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Analytical study of Coptic wall paintings in Egypt, El-Bagawat necropolis, Kharga Oasis: a case study

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Abstract

The present study aims to analyze Coptic wall paintings dating back to the late third/early fourth to the seventh century A.D. from El-Bagawat necropolis, Kharga Oasis, Egypt. The analysis was carried out by means of optical microscopy (OM), scanning electron microscopy (SEM) equipped with an energy dispersive X-ray detector (EDS), X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FT-IR) and the petrographic examination. The results allowed the identification of the stratigraphic analysis of the wall paintings, their chemical composition and the painting technique employed. On the other hand, the results permitted a comparison between the Coptic wall paintings and those from the Pharaonic, Ptolemaic and Roman periods. The obtained results will enrich our knowledge concerning some painting materials from an important example of the Coptic art in Egypt.

Key words: Coptic Wall Paintings; EL-Bagawat necropolis; Kharga Oasis; SEM-EDS, XRD; FT-IR; Green earth.

Introduction

The actual term "Copt" and accompanying adjective "Coptic" originate from the Arabic "qibt", which itself is a corruption of the Greek term "Αιγύπτιος" (Aigyptios) for the people of Egypt. Today, the term "Coptic" refers to the Christian population of Egypt (Malaty, 1992; Middleton-Jones, 2011). Christianity was probably introduced to the Kharga Oasis in the latter half of the third century or the beginning of the fourth century. The greater part of the Coptic monuments was built with mud brick. Mud-brick architecture was by no means the first use of earthen architecture in ancient Egypt (Emery, 2011). Mud-brick continued to be used for the lining for burial chambers and for roof vaulting for the subterranean portions in tombs of the New Kingdom and in the Ptolemaic, Roman, and even in Coptic tombs (Spencer, 1979; Fathy, 1989; McHenry, 1996; Kemp, 2000).

The early Christian necropolis of El-Bagawat (occupies a surface area of 10,000 squares) is located about 3 km from the centre of Kharga Oasis. The Kharga Oasis is located to the west of the Nile valley 550 kilometres to the South of Cairo. El-Bagawat necropolis is perhaps the oldest major Christian cemetery in the world; it consists of a vast expanse of domed mud brick mausoleums and underground galleries dating back to the fourth century A.D., which were built over the site of an earlier Egyptian necropolis of pit graves (Fakhry, 1951). The architectural style of the 263 tomb-chapels varies from simple one-room structures to family mausoleums with ornate façades enhanced with faux columns and arches and domed roofs (see Figure 1). Although many of the chapels at the necropolis were undecorated and consisted simply of a single chamber built over the tomb shaft, some were

Figure 1. A map of Egypt, the location of Kharga Oasis is highlighted with a red circle. (after: http://www.maps.com/)

much more elaborate and contained plastered walls with painted biblical scenes in a strange mixture of styles while others have elements reminiscent of earlier Egyptian architecture (Zibawi, 2005). Two of the most outstanding and best preserved of the decorated chapels are named 'Chapel of the Exodus' and 'Chapel of Peace' (Capuani, 2002). Figure 2 shows general view of El-Bagawat necropolis at El-Kharga Oasis and an example of the individual chapels in addition to patterns of the wall paintings found in these chapels. The main art form in the Coptic monasteries and churches was the wall paintings (Gabra, 2000). The investigation of Coptic wall paintings is among the most attractive targets to be investigated, because few published papers are available about the painting materials and techniques used in the Coptic monuments.

The analytical investigations of the ancient painting materials bring us much information on developments in ancient technologies and the propagation of ancient cultures. It is indispensable to determine the chemical and mineralogical composition of the wall paintings before any conservation and restoration projects. All the materials used in the construction of wall paintings undergo degradation when exposed to aggressive environments. The rate and symptoms of such process are influenced by number of factors, including the properties of material itself, the natural factors and human actions. The deleterious effects of acids on historical and modern structures are complex, the reaction of carbonate stone or plasters based on calcium carbonate with sulfuric acid causes the formation of gypsum. Sulfation is the process of chemical corrosion of carbonate materials due to acid attack by H_3O^+ ions in the presence of sulfate ions in aqueous solution, and leads to the formation of gypsum (Ausset et al., 1999).

Research aims

In general, few studies have been undertaken to analyze Coptic wall paintings in Egypt (Ali,

Figure 2. a) General view of chapels of the El-Bagawat necropolis. b) An individual chapel shows one of the patterns found in the necropolis. c, d) Plastered fault and paintings of the chapel (No. 25) at the necropolis. e) An example of the wall decorations at the chapel (No. 210) at the necropolis. f) The state of conservation of the wall paintings at the necropolis.

1995; Helmi and Ali, 1995; Bolman, 2002; Lyster, 2008; Moussa et al., 2009; Ali et al., 2011; Marey Mahmoud and Papadopoulou, 2012). Many questions were raised at the beginning of this analytical research, concerning mainly the technical development of painting materials and techniques used during the Coptic age in Egypt. Moreover, although their historical and artistic importance, there is a paucity of information concerning the Coptic wall paintings of El-Bagawat necropolis at Kharga Oasis. For this, the mean research task of the present work was devoted to analyze samples of wall paintings collected from some selected chapels at the necropolis (chapels No. 25 & 210) according to the registration numbers of the chapels provided by the Egyptian supreme council of antiquities (SCA).

The sample characterization was performed using optical microscopy (OM), scanning electron microscopy (SEM) equipped with an energy dispersive X-ray detector (EDS), X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FT-IR) and the petrographic examination. The results of this study bring us useful information on painting materials and techniques used in an important example of Coptic wall paintings in Egypt. Moreover, the obtained data permit comparison between the Coptic wall paintings and those from the Pharaonic, Ptolemaic and Roman ages in respect to their structure, the chromatic palette and the painting technique. Furthermore, the results will help in establishing a conservation-restoration plan for the wall paintings at El-Bagawat necropolis.

Materials and methods

Samples

The wall paintings of the studied chapels show several deterioration forms such as cracking, blistering and detachment of the painted layers. As a result of the state of preservation of the murals, fifteen (15) tiny samples of the detached painted plasters were carefully collected and chosen for analysis. In addition, five (5) representative mud brick samples were collected in order to determine their chemical and mineralogical composition. Table 1 shows codes, description and location of the studied samples.

The analytical methodology

In this work, the analytical techniques utilized to study the wall paintings samples were SEM-EDS, XRD, FT-IR and the petrographic examination. In order to identify the stratigraphic structure of the paint layers, some cross-sections were examined by a stereomicroscope.

Optical microscopy

The stratigraphic structure of the paint layers was examined using a Zeiss (stemi DV4) stereomicroscope with a Sony camera (DSC-S85). The examination was carried out on fractured surfaces of the raw samples and also some tiny samples were embedded in epoxy resin (EpoFix) in order to prepare polished cross-sections.

Scanning electron microscopy with an EDX microanalysis detector (SEM-EDS)

The microstructure and the morphological characteristics were determined by a Quanta 3D 200i scanning electron microscope made by FEI. The microanalysis was carried out using an energy dispersive X-ray analysis (EDAX Pegasus XM4). The accelerating voltage was between 15-20 kV. Highly polished cross-sections prepared on the studied samples were examined using SEM. The investigation was carried out in the backscattered electrons mode (BSE).

X-ray diffraction analysis (XRD)

In order to determine the mineralogical composition of the plaster layers, the collected samples were ground into powder in an agate mortar. PXRD data were collected using a Philips X'Pert PW3290 diffractometer with Ni-filtered CuK_α radiation on randomly oriented samples. The counting statistics of the X-ray diffraction method were as follows: step size: 0.01° 2θ, start angle: 3°, end angle: 63° and scan speed: 0.02° 2θ/sec. The X'Pert HighScore Software 2006 was used for the semi-

Table 1. Codes, description and location of the studied samples.

No.	Colour	Label of sample	Description	Location
1	Green	Gr.1	Painted fragment	Chapel No. 25
2	Olive-green	Gr.2	Powder	Chapel No. 210
3	Light green	Gr.3	Paint flake	Chapel No. 210
4	Dark green	Gr.4	Painted fragment	Chapel No. 210
5	Red-brown	R.1	Painted fragment	Chapel No. 210
6	Red	R.2	Coloured grains	Chapel No. 25
7	Pink	R.3	Painted fragment	Chapel No. 25
8	Light red	R.4	Paint flake	Chapel No. 25
9	Yellow	Y.1	Tiny piece	Chapel No. 210
10	Yellow	Y.2	Powder	Chapel No. 25
11	Dark yellow	Y.3	Painted fragment	Chapel No. 25
12	Light yellow	Y.4	Paint flake	Chapel No. 25
13	White	W.1	Painted fragment	Chapel No. 25
14	White	W.2	Paint flake	Chapel No. 25
15	White	W.3	Painted fragment	Chapel No. 25

quantitative determination of the mineral phases. The detection limit was ± 2% w/w.

Infrared spectroscopy

Small amounts of the paint samples were removed and mixed with a KBr powder (~ 150 mg). After grinding, the mixture was pressed in an evacuated die in order to produce a pellet. FT-IR spectra were collected using a Jasco 4100 FT-IR Spectrometer, in transmittance mode, over a wave number range of 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}.

Petrographic examination

The prepared thin-sections of the plaster samples were examined by a Nikon Eclipse E600 microscope with photographic attachments include PixeLINK PL-A623 digital camera.

Results

Optical and petrographic examination

The optical examination on fragments of the plaster layers showed their stratigraphic sequence profile. Figure 3a shows photomicrograph obtained on a fraction of the plaster sample. It was clear that the paint layer is well adhered to the underlying preparation layer. Below it, a fine plaster '*intonaco*' with thickness ranges from 150 to 200 µm is clearly observed. In Figure 3b, the thick coarse plaster '*arriccio*' is clearly observed. The thickness of this layer ranges from 300 µm to 15 mm. The coarse plaster is rich in siliceous aggregates mainly of local sands and the matrix binder is mainly of lime. The petrographic analysis carried out on thin sections of the fine plaster layer (Figure 3c, d) shows that the plaster layer is texturally heterogeneous. The matrix is

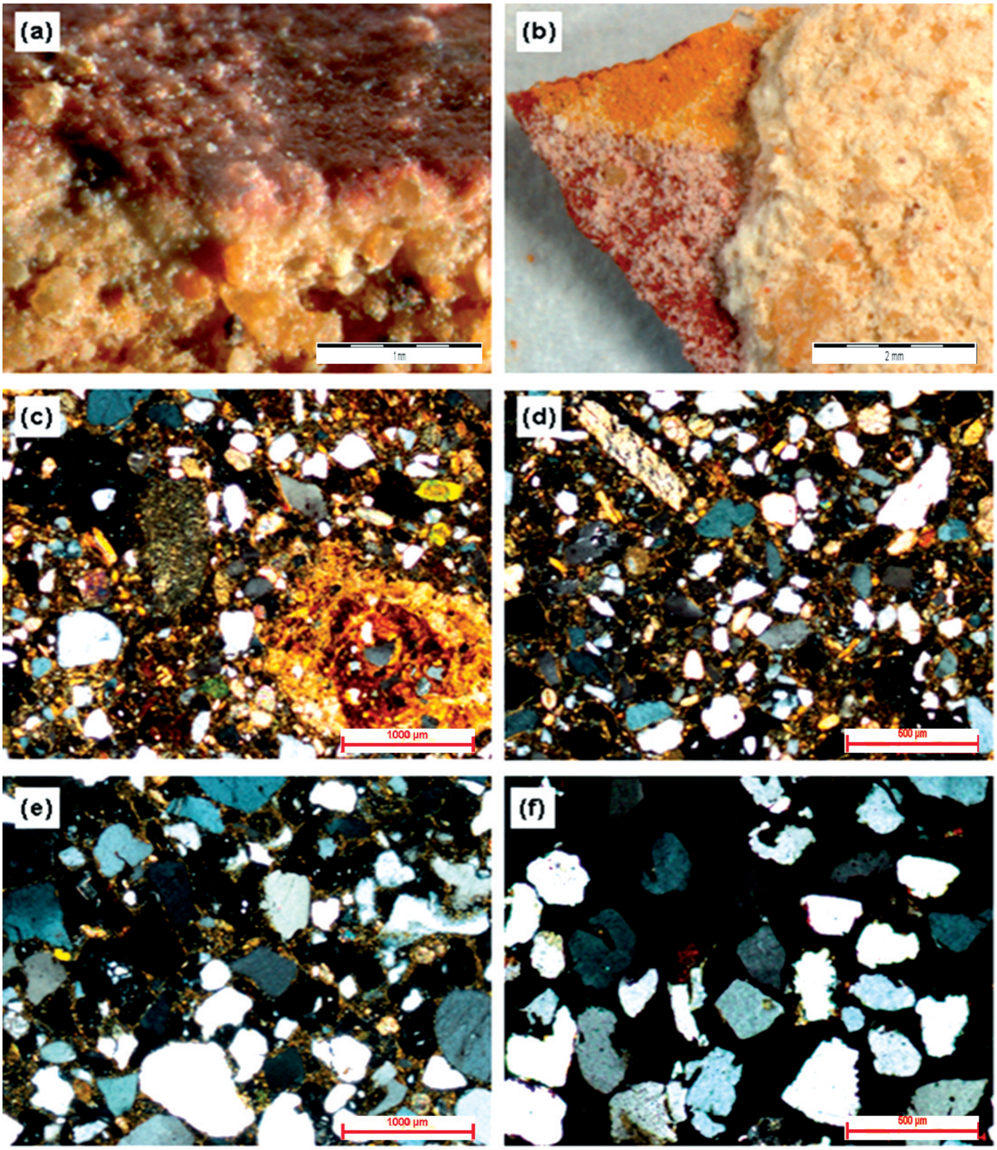

Figure 3. a) Stereomicroscopic image of polished cross-section of the plaster layer showing the stratigraphy of the different layers. b) Stereomicroscopic image showing details of the outer surface of the ground layer. c, d) Optical photomicrograph of thin sections prepared on the fine plaster layers, under cross polarized light. e, f) Optical photomicrograph of thin sections prepared on the coarse plaster layers, under cross polarized light.

based mainly on fine-grained calcium carbonate. Slightly large siliceous and calcareous aggregates are observed in the matrix. The coloured patches (mainly with light brown hues) are attributed to iron oxides associated in the plasters. Some silicate minerals (such as muscovite,

$KAl_2Si_3AlO_{10}(OH)_2$), with different colours ranges between yellow to reddish-brown hues are also noticeable. The microscopic images obtained on thin sections of the coarse plaster layer (Figure 3e, f) show aggregates of large sharp grains of quartz (SiO_2) and limestone fragments are clearly observed embedded in the carbonated matrix.

Mineralogical characterization

Table 2 shows the mineralogical composition of the studied samples. The XRD analysis on powder sample of the mud brick (Figure 4a) shows major component of quartz. Other minerals of calcite ($CaCO_3$), plagioclase (albite, $NaAlSi_3O_8$), potassium feldspar (microcline, $KAlSi_3O_8$) and clay minerals (kaolinite, $Al_2Si_2O_5OH_4$ and illite, $KAlSi_3AlO_{10}OH_2$) were also measured. The XRD analysis of the fine plaster indicates that calcite is the major component in the sample. Traces of gypsum ($CaSO_4{\cdot}2H_2O$), quartz and kaolinite were also measured. The XRD analysis of the coarse plaster (Figure 4b) shows that the sample consists mainly of quartz and calcite. In some samples, traces of kaolinite, potassium feldspar (microcline), plagioclase (albite) were also found. The render samples show major components of calcite with traces of quartz and gypsum. Concerning pigment samples, XRD analysis showed that the green pigment (sample Gr.1) consists of quartz, calcite, glauconite, gypsum and clay minerals. The red pigment (sample R.2) consists of quartz, calcite, hematite (α-Fe_2O_3), potassium feldspar, plagioclase, gypsum and clay minerals. The yellow pigment (sample Y.2) consists of calcite, quartz, goethite (α-FeOOH), potassium feldspar, plagioclase and clay minerals. The white pigment (sample W.1) contains calcite as major component with minor amounts of gypsum while traces of quartz were also found.

Table 2. The mineralogical composition of the studied samples.

Sample/Component	*Q*	*C*	*Kf*	*Pl*	*Gy*	*He*	*Go*	*Gl*	*Cl*
Mud brick	+++	+	+	+	–	–	–	++	++
Coarse plaster	+++	+	+	+	–	–	–	–	–
Fine plaster	+	+++	+	–	+	–	–	–	+
Render	+	+++	–	–	+	–	–	–	+
Green pigment	+++	+	+	+	+	–	–	+	+
Red pigment	+++	+	+	+	+	+	–	–	+
Yellow pigment	+++	++	+	+	–	–	+	–	+
White pigment	+	+++	–	–	++	–	–	–	–

Q = quartz; C = calcite; Kf = K-feldspar; Pl = plagioclase; Gy = gypsum; He = hematite; Go = goethite; Gl = glauconite; Cl = clay minerals; – = not determined; + = traces; ++ = minor constituent; +++ = major constituent.

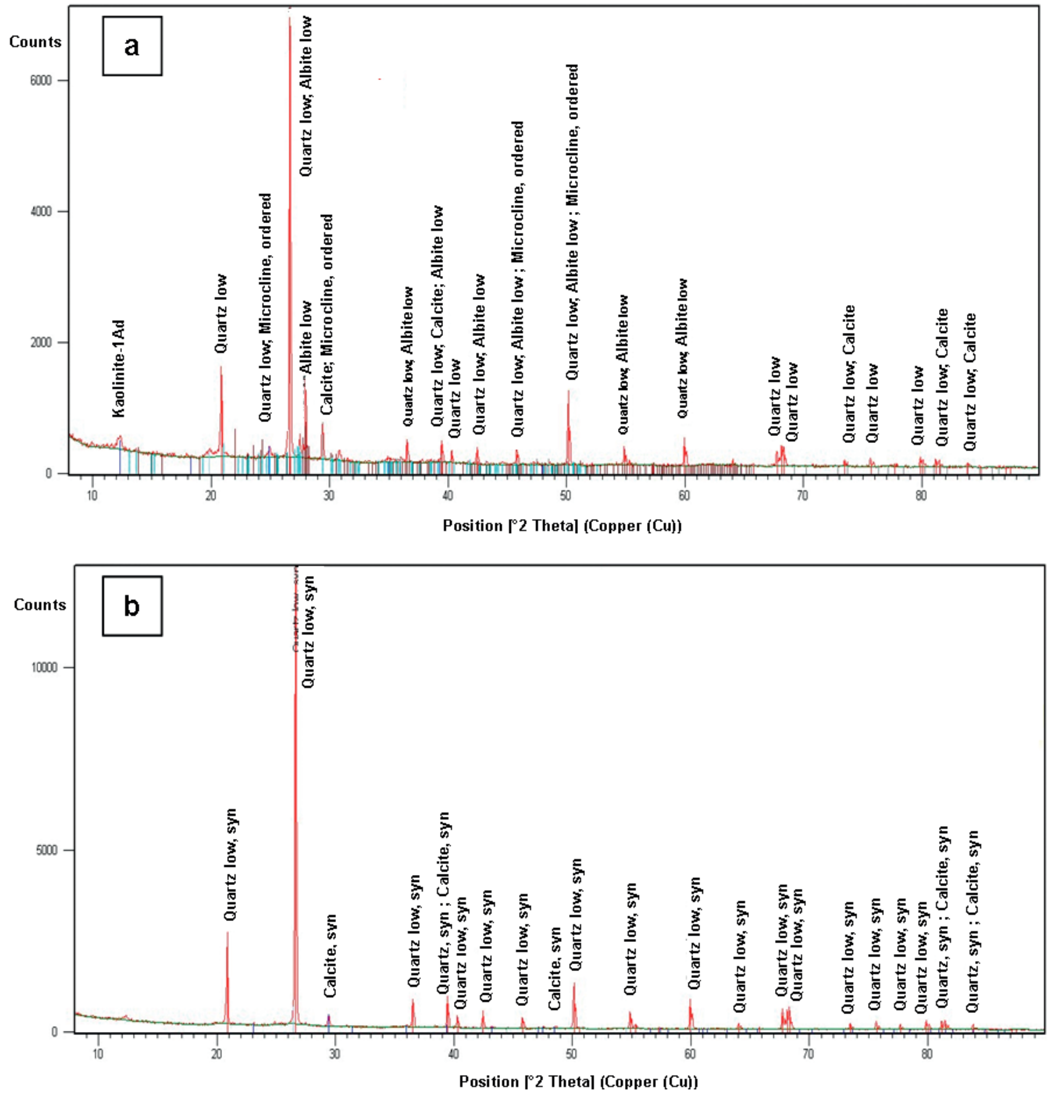

Figure 4. Representative XRD patterns of: a) mud brick sample; b) coarse plaster layer.

Microstructure and microanalysis

Figure 5 shows BSE and SEM images obtained on some paint layers. The BSE image obtained on a polished cross section of the green paint layer (Figure 5a) shows coarse aggregates of the pigment material. The elemental analysis, obtained by the EDS detector, (Figure 5b) showed that potassium, aluminium, silicon and iron were detected. Among mineral pigments, only green earth contains the above elements. Moreover, the existence of sodium detected in the EDS spectrum of the sample suggests that

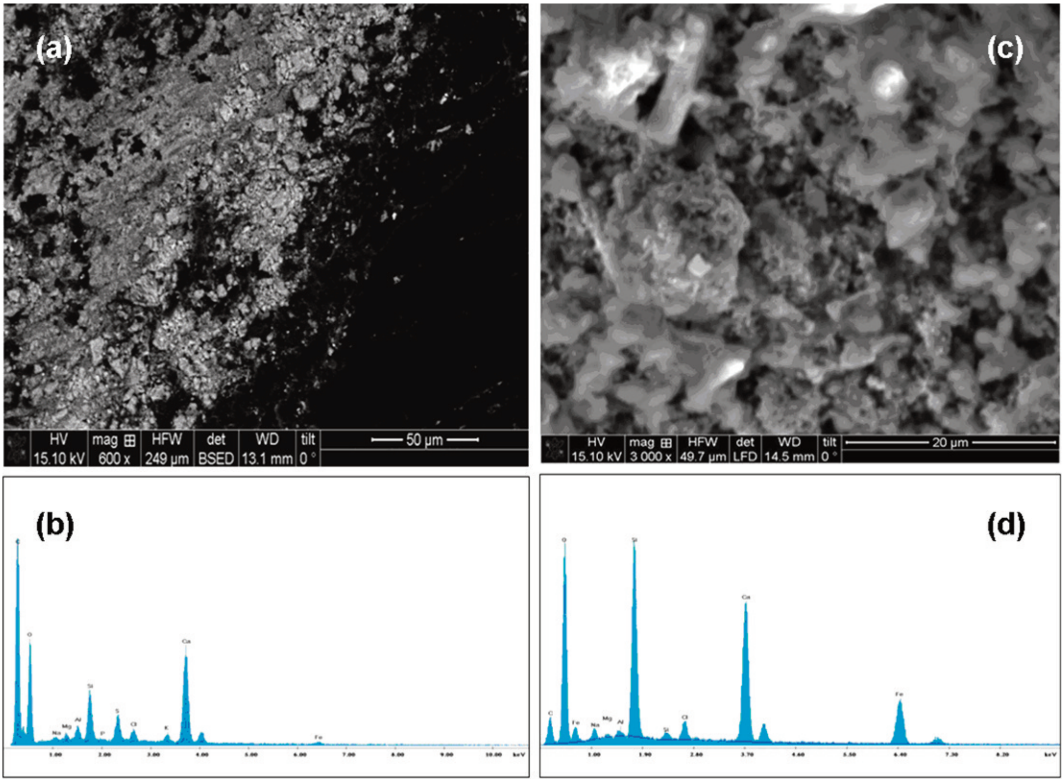

Figure 5. a) BSE image of a polished cross-section of the green paint layer (sample Gr. 1), and the EDS spectrum b) obtained on the same sample. c) SEM image of the outer surface of the yellow paint layer (sample Y.1), and the EDS spectrum d) obtained on the same sample.

glauconite was used to obtain the green colour. The detection of sulphur is probably due to the presence of calcium sulphates (gypsum) resulting from the chemical transformation of calcium carbonates in the render layer.

The SEM investigation obtained on the outer surface of the yellow pigment sample (Figure 5c) shows a heterogeneous distribution of large and small crystals of ochre and quartz. The EDS microanalysis of the sample (Figure 5d) shows that the peak of iron is present which indicates the existence of iron oxide. The contribution of silicon and aluminium suggests possible existence of an aluminosilicate material (probably the kaolinite). The BSE image obtained on the red pigment sample shows slightly fine grains of the red ochre. The EDS microanalysis of the sample affirms the presence of the beak of iron which suggests the use of iron oxides of red ochre. Minor amounts of silicon and aluminium were found, together with traces of sodium, iron and sodium were also detected. These elements probably refer to aluminosilicate materials (e.g. clays) and plagioclase (albite). The investigation of the white pigment shows fine grains of calcium carbonate. The EDS microanalysis shows high concentration of calcium in the sample. For mud brick samples, the EDS microanalysis shows major amounts of silicon with minor amounts of calcium, aluminium and iron. Other elements of sulphur, potassium, magnesium, sodium and titanium were also detected. The fine plaster layers show elemental composition with concentrations of CaO ranging from 65.54% to 74.99%. The coarse plaster layers show elemental composition with concentrations of CaO ranging from to 33.5% to 46.11%. The EDS microanalysis of the rend samples show high concentration of calcium with traces of sulphur and silicon. The SEM-EDS results obtained on the studied samples are given in Table 3.

FT-IR results

Figure 6 displays FT-IR spectra obtained on the yellow and green paint layers (samples Gr.1 and Y.1). In Figure 6a, the characteristic bands at 1419, 867, 782 and 708 cm^{-1} are all of calcium carbonate. These bands are come from the underlying ground layer. The band at 549 cm^{-1} indicates the presence of iron oxide. The outer OH groups at 3747 and 3693 cm^{-1} are attributed to amounts of kaolinite. The band at 1653 cm^{-1} is attributed to (νC = O amide I) together with the bands at 2988 and 2896 cm^{-1} attributed to methylene groups (ν_{asym} and $\nu_{sym}CH_2$) are believed to belong to a proteinaceous material. The bands at 3000-3750 cm^{-1} indicate hydroxyl group. The bands at 400-475 cm^{-1} indicate the presence of amorphous silicates. The band at 1044 cm^{-1} is attributed to in-plane Si-O stretching modes. In the FT-IR spectrum of the green pigment (Figure 6b), glauconite was characterized by the small band at 664 cm^{-1} with broad peaks in the 1110-950 cm^{-1} region. These last bands are mainly at 970 and 1055 cm^{-1}. In the region 3400-3700 cm^{-1}, three narrow bands at 3420, 3690 and 3747 cm^{-1} are present; such bands are characteristic of the stretching of hydroxyl (O-H stretching) groups depending on the nature of the cations (Moretto et al., 2011).

The bands at 913-849 cm^{-1} are attributed to Si-O stretching bands, and the bands at 1000-1100 cm^{-1} are for asymmetric Si-O-Si stretching bands. The bands at 2989 and 2896 cm^{-1} are for methylenic groups, 1646 cm^{-1} (amide I) and at 1529 cm^{-1} (δN-H amide II) for a proteinaceous material. The presence of oil was concluded on the basis of characteristic bands at 1737 and 1247 cm^{-1} (stretch, C-O-C). The plaster layers

Table 3. SEM-EDS analysis (wt%) of the studied samples.

Sample/oxide	Na_2O	MgO	$A1_2O_3$	SiO_2	SO_3	K_2O	CaO	Fe_2O_3	TiO_2
Mud brick	1.76	1.87	24.65	48.32	4.49	3.54	6.43	3.76	1.09
Coarse plaster	7.78	2.21	1.21	30.82	1.45	0.76	46.11	0.97	–
Fine plaster	2.81	1.80	3.76	5.56	7.36	2.28	74.99	1.50	1.05
Render	1.65	–	–	1.65	1.87	–	89.54	–	–
Green pigment	–	7.02	6.43	51.82	–	4.87	15.54	14.32	–
Red pigment	–	–	2.77	3.49	10.05	1.98	6.31	74.21	1.34
Yellow pigment	–	1.76	4.98	23.49	20.86	1.63	21.48	24.96	–
White pigment	–	–	–	2.67	5.79	–	91.54	–	–

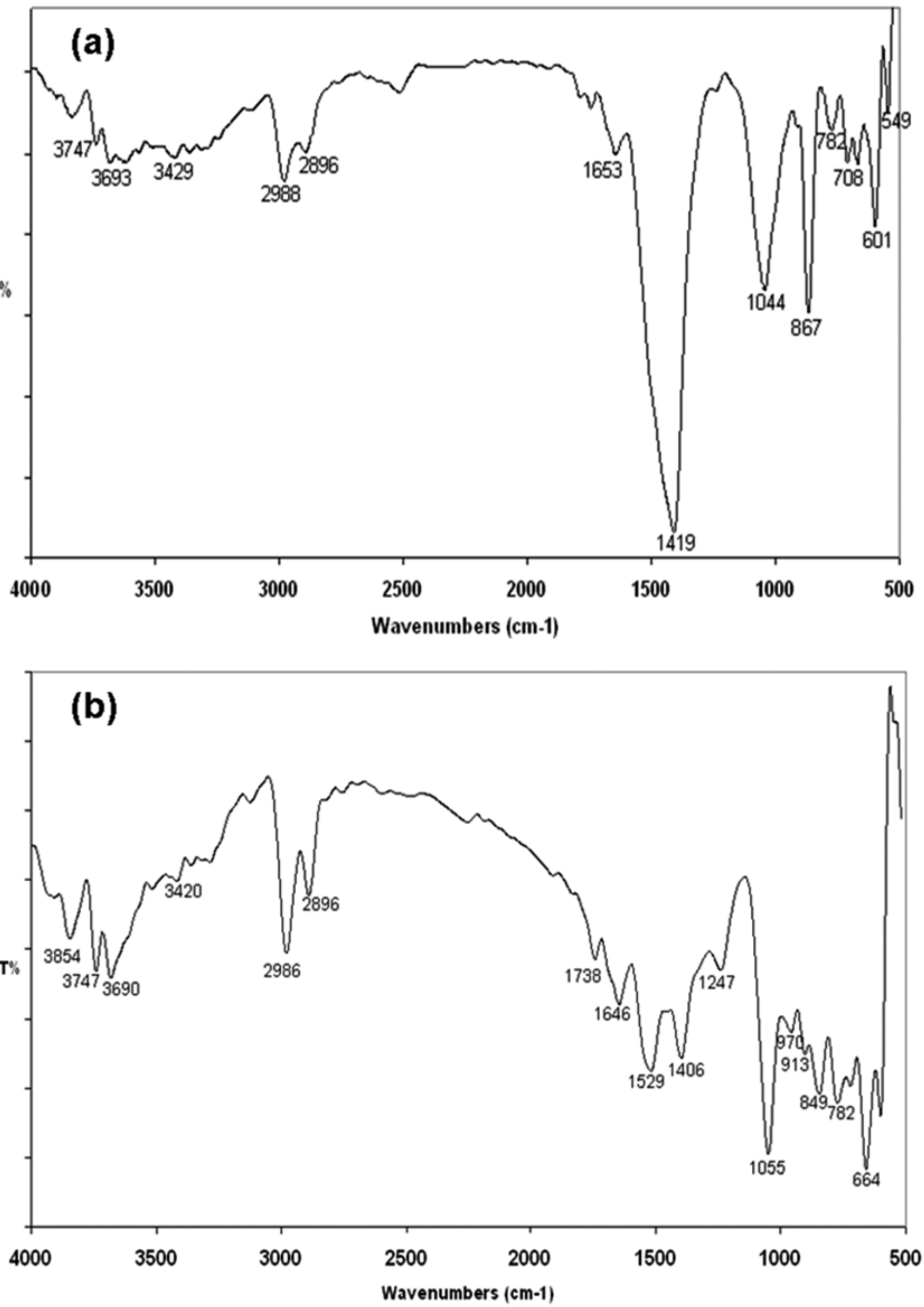

Figure 6. FT-IR (KBr) spectra recorded on some paint layers: a) The yellow paint layer (sample Y.1); b) The green paint layer (sample Gr.1).

showed characteristic bands of calcium carbonates (mainly of calcite) at 1430, 878 and 713 cm^{-1} and the band at 468 cm^{-1} is due to quartz. The bands at 3440, 1639 and 600 cm^{-1} are attributed to calcium sulphates (gypsum). For mud brick samples, quartz, kaolinite and illite were identified on the basis of the characteristic bands at Si-O stretching in the 1300-400 cm^{-1} range, the bands at 3696 cm^{-1} (Al---O-H str.), 3622 and 914 cm^{-1} (Al---O-H, inter-octahedral), 3450 and 1633 cm^{-1} (H-O-H str.), 1033 cm^{-1} (Si-O-Si, Si-O str.), 790 cm^{-1} (Si-O str., Si-O-Al str.) [(Al, Mg)---O-H], 693 and 468 cm^{-1} (Si-O str.). Table 4 summarises the results obtained from the application of analytical techniques on the studied samples.

Discussion

Paintings support

The main building material used in the necropolis is the mud brick. The XRD analysis of mud brick samples showed that quartz is the major component of the samples. Other minerals of potassium feldspar (microcline), calcite and clay minerals (kaolinite and illite) were also measured. Mud bricks should contain at least three of the following ingredients: coarse sand for strength, fine sand to lock the coarse sand in place, silt and clay as binders and a plastic medium (Kemp, 2000). Also, mud brick contains organic materials like straw which added to prevent the shrinkage of the brick (Nicolini et al., 2010). Clay minerals form an important group of the phyllosilicate or sheet silicate family of minerals, which are distinguished by layered structures composed of polymeric sheets of SiO_4 tetrahedra linked to sheets of (Al, Mg, Fe)(O, $OH)_6$ octahedra. Clay minerals have very fine particle size, usually < 2 mm. They are classified by the differences in their layered structures (Nayak and Singh, 2007). There are several classes of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite (Grim, 1968). If one tetrahedral and one octahedral sheet are bonded together the structure is called 1:1 layer silicate structure. Within the 1:1 family different species of dioctahedral (e.g. kaolinite, dickite) and trioctahedral (e.g. chrysotile) minerals exist (Madejová, 2003).

Plasters and preparation layers

The stratigraphic analysis of the plaster layers has shown that two layers are clearly distinguishable. XRD and FT-IR analyses revealed the contentious detection of calcium carbonate as the main constituent of the plasters both as binder (lime) and filler. The first plaster layer is made up of lime wash with fine grains of local silica sand. The second layer is slightly thick and prepared from lime and large grains of silica sand. Moreover, the semi quantitative SEM-EDS analysis performed on the plaster samples revealed concentrations of CaO, SiO_2, Al_2O_3, MgO, Fe_2O_3 and K_2O which suggests that a non-hydraulic lime with low hydraulic compounds was used to prepare the plaster layers.

Organic fibres of straw were used in the plaster layers. These fibres have traditionally been used to improve the tensile strength (Elsen, 2006). Ali et al. (2011) reported that quartz, calcium sulphate (gypsum) and calcium carbonate were used to make the ground layer of wall paintings coming from the monastery of St. Jeremiah in Saqqara and preserved now in the Coptic museum in Cairo (no. 7953). In their study of Coptic plasters from the Monastery of St. Simeon (Deir Anba Hatre), Aswan, Upper Egypt, Marey Mahmoud and Papadopoulou (2012) showed that the ground layer consists of aragonite and calcite with traces of gypsum, quartz and clay minerals. Non-hydraulic or aerial lime, so-called since the phenomenon of crystallization can take place only in the presence of air (hence the slowness to set and the possibility of storing large quantities of slaked

Table 4. Summary of the results obtained from analytical methods applied on the studied samples.

Sample	XRD	SEM-EDS	FT-IR
Mud brick	Quartz, calcite, plagioclase, potassium feldspar, kaolinite and illite	Si, Ca, Al, K, Fe, Ti, Mg, Na, S	Quartz, kaolinite and illite show characteristic bands at Si-O stretching in the 1300-400 cm^{-1} range, the bands at 3696 cm^{-1} (Al---O-H str.), 3622 and 914 cm^{-1} (Al---O-H, inter-octahedral), 3450 and 1633 cm^{-1} (H-O-H str.), 1033 cm^{-1} (Si-O-Si, Si-O str.), 790 cm^{-1} (Si-O str., Si-O-Al str.) (Al, Mg)---O-H), 693 and 468 cm^{-1} (Si-O str.)
Coarse plaster	Quartz and calcite. Traces of kaolinite, potassium feldspar (microcline), plagioclase (albite)	Si, Ca, Al, K, Fe, Mg, Na	
Fine plaster	Calcite, traces of gypsum, quartz and kaolinite	Ca, Si, S, Al, K, Fe, Mg, Na, Ti	Characteristic bands of calcium carbonates at 1430, 878 and 713 cm^{-1} and the band at 468 cm^{-1} is due to quartz. The bands at 3440, 1639 and 600 cm^{-1} are attributed to calcium sulphates (gypsum).
Render	Calcite with traces of quartz and gypsum	Ca, Si, S, Na	
Green pigment	Quartz, calcite, glauconite, gypsum and clay minerals	Si, Al, K, Fe, Ca, Mg, K	Glauconite was characterized by the small band at 664 cm^{-1} with broad peaks in the 1110-950 cm^{-1} region. These last bands are mainly at 970 and 1055 cm^{-1}
Red pigment	Quartz, calcite, hematite, potassium feldspar, plagioclase, gypsum and clay minerals	Si, Al, Fe, S, K, Ti	Red ochre presented bands at 690 and 555 cm^{-1} are attributed to iron oxide, the bands at 3696 and 3622 cm^{-1} are due to kaolinite
Yellow pigment	Calcite, quartz, goethite, potassium feldspar, plagioclase and clay minerals	Si, Al, Fe, S, K, Mg, Ti	Yellow ochre showed bands at 549 cm^{-1} indicates the presence of iron oxide. The outer OH groups at 3747 and 3693 cm^{-1} are attributed to amounts of kaolinite
White pigment	Calcite, gypsum with traces of quartz	Ca, Si, S	Characteristic bands of calcium carbonates at 1407 and 872 cm^{-1}

lime) (Adam, 1994; Toprak, 2007). The detection of sulphur in the samples suggests the transformation of calcium carbonates in the plaster layers to gypsum ($CaSO_4{\cdot}H_2O$) as confirmed by XRD analysis. The materials used in old restoration interventions of the wall paintings at the necropolis probably helped in the occurrence of this process.

Green pigment

Papers have been published on the characterization of Coptic wall paintings, all of which suggest that earth pigments are the main components of the chromatic palette used in these murals. The XRD, EDS and FT-IR analyses confirmed the green pigment as green earth and specifically of glauconite. Indeed, in the celadonite composition, the percentage of aluminium is lower (0-0.2%) with respect to glauconite (0.3-0.8%) (Moretto et al., 2011). Glauconite chemical composition is approximately (K, Na) (Fe^{3+}, Al, Mg)$_2$ (Si, Al)$_4$O$_{10}$(OH)$_2$, similar to celadonite, but with a great content of aluminium due to a partial substitution of Al^{3+} for Si^{4+} in the tetrahedrally coordinated layer (Aliatis et al., 2008). Other greenish clayey minerals can be incorporated into pigments labelled and included in “green earths” pigments, e.g.: greenish smectites, chlorites, serpentines and pyroxenes with accessory minerals (e.g., quartz, calcite, goethite and feldspars) (Hradil et al., 2003; Aliatis et al., 2008).

Red pigment

The red pigment was identified as red ochre. The EDS microanalysis showed high concentrations of iron are present. A small contribution of silicon and aluminium may indicate the presence of aluminosilicate materials (e.g. clays). The various shades of ochre are determined by several factors: the average size of crystallites, the corresponding dispersion; their proportion with respect to the presence of other chemical components such as aluminosilicate materials and other minor components (calcite, gypsum, etc.) (Ramos et al., 2008). Moussa et al. (2006), in their study of Coptic wall paintings in Al Qurna and Wadi El Natrun-Egypt, reported that the red pigment is hematite and the brown pigment is hematite of Aswan.

Yellow pigment

The FT-IR and XRD analyses revealed that the yellow pigment was identified as yellow ochre. The hue of goethite is affected by its crystallinity and elemental purity. Ali et al. (2011) showed that manganese was added in the form of MnO to obtain dark yellow colour in wall paintings at the Coptic museum in Cairo.

White pigment

From the XRD and FT-IR analyses, the white pigment was identified as calcite. EDS analysis showed high concentration of calcium in all the studied samples. Traces of gypsum were also found in some samples.

Painting technique

From the FT-IR analysis, the use of a proteinaceous binder (probably of animal glue) was recorded. In some cases, the content of animal glue was not confirmed because the amide I and II bands are masked by the broad bands of calcium sulphate, oxalate and carbonate. That suggests that *al secco* technique was used as painting technique. *Al secco* technique is used for painting on dry plaster with pigments mixed with different types of organic binders (Hein et al., 2009).

Conclusions

Different analytical techniques such as OM, SEM-EDS, XRD, FT-IR and the petrographic examination were applied to answer some questions concerning materials and techniques used in Coptic wall paintings from El-Bagawat necropolis, Kharga Oasis, Egypt. The results showed that the main building material in the necropolis is the mud brick. The mud brick samples consist mainly of quartz with other minerals of calcite, plagioclase (albite), potassium feldspar (microcline) and clay minerals (kaolinite and illite) were also measured. Concerning the plaster layers, the results showed that the plaster layers used in the examined wall paintings are based mainly on lime. The results indicated that calcite is the predominant phase found in the fine plaster '*intonaco*' with traces of quartz and kaolinite. The coarse plaster '*arriccio*' consists mainly of silica sand with minor amounts of calcite. Traces of kaolinite, potassium feldspar (microcline), plagioclase (albite) were also found. The render samples show major components of calcite with traces of quartz and gypsum.

In comparison with the Pharaonic plasters, the stratigraphy of the studied Coptic wall paintings is almost the same and in all cases it depends mainly on the quality of the painting support. The walls of the chapels at the necropolis are decorated with a chromatic palette based mainly on earth pigments. The results revealed the green pigment as green earth (specifically of glauconite), the red pigment as red ochre (hematite, α-Fe_2O_3), the yellow pigment as yellow ochre (goethite, α-FeOOH) and the white pigment as calcite with minor amounts of gypsum. The XRD and FT-IR analyses showed the continuous detection of calcium carbonates in all the examined samples. Moreover, an indication of a proteinaceous binder (probably of animal glue) was found which suggests that *al secco* technique was applied in the studied wall paintings. The results will be used in the conservation-restoration interventions of these wall paintings. In conclusion, the investigation of additional samples will be of importance to improve our knowledge of the materials used in the Coptic wall paintings in Egypt.

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