

End of Bachelor Degree Project

## Bachelor Degree in Chemical Engineering

# Experimental Study of the Egyptian blue degradation by the copper chloride cancer

Memory

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## Abstract

Egyptian blue, which was the first synthetic pigment to be used in antiquity, consists of crystals of calcium-copper tetrasilicate. Based on previous investigations and literature synthesis recipes, different experiments to obtain this pigment have been made using the analytical techniques Raman and XRD. The main aim of this work was the study the pigment degradation by the copper chloride cancer and to investigate the application of Raman to the identification of ancient pigments.

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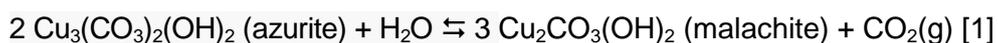
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## Introduction

The ancient Egyptians sought eternal durability in decorating their tombs, temples, and diverse sacred objects. This is probably a plausible explanation for their restlessness in manufacturing new pigments, introducing technical innovations, and their eagerness to improve the quality of their decorative products. Already in the Predynastic Period (before the 3000 BC) and the early Old Kingdom (3000-2800 BC), they used pigments made of minerals or solids easily found in the landscape for their paintings in tombs and temples. For the black color they collected the soot from the kitchen pots or saucepans, although in some cases they used grinded galena as well. Red and yellow colors were obtained by crushing ochres, mixtures of different minerals that contain an iron oxide or oxyhydroxide which is the responsible of the color. Red ochre contains the red mineral hematite ( $\text{Fe}_2\text{O}_3$ ), while yellow ochre contains goethite or limonite ( $\text{FeO}\cdot\text{OH}$ ). Other red pigments used from the New Kingdom (from 15<sup>th</sup> century BC) were realgar (AsS polymorph), minium ( $\text{Pb}_3\text{O}_4$ ) and cinnabar ( $\text{HgS}$ ). White color was obtained from gypsum ( $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ ) and calcite ( $\text{CaCO}_3$ ), although from the Middle Kingdom (from 20<sup>th</sup> century BC) the brightest whites were obtained by using the mineral huntite ( $\text{CaMg}_3(\text{CO}_3)_4$ )<sup>1</sup>.

However, Ancient Egyptians, as other ancient civilizations, could not find in the landscape an appropriate mineral in the necessary quantity for the blue color. One of the available minerals was azurite (a basic copper carbonate), which was demonstrated to be used from the Neolithic in Çatal Höyük and Azmak (Turkey) and perhaps also in Crete. However, was not widely used in the antiquity probably because azurite is not stable in ambient conditions and spontaneously transforms to the green mineral malachite (a basic copper carbonate  $\text{CuCO}_3\text{Cu}(\text{OH})_2$ ) according to reaction 1.



Another mineral that could potentially be used as a pigment was lapis lazuli, which came from the Sar-i-Sang mines in Badakhshan (present Afghanistan). In the Neolithic, grinded lapis lazuli was used as a pigment in Afghanistan, Pakistan and Turkmenistan, near the specialized workshops for the mineral. Although lapis lazuli was a much appreciated good and arrived to Egypt as early as in Nagada II (ca. 3300 BC) it was never used in Egypt as a pigment, perhaps because of the difficulty to obtain a blue powder of lapis lazuli by grinding, since the powder is only blue at a relatively small particle size.

The solution of the Ancient Egyptians to the problem of disposing of a mineral that could be used as a blue pigment was the synthesis of a new mineral called cuprorivaite ( $\text{CaCuSi}_4\text{O}_{10}$ ), the well-known "Egyptian Blue", which was adopted by almost all the civilizations of the Mediterranean and the Near East.

The Egyptian blue was used as the blue pigment in Egypt since the 3rd dynasty (ca. 2600 BC) in the south tomb of King Djoser and it was later widely used in ancient Egyptian paintings.<sup>2</sup> The manufacture of this pigment achieved high quality already in the Old Kingdom. The copper ingredient (malachite, azurite or bronze) was added to different mixtures of lime, and silica. The mixtures were then heated with salt flux or potash and brought to fusion. The product is a multiphase mixture of cuprorivaite ( $\text{CaCuSi}_4\text{O}_{10}$ ), silica phases (quartz, tridymite, cristobalite), a cuproan alkali- and chlorine- bearing silicate glass, a copper oxide phase, and some unreacted bronze residues (depending on the time of manufacture arsenic, tin, and lead compounds)<sup>1</sup>.

Although this pigment is still preserved on ancient Egyptian monuments and works of art, neither a representation nor a description of the manufacturing process has been found in Egypt, yet.<sup>3</sup> A small pot containing the pigment was found during the excavations at Pompeii (Figure 1), in 1814 it was examined by Sir Humphrey Davy and analysed by Fouqué, who identified the compound as the calcium-copper tetrasilicate  $\text{CaCuSi}_4\text{O}_{10}$ . Subsequently, using X-ray diffraction analysis (XRD), Pabst and Mazzi and Pabst confirmed the identification of Egyptian blue as cuprorivaite, and established that Egyptian blue and the rare natural mineral cuprorivaite were the same material<sup>4</sup>.

After the discovery of pure blue pigments in Pompeii, Numerous scientific studies concerning the blue pigment began at the turn of the 19th century and are still being performed today.<sup>3</sup>



*Figure 1 Pot of calcium copper silicate 'Egyptian Blue' pigment from Pompeii.*

The first qualitative analyses of the pigment were undertaken by Chaptal (1809) and Davy (1815)<sup>5</sup>. The first systematic laboratory replications of the Egyptian blue pigment were undertaken by Laurie et al. (1914) These and subsequent laboratory replications by Chase (1987), Ullrich (1997), and Tite et al.(1984) established that Egyptian blue pigment



can be readily produced by firing a mixture of quartz, copper oxide, and lime together with a small amount of alkali (typically 0.2–5 wt% Na<sub>2</sub>O) at a temperature in the range of 900°C–1000°C<sup>4</sup>. The best approach to antique fabrication was given by Laurie, McLintock and Miles (1914) and the crystal structure was determined in 1959 by A. Pabst.<sup>6</sup>

In general, Egyptian Blue is a very stable pigment being resistant to most acids and to the alkaline environment of lime mortars; it is also resistant to fading in strong light and there are examples to be seen in Egypt which have been exposed for thousands of years without loss of color<sup>7</sup>. However, basic copper chloride compounds were first detected in ancient Egyptian paintings from the Middle Kingdom. Subsequently, Riederer reported atacamite (CuCl<sub>2</sub>·3Cu(OH)<sub>2</sub>) formation in stone reliefs from tombs of the 11th Dynasty in Deir el Bahari (1972)<sup>1</sup>, this mineral seems to be a degradation of a blue pigment instead of an actual pigment.

In the last 10 years different experiments for the reconstruction of ancient manufacture have been made. Many details were cleared up, but some aspects are still open for investigation like the degradation of the pigment and its transformation to a green color or sometimes to a black one.

In order to investigate, characterize and identify the Egyptian blue in a non-invasive way, The Raman microscopy analytical technique will be used.

## Project Objectives

The objectives of the present work are as follows:

- The synthesis of the Egyptian blue compatible with the ancient Egyptian technology, employing chemicals or natural Egyptian compounds as raw materials in different experimental conditions.
- The application of FT-Raman spectroscopy and visible Raman microscopy to the non-destructive analysis of the pigment.
- Research about the Copper Chloride Cancer phenomenon in the ancient Egyptian wall paintings.
- A comparison of the Raman spectra of color samples from an Egyptian old piece.
- A study of the Raman spectra of azurite, Lapis lazuli, malachite, and tenorite (a Copper oxide CuO).



## Experimental study

The synthesis of the Egyptian blue needs a copper source that could be different copper minerals such as malachite and tenorite. For this reason, also a previous study of these minerals was carried out, including their Raman spectra and their likely degradation products.

Because the degradation experiments of Egyptian Blue in this work are based on the effect of high-chloride dissolutions at acidic pH, malachite and tenorite will be also put in contact with these solutions in order to detect their possible degradation products. In this sense,  $5 \text{ mol}\cdot\text{dm}^{-3}$  NaCl solutions were prepared at pH=3.

## Raman microscopy

### Introduction

The study of art objects by Raman microscopy is a recent area of research since the first reports were published in 1984. They concerned the identification of pigments. The increasing number of papers during the last five years reflects the extension of this analytical technique. Since Raman microscopy is an optical spectrometry, it has two main characteristics which suit very well to such studies. First, the analysis is non-destructive. It can be performed without sample preparation. Neither special coating nor a controlled atmosphere is necessary. The analysis causes neither damage nor alteration, so it is possible to continue the investigation of the same sample, even on the same spot, with another laser wavelength or with another technique.

The second advantage is the capability to focus the excitation beam on a very small spot, whose diameter depends on the selected laser wavelength and the aperture of objective, typically  $\sim 1 \mu\text{m}$ . Besides, with the same optical microscope and the same focus point, it is possible to lighten the pictorial layer both with a white light, for observation and choice of grains seen with their true colors, and with a laser beam, for analysis of these grains.

The Raman analysis gives molecular information and leads to an unambiguous identification. The main problem is the high level of background fluorescence in many experiments on artefacts. It occurs often in impurities or organic materials of the sample. This problem is difficult to solve.

The identification of compounds by Raman spectroscopy relies on the comparison between their Raman spectra and a database of reference spectra. Each compound is characterized by spectral fingerprint. The wavenumbers of the bands are constant whatever the experimental procedure, but their relative intensities in the spectrum may be affected by several factors.

The Resonance Raman Effect leads to an enhancement of some bands, Another phenomenon, which can affect the relative intensities in a Raman spectrum, is the orientation of a crystalline compound with respect to the direction of the electric field of the excitation laser.<sup>8</sup>

### **Experimental procedure**

The procedure to analyze components is to obtain Raman spectra directly from the artifacts without sample preparation. Therefore the object has to be brought to the laboratory, put on the stage of the microscope and then analyzed.

It is better to use an objective with a long focal length. The visual examination and Raman analysis of the object may be done for numerous points in order to control its homogeneity.<sup>8</sup>

### **Raman spectra**

Fourier-transform Raman spectra were obtained using a B&W TEK infrared spectrometer with an FRA 106 Raman module attachment and dedicated Raman microscope. Excitation was effected using 785 nm radiation from a Nd:YAG laser operating with a maximum power of 495mW, although laser powers at the sample of about  $100\pm 200$ mW were typical of those used here.

Laser powers were kept as low as possible to avoid laser-induced sample degradation.

Raman measurements were performed by properly setting the acquisition time (typically, between 5 and 30 s) and the number of spectra to be averaged (from 5 to 20) in order to obtain a signal-to-noise ratio as high as possible. Raman spectra were mainly collected within the  $0\text{--}1400\text{ cm}^{-1}$  wavenumber range with a spectral resolution of about  $3\text{ cm}^{-1}$ .

A large number of Raman measurements were performed on each sample by focusing the laser on different points. Generally, reliable Raman spectra were collected by



focusing the laser on particles of well-defined color and shape. In several measurements no clear Raman signals were detected.

## Malachite

### Raman spectra of the malachite

Malachite is perhaps the oldest known bright green pigment. It is the natural basic copper carbonate and is similar in composition to the blue basic copper carbonate, azurite. It was known in Ancient Egypt because different malachite mines worked in antiquity have been found in Egypt, especially at the Sinai Peninsula. Malachite was used in ancient Egypt for eye-paint as early as predynastic times and was found on Fourth Dynasty tomb paintings. Curiously, malachite was not used in paintings extensively as azurite in Europe<sup>8</sup>.

To compare the composition of the malachite and the Egyptian Blue obtained later, a Raman analysis resulted in the spectra shown below (Figure 2). The bands of the malachite spectra are attributed to CuO vibrations up to  $600\text{ cm}^{-1}$ ,  $\text{CO}_3$  vibrations up to  $1500\text{ cm}^{-1}$  and OH stretching at  $3500\text{ cm}^{-1}$ . Two peaks are observed at  $291$  and  $1621\text{ cm}^{-1}$ .

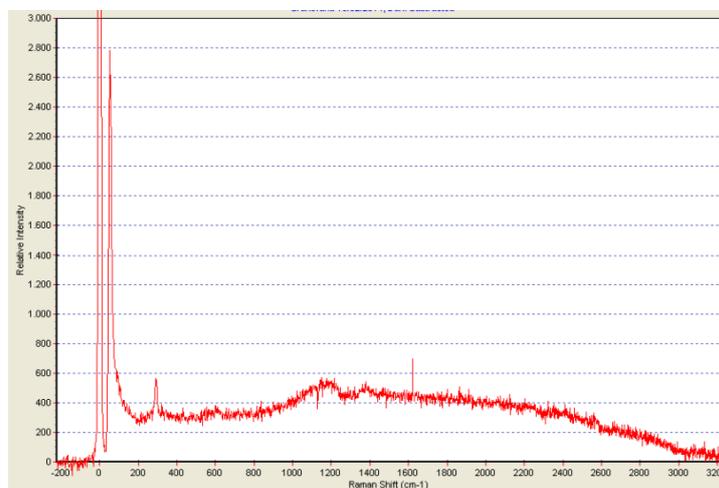


Figure 2 Raman spectra of Malachite

Unfortunately, malachite suffers burnings due to the laser application during the analysis that could be a result of a possible degradation (Figure 3). This alteration could be the reason why the Raman spectra does not show all the characteristic peaks of malachite<sup>9</sup> and gives the  $291\text{ cm}^{-1}$  band attributed to CuO. The explanation would be that a laser-induced degradation of malachite to tenorite had happened according to this reaction

[2].

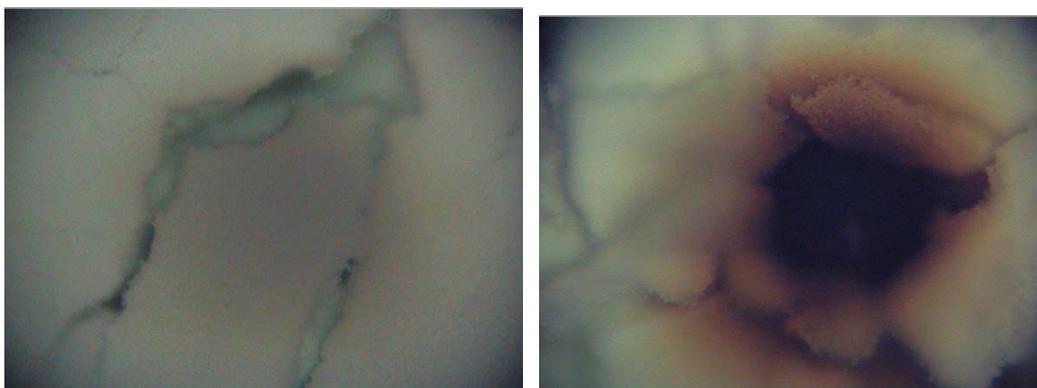


Figure 3 Left: before applying laser on malachite. Right: the effect of laser on malachite.

#### Influence of the 5 mol·dm<sup>-3</sup> solution on malachite

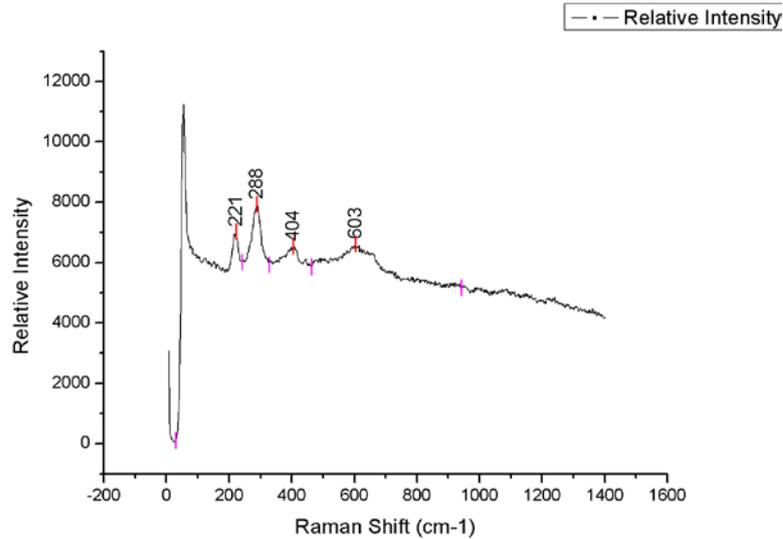
Malachite is dissolved in hydrochloric acid and crystals of a new component are observed (Figure 4). The following reaction describes the dissolution of malachite [3]<sup>10</sup>:



Figure 4 **Left**: the original aspect of malachite. **Right**: after being in acid solution for 1 week.

The Raman spectrum of the malachite after being in contact with the brine solution at acidic pH can be seen in figure 5.





*Figure 5 Raman spectra of the malachite after acid attack*

In comparing the two spectra, a new peak at  $221\text{ cm}^{-1}$  is observed. This band may be assigned to the longitudinal Cu-Cl optic vibration.<sup>10</sup>

## Tenorite

The Raman spectra of tenorite before and after acid attack are similar (Figures 6 and 7) with the same strong peak at  $297\text{ cm}^{-1}$ . This big similarity could be due to the low reactivity of the copper oxide that is already noticed by the absence of any change in its original aspect.

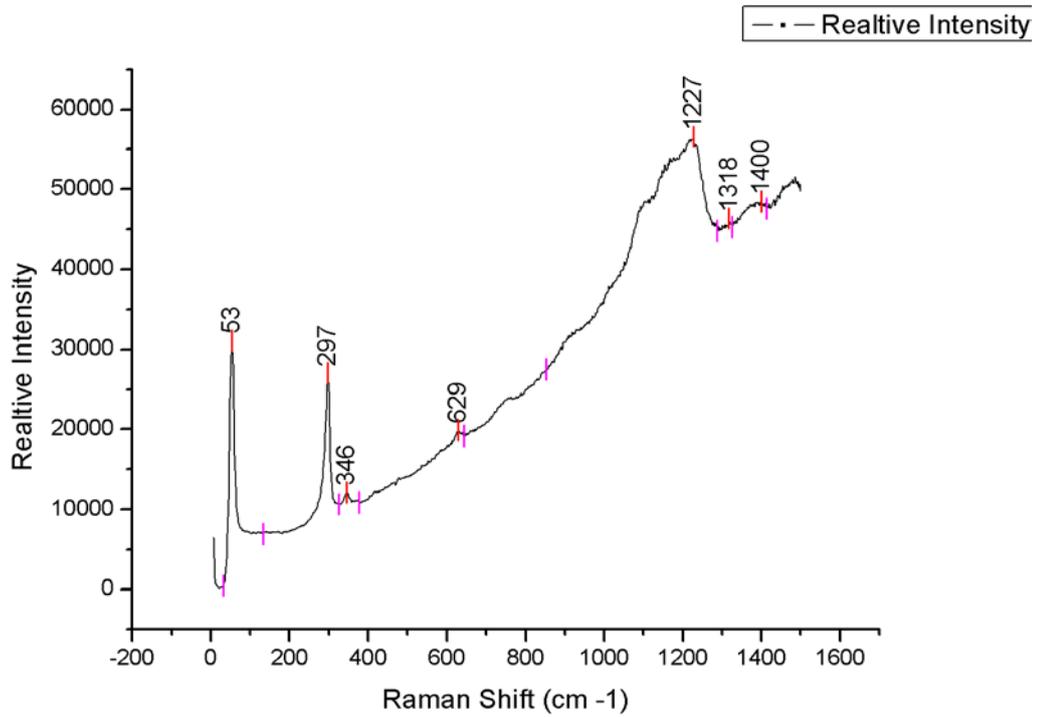


Figure 6 Raman spectrum of the tenorite before any reaction.

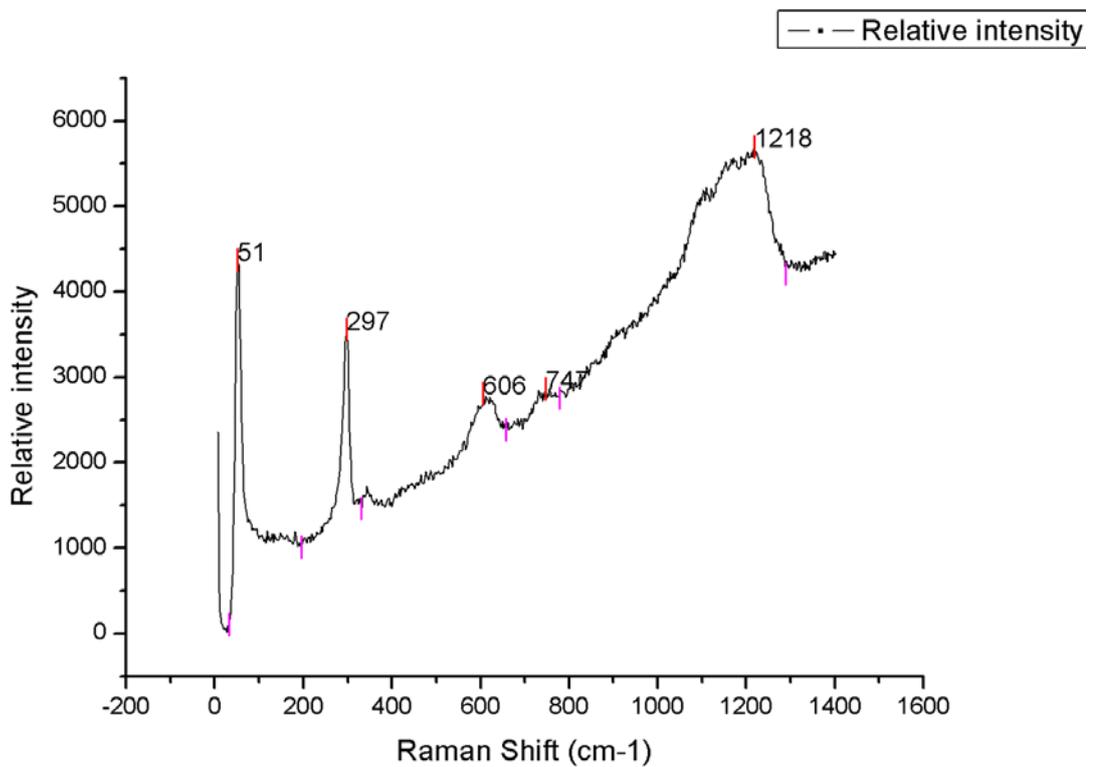


Figure 7 Raman spectrum of the tenorite after acid attack



# Synthesis of the Egyptian Blue

## Materials

### Muffle oven and crucibles

Used muffle and crucibles are shown in Figure 8, crucible material was porcelain.



*Figure 8 the used muffle and crucibles in the synthesis*

To manufacture Egyptian blue, a steady supply of oxygen is essential; thus production in an open crucible is desirable. It is necessary to maintain a constant temperature over the entire production period.

As reported by many authors, if the temperature exceeds 1000°C and/or a reducing atmosphere exists, the green frit may be obtained.<sup>6</sup>

### Reagents

Chemicals were of analytical grade. Egypt sand brought from Alexandria was used in just one case. Basic copper carbonate identified as malachite, copper oxide as cuprite [copper (II) oxide], calcium carbonate, sodium carbonate and amorphous silica, were employed as pure chemical compounds.<sup>11</sup>

### Sample composition

Five basic mixtures, characterized by different amounts of the synthesis reagents, were chosen to evaluate the influence of chemical conditions on the characteristics of the produced pigments. (Table I)

Table 1 Composition of standard mixture (in grams)

Chemical formula	$CuCO_3Cu(OH)_2$	$CuO$	$CaCO_3$	$Na_2CO_3$	$NaHCO_3$	$SiO_2$
Mixture A	2.500	-	1.100	0.608	-	7.201
Mixture B	1.401	-	2.500	0.624	-	7.207
Mixture C	-	2.004	2.500	2.026	-	6.002
Mixture D	1.738	-	1.453	-	0.821	6.022
MixtureE*	-	0.503	1.010	0.506	-	4.003

\* The mixture E was the only case with 3 grams of Egyptian sand added.

Sodium carbonate was added as a flux and then mixtures were heated in a muffle furnace at controlled temperature.

### Experimental conditions for melting

These raw materials were ground to a fine powder and then mixed.

Two different series of experiments were carried out depending on the heating time:

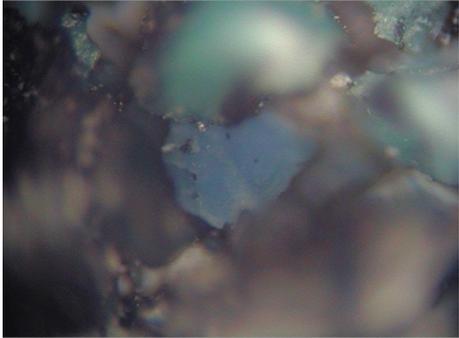
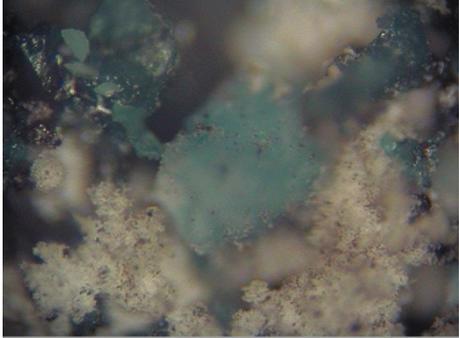
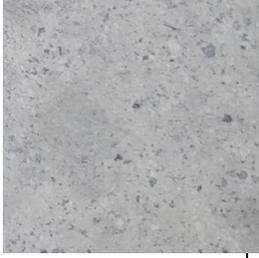
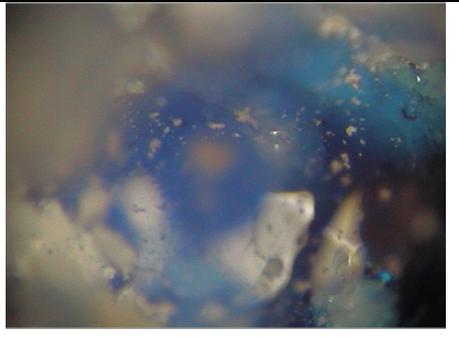
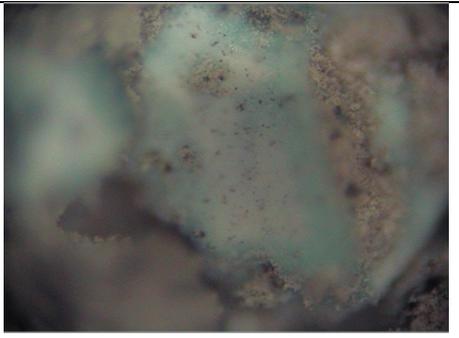
- In the first one, mixtures A, B, C and D were introduced in a first step into the muffle at room temperature, heated for 4 hours at 860 °C, and left to cool down overnight. In the second step, they were reintroduced into the muffle for additional 8 hours at 860 °C.
- In the second one, mixtures A, C and E were heated for 24 hours at 860 °C.

### Results and discussion

The results obtained in the first experiments (after the first and second heating process) are shown in Table 2 and in general show the appearance of different blue shades particles dispersed in black particles. Since the samples A, B and D were prepared from the same components, but at different ratios, after leaving the muffle, had nearly the same look. Sample C, which is different from A, B, and D by the replacement of malachite with copper oxide, had a different look, the blue particles were more abundant and the blue tone was very different than the other samples.



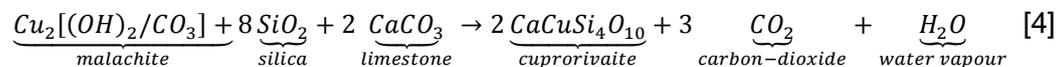
*Table 2 Summary the visual characters of the produced pigments after the first and the second heating process.*

Sample	Before melting	After melting (Camera Shot)	After melting ( microscope)
A			
B			
C			
D			

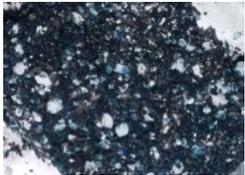
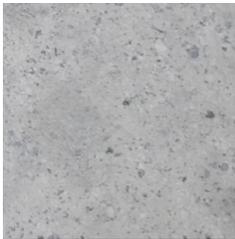
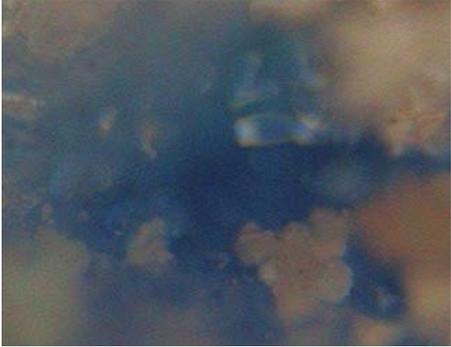
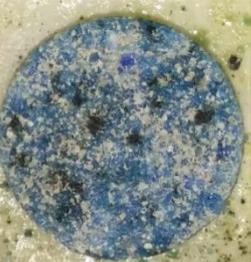
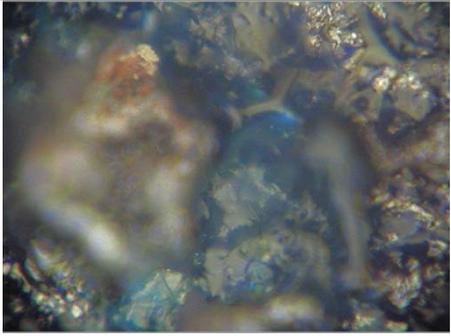
In the second series of experiments, shown in Table 3, the colors take more intensity in

the case of A and C. For the mixture E, the blue tone and texture looks more like the product got from the mixture C than the one from A.

The general reaction of synthesis<sup>12</sup> can be described by the reaction [4].



*Table 3 Summary the visual characters of the produced pigments after the third heating process.*

Sample	Before melting	After melting (Camera Shot)	After melting ( microscope)
A			
C			
E			



## Identification of the Egyptian Blue and its degradation products

In this project, Raman and X-ray Diffraction were used as analytical methods for the identification of the different products. The Raman analyses were carried out at the Department of Chemical Engineering at the ETSEIB, while the X-ray Diffraction ones were sent to the laboratory of the University of Barcelona.

For comparison, literature values of the Egyptian blue Raman lines<sup>13,14</sup> are 136, 358, 431, 572, and 1086  $\text{cm}^{-1}$ .

### Sample A

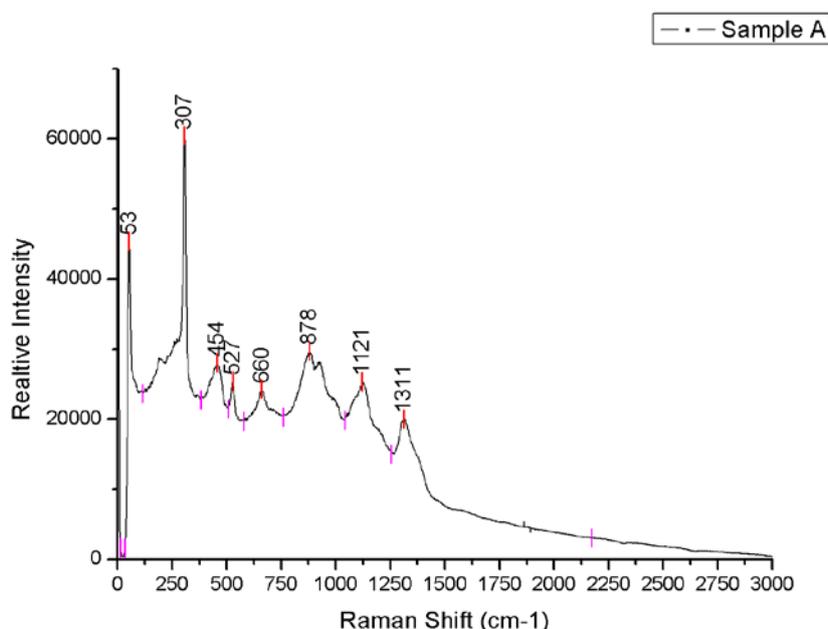


Figure 9 Raman spectra of a blue point from sample A after 12 hours in muffle.

In the figure 9, the strongest Raman lines appear at 53 and 307  $\text{cm}^{-1}$ . The peak frequencies of the low-intensity lines (around 454, 527, 878, 1121 and 1311  $\text{cm}^{-1}$ ) are affected by some uncertainty. In several of the collected spectra the 454  $\text{cm}^{-1}$  line characteristic of low-crystalline,  $\alpha$ -quartz, was also observed.

The comparison of the spectra reported in Figure 9 with the literature data cannot show that the blue grains are Egyptian blue. The observed peak frequencies are not in a really good agreement with the literature data. It is worth noting that, in comparing Raman

spectra measured on samples, measurements performed on micro-crystals with different orientations can give considerable variations in the relative intensity of the peaks because of polarization effects.<sup>15</sup>

In discussing the Raman spectra of Egyptian blue, it is worth recalling that this synthetic pigment is obtained by firing a mixture of compounds containing silica sand, calcium carbonate, and copper oxide with a soda flux. This produces blue crystals embedded in a silica-rich vitreous matrix, and the blue pigment powder is obtained by milling this compound. This explains the strong heterogeneity observed in the blue samples and the observation of the  $\alpha$ -quartz line.

### Sample C

In the figure 10, the peak frequencies of strongest Raman lines are at 51, **357**, 855, 1263 and 1352  $\text{cm}^{-1}$ . In this case, the 357  $\text{cm}^{-1}$  is one of the characterizing bands of the cuprorivaite<sup>15</sup>.



Figure 10 Raman spectra of a blue point from sample C after the first heating process.



## Sample D

In the figure 11, in the Raman spectra the peak frequencies of strongest Raman lines are at 51 and 307  $\text{cm}^{-1}$ . Again, the observed peak frequencies are not in agreement with the literature data. So it is not possible to confirm the formation of Egyptian blue by using Raman.

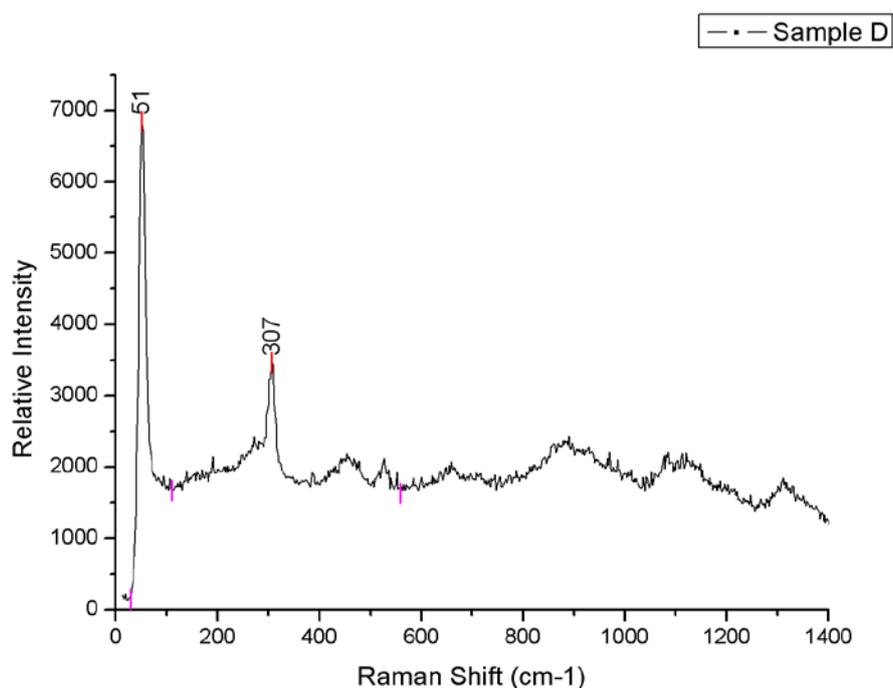


Figure 11 Raman spectra of a blue point from sample D after the first heating process.

## X-ray diffraction analysis (XRD)

Due to the fact that Raman seemed not to be a technique which permits the identification of the Egyptian Blue, XRD measurements were performed using a Goniometer=PW3050/60 diffractometer with Ni filtered  $\text{Cu-k}_\alpha$  radiation.

Figure 12 shows the Raman spectra of sample A after 24 h of heating at  $860^\circ\text{C}$ . The comparison of this with the literature data allows the confirmation of the presence of the cuprorivaite because of the triplet observed at  $20^\circ$ <sup>15</sup>.

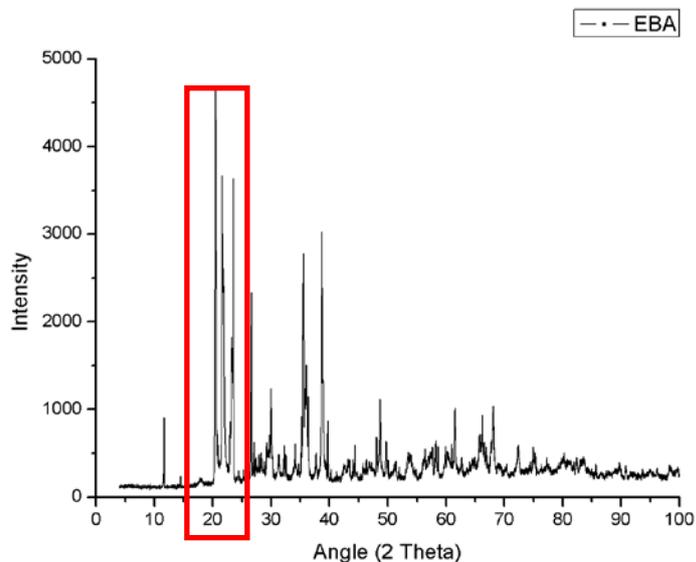


Figure 12 Identification of the synthesized pigment from the mixture A after 24 hours heating process.

On the other hand, the characteristic triplet band of cuprorivaite is not so well appreciated in the spectra of the sample C after 24 hours heating process at 860°C (Figure 13).

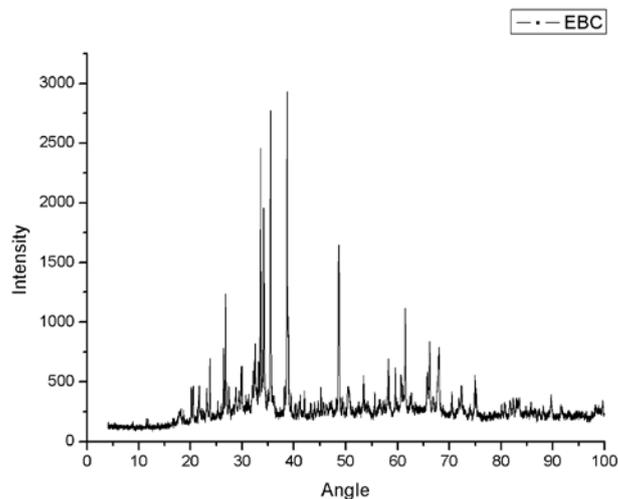
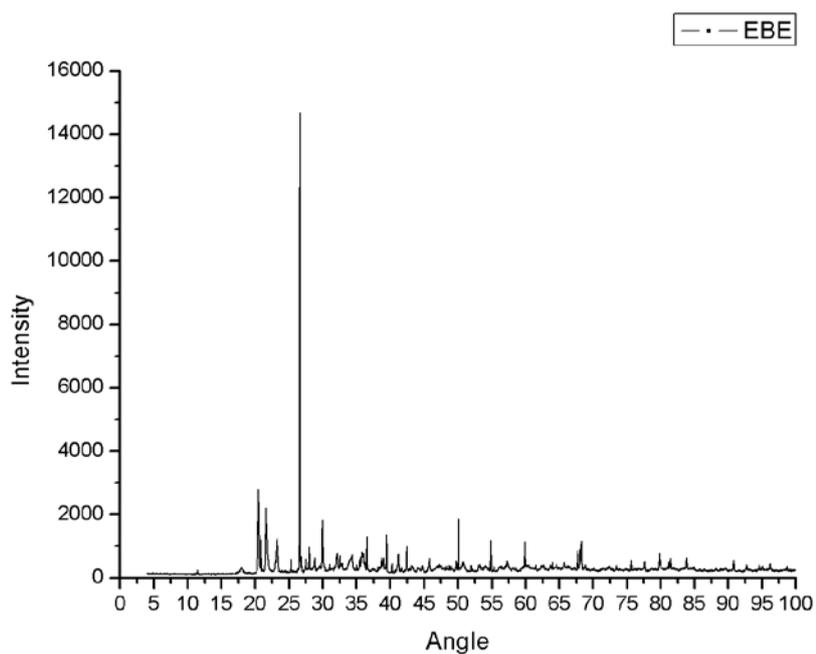


Figure 13 Identification of the synthesized pigment from the mixture C after 24 heating process.

Finally, the comparison of the spectra reported in figure 14 from the mixture E after 24 hours of heating with the literature data allows the confirmation of the presence of Egyptian Blue, but it seems that at a lower concentration than in the case of the sample A. The use of the Egyptian sand has been the cause of the appearance of a strong peak characteristic of the calcium carbonate, because Egyptian sands are usually rich in  $\text{CaCO}_3$ .<sup>16</sup>





*Figure 14 Identification of the synthesized pigment from the mixture E after 24 hours heating process*

## Degradation of the Egyptian Blue

In spite of the agreed stability of the Egyptian Blue pigment against the environment, there are different reports that show the presence of other minerals, especially basic copper chlorides,  $\text{Cu}_2(\text{OH})_3\text{Cl}$ , which have been attributed to the degradation of such pigments. Basic copper(II) chlorides are found in nature in three different phases: botallackite (monoclinic), atacamite (orthorhombic) and paratacamite (rhombohedral) (Pollard et al. 1989).

The degradation by formation of basic copper chlorides has been observed in Egyptian artifacts not only where the Egyptian Blue pigment was used but also in artifacts painted with Green Frit and in objects made of faience (Schiegl et al., 1989). The mechanism of degradation is similar in both cases, starting with the devitrification of the glass phase followed by the decomposition of the residual material to form the basic copper chlorides. According to Schiegl et al. (1989) the degradation is high in objects from the Egyptian Old Kingdom (degradation was detected in all the artifacts studied), medium to high in objects from the Middle Kingdom and low to medium in artifacts from the New Kingdom. In particular, the degradation of some of the faience tiles found under the king Djoser step pyramid in Saqqara is very high, and the 'green' tiles seem to be blue tiles which have been degraded (in some cases, the glaze has disappeared and the tiles are white due to the core of the faience). The authors affirm that green faience was never used by the Egyptians, on the contrary, all the green faience in Egyptian objects is the product of the chemical degradation of the copper compounds to basic copper(II) chlorides. A recent work, focused on the degradation patterns of the king Djoser faience tiles, corroborates these findings and, in addition, shows that in some of the blue tiles the glaze was composed of Egyptian Blue (Moussa and Ali, 2013).

This color alteration of Egyptian blue faience depends on the presence of the water-soluble salts in conjunction with Egyptian blue and its ability to discolor according to bronze disease the result of the presence of chlorides which catalyzes the decay process.

The color alteration of the blue pigments indicates precipitation from migrating solutions after removal of copper and chlorine from the pigment layer.

The chloride ion replaces the hydroxide ion and forms a soluble metal chloride, which has a hygroscopic nature. This effect is very deleterious in the presence of Egyptian blue cuprorivaite, as a pigment material that's why the color change phenomenon of the Egyptian blue into green color has called "copper chloride cancer"<sup>1,2</sup>



## Experiments

After the synthesis of the Egyptian blue, the samples A and C were chosen for the study of the high concentrated acid solution effect and the possible degradation.

The test consisted of adding a small amount (between 2-3 g) of the products obtained in the synthesis (Sample A and C) to a 10% concentrated hydrochloric acid solution (about 3 ml).

## Results

After about 10 days, the result was impressive. In the case of sample A (Figures 15 and 16), almost 100% of the blue color turned to green, while in the case of sample C (Figure 17) the change was not as significant as in the case of A. It took about 3 days more to the green color to appear and the proportion of the green color did not exceed ~10% of the total sample.



Figure 15 **left:** Sample A before acid attack, **right:** Sample A after acid attack.

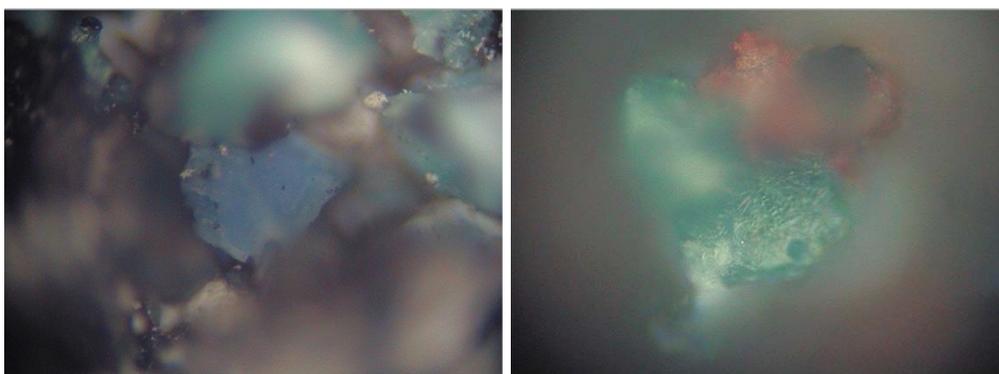


Figure 16 **left:** A microscope photo of the Egyptian Blue mixture A obtained after 12 hours of muffle heating. **Right:** after leaving it in concentrated acid solution.



Figure 17 **left:** Sample C before acid attack, **right:** Sample C after acid attack.

## Discussion

Although the experiments were carried out using artificial brine (very acidic brines are unusual in Egypt), the formation of degradation products (or secondary solid phases) has been demonstrated. This process of degradation could be related to the 'copper chloride cancer', the formation of basic copper chlorides such as atacamite  $[\text{Cu}_2\text{Cl}(\text{OH})_3]$  due to the migration of Cu ions through the NaCl solution, which at relatively high chloride concentration produces the precipitation of atacamite, which changes after losing water to a powder of paratacamite, or to a material known as wollastonite green  $(\text{CaCu})_3(\text{Si}_3\text{O}_9)$ .

The disease develops in stages: It starts with the devitrification of the glass phase in Egyptian Blue, followed by decomposition of the residual material. Migration of chlorine-bearing solutions leads to reaction with copper in the residual glass. The copper and chlorine bearing solutions will then react with calcite and precipitate basic copper chloride to form atacamite. These solutions may also migrate to the surface of the pigment layer to deposit at atacamite or paratacamite.<sup>1,2</sup>

The X-ray diffraction analysis of the sample A before and after the acid attack gives the spectra shown in figure 18. The triplet of cuprorivate is still shown which means that the degradation did not affect the whole bulk of the pigment and the basic copper chloride formed is just a layer. Another possible explanation is that the new phase formed on the surface of the pigment is amorphous, unidentifiable by X-ray Diffraction.



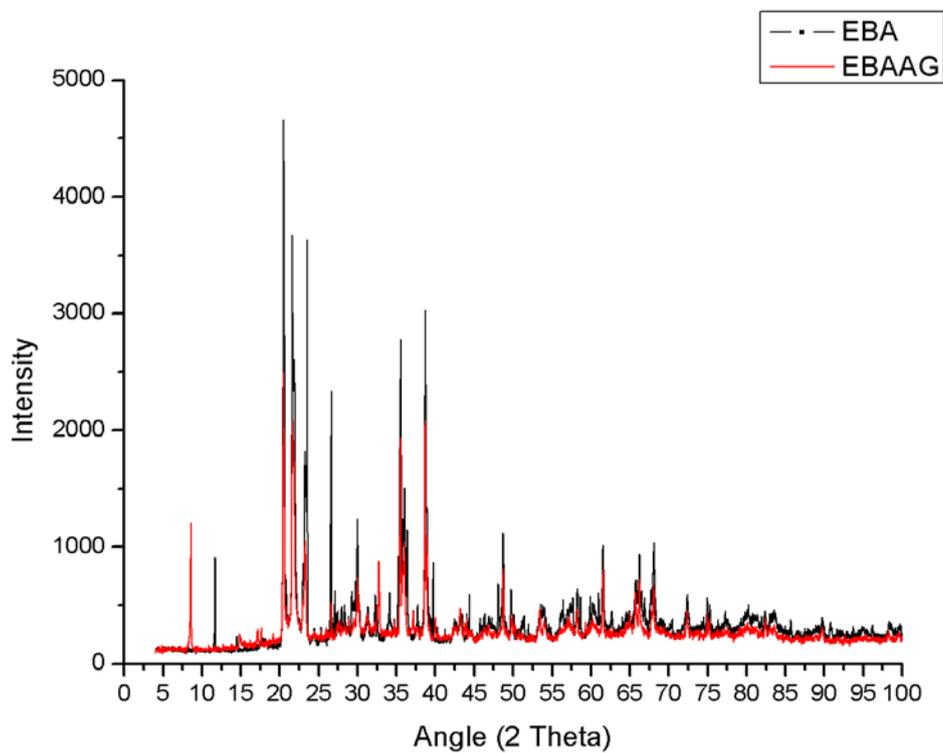


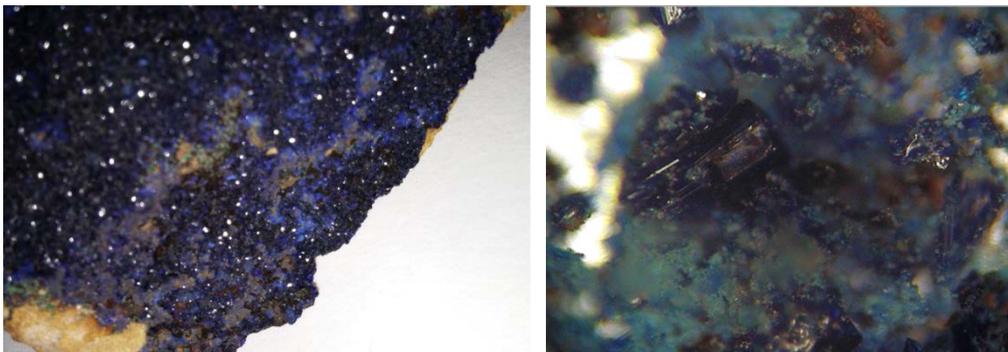
Figure 18 X-ray spectra of sample A before (EBA) and after being in concentrated acid solution (EBAAG).

## Other Applications of Raman analyses on ancient pigments

Due to the fact that Raman analysis under the conditions described above seems not to give reliable results on the identification of the Egyptian Blue, in this work also other minerals which could be used for the blue pigment in antiquity have been analyzed. In addition, a 'possible' ancient fragment of a painted pottery has also been analyzed in order to evaluate the actual application of the Raman on ancient pigments

### Azurite

Azurite (Figure 19) is a natural mineral pigment whose chemical composition is basic copper carbonate ( $\text{CuCO}_3\text{Cu(OH)}_2$ ). It was largely employed in paintings particularly around the middle Ages and the Renaissance, both in Europe and in the East. It presents an intense blue color whose hue depends on the grain size, the smaller grains producing a paler blue color.<sup>10</sup> It was a mineral known in Ancient Egypt and although some reports indicated that it was used as a blue pigment it seems nowadays that it was misidentified.



*Figure 19 Azurite mineral*

Micro-Raman spectroscopy has been used as a non-destructive technique to investigate azurite and gives the following spectra in figure 20.



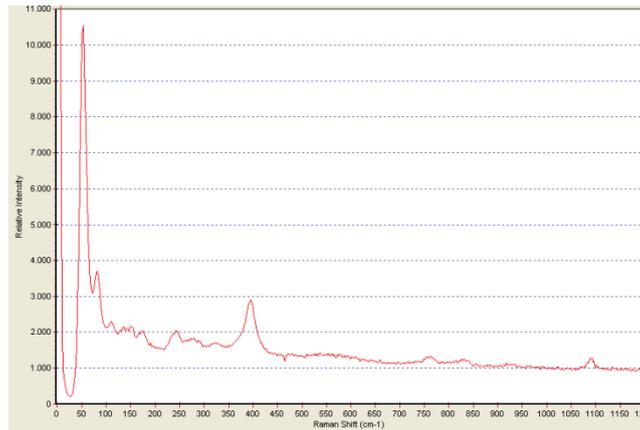


Figure 20 Azurite Raman Spectra

In this case the spectra matches perfectly with the literature data, where the strongest peaks at 402 and 1099  $\text{cm}^{-1}$  are clearly shown<sup>10</sup>.

As happened with the malachite a laser-induced degradation of azurite was detected by progressively increasing the laser power on the sample (figure 21). The blackening of azurite is due to thermal alteration which causes its degradation into tenorite (E. Mattei 2007), as happen in the case of malachite. The reaction 5 describes the degradation process.<sup>10</sup>

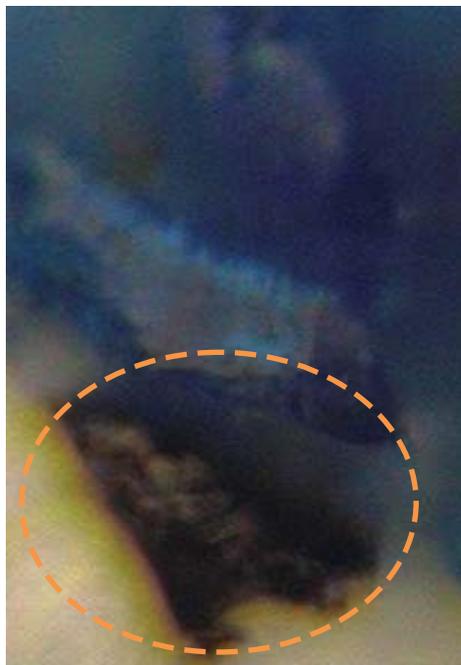
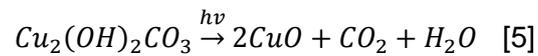


Figure 21 laser-induced degradation of azurite.

## Lapis lazuli

Lapis lazuli is the name given to the typical lazurite rich rock (figure 22), also containing calcite, pyrite, and other silicate minerals, such as diopside, forsterite, muscovite and wollastonite.

The rare and thus expensive lapis lazuli has been mined for centuries principally from Afghanistan. The pigment, called “ultramarine” from the Renaissance, was extensively used in miniatures in the Middle Ages in the west and in the Islamic world, and in pictures and frescos. They were highly valued by ancient cultures in Mesopotamia, Egypt, Greece, China and Rome.

Lapis lazuli was also known in Egypt and it was the most appreciated semi-precious stone, although it was never used as a pigment because of the difficulties of its grinding.

16



*Figure 22 A Lapis Lazuli rock*

Figure 23 shows the Raman spectrum of a fragment of lapis lazuli, with a peak at  $548\text{ cm}^{-1}$ , which is attributable to the lazurite. The Raman spectrum is relatively complicated, with different peaks because lapis lazuli is not a mineral but a rock, because it is made up from various other minerals.



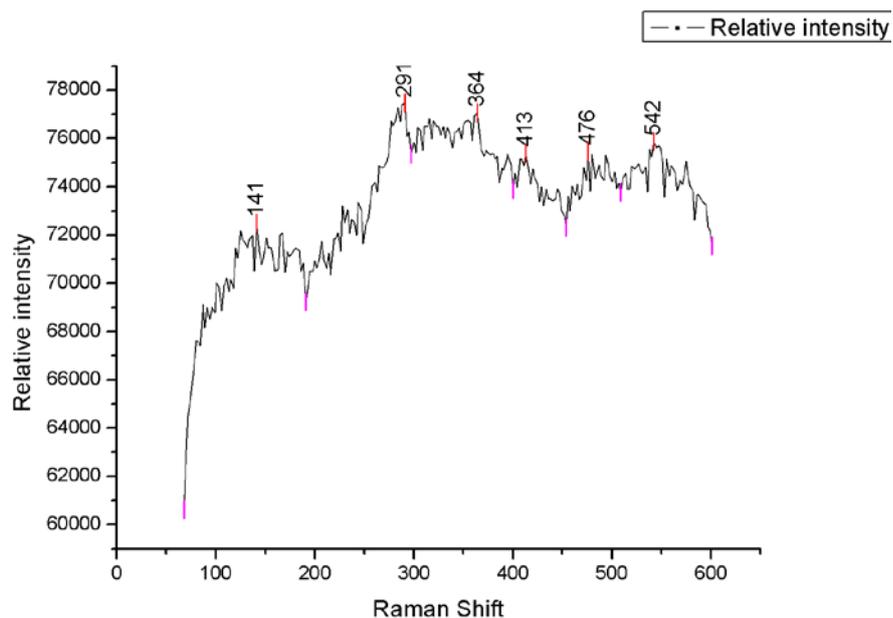


Figure 23 Raman spectra of a lapis lazuli rock.

## Ancient Egyptian pottery fragment

As part of the analytical survey of this work, yellow, red, black and blue pigments from a fragment of pottery from the Malqata palace (figure 24) was analyzed using Raman. The Malqata Palace was founded by Amenhotep III during the 18<sup>th</sup> Dynasty (ca. 1390 BC), and is located on the West Bank of Luxor (670 km south from Cairo), Egypt,.

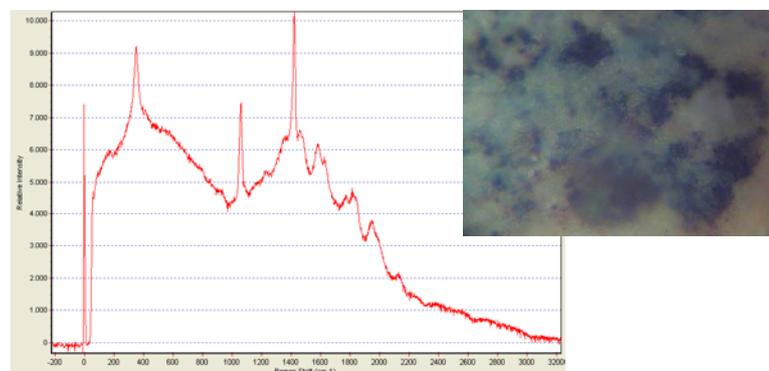
The details of the Raman vibrational spectroscopic analysis of the pigments are shown below.



Figure 24 Pigments from ancient Egyptian pottery fragment

## Blue color

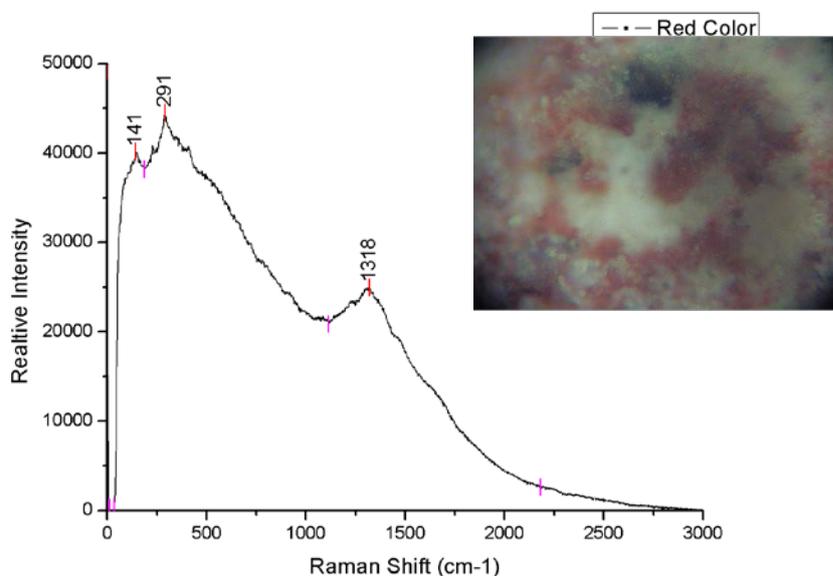
The blue pigment sample gave a Raman spectrum (Figure 25) with characteristic peaks at 350, 1062 and 1424  $\text{cm}^{-1}$  of malachite.<sup>8</sup>



*Figure 25 Raman spectra of the blue pigment from ancient Egyptian funerary artefact.*

## Red color

The red pigment sample gave a Raman spectrum (Figure 26) with characteristic peaks at 141, 291 and 1318  $\text{cm}^{-1}$  of Hematite, the mineral form of iron (III) oxide ( $\text{Fe}_2\text{O}_3$ ), the iron component of the Red Ochre.<sup>17</sup>

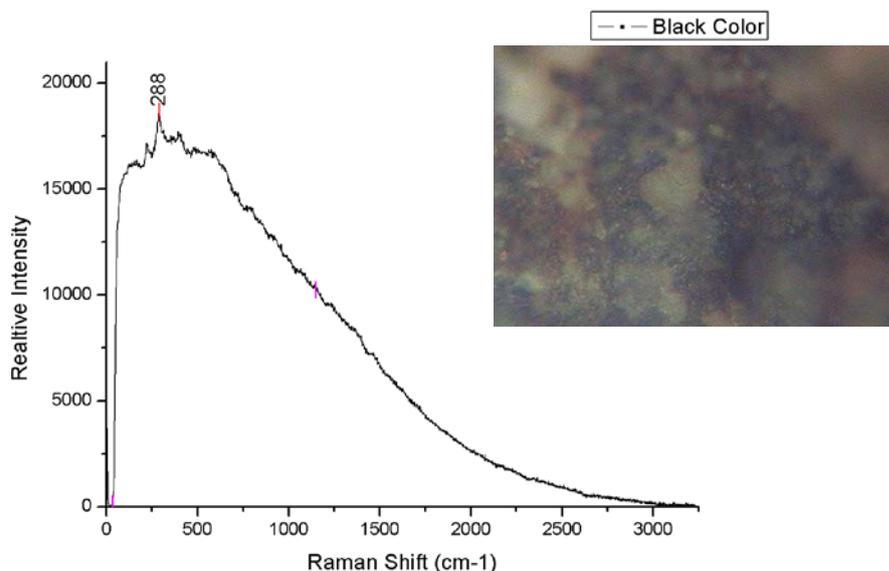


*Figure 26 Raman spectra of the red pigment from ancient Egyptian funerary artefact*



## Black color

The black pigment sample gave a Raman spectrum (Figure 27) with characteristic peak at  $288\text{ cm}^{-1}$  perhaps due to the presence of Vermilion as a brilliant red pigment originally made from the powdered mineral cinnabar. The chemical formula of the pigment is  $\text{HgS}$  (mercury-II sulfide). Mineral (cinnabar) may undergo a light induced transformation to black  $\alpha'$ - $\text{HgS}^{18}$ . However, this kind of spectra could also be attributed to the presence of organic species, such as organic carbon.

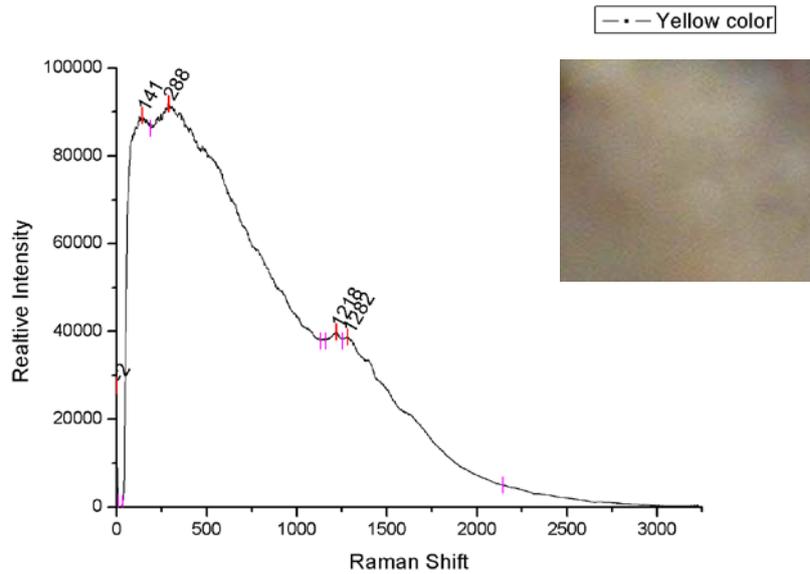


*Figure 27 Raman spectra of the black pigment from ancient Egyptian funerary artefact*

## Yellow color

The white yellowish pigment sample gave a Raman spectrum (Figure 28) with characteristic peaks at  $141$ ,  $288$ ,  $1218$  and  $1282\text{ cm}^{-1}$  which means that probably the surface layer was composed of calcite ( $\text{CaCO}_3$ ).<sup>19</sup>

The aspect of all the spectra obtained has this parabolic curve which shows that an organic material was used in the painting of those walls. In most cases, pigments was mixed with an organic binding medium such as Arabic gum, egg or animal glue and applied onto the surface of objects.



*Figure 28 Raman spectra of the yellow pigment from ancient Egyptian funerary artefact*

The composition of the pigments of this fragment is not conclusive to deduce its originality, especially because of the presence of vermilion, because this pigment was used in Ancient Egypt only some centuries after the life of Amenhotep III and his descendants. More analyses of the black areas of the artefact would be necessary. The other components, red ochre, malachite (for a green color instead of a blue color) and calcite, would fit perfectly well with the pigments used by the Ancient Egyptians.



## Economical study

The project was funded by the Polytechnic University of Catalonia, with an approximate cost of 7.113,07 €, which covers the working hours of the investigator, a total of 600 hours, 25 hours for each credit of the 24 credits dedicated to the project, covers as well all the materials used and devices needed<sup>20</sup>.

Table 4 the different cost concepts of the project.

		unit	Unit Price [€/unit]	Quantity[unit]	Total [€]
Working Hours		hour	10,00	600	6000,00
Materials	Basic copper carbonate (malachite)	gram	0,11	10,00	1,14
	Copper oxide (Tenorite)		0,22	10,00	2,23
	Calcium carbonate		0,09	8,56	0,80
	Sodium carbonate		0,28	2,03	0,57
	Sodium bicarbonate		0,04	0,82	0,03
	Silica		0,06	30,44	1,74
	Sodium Chloride		0,35	150,00	52,55
Analytical techniques	Raman	Analysis	45,70	20,00	914,00
	X-Ray		35,00	4,00	140,00
Total [€]					7.113,07

## Environment Impact

The quantity of wastes released from this work is very small because the analytical techniques used did not need a complicated preparation of the sample. In addition, because of the own characteristics of the work (fabrication of an ancient pigment from 'landscape' minerals) most reactives used are easily found in the territory.

During the synthesis process carbon dioxide is liberated. The environmental effects of carbon dioxide are of significant interest. It increases the greenhouse effect which causes extreme weather changes, a global temperature increase, the loss of ecosystems and potentially hazardous health effects for people.

The use of copper components has its environment effects, although the quantity of copper released to the environment in this work was very low because of the low solubility of most copper solids used. Copper does not break down in the environment and because of that it can accumulate in plants and animals when it is found in soils. On copper-rich soils only a limited number of plants have a chance of survival. Copper can seriously influence the proceedings of certain farmlands, depending upon the acidity of the soil and the presence of organic matter. Copper can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms. The decomposition of organic matter may seriously slow down because of this. When the soils of farmland are polluted with copper, animals will absorb concentrations that are damaging to their health.<sup>21</sup>

Calcium carbonate is a constituent of natural soils. Dissolved calcium carbonate dissociates into calcium and carbonate ions. Calcium ions will be assimilated by living organisms in the water and the carbonate will become part of the carbon cycle. Calcium carbonate is not toxic for the environment. Calcium is an essential element for all living organisms. Effects on plants can differ due to their preference for calcium rich or calcium poor soils.<sup>22</sup>

In water, sodium bicarbonate dissociates into sodium and bicarbonate ions. If the pH is decreased then carbonic acid,  $H_2CO_3$ , can be formed, in equilibrium with  $CO_2(g)$ . If sodium bicarbonate is released to soils, decomposes to  $CO_2$  or precipitates as a calcium or metal carbonate, forming complexes or staying in solution in water. Both sodium and bicarbonate have a wide natural occurrence. Sodium bicarbonate is not considered to be environmentally hazardous or toxic.<sup>23</sup>

Silicon dioxide consists of diatomaceous earth, a naturally-occurring material. Its primary component, silica, is found in common minerals like quartz, sand and agate. Silica gel is simply an amorphous form of silicon dioxide. These materials are ubiquitous, and unlikely to react chemically with any other substances in the environment.<sup>24</sup>



## Impact on human heritage

Color alteration of Egyptian blue faience depends on the presence of the water-soluble salts in conjunction with Egyptian blue and its ability to discolor through the formation of basic copper chlorides. The first discovery of the Egyptian Blue degradation indicated a developing archaeological disaster due to the advanced stage of the copper chloride cancer. This disaster is now full in action and the final result is walls barren of any blue or green paint.

Only paintings of natural minerals, e.g. white, red, brown, and yellow may survive this process. These features are well developed in several tombs e.g. Tomb of Mereruka (6th Dynasty) in Saqqara. The result may be even more disastrous for polychromic reliefs, since precipitation of basic copper chloride in the stucco or plaster will also take place below the neighboring white, yellow, red, and brown pigments, thus destroying them all together.

The attack of the cancer does not terminate after dislocation of the objects to museums or archaeological collections. It continues there perhaps more vigorously depending on the degree of humidity. Rescue of numerous tombs is even too late e.g. the Tombs of Princess Idut (6th Dynasty) and Nefer (5th Dynasty) in Saqqara. Depending on the degree of humidity, which is also in many cases a direct function of the number of tourists visiting the tombs, the blue and green paints vanish in a few decades but at most in one century.

It may take only a few decades to entirely destroy the once beautiful blue faience tiles of the Zoser pyramid and the South Tomb (and the tiles in collections). The cancer is also in an advanced stage in numerous tombs of the New Kingdom. Just to mention a few examples: Amenophis II (18th Dynasty), Sethos I (19th Dynasty), Merenptah (19th Dynasty), Ramses III (20th Dynasty), Ramses IV (20th Dynasty), and Ramses VI (20th Dynasty) ... etc<sup>1</sup>.

Despite its relatively young age, the Tomb of Petosiris in Tuna el Gabal (4th century BC) is in a considerably hopeless condition. The disease is also in a far advanced stage in a large number of tombs of the Old and Middle Kingdom.

A great number of objects in the Egyptian Museum in Cairo show symptoms of the copper chloride cancer e. g. painted stone reliefs, decorated wooden artifacts, and glazed ware. Consequently, a systematic survey of the degree of deterioration in tombs, temples, museums, and archaeological collections is needed before it is too late.

A restudy of restored objects and decorations in tombs (e.g. Queen Nefertari) is also an imperative to explore if the chemicals used during restoration did accelerate or stop the

process of basic copper chloride formation. These restorations took place before discovery of the cancer. The formation of basic copper chloride leads to considerable change in the hue of colors in the decorated reliefs.

Consequently, the color of the decorations on the walls is not the same as the ancient Egyptian artists once painted them. The conservation projects in some tombs, dedicated to avoid the pigments deterioration (e.g. Queen Nefertari Tomb) are a successful way to stop such degradation.<sup>25</sup>

In spite of these first studies on the likely degradation of the Egyptian pigments on the walls of the ancient monuments, there are not studies at laboratory scale of the degradation of Egyptian Blue freshly synthesized, which can be very helpful on the understanding of the degradation patterns in real samples. Is at this point where this work starts a new line of studies which should be continued and complemented in the future.



## Conclusions

- 1) Heating a mixture constituted by siliceous sand, lime (or calcareous sand) and copper compounds (minerals or bronze fragments) in the presence of a flux (soda, natron or plant ash) at temperature around 860 °C and no more than 950 °C for 24 hours, is a valid recipe to synthesize the Egyptian blue. The product varies depending on the proportions used of each component, the temperature and the duration of the process. The use of malachite or tenorite produces neither the same color nor the same composition.
- 2) The main problem in this project was the identification of the products, since the Raman spectroscopy did not get enough information probably because of the laser used for the excitation, peaks in many cases were not clear enough to compare it with the references data. In addition, sometimes a single component has many slightly different spectra in different scientific papers and Raman databases or in some cases, two or more components have a same characteristic band, sometimes because of the variations of the spectra with the position of the crystals in the sample. The type of laser and the wavelength applied by other investigators is another important factor in the low similitude between same component spectra. For this reason, in this project X-ray Diffraction was also used in order to identify the components of the sample. The problems of Raman could be solved by changing the laser wavelength in order to separate the Raman and the fluorescence spectra since electronic fluorescence is excited by a specific wavelength, whereas the Raman spectra varies in wavelength like the laser excitation.
- 3) At acidic pH and in the presence of high-chloride brine, Egyptian Blue seems to degrade to a green-component. Although the main degradation of the Egyptian Blue in archaeological samples is the green mineral atacamite, in this project atacamite was not detected, perhaps the solid formed was amorphous or the quantity formed was very low.
- 4) The degradation of the Egyptian Blue has been observed in this work at acidic pH, because brines analyzed in Egypt are usually neutral or slightly alkaline future experiments should be carried out at higher pH values. Considering that the degradation in the monuments is especially observed in very old samples (Old Kingdom, ca. 2500 aC) it is probable that pH has a kinetic effect on the degradation.
- 5) The results of the pigments analysis of the Ancient Egyptian pottery fragment was in concurrence with the literature, the identification of the red color as a hematite was part of this concurrence whereas the identification of the blue one as malachite contradicts the Egyptian blue expectation, actually, what it seemed

visually to be blue was probably originally pale green (Ancient Egyptians used malachite for the pale green). More work is necessary in order to identify the pigment for the black color; perhaps the existence of organic carbon avoids a reliable Raman analysis.



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