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ANALYTICAL PHYSICOCHEMICAL SURVEY OF THE RECENTLY EXCAVATED MURALS AT THE TOMB OF IWRAKHY/HATIA AT SAQQARA, EGYPT

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ABSTRACT

Present work presents an analytical survey of the murals at the tomb of Iwrakhy/Hatia (1550 BC-1077 BC). The owner was a noble lived during the ruling era of king Ramses II (reigned 1279-1213 BC), discovered during the Cairo University excavation season of 2018 at Saqqara area. New evidence is produced for the use of lead ores abreast with hematite as a source of red pigments, moreover; as well as proof of the mixing process of goethite with orpiment to get a gold-like colour. Stones, mortars, plasters and pigments were investigated using the digital microscope and the scanning electron microscope, and X-ray diffraction, SEM-EDX, while the paint medium was examined using the FTIR and Raman spectroscopy. Mortars and rendering layers are composed of gypsum, the latter is the ideal arriccio for the tempera murals and for the dry Egyptian climate; crushed limestone and quartz were added to gypsum as fillers. The red pigment is hematite mixed with lead; this represents a new discovery in the new kingdom murals. Yellow pigment is goethite mixed with orpiment, a rare case of the ancient Egyptian trials for gaining the effect of gilding on the walls, trying to imitate the common tradition in painting coffins. Regarding the blue pigment it is Egyptian blue containing high amounts of wollastonite and atacamite, blue is turned into greenish due to the presence of halite, animal glue was used as a paint medium in the studied tomb.

KEYWORDS: Mural paintings; Saqqara; Excavations; Iwrakhy; Egyptian blue; SEM-EDX, FTIR, XRD, Raman.

1. INTRODUCTION

Saqqara locates at 29.87˚ N and 31.21˚ E, also known as Sakkara or Saccara, the area is about 183 km^2; it attains a length of approximately 4.5 miles and a width doesn't exceed 1 mile, the whole area is about 48-52.5m ASL (above sea level), it is about 30 kilometres southwest of Cairo. The climate of Saqqara is distinguished by its high daily and annual range of temperature, while topographically; the area is almost a flat land containing some important heights, surrounded by the flood plain and the flood basin of the river Nile silt, the surficial quaternary sediments in the area are 43% marine deposits, 2% Aeolian deposits and 55% are mixed deposits (marine with wind effect), the common rock in the area is the clayey limestone containing high amount of concretions with a high stratification appearance (Ali, 1993; Godziejewski, 1999; Hamdan, 2000; Moussa, 2001). Saqqara used to serve as a necropolis for the ancient Egyptian capital Memphis (Graindorge, 2005), the use of the first faience tiles pigmented with the first man-made pigment in history (Egyptian blue) started first on the walls of Saqqara tombs (Moussa and Ali, 2013). The tomb of Iwrakhy was recently discovered during the excavation season of the faculty of Archaeology-Cairo University at Saqqara in 2018 (Fig. 1), the tomb dates back to the new kingdom era (1550 BC-1077 BC, Schneider, 2008), the tomb owner was a noble lived during the ruling era of king Ramses II (reigned 1279-1213 BC, Reeves, 1990; Reeves and Wilkinson, 1996; Reeves, 2006). Iwrakhy, according to the hieroglyphic inscriptions upon the studied mural (El-Aguizy, 2018), was "the head of the army" and "the royal envoy to all the foreign countries". The studied mural is decorated with inscriptions and hieroglyphic letters coloured in red, yellow and blue, its dimensions are about 140 cm width, 75cm height and 60cm thickness, the mural is located at the left wall of the entrance to the main hall of the tomb (Fig. 2). The current study aims essentially to investigate the building materials of Iwrakhy tomb from the new kingdom at Saqqara area in order to point out the current state of durability of these materials; the study also aims to assess the chemical composition of the used building materials in the studied tomb (stones, mortars, plasters, pigments and media). Across assessing the chemical contents of the pigment materials, the study aims to point out if there are new trends in the wall painting technique or in the recruiting of the row materials. This is useful, both, for correctly analysing the technology of wall painting in this era, and for the development of damage hazards affecting building materials at Saqqara area. Similar studies have been reported elsewhere (e.g., Ashkenazi et al., 2021; Al-Emam et al., 2015; Medhat Abdallah et al., 2020; Vázquez de Ágredos-Pascual et al., 2019; Liritzis et al., 2015).

Figure 1. The excavation site of Cairo University at Saqqara (Google earth).

Figure 2. The studied mural from Iwrakhy tomb during excavation, Saqqara

2. SAMPLING AND METHODS

Stones, mortars, plaster, and pigments from the studied tomb; have been sampled and laboratory analysed to determine their chemical composition. Samples were investigated using the digital microscope and the scanning electron microscope, they were also analysed using X-ray diffraction, SEM-EDX, while the paint medium was examined using the FTIR spectroscopy and Raman spectroscopy. The used scanning electron microscope is Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 Kv, magnification 14x up to 100,0000 and resolution for Gun.1n). Tilts (0.00); take-off: (36.47); ampt (35.0); detector type (SUTW-sapphire); resolution (129.87), FEI Company, Netherlands. Samples were grinded and pulverized; X-ray diffraction (XRD) analysis was performed using these powdered samples of the above-mentioned building materials using a Philips (PW1840) diffractometer with Ni-filtered Cu-Kα radiation. The samples were scanned over the 5-60° 2θ intervals at a scanning speed of 1.2° min-1. A quantitative estimate of the abundance of the mineral phases was derived from the XRD data using the intensity of certain reflections and external standard mixtures of minerals compared to the JCPDS standards of 1967. Raman scattering spectra were recorded on a LABRAM-HR Raman spectrometer excited with a 514.5 nm Ar + laser, moreover; mass contents were measured by thermal gravimetric analysis (SDT Q600), field-emission scanning electron microscopy (SUPRA 40 ZEISS, Germany, SEM-EDS). The FTIR analysis involved the evaporation of the sample solution (using a solvent such as: chloroform, ether, dichloromethane) onto a KBr salt plate and acquisition of the spectrum from the thin film remaining. The estimated time to obtain spectrum from a routine sample varies from 1 to 10 minutes (Hsu, 2000). Additionally, liquids, dried residues, viscous materials, films, and other sample matrices can be accommodated. The testing is generally performed in accordance with ASTM E334. The FTIR aids in identifying chemical bonds, and thus chemical composition of materials. FTIR works best when the sample matrix is either homogeneous; or composed of only a few materials. Mixtures of multiple materials tend to "confuse" the library search function due to complexity of overlapping spectral fingerprints. The paint medium sample was analysed as KBr pellet by a JASCO FTIR spectrometer (model 460, 400 – 4000cm−1, 4cm^{-1} resolution), in the transmission mode. Samples were investigated using digital USB light optical microscope (USB 2.0 interface, Linux, Max OS and above 10.5.5), from 10x – 500x, model: PZ01, Fig.3 shows the locations of the analysed samples from the studied mural in Iwrakhy tomb.

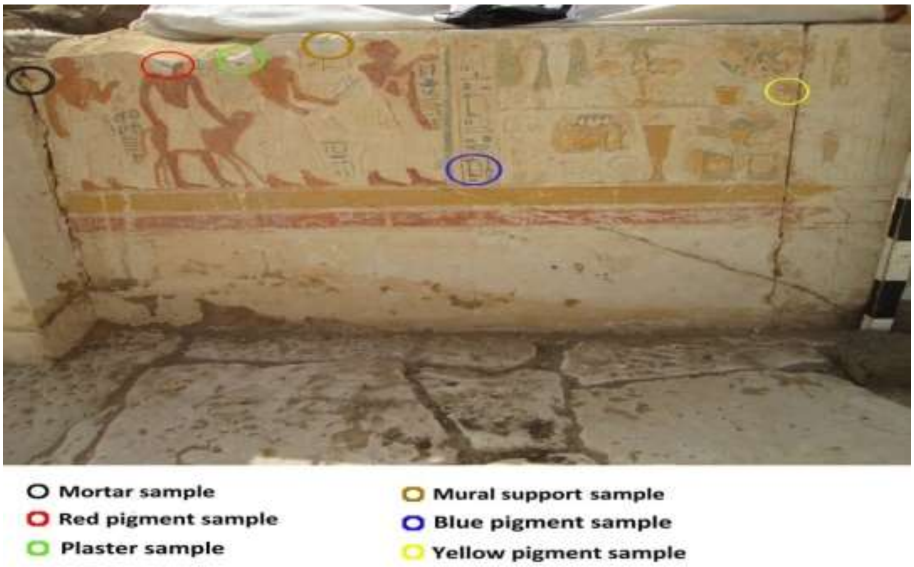

Figure 3. The locations of the analysed samples from the studied mural.

3. RESULTS AND DISCUSSION

3.1. *Investigation*

Based on the data obtained from the field investigation; and from the light optical microscope; building materials in the studied tomb are showing different degradation patterns amongst: powdering of the paint layers; detachment of the paint layer "flaking"; loss of the paint layers; chromatic alterations; natural deposits (dust, insects' broods and blood; efflorescence; black shadows on the white washing looks like fungal colonies); plistering; spalling of pigments' surfaces; black spots; discoloured area without any pictorial layer under them; gaps as a result of losing pictorial layer because of humidity, salt efflorescence; detachment of the pictorial layer (Fig. 4 A-F).

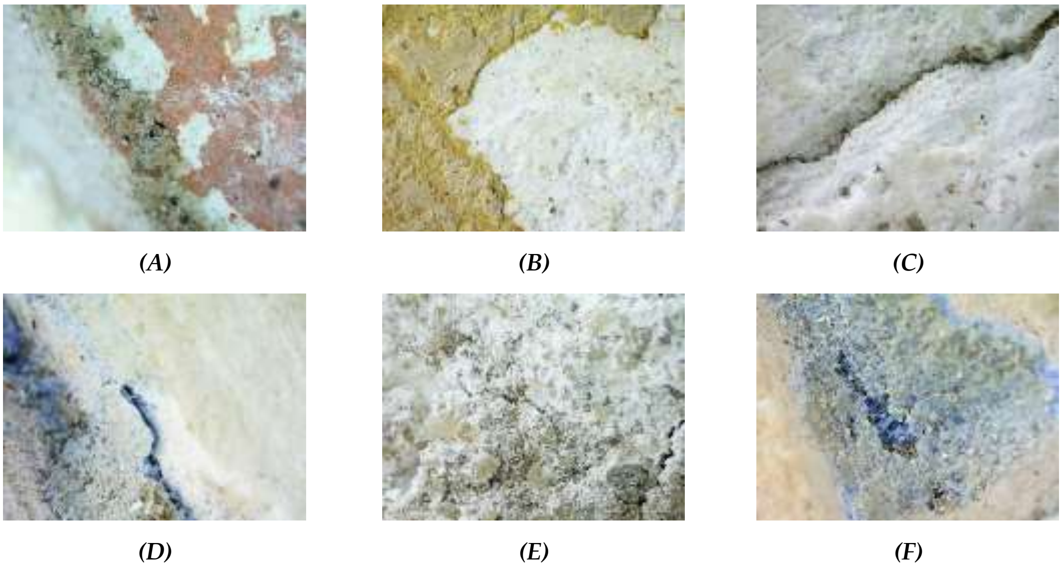

Figure 4. The deterioration symptoms observed by the digital microscope investigation: (A) Loss of the red pigment and chalking of the pictorial layer with salty deposits. (B) Loss in yellow pigment and gaps as a result of losing pictorial layer because of humidity. (C) A cracks in the pictorial and rendering layer. (D) Separation and discolouring of the blue pigment with salty deposits. (E) Clay and Sandy calcifications are indicated above the pictorial layer. (F) Loss, fading and detachment of the blue pigment.

The same samples were investigated using scanning electron microscope (SEM), the results has detected the same fragility and loss of cohesion in the studied building materials, the examination of the limestone support sample; shows the lack of cohesion between the granules, the appearance of interstitial spaces and calcification of salts (Fig. 5 (A)), the investigation of the rendering layer sample; has shown the lack of cohesion between its grains, the existence of voids and micro cracks (Fig. 5 (B)), concerning mortars; it also shows lack of cohesion and fragility in addition to the crystallization of salts among its components (Fig. 5 (C)). As for pigments, the microscopic investigation of the yellow one shows the fragility of the pigment grains due to the loss of paint medium, voids and salt crystals are also common in the sample (Fig. 5 (D)), blue and red pigments are suffering the same symptoms such as the yellow one (Fig. 5 (E, F)). Pigments are the first and quite often the major agents binding the painting with the viewers, pigments are the first to suffer at the aging of a painting. Often starting with fading, colour changes after a certain time may heavily damage the whole paint. Old painting collections in the world museums protected strictly because of painting vulnerability by many detrimental, external and internal impacts. Both two conditions had enough time to exhibit heavy changes really occurred in pigments and paints (Zilbergleyt, 2005). Salt crystallization, salt efflorescence and the dryness of paintings in addition to delamination are common symptoms in the ancient Egyptian murals, pigments can spall, become friable when the paint medium dries, and discolour, plasters crack deforming the aesthetic appearance of the mural paint.

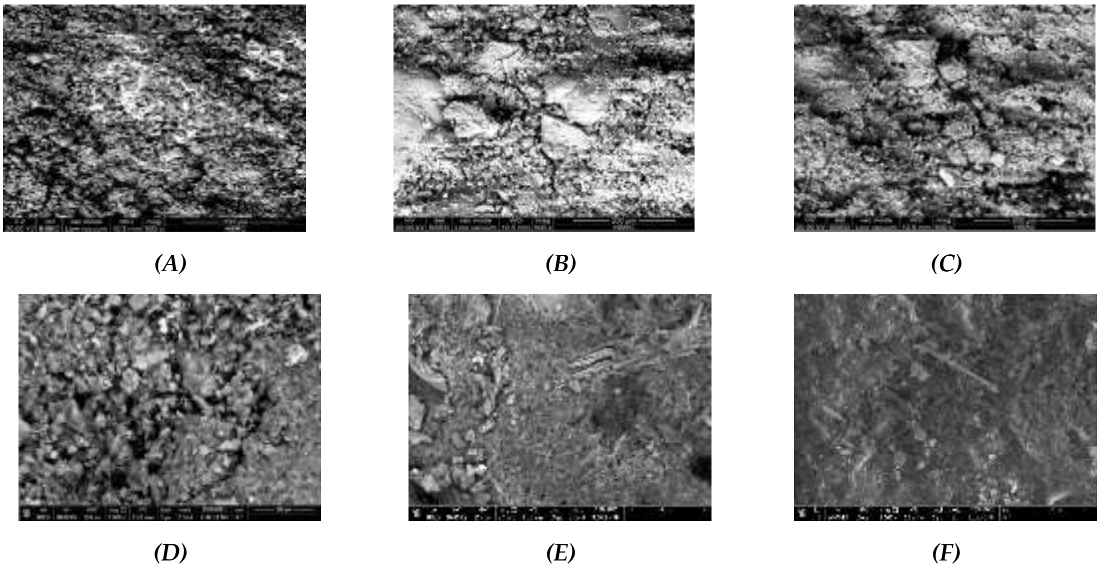

Figure 5. Scanning electron micrographs showing the deterioration symptoms observed by the scanning electron microscope investigation: (A) The limestone support sample. (B) The plaster "rendering layer" sample. (C) The Mortar sample. (D) The yellow pigment sample. (E) The blue pigment sample. (F) The red pigment sample.

3.2. *Analyses*

Weathering effects on the physical and mechanical properties of natural building materials of monuments cause stability problems. These properties cannot be easily studied using the common methods used for investigation, because these methods need a big quantity of testing material. So, the use of non-destructive techniques for determining the physical and mechanical properties of building materials is very important, as a small quantity of testing material is needed (Christaras, 2003). According to the analyses carried out by mean of XRD, the building materials used in the tomb of Iwrakhy are protraction to those used throughout the ancient Egyptian civilization, limestone quarries such as Tura, Saqqara and Giza were the main source for building stones in Egypt for millennia, these quarries have some veins "formations" of pure limestone, however Max limestone quarries; west of Alexandria -Tertiary formations: mainly Eocene but also Paleocene and Pliocene- are distinguished by the presence of dolomite and halite (Klemm et al., 2001; Harrell and Storemyr, 2009). The XRD analysis supports that the used building stone in the studied tomb; was derived from Tura quarries because it is a pure calcite one, the sample consists of 100% calcite $CaCO_3$ (Fig. 6). The same results were emphasized by mean of SEM-EDX, the sample composes of about 82% calcium (Ca), 9% Silicone (Si), 4% sulphur (S), 2% Iron (Fe) and 1% Magnesium (Mg) with some traces (2%) of aluminium (Al) and chlorine (Cl) (Fig.7).

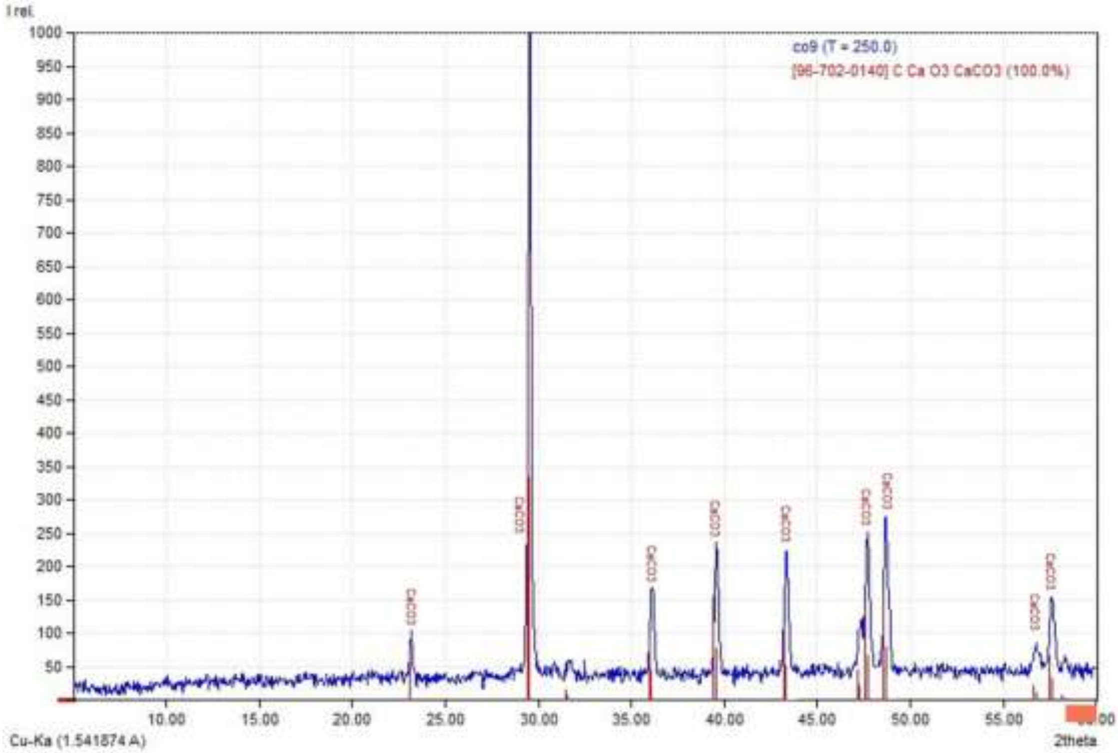

Figure 6. XRD pattern of the studied limestone sample from Iwrakhy tomb; the stone is a fine pure limestone.

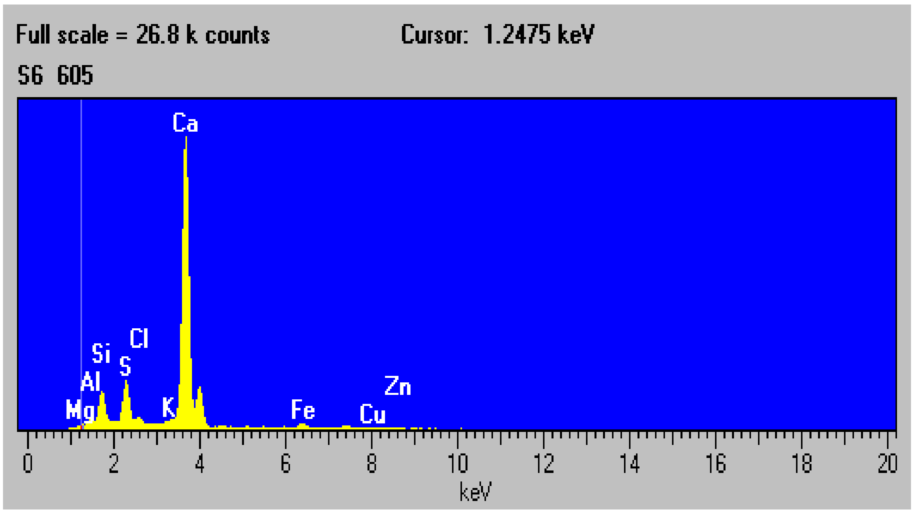

Figure 7. Scanning electron spectra of the studied limestone sample from Iwrakhy tomb.

Concerning mortars and plasters in ancient Egypt; they appear to be basically processed gypsum, they usually have a small percentage of sand and limestone powder thus; supporting the concept that gypsum was used as processed: gypsum 70%-90%, crushed limestone 8%-17%, sand 2%-8% (Snell and Snell, 2000), the aforementioned theories were supported by the results obtained from the XRD analyses, the mortar sample from the tomb of Iwrakhy consists of 71% gypsum ($CaSO_4 2H_2O$), 27% crushed limestone (calcium carbonate $CaCO_3$) and 2% quartz SiO_2, with some traces not exceeding 1% of sodium chloride salt (halite NaCl, Fig. 8).

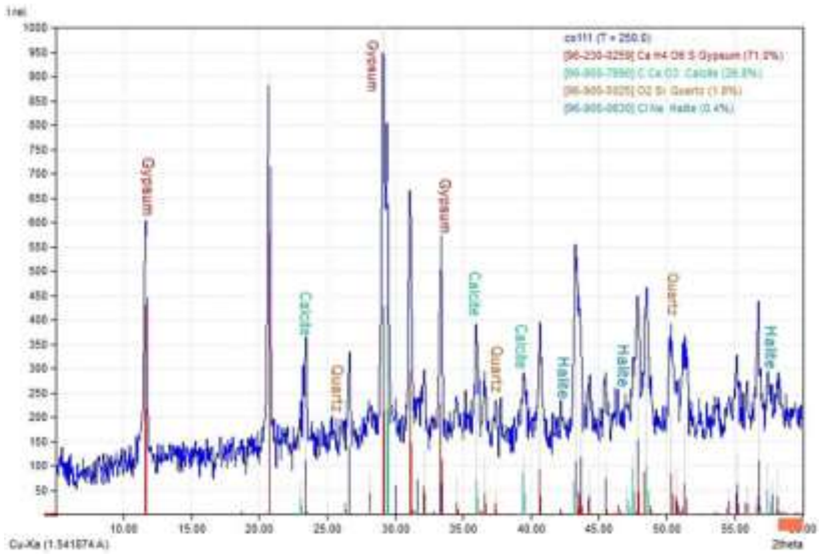

Figure 8. XRD pattern of the studied mortar, the mortar composes mainly of gypsum, crushed limestone and sand, halite is a deterioration product.

The previous results were assured by mean of SEM-EDX; the sample composes essentially of about 50% calcium (Ca), 32% sulphur (S), 8% silicone (Si), 5% iron (Fe), 2% aluminium (Al) and 2% chlorine (Cl) with some traces of zinc (Zn), magnesium (Mg) and potassium (K) (Fig.9).

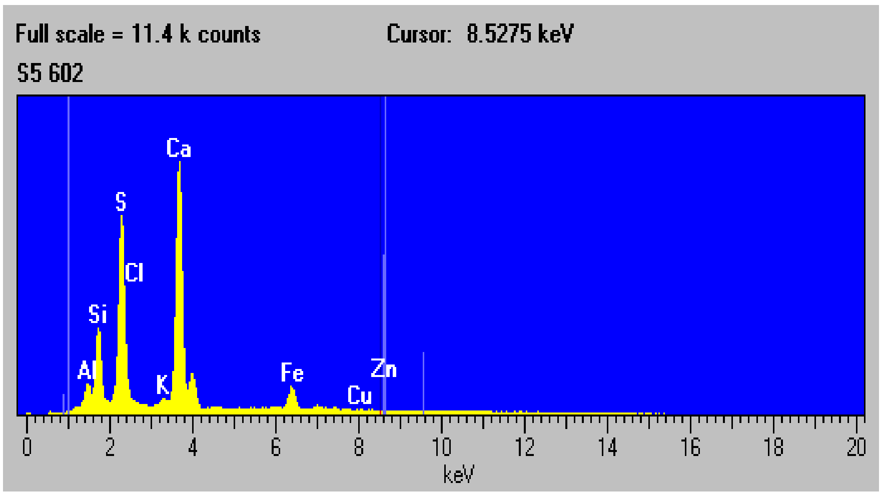

Figure 9. Scanning electron spectra of the studied mortar sample from Iwrakhy tomb.

The analysis of the plaster layer in the studied tomb, shows that it consists of 70% gypsum ($CaSO_4 2H_2O$), 26% calcite $CaCO_3$, 2% quartz SiO_2 and 2% halite NaCl (Fig. 10), the previous results were assured by mean of SEM-EDX; the sample composes essentially of about 44% oxygen (O), 26% calcium (Ca), 14% sulphur (S), 6% silicon (Si), 6% iron (Fe), 2% aluminium (Al), 2% chlorine (Cl) with some traces of zinc (Zn), cupper (Cu) and potassium (K) (Fig.11).

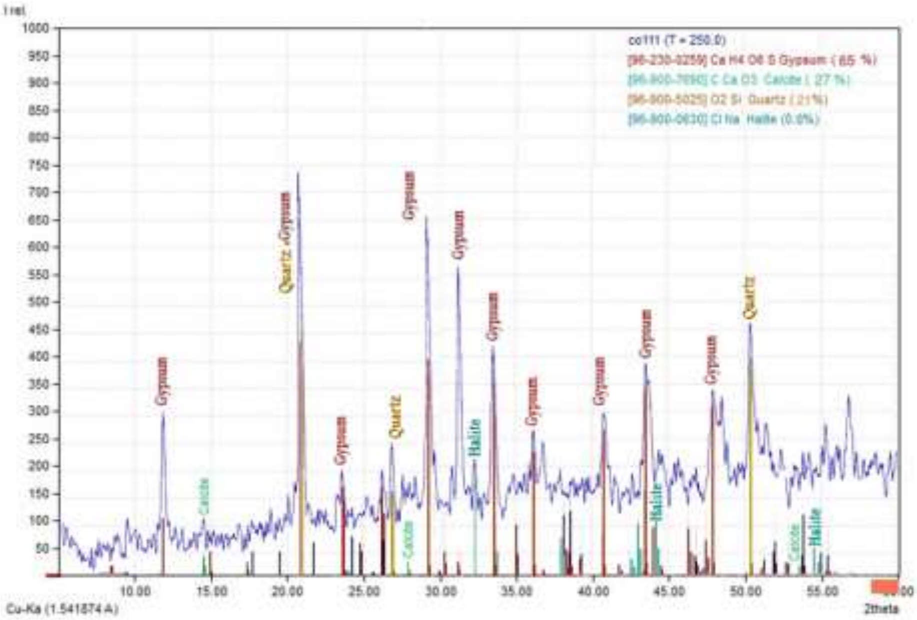

Figure 10 XRD pattern of the studied plaster sample; the plaster composes mainly of gypsum as a binder, crushed limestone and sand are fillers, halite is a deterioration product.

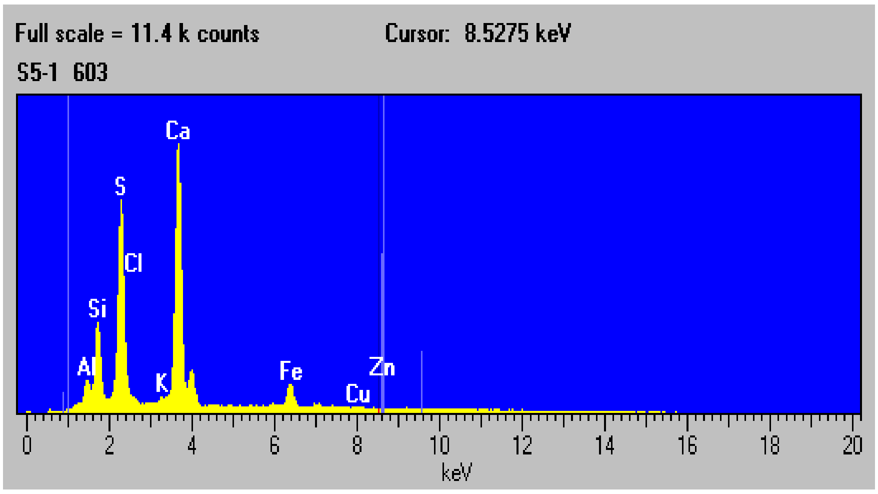

Figure 11. Scanning electron spectra of the studied plaster sample from Iwrakhy tomb.

Salt is considered one of the most serious problems facing the murals inside the ancient Egyptian tombs, due to the multiplicity of its sources and the rapid growth of its crystals, as well as the distinctive porous composition of most building materials and the dry environmental conditions, which are a suitable medium for this weathering (Kloppmann et al., 2011), renders and mortars of old buildings are particularly susceptible to salt weathering, this process eventually ends up with the powdering and erosion of the superficial layers and/or flaking and cracking of in-depth layers with detachment of large parts of the rendering (Nogueira et al., 2020), movement of the saline solutions depends on many factors, the essential aspect is the chemical composition of the salts, which determines their solubility, migration and conditions of crystallization in case of decreased humidity/moisture, the process is affected by the composition of the subsoil structure, level and nature of the subsoil's pore system (Perinkova et al., 2021), the size of the pores influences the progression of rising damp, what will happen in this situation is that the water during its capillary ascension will carry dissolved salts to higher levels. When the surface of the wall is reached, the water evaporates, the salts crystallize with increase of volume, are deposited there, progressively decreasing the size of the pores. This decrease in pore size will hinder the evaporation of water and a higher capillary rise will occur (Torres, 2018), in most cases salt weathering is related to repeated cycles of dissolution-crystallization of salts in the porous system of materials. However, some salts present several stable phases, in these cases; changes in the relative humidity of the surrounding environment can cause the transformation and recrystallization of an unstable phase into a new stable phase. Consequently, when a stone weathering is related to the presence of hydratable salts, damages can be caused by either crystallization or hydration pressures, increasing the sensitivity of the stone weathering to the extrinsic characteristics of the salt-rock system (Martinez et al., 2021), concerning rock-cut tombs; the highest risk is represented by cycles of salt crystallization/dissolution and hydration/dehydration produced by wetting/drying, the resulting stresses may be caused by the changing state of one phase or transitions between two salts with different degree of hydration. In winter, salt weathering can combine with the freeze-thaw damage associated with sub-zero temperatures. These cycles generally happen on the rock surface or within the near-surface layers, producing: scaling, peeling, disintegration; micro-cracking and splintering (Germinario and Oguchi, 2021).

The pigments used by the ancient Egyptians constitute the most diverse pigment palette of the ancient world, the identification of ancient Egyptian pigments is often aggravated by chemical interactions between pigment and binder media, or between the pigment and environmental pollutants, or both (Scott, 2016), the results obtained from the XRD analyses, proves that the red pigmented sample from the tomb of Iwrakhy consists of 79% hematite (Fe_2O_3), 16% gypsum ($CaSO_4.2H_2O$) and 5% goethite (FeO_2) (Fig.12).

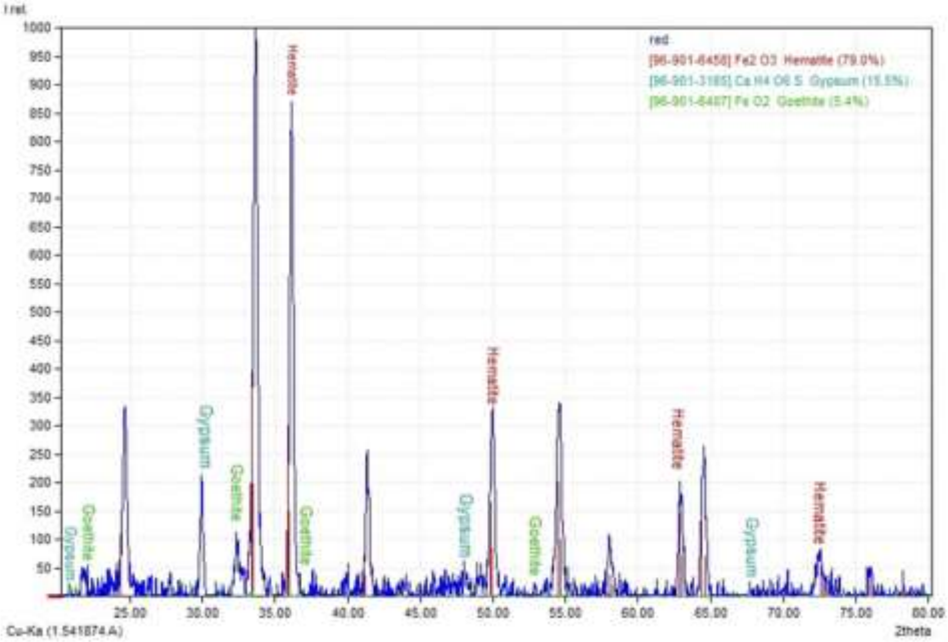

Figure 12. XRD pattern of the studied red pigment sample; the pigment is hematite, gypsum is from the rendering layer, goethite is the underlying pigment for high coverage.

The previous results were also detected by mean of SEM-EDX (Fig. 13), the samples consists of about 41% carbon (C), 33% oxygen (O), 18% lead (Pb), 6% iron (Fe) and 2% silicon (Si). Geologically, hematite ores may be mixed with lead ores (Marketou et al., 2019). Although there is no lead compounds detected by mean of XRD analysis, nevertheless the high amount of lead (Pb) detected in the sample due to the SEM-EDX analysis, doesn't preclude the use of lead compounds mixed with hematite as a source of red pigment especially in the New Kingdom era, further studies are needed regarding this proposition. The principal red pigments in Egypt are of two main types, red iron oxide (hematite) and red ochre (hydrated iron oxide, perhaps partially dehydrated goethite). Natural iron oxides occur plentifully in Egypt and then anhydrous and hydrated oxides could be used as red pigments without any heat treatment (Calza et al., 2007, Miriello et al., 2021), historical documents reveal that artists have long known that yellowish brown ochre can be converted to a bright red by heating, early studies demonstrated that brownish goethite, FeO(OH), is dehydrated to red hematite (Fe_2O_3), by heating above 300 °C (Lin et al., 2021), the use of fire technology for transforming yellow goethite into red hematite was common, intentional and consolidated practice in Prehistoric settlements. The intentional fire use technology for transforming goethite-rich minerals (yellow ochre) into hematite (red ochre) was an important human achievement, a sort of engineering tool (Cavallo et al., 2021). Photochemical degradation, heat and moisture contributed as oxidizing factors in the discolouring phenomenon of the brown pigment in some ancient Egyptian murals. The presence of calcium iron sulphate hydroxide hydrate [$Ca_6Fe_2(SO_4)_3(OH)_2.26H_2O$], is a result of the reaction between gypsum (the rendering layer) and red hematite due to the climatic conditions (Moussa et al., 2009). Recent studies investigated the role of water and hematite on the stability of tempera paint layers; it was pointed out that the destabilization and structure modification of tempera murals, in the presence of hematite, is ascribed mostly to a water redistribution in the pigmented paint layer. This effect is more evident at low humidity ranges and at high pigment percentages (Mahmoud 2011; Saitta et al., 2020).

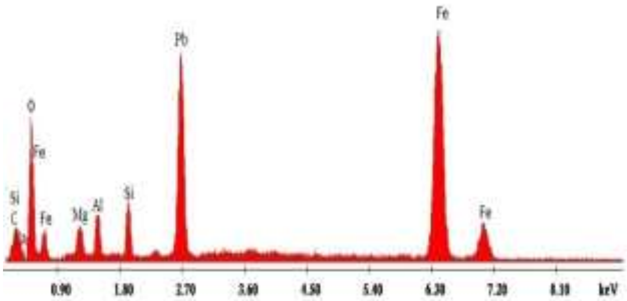

Figure 13. Scanning electron spectra of the studied red pigment sample from Iwrakhy tomb.

Ochres are among the earliest materials used in painting, since prehistoric times. The mural paintings at the Altamira (Cantabria, Spain) and Lascaux (Dordogne, France) sites are considered the most ancient evidence (see, also: Katsaros et al., 2009; Castagnotto et al., 2021). Regarding the yellow pigment, this colour is most commonly found to consist of yellow ochre, comprising of iron bearing material, notably goethite [the alpha form of [FeO(OH)] and limonite (the yellow to brown hydrous oxide) together with varying amounts of clay and siliceous matter (Lucas, 1962; Lee and Quirke, 2001). These pigments were widely spread all-over Egypt, extending from the north into the Nubian ancient sites, all yellows from all locations at Sai Island in Nubia were identified as yellow ochre (Fulcher and Budka, 2020). As for the studied yellow pigment sample from the tomb of Iwrakhy, the XRD method (Fig. 14) proved that the samples composes of about 90% wollastonite ($CaSiO_3$) and 10% goethite [FeO(OH)]. Recently, a wide attention is paid to wollastonite; this pigment is remarkable for several properties. Firstly, in contrast with traditional pigment powders it has a wide band gap; therefore, wollastonite almost does not absorb any solar electromagnetic radiation. It is possible to obtain wollastonite-based coatings with low absorption of solar radiation (Mikhailov et al., 2021), regardless of the ancient knowledge about the previous properties. We suggest that this pigment was added to goethite to gain a bright, shiny, and gold-like pigment.

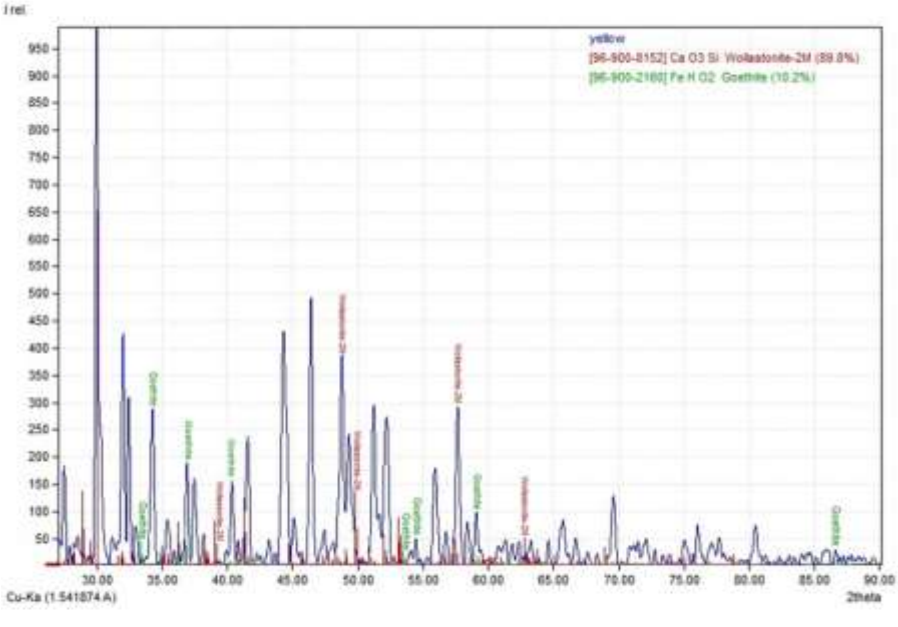

Figure 14. XRD pattern of the studied yellow pigment sample; the pigment is mainly goethite.

New findings were detected by mean of SEM-EDX (Fig. 15). The yellow pigment sample composes of about 40% oxygen (O), 22% iron (Fe), 19% sulphur (S), 11% arsenic (As), 5% carbon (C) and 3% traces of aluminium (Al) and magnesium (Mg). Arsenic and sulphur are indicators for the orpiment yellow pigment (As_2S_3). Orpiment is typically unstable in the environment, especially under alkaline and oxidizing conditions, which is a significant barrier to fixation of arsenic present in metallurgical waste streams in the form of arsenic trisulphide (Mirazimi et al., 2021). Because of its deep yellow colour, orpiment has been used for centuries as a yellow pigment, natural orpiment (As_2S_3) or realgar (α-As_4S_4) have been used in polychrome artworks for centuries, especially in Egypt and Asia. Furthermore, arsenic sulphide pigments have also been identified in European paintings (Vermeulen et al., 2018). The use of orpiment as a pigment ended almost entirely with the advent of the cadmium yellows, orpiment is also known as "King's Yellow", "Chinese Yellow" and "Yellow Orpiment", in the Egyptian murals; orpiment has been mixed with goethite for a bright yellow colour (Noll, 1978).

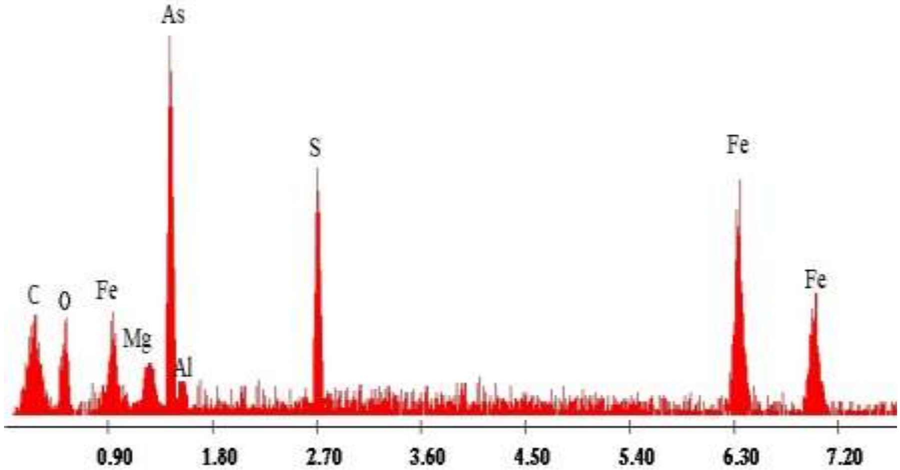

Figure 15. Scanning electron spectra of the studied yellow pigment sample from Iwrakhy tomb.

Egyptian blue (EB) was the dominant blue pigment in ancient Egypt, that vitreous blue compound was the earliest known synthetically produced pigment. Ancient texts by Pliny mention the existence of various kinds of caeruleum which may be EB. Egyptian blue is also recorded by the ancient author and architect Vitruvius (Rodler et al., 2017), this blue pigment was identified later on in many ancient artefacts allover the world. EB found outside Egypt was not imported from Egypt as a final product, only the raw materials were imported and then melted or manufactured locally (Moussa, 2012). EB was commonly believed to have disappeared from Western Europe following the upheaval of the disastrous fall of the Roman Empire, despite in several subsequent studies this hypothesis proved to be partially erroneous (Nicola et al., 2018). Recent studies have detected EB in the paint layer of the “Birch Spring” painting by Robert Falk (1907 AD); they have also found the pigment in the paints of the sketch drawn on the canvas back side; this is probably the first discovery of EB in a 20th century work of art (Pisareva et al., 2021). Concerning the studied blue pigment sample from the tomb of Iwrakhy, the XRD method proved that the samples composes of about 78% wollastonite ($CaSiO_3$), 12% atacamite [$Cu_2Cl(OH)_3$], 5% cuprorivaite ($CaCuSi_4O_{10}$) and 5% halite (NaCl) (Fig.16).

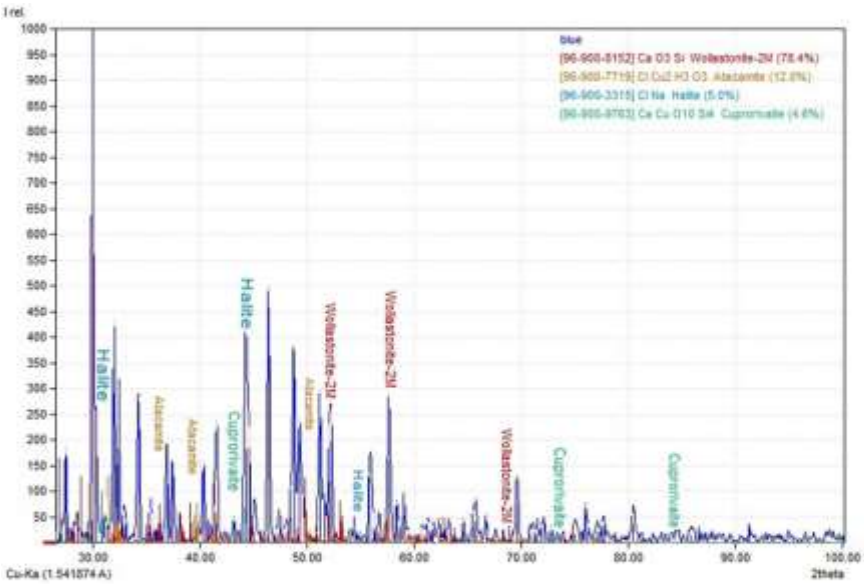

Figure 16. XRD pattern of the studied blue pigment; the pigment is mainly Egyptian blue; other compounds are colour alteration products.

The high amounts of wollastonite and atacamite in the sample are indicators for the colour change of EB, which depends on the presence of the water-soluble salts in conjunction with the pigment and its ability to discolour according to bronze disease (Moussa and Ali, 2013). Halite is already detected in the sample. Chromatic alteration of the EB was the subject of many previous studies, most of these studies ascribe this phenomenon to the effect of halite salt. Recent studies introduced a new reason for chromatic alteration of the EB, this is concerned with the growth of fungal and bacterial species which use these copper based pigments as a nutrient and as a main source for carbon and energy (Moussa et al., 2021). Even during fabrication of the EB, the presence of sodium chloride inhibits the formation of cuprorivaite in such a way as changing the colour of the pigment obtained, which implies that there was a cleaning step before the fabrication of the pigment (Giménez et al., 2017). Depending on the SEM-EDX analysis (Fig. 17), the blue pigment sample consists of about 30% carbon (C), 25% oxygen (O), 20% cupper (Cu), 15% calcium (Ca) and 10% silicon (Si), although there is no chlorine (Cl) or sodium (Na) detected by mean of SEM-EDX, but the microscopic investigation of the sample shows the chromatic alteration of the sample in addition to the spongy appearance of the pigment material (Fig. 18).

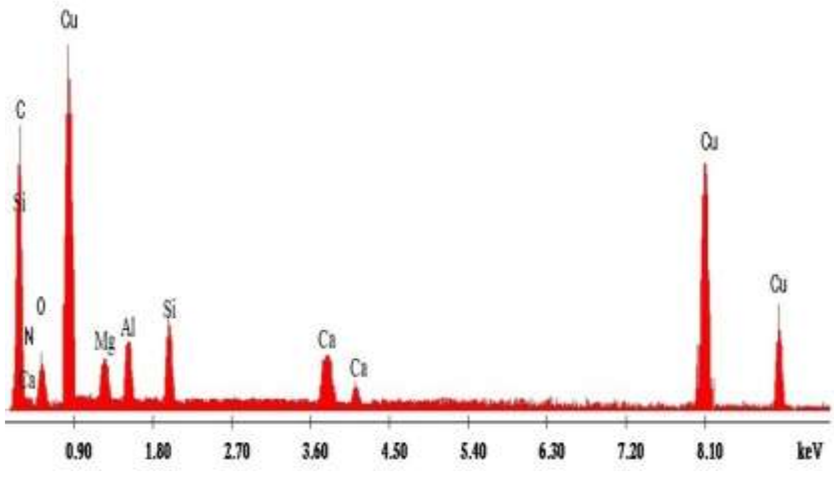

Figure 17. Scanning electron spectra of the studied blue pigment sample from Iwrakhy tomb.

Figure 18. The chromatic alteration observed in the blue pigment sample by the digital microscope investigation, 60x.

The identification of binding media in paintings is one of the most difficult questions an art conservator or restorer may address to an analytical chemist. The basic problem lies in the small amount of sample available and its low purity. In addition, the sample is often not homogeneous; as it is a complicated mixture of materials which underwent changes during aging or because of conservation treatments (Casoli et al., 1995; Moussa 2007). The FTIR analysis carried out on a blue pigment sample proved that the used paint medium in the tomb of Iwrakhy is animal glue. Animal glue is considered to be the most commonly used binder from a very early period, glue was prepared by boiling animal bones, hides and connective tissues. The main sources of glue in ancient Egypt are not known but could have included various animals and fish (Granzotto and Arslanoglu, 2017). The sample has shown the (O-H) stretching bands of gypsum at 3549.34 cm^{-1} and 3405.67 cm^{-1}, while the (S-O) stretching band of gypsum was detected at 1623.787 cm^{-1}. Moreover, the (C=O) stretching band of animal glue was detected at 1138.76 cm^{-1} (Fig.19).

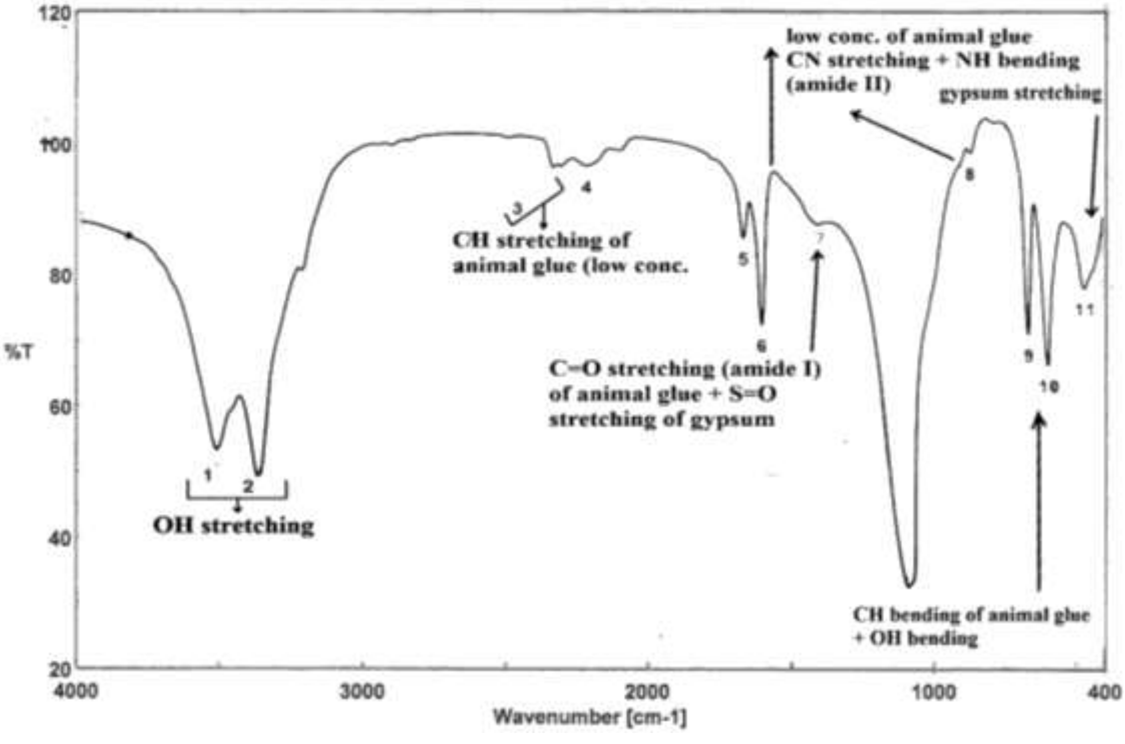

Figure 19. FTIR spectrum of the blue pigment sample from Iwrakhy tomb. The atomic bonds are shown related to stretching and bending (X-axis = Wavenumber cm-1, Y-axis = Transmittance %)

The former results were emphasized by mean of Raman spectroscopy (Fig. 20), the studied blue pigment sample consists of quartz (amorphous) and Egyptian blue, the quartz Raman shift peaks were recognized at 207.66 cm^{-1}, 262.49 cm^{-1}, 354.07 cm^{-1}, 393.08 cm^{-1}, 464.31 cm^{-1}, 512 cm^{-1}, 600.52 cm^{-1}, 808.02 cm^{-1} and 865.13 cm^{-1}. The Egyptian blue shift peaks were recognized at 403.26 cm^{-1} and 526.21 cm^{-1}. Finally, the Raman shift peaks of the animal glue paint medium were recognized at 622.60 cm^{-1}, 1005 cm^{-1} and 1126.11 cm^{-1}.

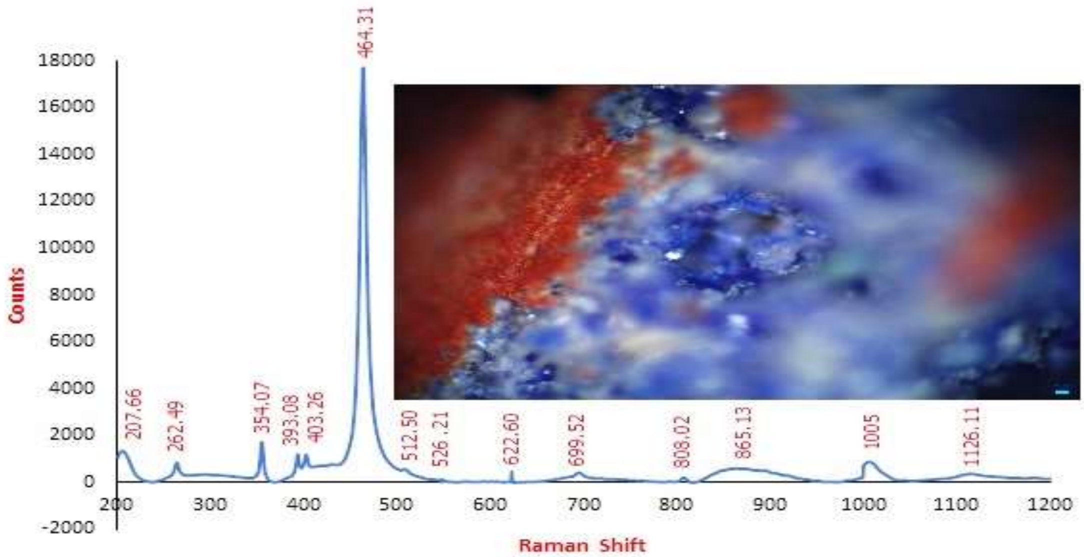

Figure 20. Illustrated Raman spectra of the blue pigment sample with a confocal image for the tested area.

4. CONCLUSION

Based on the investigations and analyses carried out upon the studied tomb, new evidence for the use of lead ores abreast with hematite as a source of red pigments is produced and emphasis is given to the mixing process of goethite with orpiment to get a gold-like colour. The analytical physicochemical survey indicated that the main component of the foundation stone (support) is calcite, which is further verification for the advanced knowledge about geology in ancient Egypt. Mortars and rendering layers are composed of gypsum, the latter is the ideal arriccio for the tempera murals and for the dry Egyptian climate; crushed limestone and quartz were added to gypsum as fillers. Red pigment is hematite with high amount of lead which may be naturally found in the hematite ores or may be used as a lead compound pigment, though further investigation is needed concerning this point of view. Yellow pigment is goethite mixed with orpiment, the ancient Egyptian tried to get the effect of gilding by mixing these two pigments together, this technique is commonly used in painting plastered coffins, in the studied tomb. This may be one of the first trials on the walls. Regarding the blue pigment it is the known Egyptian blue containing high amounts of wollastonite and atacamite; blue is turned into greenish due to the presence of halite. Last, animal glue was detected as a paint medium by mean of FTIR and Raman spectroscopy.

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