

TECHNICAL EXAMINATION AND STATE OF CONSERVATION OF WALL PAINTING AT THE THEBAN TOMB TT15 AT DRA' ABU EL-NAGA NECROPOLIS, WESTERN THEBES, LUXOR, EGYPT

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Abstract

The Theban Tomb TT15 is located in Dra' Abu El-Naga', part of the Theban Necropolis, on the west bank of the Nile, opposite to Luxor, just by the entrance of the dry bay that leads up to Deir El-Bahri. The tomb was discovered in 1908 by Howard Carter and Lord Carnevon. Its walls were made of mud bricks and decorated with paintings dated from 18th dynasty Pharaoh. The tomb and its paintings are in a critical condition of deterioration due to surrounding damage factors, as well as the weakness of the building materials used in its construction. No publications are available on materials and techniques used in this tomb. To protect these paintings and to provide more conclusive information regarding the date of the painting scenes, painting materials and techniques have been studied. This study aimed at using different analytical techniques to characterize original and decayed materials from the mural paintings of TeTiky tomb and define the degradation pathways threatening their conservation. The analytical data obtained by Raman spectroscopy, X-Ray florescence (XRF), Light Optical microscopy (LOM), and Scanning electron microscopy (SEM) attached with X-ray Microanalysis (SEM-EDS), FTIR and X-ray diffraction. The results indicated that, the wall painting technique is typical of 18th dynasty Pharaoh paintings and includes multiple layers of gypsum mixed with calcite. Analytical results demonstrate also, the Egyptian painter used locally sourced materials for pigments as Egyptian blue and its various color tones, red and yellow ochre, etc... The binding media is a kind of animal glue (tempera technique). The results obtained for this case of study also highlight the important inference to consider in future conservation project.

Keywords: Wall painting; Luxor; Mudbrick; Pigments; Deterioration; Analysis; Raman

Introduction

Archaeological Background

The TeTiky tomb (No. 15) is in the west of the necropolis of Dra' Abu El-Naga. Dra' Abu El-Naga' Necropolis lies on the western bank of the Nile at Luxor. Dra Abu El-Naga is a small hill approximately 1.0km in length and 250m in width. Its boundaries are the valley of Deir El-Bahari to the south, the wadi Biban El-Moluk that leads to the Valley of the Kings to the north, and El-Tarif along its north-eastern border [1]. Topographically, Dra Abu El-Naga consists of two different parts, a flat area close to the cultivation land, and a hilly zone. It is linked to the location of the necropolis just across from the Temple of Karnak. Necropolis of Dra Abu El-Naga is one of the longest operating cemeteries in ancient Egypt. The oldest burial at the site has been dated to around 2000 BC during the Middle Kingdom and it was used

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continuously up until early Coptic Christian times. This area of the necropolis is characterized by several groups of tombs, including clusters where the mudbrick remains of tomb superstructures are quite well preserved. The necropolis is remarkable for the range of social status to be found at the site from humble burials to tombs of high-ranking officials and even some kings and queens of the 17th and 18th dynasties. Excavations continue at the site until now. One of the unique tombs in the necropolis of Dra' Abu El-Naga is TeTiky tomb (No. 15). It was discovered in 1908 by Howard Carter and Lord Carnevon. The Theban Tomb TT15 is in Dra' Abu El-Naga'. According to some opinions of archaeologists, the tomb may well have been intended as the burial place of the Ancient Egyptian Tetiky, who was Mayor of Thebes, during the reign of Ahmose I, during the early Eighteenth dynasty. Tetiky was the son of Rahotep Overseer of the harem of the Lake and Sensonb, Tetiky's wife is named Senbi [2]. The tomb consists of a main vaulted entrance that leads to another unpainted vaulted entrance leading to the main rectangular hall, this hall takes measures 5.30m length × 2.42m width and the rising ceiling of the earth about 2.38m (Fig. 1) with vaulted ceiling which decorated with unique decoration painted on it in the middle represented geometric decoration and the shape of the bark of wood (torsion or trunk) (Fig. 2).

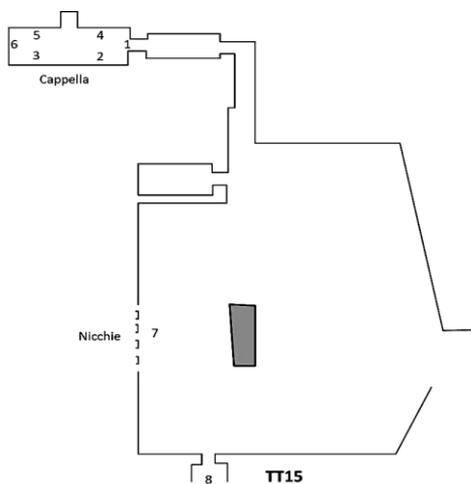


Fig. 1. Floor plan of the tomb TT15 at Dra' Abu El-Naga Necropolis

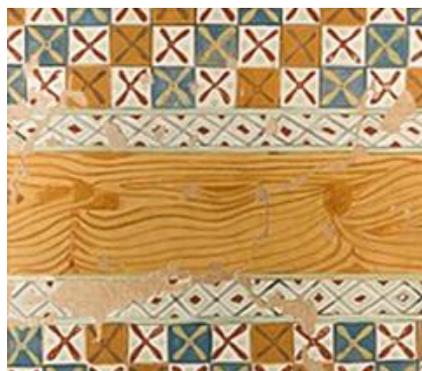


Fig. 2. Geometric decorations and the shape of the bark of wood decoration at the ceiling of the tomb TT15

The north side of this hall contains a painted niche. The walls and the niche were decorated with very important mural paintings. The decoration in this tomb shows an early depiction of the King's Wife Ahmose-Nefertari, offering to Hathor, and wearing as yet the gazelle headdress of a lesser wife, moreover, the paintings of the depicted episodes comprise funeral scenes with ancient Egyptian gods, the owner of the tomb and his wife, daily life scenes as cultivation and working in fields, hunting, fishing, and food cooking, preparing of beer, offering and burial scenes, historical texts which comprise funeral scenes with ancient Egyptian gods and cartouches with hieroglyphic inscriptions.

TeTiky tomb was built of mud brick and the walls were plastered with mud mortar tempered with chaff and given a coat of gypsum plaster which acted as a ground for the painted decoration. The wall plaster consists mostly of more than one layer with thickness ranges between 1.5 and 3cm in most areas (Fig. 3). some walls carried out with up three plaster layers with variety thickness, the variety of the wall plasters thickness resulted from the unevenness of the mud-brick surfaces under those plaster layers, the upper layer is a white ground, approximately 1-2mm thick, on which the polychrome painting was executed, and the white

ground contains fine gypsum and aggregate of fine sand to facilitate brushing. The polychrome painting was executed on the outside gypsum plaster. The paints were based on an organic binder and traditional pigments (blue, red, yellow, black, white, and gray). No publications are available on materials and techniques used in the tomb or previous conservation work that had been done. According to information provided by the Archaeological in Dra' Abu El-Naga during the past years, the tomb has undergone few restorations works, the most recent in 2015. Despite a lack of detailed documentation, the tomb was clearly subjected to unscientific treatment works which led to further deterioration and damage. This paper aims to obtain useful information about the materials, painting technique, the type, and the extent of the degradation processes and to detect the materials used in previous interventions to obtain detailed knowledge about the original materials used for the construction and decoration of architectural surfaces in the TT15 tomb. The obtained results will be used in establishing a conservation plan of the wall paintings in TeTiky tomb. Integrated investigations were implemented on selected plaster fragments collected from the painted layers, a ground layer, mudbrick support, and deterioration products from TT15 tomb one of the most important buildings in Dra' Abu El-Naga.



Fig. 3. The stratigraphy of mural painting at TeTiky tomb:
 a. portion of the image of the tomb, the stratigraphy of the preparation can be seen in the damaged portions of the painting; b. The stratigraphy of the mural painting at TeTiky tomb;
 1. mudbrick support; 2. coarse mud and straw plaster; 3. fine mud plaster;
 4. The upper plaster carries a polychrome painting

Degradation forms of the TeTiky tomb

The wall paintings in TeTiky tomb are in a critical state of conservation, it has been constantly undermined by the destructive effects of many degradation phenomena as variation in temperature and humidity, salts, insects, and micro-organisms, which have disastrous effects on the stability and integrity of the wall painting. More subtle changes arising from the presence of human beings, e.g., looting, theft, demolition, and fault restoration work by unstable materials and the instability of the pigments or pigment mixtures with time, also produced dramatic deterioration in wall paintings [3-6].

Even though the excavation of Dra Abu El-Naga offered a full and unique tomb with unique scenes, the removal of debris triggered the activation of several deterioration processes. Dampness and heat are the main considerations influencing the durability of mural paintings in the tomb; dampness starts compound, physical, and biological measures either by itself or by moving the substances that participate in deterioration mechanisms [3-8], wide fluctuation in temperature are noticed from outside to inside also. Also, fluctuations, water penetration, high water table, leaching processes triggered by rainwater, exposure to sunlight, the capillary rise of soluble salts from the soil, wind abrasion, atmospheric pollution, biological colonization are just

a few of the many factors causing the irremediable loss of unique pieces of a wall painting at the tomb.

In addition to the irreversible impact of misguided and piecemeal conservation interventions and weakness of the building materials (mudbrick) used in construction have had a devastating effect at wall painting on the tomb. Also, environmental mechanisms and emphasizes structural decay mechanisms as well, including structural movements, shrinkage and cracking, moisture and thermal movement, density relaxation, and load redistribution caused the cracking and collapse of parts of the walls in the tomb. Extensive degradation was observed on a wall painting at the tomb and the wall painting exhibits the most intense degradation problems, mainly consisting of:

- Displacement, leaning, collapse in the lower part of the wall and moderate cracks are found along the tomb walls (Fig. 4a), also bulges of the upper wall of the niche (Fig. 4b) due to subflorescence in between plaster layers.
- Network of microcracks (Fig. 5a) and missing parts of wall painting in different parts of the wall of the tomb were clearly noted which affect the tomb's integrity (Fig. 5b).



Fig. 4. a - Displacement, leaning of the wall:
b - bulges or swelling of the upper wall of the niche the TeTiky tomb



Fig. 5. a - Network of micro cracks associated with detachments of the mud plaster;
b - missing part of wall painting which affects their integrity

- The most common types of deterioration observed on wall paintings in the tomb is detachments of the mud plaster from mudbrick support (peeling) (Fig. 6a), abrasion of the paint layer (Fig. 6b), crumbling, surface erosion and failure of the plaster (Fig. 6c) and the brittle plaster collapsed and was crushed (Fig. 6d).
- Salt efflorescence was clearly observed at the surface, and crypto efflorescence salts were observed between the mud plaster and mudbrick support, which deteriorated the wall plaster in various degrees from one area to another. Separation of the wall plaster layers, partially or completely, is caused by the crystallization of the salts (Fig. 7a and b).

- Chromatic alterations are widely distributed in the mural painting in the tomb, essentially greyish in color, which ascribed to the deposition of debris, dust, and other fine particulates at the surface (Fig. 8a and b).

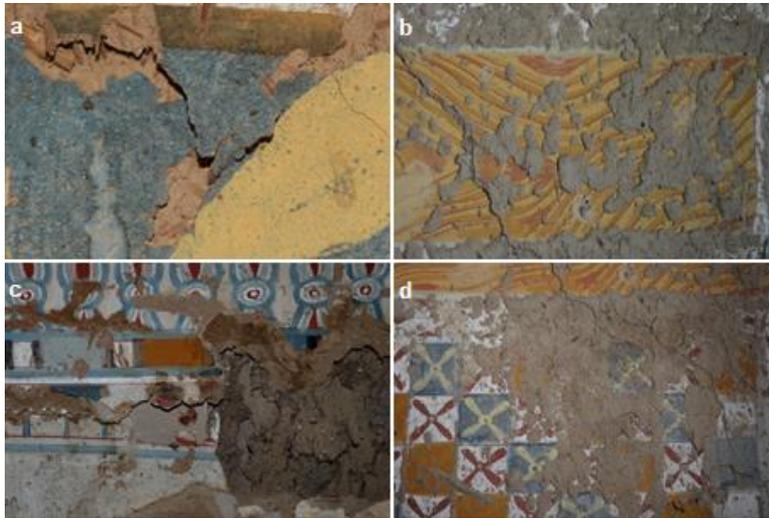


Fig. 6. a - peeling of the paint layer; b - abrasion of the paint layer; c - crumbling of the mud plaster; d - the brittle plaster collapsed and was crushed



Fig. 7 a, b - accumulation of soluble salts at the mudbrick



Fig. 8. a, b - The accumulation of dirt on a surface leading to discoloration

- Mural paintings in tombs are exposed to deterioration due to the composition of these paintings, it was well established that mud plaster containing organic materials such as chopped straw (Fig. 9a) provides a rich and suitable food source for insects, so many areas

show extensive holes and gaps in the ground layer (Fig. 9b) due to the insect attack, which feeds on the chopped vegetable matter at the mud plaster and mudbrick support.

- Infiltration of rain and wastewater (from sewage leakage from sewage septic tanks installed by the people at the top of the tombs) within joints and cracks of the ceiling of the tomb cause dissolving clay and gypsum in gray opaque encrustations that hidden paintings (Fig. 10a), also the wall paintings in the tomb present visible discoloration in appearance (Fig. 10b) due to the prolonged action of microorganisms [9].

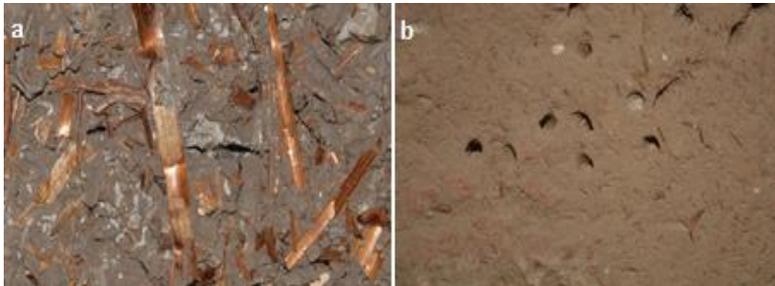


Fig.9. a - straw in mud plaster; b - extensive holes and gaps due to the insect attack



Fig. 10 a - infiltration of rain and wastewater by ingress through cracks; b - discoloration in appearance due to the prolonged action of microorganisms

- Damage caused by deliberate or unintentional human acts were represented in the tomb of TeTany in different features as; desolation of many parts of the tomb during the demolition of houses in the old Qurna (Fig. 11a), also many wall painting parts at TeTiky tomb has been damaged due to looting, theft and demolition, the thieves cut off some parts of the mural in the tomb (Fig. 11b) for trafficking and the Louvre have recently returned several decorated sections from the tomb [10]. In addition, using inappropriate materials through ignorance of mudbrick techniques and the incompatibility of materials trying to protect the tomb by using cement, linen with gypsum mortar and organic binders which affected by biodeterioration (Fig. 11c and d).



Fig. 11. a- desolation of many parts of the tomb during the demolition of houses in the old Qurn:
 a and b - some parts of the mural were cutting off in the tomb for trafficking;
 c - Portland cement and organic binders affected by biodeterioration; d - Gypsum mortar with linen

Experimental part

Samples

A few tiny wall painting samples were collected from seriously damaged areas and stored. Chosen representative samples including different visible colors were collected to provide stratigraphic information of paint layers and substrate layers. Mudbrick support, kinds of plaster, pigments from detached parts of the paintings and the deteriorated residual on the wall painting surface were collected (fig.12), it was cared to collect samples as small as possible in size. The samples analyzed by analytical laboratory systems, provided useful information about the origins of wall painting materials and some of the degradation processes threatening the conservation state of the tomb.



Fig. 12. Fragment of plaster with different pigments from TeTiky tomb, white, black, red, yellow, dark blue and grey

Methods

Cross sections (20 μ m thickness) were prepared to investigate the underlying stratigraphy of the wall paintings in the tomb. This preparation requires the samples embedding in Araldit 1092 followed by abrasion and polishing of the specimen, trying to obtain plain surface.

LOM

Light optical stereo microscopy (LOM) was conducted on optical microscopy (OM) using (Leica DM 1000) equipped with a Leica EC3 digital camera under a magnification of 40x to 100x.

SEM-EDS

weathered wall painting samples were analyzed with scanning electron microscopy coupled with dispersive X-ray spectroscopy (SEM/EDS). The SEM JEOL JSM 5410 was fitted

with an energy dispersive X-ray spectrometer (EDS) INCA PentraFETx3, Detector model 6587. Images and elemental analyses were obtained at accelerating voltage of 5-50kV and at low vacuum (40Pa) lifetime >50sec, CPS = 4000 and working distance 7mm used to obtain information on the elemental composition of the sample, since this technique requires a very small number of samples tested with the selection of the part to be examined and analyzed [11-13].

XRD

The mineralogical composition of all the samples was obtained by Philips X-ray PW 1840 diffractometer for semi-quantitative mineralogical analyses with radiation $\text{CuK}\alpha_1 = 1545\text{\AA}$, operating at 40mA, 40kV, investigating range 2θ $4.0100^\circ - 72.4900^\circ$, divergence and detector slits of 1.54060° , 1.54439° 2 step size, and time for step of 1s. The XRD profiles were measured in 2θ goniometer steps for 0.300s.

Raman

The collected paint samples have been examined with μ Raman spectroscopy. Raman spectroscopy data were mostly useful for identification of the materials used for the wall painting [14]. Micro-Raman spectra were recorded using a laser power at the sample of about 0.3 mW and objective lens of 50 \times magnification of an Olympus microscope. The Raman analyses have been carried out with a Senterra (Bruker) and a laser at 785nm, at a power ranging from 5 - 25mW according with the thermal stability of the compounds to be investigated and Charge Coupled Device (CCD) (-65°C) detector cooled by the Peltier effect at 200°K . A Jasco 2000 spectrometer combined with an Olympus microscope, cooled with liquid nitrogen has been also used with a laser at 1000 nm and a power range lower than 50mW. The spectra have been generally recorded between 1200 and 150cm^{-1} . For each paint fragment an average of 30 particles has been analyzed, with a varied collection time according to the magnitude of the scattering signal. It was attached with Olympus U-TV1x-2 camera.

FTIR

The chemical composition of the binding media was determined by using mid infrared (Mid IR) spectroscopy A PerkinElmer Spectrum 100 FTIR-ATR with a diamond crystal. The binder was finely ground in an agate mortar. 0.5mg of this mixture was then dispersed and further ground in about 70mg of KBr and pressed into pellets under about 10 tons/cm^2 pressure. Spectra were acquired between $400 - 5000\text{cm}^{-1}$.

Results

LOM photos of the cross-section sample from TeTiky tomb pointed out that, the underlying stratigraphy of the wall painting consists of coarse mud and straw plaster that was applied on the mudbrick walls in a layer approximately 1:2cm thickness, followed by a layer of a finer plaster containing fine clay and sand supplemented with a variety of chopped vegetable matter, the outer layer of fine gypsum plaster that functions as pigments support carrying the white ground color and other pigments (Fig. 13a and b). The photos revealed a network of gaps, missing parts, microcracks in the plaster and paint layer, and accumulation of extraneous material as dust, bird droppings on a surface leading to discoloration. The investigation of the yellow pigment sample shows the canary hue of the pigment which is applied in form of a single layer on the plaster layer, acclimation of extraction of insects and salts coated the yellow paint layer (Fig.14a and b). The investigation of the white pigment sample shows the presence of extensive holes and gaps in the ground layer resulted from Insect's attack (Fig. 15a). The investigation of the green pigment sample shows pale hue tends to gray, in addition to the weakness of the pigment (Fig. 15b and c). The investigation of the red pigment sample shows a thick layer of the paint layer with dark grains embedded in the layer and hairline crack observed clearly (Fig. 15d).

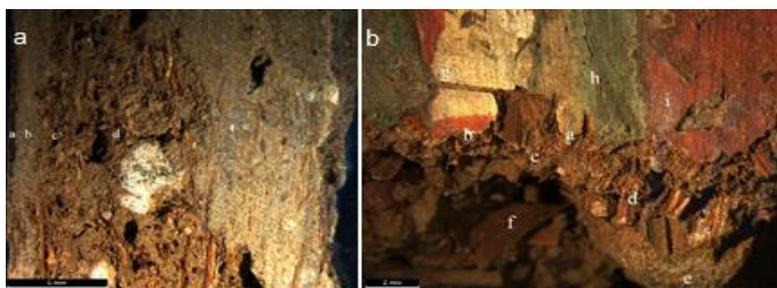


Fig. 13. Optical microphotographs of wall painting sample from **TeTiky tomb**, showing, the stratigraphy of wall painting: a - paint layer; b - gypsum preparation layer; c - mud fine plaster; d - mud coarse plaster; e - mud brick support; f - straw mixed with mud mouratr and plaster; g - white pigment, h-green pigment; i - red pigment

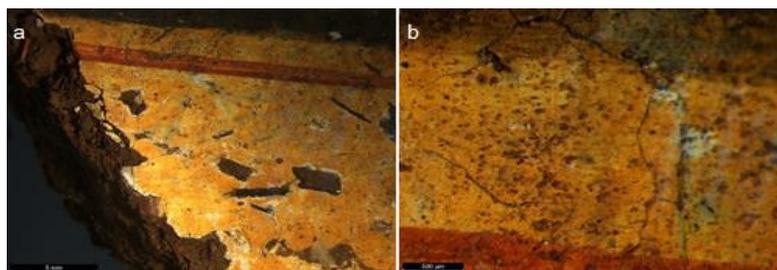


Fig. 14. Optical microphotographs of yellow pigment sample from TeTiky tomb, showing network of cracks, accumulation of extraneous material as dust, bird droppings on a surface

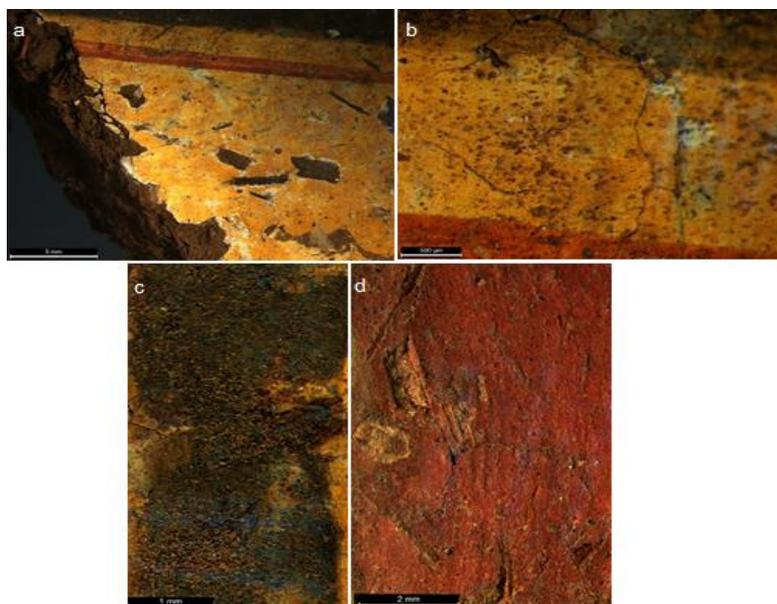


Fig. 15. Optical microphotographs of different pigments sample from TeTiky tomb, showing deterioration phenomena as network of microcracks, extensive holes, gaps and missing part of wall painting which affects their integrity, salt crystals on the surface

Mineralogical composition data of the wall painting samples is shown in figure 16. XRD data of the clay plaster (Figs. 16 and 17) indicates that quartz (SiO_2), calcite (CaCO_3), phyllosilicates and kaolinite - $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$ compose mainly the ground layer. Most of the

studied samples display the kaolinite occurrence, moreover only some layers of the multilayer plaster exhibit kaolinite minerals. The kaolinite presence in the samples can suggest the plaster manufactured from locally available raw material sources.

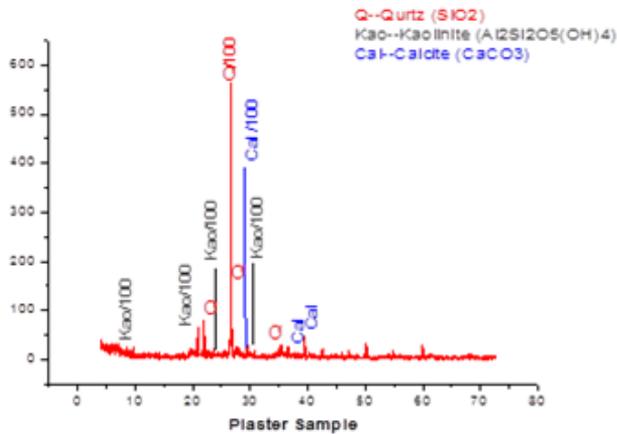


Fig. 16. XRD pattern of mud plaster from TT15 tomb

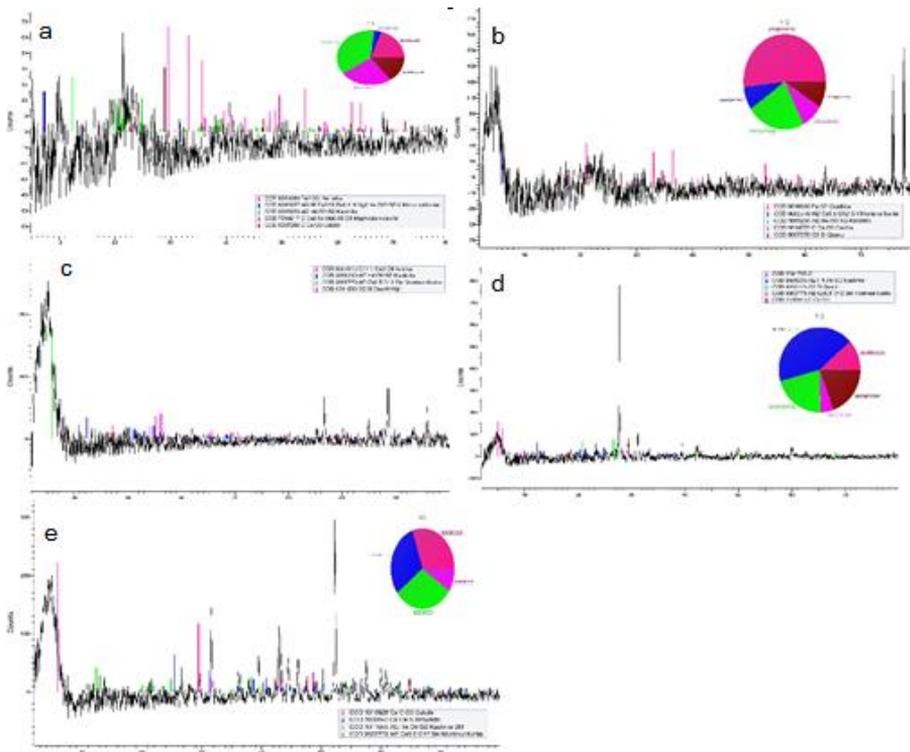


Fig. 17. XRD pattern of pigments sample from TT15; a- XRD pattern of red pigment, b- yellow pigment, c- blue pigment, black pigment, d- white pigment, e- mud Plaster

Pigments samples

Mineralogical composition data of the pigment samples (Fig. 17) indicated that, the pigments in TeTiky tomb were those traditionally used in ancient as well as classical times and the differences found may be related to the impurities as well as the geological sources of the pigments used.

Red pigment: samples consist of a mixture of hematite - Fe_2O_3 , montmorillonite - $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$, kaolinite - $\text{Al}_4(\text{Si}_4\text{O}_{10}) \cdot (\text{OH})_8$, magnesium calcite - $\text{CaMg}(\text{CO}_3)_2$ and calcite - CaCO_3 .

Yellow pigment: consists of a mixture of goethite - FeOOH , montmorillonite $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$, kaolinite - $\text{Al}_4\text{Si}_4\text{O}_{10} \cdot (\text{OH})_8$] and quartz - SiO_2 .

Blue pigment: contain azurite - $\text{Cu}_2\text{CO}_3(\text{OH})$, montmorillonite - $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$, kaolinite - $\text{Al}_4(\text{Si}_4\text{O}_{10}) \cdot (\text{OH})_8$, quartz - SiO_2 .

Black pigment: contains carbon C, Montmorillonite ($\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$, kaolinite - $\text{Al}_4(\text{Si}_4\text{O}_{10}) \cdot (\text{OH})_8$, Quartz SiO_2 and traces of calcite.

White pigment: sample consists of a mixture of and calcite - CaCO_3 , anhydrite - CaSO_4 , ontmorillonite $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ and kaolinite - $\text{Al}_4(\text{Si}_4\text{O}_{10}) \cdot (\text{OH})_8$.

SEM-EDS examination in table 1 and figure 18 the results of the analysis carried out on the wall paintings from the tomb of GTT19.

Table 1. EDS analysis results of pigment samples

Sample	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Cu	C
Red pigment	3.29	4.48	8.68	24.12	6.97	8.29	0.97	1.93	25.09	0.93	14.87	0.60	-----
Yellow Pigment	1.56	16.18	12.36	19.86	4.28	11.46	1.63	0.81	19.08	0.60	11.73	-----	-----
Blue pigment	2.62	8.08	4.87	15.05	6.47	12.05	2.47	1.13	40.30	-----	6.11	0.13	-----
Green pigment	-----	-----	-----	44.51	2.33	5.19	-----	-----	32.67	-----	3.97	13.66	-----
Black pigment	-----	2.21	2.97	20.71	-----	0.94	1.08	-----	15.08	-----	2.99	10.68	41.01
White pigment	2.33	26.50	3.32	7.96	6.30	19.42	1.82	0.88	29.32	-----	2.14	-----	-----

Mudbrick support: EDX pattern of preparation layer showed presence of S (60.24%) Ca (8.35%), Si (8.54%) and Al (3.04%), (Fig. 16a) so the preparation was gypsum plaster layer consisted of gypsum, limestone powder and fine aggregates of sand, and presence of Al and Si may be ascribed to clay minerals from the inner layer of plaster.

Red pigment: EDS pattern of red pigment pointed out presence of Fe (14.87%), Al (10.77%), Si (24.12%), K (1.39%), P (6.97%), Cl (0.97%), Ca (25.09%), Ti (0.93%) and Cu (0.60%). The beak of iron suggests the use of iron oxides (probably hematite, Fe_2O_3) as coloring material (Fig. 16b). The contribution of silicon and aluminium indicates the presence of aluminosilicate materials from inner plaster.

Yellow pigment: EDS microanalysis of the yellow pigment shows the detection of Fe (6.06%), Al (6.23%), K (0.81%), Mg (20.85%), Ca (29.61%), S (11.28%), P (6.15%), Ti (0.69%) Na (2.06%) and Cl (2.02%) (Fig.16c) The peak for iron indicates the existence of iron oxide (probably goethite, FeOOH). Presence of Na and Cl point out the salt of sodium chloride.

Blue pigment: The EDS pattern from the blue pigment obtained, showed presence of Cu (0.31%), Ca (6.10%), Si (53.85%), Al (11.66%), S (1.090%), Mg (3.84%), Na (2.17%), and Cl (0.61%), so Egyptian blue is the most probable blue pigment (Fig. 16d).

Green pigment: The EDS spectrum of green sample evidenced the presence of Cu (13.66%), Ca (32.687%), Si (44.51%), S (5.19%) and Fe (3.97%), that probably suggests the use of malachite $\text{Cu}_2(\text{CO}_3) \cdot (\text{OH})_2$ for green pigment, potassium, aluminium, silicon, and iron were detected (Fig. 16e).

Black pigment: EDX patter of black pigment (sample 7) showing presence of C (41.01%), Al (2.97%) Mg (2.21%), Fe (2.99%), Cu (10.68%), Ca (15.08%), Cl (1.08%), Si (20.71%), this declare that carbon is the most probable as a black color (Fig. 16f).

White pigment: EDX pattern of white sample from the tomb of TT15 pointed out presence of Ca (29.32%) and S (19.42%), so white pigment gypsum may be used, and confirmed by SEM micrograph showed fibrous crystals, the main feature of gypsum (Fig. 16g).

Raman spectroscopic analysis of pigment samples

Micro-Raman spectroscopy was used as a complementary technique to study some pigments and white ground layer.

The white ground layer bands yielded the characteristic Raman of gypsum - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (1008cm^{-1}) which was found in every sample. Calcium carbonate - CaCO_3 (1086cm^{-1}) was detected in also in all samples.

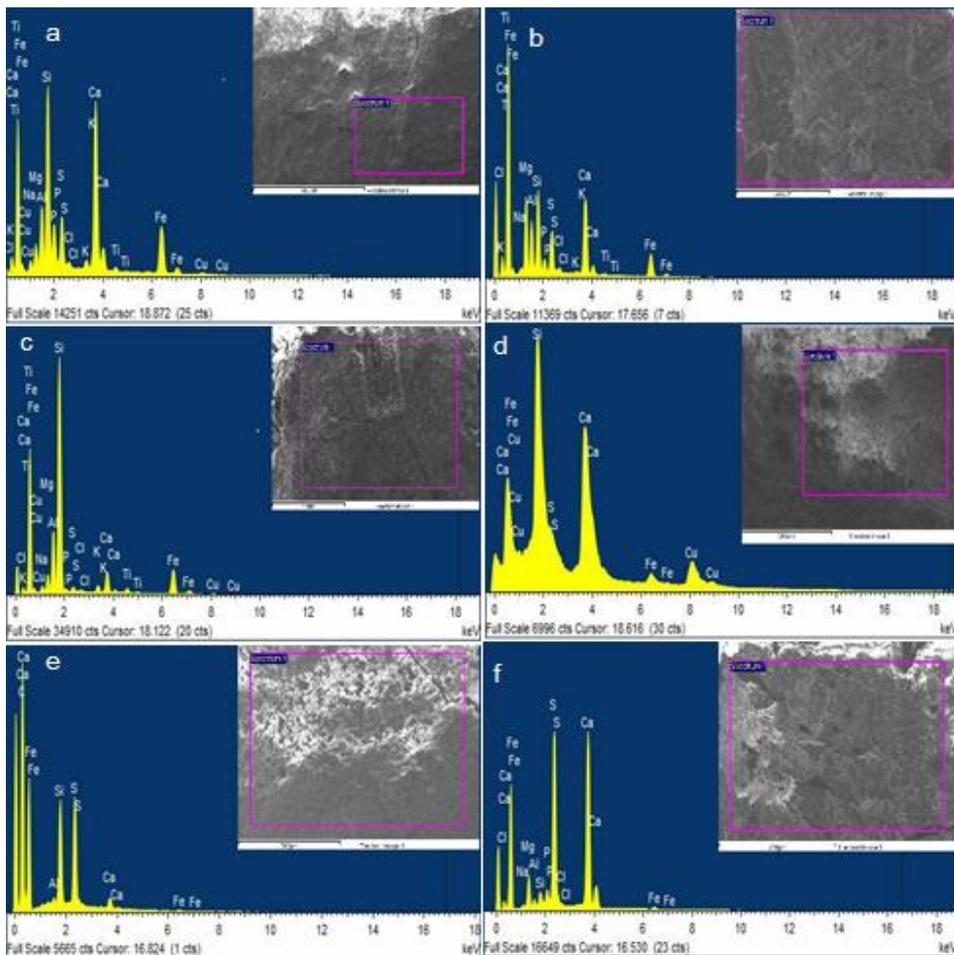


Fig. 18. EDS spectra of the pigment samples from TeTiky tomb:
 a - red pigment; b - yellow pigment; c-blue pigment; d - green pigment;
 e - black pigment; f - white pigment

A μ -Raman spectrum recorded on the red pigment (Fig. 19a) shows the characteristic bands at $\sim 226, 298, 408$ and 614cm^{-1} are attributed to hematite.

A μ -Raman spectrum recorded on the yellow pigment (Fig. 19b) shows the characteristic bands at $\sim 247, 280, 302, 386, 460$ and 506cm^{-1} were recorded, which refers to goethite.

A μ -Raman spectrum shows the characteristic bands of Egyptian blue (calcium copper silicate, $\text{CaO}\cdot\text{CuO}\cdot 4\text{SiO}_2$) (fig.19c). Egyptian blue is identifiable through the characteristic bands at $1022, 965, 563, 538, 510, 497, 412, 328, 361, 241\text{cm}^{-1}$. The band at 1086cm^{-1} is attributed to calcite - CaCO_3 . Few spectra at 200 and 400cm^{-1} is probably due to the presence of quartz and amorphous silica.

A μ -Raman spectrum of the black pigment (Fig. 19d). There are peaks at 1355 and 1592cm^{-1} , indicating that carbon was used in the pigment.

A μ -Raman spectrum of the white specimen (Fig. 19e), which contains peaks at $281, 711$ and 1085cm^{-1} . The Raman peak wavenumbers of the white pigment are in very good agreement with those of calcite.

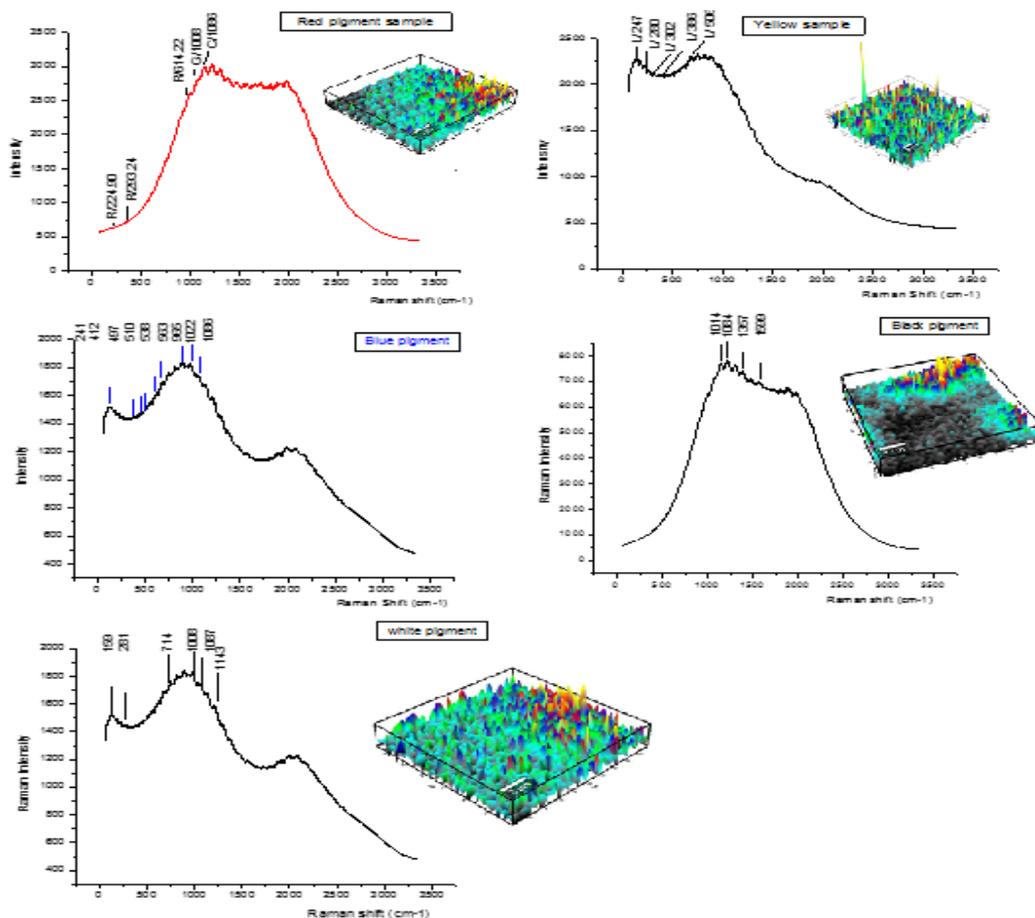


Fig. 19. μ - Raman spectra of the pigment samples of TeTiky tomb red sample: a - yellow sample; b - blue sample; c - black sample; d - the white sample

Binding media

FT-IR spectra from the red pigment gave intensive band at 3620 and 3432cm^{-1} the signature of stretching band of (OH) group, 1630cm^{-1} is the fingerprint region of bending band of (OH) group 1430cm^{-1} is the stretching band of (C-H) group, 1120cm^{-1} , 790cm^{-1} , 640cm^{-1} , 440cm^{-1} are characterized of C-O stretching bands (Fig. 20a) FT-IR spectra from a yellow pigment gave intensive band at 3420cm^{-1} , 1626cm^{-1} , 1340cm^{-1} , 1022cm^{-1} and 462cm^{-1} (Fig. 20b). From the above-mentioned results, so Arabic gum is highly recommended to be the binder of these pigments.

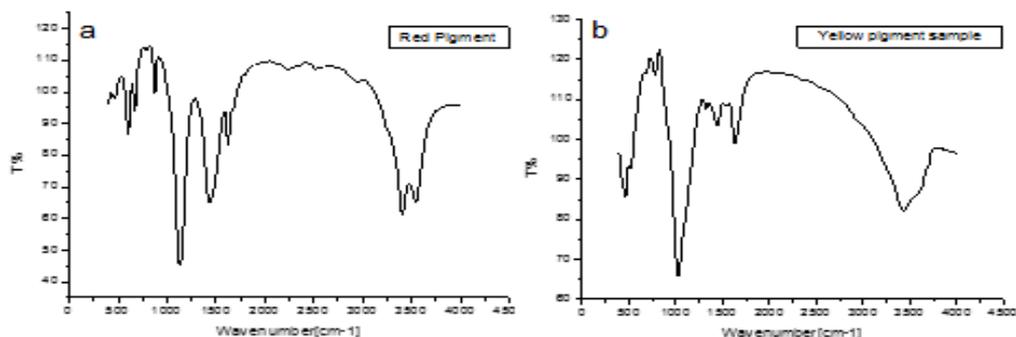


Fig. 20. FTIR spectra: a - red pigment sample; b - yellow pigment sample of pigments samples from TeTiky tomb

Discussion

Field investigations revealed that the TeTiky tomb was built of mud brick and the walls were plastered with mud mortar tempered with chaff and given a coat of gypsum plaster which acted as a ground for the painted decoration. The painted walls of the tomb were painted with funeral scenes.

Field investigations and lab analyses revealed that the condition of the paintings at the TeTiky tomb was disastrous, it has many deterioration phenomena such as Displacement, leaning, bulges of the upper wall of the niche, collapse in the lower part of the wall, and moderate cracks are found along the tomb walls. If heavy rain or new movement activity should occur, the cracks will increase in number and size, forming wall segments separated by cracks. These segments will move independently, shifting until the partial or total collapse of walls and roofs occurs. In addition, networks of micro-cracks and Hairline cracks were observed clearly due to environmental causes, vibrations, or internal and external stresses. Salts are considered one of the most dangerous degradation agents in the tomb [3-6]. Accumulation of salts between the mudbrick support and preparation layer of wall paintings are spread in all walls of the tomb, this resulted in the separation of the preparation layers from the adobe support [15], there are several sources of salts in wall paintings and many factors that may contribute to this process as environmental conditions, materials used for restoration (Portland cement and Gypsum) and rising damp [16]. The principal mechanism by which paints on earthen plaster on TeTiky tomb deteriorate is the loss of mechanical strength, as a result, paints lost adhesion to the wall between layers, or internal cohesion whereby the paint disintegrated to powders. Mural paintings in tombs are exposed to deterioration due to the composition of these paintings, it was well established that mud plaster containing organic materials such as chopped straw provides a rich and suitable food source for insects, like silver fishes who thrives on it by making holes into the soft mortar, in addition, the following year's murals was infested by termites feeding on the plant fibers in bricks and mud plaster, causing the painted layer to become detached from the support and many areas show extensive holes and gaps. The movement of the insects within the mud mortar makes it weak and prone to fall [17]. Microorganisms play an important and substantial role in alteration processes that occur in the TT15 tomb, visual examination revealed that the mural paintings in the tomb present visible discoloration in appearance due to the prolonged action of microorganisms, the tomb had many reasons encourage the microbial (e.g.) the atmospheric conditions of the tomb have favored the growth of microorganism, the composition of these paintings, it was well established that mud plaster containing organic materials such as chopped straw provides a rich carbon source for microbes growth [18], infiltration of rain and wastewater (from sewage leakage from sewage septic tanks installed by the people at the top of the tombs) within joints and cracks of the ceiling of the tomb. The tomb has been damaged due to looting, theft, and demolition, the thieves cut off some parts of the mural in the tomb for trafficking and the Louvre has recently returned several decorated sections from the tomb. In addition, the destruction of many parts with its mural painting during the demolition of houses in the old Qurna area.

No suitable means of pest control and consolidation were used at the tomb. Inappropriate materials through ignorance of mudbrick techniques and the incompatibility of materials were used trying to protect the tomb, missing parts of plaster were replaced with plaster-of-Paris or Portland cement and the cracks were restored with unsuitable linen filler and gypsum which caused a lot of damage and there was no opportunity for emergency conservation treatment. The lab analysis revealed that the paints in the TeTiky tomb were based on an organic binder (Arabic Gum) and traditional pigments as red hematite ochre in red paints, goethite ochre in yellow paint, vegetable black in black paint, Egyptian blue in blue paint, and a mixture of calcite and anhydrite in white paint. Anhydrite was detected in plaster samples and white pigment which may indicate that the gypsum has completely changed into anhydrite [19], Transformation of hydrated gypsum into anhydrite takes place spontaneously in dry, hot climate "as Luxure climate". As a result, the mechanical strength of gypsum plaster may be sharply reduced [20, 21].

FT-IR Spectroscopy analysis indicated that Arabic Gum was used as a binder of these pigments. Plant gums are polysaccharide vegetable emissions that can be tapped from entry points in plants. Plant gums utilized for restricting media are delivered by an assortment of trees and bushes [22]. The most widely available gums in ancient Egypt were acacia gum (from *Vachellia spp. and Senegalia spp.*) and gum tragacanth (from *Astragalus spp.*), while locust bean gum, tamarind gum and cherry gum have also been suggested [23].

Conclusions

Theban Tomb TT15 at Dra' Abu El-Naga Necropolis, Western Thebes, Luxor, Egypt has been exposed to many factors of damage, whether they are endogenous factors resulting from the use of weak materials in the carrying out of wall painting in the tomb, such as the mud-brick support or clay plaster layers, or environmental exogenous factors represented by the high temperatures, Changes in degrees of relative humidity, insects and microorganisms ... etc. that characterize the Luxor area of human factors was represented in the lack of maintenance of the tomb or the use of appropriate materials in maintenance operations such as the use of gypsum mortar or Portland cement, which led to many different aspects of the damage, whether physical or chemical transformations in the components of the wall paintings, which led to the weakness of its components and the loss of many components.

Scientific studies and examinations confirmed the bad condition of the wall painting in the TT15 tomb reached and the chemical and physical changes that occurred to the components of the painting layer in it, which warn of greater damage if maintenance operations were not carried out.

The necessity to prepare a restoration and conservation plan for the TT15 tomb that includes documentation of the tomb's painting, the bad condition that the tomb has reached, and to carry out cleaning, fixing, and consolidation operations for the wall paintings in the tomb so that we can save this tomb with its very beautiful wall paintings that talk about an important part of Egypt's archaeological heritage.

References

- [1] T. Bardají, A. Martínez, S. Sánchez, H. Pethend, D. García, S. Cuezvaf, C. Cañaverasg, A. Jiménez, *Geomorphology of Dra Abu el-Naga (Egypt): The basis of the funerary sacred landscape*, **Journal of African Earth Sciences**, **131**, 2017, pp. 233-250.
- [2] * * *, **Topographical Bibliography: The Theban Necropolis**, Porter and Moss, 2020, pg 26-27
- [3] S. Abdelaal, R. Yamani, M. Abdel-Fatah, I.G. Sandu, *Salt Weathering of Imni Tomb. Problem Identification and Characterization*, **International Journal of Conservation Science**, **10**(4), 2019, pp. 661-680.
- [4] S. Abdelaal, I.C.A. Sandu, *Assessment of protease in cleaning of bat blood patches from ancient Egyptian wall paintings and surface inscriptions*, **International Journal of Conservation Science**, **10**(3), 2019, pp. 459-474.
- [5] I.C.A. Sandu, P. Spiridon, I. Sandu, *Current studies and approaches in the field of cultural heritage conservation science. harmonising the terminology in an interdisciplinary context*, **International Journal of Conservation Science**, **7**(3), 2016 , pp. 591-606.
- [6] I. Sandu, C.T. Iurcovschi, I.G. Sandu, V. Vasilache, I.C. Negru, M. Brebu, P.S. Ursu, V Pelin, *Multianalytical Study for Establishing the Historical Contexts of the Church of the Holy Archangels from Cicau, Alba County, Romania, for its Promotion as a World Heritage Good I. Assessing the preservation-restoration works from the 18th century*, **Revista de Chimie**, **70**(7), 2019, pp. 2538-2544.
- [7] L. Addleson, C. Rice, **Performance of Materials in Buildings**, Butterworth-Heinemann Ltd., Oxford, 1991.

- [8] A. Moussa, M. Badawy, N. Saber, *Chromatic Alteration of Egyptian Blue and Egyptian Green Pigments in Pharaonic Late Period Tempera Murals*, **Scientific Culture**, 7(2), 2021, pp. 1-15
- [9] B.L. Harris, D.W. Hoffman, F.J. Mazac, **Reducing the Risk of Ground Water Contamination by Improving Household Wastewater Treatment**, Texas Agricultural Extension Services, Texas A&M University System, College Station, Texas, 2011, pp.1-12, <http://agrifile.org/lubbock/files/2011/10/2074410-B6029.pdf>
- [10] * * *, **France's Louvre Museum returns five frescoes to Egypt**, <http://news.bbc.co.uk/2/hi/europe/8412762.stm> .
- [11] A.M. Saviuc-Paval, I. Sandu, I.M. Popa, I.C.A. Sandu, V. Vasilache, I.G. Sandu, *Obtaining and Characterization of Ceramic Pigments for Polychrome Artistic Elements II. Microscopic and colorimetric analysis*, **Revista de Chimie**, 63(2), 2012, pp. 170-178.
- [12] A.M. Saviuc-Paval, A.V. Sandu, I.M. Popa, I.C.A. Sandu, A.P. Berteau, I. Sandu, *Colorimetric and microscopic study of the thermal behavior of new ceramic pigments*, **Microscopy Research and Technique**, 76(6), 2013, pp. 564-571.
- [13] A.M. Saviuc-Paval, I. Sandu, I.M. Popa, I.G. Sandu, V. Vasilache, A.V. Sandu, *Obtaining and Characterization of Ceramic Pigments for Polychrome Artistic Elements I. Synthesis and SEM-EDX and mu-FTIR Analysis*, **Revista de Chimie**, 63(1), 2012, pp. 40-48.
- [14] G. Howell, M. Edwards, R. Wolstenholme, S. David, C. Brooke, M. Pepper, *Raman Spectroscopic Analysis of the Enigmatic Comper Pigments*, **Analytical and Bioanalytical Chemistry**, 387, 2007, pp. 2255-2262.
- [15] N. Bader, A. Ahmed, *Identification and Conservation State of Painted Wall Plasters at the Funerary House in Necropolis of Tuna El-Gebel, El-Minia-Upper Egypt*, **Open Journal of Geology**, 7(7), 2017, pp. 923-944. DOI: 10.4236/ojg.2017.77063.
- [16] N. Bader, W. Al-Gharib, *Restoration and Preservation of Engraved Limestone Blocks Discovered in Abu Mousa Excavation, Suez- Egypt*, **International Journal of Conservation Science**, 4(1), 2013, pp. 25-42.
- [17] M. Singh, B. Arbad, *Ancient Indian Painting Recipes and Mural Art Technique at Ajanta*, **International Journal of Conservation Science**, 5(1), 2014, pp. 35-50.
- [18] Y. Su, Z. He, Y. Yang, S. Jia, M. Yu, X. Chen, A. Shen, *Linking Soil Microbial Community Dynamics to Straw-Carbon Distribution in Soil Organic Carbon*, **Scientific Reports**, 10, 2020, Article Number: 5526. DOI:org/10.1038/s41598-020-62198-2.
- [19] A.E. Charola, J. Puhlinger, M. Steiger, *Gypsum: A review of its role in the deterioration of building materials*, **Environmental Geology**, 52(2), 2007, pp. 339-352. DOI: 10.1007/s00254-006-0566-9.
- [20] A. Klimchouk, *Dissolution and Conversions of Gypsum and Anhydrite*, Chapter 4, **Speleogenesis: Evolution of Karst Aquifers** (Editors: Alexander B. Klimchouk, Derek C. Ford, Arthur N. Palmer, Wolfgang Dreybrodt), Publisher: National Speleological Society, Huntsville, Alabama, 2000, pp.160-168.
- [21] H. Milsch, M. Priegnitz, G. Blocher, *Permeability of Gypsum Samples Dehydrated in Air*. **Geophysical Research Letters**, 38, L18304.
- [22] C. Brøns, K. L. Rasmussen, M. M. Di Crescenzo, R. Stacey, A. Tenorio, *Painting the Palace of Apries I: ancient binding media and coatings of the reliefs from the Palace of Apries, Lower Egypt*, **Heritage Science**, 6, 2018, pp.2-20.
- [23] R. Newman, M. Serpico, *Adhesives and binders*, **Ancient Egyptian Materials and Technology** (Editors: P.T. Nicholson and I. Shaw), Cambridge University Press Cambridge, 2000, 476p.

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