Ge-conservación
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# Material characterization and restoration of mural paintings of El-Muzzawaka Tombs, Dakhla Oases, Egypt

**Mona F. Ali, Hanaa Shawki, Hussein Marey Mahmoud**

**Abstract:** The present study demonstrates scientific procedures applied to study mural paintings in two Graeco-Roman tombs of El-Muzzawaka, Dakhla Oases, Egypt. First, a series of analytical methods was applied to determine the chemical and mineralogical composition of pigment and plaster samples collected from the studied tombs. The analyses were performed by means of digitalized optical microscopy (OM), polarized light microscopy (PLM), scanning electron microscopy attached with X-ray microanalysis detector (SEM–EDS), X–ray diffraction analysis (XRD), and Fourier transform infrared spectroscopy (FT–IR). Analyses of the pigment samples revealed Egyptian blue, Egyptian green, green earth, black magnetite, and red/yellow ochres. The paintings were applied on a coarse plaster layer made of gypsum, anhydrite, calcite, and quartz. The preparation layer was made of two phases of calcium sulphate (gypsum and anhydrite). Further, the detection of an organic binder, of gum Arabic, confirms the application of tempera technique. The results showed that the bed rock samples contain variable amounts of quartz, anhydrite, montmorillonite, kaolinite, gypsum, and sodium chloride (halite). In situ observations showed several deterioration forms on the studied mural paintings. The destructive climatic condition of the region and the defects of the rock structure have contributed seriously in the deterioration process. Based on experimental tests, multi restoration procedures were applied in form of cleaning, reattaching paint flakes, applying injection grouts to detached layers, reconstruction of missing parts in the plaster, repair of wide-open cracks, and final protective consolidation of the painted surfaces. Further, recommendations to minimize any future damage were discussed.

**Keyword:** Dakhla Oases, El-Muzzawaka Rock tombs, mural paintings, SEM–EDS, XRD, FT–IR, deterioration, restoration

## Caracterización de materiales y restauración de pinturas murales de las tumbas de El-Muzzawaka, Dakhla Oases, Egipto

**Resumen:** El presente estudio demuestra procedimientos científicos aplicados al estudio de pinturas murales en dos tumbas grecorromanas en El-Muzzawaka, Dakhla Oásis, Egipto. Primero, se aplicó una serie de métodos analíticos para determinar la composición química y mineralógica de las muestras de pigmento y yeso recolectadas de las tumbas estudiadas. Los análisis se realizaron mediante microscopía óptica digital (OM), microscopía de luz polarizada (PLM), microscopía electrónica de barrido acoplada a un detector de microanálisis de rayos X (SEM-EDS), análisis de difracción de rayos X (XRD) y infrarrojo por transformada de Fourier. espectroscopia (FT-IR). El análisis de las muestras de pigmento reveló azul egipcio, verde egipcio, tierra verde, magnetita negra y ocre rojo / amarillo. Las pinturas se aplicaron sobre una gruesa capa de yeso a base de yeso, anhidrita, calcita y cuarzo. La capa de preparación estaba compuesta por dos fases de sulfato de calcio (yeso y anhidrita). Además, la detección de un aglutinante orgánico, la goma arábiga, confirma la aplicación de la técnica de revenido. Los resultados mostraron que las muestras de lecho rocoso contienen cantidades variables de cuarzo, anhidrita, montmorillonita, caolinita, yeso y cloruro de sodio (halita). Las observaciones in situ mostraron varias formas de deterioro en las pinturas murales estudiadas. La condición climática destructiva de la región y los defectos en la estructura de la roca han contribuido seriamente al proceso de deterioro. Sobre la base de pruebas experimentales, se aplicaron múltiples procedimientos de restauración en forma de limpieza, reposición de escamas de pintura, aplicación de juntas en capas desprendidas, reconstrucción de partes faltantes en el yeso, reparación de grietas abiertas y consolidación protectora final de superficies pintadas. Además, se discutieron recomendaciones para minimizar cualquier daño futuro.

**Palabras clave**: Oasis de Dakhla, tumbas rupestres de El-Muzzawaka, pinturas murales, SEM–EDS, XRD, FT–IR, deterioro, restauracion

## Caracterização dos materiais e restauro de pinturas murais das tumbas de El-Muzzawaka, Dakhla Oases, Egito

**Resumo**: O presente estudo mostra os procedimentos científicos aplicados ao estudo de pinturas murais de duas tumbas greco-romanas de El-Muzzawaka, Dakhla Oásis, Egito. Numa primeira fase aplicaram-se diversos métodos analíticos para determinar a composição química e mineralógica de amostras de pigmento e gesso recolhidas das tumbas estudadas. As análises foram realizadas por meio de microscopia ótica (OM) digital, microscopia de luz polarizada (PLM), microscopia eletrónica de varrimento acoplada a detector de raios X (MEV - EDS), análise por difração de raios X (DRX) e espectroscopia de infravermelho por transformada de Fourier (FTIR). As análises das amostras de pigmento revelaram azul egípcio, verde egípcio, terra verde, magnetita preta e ocres vermelho / amarelo. As pinturas foram aplicadas sobre uma camada de gesso grosso constituída por gesso, anidrite, calcite e quartzo. A camada de preparação é composta por duas fases de sulfato de cálcio (gesso e anidrite). Além disso, o recurso à técnica a têmpera é confirmada pela deteção de um aglutinante orgânico, a goma-arábica. Os resultados mostraram que as amostras de leito rochoso contêm quantidades variáveis de quartzo, anidrite, montmorilonite, caulinite, gesso e cloreto de sódio (halite). As observações in situ mostraram várias formas de deterioração nas pinturas murais estudadas. A condição climática destrutiva da região e os defeitos da estrutura rochosa têm contribuído seriamente para o processo de deterioração. Com base em testes experimentais forma usados múltiplos procedimentos de restauro, designadamente limpeza, fixações, consolidação por injeção, reconstrução de partes do gesso em falta, reparação de fissuras abertas e consolidação protetora final das superfícies pintadas. Além disso, foram discutidas recomendações para minimizar quaisquer danos futuros.

**Palavras-chave:** Dakhla Oásis, tumbas de Rocha El-Muzzawaka, pinturas murais, SEM - EDS, XRD, FTIR, deterioração, restauro

## Introduction

El-Muzzawaka necropolis is a significant cut-rock archaeological site in the Dakhla Oases located in the Western Desert of Egypt (Figure 1a). The necropolis is highly attributed to the Roman occupation of the Oases (Bashendi 2009). There is a number of five hundred tombs in the site, which was discovered into three levels of the hill cliffs. By early the 19th century, some travellers to the Oases have reported several rock tombs and other tombs built of brick. In 1908, the tombs were first reported by Herbert Winlock, an American archaeologist. Later in 1972, Ahmed Fakhry, an eminent Egyptian archaeologist, rediscovered and documented the tombs. These tombs were cut in the rock using different styles, including square, rectangular and oval shapes. The schematic plan of the tombs is very simple that contains single burial chamber or two chambers connected together with a doorway with niches to host mummies [Figure 1b]. The most important tombs in the site are the tombs of Petosiris and Petubastis. The tomb of Petosiris has two chambers and probably dates back to the early of the second century A.D. (Whitehouse 1998). While, the tomb of Petubastis dates back to the first century A.D and consists of a featured decorated single chamber. Notably, the tombs were decorated with scenes that represent both Pharaonic and classical artistic styles (e.g. Zodiac ceiling) (Neugebaure 1982).

## Geologic setting

The Dakhla Oases are located in the Western Desert of Egypt (about 800 km south of Cairo). Based on geological literature data, the Oases of the Western Desert were formed due to the thickness of hard limestones and the groundwater table (Plyusnina et al. 2016). Stratigraphically, the Nubian sandstone formation forms the base of the geological structure of the studied area (Soltan 1999). Dakhla Oases were formed on several sedimentary rocks, Cenomanian to Palaeocene age. A main geologic part in the site is the Dakhla

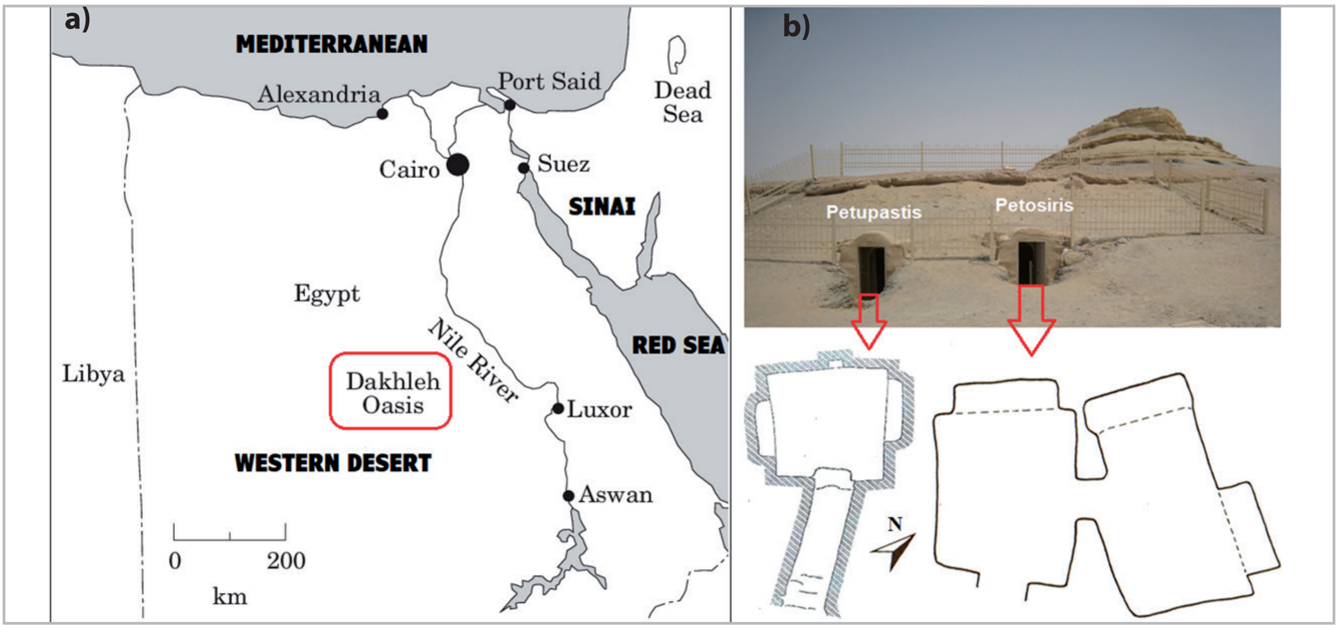


**Figure 1**.- (a) Map of Egypt, location of the Dakhla Oases is highlighted with a red rectangle. (b) View of El- Muzzawaka rock tombs, the arrows show schematic plans of the studied tombs.

Formation Shale, which measures a 230 m thickness of shales and mudstones. Further, Eocene Limestone plateau contributes largely not only in the Dakhla Oases, but in the whole Western Desert. In Figure 2, the geological structure of the hills is clearly observed. It is noticed that the rock is characterized with laminae interventions of gypsum and anhydrite (Helmi 2000). Besides, the occurrence of chert nodules together with clay minerals was also reported.

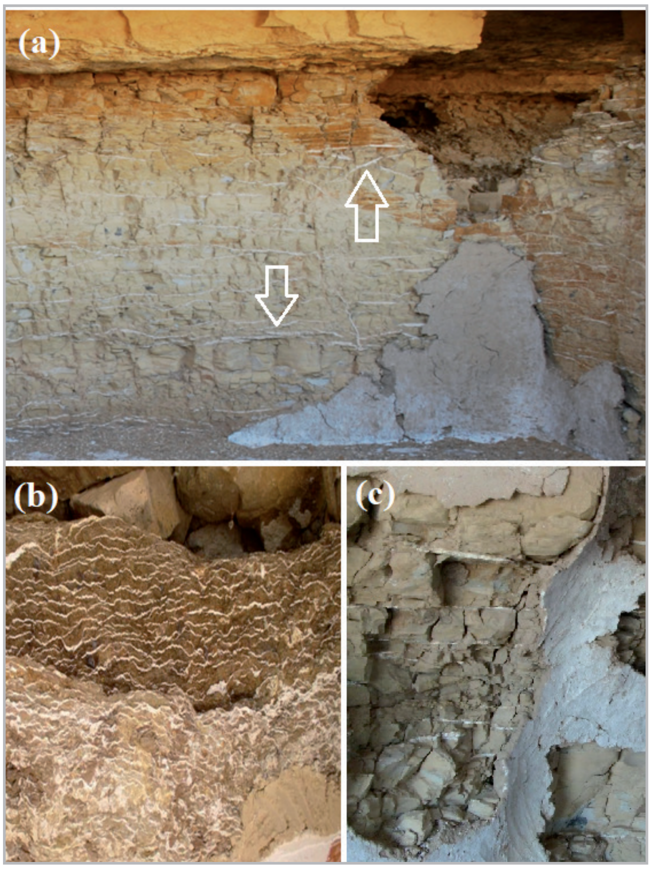


**Figure 2**.- (a) laminate layers of gypsum-anhydrite in the geological structure of the tombs, (b) chert nodules are observed in the rock structure, (c) Detachments of plaster layers due to the heterogeneity of the geological structure.

In fact, several researches have studied ancient Egyptian and Graeco-Roman sites in the Western Desert of Egypt. The Dakhla Oases Project has achieved systematic archaeological-conservation expeditions to many sites in the Dakhla (http://dakhlehoasisproject.com/). Important activities have been undertaken to study and conserve mural paintings at the Amheida site from the Roman age. Building materials of mud brick and limestone were studied from the site of Ain el-Lebekha at Kharga Oasis (the 2nd and 5th centuries AD) (Abdel Aal 2019). Multi-analytical techniques were used to identify painted fragments from Qasr el-Ghuieta temple at Kharga Oasis (from the Late Period and the Ptolemaic era) (Marey Mahmoud 2014). Common pigments were identified in the site, mainly Egyptian blue, ochre pigments, and green earth. In addition, pigment mixtures were used to create specific color hues. Additionally, an extensive coloring palette was used in the Roman temple of Dier-El Hagar at the Dakhla Oases. The findings were almost similar to those of the ancient Egyptian temples (Marey Mahmoud et al. 2019). In 1998, the Supreme Council of Antiquities of Egypt (SCA) decided to close the tombs of Petosiris and Petubastis to public due to serious geotechnical problems. In fact, the geological structure of the area, mainly the marl-shale formation -which has the potential to expand and shrink dramatically- usually results in form of a serious structural damage. Figure 3 illustrates some deterioration forms recorded on the studied murals.


**Figure 3**.- Examples of deterioration forms on the wall decorations of El-Muzzawaka tombs (e.g. plaster loss and several cracks) (a), (b) the tomb of Petosiris, (c), (d): the tomb of Petubastis.

Further, the rock structure displays several faults, major cracks and heavy rock slabs which cause catastrophic rock collapse and loading of overburden on the pillars and ceilings of the tombs. In old restorations of the tombs, metal framing elements were added to reinforce the ceilings of the tombs. Unfortunately, these iron bars caused additional pressure and induced weakening to the ceilings and the painted plasters [Figure 4].


**Figure 4**.- (a) geotechnical defects in the rock structure of the areas, (b) failure of the ceiling of the tombs and the iron bars used in old restorations of the tombs.

The main task of the present study was determined to study painting materials from El-Muzzawaka tombs at the Dakhla Oases and to examine their state of preservation. Afterwards, the results of the analytical methods conducted on stone and painted layers were interpreted and discussed. Thus, a restoration-conservation project was applied to preserve the murals and to minimize the main forms of damage.

## Materials and methods

**—***Samples*

Four rock samples were collected from the rock cliffs. Samples of painted flakes and small-size fragments were collected. The sampling process respected the sate of preservation of the painted walls. To cover the chromatic hues used in the tombs, six samples were collected from the tomb of Petosiris (with approximate dimensions of 0.5 cm to 2 cm), together with seven samples collected from the tomb of Petubastis (with approximate dimensions of 0.5 cm to 1 cm).

**—** *Restoration products*

- Kemtekt 20: a ready-to-use silicon polymer, produced by CMB Group, Egypt.
- Addicrete BVD: Sodium Gluconate, produced by CMB Group CMB Group, Egypt.
- Primal AC33: an acrylic emulsion based on ethyl acrylate-methyl methacrylate co-polymer, produced by Rohm and Hass Co., USA.
- Microballoon: a bulking agent of hollow glass particles, produced by C.T.S Italy.
- Bentonite: an aluminium phyllosilicate clay.
- Butanone: methyl ethyl ketone, produced by Sigma-Aldrich.
- Repair mortar: a traditional mortar was used to re-fill the missing parts in the plaster layers. The mortar is based on quicklime, crushed marl and washed river sand.

**—** *Optical microscopy*

The samples were first observed by an USB digital microscope (HD Color Comos Sensor, High Speed DSP). Also, some thin sections of rough rock and plaster layers were prepared and observed using a Polarizing/ Dispersion Microscope Eclipse LV100- UDM-POL/DS.

**—** *Scanning electron microscopy*

The morphological behaviour of stone and plaster samples was investigated by a JEOL JSM-840A scanning electron microscope (SEM). The operating conditions of the microscope were set at a voltage reached 20 kV and probe current of 45 nA. The chemical analysis of the contained elements in the samples was determined using an energy-dispersive X-ray spectrometer (EDS).

**—** *FT-IR analysis*

Few milligrams of the powdered paint samples were removed for FT–IR analysis. KBr discs were analyzed in the transmittance mode using a Shimadzu (AA-6300) Fourier transform infrared spectrometer. The spectrometer was operated in the mid-IR region (4000-400 $cm^{-1}$).

**—** *X-ray diffraction analysis*

The mineral components of samples were measured by X-ray diffraction analysis technique (XRD). Stone and plaster powder samples were scanned on a XRD Philips Diffractometer type (Pw1840) using CuKα1 radiation (with λ=1.540562 Å) at 40 kV and 50 mA.

## Results and discussion

Table 1 shows the main components determined for the studied samples.

**—***Characterization of bed rock samples*

SEM micrograph recorded on a bed rock sample shows heterogeneous distribution of siliceous aggregates together with clay clusters [Figure 5a]. The elemental analysis of the sample, performed by EDS analyzer, indicated the detection of iron (Fe), silicon (Si), calcium (Ca), aluminium (Al), sulphur (S), sodium (Na), potassium (K), and chlorine (Cl) [Figure 5b]. The XRD analysis of the sample measured minerals of quartz ($SiO_2$), calcite ($CaCO_3$), anhydrite ($CaSO_4$), montmorillonite $(Na, Ca)_{0.3}(Al, Mg)_2Si_4O_{10}(OH)_2 \cdot n(H_2O)$, kaolinite ($Al_2Si_2O_5(OH)_4$), gypsum ($CaSO_4 \cdot 2H_2O$), and sodium chloride (halite, NaC1) [Figure 6].

In her study of the deterioration mechanisms affecting El-Muzzawaka tombs, Helmi (2000) demonstrated that the serious damage of the tombs is highly linked to the swelling of smectite clay minerals (e.g. montmorillonite) and the transformation of gypsum into anhydrite occurred between the clay layers. Well, the deterioration becomes more destructive in the presence of salts.

Thus, the osmotic swelling of clays, in combination of the crystallization/hydration pressure of salts, will result in form of several cracks and detachments of the plaster layers (Marey Mahmoud 2010).

**Table 1**.- Summary of the main findings obtained from the analytical methods of the studied samples.

| Sample | Tomb of Petubastis | Tomb of Petosiris |
|---|---|---|
| | Component | |
| Bed rock | Quartz ($SiO_2$), Anhydrite ($CaSO_4$), Calcite ($CaCO_3$), Montmorillonite $(Na, Ca)_{0.3}(Al, Mg)_2Si_4O_{10}(OH)2 \cdot n(H_2O)$, Kaolinite ($Al_2Si_2O_5(OH)_4$), Gypsum ($CaSO_4 \cdot 2H_2O$), Halite (NaCl) | |
| Plaster layer | Anhydrite, Quartz, Calcite, Gypsum | |
| Render | Gypsum, Anhydrite | |
| Blue pigment | Egyptian blue ($CaCuSi_4O_{10}$) | - |
| Green pigment | Dark green: Egyptian blue and yellow ochre; Light green: Green earth (celadonite) | Egyptian green [$(Ca,Cu)_3Si_3O_9$] Green earth (celadonite) |
| Red pigment | Red ochre ($\alpha Fe_2O_3$, clay minerals and quartz) | |
| Yellow pigment | Yellow ochre ($\alpha FeO \cdot OH$, clay minerals and quartz), | |
| Black pigment | Magnetite ($Fe_3O_4$) | |
| Paint binder | Gum Arabic | |
| Deterioration forms | Sodium chloride (NaCl) in both tombs and atacamite ($Cu_2Cl(OH)_3$) in the green pigment from the tomb of Petubastis | |

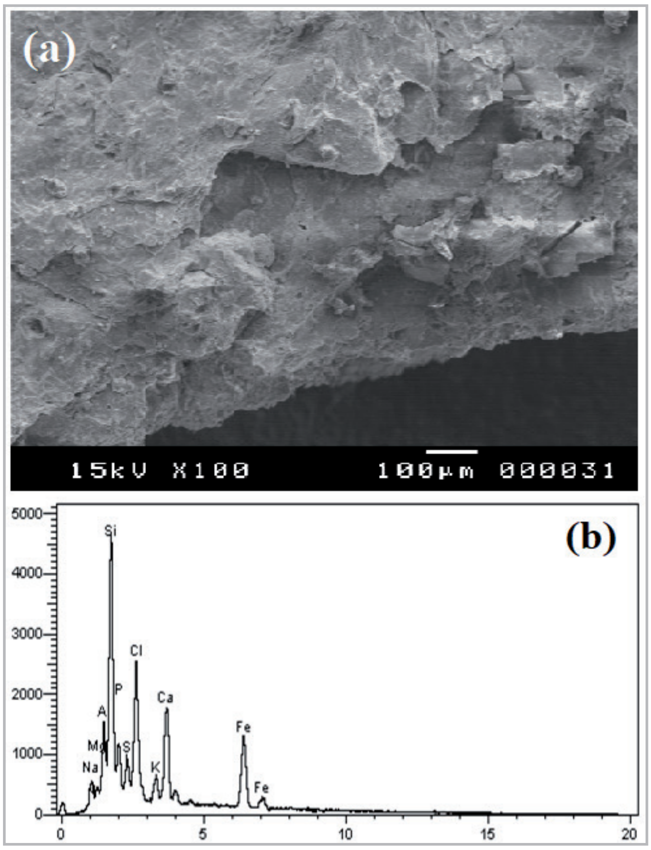


**Figure 5**.- (a) SEM micrograph shows morphology of the studied rock sample. (b) An EDS spectrum of the sample.

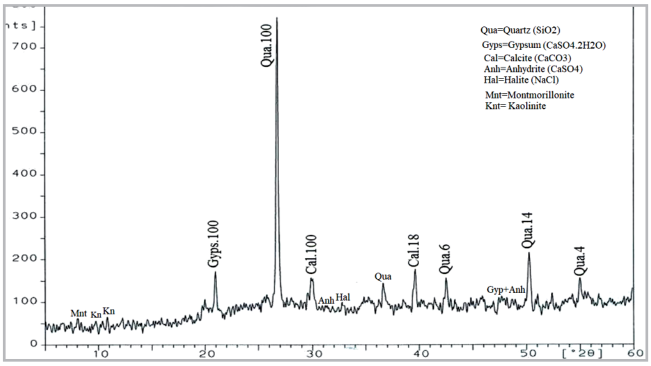


**Figure 6**.- XRD pattern of the bed rock sample.

**—*Characterization of plaster samples***

The optical examination on a cross-section of rough plaster sample from the tomb of Petubastis shows irregular layer with large sub-rounded quartz grains blended with the white binder [Figure 7a]. The petrographic description of the plaster sample revealed large siliceous granules with different shapes embedded in the binder [Figure 7b]. The EDS spectrum measured on the sample shows high concentrations of calcium (Ca) and sulphur (S). Elements of silicon (Si), aluminium (Al), iron (Fe), potassium (K), and chlorine (Cl) were also noticed [Figure 7c]. While large voids and high porosity of the matrix were observed in the SEM micrograph of the sample [Figure 7d].

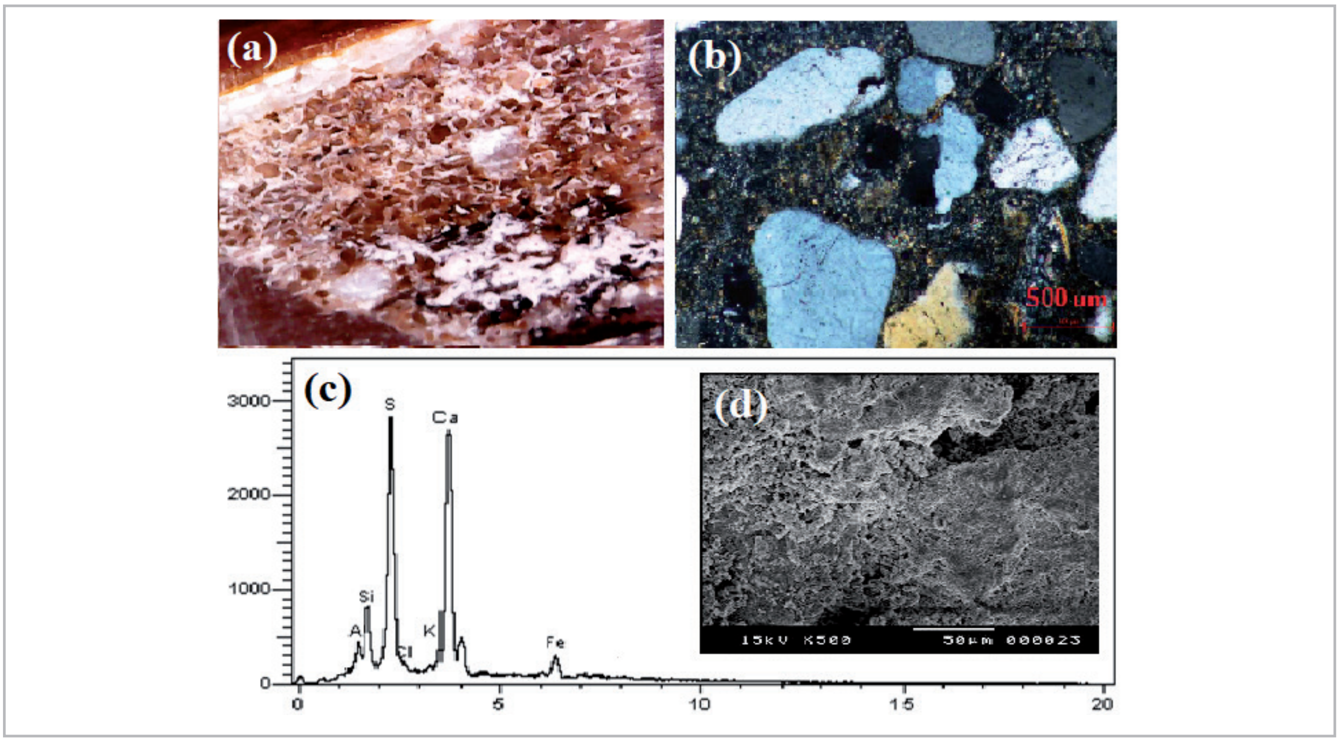


**Figure 7**.- (a) Microscopic image obtained on a rough cross-section of the plaster layer from the tomb of Petubastis, (b) Petrographic examination of thin-section of the sample. (c) An EDS spectrum of the sample. (d) The morphological feature of the sample though SEM.

Mineralogy of the plaster samples from the tomb of Petubastis, analyzed by XRD, showed that anhydrite is the major component while quartz is the secondary mineral contained in the sample. Accessory minerals of calcite ($CaCO_3$), gypsum, and sodium chloride (halite) were also determined. As well, the XRD results of the plaster samples from the tomb of Petosiris showed similar results to the samples of the tomb of Petubastis. Accordingly, the plaster layers were built up using anhydrite and gypsum. While, quartz and limestone were added as aggregates. The preparatory layer was almost of pure gypsum with traces of quartz. Geologists have reported that gypsum and anhydrite were obtained from quarries along the Red sea coast, and from the Fayoum Depression in the Western Desert (Harrell 2014). As well, another possible source for gypsum, from the gypsite deposits near Amarna (about 270 km south of Cairo), was also suggested (Harrell 2017).

**—***Characterization of pigments*

• Red pigments

The morphological investigation of red pigment sample from the tomb of Petosiris shows slightly fine pigment grains while the elemental analysis revealed major amounts of sulphur (S) and calcium (Ca), representing the render layer. Elements of iron (Fe) together with silicon (Si), aluminium (Al), chlorine (Cl), and potassium (K) were detected. Based on these results, the pigment was identified as red ochre (αFe2O3). Further, characteristic groups of silicates, sulphates, carbonates and carbohydrates were reported in the FT–IR spectrum [Figure 8].

As given in Figure 9, almost the same results were obtained for the red pigment samples from the tomb of Petubastis. Factually, ochre pigments are by far the most commonly pigments used from the pre-Dynastic period of ancient Egypt.

• Yellow pigments

Yellow pigment samples from both tombs were analyzed and compared. The SEM micrograph recorded on yellow pigment sample from the tomb of Petosiris shows fine pigment grains together with large siliceous particles. The elemental analysis showed the detection of high concentration of iron (Fe), referring to iron-based material. Other elements of calcium (Ca), sulphur (S), silicon (Si), aluminium (Al), and chlorine (Cl) were measured. The FT–IR spectrum collected on the sample represented intense peaks of silicates [Figure 10]. For this, the pigment was identified as goethite (hydrated iron oxide, αFeOOH) together with an aluminosilicate material. In Figure 11, analyses performed on the yellow pigment sample from the tomb of Petubastis, are given. The same results of the yellow pigment of the tomb of Petosiris were reported. But, low iron concentration in the EDS analysis was detected for the yellow pigment sample from the tomb of Petubastis. Iron ore deposits occur in sandstone pockets along the Nile valley, Bahariya oasis, Aswan, and in some locations in Sinai. Also, goethite-rich deposits -with high quantity of $Fe_2O_3$- were reported in the Dakhla Oases (El-Desoky et al. 2015).

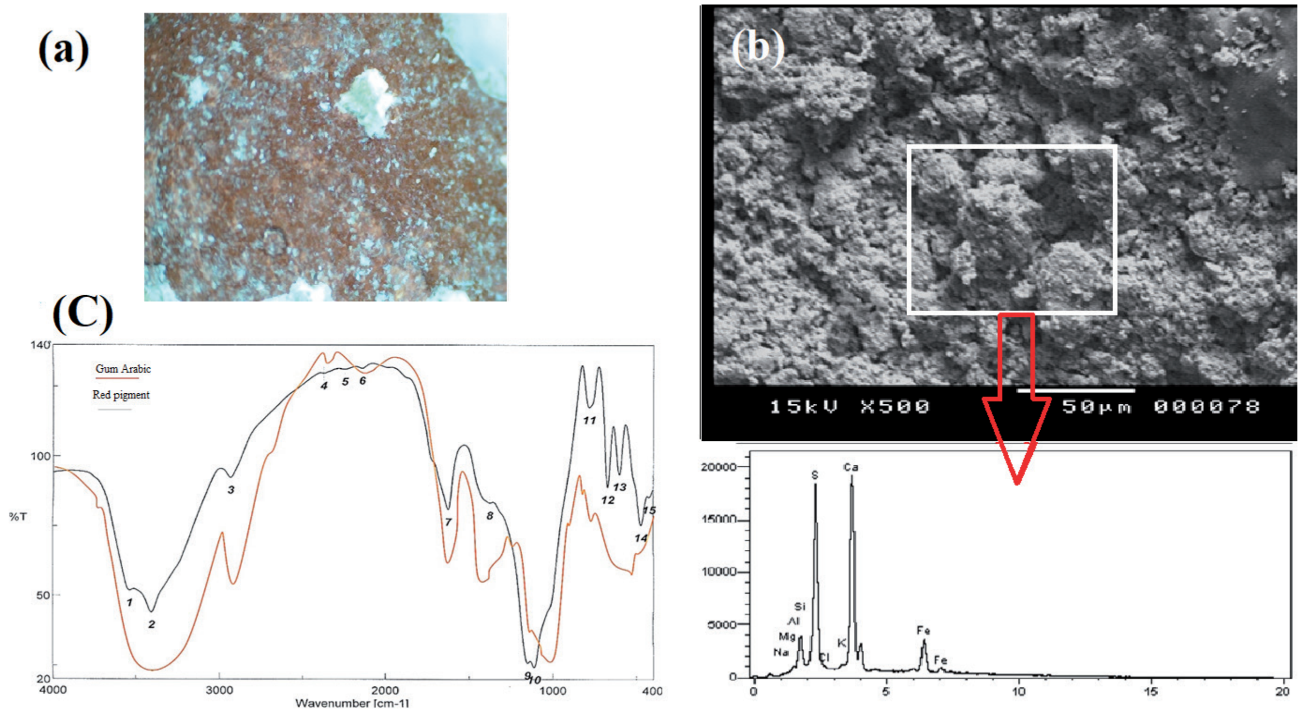


**Figure 8**.- (a) Microscopic image obtained on the red pigment from the tomb of Petosiris, (b) SEM-EDS analysis of the sample. (c) A transmittance FT-IR spectrum recorded on the sample.

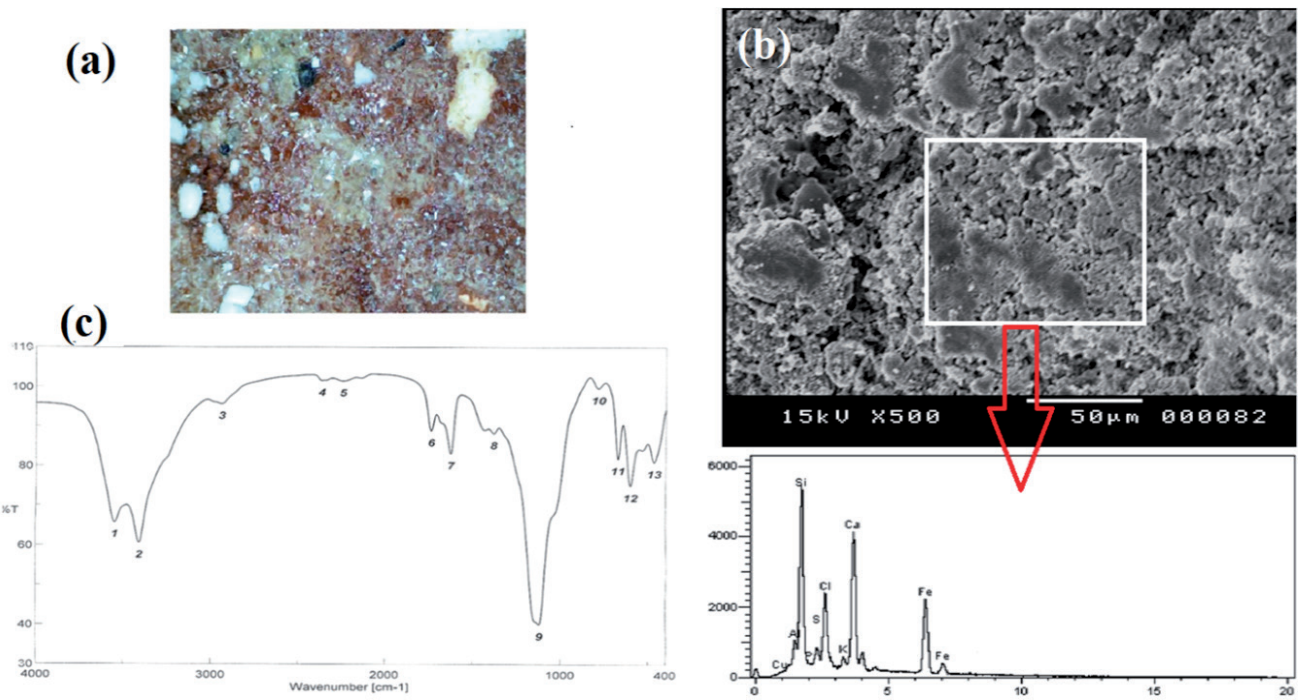


**Figure 9**.- (a) Microscopic image obtained on the red pigment from the tomb of Petubastis, (b) SEM-EDS analysis of the sample. (c) A transmittance FT-IR spectrum recorded on the sample.

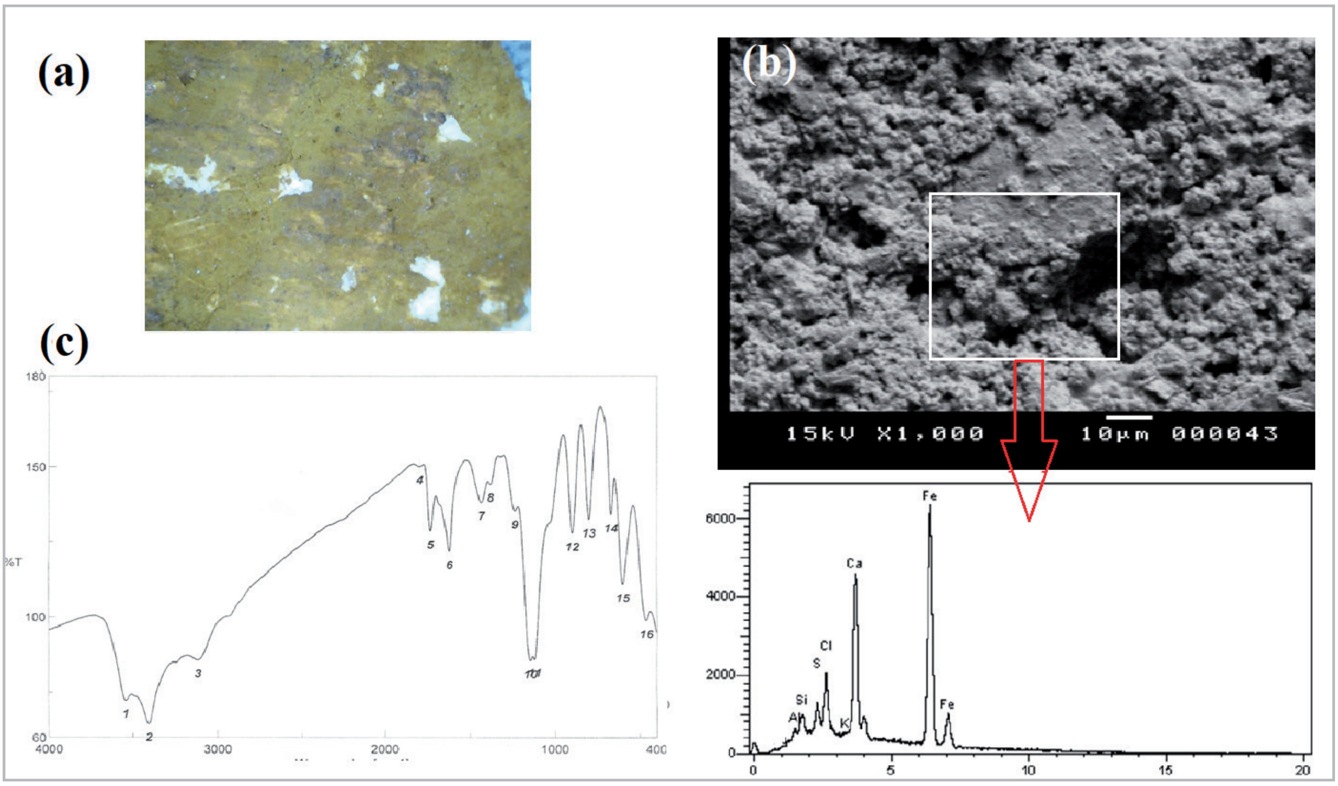


**Figure 10**.- (a) Microscopic image obtained on the yellow pigment from the tomb of Petosiris, (b) SEM-EDS analysis of the sample. (c) A transmittance FT-IR spectrum recorded on the sample.

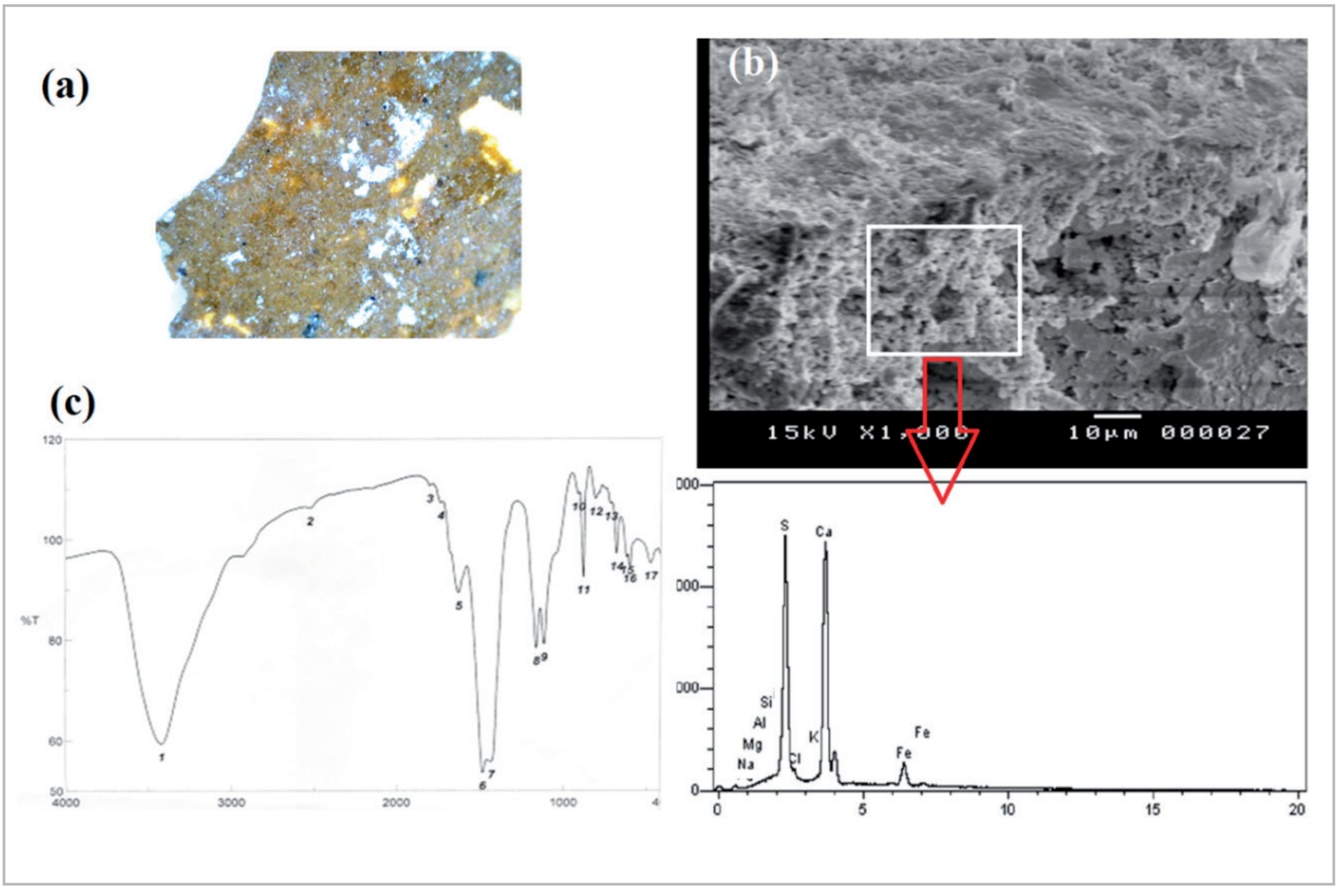


**Figure 11**.- (a) Microscopic image obtained on the yellow pigment from the tomb of Petubastis, (b) SEM-EDS analysis of the sample. (c) A transmittance FT-IR spectrum recorded on the sample.

• Blue pigment

A tiny blue paint sample from the tomb of Petubastis was collected and analyzed. The optical examination on the sample shows dark blue grains scattered in the matrix. Also, light blue areas were also observed, probably resulted from the dilution of the blue grains in the white binder [Figure 12a]. In the SEM micrograph of the sample, multi-size coarse crystals together with large quartz grains were observed [Figure 12b]. The EDS analysis on the sample showed the existence of silicon (Si), calcium (Ca) and copper (Cu), which are remarkable for cuprorivaite (calcium copper tetrasilicate). Blue cuprorivaite crystals are the responsible chromophore in the synthetic Egyptian blue pigment that usually produced at a temperature below 1000 °C (Ali 2003; Hatton et al. 2008; Hedegaard et al. 2019). The FT-IR spectroscopic analysis of the sample showed that the Si–O–Si stretching vibrations of the pigment are situated in the spectral region between 900 and 1100 $cm^{-1}$ [Figure 12c].

• Green pigments

Different green hues were observed in the studied tombs. The microscopic image recorded on a dark green pigment from the tomb of Petubastis showed multi-colours coarse grains. The morphological profile of the dark green pigment represents a dense massive matrix. The EDS analysis of this dark green allowed the identification of a variety of elements [Figure 13a]. Silicon, calcium and copper are likely due to the Egyptian blue pigment. The peak of iron -detected in the spectrum- suggests the presence of iron-based pigments. For this, most probably that the green hue was created by adding amounts of yellow ochre to the Egyptian blue pigment (Scott 2016). In addition to that, chlorine ions were reported in a high concentration in the sample which reflect the serious damage occurred to the murals. Likely, some of the green hues are resulted from the transformation of Egyptian blue into basic copper chloride (atacamite, $Cu_2Cl(OH)_3$) (Schiegl et al. 1989). The SEM micrograph of the light green sample shows heterogeneous matrix with coarse grains and the EDX analysis showed the presence of iron (Fe), silicon (Si), calcium (Ca), sulphur (S), potassium (K), aluminium (Al) (Fig. 13b). These elements refer to the green earth pigment, and mainly of celadonite, due to the absence of sodium.

A dull olive-green pigment was collected from the Petosiris tomb [Figure 14a]. The morphology of the sample showed the distribution of large aggregates. However, the EDS analysis of the pigment showed the presence of copper (Cu), silicon (Si), calcium (Ca), perhaps related to the Egyptian green pigment [Figure 14b]. Egyptian green is a synthetic pigment based on silica-rich copper glass and its manufacturing process required large amounts of alkali

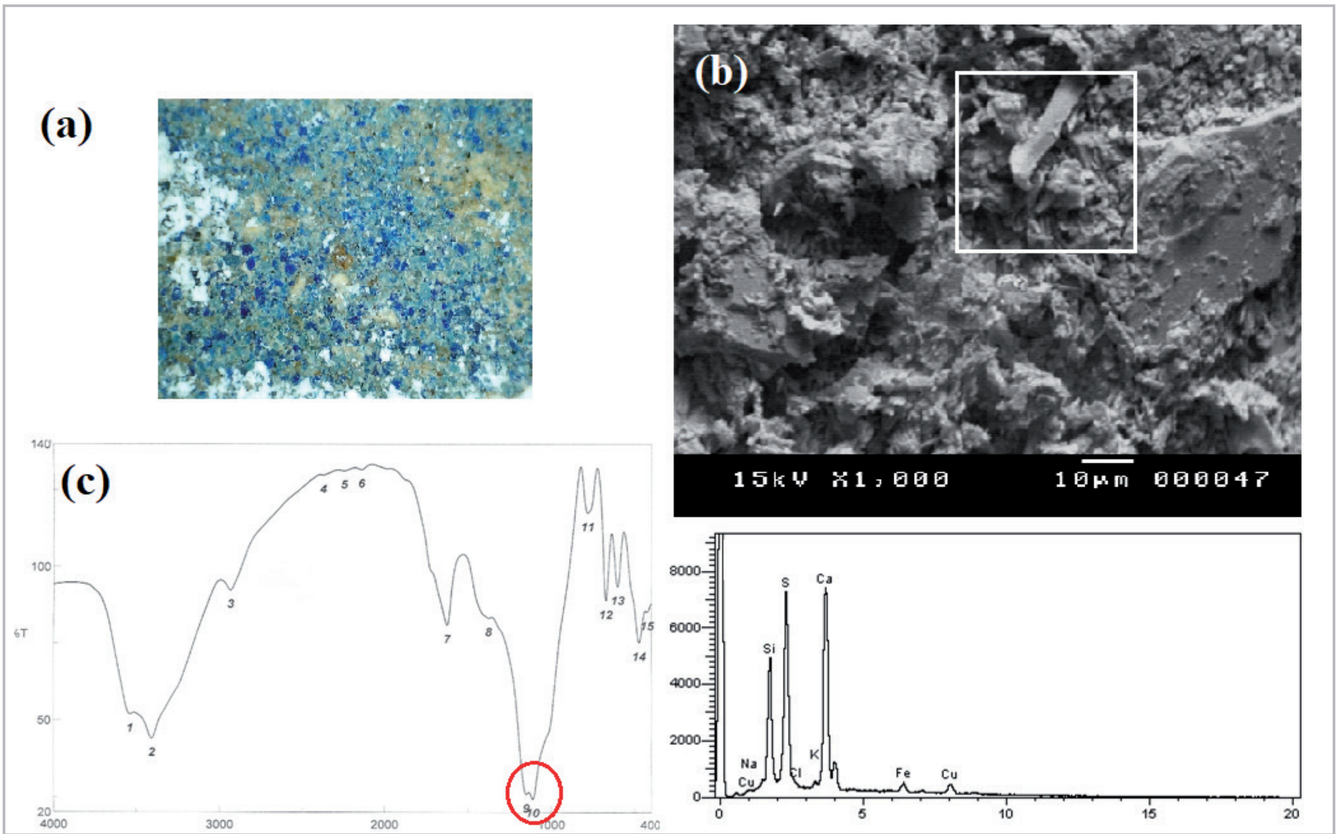


**Figure 12**.- (a) Microscopic image obtained on the outer surface of the sample. (b) SEM micrograph and EDS spectrum of the blue pigment sample. (c) FT-IR spectrum recorded on the sample (silicate group is highlighted by a red circle).

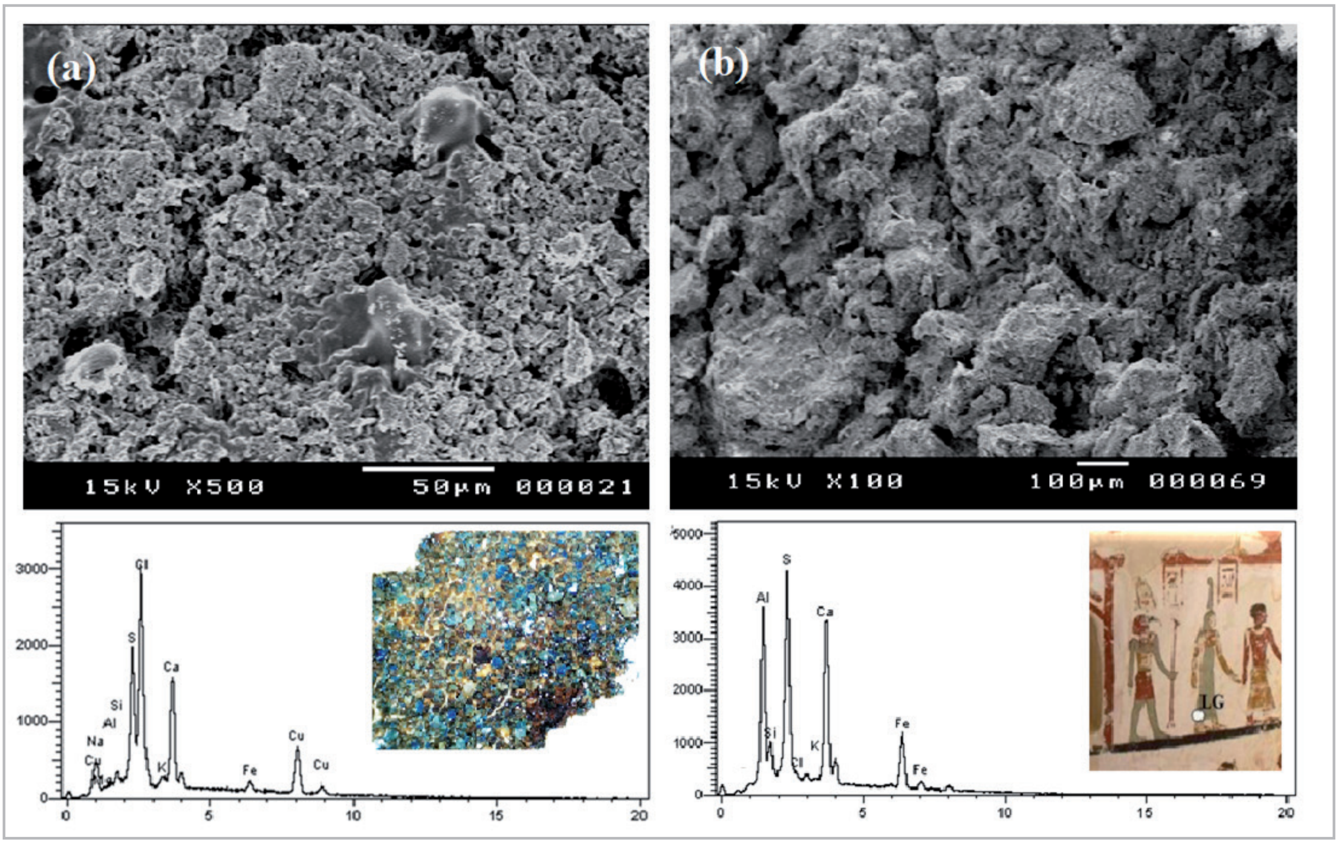


**Figure 13**.- SEM micrograph and EDS spectra obtained on the green pigments from the tomb of Petubastis. (a) dark green pigment. (b) light green pigment.

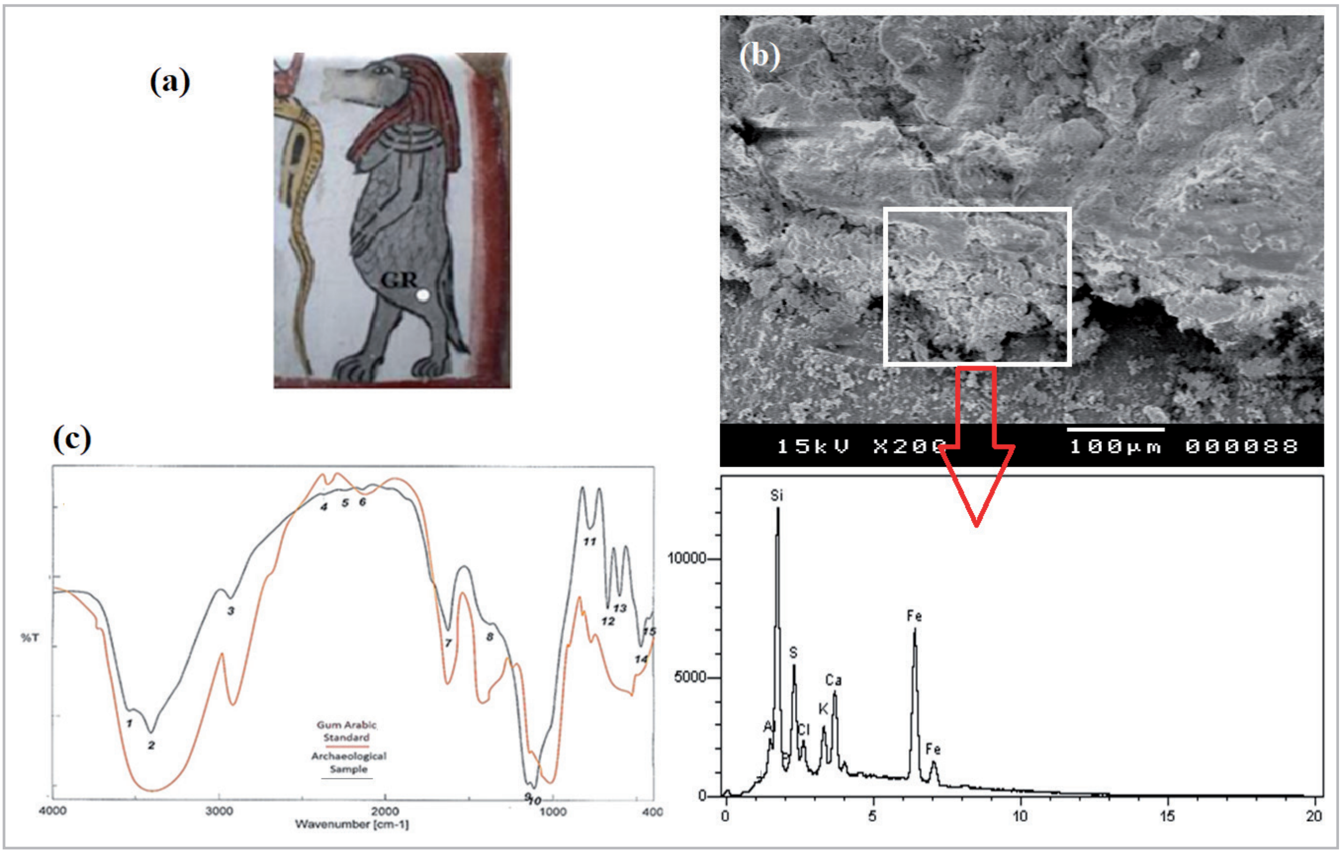


**Figure 14**.- (a) Location of the green pigment sample from the tomb of Petosiris. (b) SEM micrograph and EDS spectrum of the pigment sample. (c) FT– IR spectrum recorded on the sample (compared with a standard spectrum of gum Arabic).

and high temperature (Pagès-Camagna and Colinart 2003). Elements of sulphur (S), chlorine (Cl), iron (Fe), aluminium (Al), and potassium (K) probably corresponding to green earth. The spectroscopic molecular analysis of the sample [Figure 14c] shows characteristic asymmetric Si–O–Si stretching vibration at 1115 and H–O–H bond at 1640 cm$^{-1}$ while the R–O–H bending is occurring at 799cm$^{-1}$ (where R is an octahedral ion). Most probably that these bands are attributed to the mineral celadonite [$K(Mg,Fe^{2+})(Fe^{3+},Al)Si_4O_{10}(OH)_2$].

• Black pigments

The black pigment in the studied tombs was identified as magnetite ($Fe_3O_4$). As shown in Figure 15, the EDS microanalysis of the black pigment samples showed high amounts of iron, and no carbon was detected. It is well known that carbon-based blacks were the most black pigments used in ancient Egypt. However, black pigment of magnetite was identified, along with other iron oxides by the Raman spectrometer, in prehistoric rock art paintings in the area of Gilf Kebir in the southern corner of the Western desert (Darchuck et al. 2011). Magnetite is characterized by a dark gray to deep black hue. Historically, the Western desert is well known with iron ores deposits and it had given a particular importance during the Roman age (Boozer 2020).

*—The organic binder and painting technique*

FT-IR spectra collected on several paint samples from the studied tombs showed characteristic bands of an organic material. The bands at 3406 and 1620 cm$^{-1}$ are for hydroxyl group stretching (O–H), while the bands at 2935 and 1430 cm$^{-1}$ are for C–H bending. The band at 1074 cm$^{-1}$ is for C–O stretching and a carbonyl group in the distinguishing glues area was observed at nearly 1370 cm$^{-1}$. Thus, gum Arabic most probably was used as a binder for the murals. This kind of gums is collected from the *Acacia Senegal*, which distributed in Eastern Africa and North of Sudan (Vallance 1997). Gum Arabic is a complex polysaccharides, consisting mainly of glactose, arabinose, rhamnose, and glucoronic acid with some content of proteins (Brøns et al. 2018). The detection of gum Arabic confirms that tempera technique was used to decorate the tombs. Tempera was a favourite painting technique in the ancient Egyptian decorations. In this technique, the powdered pigments are usually mixed with an organic medium which allows the adhesion between the pigment particles and the render layer (Marey Mahmoud et al. 2019).

*— Restoration of the murals*

The studied site is suffering from several deterioration factors. Different clay minerals, mainly of montmorillonite,

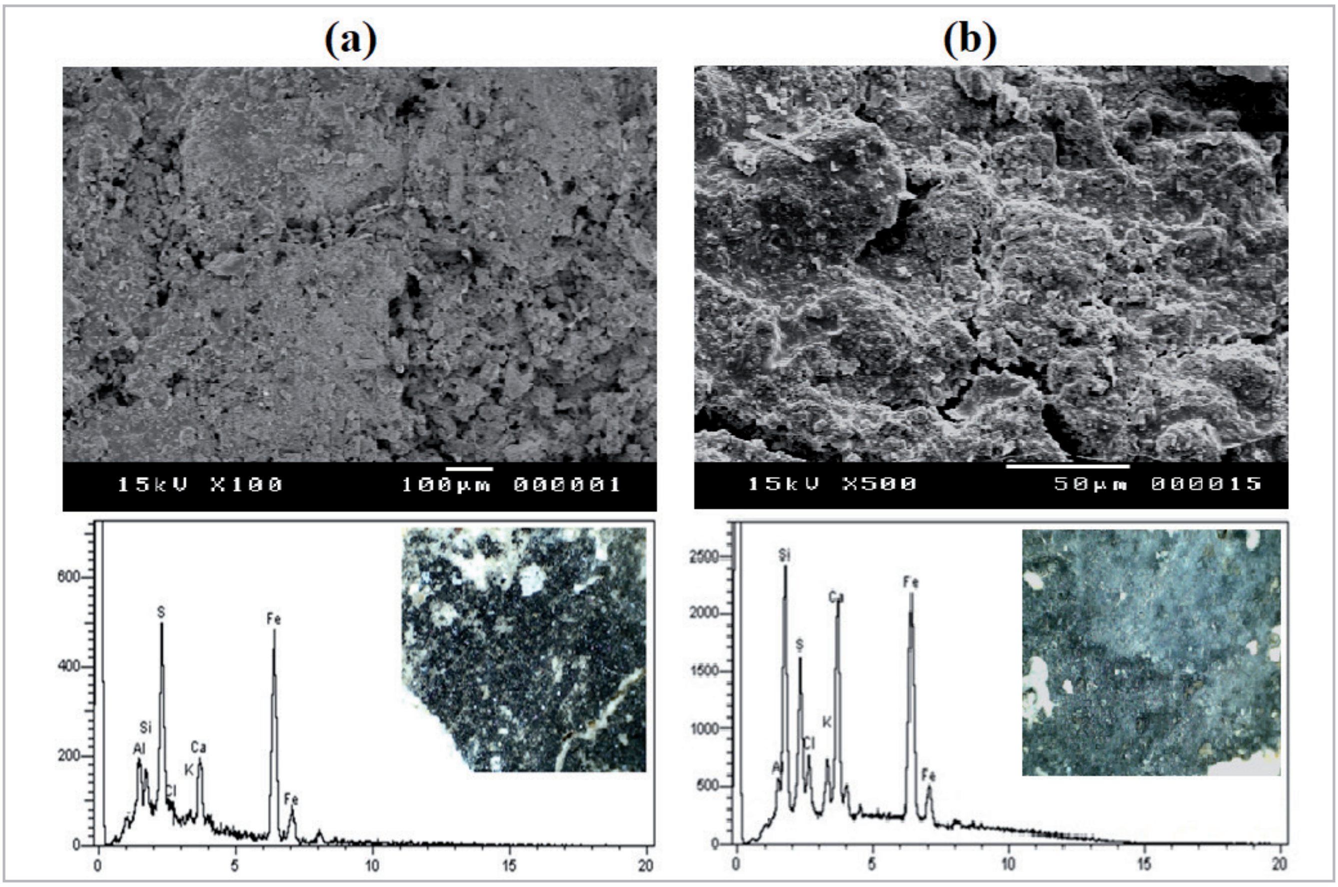


**Figure 15**.- SEM micrographs and EDS spectra of the black pigments from the tomb of Petubastis (a), and the tomb of Petosiris (b).

are occurring in the rock structure. Further, overlapping of gypsum and anhydrite laminate between the clay layers is a critical destructive factor. The swelling of clay minerals, in addition to the transformation of calcium sulphate phases contained in the layers, produce a dramatic pressure onto the tombs walls (Helmi 2000). Taking into account the arid climatic conditions of the area (average of air temperature= 42 °C), this leads to crumbling and disintegration of the ceiling in addition to cracking and detachments of the paint layers. Not only that, but the heterogeneity of the physical structure of the mural paintings is contributing in the deterioration process. As well, the analytical methods conducted on the tombs showed the crystallization of destructive salts, especially of sodium chloride (halite, NaCl). As previously shown in Figure 3, several deterioration forms were documented in the studied tombs. These forms can be summarized as follows:

a) The tomb of Petosiris:

- Micro and wide cracks in the Western/Northern wall and in the ceiling of the tomb.
- Shinny appearance of the painted surfaces due to old treatment with Paraloid B72, in a high concentration.
- Several detachments and crumbling of the paint layers.
- Paint flaking and pigment materials loss in the inner chamber.
- Recent graffiti on the Western wall of the front chamber and on the ceiling of the tomb.

b) The tomb of Petubastis:

- Problems of old restoration of the ceiling of the tombs using unstable metal bars and Portland cement mortars.
- Wide and micro-cracks in the Northern and Western walls of the tomb.
- Salt efflorescence on the painted surfaces.
- Detachments in the Northern wall of the tomb and crumbling of the ceiling.

As a result, several restoration procedures were necessary to stabilize the condition of the damaged murals in the tombs. The restoration steps varied according to the state of preservation for each wall. Such operations included cleaning, reattaching of flaking paints, application of injection grouts to detached layers, reconstruction of missing parts in the plaster, repair of wide-open cracks, and consolidation of the painted surfaces. Figure 16 displays some procedures applied to restore the murals of the studied tombs.

• *Reattaching flaking paints*

One of the challenging issues with tempera paintings is the detaching of tiny flakes from the underlying ground. First, clearing away the dust from the outer surface was done by soft brushes followed by wetting the detached flake by an ethyl alcohol. To reattach these flakes, a drop of an acrylic-based emulsion of Primal AC 33 was mounted at the underside in the separated point. Flattening the flake was made by a ball of absorbent cotton. Then, a gentle pressing using a silicon paper sheet and spatula was performed to re-adhere the detached flake to the wall.

• *Cleaning process*

One of the necessary steps in the restoration project was the cleaning of several accumulations and damaged layers formed onto the walls. Unfortunately in old restorations, a high concentration of an acrylic polymer (e.g. Paraloid B72: ethylmethacrylate/methyl-acrylate co-polymer) was used as a protective layer. The contribution of ageing processes of the polymer led to the formation of a dense damaged layer on the surface, which seriously caused aesthetic damage and several flakes. To remove these layers, a cleaning solvent agent based on butanone (methyl ethyl ketone) was used (Lee et al. 2018). The cleaning process was applied as follows:

a) cotton q-tips were soaked into the cleaning solution for a minute, then they were used for wetting the polymer layers to be easily removed; b) in some areas, tissue papers were immersed in the cleaning solution and applied directly onto the surface. The tissue poultices helped to soften the polymer layers, which then were removed easily using a scalpel.

• *Injection grouts*

For plasters that suffer from detaching and crumbling, injection grouts are usually applied (Baglioni et al. 1997). A series of experimental procedures were performed on different suggested formulas. Comprehensive laboratory tests were undertaken to define the physical and mechanical properties of the restoration mortars and injection grouts. Based on the chemical-mineralogical characterization of the paint layers, a number of restoration mortars and grouts was prepared. The grouts were tested according to related international standards (Kemp 2009). The experiments showed that the best formula is the one consists of: 1 part slaked lime, 2 parts powdered sand (300 μm), 1 part microballoon, 1 part bentonite and 1 part Addicrete BVD. This formula showed satisfactory results in terms of the physical and mechanical properties. Before injecting the grout, a dry cleaning by an air blower was applied. The injection formula was applied using plastic syringes (with size of 5 cm to 60 cm). To ensure a good penetration of the grout, the edges of the plaster layers were closed prior to the injection process.

**Figure 16**.- Shows representative restoration procedures applied for the murals in the tomb of Petubastis (a) and the tomb of Petosiris (b).

• *Cracks repair*

For the narrow cracks, an initial cleaning with a solution of water and ethyl alcohol was applied. Then, a diluted emulsion of Primal AC 33 (1:4 in water) was injected into the cracks using a syringe. But for the wide-open cracks, a restoration mortar was essential. The cracks were cleaned mechanically, by soft brushes and air blowers, to remove the damaged remains. Then, a restoration mortar consists of slaked lime, sand, clay, and Primal AC33 was applied using a metallic spatula.

• *Reconstruction of missing parts*

The missing parts in the plaster layers were re-filled using a restoration mortar. The deteriorated remains were removed and then the voids were wetted before applying the mortar. A compatible mortar similar to the original plaster layer was used. Before applying the mortar, the stability of the plaster edges was tested and the friable areas were subjected to a topical consolidation treatment. Then, the mortar was applied in form of multi-layers with the aid of mechanical compressing using a metallic spatula to ensure a good cohesion with the underlying substrate.

• *Final consolidation*

A final consolidation treatment was applied to strengthening the damaged pictorial surfaces and to minimize any future deterioration. This application was performed using a Kemtekt 20 ready-to-use silicon polymer. The consolidation was applied by a soft brush, then it was repeated for three times, with an intervention of 7 days between each application [Figure 17].

**Conclusion**

In the present case study, analytical techniques of OM, PLM, SEM–EDS, XRD, and FT–IR were used to identify the mural paintings of El-Muzzawaka tombs, Dakhla Oases, Egypt. The results allowed collecting information regarding the chemical, mineralogical and petrographic characteristics of the studied murals. The analysis of pigment samples from the tombs of Petubastis and Petosiris showed almost similar materials. Yellow and red ochres were identified in both tombs. While, the blue pigment in the tomb of Petubastis was of Egyptian blue. A mixture of Egyptian blue and yellow ochre was used to produce the green pigment in the tomb of Petubastis. However in the same tomb, indications on the presence of green earth (of celadonite), were reported. The green pigment in the tomb of Petosiris is probably made of Egyptian green and green earth. The black pigment in both tombs was obtained from iron oxide (magnetite). Also, an organic binder, probably gum Arabic, was identified by FT–IR, suggesting the use of tempera technique for the murals. The paintings of the tombs were executed on a thin anhydrite-gypsum render layer. This layer is laying on a coarse plaster, consists mainly of gypsum, anhydrite and quartz. However, calcite was also reported in the samples, most probably was added as a crushed limestone to the plaster formula. The geological structure of the area is affecting, severely, the painted walls of the tombs. Expandable clay minerals of montmorillonite, in addition to the crystallization of sodium chloride (halite) and calcium sulphate phases (gypsum and anhydrite), are the major deterioration factors. Several detachments/ crumbling of the plaster layers, paint flakes, cracks and missing parts of the plasters were remarked. For this, an integrated restoration intervention was applied to repair the damage of the murals. Multi-step procedures were applied in form of: stabilizing the paint flakes, injection grouts to the detached layers, reconstruction of missing

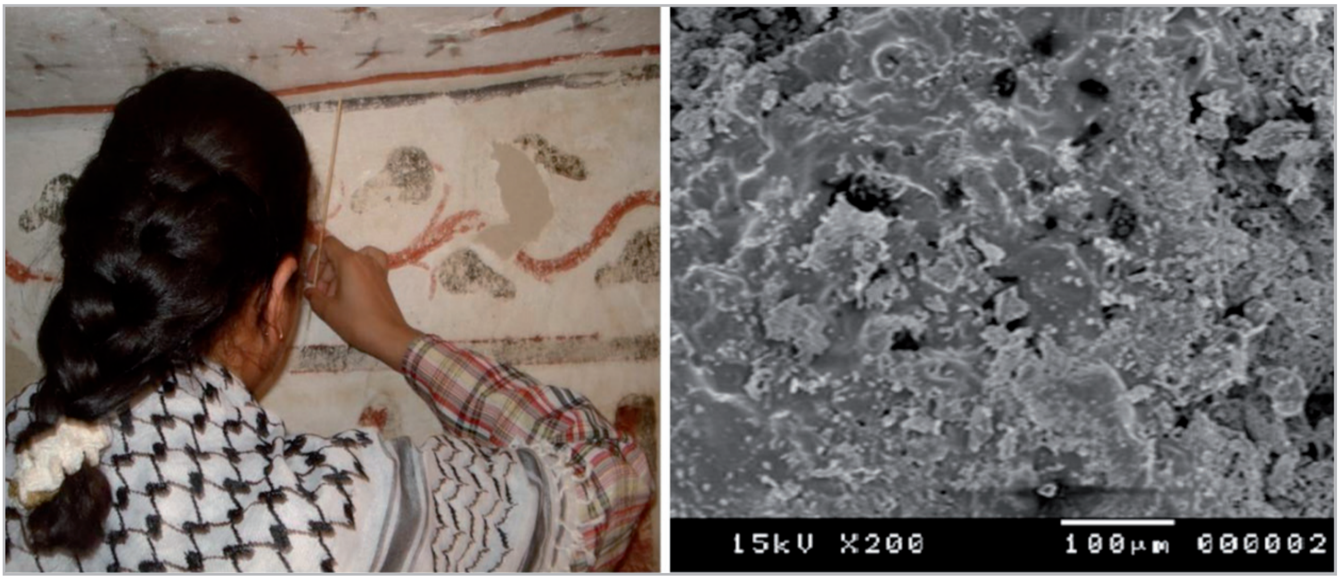


**Figure 17**.- Stabilizing friable areas of the murals (a), and SEM micrograph shows the good cohesion of the inner matrix of the murals after the consolidation process (b).

parts in the plaster layers, repair of cracks, and a final consolidation to the painted surfaces. As it is widely agreed that the environmental setting is a key factor for the long-term preservation of the murals. For this, a periodic maintenance is highly required to fully understand the performance behavior of the murals in connection to the microclimate of the tombs. In fact, controlling the levels of relative humidity (RH%), temperature, and light irradiation, in addition to minimizing the visitors to the site, are highly proposed.

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