Original article

ANALYTICAL STUDY OF TWO WALL PAINTINGS FROM KOM OSHIEM EXCAVATION (EL-FAYOUM- EGYPT).

Bakr, A. A. & Brania, A.A.
Department of Conservation, Faculty of Archaeology, Cairo University, Egypt
amanymbakr@hotmail.com

Abstract

This paper presents an analytical study of two wall paintings dating back to the 3rd Century A.D. Both wall paintings were discovered at kom Oshiem (El Fayoum, Egypt) in 1975 by the Faculty of Archaeology excavation mission, Cairo University. The study involved identification of the pigments, plaster layers and binding media. Several analytical methods were employed for the identification process such as light optical microscopy (LOM), Scanning electron microscopy equipped with energy dispersive X-ray analyzer (SEM-EDS), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The obtained data will be used to evaluate the deterioration status of the wall paintings and define suitable treatment methods.

1. Introduction

In 1975, a mission attached to the Faculty of Archaeology at Cairo University that had been excavating at Kom Oshiem (El Fayoum, Egypt) has exposed many wall paintings dating back to the 3rd Century A.D. The discovered wall paintings were stored in the Faculty of Archaeology excavation mission storages in El Fayoum state. The wall paintings have no registration names. Two wall paintings were selected to identify their main components for conservation purposes. The first wall painting (1) is fixed on a background of modern mortars and surrounded by a wooden frame with the size of 120 cm x 60 cm. The second wall painting (2) has no frame and its outer size is 100cm. x 80 cm. Both wall paintings are in a very bad state of conservation. The first one

has disintegrated surface with exfoliated colored layer in flakes shapes in several areas. Cracks in different size and shape are dispersed all over the surface, fig. (1 a, b, c, d). The drawn shapes are indistinct because of the accumulation of dust and air particles. Wall painting (2) is more severely deteriorated than the first one. The painted layer and the underneath support lost their cohesion and separated into many pieces. The painting was found upside down and in a very bad condition. Drastic attempts to remove this wall painting most likely have caused this state of deterioration. The wall painting was turned over carefully to document the status of the colored layer, fig. (2a, b, c, d). A piece of lawn was adhered on the colored layer trying most probably to save the remains of colored layer.
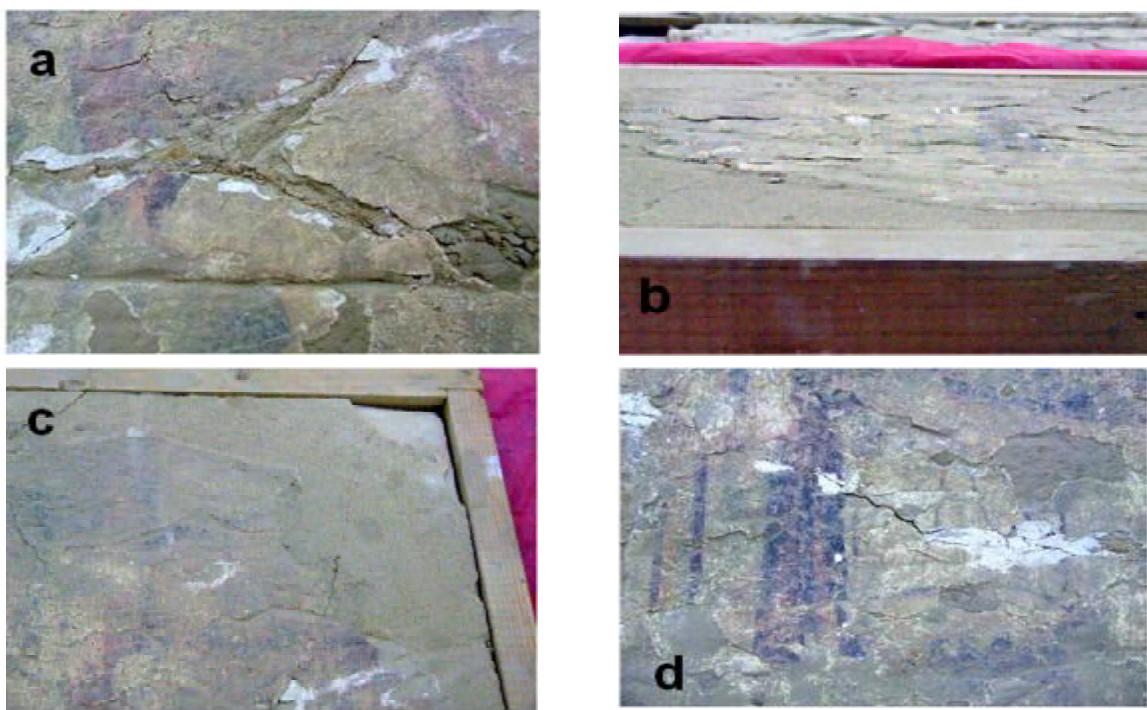
Figure: 1(a, b, c, d) details from the 1st wall painting show exfoliation, missing parts (a, b and c) and cracks (d).
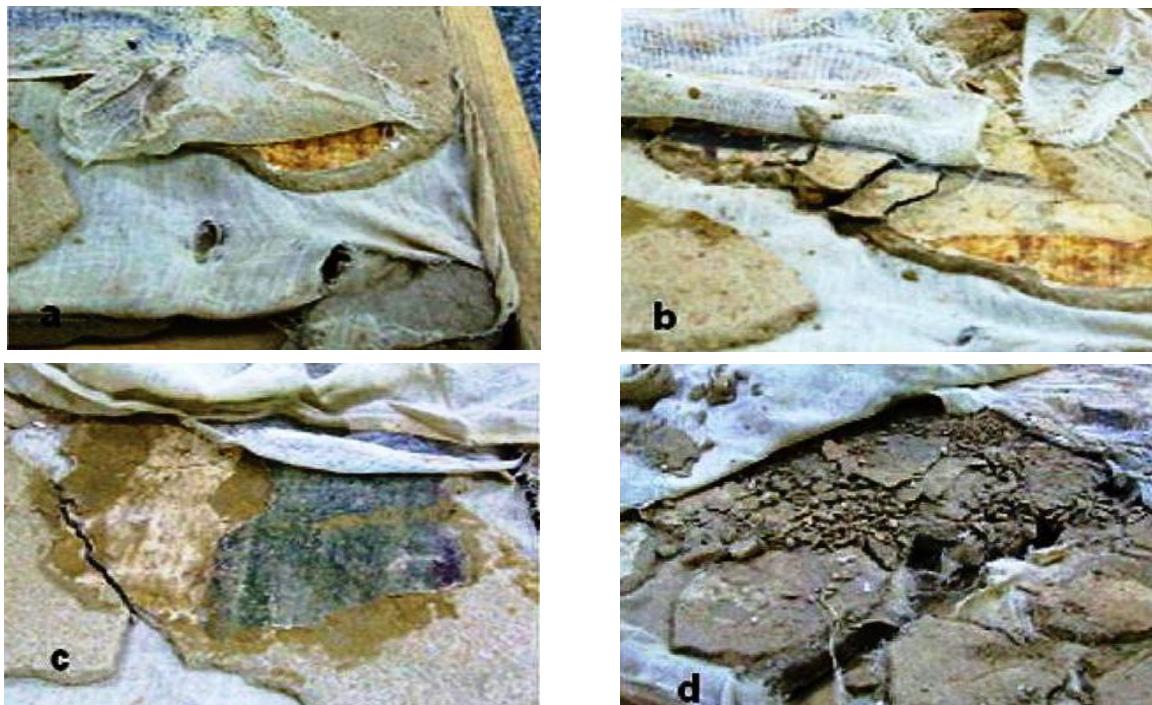

Figure: 2 (a, b, c, d) sow some details from the 2nd wall painting show some colored parts covered with lawn cloth. Deteriorated and separated parts seen all over the painting.

The aim of this study is to characterize the components of the pictorial surface which consists of pigments, the binding media and the substrate in which immersed. The chemical composition of these materials can offer substantial information about the techniques that were used in its execution. The deterioration products detected during this study help to interpret many of deterioration phenomena appear all over the wall paintings. The information obtained is also required for conservation works.

2. Materials and methods

2.1. *Sampling*

Samples representing the used pigments and the substrata were taken from both wall paintings. The samples were first described to register their general appearance by means of optical microscopic observation (LOM). Red, green and black samples were collected from the first wall painting, fig. (3a, b, c). Yellow, red, green and black samples were collected from the second wall painting, Fig. (4a, b, c). Some samples representing the substrata under the colored layer were taken from both wall paintings.

2.2. *Methods:*

Investigations of the collected samples were performed using the following methods: -Light optical microscopy (LOM). -Scanning electron microscopy (SEM) using Philips (XL30) microscope, equipped with EDX micro-analytical system. -X-ray powder diffractometry (XRD) using Philips PW 1840 diffractometer with Cu radiation. -Fourier-transform infrared spectrometry (FTIR) using JASCO FT\IR–460 plus spectrometer.
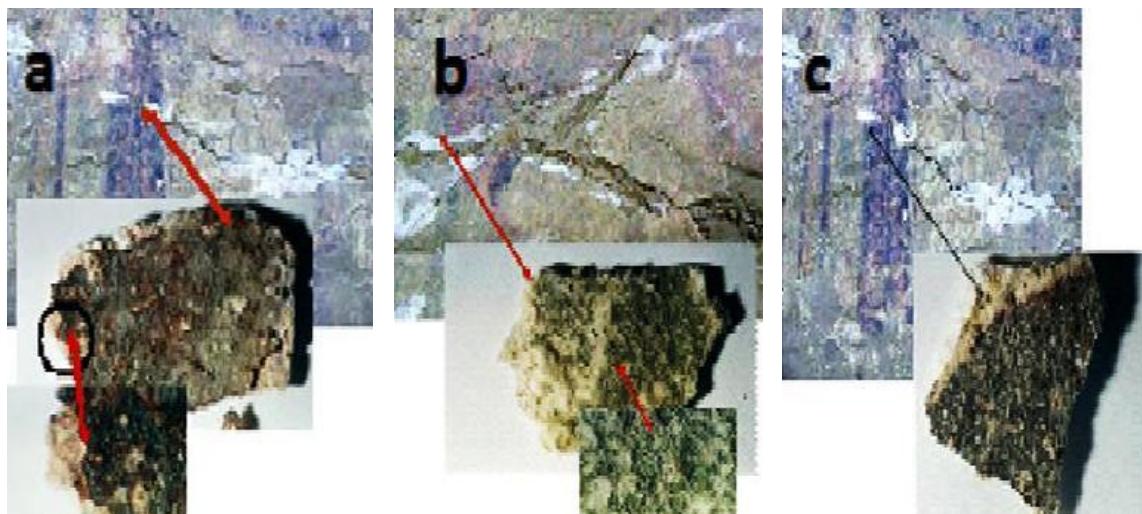

Figure: 3 Shows the studied samples taken from the first wall painting by LOM. (a) Shows the dark red sample, (b) shows the light green sample and (c) shows the black sample.
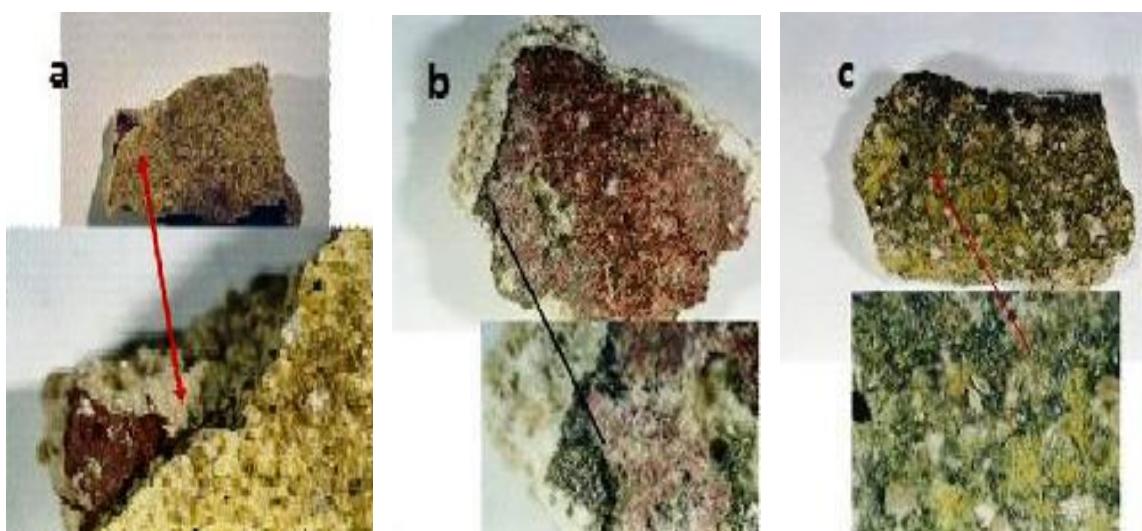

Figure: 4.Shows the studied samples, taken from the second wall painting. (a) Shows the yellow sample, the arrow point to the red layer under the yellow paint (b) shows the dark red sample, (c) shows the light green sample

3. Results:

3.1. *The samples of the first wall painting:*

3.1.1. Dark red pigment.

The SEM-EDX examination showed the coarse morphology of the surface, fig. (5a) and the inhomogeneous distribution of the studied elements. The results of microanalysis EDX, table (1) showed that silicon (Si), iron (Fe) and calcium (Ca) are the main elements; their values are 28.76%, 25.42% and 12.68%, respectively. Small amounts of S, K, AL, Mg, P, Na and Cl were detected all over the sample, their values are 9%, 6.47%, 6% , 3%, 2.84%, 2.90% and 2.20%, respectively. Calcium and Sulphur are related mainly to calcium sulphate and Na, Mg and Cl are probably related to the presence of some salts, e.g. NaCl or Mg Cl_2, or together with Al and Si to some clay minerals. The XRD analysis of the red pigment showed the presence of akaganeite (ßFeO.OH), which is a polymorph of goethite (α-FeOOH), and gypsum ($CaSO_4.2H_2O$), fig (6).

3.1.2. Green pigment.

The SEM-EDX examination showed inhomogeneous composition of the sample. Some grains of different size and shape embedded in the fine-grain matrix, fig. (5b). The EDX analysis, table (1) shows that Si, Ca, and Fe are the dominant elements in the sample; their values are 27.60%, 23.47% and 23.20%, respectively. Significant amount of Al (11.71%) was recorded. Small amounts of Mg, S, Na, K and Cl are observed all over the sample, their values 3.26 %, 3 %, 2.6 %, 1.97 % and 1.92 %, respectively. The XRD analysis of the green pigment showed the presence of gypsum and quartz. No other crystalline phases related to detected elements (Fe, Si, Al, Mg and K) and the green color were detected.

3.1.3. Black pigment.

The SEM-EDX examination of the black sample showed the compact surface of the sample with some micro cracks in several areas, fig. (5c). Some grains of heavy element are distributed all over the sample. EDX analysis, table (1) indicates that Si, Fe, and Al are the dominant elements (calculated values without C and O are 35.19%, 23.27% and 14. 23%, respectively). The sample contains a considerable amount of C; its value is 11.73%. The EDX analysis of some areas containing the heavy element showed the presence of Pb in significant amount (calculated value without C and O is 13.65%). Ca, S, K, Cl, Z, Mg and Na are observed all over the sample. The amount of Sulphur compared to the amount of lead indicates that we are dealing with Pb oxides /or carbonates and not with galena (PbS).The XRD analysis of the black pigment revealed the presence of gypsum ($CaSO_4.2$ (H_2O) and quartz (SiO_2). No crystalline phases related to carbon black (graphite) or other minerals typically used to obtain a black color and agree with the presence of Pb and Fe (e.g. galena and magnetite, respectively) were detected.
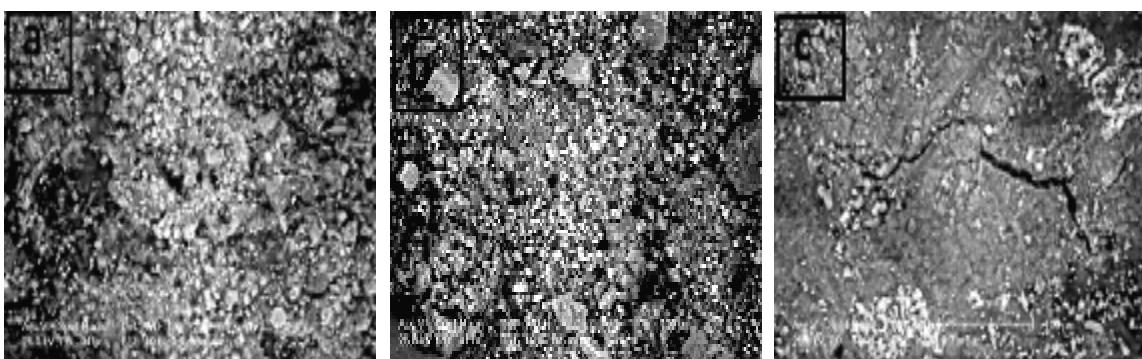

Figure 5: shows the SEM photos of the studied samples taken from the first wall painting. (a) Photo of the red sample, (b) photo of the green sample and (c) photos of the black sample.

Table 1: SEM-EDX microanalysis of the red, green and black pigments of the first wall painting.

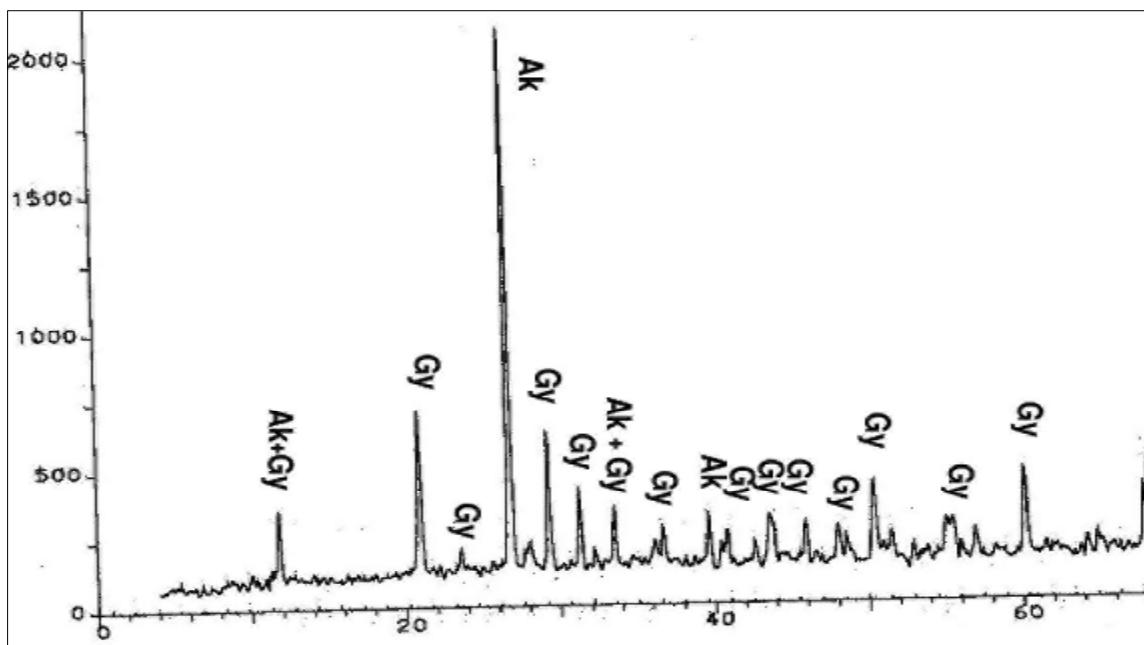| Dark red pigment		Green pigment		Black pigment	
Elements	*(In. %)*	*Elements*	*(In. %)*	*Elements*	*(In. %)*
Si	28.76	Si	27.60	Si	35.19
Fe	25.42	Fe	23.20	Fe	23.27
Ca	12.68	Ca	23.47	Al	14.23
S	9	Al	11.71	Ca	7.32
K	6.47	Mg	3.26	S	4.73
Al	6	S	3	K	3.25
Mg	3	Na	2.60	Cl	3.19
P	2. 84	K	1.97	Mg	3.04
Na	2. 90	Cl	1.92	Na	2.96
Cl	2. 20	-	-	P	0.94
-	-	-	-	Ti	0.93

Figure 6: Shows XRD patterns of the dark red sample of the first wall painting. Gy = gypsum and Ak = akaganeite

3.2. *The samples of the second wall painting:*

3.2.1. Yellow pigment.

The optical microscopy examination of the yellow colored layer sample showed the presence of a red layer under the yellow layer in some areas of the wall painting. The underneath red layer is rough and does not contain any painted figures. SEM examination showed the rough morphology of the yellow surface. The thickness of the yellow layer is ranging from 209 μm and 284 μm over the red layer, fig (7a, b). EDX analysis of the yellow paint indicates that Ca, S and Si are the main elements (calculated values without O and C are 38.69%, 29.20% and 17.61%, respectively). Al, Fe, K and Mg in small amount were detected all over the sample. EDX of the red layer showed that the Fe is a dominant element (calculated value without O and C is 71.26%), table (2). The XRD pattern of the yellow paint showed the presence of Quartz and gypsum, fig. (8a). No minerals related to the yellow color were detected. The XRD pattern of the underneath red paint showed the presence of goethite (αFeO.OH), akaganeite (βFeO.OH), and gypsum, fig. (8b).

3.2.2. Dark red pigment.

The optical microscopy examination of the dark red paint showed that the red paint was applied over the black paint in sporadic places in the wall painting. It seems that the artisan used this technique to achieve gradual hue of red color because beside this dark red area there is a red paint layer applied directly over the plaster layer. The SEM examinations of the sample show the disassembled coarse structure of the surface with embedded big grains, fig. (9a). EDX analysis showed that Si and Fe are the dominant elements (calculated value without O and C are 51.82% and 21.59%, respectively). Significant amounts of Al, Ca and K (9.71%, 5.70% and 4.69%, respectively) were recorded. Small amounts of Ti, Mg, Cl and S are observed all over the sample, table (2). The XRD analysis showed the presence of quartz and gypsum. Although Fe was detected in the EDX analysis, no minerals related to iron oxides and cause the red color were detected.

3.2.3. Green pigment

The SEM-EDX examination showed that the surface of the sample has coarse topography and inhomogeneous distribution of elements, fig. (9b). The EDX analysis, table (2) shows the presence of Si, Fe, Al and S in values 39.85%, 23.45%, 9% and 8.5%, respectively. Significant amount of Ca and K (7.93% and 7.92%) are recorded. Small amounts of Mg and Cl are observed all over the sample.

3.2.4. Black pigment

The XRD pattern of the black sample showed the presence of other types of minerals such as graphite, gypsum and quartz, fig. (10)
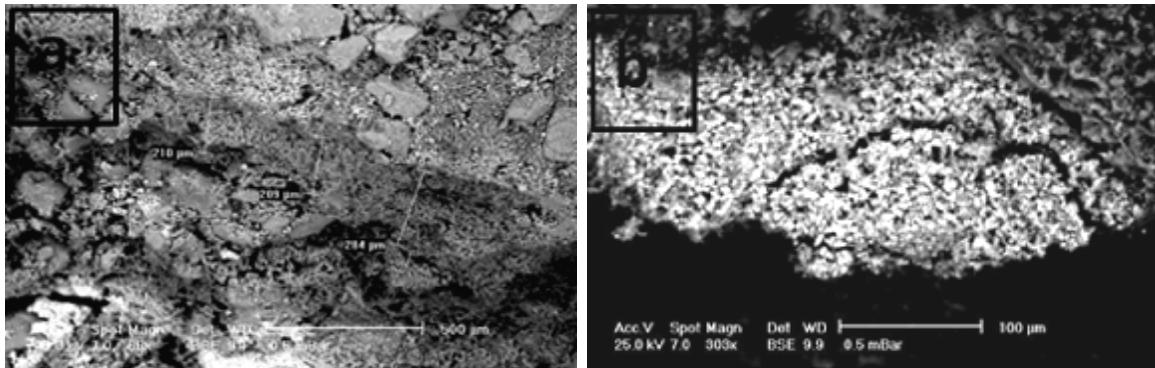

Figure 7: Shows the SEM photos of the studied samples taken from the second wall painting. (a) shows the thickness of the yellow layer that applied over the red layer, (b) the underneath red layer,
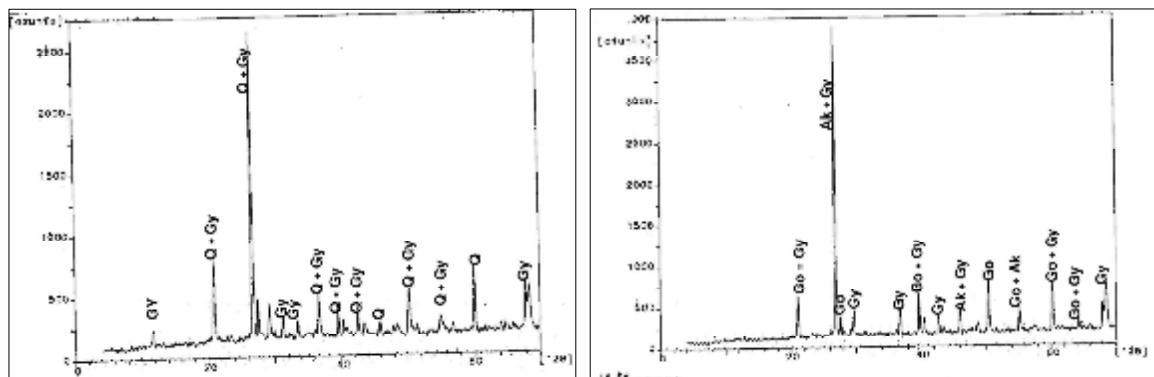

Figure 8: Shows (a) XRD pattern of the yellow sample of the second wall painting. Gy = gypsum and Q = quartz. (b) the XRD pattern of the underneath red layer sample of the second wall painting. Go = goethite, Gy = gypsum and Ak = akaganeite.
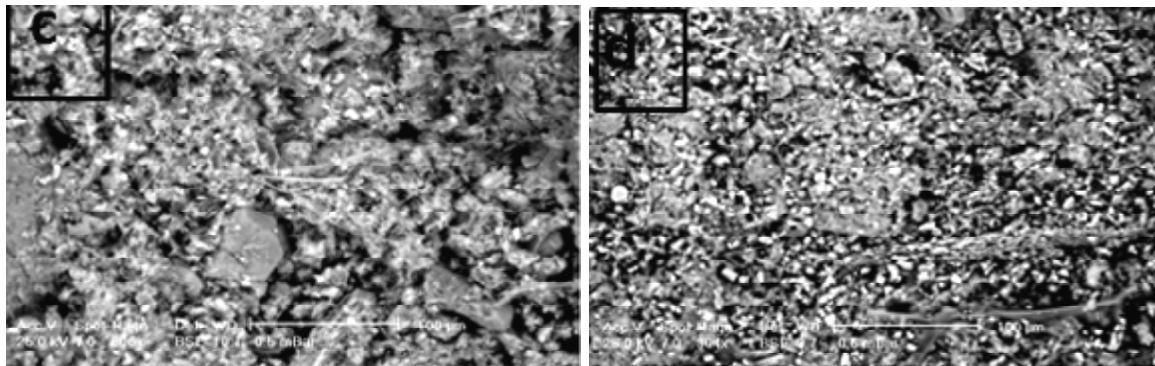
Figure 9: Shows the SEM photos of the studied samples taken from the second wall painting (a) shows the dark red sample and (b) shows the green sample.

Table 2: SEM-EDX microanalysis of the yellow, red and green pigments of the second wall painting.

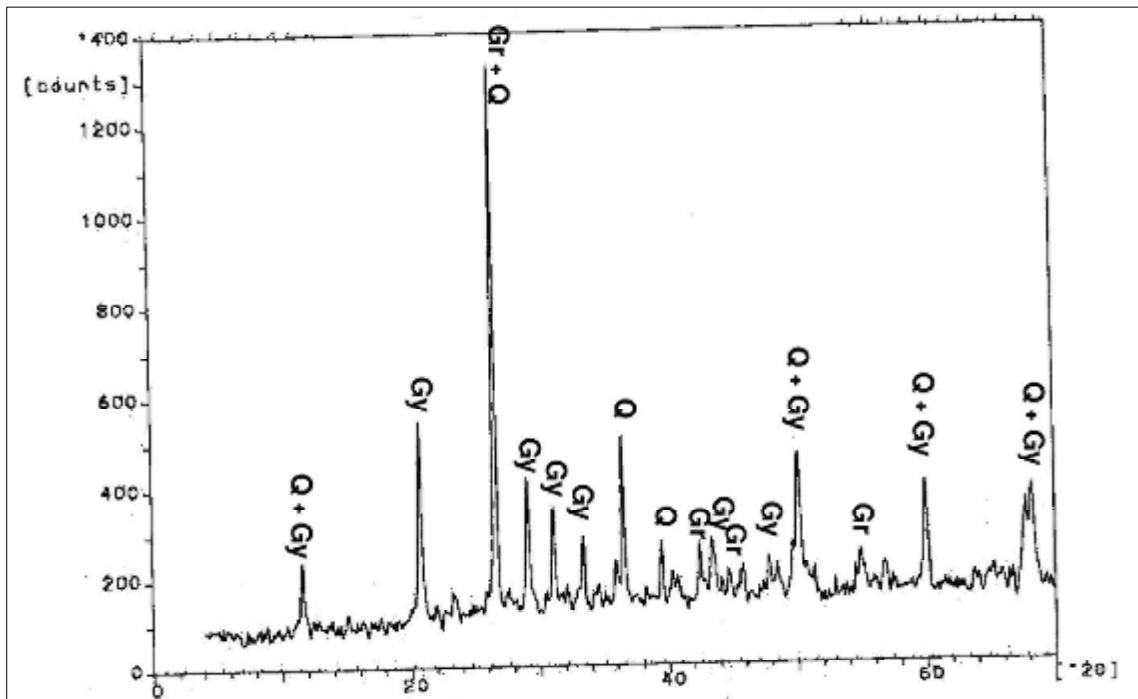| Yellow pigment		Underneath red pigment		Dark red pigment		Green pigment	
Elements	*(In.%)*	*Elements*	*(In.%)*	*Elements*	*(In.%)*	*Elements*	*(In.%)*
Ca	38.69	Fe	71.26	Si	51.82	Si	39.85
S	29.20	Si	19.26	Fe	21.59	Fe	23.45
Si	17.61	Al	6.12	Al	9.71	Al	9
Al	5.79	Ca	1.19	Ca	5.70	S	8.5
Fe	5	-	-	K	4.69	Ca	7.93
K	1.42	-	-	Ti	2.60	K	7.92
Mg	1.35	-	-	Mg	1.19	Mg	2.36
Cl	0.93	-	-	Cl	1.49	Cl	0.91
		-	-	S	1	-	

Figure 10: XRD of the black sample taken from the second wall painting. Gy = gypsum, Q = quartz and Gr = graphite.

3.3. *The underneath substrata*

The EDX analysis of many places in the colored layer showed the presence of Ca and S in remarkable amounts (calculated value without C and O are 23 – 7% and 9 – 3%, respectively) XRD analysis of the underneath substrata showed the presence of gypsum and quartz in both wall painting's layer.

3.4. *Identification of organic binding media*

Fourier-transform infrared spectrometry (FTIR) analysis was performed to detect the organic binding media. Green and red samples were taken from the first and the second wall painting, respectively. The FTIR spectrum of the samples, fig. (11) showed the absorption bands at 2924 – 2853 cm^{-1} due to C-H stretching vibrations of the aliphatic group. The band at 1374 cm^{-1} corresponds to C-H bending. The band at 1743 cm^{-1} corresponds to the carbonyl (C=O) stretching vibration from ester group. The bands at the range 1300 – 1000 cm^{-1} correspond to (C-O) stretching vibration of esters. The broad band at 769 cm^{-1} corresponds to (C-H) vibration. The observed absorption bands indicate that small amount of organic matter most probably wax [1] [2] was used. The bands related to the inorganic components of the samples have a strong effect on the strength of the characteristic bands of wax. The characteristic IR absorption bands of different kinds of wax were mentioned in details by Michele R.[3] as follow: 3600-3200 cm^{-1} (O-H stretching band), 3000-2800 cm^{-1} (C-H stretching bands), 1780-1700cm^{-1} (C=O stretching band),1480-1300 cm^{-1} (C-H bending bands), 1300-900 cm^{-1} (C-O stretching bands) and 750-700 cm^{-1} (C-H torsion bands). The wax present in both wall paintings was used most probably for preservation purpose during removing and transportation rather than used as a binding media with pigments. The wax was removed from the surface of the wall paintings after the transportation process was completed.
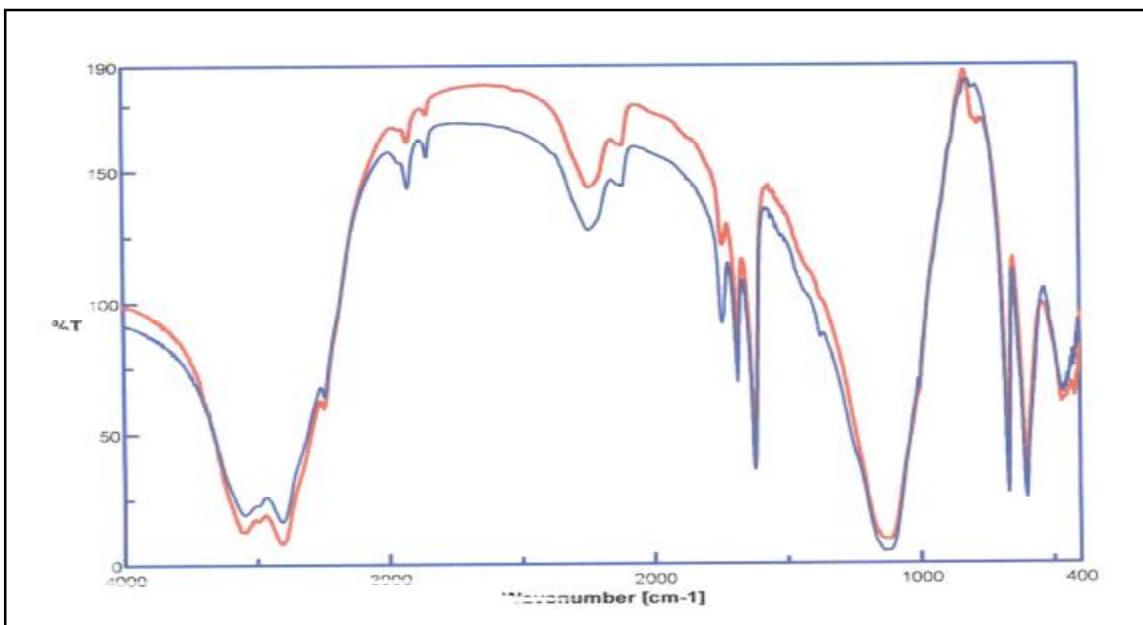

Figure11: Shows the FTIR spectra of the samples taken from the two wall paintings.

4. Discussion
4.1 *The first wall painting*
4.1.1. Dark red paint

The elemental composition of the dark red pigment (Al, Si, K and Mg - the building elements of clay minerals) and the presence of hydrous phase of iron oxides akaganeite ßFeO.OH) in the XRD analysis indicate that poor crystalline red ochre or red earth is the main red coloring substance in the sample[4][5][6]. It is well known that the red ochre is a natural earth substance, containing silica and clays (high contents of Si and Al) and owing its color to iron oxides [7][8]. The hue of red ochre is mainly due to the ratio of hydrous iron oxides e.g. goethite (αFeO.OH yellow), akaganite (ßFeO.OH brown), and unhydrous iron oxides e.g. hematite (α-

Fe_2O_3 red). The detected akaganite in the dark red sample doesn't exclude the presence of other phases of iron oxides such as hematite or goethite. The small amount and poor-crystalline of normal hematite, which is normally present in the red ochre, make its identification by XRD analysis very difficult [9]. Akaganite is a natural oxyhydroxide mineral and it is always associated with goethite and

4.1.2. Green paint

The absence of copper element that could be related to some copper compounds used to obtain green color e.g. chrysocolla and malachite. The elemental composition of the green pigment containing a considerable amount of Fe with Al, Si, K and Mg implies that green earth is the source of the green pigment. Green earth is green iron hydro silicate clays that have been used as pigments since ancient times. Green earth is often a mix of celadonite

4.1.3. Black paint

The black color of the studied black paint was obtained from the organic carbon black, either charcoal black or soot black. Bone black is rather excluded because of the absence of phosphorus in the EDX analysis. According to Gettens and Stout [7], bone black is composed of about 10% of carbon and 84% of calcium hydroxylapatite $Ca_5(PO_4)_3(OH)$, along with smaller amounts of magnesium phosphate and calcium carbonate. After heating the sample at 500 ^{o} C in muffle oven the black color disappeared, confirming the use of carbon as a black

4.2 The second wall painting

4.2.1. Yellow paint

Depending on the elemental composition (presence of Fe, Ca, Al, K and Mg) the use of yellow ochre is recommended. The hydration, poor crystalline of the minerals (irons oxides and clay minerals) forming the yellow ochre and the small amount of the used pigment hindered their identification by XRD analysis. Red ochre is used in the underneath red layer because

4.2.2. Dark red

The elemental composition of the dark red layer and the XRD analysis implies

lepidocrocite (γ-FeOOH)**.** When prepared synthetically, powdered goethite and akaganeite are yellow-brown and lepidocrocite is orange, but when formed naturally the color of iron oxyhydroxides is influenced by particle size and shape and can be various shades of yellow, orange, red or brown[10]. The presence of gypsum is due to the plaster layer underneath the red pigment.

(variations on K [(Al ^{III}, Fe ^{III}) (Fe ^{II}, Mg ^{II})]) and glauconite (AlSi$_3$, Si$_4$) O_{10} (OH) $_2$ [11]. Some other clay minerals such as chlorite and montmorillonites can be incorporated into pigments labeled as green earth [4]. The hydration, a small amount (<1%) which is, however, sufficient to produce the coloration [12], and poor crystalline of these clay minerals could have frustrated their identification by XRD analysis.

colorant [13] [14] the presence of considerable amounts of lead in the EDX analysis and the absence of galena in the XRD analysis suggests that it most probably related to lead-carbonate-mineral (e.g. cerussite $PbCO_3$ or hydrocerussite Pb_3 $(CO_3)_2(OH)_2$). Hydration or poor crystalline of the used lead-carbonate mineral could disturb their identification by XRD analysis. Lead-carbonate or white lead could be intentionally added to the black pigment to accelerate the drying process of carbon black that has poor drying properties [15] [16]**.**

of the dictation of hydrous iron oxides (goethite αFeO.OH and akaganeite ßFeO.OH) and the presence of Si, Al, K and Mg (the building elements of clay minerals) in the EDX analysis. The presence of this red layer under the yellow layer in one place in the yellow area of the wall painting and its rough surface implies that the artisan did not do it intentionally.

the use of hydro-poor crystalline red ochre in this paint. The red paint applied

over the black paint is the cause of complicated and inhomogeneous component of the taken sample that

4.2.3. Green paint
The elemental composition of the green sample containing mainly (Fe, Si Al, Ca,

4.2.4. Black paint
The presence of crystalline phase of carbon (graphite) in the XRD analysis indicates that it is the only source of the

makes the identification of the red pigment with XRD analysis very difficult.

K, Mg and Cl implies that green earth is the source of the green pigment.

black pigment in the sample. The presence of gypsum and quartz is due to the plaster layer.

5. Conclusion
From the results obtained using several analytical techniques (OLM, SEM-EDX, XRD and FTIR), the following information was deduced:

- *The red pigment used in the two wall paintings originated from red ochre containing mainly hydro-iron oxides (e.g. goethite, akaganeite) and quartz.*
- *The green earth is the source of the green color used in the two wall paintings.*
- *The yellow color used in the second wall painting was obtained from yellow irons oxides (yellow ochre).*
- *Carbon black was used to obtain the black color in both wall paintings. The crystalline phase of carbon (graphite) was detected in the second wall painting.*
- *The wax present in both wall paintings was used most likely for preservation purpose during removal and transportation rather than used as a binding media with pigments.*
- *The plaster layer is mainly composed of gypsum and quartz.*
- *Usage of the same materials (pigment, plaster layer and the organic media) in both wall paintings indicates that the paintings represent the same historical period.*
- *The documented deterioration phenomena showed that man-made deterioration factors (drastic moving, random conservation works, and bad condition of storage) play an important role in the deterioration of wall paintings.*
- *The results obtained will provide the conservators with essential information needed to select the most suitable materials and methods that can be used in conservation and restoration works.*

References:
[1] U. Knuutinen, and A. Norrman, (2000) 'Wax *analysis in conservation objects by solubility studies, FTIR and DSC*', in: 15th World Conference on Non-destructive Testing, ICNDT, Rome, Italy, pp: 15-21.

[2] D. Omecinsky, and W. G. Carriveau, (1982) '*IR investigation of resinous and synthetic varnishes*', in: AIC 10th Annual meeting preprints, Milwaukee, pp: 141-149.

[3] Michele, R., Dusan, S., James, M., (1999) *Infrared Spectroscopy in Conservation Science*, the Getty Conservation Institute, Los Angeles.

[4] D. Hradial, T. Grygar, J. Hradilova and P. Bezdickaa, (2003) *Clay and iron oxide pigments in the history of painting*, J. Appl. Clay Sci., vol. 22, pp: 223 – 236.

[5] D. Hradial, J. Hradilova and B. Hrebickova, (2002) *Clay minerals in pigments of mediaeval and Baroque paintings*, Geologica Carpathica, 53 (2), pp: 123-126.

[6] D. Bikiaris, S.Daniilia, S. Sotiropoulou, and O. Katsimbiri, (1999) '*Ochre differentiation through Micro-Raman and Micro-FTIR Spectroscopies: application on Wall Painting at Meteora and Mount Athos, Greece*', Journal of Spectrochimica Acta, vol. 56, pp: 3- 18.

[7] R. J. Gettens and G.L. Stout, (1966) *Painting materials*, a short encyclopedia, Dover Publications, New York.

[8] A. B. Olsson, T. Calligaro and S. Colinaret, (2001) *Micro-PIXE analysis of an ancient Egyptian papyrus: identification of pigments used for the "Book of the Dead',* Journal of Nuclear Instruments and Methods in Physics Research, vol. 181, pp: 707-714.

[9] Kate Helwig, (1997) *A note on burnt yellow earth pigments: documentary sources and scientific analysis Stud.* In Cons., vol. 42, pp: 181-188.

[10] L. S. Selwyn, P. J. Sirois, V. Argyropoulos, (1999) *The Corrosion of excavated archaeological iron with details on weeping and akaganéite, Stud.* In Cons., vol. 44, pp: 217-232

[11] R.J.H. Clark, (2002) *Pigment identification by spectroscopic means: an arts\science interface* J. C. R. Chimie, vol. **5**, pp: 7-20.

[12] P. Maravelaki-Kalaitzaki, and N. Kallithrakas, (2003) '*Pigment and terracotta analyses of Hellenistic figurines in Crete*', Journal Analytica Chimica Acta, vol. **497,** pp: 209-225.

[13] G.A. Mazzochin, F. Agnoli, S. Mazzocchin, and I. Colpo, (2003) '*Analysis of pigments from roman wall painting found in Vicenza*', Journal of Talanta, vol.61**,** pp: 565-572.

[14] G. A. Mazzocchin, F. Agnoli and M. Salvadori, (2004) '*Analysis of Roman age wall paintings found in Pordenone,* Trieste and Montegrotto', Journal of Talanta, vol. 64, pp: 732-741.

[15] R. J. Gettens, H. Kuhn and W. T. Chase, (1993) '*Lead White*', in: Artists' pigments, a handbook of their history and characteristics, vol. 2, Ashok Roy, Oxford University Press, Oxford.

[16] J. Winter, (1983) '*The characterization of pigments based on carbon*', Stud. In Cons., vol. 28, pp: 49-66.