ORIGINAL PAPER

SCIENTIFIC INVESTIGATION OF PIGMENTS AND BINDING FROM WOOD CEILING ABDEL RAHMAN KATKHAD, OTTOMAN PERIOD, CAIRO

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Abstract.*Abdel Rahman Katkhada Sibile was built of limestone, with ceiling of wood panels decorated with plant and geometric units with different colors. Blue color was of papagonite, red color was vermillion (HgS), white color was Barite ($BaSO_4$)and gold color was gold foil. This paint layer was carried out on gesso layer of calcite and animal glue. Calcite contained clay minerals and phosphorus as an indicator to its marine origin. Both gesso layer and paint layer were carried out onto wooden plates of Pinus.*

Keywords: *Abdel Rahman Katkhada, vermillion, papagonite, barite.*

1. INTRODUCTION

In Ottoman period, there was great interest and competition among rulers, princes, princesses and rich men in establishing the charitable establishments, such as sibiles (water distributors), hospitals and madrassa (schools). These establishments were not mere stone blocks, but they were lavishly decorated according to prevailed decoration style combined both Mumulk and Ottoman period. The ceilings within Islamic architecture are an important structural element that usually made of wood. These ceilings were of interest of artists who decorated these ceilings with different decorations: geometric and vegetable units and writings due to prohibition of figuring animal and human figures. These decoration units were carried out using different pigments on a preparatory layer of gesso on wood panels. This gesso layer was either of gypsum or lime mixed with binding medium, usually animal glue or rabbit glue [1, 2].

The pallet of the artists varied significantly and included traditional pigments such as hematite as red and brown pigment, or new pigments such as papagonite (calcium copper aluminum silicate hydrate) although little cases of using this blue pigment in decorating Islamic monuments were documented.The other red pigment is red vermillion, this pigment was imported from Minor Asia as natural occurrences and manufactured according to the technique described by Theophilus [3].Moreover, barite ($BaSO_4$) was used as white pigment, either inside Egypt or outside Egypt. In Egypt barite occurrences are usually associated with gypsum occurrences, or being in form of lenses within gypsum occurrences. In addition to its

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application as a white pigment, barite was used to protect wooden panels in the humid environment [4]. In sometimes, an opaque pigment of zinc sulfide and barium sulfate was used as inert and transparent pigment that is hard to be distinguished microscopically [5].

In the Islamic period, in particular in Mumluki and Ottoman periods, establishments in general were decorated lavishly, and because gold color is attractive in nature, so it was used in decorating ceilings of these establishments on a smooth preparatory layer [6].

Characterization of pigments, grounds and wooden panels within the ceiling of Sibile Abdel Rahman Katkhada will be described herein.

2. MATERIALS AND METHODS

2.1. MATERIALS

The Sibil of Abdel Rahman Katkhoda is dated back 1744 AD, registration no. 21 Islamic monuments, that was known in the historian records the Sibile of between the two palaces. This sibile is composed of sibiling room, entrance, annexes of sibile and reservoir (Fig. 1).

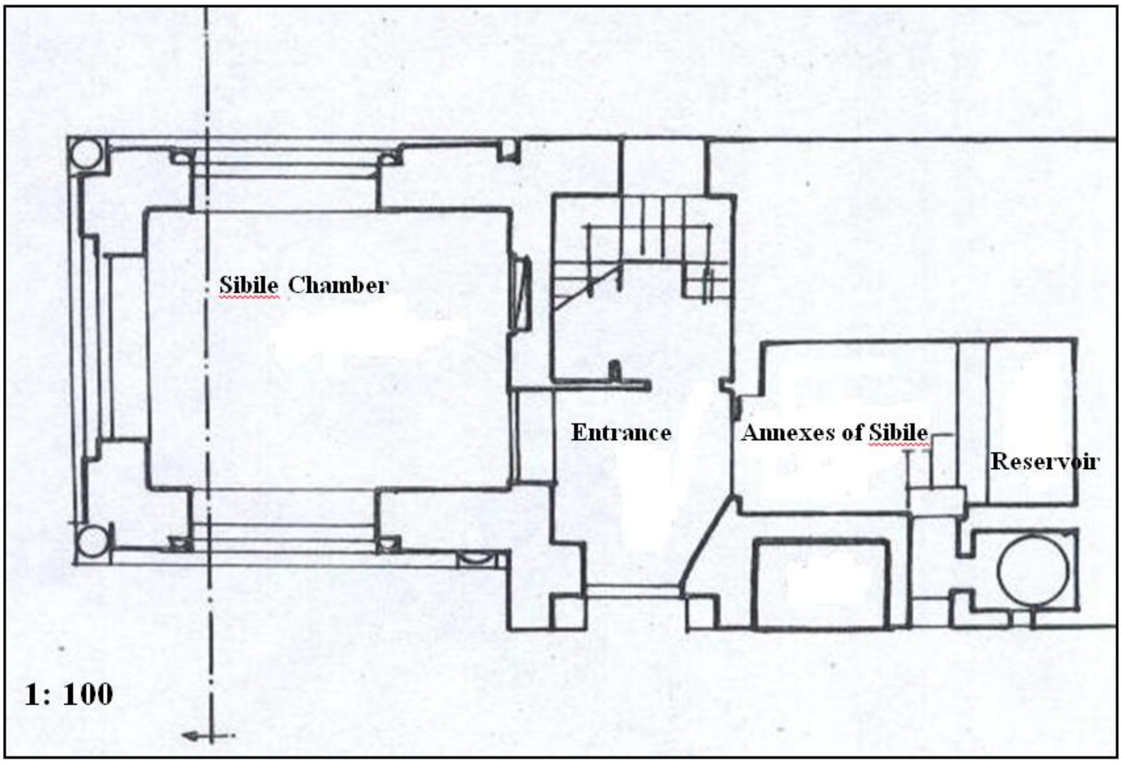


Figure 1. The plane of Sibile Abdel Rahman Katkhoda showing an entrance, annexes of Sibile and reservoir.

This Sibil was built of limestone, it ceiling is composed of two parts of wood, and the first one is 110×80 cm, the second is 115×110 cm decorated with plant and geometric units with different colors in similar to Mumluk style (Fig. 2).

a) b)

Figure 2. The ceiling of Abdel Rahman Katkhoda: a) staining of the ceiling with dusyt; b) decoration of the ceiling with geometic units.

2.2. COLOR CODE DOCUMENTATION

To put forward the conservation plane, it is important to document deterioration aspects. In this regard, color code method was used in documenting deterioration symptoms in the painted wood ceiling of Abdel Rahman Katkhoda, every deterioration symptom is identified with specific color to facilitate putting forward this plan (Fig.3).

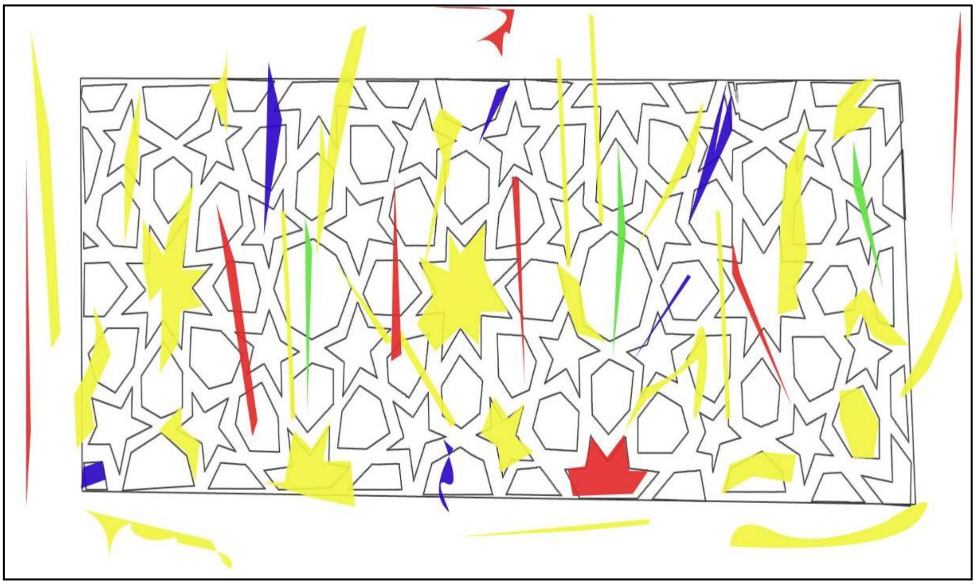


Figure 3.Color code of deterioration symptoms in the ceiling of Sibil of Abdel Rahman Katkhoda: red – paint flaking; blue – lost paintings; yellow – encrustations; green – fractures.

2.3. SAMPLING

Micro samples of white, red, brown, blue, bold and grounds were used for further investigations to identify these used pigments (Fig.4).

Figure 4. Pigment samples from the wooden ceiling of Abdel Rahman Katkhoda

2.4. METHODS

Optical microscopy

To investigate the homogeneity of paint layer and alteration of these used pigments, optical microscopy was used. Also, to identify the wood used as panels in the ceiling of Abdel Rahman Katkhoda, thin sections were made and investigated using light microscope according to [7], stained with different stains such as toluidine blue, iodine potassium iodide, sudan III, safranin 0, phloroglucinol, and ferric sulfate. These slides were compared with standard samples according to Hoadley [8].

X-Ray Diffraction (XRD)

To determine the elemental composition of different pigments, XRD Philips (PW1840) diffractometer with Ni-filtered Cu-Kα radiation was used.

Scanning Enectron Microscopy coupled with Energy Dispersive X-ray Spectrometry (SEM-EDX)

To confirm data obtained from XRD pattern of ground, SEM-EDX Quanta 200 (National Research Center, Dokky, Cairo) was used.

Fourier Transform Infrared spectroscopy (FT-IR)

To determine the binding medium and to confirm the essence of the blue pigment, FTIR Spectroscometer JASCO FT-IR 61000 (National Research Centre, Cairo) was used according to the operation instructions.

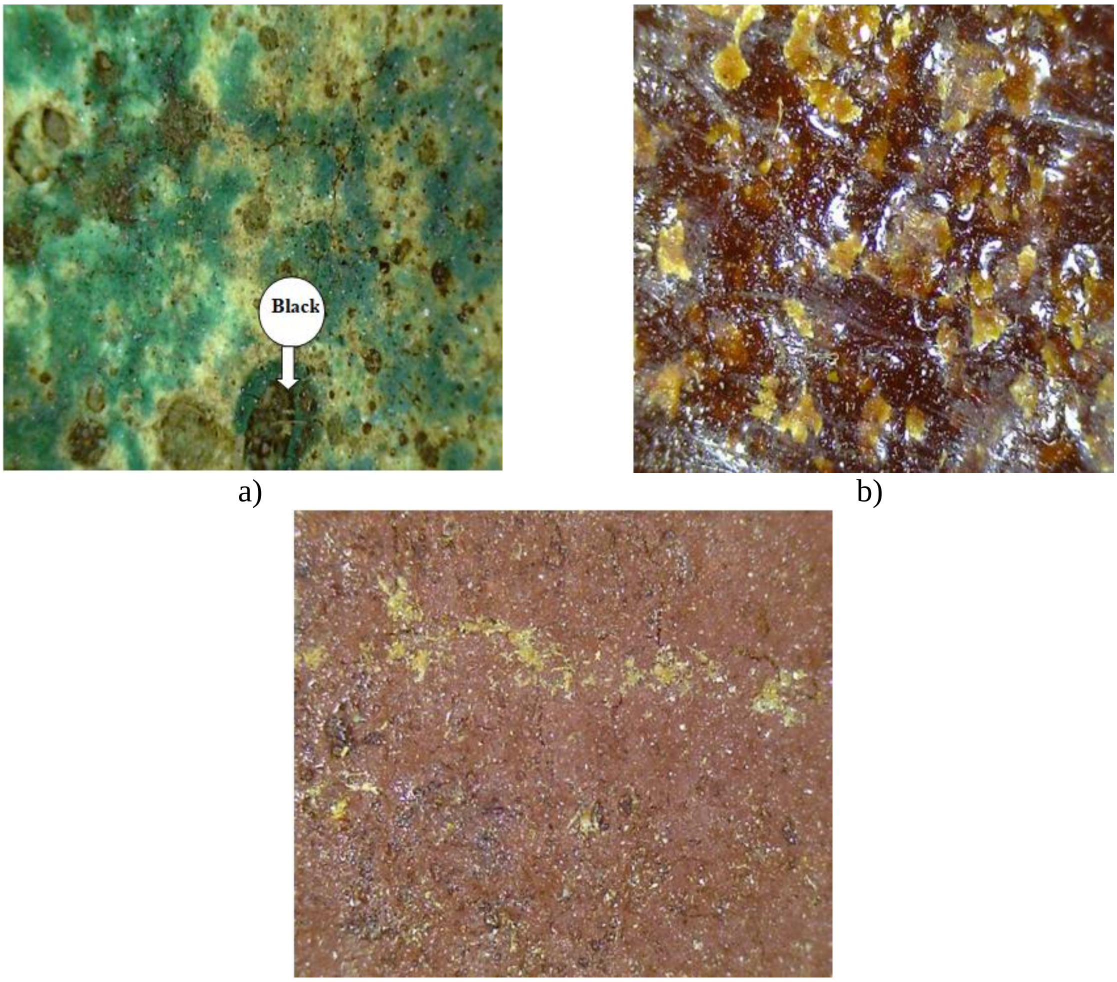
Microbiological investigations

From our survey to biodeterioration, it has been observed that microbial growth is less on red vermillion than other pigments, to confirm and explain this matter, fungi (*Penicillum* sp.) and *Streptomyces* sp. were cultured onto starch-nitrate-agar plates supplemented with vermillion, incubated for 72 hs at 28 °C, and colony forming units (cfu) of both Penicillum sp Streptomyces sp. and were counted.

3. RESULTS AND DISCUSSION

3.1. OPTICAL MICROSCOPY INVESTIGATION OF PIGMENTS

Optical microscopy investigations pointed out that blue pigment showed black spots that could be ascribed to the pollutants or precipitate clay minerals (Fig.5a). On the other hand, hematite appeared in bright color (Fig.5b).



a) b)

c)

Figure 5. Light micrograph of different pigments from Abdel Rahman Katkhoda: a) blue color; b) brown color; c) red color.

3.2. XRD INVESTIGATION OF PIGMENTS

XRD pattern of the blue pigment pointed out it is of papagonite [calcium copper aluminum silicate hydrate $CaCuAlSi_2O_6(OH)_3$] (Fig. 6). It has been well referenced that papagonite was used as a blue pigment in decoration of ceilings within Islamic buildings at least from the Fatimid period and continued till Ottoman period either in pure form or in a mixture with azurite. Papagonite was used as blue pigment in decoration the ceiling of the Hall of Moheb El Dein dated back to Ottoman period. The preference of Papagonite as a blue pigment may be ascribed to its toxicity to a wide spectrum of insects, so that it was used sometimes as insecticide [9].

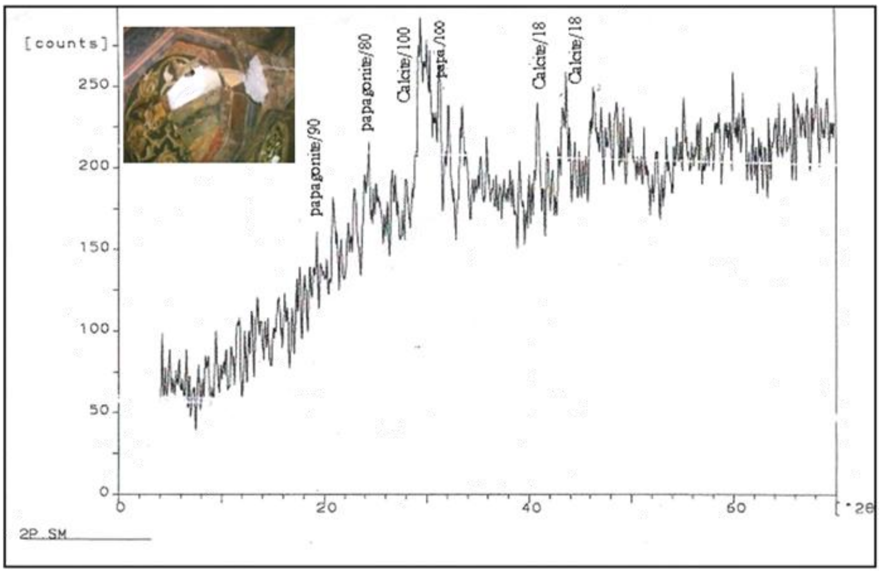


Figure 6.XRD pattern of blue pigment of papagonite.

This result was confirmed by FTIR investigation that gave intense band at 519 cm^{-1}; the bending vibrations for Si-O that is usually occur below 600 cm^{-1}. In addition,these spectra showed asymmetric Si-O-Si stretching band at 1159 cm^{-1} (Fig. 7). Also, these spectra showed an intense band at 3422 cm^{-1}, the fingerprint region of Cu that is commonly appearing at 3425 cm^{-1} [5]. Moreover, these spectra gave a band at 1415 cm^{-1} characterizing CO_3, and a band at 876 cm^{-1} characterizing O-C-O, so we could conclude that Papagonite (hydrated calcium copper aluminum silicate) is the most probable blue pigment.

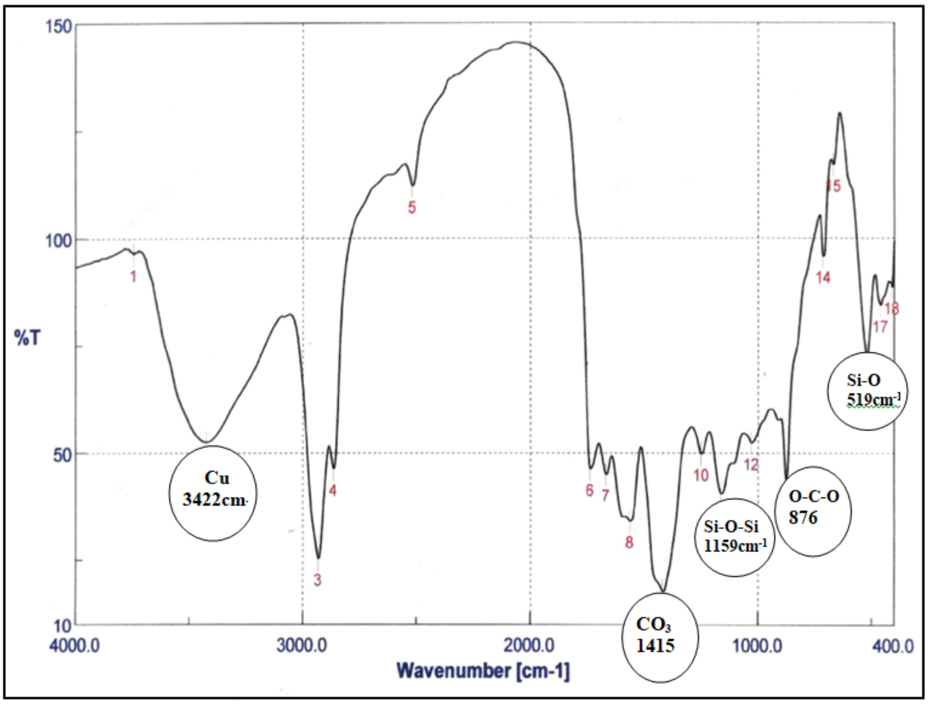


Figure 7. FT-IR spectra blue pigment.

XRD pattern of red pigment showed presence of mercuric sulphid, HgS (Fig.8), so using vermillion as a red pigment could be concluded. Historically, vermillion pigment was firstly used in the Greec-Roman period, it has been obtained from mines of Cappadocia in Minor Asia, sold with high prices in Greece-Roman marketsand and was widely used in several arte-facts[3]. Strabo differenatited between cinnbar and vermillion as red pigments, he mentioned cinnabar with μίλτος and vermilionwith χιννάζαςί., each one has specific characteristics. On the other hand, Pliny reported in 77 A.D that Roman supply of vermillion came from Sisapu (Sisopo) in Spain.

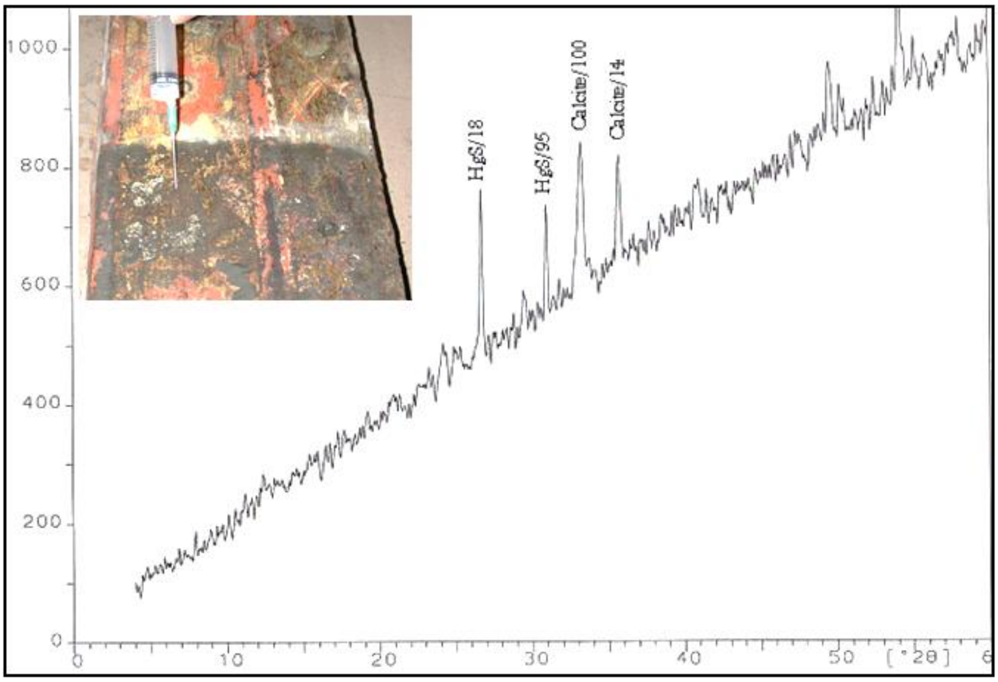


Figure 8. XRD pattern of red pigment showed presence of vermillion.

Chemically, both cinnabar and vermillion has the same chemical compositions (HgS), but vermilion (HgS) is the synthetic form of cinnabar made by a dry process which forms a darker and cooler tone, while a wet process produces the lighter German vermilion, and manufacturing of vermillion was described by Theophilus [10].

Due to higher prices of vermillion, it was mixed with hematite to reduce the cost on one hand and to increase its brightness on the other hand. In the Roman period, vermillion has also been interchanged with red ochre by Roman artists, though the ochre was preferred because of its lower cost and higher stability. In Islamic civilization, we could savely say that vermillion was used since the eighth century as red pigment [11].

Vermillion has many characteristics qualify it to be used in decoration of paintings and wood panels; it is bright and resistant to microbial growth [12]. The main disadvantage of vermillion is its darkness when exposed to light and gamma irradiation due to forming metacinnabar (β-HgS). In addition, this form of degradation of vermillion could be ascribed to the presence of halides due to forming HgCl [15], so it has been reported that both light and halides are the main factors inducing red mercury sulfide alteration [16]. The other agent of chromatic alteration of vermillion is exposure to laser power of 1.3mW at 532 nm that causes a temporary blackening, but could be turn into its original color after period of time [17].

In addition, XRD pattern of white pigment showed that it is of Barite [Barium sulphate ($BaSO_4$)] (Fig.9). Color of Barite is varied significantly; it may be white; bluish; yellow and red [18], and is slightly toxic, so it is used in cosmetics. In Egypt, there are some Barite occurrences in the Eastern Desert, and in most times associating the celestine ($SrSO_4$)occurrences. Using Barite as white pigment was put onto the evidence, it has been used as a white pigment in decorating Romanian Gospel dated back to 1740 [19], in a contemporaneous date of decorating the ceiling of Abdel Rahman Katkhoda (1744 AD). In addition to natural occurrences, $BaSO_4$ as a pigment was prepared from barite mineral via thermal reduction and leaching methods. In the thermal reduction process, barite was reduced with coal or coke to produce barium sulphide which is soluble in water between 1000°C and 1300°C in a kiln.

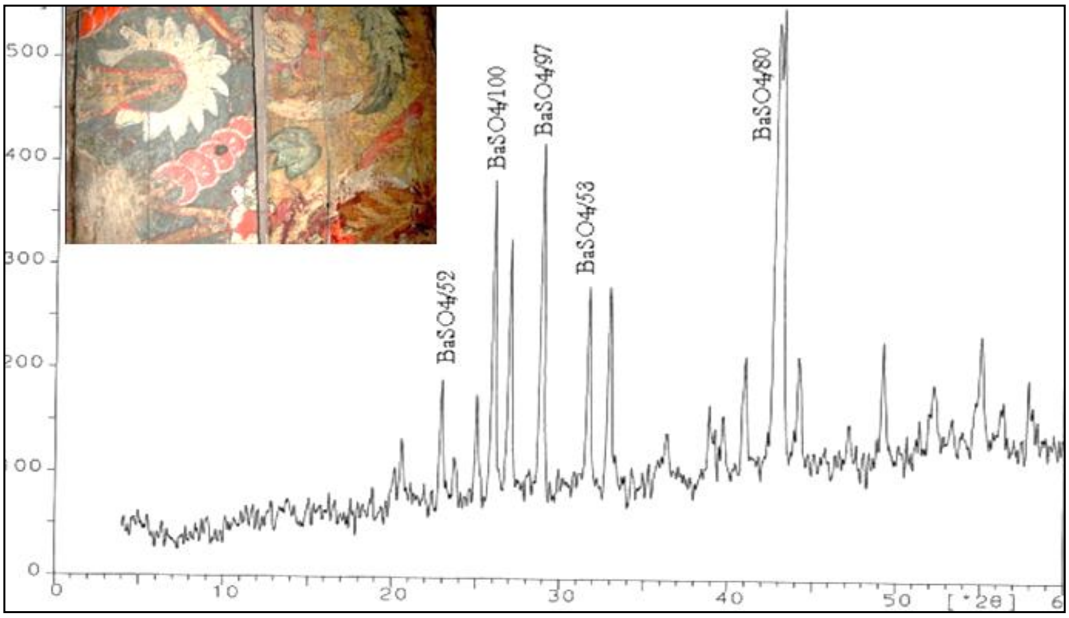


Figure 9.XRD pattern of white pigment point out presence of Barite ($BaSO_4$).

After barium sulphide was leached with water at 90°Cfor 30 minute, the obtained solution was used to precipitate $BaSO_4$ (%97 purity) by addition of Na_2SO_4. The white and green color pigments were successfully produced by using synthesized $BaSO_4$, ZnO and Cr_2O_3. The resulted white pigment of barite was intense and stable [18].

Our data derived from XRD pattern of the brown pigment pointed out presence of hematite (σ-Fe_2O_3) (Fig. 10) that was commonly used since prehistory due to its availability.

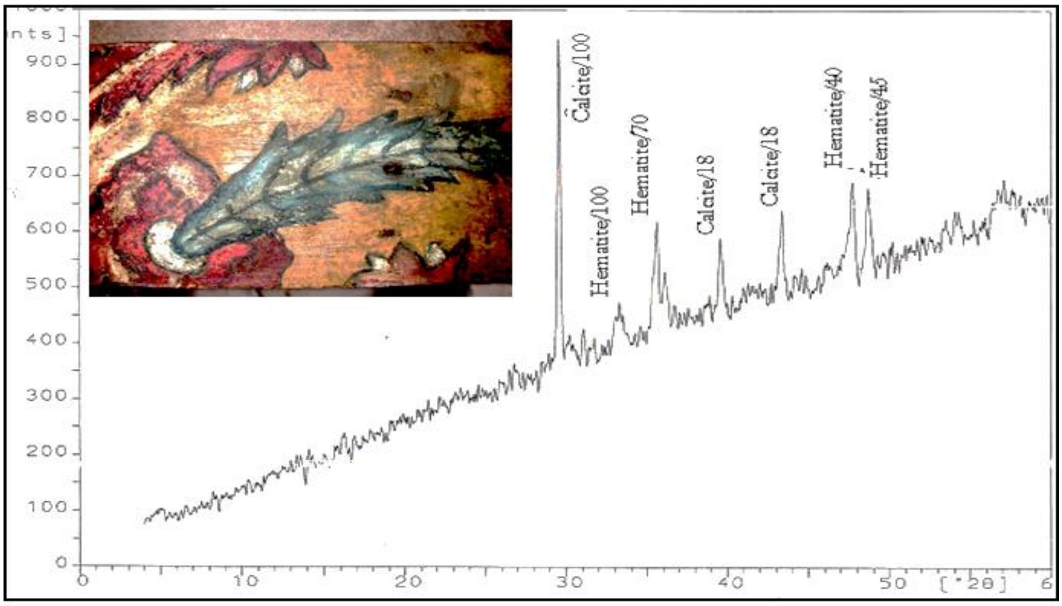


Figure 10.XRD pattern of brown pigment point out presence hematite.

The color of the ochre is notonly determined by the hematite content, but also by other minerals, such as manganese oxide and clay minerals that impart red ochre the dark color. Furthermore, the grain (or crystal) size may also influence the color [20]. In addition to natural occurrences, hematitebasedochres were at times roasted to produce more intense red hues [21].

XRD pattern of gold color pointed out presence of Au (Fig.11), so gold leaf gilding technique in decoration of the ceiling is the most probable; this technique was commonly used in the Islamic period by applying gold leaves with thickness 0.001 mm on a preparatory layer may be from lime or gypsum mixed with a binder may be of animal glue or egg yolk or called red bole [22]. In this technique gold leaves were placed side by side (and slightly overlapped on the edges), and gently pressed to show the outlines of the decoration units until finishing the decoration [23]. Moreover, XRD pattern of gold did not show Ag suggesting that gold was not alloyed.

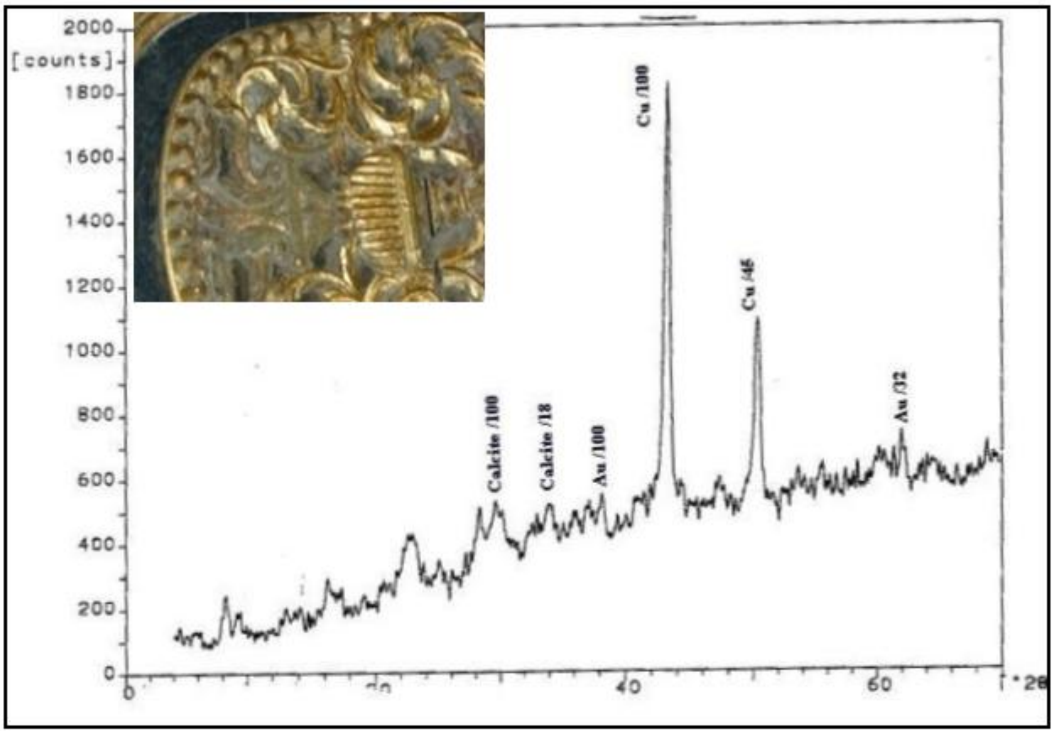
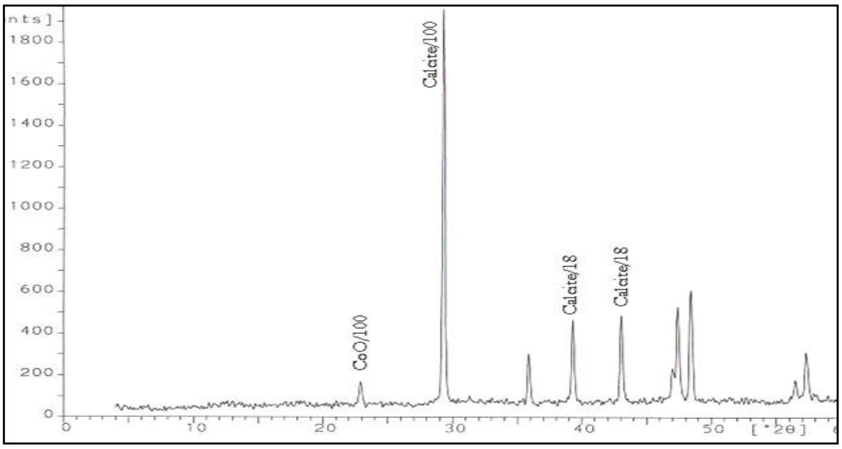


Figure 11. XRD pattern of gilding showing presence of gold (Au).

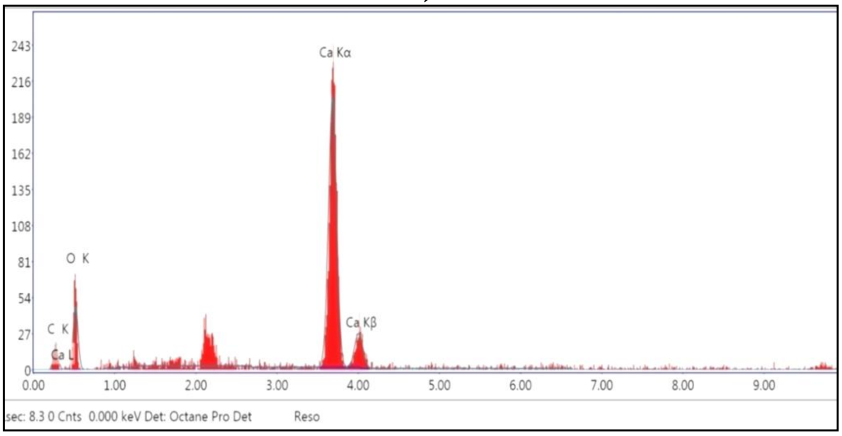
Our finding from XRD pattern of ground layer we could conclude that calcite is the main component (Fig.12a-b). It was well established that calcite mixed with a binding media in most cases of animal glue or rabbit glue (gesso) was used since Ptolemaic period as a prepartory layer to hidden knots and roughness of wood and to provide a smooth layer for painting and facilitate brushing [3, 10]. Gesso layer may not one layer, but in sometimes composed of multi layers; the inner layer is rough, sometimes contain a fraction of fine sand and crushed limes stone, but the upmost layer is smooth of fine calcite or gypsum with a portion of lime to increase its brightness.

3.3. SEM-EDX AND XRD PATTERNS OF GROUND

Confirming data obtained from XRD pattern, SEM-EDX pattern showed presence of calcite in addition to Si, Mg and P (Fig.12c). Presence of Si and Mg may be ascribed to clay minerals as impurities, and presence of P is an indicator to margin origin of lime occurrences [12-14].



a)



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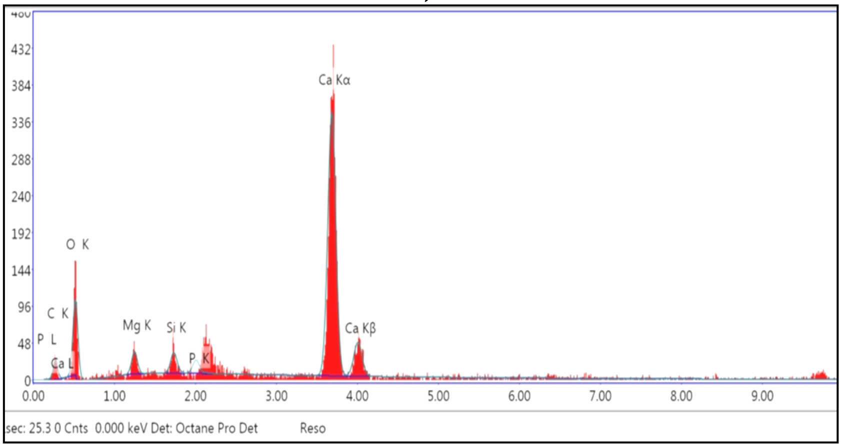

c)

Figure 12. Ground layer: (a) XRD pattern, (b-c) SEM –EDX pattern.

3.4. FT-IR SPECTROSCOPY OF BINDING MEDIA

FT-IR spectra of traces adhered to the gold foils pointed out intense band at 3350 cm^{-1}that is ascribed to N-H (amid group), this band is nearly the center of N-H group [5]. In addition, a strong band appeared at 1714 cm^{-1} characterizing aliphatic aldehyde C=O stretchingand a band at 1454 cm^{-1}characterizing carbonate group (Fig. 13), that has spectra from 1490-1370cm^{-1}[5, 24-26] suggesting using animal glue as adhesive for fixing gold foils on the preparatory layer. Animal glue is extracted from bones and nails, it was used from

Pharnonic period [2] and its manufacturing was depicted on the walls of the tomb of vizier Rakh m r3c from 18th dynasty [3].

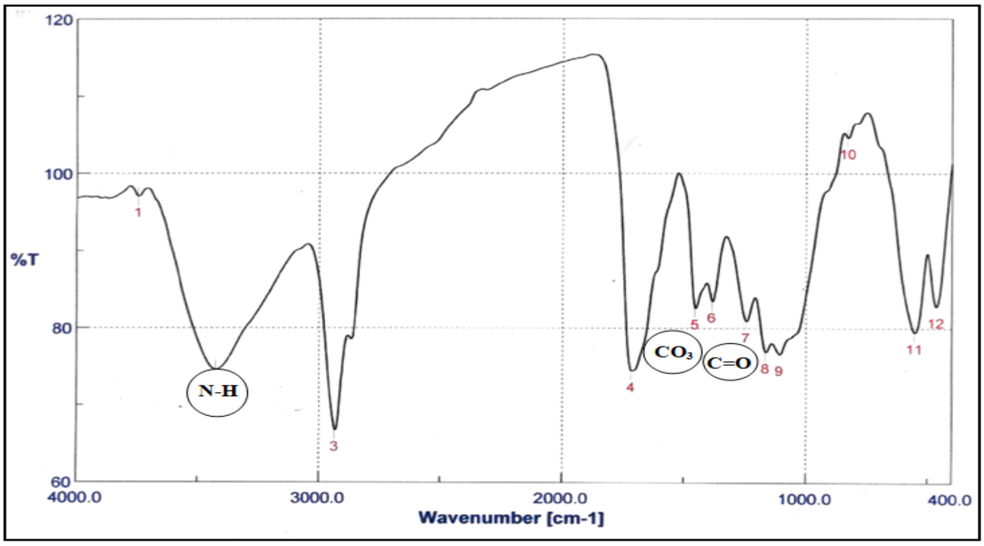

Figure 13. FT-IR spectra of traces adhered with gold foil.

3.5. MICROBIOLOGICAL INVESTIGATIONS

From microbial cultures, it has been observed that microbial growth on vermillion is less than on the other pigments estimated in cfu of fungi with olivey color and *Streptomyces* with white color (Fig.14). This could be ascribed to the matter of fact mercuric (Hg) in vermillion is toxic to a wide range of microorganisms, this phenomenon was well reported in many oil paintings [27].

On the other hand, colony forming units (cfu) of *Streptomyces* on vermillion is higher than fungi due to defense mechanisms possessed by *Streptomyces*; the most important are detoxifying enzyme activities and methylation mechanisms [28-34].

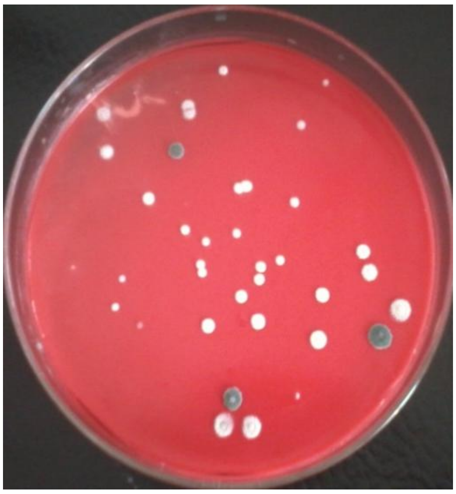

Figure 14. Effect of vermillion on both fungi and *Streptomyces.*

3.6. MICROSCOPIC INVESTIGATION OF WOOD

Microscopic investigation of wood cross section pointed out various pore arrangements; showed dense thick walled tracheids and circular growth rings with many thick walled cells [7]. In comparing these thin section micrographs with standard samples provided by Hoadley [6, 8], so we could say that striking ray fleck is apparent on the radial surface characterizing Pinus wood (*Pinus* sp.) (Fig. 15).

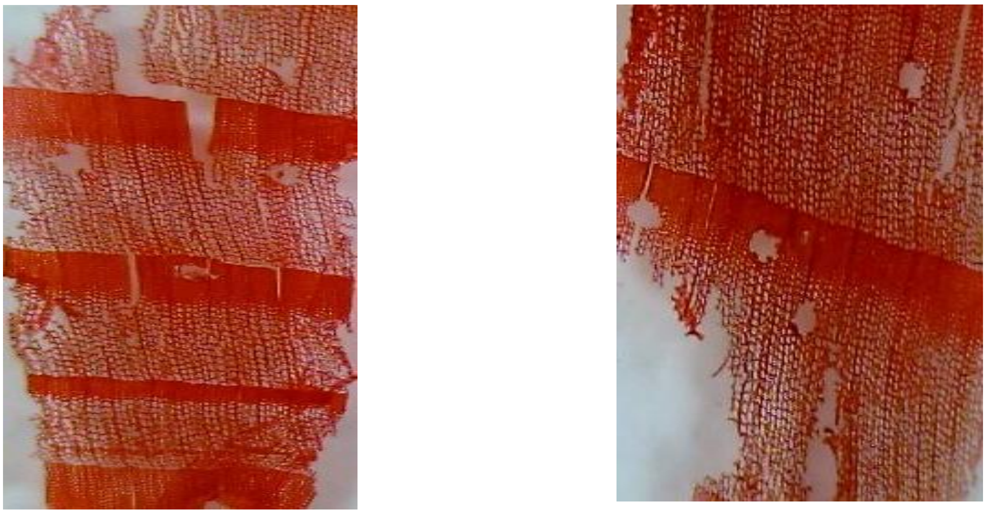

Figure 15. Thin section micrograph of wood from the investigated ceiling illustrated that it belong to the *Pinus*wood, 40X.

The pines, which comprise the genus *Pinus*; family *Pinaceae*, include avery large and diverse group of species; They typically have large-diameter resincanals whose epithelial cells are thinwalled,in contrast to the smaller resincanals and thick-walled epithelial cells ofthe Douglas-firlspruce/larch group; but we could not assign this sample to any subgroup of Pinus (P. *strobes*; P. *monticola*; P.*lambertiana*). Historically, presence of *Pinus* wood in Egypt was recorded since prehistory where two pices from Saqqara were found, but utilization of pines was common in the Islamic architecture in different items such as minbers, ceiling beams etc. Pinus wood is not a local type, but it may be imported from Syria which has commercial relation with Egypt, although some types of pinus were cultivated in gardens in Egypt, such as *Pinus pinea* and *pinus halepensis* but not on a wide scale so they could not be a source of wood [3].This preference of *Pinus* sp. wood in the Islamic architecture may be attributed to its attractive in color with yellow-reddish color and other characteristics qualifying it to be used in construction of different items such as containing a high portion of resinous materials inducing its microbial activity; strong and interlock of cellulose fibers; it softness; fine grained easily worked [7] and availability of its knots, so the preparatory layer could be adhered and interlocked strongly with wooden panels [3].

4. CONCLUSION

In conclusion, the ceiling of Sibile Abdel Rahman Katkhda was of wood, decorated with plant and geometric units using different pigments. The blue pigment is of papagonite; the red pigment is vermillion (HgS); white pigment is barite ($BaSO_4$); gold color is of gold foils. These pigments were mixed with a medium of animal glue to facilitate brushing on preparatory layer that is of calcite or slaked lime. This layer was carried out on wooden panels; thin section investigation of these panels pointed out that they are of *Pinus* wood.

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