Geopolymer Institute
2004

Geopolymer Institute, 16 rue Galilée,
F-02100 Saint-Quentin, France
www.geopolymer.org

Paper presented at the IX. International Congress of Egyptologists,
Grenoble, France,
September 6-11, Session 12.2
for publication in the Proceedings

Why Djoser's blue Egyptian faience tiles are not blue?

Manufacturing Djoser's faience tiles

at temperatures as low as 250°C?

by
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Selected blue faience tiles from Djoser's Pyramid, Saqqarah, 2700 B.C.
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Abstract

30,000 blue faience tiles were found in Djoser's funerary complex at Saqqarah (3. dynasty). It is generally assumed that the tiles underwent a self-glazing process during firing in the range of 800-850°C (C. Kieffer and A. Allibert, 1971) or by dipping in a liquid glaze (S. Schiegel, 1988). SEM microanalysis shows the presence of phosphorus in the glaze that suggests the use of the blue mineral turquoise (*mafkat*), an aluminium-copper phosphate, intensively extracted by pharaoh Djoser in the Sinai mines. Our aim was to replicate the self-glazing process with a soluble silicate binder involving a synthetic turquoise (*mafkat*) mixture made of pure aluminium phosphate hydrate and copper phosphate hydrate. We were astonished to get a turquoise blue-self-glazed ceramic, stable and identical to Egyptian faience, at a temperature as low as 250°C. Post treatment at 350°C changes the blue colour into grey-black (chemical transformation of blue copper phosphate into black tenorite CuO) that remains stable up to 800°C, where it turns back to blue. Did Djoser's ceramists use this low temperature process? Apparently yes, if we look at the colours of the tiles. It is striking to notice that in

contrary to their labelling, numerous Djoser's tiles are not blue but grey, black, blue-green and even brown, colours that we have replicated at self-glazing temperatures in the range of 250-350°C..[1]

Figure 1: Djoser's tiles are not blue but grey, black, green, blue-green and even beige. New York, Metropolitan Museum of Art 48.160.1

Introduction

There are three techniques for making faience: Application, Cementation, and Efflorescence. Application is to apply 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 which partially melts on heating. The powder reacts with the surface of the quartz core and so glazes it, though powder not in contact with it remains unaffected. The last one, the efflorescence technique, is unique in combining the glaze mixture in the core. Water-soluble alkali salts probably in the form of natron (sodium alkali) or plant ash (potassium alkali) are mixed with the siliceous core. The mixture of these ingredients is moistened and formed into a desired shape. Then, in the process of drying, the salts migrate to the surface of the object to form an efflorescent bloom. When fired at high temperature, usually above 1000°C, this layer melts and fuses with the fine quartz, copper oxide or lime to create a glassy coating. The latter method is regarded as self-glazing process.

The self-glazing-efflorescence technique was probably discovered by chance in the chalcolithic period around 3000 B.C. by the copper smiths or potters who were also dealing with the extraction of other copper containing ores, such as *mafkat*

[1] The present authors must express their sincere gratitude to the Geopolymer Institute, Saint-Quentin, France (www.geopolymer.org) for providing the financial support for the author's attending the Congress. The opportunity to perform the experimental parts of the study was afforded to the authors by the Laboratoire de Recherche sur les Nouveaux Matériaux at Cordi-Géopolymère, Saint-Quentin, France.

(turquoise). Microscopic investigations as well as x-ray diffraction analysis show that the body of the tiles is made of quartz, exclusively. On the other hand, crystobalite and tridymite are always absent. According to C. Kieffer and A. Allibert[2], the absence of these two high temperature SiO2 varieties demonstrate that the processing temperature never reached 900-920°C. It was always postulated that enameling had to occur above 1000°C[3].

But even more moderate temperatures in the range of 800-850°C are difficult to imagine in the particular task of manufacturing 36 000 tiles. The manufacturing process would have involved several industrial kilns that are not found during this period. There are also other riddles to be solved. If we admit that the self-glazing results from the efflorescence of soluble elements, we can trust chemistry to provide the right answer for the alkali salts that are all water-soluble. Yet, it is also stated that copper salts would also migrate. As far as we know, natural copper salts such as carbonate (malachite, azurite), phosphate (turquoise), silicate (chrysocolla), arsenate (olivenite) are not soluble in water. Otherwise, these minerals would not exist as copper ores. In order to render these copper salts soluble, they must undergo a chemical reaction; the latter is hard to imagine for the craftsman of the 3rd millennium B.C.

Scientific investigation shows water in the glaze

S. Schiegel presented an interesting study in 1988[4]. On faience tiles from the walls of Djoser's south tomb in Saqqarah, he prepared several cross-sections vertical to the glaze through the tile for microscopic and microchemical studies. The texture of the quartzite core and the glaze were systematically investigated using scanning electron microscopy. Chemical composition of the glaze layers was determined using energy dispersive and wavelength dispersive techniques with fully automated computer controlled electronprobe microanalyser. In his paper, he states:
"*The average glaze composition is mainly SiO2, CuO and water (13% by weight) with a minor degree: alkalis, iron, phosphorus, chlorine*".

When this investigation was presented at the Vth Int. Congress of Egyptology, Cairo, nobody in the attendance paid attention to the real meaning of this analysis. It is only recently, in 2002, that within our research work carried out on geopolymers of the alumino-silicate types (Si-O-Al-O-Si-O)n, we came back to this paper[5]. We have been struck by the presence of water: 13 % by weight. Where is the water coming from, if the glaze resulted from a process involving firing temperatures as high as 800-850°C?

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[2] Charles Kiefer and A. Allibert, Pharaonic Blue Ceramics, The Process of Self-Glazing, Archaeololy 24, pp. 107-117, 1971.
[3] Kyoko Yamahana, Synchrotron Radiation Analysis on Ancient Egyptian Vitreous Materials, Proceedings of the 25th Linear Accelerator Meeting in Japan (July 12-14, 2000, Himeji, Japan) [13C-01].
[4] S. Schiegel (1988), Vth Int. Congress of Egyptology, Cairo. Abstract of Papers, page 242-243, Investigation on faience tiles from the walls of Djoser's south tomb in Saqqarah: an approach to reveal the technique of their manufacture.
[5] Information on geopolymer chemistry may be downloaded from the Geopolymer Institute internet site at www.geopolymer.org

The only logical answer to this matter of fact suggests the use of a low temperature processing, involving temperature below 300°C, i.e. temperatures below the degradation of combined water.

A low-temperature self-glazing process involving *mafkat*

Because the above analysis found phosphorus, we made the assumption that the copper ore exploited for the making of the tiles could have been one of the *mafkat* minerals heavily exploited in the Sinai Mines during that time. The phosphorus element would generate from turquoise, a hydrated aluminum-copper phosphate, whereas additional copper would be provided by chrysocolla, a hydrated copper silicate, of the same blue-turquoise color as the genuine turquoise and very often confused with it.

It is well established that the *mafkat* mines were heavily exploited before, during and after the time of pharaoh Djoser. Yet, as S. Aufrère pointed out [6]:
« ...*Despite any rational exploitation of Mafkat, which must have run to very high quantities, there exists very few items made of turquoise (Mafkat) in the museums … we have only a trivial amount (very few) of turquoise items found by archaeology when compared with the extravagant mining expeditions undertaken at great expenses, lot of personal and equipment...*»

It seams therefore obvious that the enormous quantities of *mafkat* extracted in the mines could have been precisely used in the manufacture of the 36 000 tiles adorning the subterranean chambers of Djoser's Step Pyramid complex at Saqqarah.

Experimental method

The aim was to replicate the self-glazing process with modern soluble silicate, SiO2,K2O,Na2O and a synthetic turquoise (*mafkat*) comprising a mixture of aluminum phosphate hydrate, copper phosphate hydrate.

To a water soluble Potassium Silicate solution, molar ratio SiO2: K2O = 12:2, was added Aluminum Phosphate hydrate (5% by weight) and Copper Phosphate hydrate (4% by weight). Hardening (curing) was carried out at 60°C during 3 hours, in a closed container. After demolding, the sample was dried 1 hour long at 80°C, then heated up to 250°C, during 30 minutes. Figure 2 shows the principal results. In 2a, the sample did not contain any aluminum phosphate. It is intense blue and shows no self-glazing at all. Fig 2b shows the core of the sample after hardening and drying at 80°C. The color of the core is evenly light blue, with no migration. The migration and self-glazing occurs above 200°C, Figure 2c. The core is white and the glaze is turquoise-blue.

[6] Sydney Aufrère, L'univers Minéral dans la Pensée Égyptienne, IFAO, 1991, Vol. 2, p. 294.

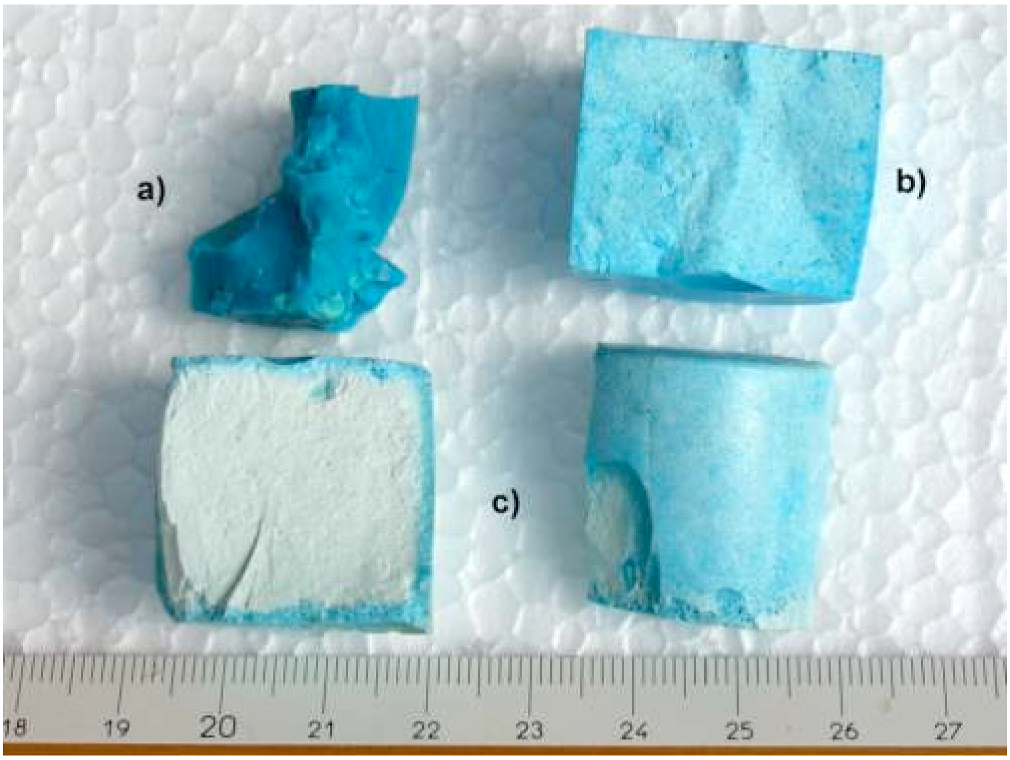

Figure 2: blue glazing (c) obtained above 200°C

The composition of the glaze has been determined with SEM-EDS (Figure 3).
The turquoise blue pigments are embedded in a matrix that has the chemical composition of a geopolymer of the type (K,Na)-Poly(Sialate-decaSiloxo), (Si-O-Al-O)-(Si-O-)$_{10}$ The matrix is similar in composition to the glaze previously analyzed by S. Schiegel.

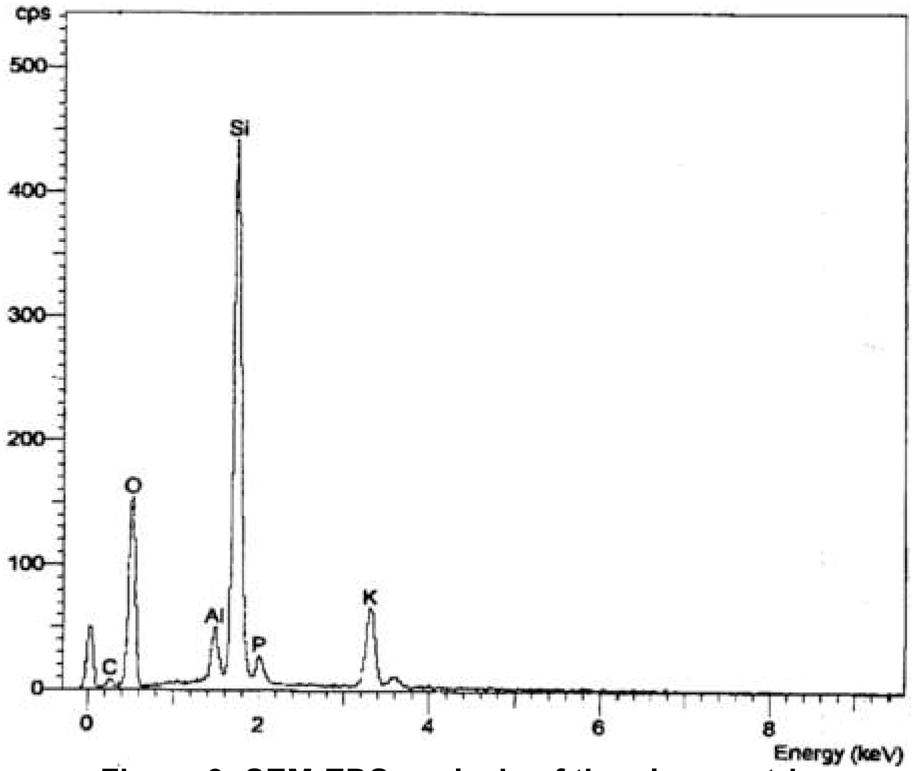

Figure 3: SEM-EDS analysis of the glaze matrix

What about black, grey, green, beige faience

We know that only small amount of Djoser's faience tiles exhibit the turquoise blue glazing. The general trend is towards green, grey-green, sometimes black, and also beige. We got a green glaze when sodium (Na) was used instead of potassium (K) (Figure 4)

Figure 4: the manufacture of blue, green, grey, black, beige glaze.

We were astonished to find that a post treatment at 350°C changes the blue or green color into grey-black (chemical transformation of blue copper phosphate into black tenorite CuO), see in Figure 5.

The black CuO tenorite remains stable up to 800°C, where it turns back to blue. In fact these results were obtained in an electrical oven with exact temperature driven device. Replication of the heat treatment performed in a ceramic kiln with a more crude temperature regulation, where the temperature may vary between 250 and 400°C (depending on the position of the samples in the kiln), provided mixed colors, grey-blue, black-blue. It is therefore obvious that in the case of heat treatment occurring in an open wood fire with flame, where the temperatures may be in the range of 200 to 400 °C, the manufactured tiles could exhibit grey-black spots or areas. As for the beige color, some iron phosphate minerals are naturally blue and could have been mistaken for turquoise. In that case, the glaze turned into beige instead of green or blue. Did Djoser's ceramists use this low temperature process?

Figure 5: heat-treatment above 350°C transforms turquoise-blue into black CuO, tenorite, with the exception of iron-phosphate that remains beige.