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# MULTI-ANALTICAL CHARACTERIZATION OF AN ANCIENT CARTONNAGE FRAGMENT FROM THE AMERICAN UNIVERSITY EXCAVATIONS: A CASE STUDY

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***Abstract***

*Cartonnage is one of the most valuable cultural heritage artifacts that are submitted to several degradation mechanisms due to their composite structure, and sensitive nature. In this paper, scientific techniques were used to estimate a cartonnage fragment. The use of non-destructive procedures was carried out to investigate the multi layered structure of cartonnage. The procedures include a Digital microscope and SEM were used to identify the support layer structure, EDS microanalysis was able to detect and identify the ground layer, Raman spectroscopy used to analyze the color layer for pigments identification, also XRF microanalysis was used for the identification of color samples, for the yellow, red, green, and black colors, the results concluded orpiment, red ochre, Egyptian green, and carbon-based pigment were found in the chromatic layer.*

***Keywords:*** *Carttonage; SEM -EDS microanalysis; Raman; XRF imaging*

## Introduction

Mummies are the most iconic artifacts from the ancient Egypt, the cartonnage cases and masks used to decorate and cover the mummified wrapped body; Cartonnage is a term used in the Egyptology for stucco layers of linen fiber or papyrus, which are more flexible for molding when applied on the irregular surfaces of the body; masks used to cover all or part of the mummified body. The stucco layer represents a ground for painting with more stability than was applied on a linen shroud. It was used by the ancient Egyptians for mummy cases. It was composed of layers of linen or papyrus which has been moistened and stuck together by using a paste. The linen or papyrus layer coated with a layer of stucco (white layer of lime plaster or gesso) [1]. Finally, when it had dried it could be painted or gilled with gold layers, therefore, it is a composite material include more than component such as cellulosic materials, ground layer, and paint layers.

Some studies reported the multilayer structure of mummy cases, the pigments and media used for the layers of linen support and the stucco layer. The pigments used in the ancient era were derive fronm natural sources, including red and yellow from iron oxide components, black from vegetable carbon black, blue and green from azurite and egyption malachite [2-4].

The multilayer structure of cartonnage is responsible for its different behavior due to natural aging process. So, it is submitted to the damage and disfiguration as the result of various deterioration factors. In many cases foxing can be observed as a result of biodegradation which is one of the most critical issue in the conservation treatments. Scientific investigations carried

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out in order to evaluate the composition, the chemical properties of the historical objects, and to identify the aspects of degradation. Some researchers study different techniques for identification the multilayer structure of cartonnage from the different historic periods [5-7].

The study aimed to identify the multi layer composition of a cartonnage fragment, from the American Excavations at Saqqara, Egypt, as well as estimating the degradation process due to the surrounding environment. Complementary techniques were carried out, such as SEM EDS, Raman spectroscopy, Portable XRF micro analysis, and FTIR for identification the layer structure of a cartonnage fragment.

## Experimental part

### *Sampling*

Samples collected from separated parts included support layer, Stucco layer, and pigments peels representing red, yellow, green, and black color. As shown in (Fig 1).


**Fig. 1.** (A) cartonnage fragment, (B, C) and (D) present the condition of cartonnage layers; cracks, missing parts, flaking of colors, and fabric brittleness

### *Methods*

*USB digital microscope*

Cartonnage fragment was examined using a USB digital microscope Dino-Lite with magnification from 20 to 500X. The observations helped to evaluate the Fibrous structure, the color layers, and to detect deterioration aspects such as cracks, flaking of colors, and missing parts.

*ESEM with Energy Dispersive X – ray Spectroscopy (SEM –EDS)*

Scanning electron microscopy – energy dispersive X-ray spectroscopy (EDX) was employed for color analysis, support layer, and stucco layer. samples were examined uncoated, using a variable pressure SEM (FEL Quanta 3D 200i Edx/thermofisher pathfinder in Grand Egyptian Museum, operated under conditions of low vacuum for acceleration voltage 20.0~30.0kv using large field detector with working distance 15~17mm.

*Micro Raman analysis*

Raman microscopy was carried out using a Raman confocal microscope, Bruker Senterra 11, magnification 20X, Resolution 4cm$^{-1}$, Laser 785nm Power 1microwatt. Neutral filters were used to avoid the damage of paper samples. The illuminating and collecting optics of the system

consists in a microscope in confocal configuration (a special long working distance 20X objective was used).

*FTIR- ATR analysis*

FTIR analysis was performed to monitor the functional groups of the fabric layer. FTIR spectra in transmission mode were collected using a Buker FTIR Spectroscopy, model Vertex 70, fitted out with ATR unit, the spectral region in the range from 400-4000cm$^{-1}$ using 4.0cm$^{-1}$ spectral resolution.

*Portable XRF Spectroscopy*

X-ray fluorescence, a portable XRF spectrometer (Elio Spectrometer, XGlabsrl, Milan, Italy), specifically designed for in-situ analyses, the detection of elements from Na to U was recorded, and the range of analysis varying between 1 and 50keV. X-ray radiation was generated using an Rh tube, with an electron accelerating voltage from 10 to 50kV and a filament current from 5μA to 200μA (Elio Device: SN177; device mode: Head, tube voltage: 40kV, time measure: 40,0s provided with manual tube current 20UA.

## Results and discussion

***Visual examination using digital microscope***

The invesigations revealed the bad condition of the stucoo layer as shown in (Figs. 2 and 3). We note cracks, missing parts, and layer detachment in some regions. We can distigiuish the coarse granula for the examined color samples due to the inorganic nature of the coloring matterial used in the paint layer. The topography of the weave used also was determined as linen fabric.

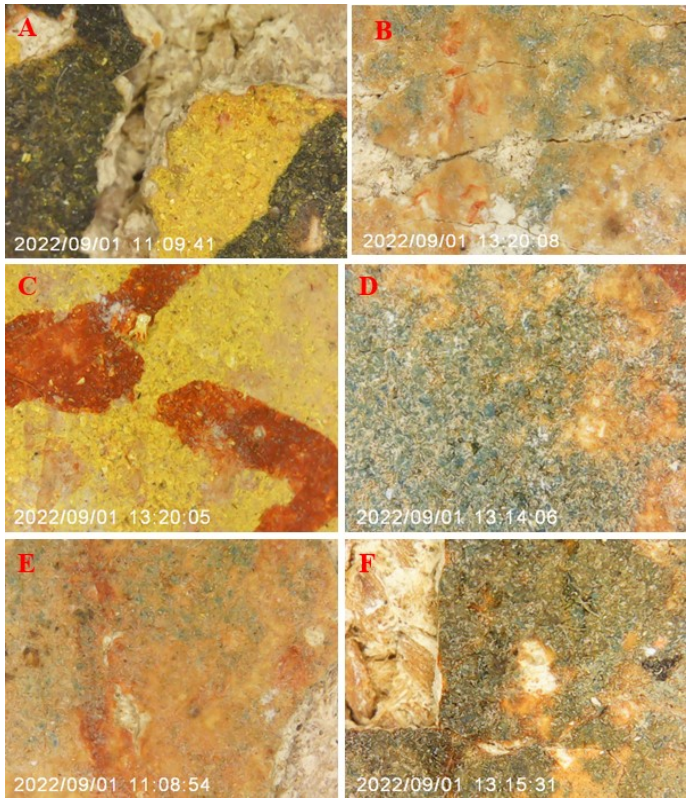


**Fig. 2.** A, B, C - show the digital microscope of the chromatic layer, we can see different color tones which suffer from fine cracks and detachments; D, E, F - show loss in both of ground and color layer

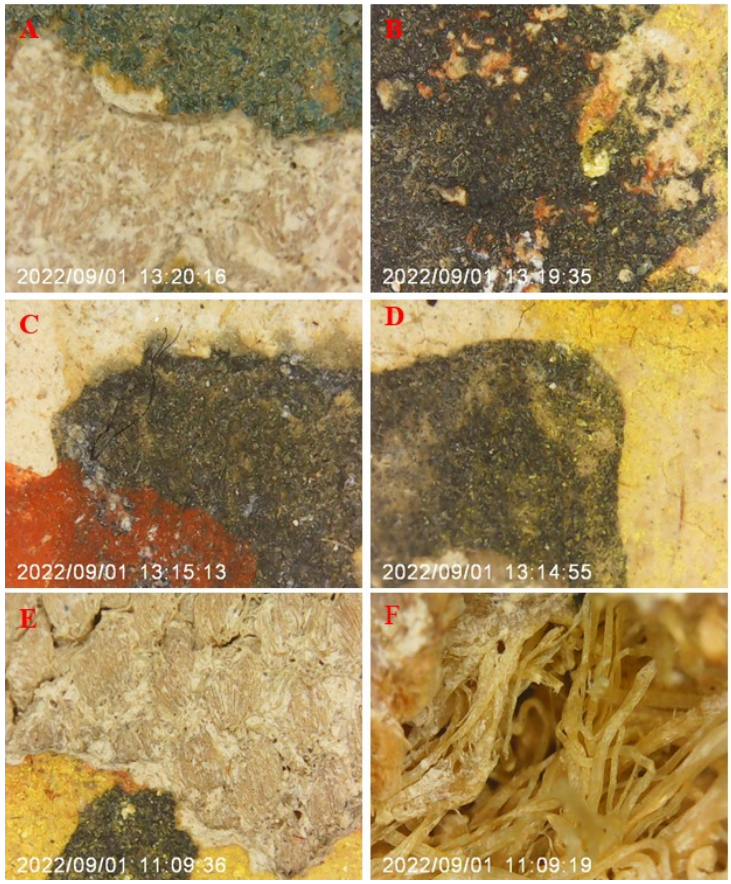


**Fig. 3.** A, B, C - show the digital microscope of the chromatic layer represents green, black, red pigments; D and E - show loss in both of ground and color laye; while F shows the bad condition of the linen weave

***SEM microscopy***

The morphological of the textile fabric using SEM, the results concluded the linen fabric in the layered structure of cartonnage. The SEM micrographs reveal the linen fabric structure, the typical nodes structure and fiber embrittlement are clearly noted in the fabric layer, the SEM analysis confirmed that the fiber structure is completely coverd with stucco layer (Fig. 4).

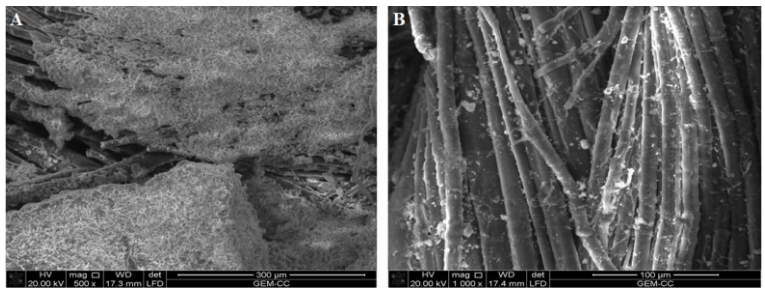


**Fig. 4.** SEM microphotographs of fabric layer covered with the ground layer appeared in fragile condition. We can see distinguish longitudinal view of linen fiber

### *SEM EDS micro analysis*

SEM provided with an energy dispersive detector (EDS) is a complementary technique used as a powerful method in conservation of culture heritage because it gives data about the surface morphology of the selected samples. The elemental analysis was carried out for the color layer, and the cellulosic support to identify its composition and element constituents the pigment used in painting. EDX microanalysis was used to detect the elemental structure of the flax the main fiber used for mummy casing (Tables 1 and 2). Scanning electron micrographs were subjected to EDS mapping. The EDS spectra (Fig 5), representing the elemental structure of the fabric layer, the sample revealed the presence of high percent of both carbon and oxygen which refer to the major elements of linen fabric composition.

**Table 1.** Show the elemental composition of the linen detected with EDS microanalysis

| Element | Wt% | At % |
|---|---|---|
| **C** | **38.31** | **48.64** |
| **O** | **47.04** | **44.83** |
| **Na** | **1.63** | **1.08** |
| **Al** | **0.67** | **0.38** |
| **Si** | **0.94** | **0.51** |
| **S** | **0.29** | **0.18** |
| **Ca** | **7.13** | **2.71** |
| **Cl** | **4.28** | **1.84** |

**Table 2.** Show the elemental composition of the ground layer with EDS microanalysis

| Element | Wt% | At % |
|---|---|---|
| C | 9.34 | 15.54 |
| O | 50.75 | 63.37 |
| Mg | 0.77 | 0.63 |
| Al | 0.51 | 0.38 |
| Si | 3.54 | 2.52 |
| S | 0.29 | 0.18 |
| Ca | 0.74 | 0.42 |
| C l | 34.06 | 16.97 |

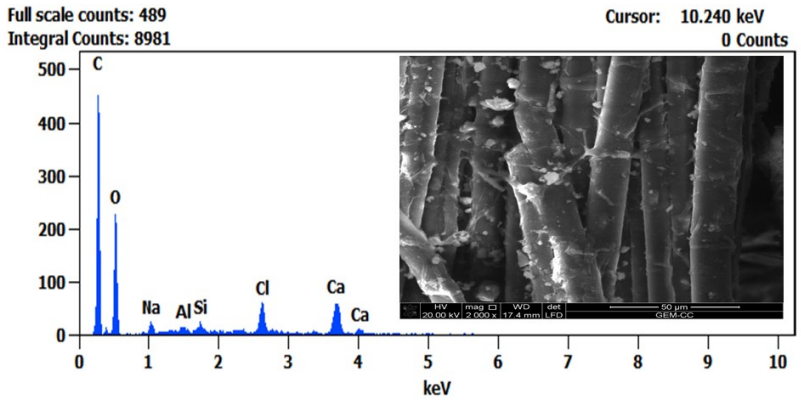


**Fig. 5.** EDS spectrum of linen weave used in the layered structure of cartonnage

The minor elements, including calcium (Ca), Aluminum (Al), Silicon (S), and Sodium (Na) were detected through the fabric layer [8, 9]. The analysis revealed that the stucco (whitewash) layer was composed of lime (calcium carbonate) due to the presence of Ca with major concentration; while Silica was found with minor percentages (Fig. 6). These results

confirmed with the FTIR analysis which revealed the characteristic bands of calcium carbonate and silica which were as follow 1106, 662, 755, 663 and 593cm$^{-1}$ (Fig.11).

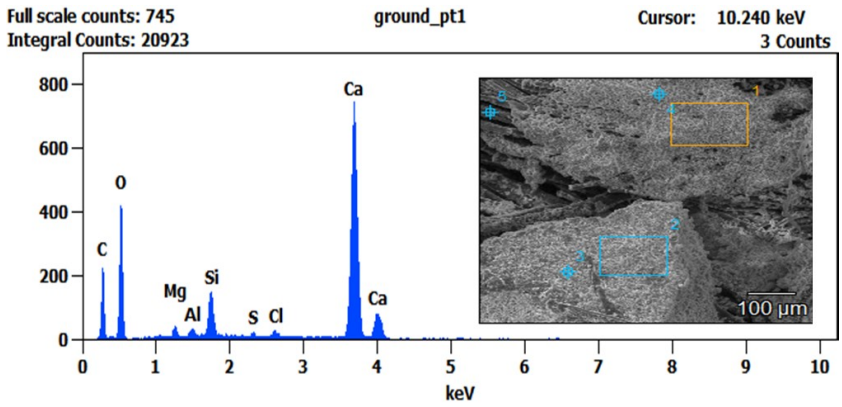


**Fig. 6.** EDS spectrum of the ground layer

***Micro Raman spectroscopy***

Raman spectroscopic analysis provides mineral detection, using a comprehensive database. (Fig. 7) shows the Raman spectrum obtained from a black region. The black pigment was possibly identified as carbon-based pigment, black pigments of vegetable sources was prepared from different kinds of charred plant substance. The characteristic bands reveal the amorphous carbon a coloring agent appeared at 1588 and 1320cm$^{-1}$.

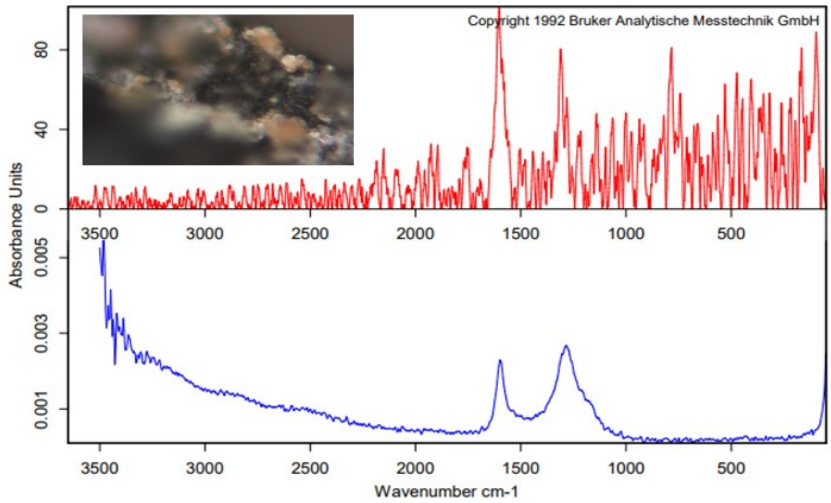


**Fig. 7.** Raman spectra detected from black pigment

The characteristic Raman spectra detected with laser type: 785nm from the yellow color sample (Fig.8). The detected bands refer to the orpiment (Arsenic sulfide $As_2 S_3$) with the characteristic bands at 354, 309, 292 and 154cm$^{-1}$, which represents the vibrtional signature of the arsenic sulphide pigment. Orpiment has been used as yellow pigment in ancient era, the data refers to the existence of sulphide minerals, due to the typical Raman signal of the various arsenic sulfide components, and it was possible to detect the natural orpiment pigment [10, 11].

Raman analysis (Figs. 9, 10) confirms the typical peaks at around 209, 292 and 382cm$^{-1}$ corresponds to hematite (iron oxide), the main component of the red ochre. The iron oxide (red ochre or hematite) which is a complex of iron oxides, clays and silica. By comparing the two spectra shifts in the spectra were noted due to the presence of clay and silica as impurities.

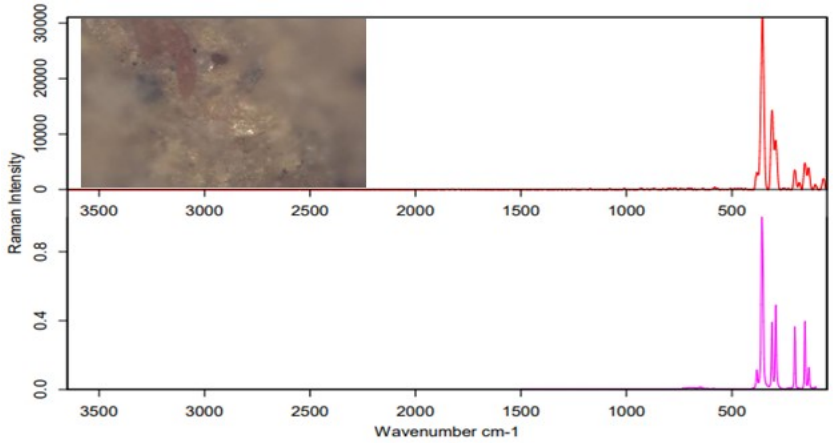


**Fig. 8.** Raman spectra detected from yellow pigment

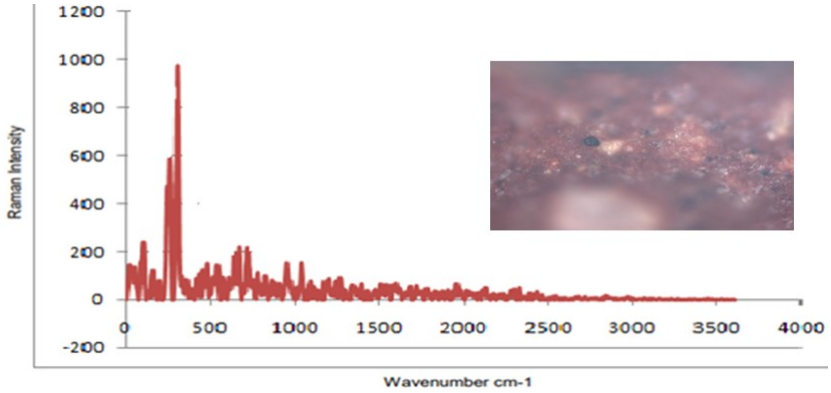


**Fig. 9.** Raman spectra detected from the red pigment

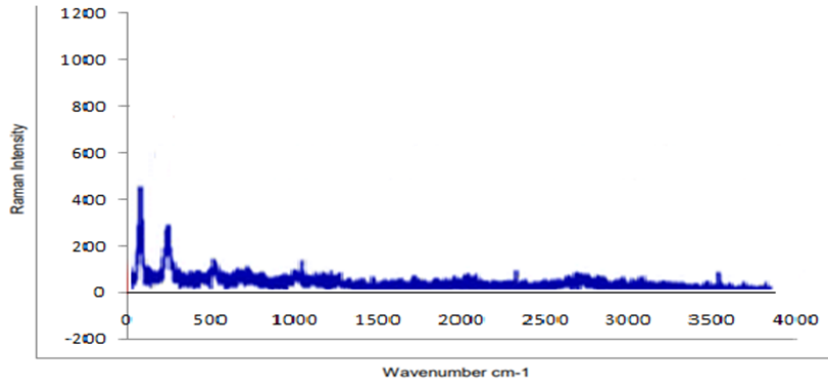


**Fig. 10**. Raman spectra of red ochre pigment (standard)

***FTIR ATR***

FTIR analysis was carried out to detect the functional groups of fabric layer and the organic media used for adhesive material. The characteristic peaks of linen are shown in Figure 11. The broad peak corresponds to hydroxyl groups -OH was detected at 3333cm$^{-1}$, the vibration stretching band of C-O- appeared at 1028cm$^{-1}$, the broad peak attributed to CH and CH2 stretching vibrations appeared at 2903cm$^{-1}$, the bands at around 1642cm$^{-1}$ which is related to C=O attributable to carbonyl groups due to cellulose oxidation (Table 3). The use of animal glue as binding media is detected by the presence of N-H bands appeared at 1543cm$^{-1}$ [12].

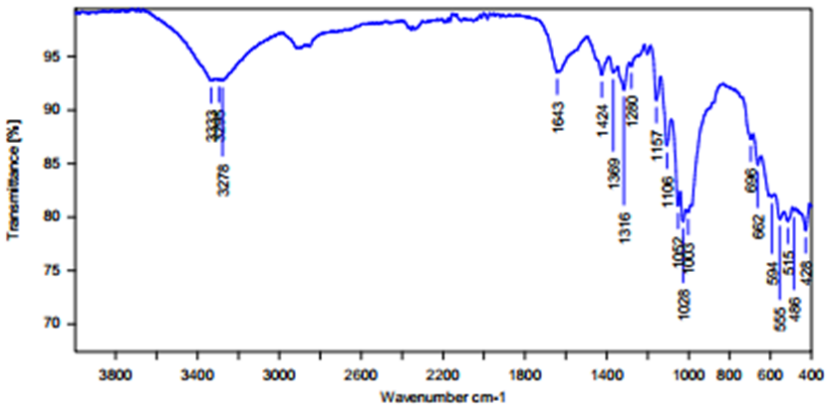


**Fig . 11.** Transmission FTIR spectra of fabric layer

**Table 3.** The vibration bands detected from the cellulosic fabric layer

| Vibration bands (wavenumder cm$^{-1}$) | Function groups |
|---|---|
| 3333 | OH, NH (Amide I) |
| 2903 | CH in the CH2 |
| 1726 | C=O |
| 1643 | Amide I |
| 1543 | Amide II |
| 1369 | COO |
| 1230 | C-O-C |
| 1157 | C-O, C-C, C-OH polysaccharides |

***Portable XRF Spectroscopy***

Pigments identification by XRF technique provides its color and mineral composition detected with the presence of major elements. Since it allows to know the historic period, to distinguish the original pigments. However, the organic colorants, or pigments contains light elemental components, cannot be directly identified by means of XRF technique.

XRF data (Table 4) corresponds to the yellow pigment used in the chromatic layer of cartonnage; we note the presence of Mg, P, S, Cl, Ca and As, the presence of these elements suggest the use of Orpiment (Arsenic sulfide $As_2S_3$) which was also confirmed by micro Raman spectroscopy. Orpiment, the yellow pigment of arsenic sulfide, was used in bright yellow or golden shades [13-15]. The mineral is found in the nature due to the geothermal sediments; it is

also found with carbonaceous stones. Several kinds of literatures mentioned the uses of orpiment as coloring matter.

**Table 4.** XRF data collected from the pigment layers

| Color | Mg% | Al% | Si% | P% | S% | Cl% | Ca% | Fe% | As% | Cu% |
|---|---|---|---|---|---|---|---|---|---|---|
| Black pigment | -- | -- | 2.13 | 0.22 | 0.78 | -- | 33.87 | -- | 0.05 | -- |
| Yellow pigment | 1.36 | -- | -- | 0.03 | 7.40 | 0.22 | 13.81 | 0.03 | 2.72 | -- |
| Red pigment | -- | 0.03 | 1.47 | 0.03 | 2.03 | 0.66 | 20.03 | 1.86 | -- | -- |
| Green pigment | -- | -- | 26.29 | 19.32 | 1.30 | -- | -- | 0.61 | 0.05 | 2.77 |
| Dark green | -- | 0.67 | 19.70 | -- | 0.91 | -- | 5.24 | 0.94 | 0.08 | 3.50 |

Regarding the other components detected with XRF Analysis, it should be observed the presence of magnesium and iron oxides with minor traces; these ensure the natural source of the yellow pigment used in the decorations since 16$^{th}$ Century BC [16, 17].

In the reddish regions, the presence of Fe it suggests the use of red ochre (Iron oxide $Fe_2O_3$). Earth oxide pigments varying from the pale yellow to the brownish red, their use as coloring matter dated back to the prehistoric periods [18, 19]. Its color is due to the presence of iron oxides, mostly goethite and hematite minerals [20-22]. The main red pigments in ancient times are of two popular types, red ochre (iron oxides) and lead oxide (red lead). Natural ochre was widely used and occurred in coloring palate, red ochre detected through XRF from the presence of high concentration of iron and calcium element beside minor traces of alum (Al) and Silicon (Si). The results also confirmed with Raman analysis, the peaks at around 209, 292 and 382cm$^{-1}$ corresponds to hematite mineral [23, 24]. The presence of calcium Ca with a major percent is due to the structure composition of cartonnage, which contained lime or gypsum. Regarding the white color, the data indicated the presence of Ca, as a major element, proposes lime (Calcium carbonate $CaCO_3$) or gypsum (calcium sulphate $CaSO_4 \cdot 2H_2O$). Lime is the main ore found in the nature and was widely used for the ground layers covered the wood panels or mummy cases [25].

In the green regions which is varying from the pale green to the dark green. The data revealed the presence of Ca, Si, S, Fe, and Cu, it suggests the use of the Egyptian green pigment with characteristic chemical composition ($CaCuSi_4O_9$). Many literatures reported the use of Egyptian green frit, green earth in the prehistoric periods for many purposes. The two green pigments were mainly used in ancient periods, are malachite green Cu $CO_3 2H_2O$ used for cosmetic ingredients, and the artificial Egyptian green dated back to the 6$^{th}$ Dynasty [26, 27].

In the black regions revealed high concentrations of Ca, Mg, P, and S, it suggests the animal source of the black pigment with typical composition ($Ca_3PO_4$) [28].

## Conclusion

The study used multi techniques to investigate the layer structure of a cartonnage fragment. Non- destructive microanalysis was performed, including SEM –EDS, XRF, FTIR, and Raman analysis. A preparation layer was applied upon the linen panel, which adhered with a binder, and appeared with colorful regions. The results proposed the use of lime (Calcium carbonate $CaCO_3$) as white stucco preceding the painting layer. The EDS analysis detected the elemental structure of the fabric layer, the sample revealed the presence of a high percentage of both carbon and oxygen which refer to the major elements of the linen fabric composition. XRF microanalysis was used for the identification of color samples, for the yellow, red, green, and

black colors, the results concluded orpiment, red ochre, Egyptian green, and carbon-based pigment were found in the chromatic layer. The green color was used in two shades, dark green and pale green, which consisted of Egyptian green, the results were also confirmed with Raman analysis. EDS and XRF microanalysis provide the elemental composition of analyzed samples, but it cannot identify the typical chemical composition of the investigated samples, However, the organic colorants, or pigments contains light elemental components, cannot be directly identified by means of XRF technique.

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