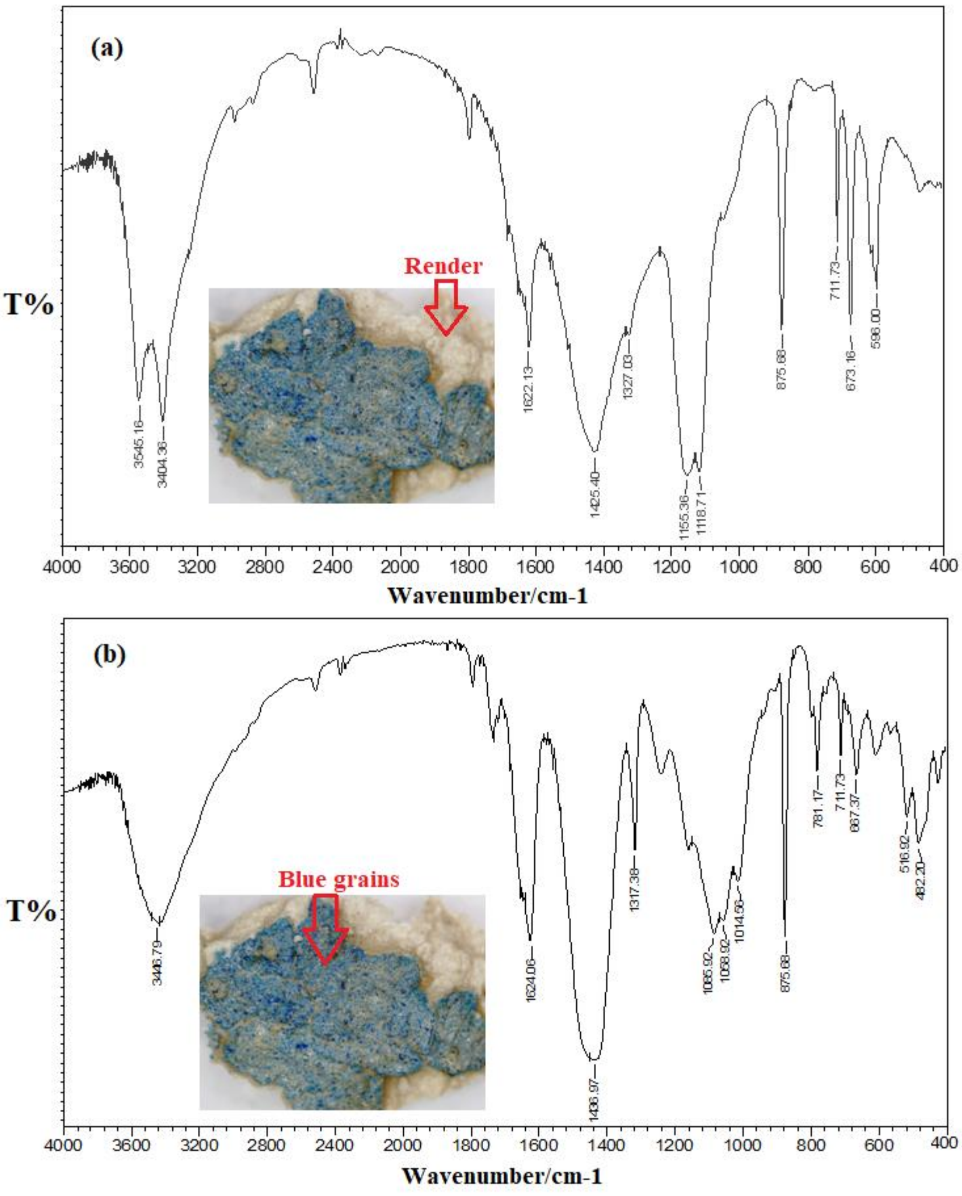

Figure 8. FTIR spectra recorded on a) render layer, b) blue paint layer.

In Fig. 8b, the FTIR spectrum recorded on the blue pigment is given. Two characteristic peaks around 1000 cm^{-1}, are mainly for the Si−O−Si stretching vibrations in the pigment matrix. The other bands observed through the spectrum are contamination minerals from the underlying render layer. The sharp band recognized at 1317 cm^{-1} is probably attributed to the CH_2 wagging mode. This band together with a small one near 1200 cm^{-1} is most likely associated with an organic matter (e.g., polysaccharides of gum Arabic) [33, 34]. The ancient Egyptian decorations were executed usually using the tempera technique by mixing the pigment fine powder with an organic binder.

3.4. MINERALOGICAL ANALYSIS BY XRD

Fig. 9 represents XRD patterns obtained on stone and pigment samples. The pattern of the stone sample shows calcite as the sole mineral contained in the sample. The blue pigment samples showed cuprorivaite as a major component in the sample together with minor amounts of quartz (SiO_2). In his study of pigments from the tomb of Nefertari, Valley of the Queens, Luxor, Saleh [35] mentioned that the blue pigment sample was of Egyptian blue mixed with wollastonite ($CaSiO_3$), quartz, and tridymite (a stable form of SiO_2) with other impurities.

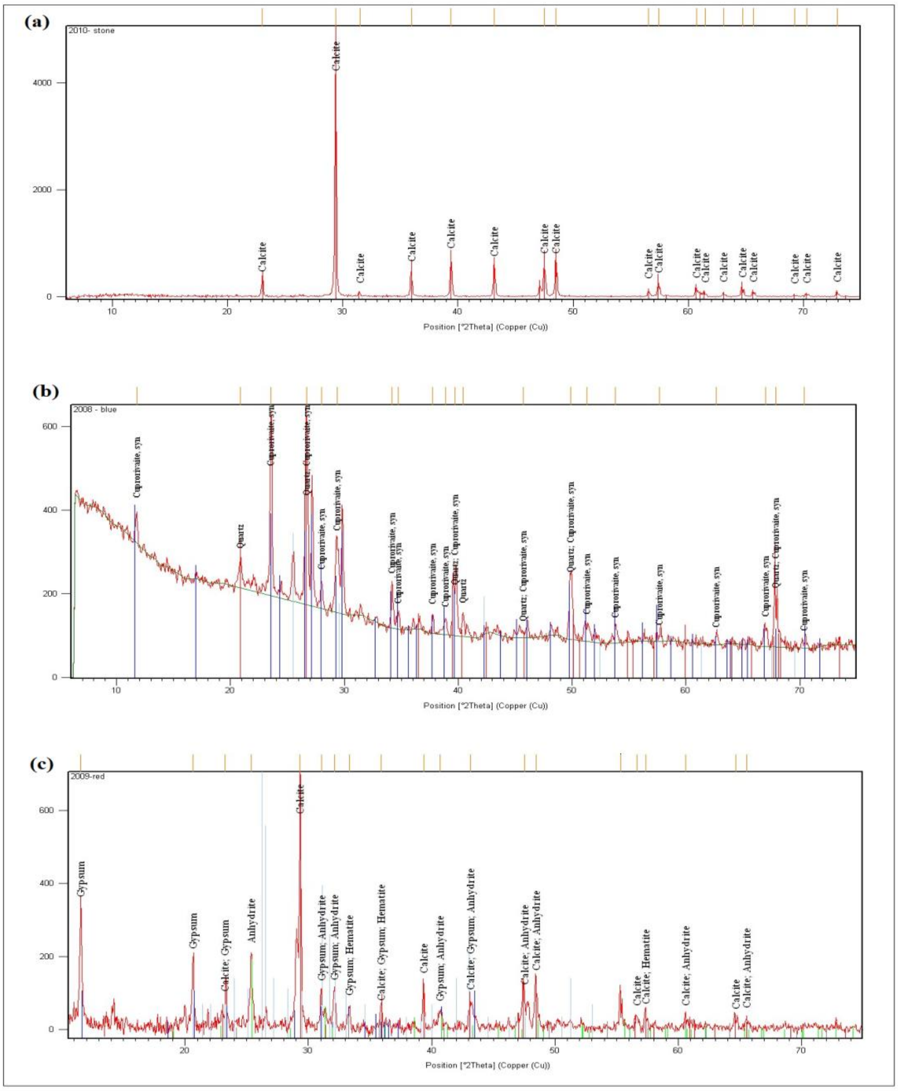

Figure 9. XRD patterns of a) rock sample, b) blue paint layer, c) red-orange paint layer.

For the red pigment sample, mineral phases of hematite, calcite, gypsum, and anhydrite were reported. Red ochre was applied extensively in wall decorations in the ancient Egyptian eras to the Roman times. Ochre usually contains hematite associated with other minerals (e.g. quartz, clay minerals (e.g. kaolinite), K-feldspar ($KAlSi_3O_8$), etc.) [36–40].

The results obtained by different analytical methods (OM, SEM-EDS, XRD and FTIR) are presented in Table 1.

Table 1. Conclusion of the results obtained from the analytical methods used to study the samples

Sample	Microscopical microscopy (OM)	SEM-EDX	XRD	FTIR
Stone support	Wackestone/packstone on micritic matrix.	Ca, Si	Calcite ($CaCO_3$)	–
Render layer	Thin layer of whitewash (up to 2 mm)	Ca, S, Si	Gypsum ($CaSO_4·2H_2O$), Calcite	Calcite bands at 1425, 875 and 711 cm^{-1}. Gypsum appears 1622 and 3404 cm^{-1}. Silicate bands around 1100 cm^{-1}.
Blue pigment	Slightly thick paint layer with coarse dark and light blue particles	Si, Ca, Cu	Cuprorivaite ($CaCuSi_4O_{10}$), Quartz (SiO_2)	Silicate bands are observed at around 1000 cm^{-1}. Other minerals of calcite and gypsum are also found.
Green pigment	A thick layer with different blue green hues and yellow particles	Si, Ca, Cu, Fe?	–	–
Red-orange pigment	Irregular cracked glossy layer with red-orange hue and black particles	Si, Fe, Ca, S	Hematite (α-Fe_2O_3), Calcite, Gypsum, Anhydrite ($CaSO_4$)	–
Black pigment	Coarse black particles are distributed together with salt patches	C	–	–

4. CONCLUSIONS

In the present study, microscopic, mineralogical, and spectroscopic methods were used for the first time to characterize some painting materials used in the wall reliefs of the Meir rock tombs of ancient Egypt. The microscopic examination allowed for obtaining useful information about the surface and the appearance of sample grains. The polarized light microscopy allowed the understanding of the stone's petrographic features as micritic-based limestone.

The surface morphology and microanalysis, through SEM-EDX, were used to investigate the render layer and pigment samples. The render layer was identified as well, by XRD and FTIR methods, as a mixture of calcite ($CaCO_3$) and gypsum ($CaSO_4·2H_2O$). The blue pigment was examined as coarse dark and light blue grains. It was concluded that the ancient Egyptian artists used synthetic Egyptian blue ($CaCuSi_4O_{10}$) to paint the tombs.

In the case of the green paint layer, most probably that a mixture of Egyptian blue and yellow ochre (α-FeOOH associated to clay minerals) was preferred. The red-orange pigment was routinely applied using red ochre (α-Fe_2O_3, associated to clay minerals).

Ochre pigments were used for decorations in ancient Egypt since the predynastic period. The black pigment was classified as carbon black (graphite), probably from a plant origin. The results are considered the first record of the pigments' origin and their chemical-mineralogical nature through an analytical approach. As an important phase in any restoration intervention, the analytical outcomes of the present study will be utilized in the conservation of the painted reliefs of the tombs.

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