# Egyptian Blue and Green Frit :

# Characterization, History and Occurrence, Synthesis

*Abstract*

The two pigments Egyptian blue and green frit form a unit in technology and history. This paper will give the evidence for the close connection between the pigments.

First they will be characterized to give an idea of the technological process which leads to those products and their synthesis (Chapter 3). The chapter about their occurrence means to give an impression of the immense importance especially of Egyptian blue in history until the end of the Roman empire, and of the discovery of antiquity during the last 150 years.

## 1. Characterization

### *a) Egyptian blue*

Egyptian blue is a crystalline substance with the formula $CaCuSi_4O_{10}$ = CaO-CuO-4$SiO_2$, and the mineralogical term « cuprorivaite ». The blue crystals grow in the form of rectangular squares, often in many layers (fig. 1). In the crystallographic nomenclature they are called « tetragonal bipyramides » (fig. 2), in the class of tetragonal sheet-silicates.

In most cases the crystals are flat and we can observe an overstressing of the 001-plane (see fig. 1). Because of the distinct habits of crystals one can estimate crystallographic data by X-ray diffraction, a method which is used routinely.

Another method to examine the phases is the remission spectroscopy or reflection spectroscopy. This method gives information about the inner binding forces of the crystals, and frequently also about the chemical basis for the colours. This method can be used for the determination of pigments on whole samples, it is a non-destructive method.

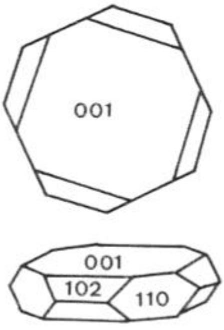


*Fig. 1. Idealized crystal of Egyptian blue.*

Other, more simple methods are optical ones, like microscopy (binocular) or polarized microscopy. In the latter the birefraction can be seen : blue or pale rose, depending on the position of the crossed nicols. With these methods a distinction between the crystals and the surrounding glass is possible. This glass is formed by the production method, which will be explained later. On the other hand one can see the difference to other blue pigments, as ultramarine is dark blue without birefraction, and azurite has a blue-green tint with only a little birefraction to green.

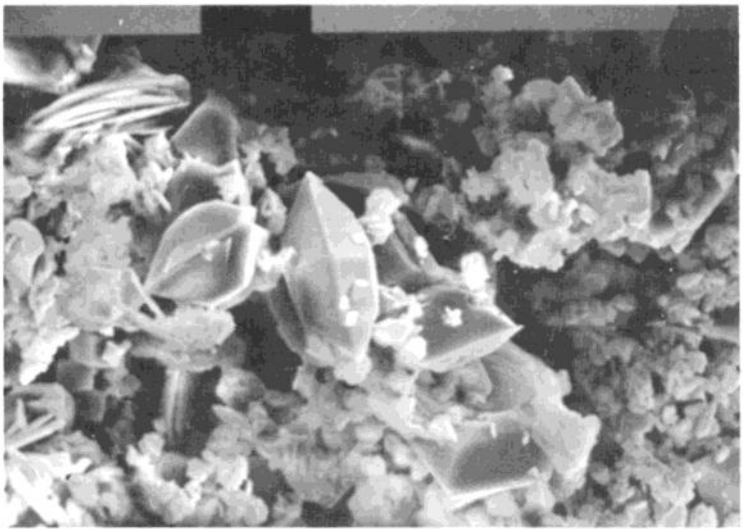

*Fig. 2. Crystals of Egyptian blue.*

All these methods of examination prove that the old term « blue frit » (or « pâte bleue ») is wrong, as « frit » means a raw product in glass manufacture without any crystal habit.

| d | 3.29 | 3.78 | 3.00 | 7.63 | $CaCuSi_4O_{10}$ |
|---|---|---|---|---|---|
| $I/I_1$ | 100 | 90 | 90 | 40 | Calcium Copper Silicate (Egyptian blue) |

Rad. CuKa λ 1.5405 Filter Dia.
Cut off $I/I_1$ Visual estimate
Ref. Pabst, Acta Cryst. 12 733 (1959)

Sys. Tetragonal S.G. P4/NNC (130)
$a_0$ 7.30 $b_0$ $c_0$ 15.12 A C 2.071
α β γ Z 4 Dx 3.09
Ref. Ibid.

ε α 1.591 n ω β 1.636 ε γ Sign -
2V D 3.06 mp Color Blue
Ref. Ibid.

May be equivalent to cuprorivaite.

| d Å | $I/I_1$ | hkl | d Å | $I/I_1$ | hkl |
|---|---|---|---|---|---|
| 7.63 | 40 | 002 | 1.970 | 20 | 314 |
| 5.22 | 15 | 102,110+ | 1.890 | 15 | 003 |
| 3.78 | 90 | 004 | 1.831 | 60 | 108 |
| 3.66 | 25 | 200 | 1.784 | 40 | |
| 3.36 | 80 | 104 | 1.758 | 20 | |
| 3.29 | 100 | 202 | 1.704 | 40 | |
| 3.19 | 50 | 211 | 1.636 | 20 | |
| 3.05 | 40 | 114 | 1.603 | 40s | |
| 3.00 | 90 | 212 | 1.573 | 5d | |
| 2.736 | 5 | 213 | 1.528 | 10 | |
| 2.629 | 40 | 204 | 1.483 | 10 | |
| 2.585 | 40 | 220 | 1.462 | 5 | |
| 2.518 | 5 | 006 | 1.456 | 5 | |
| 2.471 | 5 | 214 | 1.435 | 5 | |
| 2.386 | 20 | 106 | 1.426 | 5 | |
| 2.321 | 30 | 302,310+ | 1.398 | 20 | |
| 2.270 | 50 | 116 | 1.380 | 20 | |
| 2.136 | 10 | 224 | 1.336 | 25 | |
| 2.069 | 5 | 206 | 1.315 | 10 | |
| 2.007 | 20 | 321 | | | |

*Fig. 3. ASTM-card with crystallographic data of Egyptian blue.*

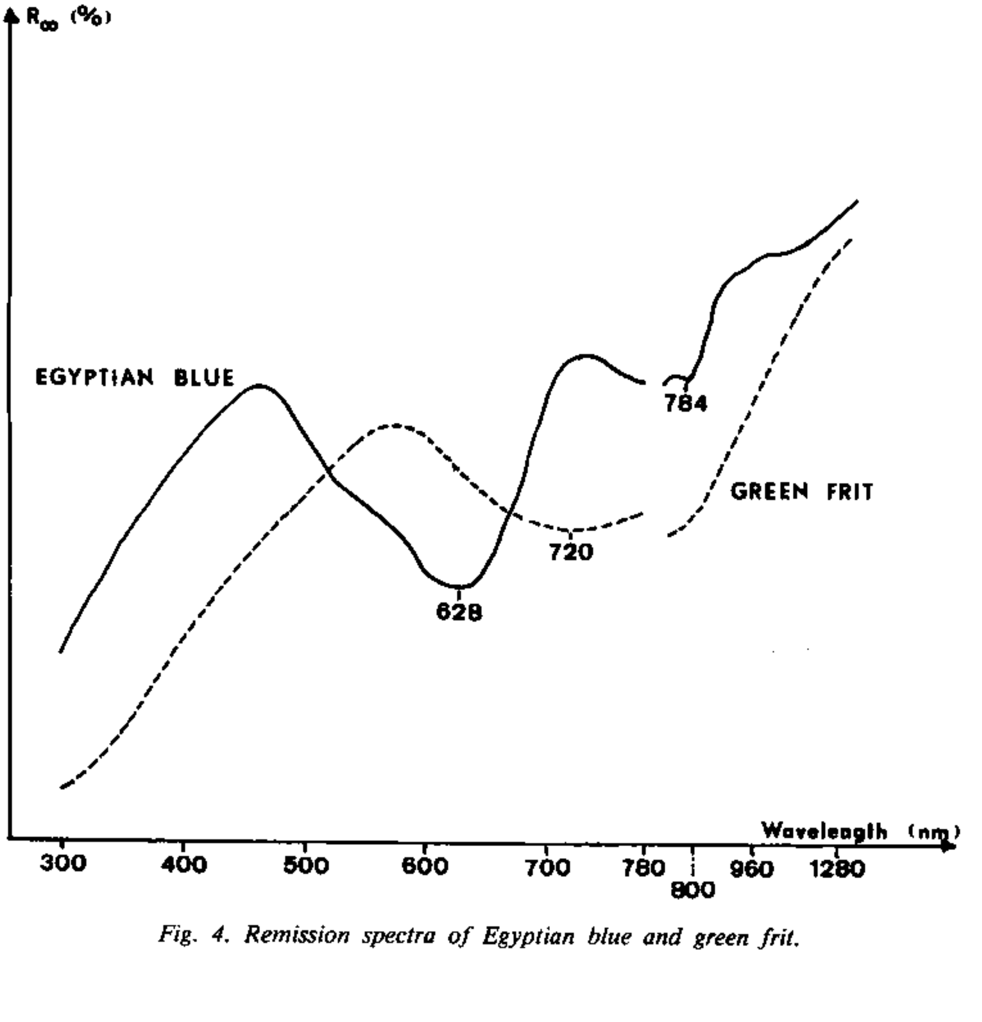


*Fig. 4. Remission spectra of Egyptian blue and green frit.*

*b) Green frit*

This pigment is more difficult to characterize as it is a glassy mass. Here the term « frit » is justified. Sometimes ground glass served as a pigment. The colour varies widely from olive-green to blue-green depending on the ingredients of the manufacture. The content of the elements silicon, calcium, copper, and sodium varies very much. Copper oxide can be found from 2 to 10 %, calcium oxide in the same range, but never in a high content in both oxides, as a ratio 1 : 1 would result in Egyptian blue. Sometimes Egyptian blue can be observed as single crystals in green frit.

*Fig. 5. Green glass as a raw pigment. Lyon, Rue des Farges, 1st century AD.*

The methods of examination are the same as for Egyptian blue. In X-ray diffraction the phase quartz may appear often or wollastonit ($CaSiO_3$) sometimes, while the remission spectrum gives a curve similar to copper glass (fig. 4). As stated before, this green frit has major glass phases, the microscope cannot give sufficient information, as glass is isotropic. Because of these difficulties the literature comes to different conclusions as regards « copper borate », « chrysocolla », « copper compound ». I assume that in most cases these pigments are green frit.

## 2. History and occurrence

Egyptian blue appears as a pigment during the 4th dynasty in Egypt (2.500 B.C.) as coloration of the « pyramid texts ». In Mesopotamia we can suppose an invention at the same time, perhaps even earlier, as the finds of shells with pigments from Kish suggest. We can only speculate about how this invention came about. The earlier steps are glazed steatite and Egyptian faience (quartz body with glaze). Along with this, copper becomes an important material ; a technique for melting this metal was developed some time earlier. As one needs about 10 % copper besides calcareous sand and melting materials (flux), I think that the pigment Egyptian blue had its first technological position between glazes and copper melting. Green frit was « invented » some time later, during the 6th dynasty.

Another proof for this statement are the (later) cuneiform glass texts from the library of Ashurbanipal (8th century B.C.), which are certainly of an earlier origin. There Egyptian blue (« ᵃuknu ») is the last stage of a series of production steps, from semi-molten frit via blue glass. In every step the glassy mass was ground to give a better reaction and mixed with additional copper and calcium compounds. So at the last step one got the high content of 10 % CuO and 10 % CaO.

The reason for the rare finds of applied Egyptian blue in Mesopotamia is the bad preservation of wallpaintings due to the humid climate in comparison with the dry climate of Egypt. The fact that there was an exchange between the two kingdoms is shown by the mention of « Egyptian blue from Bbr » as a tribute from Mesopotamia on Egyptian walls. The old Egyptian name « ḫsbḏ » was also used for lapis lazuli. This gives the impression that Egyptian blue (and later on blue glass) was an imitation of the precious stone from Badakhshan, which was the colour of divine hair in Egyptian and Mesopotamian mythology. Blue forms a contrast in colour to the brown land. The finds of Tell el-Amarna will be discussed in chapter 3. Egyptian blue and green frit were fixed with lime or plaster on walls, wooden objects, uncovered stone, and sometimes ceramics. They could be applied only cold, as they would result in a glaze when burnt. Both pigments were used with short interruptions until Roman times in Egypt and the Near East.

Greece imported Egyptian blue from Minoan times onward (« kyanos »). Romans distributed Egyptian blue across the whole empire, from Africa to Britain and Norway. Vitruvius, in his book « De architectura » describes the production of « caeruleum » : Sand, soda, and copper compounds are ground to fine powder, moistened and formed into balls (for details see chapter 3). These balls were heated after drying in pots. The factory of Vestorius at Napoli, where Vitruvius had observed this procedure, had produced glass also. As the factory is situated at the Volturnus river, calcareous sand must have been used. This fact was missed by Vitruvius and later transcribers in medieval times only got green frit by using this recipe.

The pigment Egyptian blue vanished mainly with the end of antique traditions and technology during the 4th century AD. After the present state of research the Byzantine world yielded only a poor quality of Egyptian blue (Sardis, 6th century AD). Another « island » of further employment is northern Italy and the Alps until the 9th century AD. The penetration of Islam caused the change to ultramarine. This pigment, made from lapis lazuli, was first used ca. 500 AD in central Asia, where it is found. In Ktesiphon it had been excavated in layers of the 6th/7th century, and in Europe according to our present knowledge we find it used first at the beginning of the 12th century. This gap will, it is hoped, be filled by further investigations by the author. A usage of ultramarine before the 5th century AD cannot be assumed, as no-one would grind the very precious stone lapis lazuli to get a blue pigment, when Egyptian blue was more easily obtained.

After checking the adverse statements given in the literature, I was able to prove that these opinions must have been based on only a cursory glance. Examples are : the sarcophagus of Aghia Triada (Crete), Etruscan wallpaintings, and pigments from Khorsabad, Mesopotamia.

Another use should be noted : objects made of Egyptian blue. These vessels, small figurines, beads, cylinders, and parts of divine statues appeared in two periods : from 14th to 12th century B.C. and 9th to 5th century B.C. Some of the objects were exported, like a pyxis which was found in Vulci in Etruria. This vessel, which is now in the Antikenmuseum in West Berlin, has its origin probably in Syria/Palestine in the 8th century B.C.

*Fig. 6. Beaker from Ashur ca. 13th century B.C.*

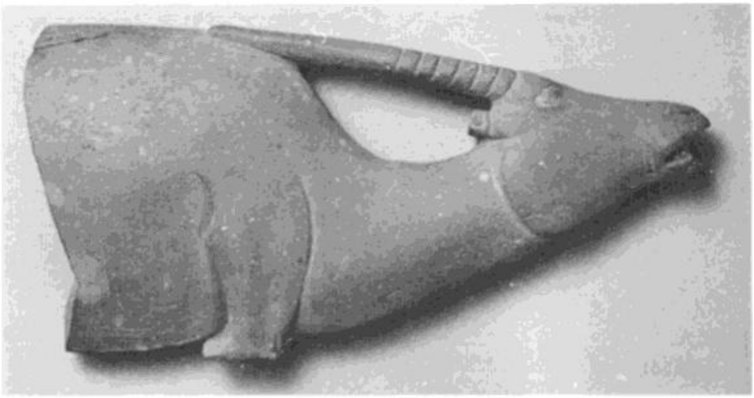

Fig. 7. Palette, 18th dyn., Egypt (Christie's auction, 1985).

## 3. Synthesis

Since Egyptian blue was an important pigment in Antiquity, it has been studied for a long time. With the increase of interest in Antiquity Chaptal started about 1804 and Sir Humphrey Davy investigated it in 1815. In the 1880s, mineralogists in France became interested in it, and in 1889, Fouqué established the composition as the calcium copper tetrasilicate $CaCuSi_4O_{10}$. He also synthesized the mineral. The best approach to antique fabrication was given by Laurie, McLintock and Miles in 1914. The crystal structure was determined in 1959 by A. Pabst. In the last 10 years diverse experiments for the reconstruction of ancient manufacture have been made. Many details were cleared up, but some aspects are still open for investigation.

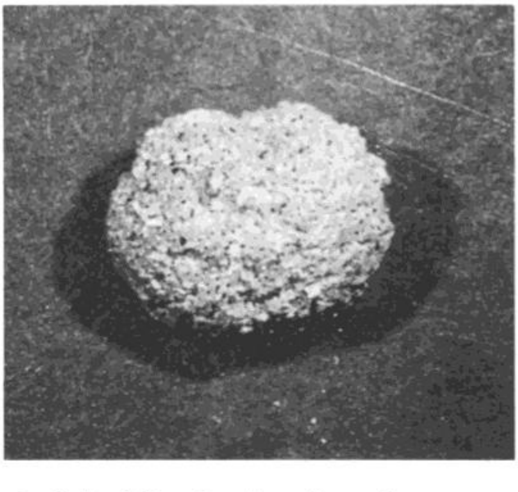

Fig. 8. Ball of Egyptian blue, Lyon, 1st century AD.

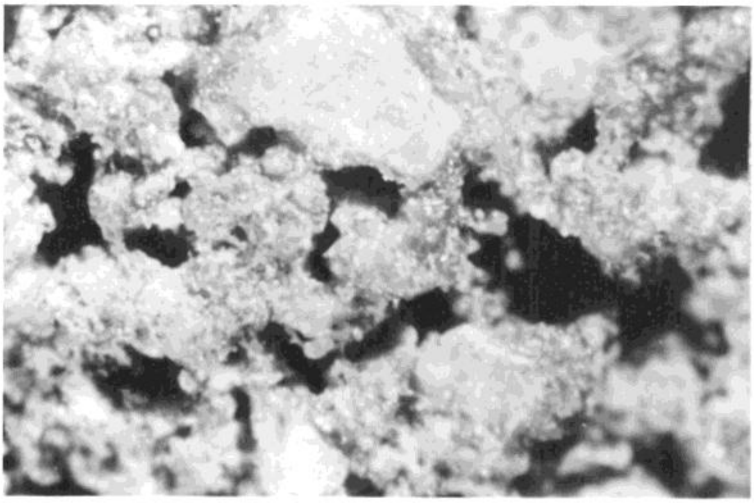

*Fig. 9. Ball of Egyptian blue (the same as fig. 8), quartz grains (white) with surrounding Egyptian blue.*

The quite frequent finds of raw pigments give an idea of the material used in Antiquity. Some are prepared by mixing with lime in pots, but the unground balls of Egyptian blue of the Roman time bear more information about the ancient technology. They show that Vitruvius' description gave a true account.

In Egypt the pigments were produced in crucibles, as the finds of Tell el-Amarna show. This archaeological material from a glass factory excavated by W.M.F. Petrie includes lumps of frit, raw glass, glass rods, green frit, and Egyptian blue, sometimes still in their crucibles. This strengthens the hypothesis that glass, green frit, and Egyptian blue were produced at one factory. In the Roman empire this makes sense, as a production at different places is cheaper than a longdistance transport of raw pigments. Taking into account all these indications I have reconstructed the process by which Egyptian blue was created. Its composition consists of quartz (in the form of sand), lime (either as limestone or lime-containing sand), copper compounds (copper ores or bronze waste), and, as melting agent, natural soda from Wadi Natrun in Lower Egypt (with different sodium compounds). These raw materials should be ground to a fine powder and mixed in the ratio 5 : 2 : 2 : 1. After heating the mixture in a crucible at a temperature of 900°-950° C for 24 tot 48 hours, a glassy mass, intensive blue in colour, results, of which a high proportion is Egyptian blue. If this mass is ground and tempered again, the proportion of Egyptian blue increases, and the colour intensifies.

Analysis of pigments from various sources suggests that Egyptian blue can also be obtained via the intermediate stages of semi-molten frit, glass, and the pigment itself, as described in the cuneiform texts.

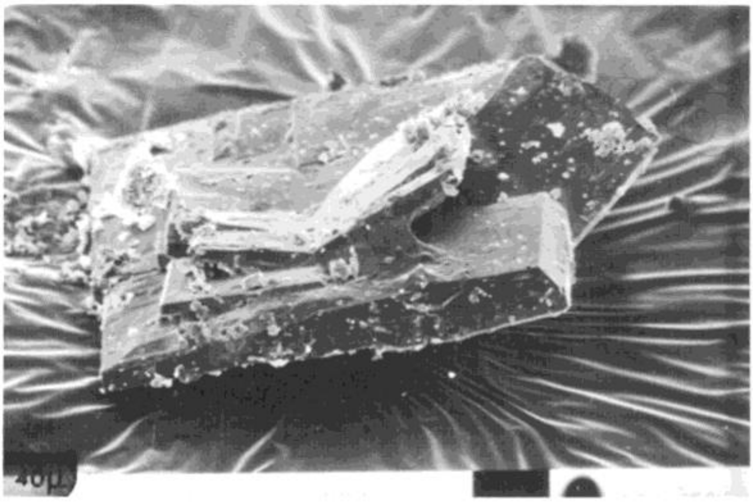

*Fig. 10. Egyptian blue crystal, obtained by hydrothermal growth.*

If the temperature exceeds 1000° C and/or a reducing atmosphere exists (*i.e.*, if the fire smokes inside a closed kiln), the green frit may be obtained by « misburning ». If the ratio of lime to copper is not 1 : 1, green frit is also produced.

To manufacture Egyptian blue, a steady supply of oxygen is essential ; thus production in an open crucible is not only possible but desirable. It is crucial to maintain a constant temperature over the entire production period, such as could be achieved by blowing air into the crucible.

In chemistry this process is called « diffusion in melts », as we can observe melted rims around quartz grains, where the reaction to Egyptian blue takes place. This is the scientific explanation for the connection of glass and Egyptian blue or green frit.

When a painter used the pigment, he controlled the colour by grinding ; coarsely ground Egyptian blue yields a dark shade ; finely ground, a lighter tone.

For objects Egyptian blue was ground and reheated in a mould, sometimes with an inner core, which was scratched off as used in the sand more technique for glass vessels in Egypt. In a final step the object is carved.

Single crystals of Egyptian blue can be obtained by the hydrothermal crystallization method, where water is heated under pressure of some kbar (1 kbar = 1000 bar, 1 bar = atmospheric pressure) to temperatures around 400° C. This is a process which possibly gave the natural, single crystals at Vesuvius in Italy.

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