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Investigation and Characterization of two Painted Limestone Stelae, Egyptian Museum, Cairo, Egypt

Seham Ramadan[a]*, Gamal Mahgoub[a], Abeer F. ElHagrassy[a], Mohamed S. Abdel-Aziz[b] and Eid Mertah[c].

[a]*Conservation Department, Faculty of Archaeology, Fayoum University, Egypt.*
[b]*Microbial Chemistry Department, National Research Centre, Cairo, Egypt.*
[c] *Conservation Laboratory, Egyptian Museum, Ministry of Tourism and Antiquities, Giza,Egypt.*

Abstract

In this framework, a multi-analytical approach was used to map and identify the types of pigments used on two polychrome limestone stelae from the Middle Kingdom, of two officials named of Henu, son of Sobek-Hetep [CG 20212] and Imeny, son of Neb-Ieyou [CG 20594]. This study provides a deeper understanding of the painting techniques, and the condition of the objects. The painted layers on the stone were analyzed by using several analytical methods such as Scanning Electron Microscopy Coupled with Energy Dispersive X-Ray Detector (SEM-EDX), portable x-ray fluorescence (pXRF), x-ray diffraction (XRD) and Fourier Transform Infrared (FTIR)). The Portable noninvasive systems allowed accurate analysis of the employed pigments in both objects. Pigments including Egyptian blue, Egyptian green, goethite, hematite, calcite, and carbon black were detected in both painted stelae under investigation, by both scientific analyses and multispectral imaging.

Keywords: Portable x-ray fluorescence; Egyptian blue; Egyptian green; hematite; particular visible-induced luminescence; IR radiography; UV radiography.

1. Introduction

The combination of biotechnological an analytical approach could play an important role in protecting and preserving cultural heritages for future generations. Painting identifications include determination of the composition of the pigments, binders, the method of their application, as well as investigate the modality used to execute the artwork. In addition, the modifications induced by natural processes may substantially change the physical and chemical characteristics of the original materials and their stability over the centuries in such a way that the understanding of the painted surface can be rather difficult [1]. The analysis of the pigments used in paintings is important for conservation procedures since it can help to distinguish the original materials from retouching or later additions. [2]. In case of painted stones, paint analysis usually begins with visual observation, for the purpose of locating representative areas for analysis. The optical microscopy helps in gathering information about the thickness and sequence of paint layers, pigments and texture of those layers [3]. In order to study the morphology and chemical composition of the samples, scanning electron microscopy is usually used and the elemental microanalysis by SEM–EDX is always a valuable preliminary orientation [4].

The analytical identification of a pigment by means of the portable X-ray fluorescence (pXRF) technique involves its color and the composition (presence of specific key elements). Photoluminescence, as well as visible-induced luminescence (VIL) imaging, provides a quick and powerful tool for the spatial characterization of Egyptian blue. It can be easily applied to objects in museum collections or in situ. It is based on the property of Egyptian blue (EB) to absorb visible light and luminesce in the near-infrared region [٥-٦]. The IR signal penetrates through various types of patinas, including dirt and deteriorated varnishes, thus detecting Egyptian blue even when it is not visible at all. This was very useful in reading painted surfaces stelae that were completely obliterated by the overlying material. In certain instances, Egyptian blue is mixed with other pigments in order to produce different colors. In these

*Corresponding author e-mail: srm03@fayoum.edu.eg.; (Seham Ramadan Mahmoud).
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cases, VIL is useful in detecting Egyptian blue even when the colour of the surface is other than blue [٦].
The aim of the present work was to study pigment and stone samples collected from two polychrome limestone stela from dynasty 12 (Middle Kingdom) using different analytical techniques.

1.1 Historical background of selected artifacts

The first case study is a painted limestone rectangular funerary stela of Henu, son of Sobek-Hetep (Cairo CG 20212) .This is the most common name in the Middle Kingdom "Sobekhotep, (Figure1A). The painted stela was discovered in 1861 during the excavations by A. Mariette (director of the Egyptian Antiquities Service) in North Abydos, more specifically in the "Northern Cemetery." The stela dated back to the dynasties 12 (Middle kingdom). The object's dimensions are 26 cm in height and 15.5 cm in width.
The second case study is a painted limestone rectangular funerary stela with cornice of Imeny son of Neb-Ieyou [Cairo CG 20594] [7] (Figure1B). The provenance is identical to the previous one. A. Mariette dated it to the same period. The painting dimensions are 26 cm in length and 26 cm in width.

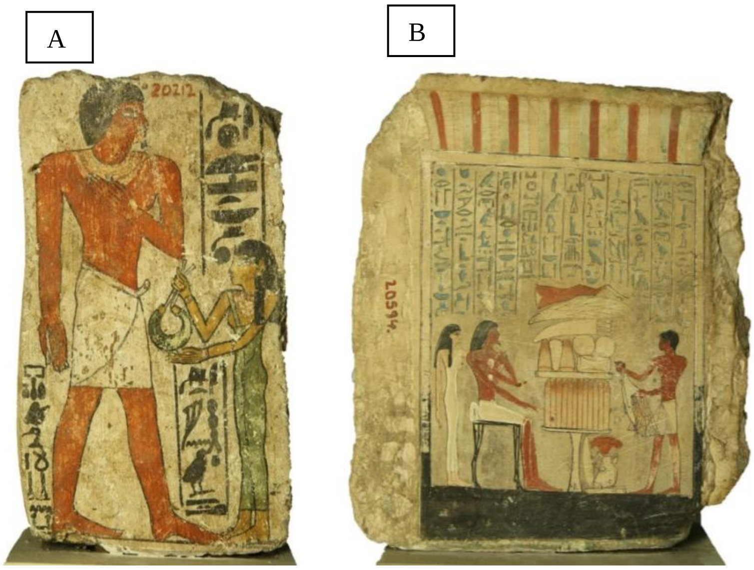

Figure 1. (A) Stela of Henu, son of Sobek-Hetep [Cairo CG 20212]. (B) General views of the Stelae of Imeny, son of Neb-Ieyou [CG 20594].

2. Material and methods

2.1Technical photography

Technical photography is popular in this field because of its simplicity. Visible-reflected (VIS) images correspond to standard photography and record the reflected light in the visible region (400-700 nm) from an object when it is luminescence (UVL) records the emission of light (luminescence) (UVL) record the emission of a light (luminescence) in the visible region (400-700 nm) from an object when it is illuminated with Ultraviolet radiation. This technique is used to investigate the distribution of luminescent materials, such as binding media and pigments. Some inorganic materials also show luminescence properties. Visible-induced infrared luminescence (VIL) images record the Egyptian blue that has the property of absorbing visible radiation and reemitting infrared (IR) radiation in the 800–1000 nm range with a peak at c. 910 nm (visible-induced luminescence).

2.2Scanning electron microscopy-energy dispersive x-ray analysis (SEM-EDX)

Scanning electron microscopy coupled with dispersive energy -Detector (SEM–EDS). Using SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K.V., magnification14x up to 1000000 and resolution for Gun.1n).SEM-EDX was used to study the morphology of the sample, the mineralogical composition, the micro-textural composition of the sample, and for the identification of chemical elements of the paint layer and the preparation layers.

2.3 Portable X-Ray fluorescence Spectrometer (pXRF)

XRF measurements were performed with a portable X-Glab ELIO spectrometer using Excitation source: Transmission x-ray generator 5-200 µA, 10-40 kv, rh anode "Ag, Au, MoW", 1 mm or 2mm collimator, filters set. Elio portable XRF analysis (PXRF) is compact detection head for energy dispersive X-Ray fluorescence applications. Designed for in-site analysis. Detection head large-area silicon drift detector: 25 MM2 XRF detectors, 130 eV at Mn Ka with 10 kcps input photon rate (high-resolution mode), 170 eV at Mn Ka with 200 Kcps input photon rate "fast mode".

2.4 X-Ray Diffraction Spectroscopy (XRD)

We collected a few chips of the stone that had fallen from the pieces, and grinded them into powder in an agate mortar, in order to analyze them. The X-ray diffraction method provided us with their mineralogical composition. XRD measurements were performed with an analytical X-Ray diffraction equipment model X pert PRO with monochromator, cu-radiation (ʎ=1.542 ◦A) at 50 K.V., 40 M.A. and scanning speed 0.02 ◦\sec. The reflection peaks were between 2º = 2◦ and 60◦, corresponding spacing (d, A) and relative intensities (1\1◦) were obtained.

2.5 Fourier Transforms Infrared Spectroscopy (FTIR)

FTIR was used to identify the medium employed in the paint and preparation layers. Identifying the medium helps to know the technique used (is the technique fresco or tempera) The collected powder was subsequently homogenized with KBr in an agate mortar (0.5 mg of the encrustation with 150 mg of anhydrous KBr) and pressed by means of a vacuum hydraulic press to obtain a pellet. Then, the transmittance FT–IR spectra were collected using Perkin-Elmer Spectrum One FT–IR and Nicolet 6700 FTIR spectrometers in a range 4000– 400 cm-1 at a resolution of 4 cm^{-1}.

3. Results and discussion

3.1 Technical photography

Multispectral imaging is a non-destructive tool for the identification of paint materials, as well as added materials from previous conservation procedures. Imaging also informs us about their spatial distribution in an artwork [8]. Ultraviolet induced luminescence imaging can reveal the distribution of luminescent materials, which includes many modern conservation materials [9,10].
On the stela CG 20212, infrared imaging (Figure 2b) revealed black outlines, which did not clearly appear in the visible light due to the negative impacts of the damage, and areas of red pigment appeared darker when exposed to ultraviolet radiation. This may suggest that the red pigment is red ochre (colored by hematite, Fe_2O_3), consistent with the strong quenching properties of iron-based pigments [11] (Figure2c). Materials containing copper or carbon are opaque under UV emission and appear black [12].

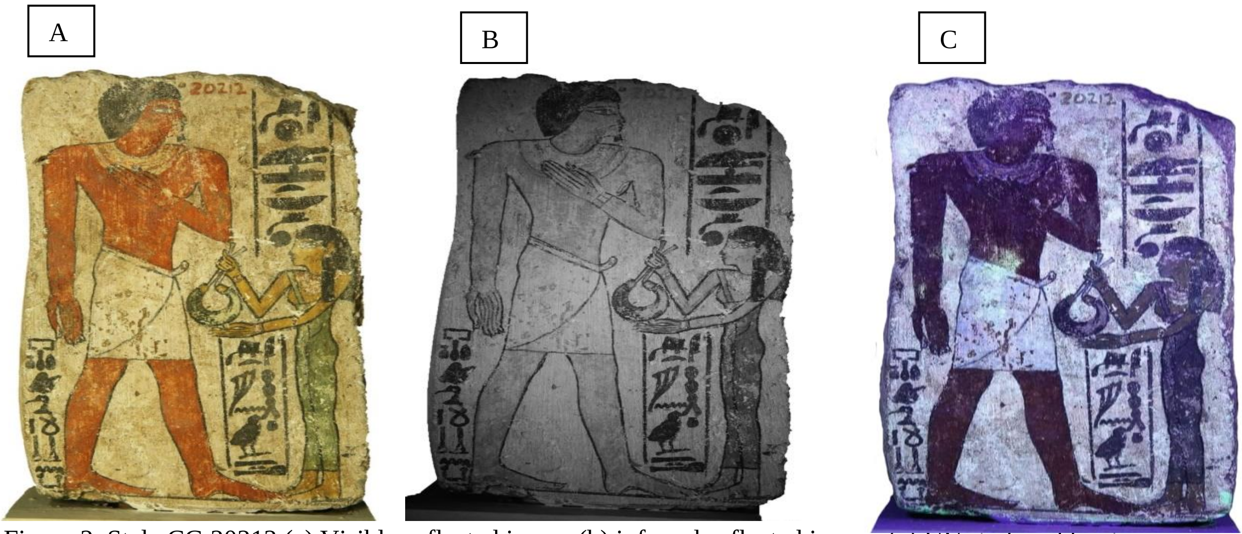

Figure 2. Stela CG 20212 (a) Visible-reflected image (b) infrared-reflected image, (c) UV- induced luminescence image.

On the stela CG 20594**:** UV was used to investigate the distribution of luminescent materials, such as organic binders and colorants. Some inorganic materials also show luminescence properties, many areas showed green patches on the surface from quite a luminescent material. This luminescence presumably relates to previous restoration materials or repainting or retouching areas (Figure 3b) [13].

The IR signal penetrates through various types of patinas, including dirt and deteriorated varnishes; this is very useful in reading painted inscriptions on wall paintings that were completely obliterated by the overlying material (Figure3c). Visible-induced luminescence (VIL) imaging provides a quick and powerful tool for the spatial characterization of Egyptian blue. It can be easily applied to objects in museum collections or in situ. Photoluminescence of Egyptian blue or visible-induced luminescence (VIL) is a powerful imaging technique applicable mostly to Egyptian Blue. It is based on the property of Egyptian blue to absorb visible light and luminesce in the near-infrared region.

Visible-induced infrared luminescence (VIL) images record the Egyptian blue has the property of absorbing visible radiation and of reemitting infrared (IR) radiation in 800–1000 nm range with a peak at c. 910 nm (visible-induced luminescence).The emission by the Egyptian blue pigment is strong (cuprorivaite is the strongest IR emitter at a molecular level currently known, emission of radiation (luminescence) in the infrared region (700-1100 nm) from a subject, when this is illuminated with visible light. This image characterizes the spatial distribution of pigments such as Egyptian blue. This technique is very sensitive and can reveal even single particles of pigments. VIL imaging allows easy differentiation between Egyptian blue and other blue pigments such as the artificial ultramarine pigment [٦]. This emission from Egyptian blue appears as white or very pale areas in the VIL image, while all other materials appear black or dark grey. In this case, the visible induced infrared luminescence images (Figure 3d) showed that the blue pigment appeared as bright white, while all other materials appear dark. The luminescence of such areas could indicate the presence of Egyptian blue

A

B

C

D

Figure 3. Stela CG 20594 (a) Visible-reflected image, (b) UV-induced luminescence image. The luminescence presumably relates to previous restoration materials or repainting or retouching areas, (c) Infrared-reflected (IRR) images, with the reflected radiation in the infrared region (700-1100 nm), (d) VIL image. The bright white areas on the image indicate the presence of Egyptian blue.

3.2 SEM- EDX results

The results of the Scanning Electron Microscope – EDX of the painted surfaces illustrated some aspects of damage, including general weakness, cracks, and flaking of the surface. We studied samples of the stone that had fallen off from the piece and analyzed them in order to understand the mineralogical chemical composition of the support, as well as the deterioration mechanisms of the whole stela.

Sample1: stela CG 20212. Scanning electron microscope was used to identify the morphological aspects of stone samples. The SEM investigation shows fine and large grains distributed into the micrograph (Figure4,A.B).The EDX microanalysis

shows major amounts of Calcium with minor amounts of magnesium and Silica It explains that consists of calcium (Ca), magnesium (Mg), which is the calcium carbonates $CaCO_3$, the main component of limestone, (Figure 5\Table 1.).

Sample 2: stela CG 20594. SEM micrograph on the sample represented fine-grained matrix with the absence of siliceous aggregates (Figure 4,C,D), the EDX spectrum of the sample shows a major content of calcium with atomic concentration reached 12.6% and Traces of chlorine (Cl, 0.33%), sodium (Na, 0.48%) and sulphur (S, 2.03%) were detected in the sample, which confirm halite salts (NaCl) and Gypsum ($CaSO_4 \cdot 2H_2O$.) (Figure 6\ Table2).

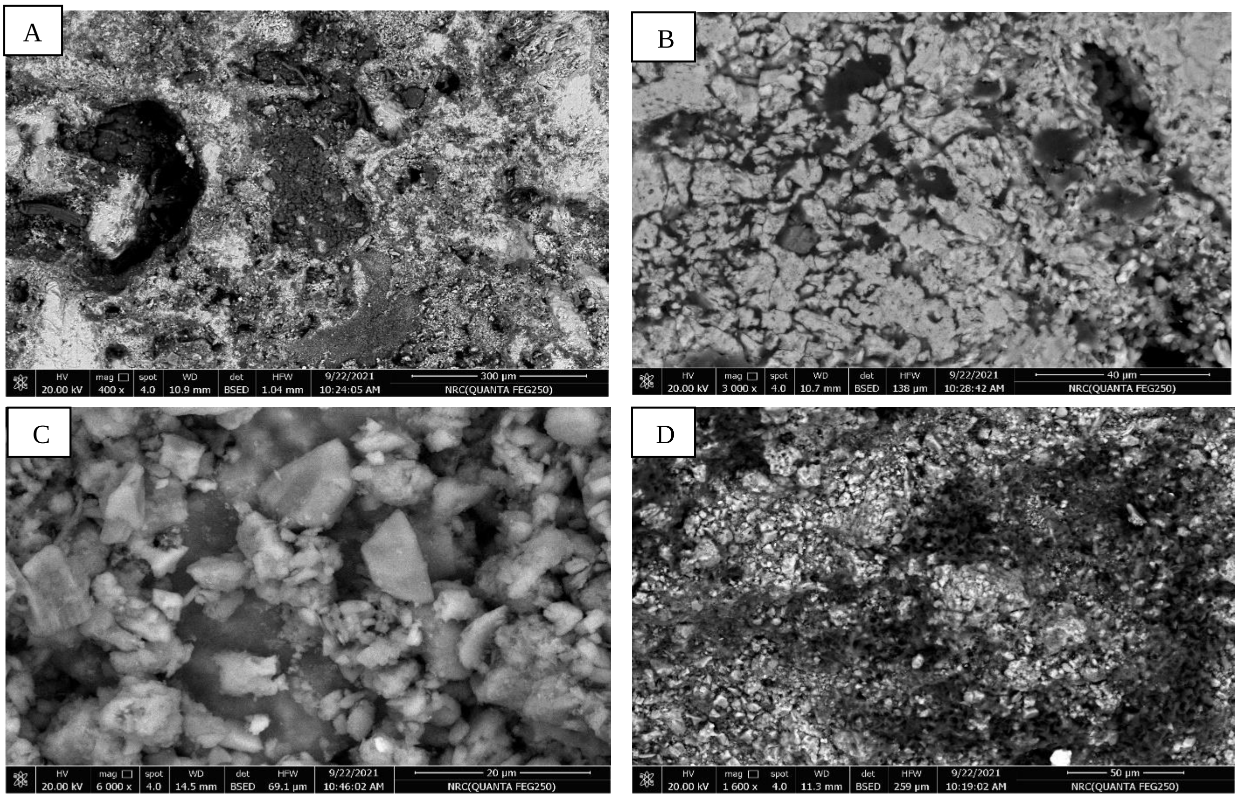

Figure 4. ESEM images obtained on the outer surface of the studied samples (a,b) Show SEM micrographs of stone and appears the pore in the grains stone 1500x and 3000x. (c.d) Show SEM micrographs of some deterioration aspects in the stone surfaces 6000x and 1600x.

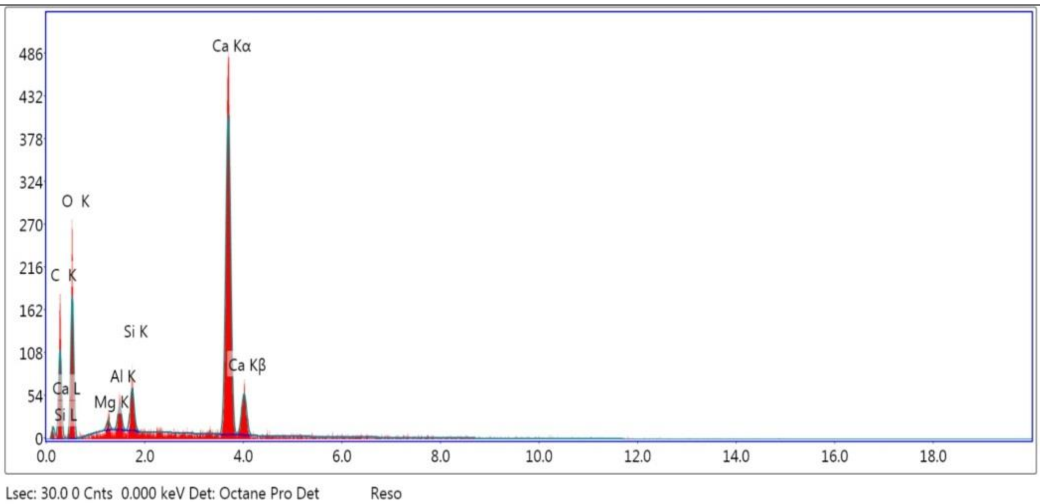

Figure 5. SEM-EDS chart shows the composition of the limestone support of the stela CG 20212.

Table 1. Elemental analysis of the stela CG 20212.

Element	Wt %	Atomic %	Net Int	Error %
C K	21.09	31.89	53.41	9.82
O K	46.07	52.29	92.5	11.89
Mg K	0.79	0.59	8.99	29.19

Al K	1.45	0.98	21.12	14.7
Si K	2	1.29	34.8	10.93
Ca K	28.8	12.96	329.41	2.62

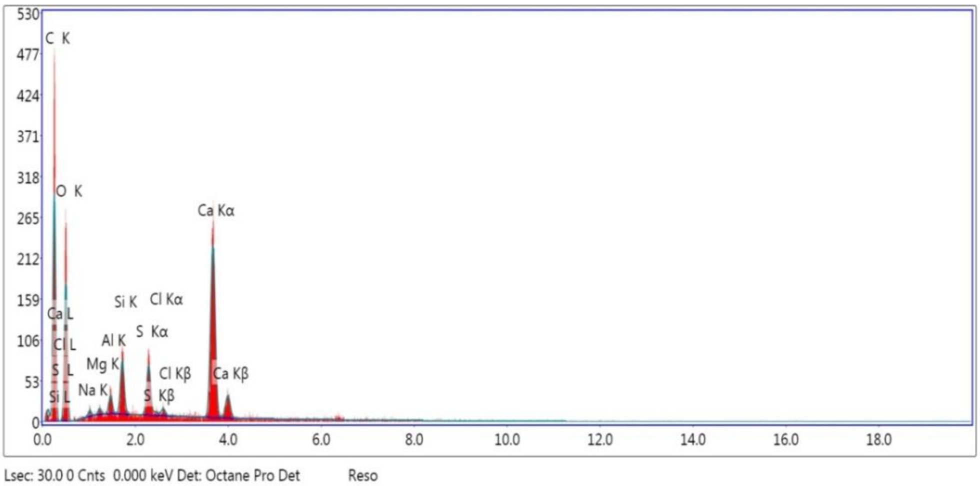

Figure 6. SEM-EDS chart shows the Salts crystallized found within the granules of the lime stone of the stela CG 20594.

Table 2. The results of elemental analysis the Salts crystallized found within the granules of the lime stone of the stela CG 20594.

Element	Wt %	Atomic %	Net Int	Error %
C K	45.51	57.73	142.7	8.6
O K	36.19	34.47	92.29	11.87
Na K	0.48	0.32	4.11	66.27
Mg K	0.26	0.17	4.23	64.72
Al K	0.71	0.4	14.31	18.52
Si K	1.89	1.02	44.47	8.65
S K	2.03	0.96	44.89	9.74
Cl K	0.33	0.14	6.66	44. 4
Ca K	12.6	4.79	6.66	3.46

3.3XRF analysis

The possible pigments used in the decorative stela were identified by the presence of key elements in the spectra associated with the color of the analyzed areas (see table 3 which summarizes the XRF analysis results for the stela CG 20212. The following elements were identified in all spectra: Ca, Fe and Sr. The presence of calcium (Ca) is related to use of the limestone, which is constituted by this material [14]. The Calcium carbonate $CaCO_3$, it's the composition of the limestone of the stela, and some other trace elements identified in the spectra as the case of Fe and Sr, can be considered as impurities from limestone (figure 7A). Most of the trace elements identified in the spectra as the case of K, Sr, Ti and Fe can be considered as impurities from the raw materials employed in the manufacture of the pigments by the Egyptian craftsmen [15].

In (Figure 7B) the XRF spectrum of the red pigment shows the presence of calcium (Ca), strontium (Sr), iron (Fe) and silica (Si). The presence of the iron (Fe) element suggests that red iron oxides were used to make the red pigment (hematite Fe_2O_3), also showed the strong contribution of Si which indicated the existence of an aluminosilicate material, probably from the clay minerals associated with ochers [16].

Portable X-ray fluorescence spectrometry of the green pigment from the painted stela CG 20212 detected the presence of silica (Si) and copper (Cu) indicating the use of a copper based pigment, most probably Egyptian green ($(CaCu)SiO_3$), the presence of iron (Fe), (Cl) and (Ti) are as minor elements in the sample (Figure 7C) [17]. The Egyptian principal green pigment has been synthesized from the same components as the Egyptian blue but requires very precise estimation of ratios of components and a much higher temperature. The green (green frit) is a heterogeneous material, and it was characterized by the presence of para-wollastonite $CaSiO_3$ crystals smaller than 10 µm and residual silica (quartz or tridymite or cristobalite) [18].

Earth pigments are varying from dull yellow to red and brown are commonly called ochres. The color is given by the presence of different iron oxides, mainly goethite and hematite; sometimes the pigment is brownish due to manganese oxides. The chemical responsible for the yellow color is ferric oxide monohydrate ($Fe_2O_3.H_2O$), and it is found mixed with silica and clay. The pigment, which is essentially yellow clay, is produced by grinding and washing [19, 20].

In (figure 7D) the XRF spectrum of the yellow pigment showed the presence of some elements such as: (Fe, Ca, Si, K, Ti, Sr, Cl) which refer to the presence of hydrated iron oxide, FeO(OH) (goethite) with the presence of a percentage of calcite and other elements, and this is due to the limestone. In this case, yellow ochre was identified in the stela.

The microscopic investigation of the black pigment indicated very fine and even particles and did not show any fibrous structure, so it was possible to exclude a burnt vegetable origin for the black pigment. In the XRF spectrum of the black samples presented a high intensities of Ca in the spectra (the main element of Calcium carbonate $CaCO_3$ of the limestone of the stela) and no elements detected for the black color, which suggests the use of Carbon black as a black pigment (Figure 7E).

Ca, Fe presented the highest concentration in the white pigment. The possible pigment in this case is calcium carbonate (Figure 7F).

Table 3. Summarizes the XRF analysis results for the different pigments on the stela CG 20212.

Color	XRF
Stone	Ca – Fe - Sr
Black	Ca - Si - Fe - Ti - Sr
Red	Ca - Fe - Sr - Cl - Zn
Green	Ca - Si - Cl - Cu - Fe - Ti - As - Sr
Yellow	Ca - Si - Cl - Cu - Fe - Ti - Sr - As
White	Ca - Fe - Sr

In table 4, you can see the summarizes of the XRF analysis results for the stela CG 20594, the presence of calcium (Ca) indicates that the stela is made of calcium carbonate ($CaCO_3$), with some traces of iron (Fe) stone (figure 8A). XRF also allowed the identification of iron (Fe) on all red samples, indicating that the red pigment used is most probably red ochres (hematite Fe_2O_3). The chart indicates also the presence of calcium (Ca) and silicon (Si), which compose the stone of the stela under the paint (Figure 8B). The presence of metals like titanium (Ti), and (Sr) are impurities from the ochres [21].

Table 4. Summarizes the XRF analysis results for the different pigments on the stela CG 20594.

Color	XRF
Stone	Ca – Fe - Sr
Red	Ca - Si - S - Fe - Ti - Sr
Black	Ca - Si - S- Fe – Ti – Sr
Blue	Si - Ca - S - Cu - Fe - Ti - As - Sr
Orange	Ca - Si - S - k - Fe - Ti - Sr
White	Ca - Si – S - Fe - Sr

In the blue regions, the spectra (Figure 8C) exhibited high intensities of silicon (Si), copper (Cu) and calcium (Ca), characteristic elements of the Egyptian blue pigment (cuprorivaite). Therefore, the possibilities in this case are Egyptian blue ($CaCuSi_4O_{10}$) also known as calcium copper silicate or cuprorivaite,). Taking into account that azurite was rarely employed as a blue pigment in Egypt [22]. Egyptian blue was used at least for 3000 years as a valuable pigment. It was spread all around the Mediterranean basin and disappeared after the 7th century AD. The Egyptian blue was characterized by the presence of cuprorivaite ($CaCuSi_4O_{10}$), a blue tabular crystal about 15µm to 30µm in length, residual silica (quartz and or tridymite) and an amorphous silica-rich phase [18].

In the areas of the painted surface with orange color, the presence of high intensities of iron (Fe) in the spectra suggests the use of ochre pigments based on iron oxides. It could be a mixture of yellow ($Fe_2O_3.H_2O$) and red ochre (Fe_2O_3) or mixing a red pigment with a white or a unique compound presenting orange color. Ochre pigments can be found in the nature in a great variety of shades from yellow to red, including brown (Figure 8D).

Analysis by portable XRF of the black pigment showed Ca, Si, Fe, S and other elements Ti and Sr, thus elements already at the composition of the stone itself and that indicating the black pigment is most probably a carbon black [23] (Figure 8E). In the white pigment Ca, Si, S presented the highest concentration. The possible pigments in this case, are calcium carbonate ($CaCO_3$) or gypsum (calcium sulfate $CaSO_4.H_2O$). Calcium carbonate and calcium sulfate and calciferous clay are reported to have been used in ancient Egypt for white pigments (Figure 8F).

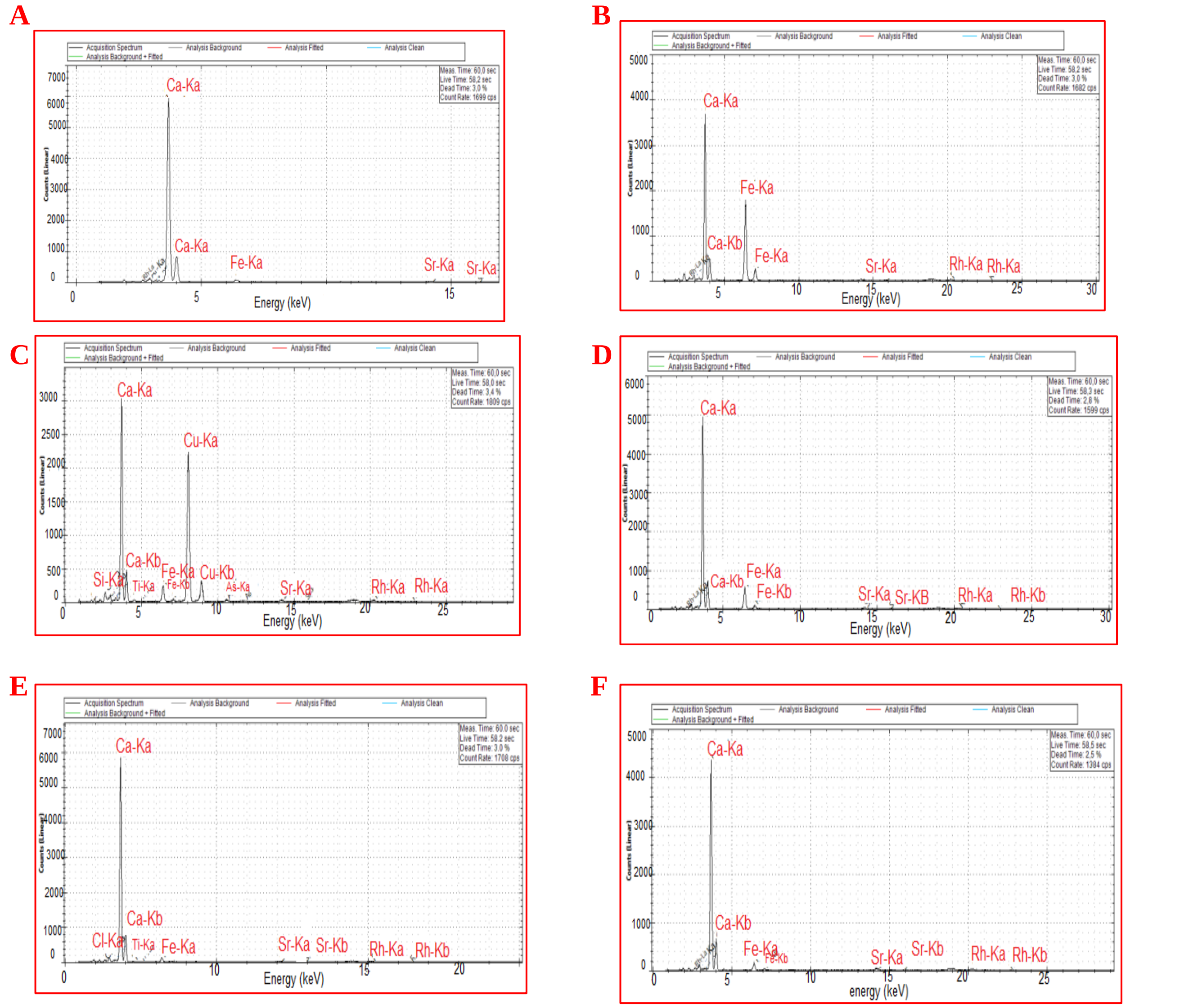

Figure 7. XRF spectra of the pigments of stela CG 20212: A) XRF spectra of the stone, B) XRF spectra of the red pigment, C) XRF spectra of the green pigment, D) XRF spectra of the yellow pigment, E) XRF spectra of the black pigment, F) XRF spectra of the white pigment.

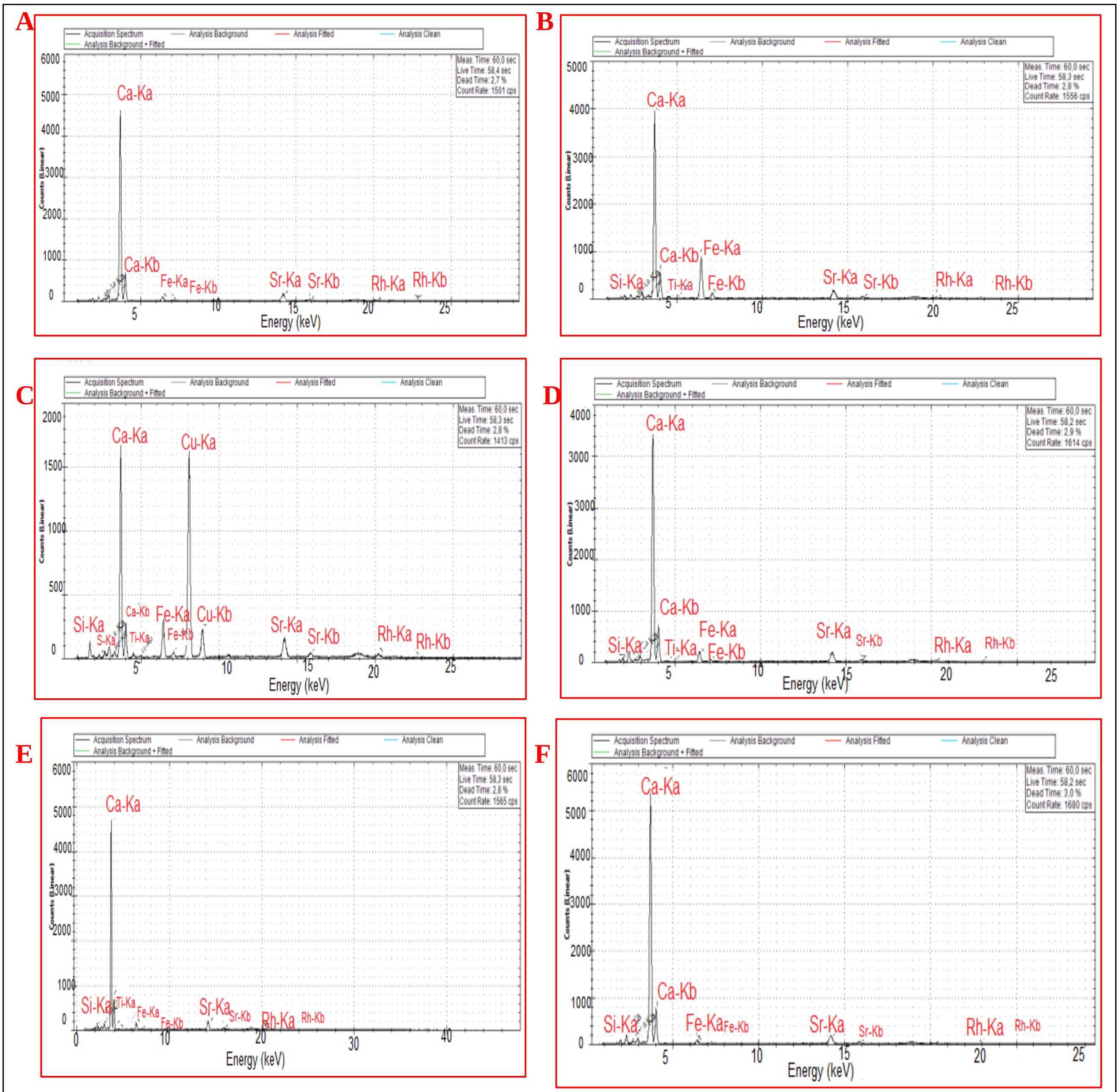

Figure 8. XRF spectra of the pigments of stela CG 20594: A) XRF spectra of the stone, B) XRF spectra of the red pigment, C) XRF spectra of the blue pigment, D) XRF spectra of the orange pigment, E) XRF spectra of the black pigment, F) XRF spectra of the white pigment.

3.4 XRD analysis

We studied samples of the stone that had fallen off from the stela and analyzed them in order to understand the mineralogical chemical composition of the support, as well as the deterioration mechanisms of the whole stela, to allow a full characterization of the paintings materials and support layer.

Sample 1, from stela CG 20212: The mineralogical analysis using X-ray diffraction method measured calcite ($CaCO_3$, 80%) and a small amount of sodium chloride (NaCl) as well as calcium sulfate $CaSO_4.2H_2O$ (gypsum) (Figure 9\ table 5). Limestone was a major building material used in constructing several monuments structures. The amounts of sodium chloride or halite detected in the stone samples occur as natural impurities in sedimentary rocks [2٤]. Sample 2, from stela CG 20594: The XRD analysis revealed quartz in the investigated limestone sample. Calcium carbonate ($CaCO_3$) was detected as major mineral component, while few low-intensity peaks represented dolomite phase. The most intense peaks for quartz, calcite, and dolomite were observed (Figure10\table6).

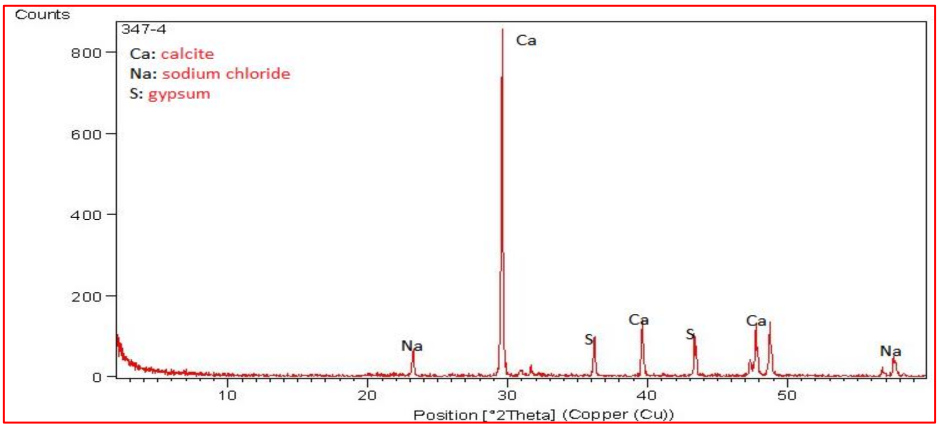

Figure 9. shows the XRD of the stone and confirmed its nature as dolomite limestone, with the presence of a small amount of sodium chloride (NaCl) and calcium sulfate $CaSO_4.H_2o$ (gypsum).

Table 5: Summarizes the XRD analysis results for the stone, stela CG 20212.

Number of cards	compound Name	Chemical Formula	SemiQuant [%]
01-089-1305	Calcite	$CaCO_3$	80
05-0628	Sodium chloride	NaCl	10
00-006-0046	Gypsum	$CaSO_4.2H_2O$	10

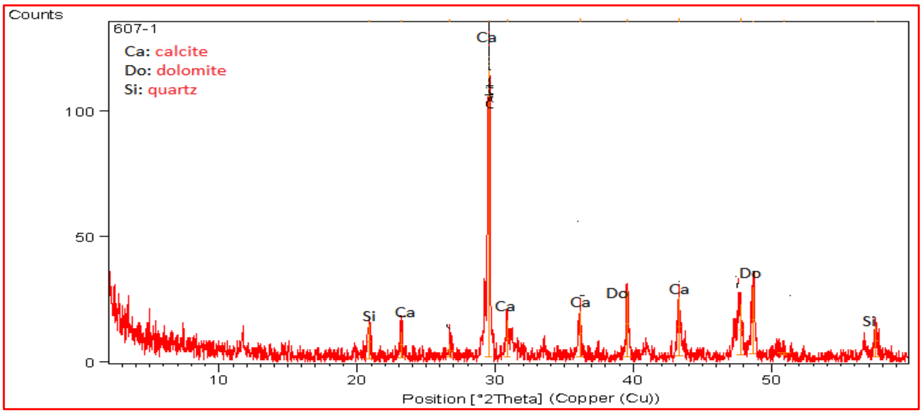

Figure 10. X-ray diffraction pattern of the analyzed limestone sample showing calcite as a major mineral phase followed by quartz and dolomite phases.

Table 6. Summarizes the XRD analysis results for stone, stela CG 20594.

Number of cards	compound Name	Chemical Formula	SemiQuant [%]
01-086-2335	Calcite,	$CaCO_3$	78
00-034-0517	Dolomite, ferroan	$Ca(Mg, Fe)(CO_3)_2$	11
01-085-0865	Quartz, syn	SiO_2	11

3.5 Fourier Transform Infra-Red (FTIR)

We analyzed the components of the painted layer of a chip which had fallen from the stela CG 20212.

By comparing the functional groups of these samples with the standard functional groups of gum Arabic and animal glue, it became clear that animal glue had been in the pigment layer (figure 11 and table 7). The characteristic bands for the identification of the animal glue as the main organic binder in the painting samples were 3200-3400 cm^{-1} N-H stretching bending, and 300-2800 cm^{-1} C-H stretching bands, as well as others, e.g. and 1600 cm^{-1} C=O stretching, and 1560 cm^{-1} C-N-H bending band and C-H bending band 1429 cm^{-1} [25\26].

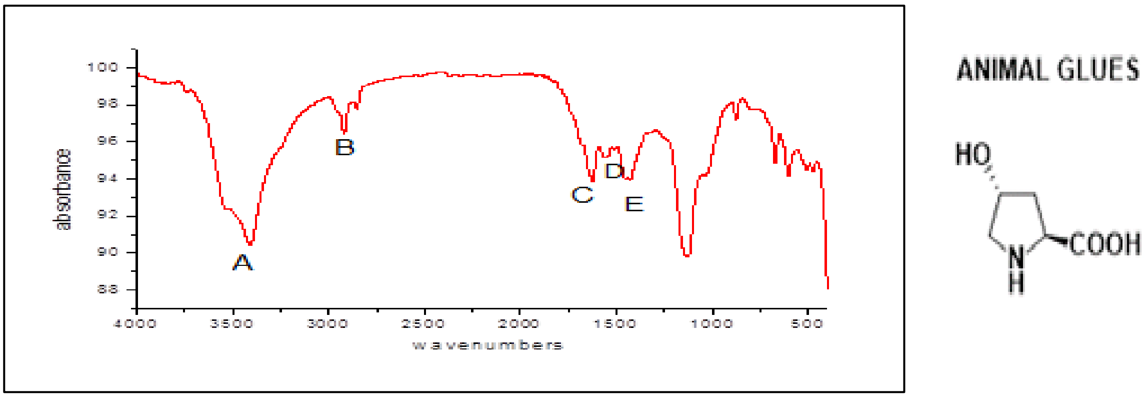

Figure 11. FTIR results showed that the animal glue as organic binder.

Table 7. The main functional groups obtained from the color layer.

N	Functional Groups bands	cm-1	Substance
A	N-H stretching (bending	3408	Animal Glue
B	C-H bending(Amide II)	2920	Animal Glue
C	C=O stretching	1623	Animal Glue
D	C-N-H bending band	1560	Animal glue
E	C-H bending band	1429	Animal glue

4. Conclusion

For this analysis, we used SEM.EDX, pXRF, XRD, FTIR techniques and technical photograph, in order to identify the pigments and stone used on two painted limestone stelae from the Middle Kingdom from Abydos (Upper Egypt). The stelae were discovered during the excavation by A. Mariette in 1861 in north Abydos. More precisely, they come from the northern cemeteries. The results showed that the pigments used were Egyptian blue, red ochre (hematite), yellow ochre (goethite) and carbon black, Egyptian green and Calcium Carbonate. In some areas of stela GC 20212, a mixture of pigments was employed in order to obtain a distinct hue as orange pigment. The animal glue was used in the different painting surfaces as the medium. The findings of this study are in accordance with previous analyses of ancient Egyptian pigments, which indicate the continuous use of artificial and natural earth pigments. By Visible-induced infrared luminescence (VIL), Egyptian blue appeared as white or very pale areas in the VIL image, while all other materials appeared black or dark grey as could be seen in stela CG 20594.

5. References

1- Regazzoni, Lucia, Giovanni Cavallo, Danilo Biondelli, and Jacopo Gilardi. "Microscopic analysis of wall painting techniques: laboratory replicas and Romanesque case studies in southern Switzerland "Studies in Conservation 63, no 6 (2018).p326.

2- Klockenkämper, R., A. Von Bohlen, and Luc Moens. "Analysis of pigments and inks on oil paintings and historical manuscripts using total reflection x-ray fluorescence spectrometry." X-Ray Spectrometry 29, no. 1 (2000): pp119-129.

3- Silva, Cynthia L. "A Technical Study of the Mural Paintings of the Interior Dome of the Capilla de la Virgen del Rosario, Iglesia San José, San Juan, Puerto Rico." (2006).p39.

4- Franquelo, María Luisa, Adrian Duran, Liz Karen Herrera, MC Jimenez De Haro, and J. L. Perez-Rodriguez. "Comparison between micro-Raman and micro-FTIR spectroscopy techniques for the characterization of pigments from Southern Spain

Cultural Heritage." Journal of Molecular structure 924 (2009): pp404-412.
5- Chiari, Giacomo. "Photoluminescence of Egyptian blue." The Encyclopedia of Archaeological Sciences (2018): pp1-4.
6- Verri, Giovanni, David Saunders, Janet Ambers, and Tracey Sweek. "Digital maping of Egyptian blue: conservation implications." Studies in Conservation 55, no. sup2 (2010): pp220-224.
7- Lange, Hans Ostenfeldt. Grab-und Denksteine des mittleren Reichs im Museum von Kairo. Reichsdruckerei, (1902).pP235.
8- Delaney, John K., Elizabeth Walmsley, Barbara H. Berrie, and Colin F. Fletcher. "Multispectral imaging of paintings in the infrared to detect and map blue pigments." Scientific examination of art: modern techniques in conservation and analysis (2005): pp120-136.
9- Grant, M.S. The use of ultraviolet induced visible fluorescence in the examination of museum objects, Part II. National Park Service. Conserve O Gram, (1/10), (2000).p.4.
10- Verri, Giovanni, M. Gleba, J. Swaddling, T. Long, J. Ambers, and T. Munden. "Etruscan women’s clothing and its decoration: the polychrome gypsum statue from the ‘Isis Tomb’at Vulci." The British Museum Technical Bulletin 8 (2014): pp59-72.
11- Dyer, Joanne, Elisabeth R. O’Connell, and Antony Simpson. "Polychromy in Roman Egypt: a study of a limestone sculpture of the Egyptian god Horus." British Museum Technical Research Bulletin 8 (2014): p93.
12- Pagès-Camagna, Sandrine, Eric Laval, Daniel Vigears, and Adrian Duran. "Non-destructive and in situ analysis of Egyptian wall paintings by X-ray diffraction and X-ray fluorescence portable systems." Applied Physics A 100, no. 3 (2010): pp671-681.
13- Hain, Miraslov, Jn Bartl, and Viado Jacko). "Multispectral analysis of cultural heritage artefacts." Measurement Science Review 3, no. 3 (2003): pp9-12
14- Calza, Cristiane, M. J. Anjos, SMF Mendonça De Souza, A. Brancaglion Jr, and Ricardo Tadeu Lopes. "X-ray microfluorescence with synchrotron radiation applied in the analysis of pigments from ancient Egypt." Applied Physics A 90, no. 1 (2008): pp75-79.
15- Paternoster, Giovanni, Raffaele Rinzivillo, Felice Nunziata, Emilio Mario Castellucci, Cristiana Lofrumento, Angela Zoppi, Anna Candida Felici et al. "Study on the technique of the Roman age mural paintings by micro-XRF with polycapillary conic collimator and micro-Raman analyses." Journal of Cultural Heritage 6, no. 1 (2005): pp21-28.
16- Berry, Michelle. "A study of pigments from a Roman Egyptian shrine." AiCCM Bulletin 24, no. 1 (1999): pp1-9.
17- Castro, L.N.C., Calza, C., Freitas, R.P., Brancaglion, A. and Lopes, R.T., October. Analysis of Ancient Egypt artifacts using X-Ray Fluorescence. In IMEKO Int. Conf. Metrol. Archeol. Cult. Heritage, MetroArcheo (Vol. 2016). p121.
18- Mahmoud, Seham Ramadan. "Impact of weathering on the chemical and mineralogical composition of ancient Egyptian copper-based pigments with application on treatment and conservation of some painted archaeological Stelae." master diss., University of fayoum, Egypt. (2019) .Pp.25-31.
19- Barnett, John R., Sarah Miller, and Emma Pearce. "Colour and art: A brief history of pigments." Optics & Laser Technology 38, no. 4-6 (2006): pp445-453.
20- Hradil, David, Tomáš Grygar, Janka Hradilová, and Petr Bezdička. "Clay and iron oxide pigments in the history of painting." Applied clay science 22, no. 5 (2003): pp223-236.
21- Gil, M., Carvalho, M.L., Seruya, A., Candeias, A.E., Mirão, J. and Queralt, I.,. Yellow and red ochre pigments from southern Portugal: Elemental composition and characterization by WDXRF and XRD. Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 580(1), (2007).pp.728-731.
22- Scott, D.A.,. A review of ancient Egyptian pigments and cosmetics. Studies in Conservation, 61(4), (2016).pp.185-202.
23- Valadas, S., A. Candeias, J. Mirao, D. Tavares, J. Coroado, Rolf Simon, A. S. Silva, M. Gil, A. Guilherme, and M. L. Carvalho. "Study of mural paintings using in situ XRF, confocal synchrotron-μ-XRF, μ-XRD, optical microscopy, and SEM-EDS—the case of the frescoes from Misericordia Church of Odemira." Microscopy and Microanalysis 17, no. 5 (2011): p702.
24- Ali, Mona F., Hazem El-Shafey, and Hussein Marey Mahmoud. "Multianalytical Techniques of Al-Bimaristan Al-Mu'ayyidi Mural Painting At Historic Cairo: Contribution to Conservationand Restoration." Scientific Culture 7, no. 2 (2021): pp33-48.
25- Mahmoud, Hussein H. Marey. "Investigations by Raman microscopy, ESEM and FTIR-ATR of wall paintings from Qasr el-Ghuieta temple, Kharga Oasis, Egypt." Heritage Science 2, no. 1 (2014): p9.
26- Ramadan, Seham, Gamal Mahgoub, Mohamed S Abdel-Aziz, Austin Nevin, and Abdelrazek Elnaggar. "Study of the Antifungal Effects of Copper-based Pigments and Synthesized Nanomaterial on Mural Painting-deteriorated Fungi in the Egyptian Museum in Tahrir." (2019).p62.