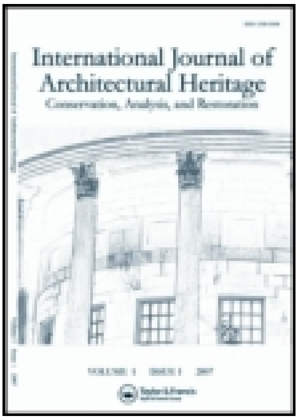

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COLOR ALTERATION OF ANCIENT EGYPTIAN BLUE FAIENCE

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Four different colored faience tiles were found in South Tomb of King Djoser in Saqqara, Egypt. The tiles suffer from various deterioration aspects, mainly color alteration, which occurred as a result of the reaction between present salts and the free copper ions of blue faience and changing it into greenish blue, dark green, and light green. The aim of this work is to study the color change phenomenon of ancient Egyptian blue faience, used in the construction and decoration of the walls in the south tomb of King Djoser–Saqqara by means of light optical microscope (LOM), x-ray diffraction spectroscopy (XRD), and scanning electron microscopy/energy dispersion X-ray (SEM EDX) analysis . The obtained results revealed that the pigment material cuprorivaite ($CaCuSi_4O_{10}$) was used in glazing the tiles and imparted the blue color. Other blue pigment materials were used in conjunction with Egyptian blue such as turquoise [$CuAl_6(PO_4)_4(OH)_8.4H_2O$]. The results indicate that the first trials for producing Egyptian blue were not in the 4th dynasty as it has been declared by previous authors.

KEY WORDS: faience, x-ray diffraction (XRD) analysis, scanning electron microscopyenergy dispersion x-ray (SEM EDX) analysis, Egyptian blue, turquoise, discoloring

1. INTRODUCTION

The term *faience* has been described as "a long-standing misnomer for a composite material consisting of a sintered quartz body and a glaze" (Moorey, 1994). Faience, the oldest synthetic material used strictly for decorative and ritual objects, is conservatively dated to 4500–4300 BC. The development of faience and of glazed stones was almost contemporaneous, followed approximately 1400 years later by Egyptian Blue, then by glass around 2400 BC (Foster, 1979; Moorey, 1985). Egyptian faience is non-clay-based ceramic displaying surface glaze, which creates a bright luster of various colors. The elected colors of the glazes varied within an array of blue-green hues.

Three techniques can be used to make faience: *application*, *cementation*, and *efflorescence* (Vandiver, 1983). *Application* is applying a glazing powder or slurry to the faience core. *Cementation* is also known as *Qom technique*. The unglazed dry faience core is buried in a glazing powder that partially melts on heating. The powder reacts with the surface of the quartz core and glazes it, although powder is not in contact with it and the core remains

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unaffected. The last technique, *efflorescence*, is unique in combining the glaze mixture in the core (Davidovits and Davidovits, 2004). Mazzocchin et al. (2004) performed three dry methods to produce Egyptian blue. The stoichiometric method uses Na_2CO_3 as a flux, while the Schippa and Torraca recipe and the Bolognese method use $NaHCO_3$. Mazzocchin et al. further mentioned that good results in color and yields were obtained by using the Schippa and Torraca recipe with the stoichiometric molar ratio and with the Bolognese method at 860° C.

The aim of this study is to investigate the color change phenomenon that occurs in ancient Egyptian blue faience, including the identification of the used glaze materials. The results will be used to detect the first trials of producing artificial copper pigments.

2. SAMPLING AND METHODOLOGY

Four different blue colored glazed faience pieces from the south tomb of King Djoser were sampled for laboratory analyses to determine their composition. Two samples were taken from each piece—one for x-ray diffraction (XRD) analysis and the other for scanning electron microscopy/energy dispersion x-ray (SEM-EDAX) analysis. XRD was performed on powdered samples of the core and glaze materials in addition to the mortar used to adhere the tiles into the walls, using a Philips (PW1840, The Netherlands) diffractometer with Ni-filtered Cu-Kα radiation. The samples were scanned over the 0–60° 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 (Joint Committee on Powder Diffraction Standards [JCPDS] standards of 1967); the detection limits of the method were ± 1 w/w %.

The same samples were studied using SEM-EDAX, which was performed using a Fei company device (Version Quanta 200, Japan), with specifications of: Kv: 24.98; tilt (0.00); take-off: (36.47); ampt (35.0); detector type (SUTW-sapphire); resolution (129.87). The cross section was carried out using a stereomicroscope (stemi dr 1663 zeiss, Germany).

3. RESULTS

3.1. XRD and SEM-EDAX Analyses

3.1.1. Faience Samples The four different blue colored glazed samples are shown in Figure 1) (1a-d). The XRD analysis of the glaze of the first sample (1a) revealed that the sample contains approximately 50% quartz (SiO_2), 37% Egyptian blue ($CaCuSi_4O_{10}$), 5% turquoise [$CuAl_6(PO_4)_4(OH)_8.4H_2O$], 5% paratacamite [$Cu_2Cl(OH)_3$] and 3% calcite ($CaCO_3$) (Figure 2a). The SEM-EDAX of the same glaze material detected the presence of approximately 52% silicon (Si), 17% copper (Cu), 16% calcium (Ca), 5% chlorine (Cl), 5% magnesium (Mg), 3% phosphorus (P), 2% sodium (Na). According to the XRD results, the core of the sample contains 94% quartz, 2% gypsum ($CaSO_4.2H_2O$), 2% anhydrite ($CaSO_4$), and 2% halite (NaCl) (Figure 2c). The SEM-EDAX analysis showed that the core contains 81% silicon, 10% calcium, 3% aluminum (Al), 2% magnesium, 2% sodium and 2% traces of potassium (K), and chlorine (Figure 2d).

In the second sample (1b), the XRD analysis of the glaze detected approximately 92% Egyptian blue, 4% turquoise, and 4% truscotite $Ca_7Si_4O_{10}Si_8O_{19})(OH)_4.H_2O]$ (Figure 3a). The SEM-EDAX analysis of the same glaze revealed the presence of approximately 30% silicon, 20% sodium, 22% copper, 10% calcium, 5% phosphorus, 5% chlorine,

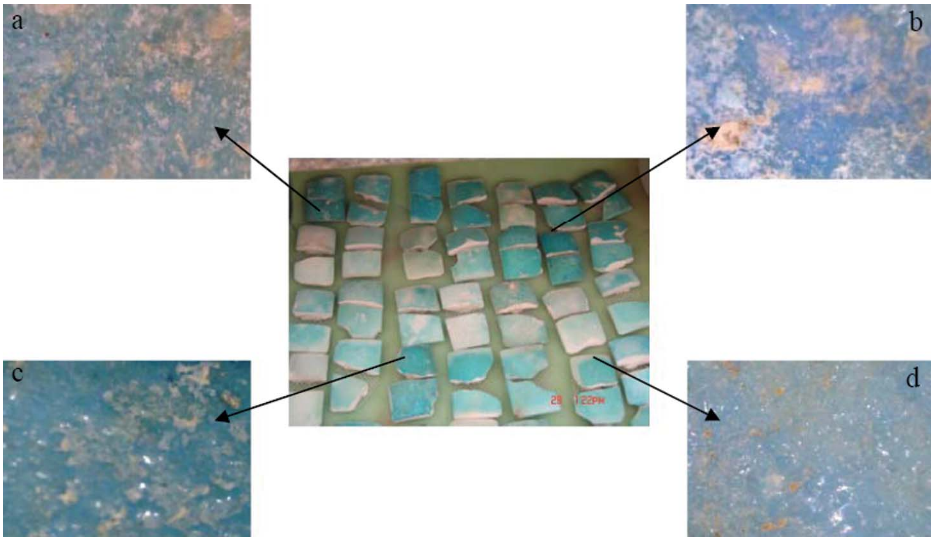

Figure 1a-d. Photographs of the studied four different colored faience tiles from the south tomb of King Djoser (3rd dynasty) (color figure available online).

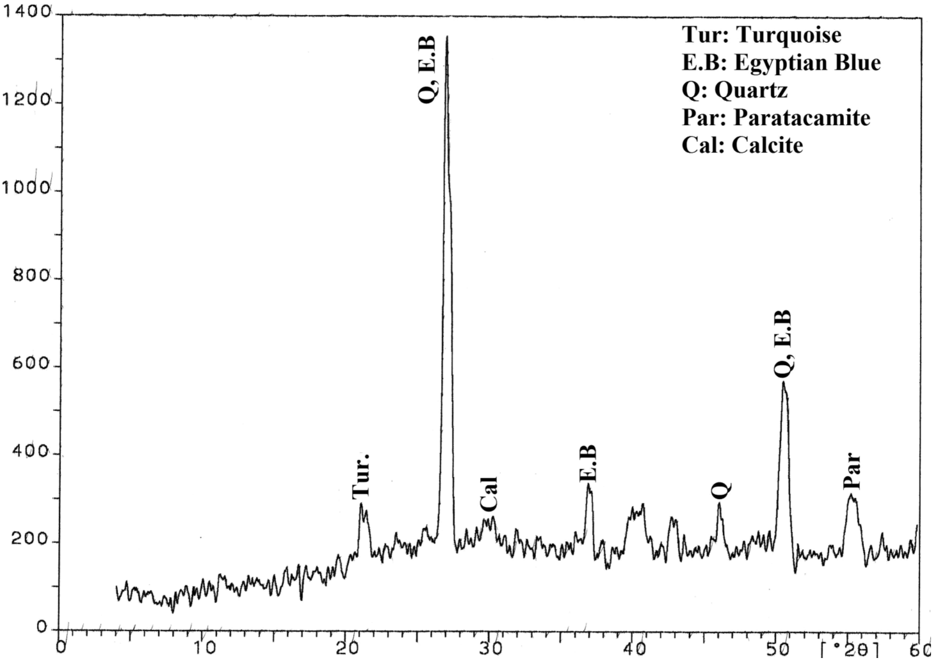

Figure 2a. Graph of X-ray diffraction (XRD) analysis pattern of the glazed face in sample 1a.

4% magnesium, 2% aluminum and 2% traces of iron (Fe), nickel (Ni) and potassium (Figure 3b). The XRD analysis showed that the core of the sample contains 97% quartz and 3% gypsum (Figure 3c). The SEM-EDAX analysis of the same core detected approximately

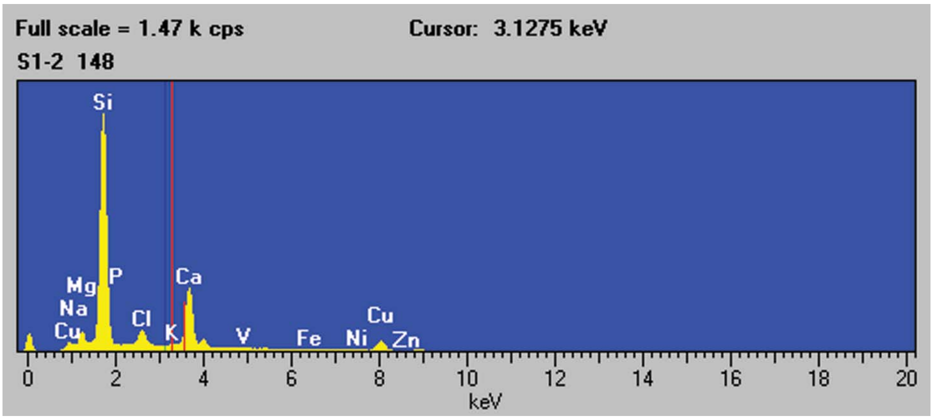

Figure 2b. Graph of scanning electron microscopy/energy dispersion x-ray (SEM-EDAX) a spectra of the glazed face in sample 1a (color figure available online).

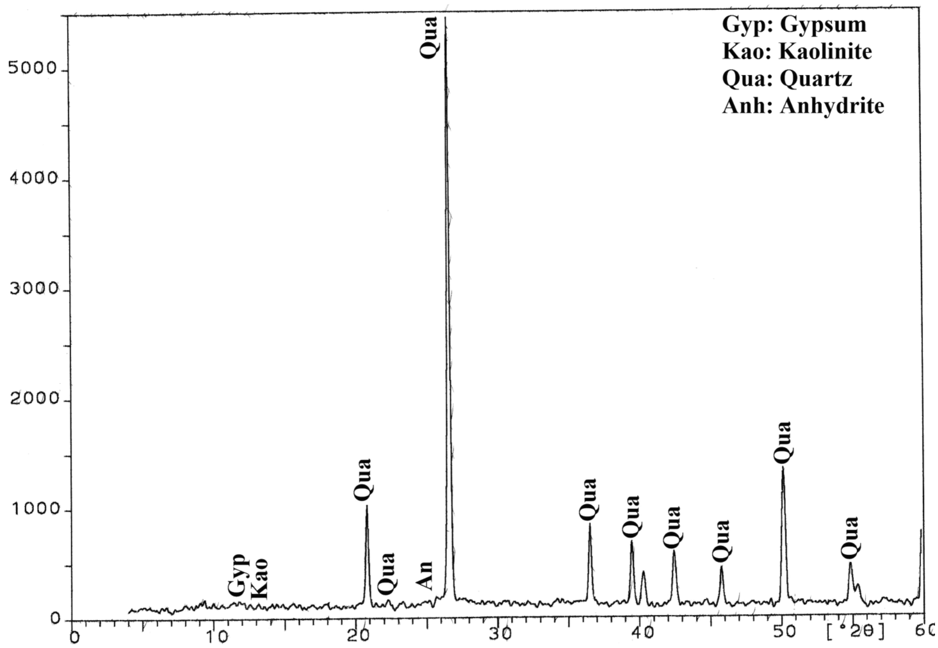

Figure 2c. Graph of XRD analysis pattern of the rendering layer upon which the glaze layer was applied in sample 1a.

44% silicon, 12% calcium, 40% oxygen (O) and 4% traces of sulfur (S), magnesium, iron, and potassium (Figure 3d).

In the third sample (1c), the XRD analysis of the glaze detected approximately 92% Egyptian blue and 8% turquoise (Figure 4a). The SEM-EDAX of the same glazed sample detected approximately 33% silicon, 12% copper, 7% sodium, 5% phosphorus, 5% magnesium, 3% chlorine, 32% oxygen, and 3% traces of potassium, iron, and nickel (Figure 4b). The analysis of the sample's core by mean of XRD detected approximately

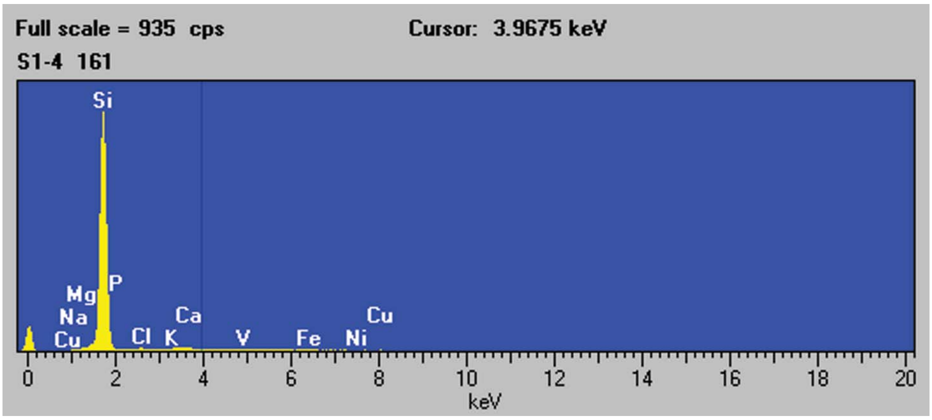

Figure 2d. Graph of SEM-EDAX spectra of the rendering layer upon which the glaze layer was applied in sample 1a (color figure available online).

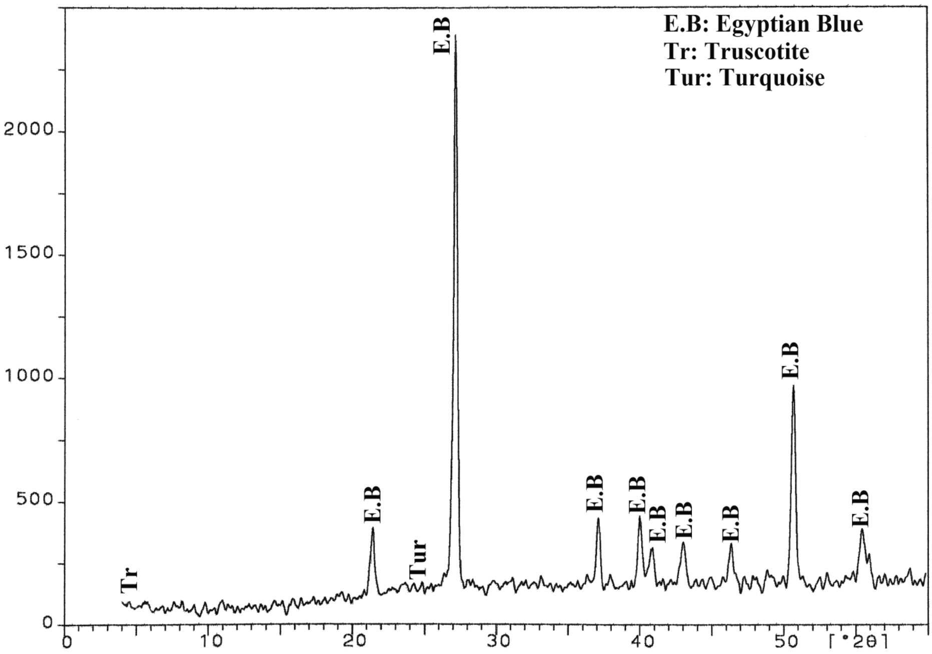

Figure 3a. Graph of X-ray diffraction (XRD) analysis pattern of the glazed face in sample 1b.

85% microcline ($KAlSi_3O_8$), 9% goethite [FeO(OH)], 3% talc [$Mg_3Si_4O_{10}(OH)_2$] and 3% truscotite (Figure 4c). The analysis of the core by mean of SEM-EDAX detected 32% silicon, 10% sodium, 7% iron, 6% magnesium, 43% oxygen, and 2% traces of potassium and chlorine (Figure 4d).

In the fourth sample (1d), the XRD analysis of the glaze detected 85% Egyptian blue, 5% turquoise, 4% paratacamite, 4% albite ($NaAlSi_3O_8$), and 2% quartz (Figure 5a). The results were emphasized by SEM-EDAX analysis, which detected 36% silicon, 5% sodium, 5% copper, 4% phosphorus, 3% calcium, 3% chlorine, 3% magnesium, 39% oxygen, and

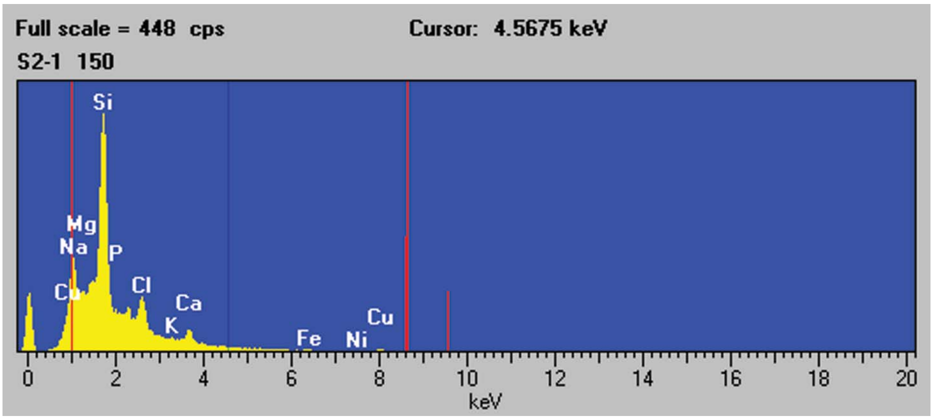

Figure 3b. Graph of scanning electron microscopy/energy dispersion x-ray (SEM-EDAX) a spectra of the glazed face in sample 1b (color figure available online).

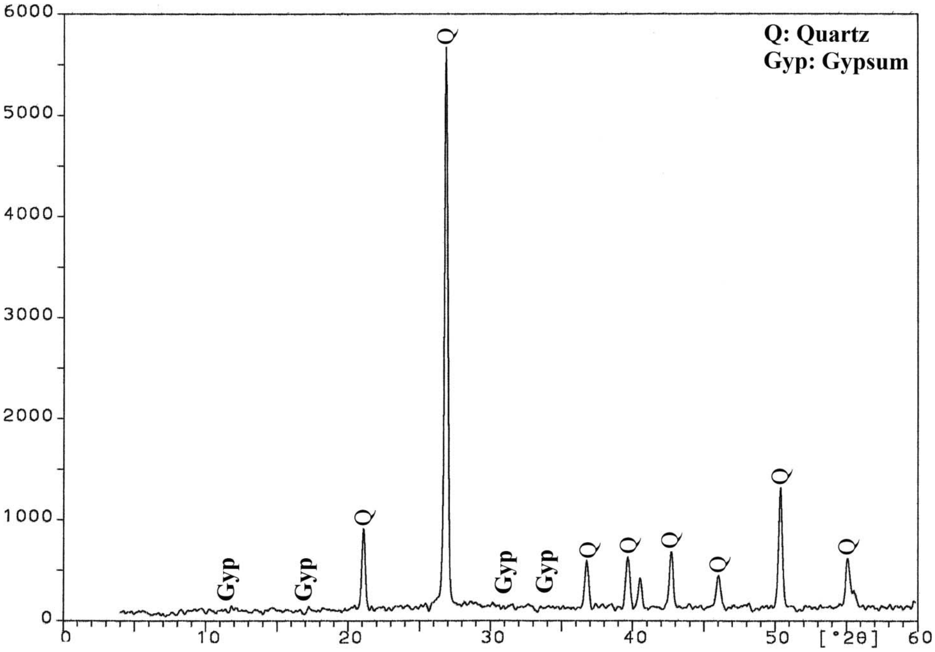

Figure 3c. Graph of XRD analysis pattern of the rendering layer upon which the glaze layer was applied in sample 1b.

2% traces of iron and potassium (Figure 5b). The core was found to be pure (100%) quartz by mean of XRD (Figure 5c). The SEM-EDAX of the core detected 44% silicon and 54% oxygen in addition to 2% traces of calcium, copper, phosphorus, chlorine, and potassium (Figure 5d).

3.1.2. Collating Mortar Samples Two representative mortar samples were collected for analysis. The first sample represents the old original mortar; and it contains 82% calcite,

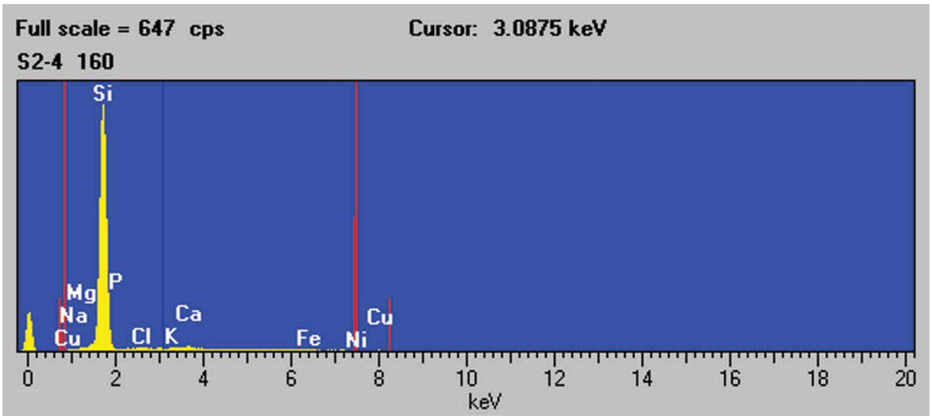

Figure 3d. Graph of SEM-EDAX spectra of the rendering layer upon which the glaze layer was applied in sample 1b (color figure available online).

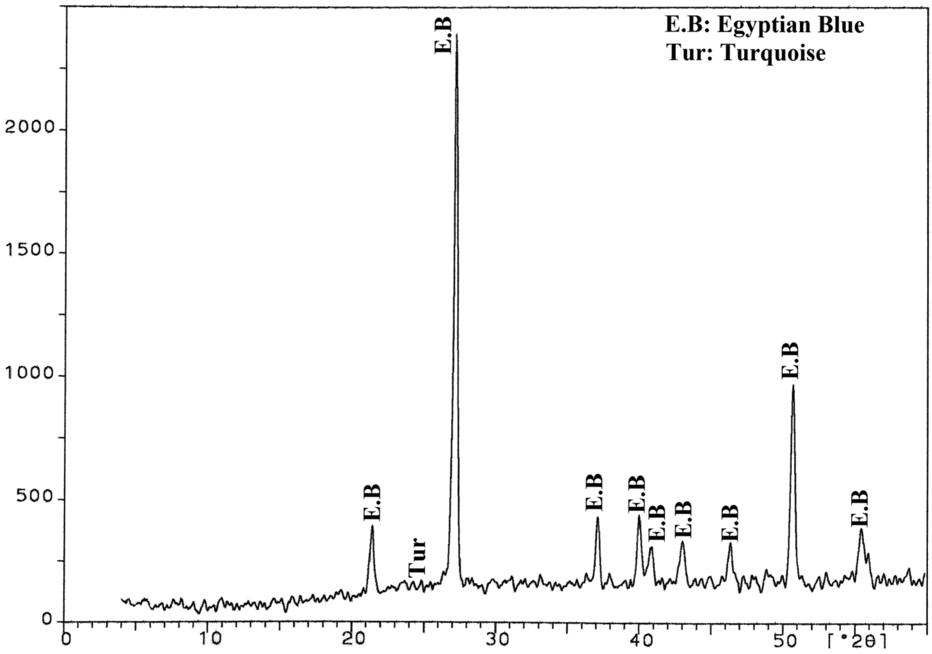

Figure 4a. Graph of XRD analysis pattern of the glazed face in sample 1c.

8% anhydrite, 6% halite, and 4% orthoclase ($KAlSi_3O_8$). The second sample represents the new mortar, which has been used in the conservation work inside the tomb and consists of 92% calcite, 4% dolomite [$CaMg(CO_3)_2$], and 4% halite.

3.2. Cross-Section Study

The cross section study revealed that the glaze layer was applied directly into the core in different thickness varying from 0.3 mm into 2 mm. The microscopic investigation

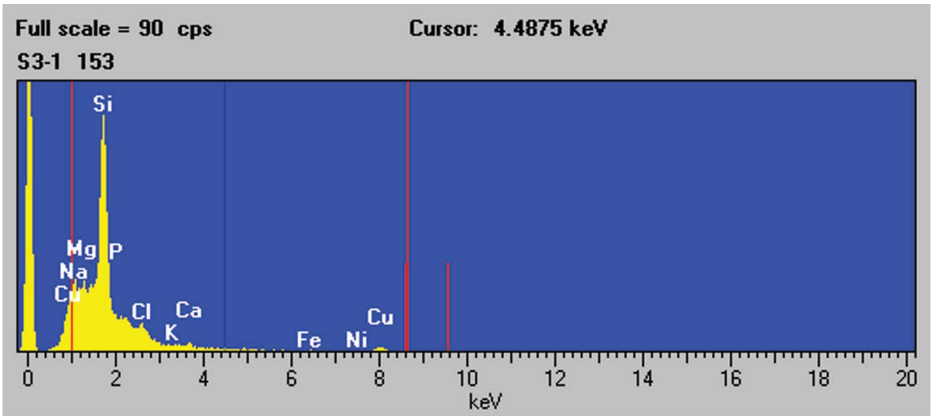

Figure 4b. Graph of scanning electron microscopy/energy dispersion x-ray (SEM-EDAX) a spectra of the glazed face in sample 1c (color figure available online).

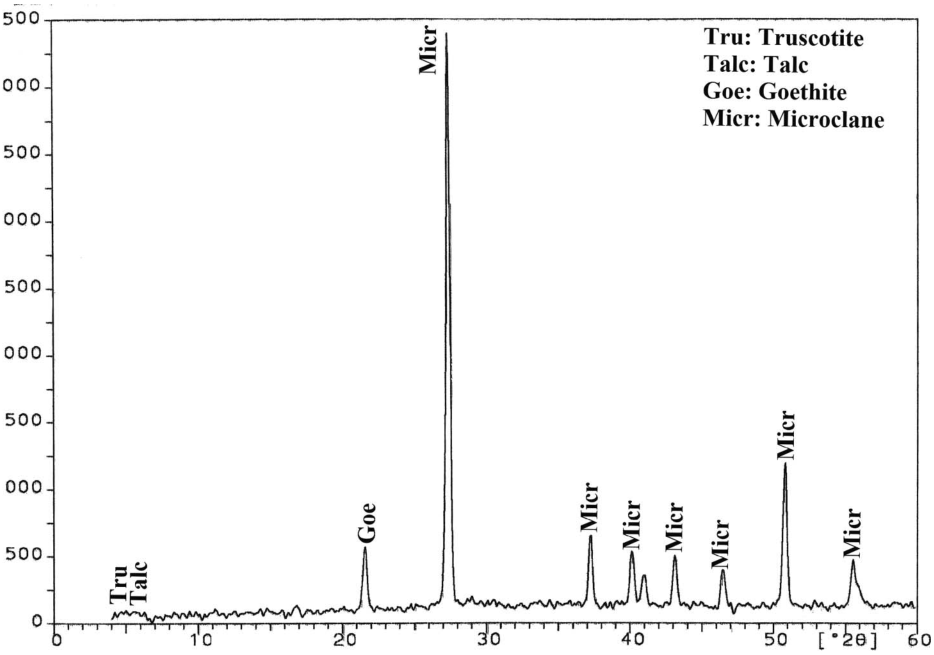

Figure 4c. Graph of XRD analysis pattern of the rendering layer upon which the glaze layer was applied in sample 1c.

of the cross section samples detected a color alteration into greenish blue, dark green, and light green color. Furthermore, the glaze took a spongy superficial appearance that may be called *glaze erosion* due to copper cancer chloride effect and the presence of copper chloride compounds (paratacamite) in the studied samples.

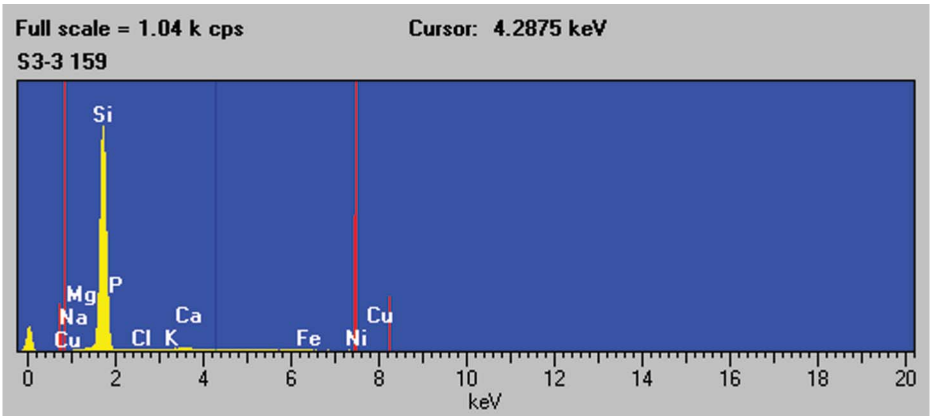

Figure 4d. Graph of SEM-EDAX spectra of the rendering layer upon which the glaze layer was applied in sample 1c (color figure available online).

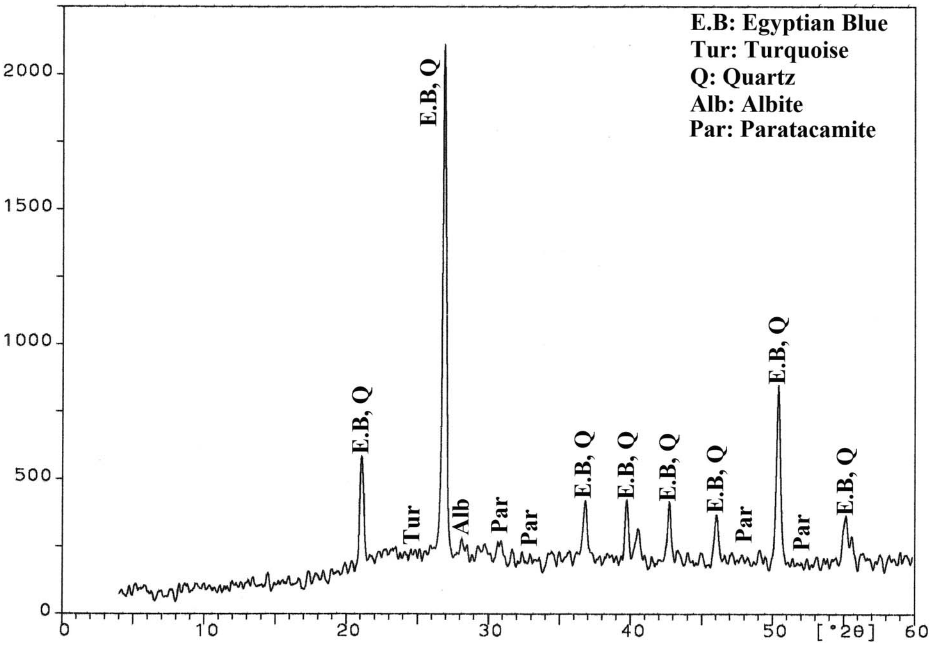

Figure 5a. Graph of X-ray diffraction (XRD) analysis pattern of the glazed face in sample 1d.

4. DISCUSSION

Pharaonic faience is made of a quartz body with an alkaline glaze achieved by one of three glazing methods: application, self-glazing by efflorescence, or self-glazing by cementation. Molding and inlaying were often used during the manufacturing (Mao, 2000). In the self-glazing process of efflorescence, the glazing materials, in the form of water-soluble alkali salts, are mixed with the raw crushed quartz of the core of the object (Kiefer and Allibert 2007; Noble 1969). As the water in the body evaporates, the salts migrate to

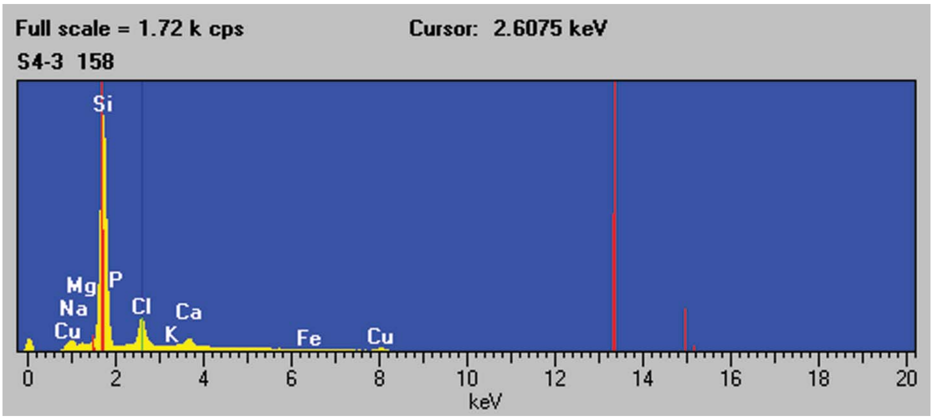

Figure 5b. Graph of scanning electron microscopy/energy dispersion x-ray (SEM-EDAX) a spectra of the glazed face in sample 1d (color figure available online).

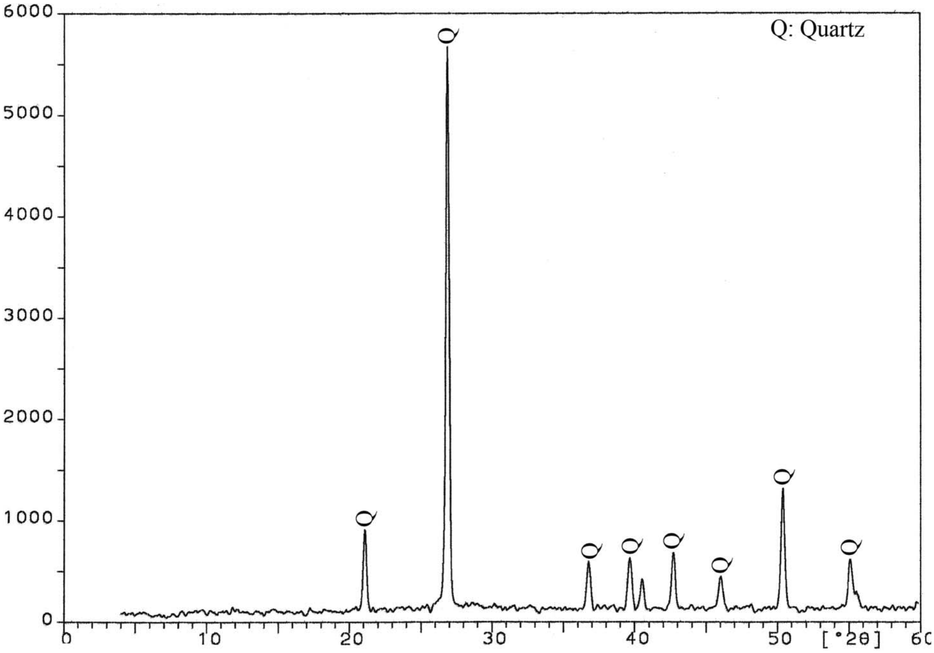

Figure 5c. Graph of XRD analysis pattern of the rendering layer upon which the glaze layer was applied in sample 1d.

the surface of the object to recrystallize, creating a thin surface, which glazes upon firing (Vandiver, 1983). These water-soluble alkali salts were probably in the form of natron or plant ash. When fired in high temperature, usually above 1000° C, this layer melts and fuses with the fine quartz, copper oxide or lime to create a glassy coating (Yamahana, 2000).

The raw materials required for manufacturing Egyptian blue are involved in the raw materials of faience; the pigment is composed during the firing process. The quality of the pigment material depends on the firing degree. Color alteration of Egyptian blue faience

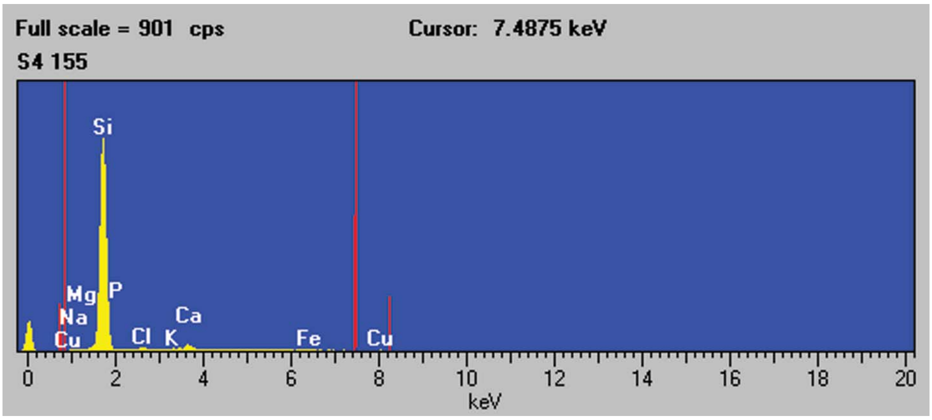

Figure 5d. Graph of SEM-EDAX spectra of the rendering layer upon which the glaze layer was applied in sample 1d (color figure available online).

depends on the presence of the water-soluble salts in conjunction with Egyptian blue and its ability to discolor according to bronze disease. The discovery of faience glazing has tentatively been associated with the copper industry. Bronze scale and corrosion products of leaded copper objects are found in the manufacture of faience pigments (Kaczamrcyz and Hedges, 1983). Davidovits and Davidovits (2004) presented a study noting a large variety of firing degree in the manufacturing process ranging from 250° C to 800° C. They further noted that the processing temperature never reached 900–920° C although even 800–850° C was difficult to imagine in the particular task of manufacturing 36000 tiles as kilns and fuel were not developed in that period of Egyptian history. They ascribed the discoloring phenomenon to that cause (firing degree). The study of Sheigel et al. (1989) was very important in declaring that the color alteration of the blue pigments indicates precipitation from migrating solutions after removal of copper and chlorine from the pigment layer. Copper chloride occurs as pseudomorphs after rhombohedral crystals of calcite with all stages between incipient and complete replacement. Sheigel et al. further concluded that all tiles were originally deep blue in color, and that green faience did not exist in the Old Kingdom. Sheigel et al. also noted that the color alteration of blue faience is the same as color alteration of blue pigments in the tombs and the temples, but did not mention if Egyptian blue was a dominant compound of the glaze layer or not.

The principal blue pigment in ancient Egypt was Egyptian blue, which is a synthetic pigment made by heating together silica, copper alloy filings or a copper ore such as malachite, lime (calcium oxide), and an alkali such as potash or natron $Na_2CO_3.NaHCO_3.2H_2O$ (Lee and Quirke, 2001). The pigment can be manufactured nowadays according to Canti and Heathcote (2002) by grounding 18 g of black copper oxide (CuO), 14 g of calcium carbonate, 60g of silica (diatomite), and 8 g of sodium carbonate together. The resultant grey powder is then fired at 850° C for 4 hours, forming a weakly sintered dark grey mass. This mass should be reground and fired at 850° C for 4 hours, followed by a refiring process at 950° C for 2 hours and further at 850° C for 5 hours. The result is a deep blue mass of crystals. These crystals should be soaked in a strong HCl solution to clean off dark residues. The working temperature must be kept between 850° C and 950° C according to a general agreement (Mazzocchin et al. 2004); however Pagès-Camagna and

Colinart (2003) noted that to produce an ideal Egyptian blue the mixture must be heated at between 870° C and 1080° C. Although Spurrell (1895) detected the presence of azurite blue pigment in three examples, no more recent corroboration of his findings (Lucas, 1962) was made eventually due to the poor quality and impermanence of azurite as pigment (Blom-Böer, 1994). Uda et al. (2002) referred to Amarna blue as a blue pigment which is believed to have been used only in the 18th and 19th dynasties, circa 1500–1200 BC; however, due to the rarity of findings, it cannot be classified as a source of blue in ancient Egypt.

Previous authors declare that Egyptian blue appeared in Egypt as early as the 4th dynasty (Lucas, 1962). However, the Max-Plank project identified it as the blue pigment in all analyzed samples dating back to the period from the 5th dynasty to the Roman period (Lee and Quirke, 2001). The present study proves that the Egyptian blue has been in use as the main source of blue pigment in Egypt since the 3rd dynasty in the south tomb of King Djoser. Turquoise was also used in conjunction with Egyptian blue, but the latter represents the dominant blue pigment component in all the studied samples. The detection of halite in some of the studied samples (sample 1 in addition to the collating mortar samples) explains the color change phenomenon of the blue faience since salt crystallization is the main conservation problem in Saqqara area, particularly in the King Djoser's complex. Geologically, salt veins are a common formation in the rocks into which this tomb was hewn.

Color alteration is a common phenomenon in ancient Egyptian blue faience. The presence of chlorides catalyzes the decay process and causes what is known as *bronze disease*. This catalysis is confirmed by the results of the SEM-EDAX analysis, which revealed the presence of almost the same amount of chlorine (Cl) in the four studied samples. 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, $CaCu(Si_4O_{10})$ as a pigment material. Schiegl (1991) and Schiegl et al. (1992) ascribed the color change phenomenon of the Egyptian blue into green color as "copper chloride cancer" (p. 398) for that reason. These researchers noted that, in the presence of chloride salts, the Chloride salt reacts with Cu which is added to the pigment's alloy, forming green copper chlorides "green atacamite $[Cu_2Cl(OH)_3]$ and paratacamite" (p. 398), which is the case of samples 1 and 4 (in which the amount of EB is lower than in samples 2 and 3). As a result of the migration of Cu and Cl ions in the NaCl solution, this process precipitates atacamite, which changes after losing water to a powder of paratacamite, or to a new pigment material known as *wollastonite green* $(CaCu)_3(Si_3O_9)$. The discoloring here is due to the instability of the Egyptian blue pigment in the glassy phase, which results from the increasing amount of silicate in the alloy.

Basic copper paratacamite or atacamite were found in green pigment samples collected from surfaces as late as the end of 12th dynasty. However, recent investigations led to the conclusion that atacamite may be a degradation product of artificial copper pigments, and that only a few examples of green earlier than the new kingdom were applied as green (Lee and Quirke, 2001). Chemically, salts in reaction with the pigment components play a catalyst role in the discoloring phenomenon.

5. CONCLUSION

Based on the results of both XRD and SEM-EDAX analyses, it has been concluded that EB is the dominant pigment material in the glazed layer of the studied faience samples.

Turquoise was also used in conjunction with EB. The present study proves that Egyptian blue was used as the main source of blue pigment in Egypt starting from the 3rd dynasty in the south tomb of King Djoser; these results are contrary to results mentioned in previous studies (Lucas 1962, Lee and Quirke, 2001). 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 detection of halite in some of the studied samples (sample 1 in addition to the collating mortar samples) explains the color change (or discoloring) phenomenon of the blue faience. Paratacamite as a deterioration product of that phenomenon was detected in both sample 1 and sample 4. The core of each studied sample has a different composition; however, quartz represents the dominant component in all four core samples. Sample 4 shows the presence of quartz only (100%) and SEM-EDAX detected 7% iron in the core of sample 3.

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