

The production technology of Egyptian blue and green frits from second millennium BC Egypt and Mesopotamia

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Abstract

The microstructures and chemical compositions of some 55 Egyptian blue and green frit samples from New Kingdom Egypt and 15th century BC Mesopotamia are determined using analytical scanning electron microscopy, the main focus being on frit cakes, powder residues, and frit vessel and bead fragments from one of the “factory areas” at Amarna in Middle Egypt. Replicate Egyptian blue frits produced in the laboratory are similarly investigated. Comparison of the microstructures of the ancient and replicate samples suggest that frit cakes are the primary product, and that these were ground to produce the powder, and then moulded to shape and refired to produce the vessels and beads. Egyptian blue and green frits are shown to be distinct pigments, the pigment produced depending on the relative proportions of copper oxide and lime in the mixtures. The bulk and glass phase compositions are used to try to infer the different sources of the quartz, lime, copper and alkali flux used in the production of frits from Egypt and Mesopotamia. An estimate is made of the scale of production of Egyptian blue frit in New Kingdom Egypt. © 2007 Elsevier Ltd. All rights reserved.

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1. Introduction

Egyptian blue frit is a multicomponent material that was produced by firing a mixture of quartz, lime, a copper compound and an alkali flux to a temperature in the range 850–1000 °C (Ullrich, 1979: 56; Tite et al., 1984). Its principal components are calcium-copper tetrasilicate crystals (i.e. $\text{CaCuSi}_4\text{O}_{10}$, cuprorivaite), which produce the blue colour, and partially reacted quartz particles bonded together by varying amounts of glass phase. Related to Egyptian blue frit is a green frit which was produced by firing a similar mixture of quartz, lime, a copper compound and an alkali flux to a temperature in the range 950–1100 °C (Pagès-Camagna and Colinart, 2003). However, in contrast to Egyptian blue frit in which the copper oxide content (CuO) normally exceeds the lime content (CaO),

the lime compound normally exceeds the copper oxide content in the green frit. In addition the alkali content tends to be higher in the green frit. In terms of microstructure, the green frit consists of a glass phase, from which wollastonite (CaSiO_3) and a high temperature polymorph of silica have crystallised, together with partially reacted quartz particles. Green frit exhibits a range of colours from green through turquoise to pale blue, and as a result, has been variously referred to as turquoise frit (Hatton, 2005) and pale blue frit (Tite, 1987).

Both Egyptian blue and green frits were used predominantly as pigments, and to a much lesser extent, for the production of small objects. In Egypt, the earliest surviving use of Egyptian blue frit was possibly in the painting from Tomb 3121 at Saqqara which is dated to the reign of ‘Ka-sen’ who was the last king of the 1st Dynasty (i.e. circa 2900 BC). However, the use of Egyptian blue frit in Egypt only became widespread by the 4th Dynasty (i.e. circa 2600 BC), after which its use continued through until the Ptolemaic-Roman period. Egyptian

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blue frit was also probably first used at much the same period in Mesopotamia, the evidence being provided by Early Dynastic III beads from the Royal Cemetery at Ur (Moorey, 1994: 187). The green frit seems to have been confined almost entirely to Egypt where it was first used in tomb paintings at the beginning of the 18th Dynasty and then continued in use into the Roman period (El Goresy, 2000).

The physical processes involved in the production of Egyptian blue frit and green frit have been investigated by means of a combination of examination by scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD) of laboratory replicate samples fired to progressively higher temperatures (Pradell et al., 2006; Pagès-Camagna and Colinart, 2003). These studies have established that, in both cases, a liquid phase is formed from which, respectively, Egyptian blue crystals ($\text{CaCuSi}_4\text{O}_{10}$), or crystals of wollastonite and high temperature polymorphs of silica (i.e. tridymite or cristobalite) nucleate and grow.

For the Ptolemaic-Roman period, we have a description of the manufacture of a blue pigment, which is clearly Egyptian blue frit, given by Vitruvius (Morgan, 1960) at the beginning of the 1st century BC in the Ten Books of Architecture. In addition, there is the production debris resulting from the manufacture of Egyptian blue frit at the site of Memphis, near Cairo, that dates to somewhere in the period from 3rd century BC to 3rd century AD. The factory area at Memphis was excavated by Petrie (1909) in the early 1900s, with further recent excavations by Nicholson (2003). This debris consists of ceramic vessels that are lined with a white slip to which a layer of Egyptian blue frit adheres. Embedded in this layer are small balls of Egyptian blue frit, up to about 15 mm in diameter. The production debris excavated from Memphis is consistent with the description of the manufacture of Egyptian blue frit given by Vitruvius in which the mixture of raw materials “is made into balls” and “The dry balls are put in an earthen jar, and the jars in an oven.” Further, on the basis of the chemical composition and microstructure of the Egyptian blue frit layer and balls, Tite and Hatton (2007) have established that the Memphis frit was made from a mixture of sand, leaded bronze scale and natron. This mixture is again consistent with the description given by Vitruvius who states that:

Sand and the flowers of Natron are brayed together so finely that the product is like meal, and the copper is grated by means of coarse files over the mixture, like sawdust, to form a conglomerate.

For the earlier periods, an extensive range of Egyptian blue and green pigment samples from wall paintings from Egyptian tombs and temples have been analysed (El Goresy et al., 1986; El Goresy, 2000; Pagès-Camagna and Colinart, 2003), together with a smaller group of Egyptian blue frit objects from both Egypt and Mesopotamia (Tite et al., 1984). However, there has, as yet, been no systematic scientific examination of material from an early site at which production debris associated with the manufacture of Egyptian blue and green frits survives.

The primary focus of the present paper is, therefore, the scientific examination of a group of Egyptian blue and green frits

from the New Kingdom site of Amarna in Middle Egypt which was occupied for a short period (second half of 14th century BC) during the 18th Dynasty. During the 19th century AD, Petrie (1894) identified and excavated some six or seven “factory areas” associated with the manufacture of glass and other vitreous materials, and one of these areas has been recently re-excavated by Paul Nicholson on behalf of the Egyptian Excavation Society (Nicholson, 2007). Together with evidence for faience production, and glass working and possibly glass production, which has been examined by Tite and Shortland (2003), considerable debris associated with the production and use of Egyptian blue and green frits has also been found. This includes frit cakes, powder residues adhering to various ceramics fragments, and fragments of frit vessels.

A SEM with attached analytical facilities was used to determine the chemical compositions and microstructures of these Amarna frit samples in order to obtain information on the raw materials used to produce the frit cakes, and on the processing involved in the production of the pigments and frit vessels. Laboratory replicates of Egyptian blue frits were produced in order to help with the interpretation of the microstructures observed in the ancient frits. The data for the Amarna frits were supplemented by comparable data for Egyptian blue and green frit samples from other New Kingdom sites in Egypt, and from 15th century BC sites in Mesopotamia.

2. Experimental procedures

2.1. Samples

The 26 frit samples from Amarna that were examined included cakes, powder residues and vessel fragments of both Egyptian blue frit (14 samples) and green frit (12 samples). The frit cakes are generally circular, no more than 100 mm in diameter and 20 mm in thickness, and similar to those described by Weatherhead and Buckley (1989). The powder residues are found inside small ceramic vessels or as thin layers adhering to ceramic fragments. The frit vessel fragments examined were too small to establish the original size and shape of the vessel. However, judging by surviving complete vessels and larger fragments, most Egyptian blue frit vessels were smaller than 100 mm in height.

The other New Kingdom frit samples from Egypt included 18 cakes of both Egyptian blue and green frits from Thebes (18th Dynasty), Karnak (18th Dynasty) and Zawiyet Umm el-Rakham (19th Dynasty), and a single Egyptian blue frit bead from Zawiyet Umm el-Rakham. The frit samples from Mesopotamia, which date to the 15th century BC, included two cakes and six beads of Egyptian blue frit from Tell Brak and Tell Rimah.

2.2. Determination of microstructures and chemical compositions

The Egyptian blue and green frit samples were all examined in polished cross-sections in a Cameca analytical SEM

(SU30) using the backscatter detector mode (BSE) with which the different phases present can be distinguished on the basis of their atomic number contrast (e.g., quartz appears dark compared to the higher atomic number Egyptian blue crystals and glass phase). For the Egyptian blue frits from Amarna, the minimum and maximum lengths of the Egyptian blue crystals, and diameters of the partially reacted quartz particles were estimated from the SEM backscatter images (Table 1). The relative percentages of Egyptian blue crystals and partially reacted quartz particles were also estimated by image analysis of the backscatter image (Hatton, 2005:41).

The bulk compositions of the frit samples were determined by analysing areas approximately 0.3 mm × 0.3 mm using the energy dispersive spectrometer (EDS) attached to a JEOL SEM (JSM-840A) (Tables 2 and 3). The instrument was run at 15 kV and 5 nA. The resulting analytical totals were normalised to 100% to eliminate the effects of differences in porosity. Because of the overlap of sodium and copper peaks, the measured soda contents are too high. Also, because of overlapping peaks, the detection limit for tin is no better than 0.3 wt% SnO₂, otherwise the detection limits are around 0.1 wt%. The relative errors are 5–10% for major and minor elements, and up to 15% for elements present at the 1% or less level.

The glass phase when present in the frit samples was analysed using wavelength dispersive spectrometers (WDS) attached to a JEOL superprobe (JXA-8800R) (Tables 4 and 5), which had been calibrated using appropriate primary standards. The instrument was run at 15 kV and 5 nA with a spot size of 5–8 μm and a 20 s count time per element. The sodium peak was the first to be analysed in order to minimise any loss of soda during analysis. The detection limits are around 0.05 wt%, and the relative errors on the analyses are in the range 2–5% for major and minor elements, and up to 10% for elements present at the 1% or less level. Because of the

small areas of the glass phase in the Egyptian blue frits, the analyses will often include adjacent Egyptian blue particles, and when this happens, the lime and copper oxide concentrations will be too high. Both before and after a series of analyses of ancient material, the accuracy of the system was checked by the analysis of the Corning A glass standard.

2.3. Laboratory replications of Egyptian blue frit

Two mixtures of quartz powder (~71 wt% SiO₂), copper(II) carbonate hydroxide 1-hydrate (i.e. artificial malachite) (~15 wt% CuO), calcium carbonate (~11 wt% CaO) and anhydrous sodium carbonate (~3 wt% Na₂O) were prepared. In the first mixture, the quartz was “coarse” grained (<500 μm; BDH Laboratory Supplies, Poole, UK), and in the second mixture, the quartz was “fine” grained (<53 μm; Potclays Ltd, Stoke-on-Trent, UK). The quartz content of both mixtures was such that there was an approximately 25 wt% excess of quartz above that required to convert all the copper oxide and lime to the Egyptian blue mineral. The other raw materials all had a grain size of less than 53 μm, and were Analar chemicals (BDH Laboratory Supplies, Poole, UK).

These mixtures were pre-fired to 850 °C in order to decompose the carbonates and drive off water of hydration. The resulting dark grey sintered material was reground to pass through a 500 μm sieve, and compacted using a screw press to produce small circular discs, approximately 15 mm thick and 25 mm in diameter, which were fired in a laboratory furnace at 1000 °C for 1 h. The Egyptian blue frits thus produced were sectioned and examined in polished section in a SEM. Fired discs were also reground to pass through a 100 μm sieve, repelleted and refired at 1000 °C for 1 h.

3. Results and discussion

3.1. New Kingdom Amarna: microstructures and production processes

3.1.1. Egyptian blue frits

The cakes of Egyptian blue frit consist of large Egyptian blue crystals, up to about 140 μm in length (Table 1), which tend to be closely packed (Fig. 1a and b). Where it has survived weathering, thin layers of glass phase separate the Egyptian blue crystals, sometimes giving the overall appearance of a single crystal (Fig. 1a). These large clusters of Egyptian blue crystals surround partially reacted quartz particles, up to about 190 μm in diameter. Overall, in samples where the glass phase survives, the clusters tend to be linked together to form an interconnecting network of Egyptian blue crystals, partially reacted quartz particles and glass phase (Fig. 1a). When the glass phase has been almost entirely lost as a result of weathering (Fig. 1b), the surviving Egyptian blue crystals and partially reacted quartz particles are similar in abundance, morphology and distribution to those for unweathered samples. These microstructures are similar, therefore, to those of Egyptian blue frit produced in the laboratory by a single firing of replicate mixtures at 1000 °C (Fig. 1c and d). In general, the

Table 1
Size ranges and percentages of quartz particles and Egyptian blue crystals

Sample code	Sample type ^a	Size ranges (μm)				Percentages	
		Quartz particles (diameter)		Egyptian blue crystals (length)		Quartz particles %	Egyptian blue crystals%
		Min	Max	Min	Max		
UCL24684	CK	18	175	40	130	38	62
UCL25153	CK	15	180	23	100	10	90
UCL24686	CK	77	188	51	139	10	90
UCL25039	PR	10	51	27	80	25	75
UCL36464	PR	30	144	25	116	78	22
AM4	PR	9	74	27	117	37	63
AM9	PR	20	135	18	98	63	37
UCL8987	PR	20	92	10	53	21	79
ASH1893. 1-41-392	VS	6	24	6	42	10	90
ASH1893. 1-41-485	VS	7	48	8	28	31	69
UCL25155	VS	10	25	10	45	12	88
UCL36472	VS	10	38	7	65	18	82
UCL36473	VS	6	97	5	50	14	86
UCL25156	VS	10	35	3	60	22	78

^a CK, cake; PR, powder residue; VS, vessel.

Table 2
Bulk chemical compositions of Egyptian blue frits (EDS analyses normalised to 100%)

Sample code	Site	Sample type ^a	SiO ₂	CuO	CaO	Na ₂ O	K ₂ O	MgO	Al ₂ O ₃	FeO	SnO ₂	PbO	CaO/CuO	SnO ₂ /CuO	Excess SiO ₂	Excess CaO	Excess CuO	n ^b
<i>Amarna</i>																		
UCL24684 ^c	Amarna	CK	65.6	15.7	12.0	3.7	0.5	0.5	0.4	0.4	1.1	0.1	0.8	0.07	19.6	1.0		10
UCL25153	Amarna	CK	64.7	18.2	11.6	1.7	0.2	0.7	1.2	0.5	1.1	0.1	0.6	0.06	15.8		1.8	10
UCL25039	Amarna	PR	66.4	14.4	12.4	1.7	0.3	1.0	1.4	0.6	1.4	0.3	0.9	0.10	24.7	2.4		4
UCL36464 ^c	Amarna	PR	69.3	12.3	12.0	2.0	0.5	2.0	0.6	0.4	0.8	0.1	1.0	0.07	34.4	3.6		5
AM4 ^c	Amarna	PR	63.0	11.2	16.7	3.4	1.2	0.8	1.7	0.9	0.7	0.2	1.5	0.06	32.2	9.7		5
AM9 ^c	Amarna	PR	66.6	7.6	14.0	4.7	1.9	1.0	1.8	1.3	0.8	0.2	1.8	0.11	49.5	9.8		6
ASH1893.1-41-392	Amarna	VS	64.9	17.6	12.9	2.2	0.2	0.7	0.3	0.5	0.6	0.1	0.7	0.03	12.4	0.6		4
ASH1893.1-41-485 ^c	Amarna	VS	65.4	15.0	12.7	3.2	0.7	1.1	0.3	0.3	1.0	0.1	0.8	0.07	21.7	2.3		4
UCL25155 ^c	Amarna	VS	63.9	16.7	11.0	3.5	1.3	0.9	0.8	1.0	0.7	0.2	0.7	0.04	18.3		1.1	10
UCL36472 ^c	Amarna	VS	61.5	16.9	13.2	3.5	0.7	1.2	0.9	0.9	0.8	0.2	0.8	0.05	11.5	1.4		9
UCL36473 ^c	Amarna	VS	66.7	14.9	11.5	3.1	0.7	0.9	0.5	0.8	0.8	0.1	0.8	0.05	23.4	1.1		14
<i>Other Egyptian sites</i>																		
BM23178	Karnak	CK	68.4	11.8	13.9	1.4	1.1	0.9	1.2	0.9	0.3	0.1	1.2	0.03	34.8	6.0		6
BM23183 ^c	Thebes	CK	65.4	12.9	15.2	2.9	0.5	0.8	0.6	0.3	1.1	0.3	1.2	0.09	28.3	6.6		6
BM23185 ^c	Thebes	CK	66.2	13.8	14.6	2.1	0.5	0.7	0.6	0.3	0.9	0.2	1.1	0.07	25.9	5.2		7
BM23187 ^c	Thebes	CK	67.2	14.8	11.9	4.6	0.3	0.4	0.1	0.2	<0.3	0.2	0.8		24.0	1.6		8
ZURM1S311	el-Rakham	CK	78.2	6.7	8.2	2.3	0.1	2.4	0.8	0.7	0.4	0.2	1.2	0.06	62.4	3.7		18
ZURG7EZ	el-Rakham	CK	68.2	13.7	11.5	1.8	0.3	1.2	1.1	0.8	1.4	<0.1	0.8	0.10	28.7	2.0		4
ZURM124	el-Rakham	CK	72.0	6.2	12.5	2.9	0.1	4.7	0.4	0.5	0.6	0.2	2.0	0.10	58.8	9.0		11
ZURM1S32	el-Rakham	CK	78.2	4.4	8.7	2.4	0.1	4.8	0.6	0.3	0.4	0.1	2.0	0.09	71.1	6.1		14
ZURM1S411	el-Rakham	CK	64.6	10.8	12.2	3.7	0.1	6.3	1.0	0.4	0.9	<0.1	1.1	0.08	36.5	5.3		9
ZURM1S415	el-Rakham	CK	71.7	8.8	10.2	3.8	<0.1	3.2	1.3	0.5	0.5	0.1	1.2	0.06	49.9	4.4		13
ZURK1000	el-Rakham	BD	73.6	5.5	10.5	3.0	0.1	5.1	0.9	0.5	0.6	0.2	1.9	0.11	63.7	7.4		11
<i>Mesopotamia</i>																		
HH65	Tell Brak	CK	77.1	10.6	7.5	1.2	0.4	1.1	0.9	0.6	0.5	0.1	0.7	0.05	47.4	0.1		4
TR4747A	Tell Rimah	CK	70.1	15.0	8.6	1.4	0.3	2.5	0.8	0.7	<0.3	0.3	0.6		35.4		3.0	4
TR4747B	Tell Rimah	BD	75.5	10.2	8.3	1.2	0.6	1.4	0.8	1.5	0.3	0.1	0.8	0.03	47.5	1.2		4
TR5517	Tell Rimah	BD	73.9	11.6	9.7	1.4	0.6	0.9	0.8	0.8	0.3	<0.1	0.8	0.03	40.8	1.6		4
TR5579	Tell Rimah	BD	76.8	5.5	5.2	1.3	2.5	2.7	4.4	1.3	<0.3	0.1	0.9		68.8	1.5		4
TR5579A	Tell Rimah	BD	82.5	3.5	4.0	1.1	2.2	1.9	3.1	1.4	0.3	<0.1	1.1	0.09	79.9	1.7		4
TR5572a	Tell Rimah	BD	78.9	8.7	8.0	1.1	0.5	0.8	0.8	0.6	0.4	0.2	0.9	0.05	55.1	2.0		4
TR5572b	Tell Rimah	BD	72.2	11.1	9.4	1.4	1.1	1.5	1.6	1.1	0.3	0.3	0.8	0.03	41.8	1.7		4

^a CK, cake; PR, powder residue; VS, vessel; BD, bead.

^b n, number of analyses.

^c See Table 4 for WDS analyses of glass phase.

Table 3
Bulk chemical compositions of green frits (EDS analyses normalised to 100%)

Sample code	Site	Sample type ^a	SiO ₂	CuO	CaO	Na ₂ O	K ₂ O	MgO	Al ₂ O ₃	FeO	SnO ₂	PbO	CaO/ CuO	SnO ₂ / CuO	n ^b
<i>Amarna</i>															
UCL25041 ^c	Amarna	CK	67.3	8.3	14.8	6.5	0.4	0.6	0.9	0.6	0.5	0.1	1.8	0.06	6
UCL25044 ^c	Amarna	CK	62.0	6.1	23.6	4.4	1.4	0.5	0.8	0.5	0.5	0.1	3.9	0.08	6
UCL36466 ^c	Amarna	CK	71.9	6.8	12.3	5.1	0.7	1.2	0.5	0.4	0.6	0.5	1.8	0.09	9
UCL36467 ^c	Amarna	CK	74.1	5.5	16.7	1.3	0.3	1.0	0.1	0.2	0.6	0.1	3.0	0.11	4
UCL36468 ^c	Amarna	CK	83.4	3.7	8.9	1.0	0.3	0.9	0.3	0.6	0.8	0.1	2.4	0.22	4
UCL24690 ^c	Amarna	PR	72.8	6.4	13.9	5.1	0.2	0.5	0.3	0.3	0.4	0.1	2.2	0.06	4
AM5 ^c	Amarna	PR	76.4	5.3	10.5	4.7	<0.1	<0.1	2.5	0.3	<0.3	0.1	2.0		6
AM6 ^c	Amarna	PR	80.3	4.3	8.1	3.1	0.2	0.2	3.0	0.3	0.3	0.2	1.9	0.07	3
AM7	Amarna	PR	73.8	5.1	11.8	6.0	<0.1	<0.1	2.2	0.3	0.4	0.4	2.3	0.08	3
AM8 ^c	Amarna	PR	76.0	2.2	17.8	2.1	0.1	<0.1	0.7	0.7	0.3	0.1	8.1	0.14	6
AM10 ^c	Amarna	PR	70.2	6.5	18.3	2.2	0.6	0.5	0.3	0.6	0.7	0.1	2.8	0.11	4
UCL25157 ^c	Amarna	VS	71.6	4.4	17.5	3.8	0.5	1.0	0.6	0.4	<0.3	0.1	4.0		6
<i>Other Egyptian sites</i>															
BM23186 ^c	Thebes	CK	70.4	5.7	14.5	6.4	0.9	0.4	0.5	0.2	0.8	0.1	2.5	0.02	8
BM23188 ^c	Thebes	CK	69.5	6.3	13.9	7.7	0.2	0.6	0.5	0.3	0.7	0.3	2.2	0.05	6
BM31118 ^c	Thebes	CK	68.6	7.0	14.1	6.7	1.0	0.6	0.8	0.3	0.6	0.3	2.0	0.04	6
ZURM1S313	el-Rakham	CK	72.9	4.4	12.5	2.9	<0.1	5.8	1.2	0.3	<0.3	<0.1	2.8		6
ZURM1S38	el-Rakham	CK	87.3	2.1	4.1	1.1	<0.1	3.0	1.1	1.3	<0.3	<0.1	2.0		6
ZURM1S413	el-Rakham	CK	77.7	2.5	7.2	3.5	<0.1	6.1	1.9	0.6	0.5	<0.1	2.9		8
ZURM1S48	el-Rakham	CK	68.9	2.0	19.0	2.5	<0.1	5.5	1.4	0.7	<0.3	<0.1	9.5		6
ZURM1C5	el-Rakham	CK	76.6	9.1	4.8	1.6	0.1	4.8	1.5	0.6	0.9	0.1	0.5	0.01	9

^a CK, cake; PR, powder residue; VS, vessel.

^b n, number of analyses.

^c See Table 5 for WDS analyses of glass phase.

Egyptian blue crystals in the ancient cakes are closer in size to those for replicate mixtures based on coarse grained quartz (majority greater than 100 µm in length/diameter) (Fig. 1c) than those based on fine grained quartz (average around 50 µm in length/diameter) (Fig. 1d).

The powder residue samples of Egyptian blue frit differ from the cakes in that the areas of closely packed Egyptian blue crystals, partially reacted quartz particles and glass phase are now fragmented (Fig. 2a and b). The lengths of the Egyptian blue crystals in the difference frits vary between up to about

50 µm for UCL8987 and up to almost 120 µm for AM4 (Table 1). Similarly, the diameters of the quartz particles vary between up to 50 µm for UCL25039 and up to about 140 µm for UCL36464. These microstructures are, therefore, comparable to that of a replicate frit (Egyptian blue crystals up to 60 µm in length and quartz particles up to 100 µm in diameter) resulting from refiring to 800 °C of ground primary frit, produced from a mixture based on fine grained quartz (Fig. 2c).

The fragments of Egyptian blue frit vessels consist of clusters of small Egyptian blue crystals, with maximum lengths in

Table 4
Chemical compositions of glass phase in Egyptian blue frits (WDS analyses normalised to 100%)

Sample code	Site	Sample type ^a	SiO ₂	CuO	CaO	Na ₂ O	K ₂ O	MgO	Al ₂ O ₃	FeO	SnO ₂	PbO	Na ₂ O/ K ₂ O	Na ₂ O/ MgO	n ^b
<i>Amarna</i>															
UCL24684	Amarna	CK	64.0	8.45	12.85	7.21	1.66	0.81	2.03	1.18	1.79	0.06	4.3	8.9	13
UCL24686	Amarna	CK	65.9	17.27	3.58	6.65	4.02	0.35	0.40	0.56	0.01	1.30	1.7	19.0	7
UCL36464	Amarna	PR	69.6	7.46	4.93	7.84	2.95	1.06	2.45	1.34	2.31	0.01	2.7	7.4	10
AM4	Amarna	PR	59.9	6.90	26.03	3.09	0.81	0.43	1.18	0.62	0.95	0.04	3.8	7.1	34
AM9	Amarna	PR	64.7	7.66	10.02	5.43	2.52	1.38	4.71	3.16	0.38	0.05	2.1	3.9	18
UCL8987	Amarna	PR	60.2	9.17	23.54	4.24	0.94	0.21	0.61	0.33	0.71	0.05	4.5	20.3	6
ASH1893.1-41-485	Amarna	VS	59.3	5.98	24.11	4.66	1.55	0.64	2.23	0.65	0.85	0.04	3.0	7.2	8
UCL25155	Amarna	VS	68.5	0.15	20.59	5.66	1.78	0.52	0.91	1.15	0.68	0.04	3.2	10.9	5
UCL36472	Amarna	VS	60.9	0.17	29.50	5.19	1.03	1.09	1.11	0.81	0.20	0.03	5.0	4.8	10
UCL36473	Amarna	VS	68.1	1.51	21.76	3.80	1.27	0.88	0.88	0.98	0.80	0.01	3.0	4.3	7
UCL25156	Amarna	VS	64.3	10.90	19.33	2.21	0.46	0.59	0.78	0.65	0.79	0.03	4.8	3.8	4
<i>Other Egyptian sites</i>															
BM23183	Thebes	CK	56.0	5.26	29.90	4.24	0.94	1.05	1.05	0.42	1.11	0.04	4.5	4.0	9
BM23185	Thebes	CK	55.9	7.53	27.90	6.02	0.63	0.46	0.62	0.27	0.59	0.06	9.6	13.1	6
BM23187	Thebes	CK	67.3	13.09	6.63	10.36	1.17	0.34	0.34	0.54	0.04	0.18	8.8	30.4	7

^a CK, cake; PR, powder residue; VS, vessel.

^b n, number of analyses.

Table 5
Chemical compositions of glass phase in green frits (WDS analyses normalised to 100%)

Sample code	Site	Sample type ^a	SiO ₂	CuO	CaO	Na ₂ O	K ₂ O	MgO	Al ₂ O ₃	FeO	SnO ₂	PbO	Na ₂ O/ K ₂ O	Na ₂ O/ MgO	n ^b
<i>Amarna</i>															
UCL25041	Amarna	CK	67.4	0.10	20.05	9.39	0.65	0.56	1.05	0.36	0.44	0.01	14.4	16.6	5
UCL25044	Amarna	CK	66.9	0.15	20.45	7.23	2.31	0.51	1.28	0.43	0.67	0.03	3.1	14.2	5
UCL25038	Amarna	CK	80.4	0.24	2.14	11.91	1.91	0.71	1.31	0.76	0.59	0.04	6.2	16.7	3
UCL36466	Amarna	CK	71.1	6.18	10.79	9.21	0.65	0.51	0.82	0.35	0.37	0.01	14.1	18.0	7
UCL36467	Amarna	CK	77.2	0.20	3.84	10.04	4.22	0.83	2.42	0.40	0.79	0.02	2.4	12.1	1
UCL36468	Amarna	CK	75.1	0.15	4.13	11.53	3.40	0.59	3.41	0.86	0.78	0.01	3.4	19.5	5
UCL24690	Amarna	PR	68.1	0.11	19.12	9.95	0.37	0.50	0.86	0.34	0.65	0.03	26.7	19.8	5
AM5	Amarna	PR	59.7	9.08	21.90	7.13	0.27	0.29	0.99	0.35	0.26	0.01	26.1	24.3	5
AM6	Amarna	PR	66.2	9.94	10.95	8.74	1.44	0.48	1.03	0.47	0.76	0.03	6.1	18.3	4
AM8	Amarna	PR	55.9	4.35	34.47	2.43	0.73	0.35	0.55	0.71	0.45	0.09	3.3	6.9	6
AM10	Amarna	PR	56.2	7.95	28.83	3.74	1.08	0.45	0.71	0.44	0.51	0.12	3.5	8.3	6
UCL25157	Amarna	VS	65.7	0.10	23.28	8.22	0.68	0.39	1.03	0.57	0.02	0.03	12.1	20.9	5
<i>Other Egyptian sites</i>															
BM23186	Thebes	CK	67.5	12.06	4.20	11.32	2.22	0.40	1.27	0.36	0.65	0.04	5.1	28.2	8
BM23188	Thebes	CK	62.7	8.94	17.28	8.39	0.24	0.31	0.92	0.35	0.83	0.03	35.1	27.2	6
BM31118	Thebes	CK	62.6	8.01	17.90	8.23	1.26	0.36	0.82	0.24	0.54	0.05	6.5	22.9	7

^a CK, cake; PR, powder residue; VS, vessel.

^b n, number of analyses.

the range 30–65 µm (Table 1), and partially reacted quartz particles, with maximum diameters in the range 25–100 µm, that are bonded together with a glass phase (Fig. 3a and b). These clusters are linked together so that they form an extended interconnecting network. The microstructures of the vessels are similar, therefore, to those of replicate frit resulting from refiring to 1000 °C of ground primary frit, produced from mixtures based on either coarse or fine grained quartz (Fig. 3c and d). The principal difference is that acicular high temperature silica polymorphs are present in the replicate frit samples suggesting that the Amarna vessels were refired to temperatures well below the 1000 °C used in refiring the replicate frits.

In making the comparisons between the microstructures of ancient and replicate frits, it should be emphasised that, where significant glass phase survives in the ancient samples, its distribution with respect to the Egyptian blue crystals and partially reacted quartz particles is exactly as observed in the replicate samples. Furthermore, the analytical totals for this glass phase are always very close to 100%. Therefore, it appears that, in the ancient frits, either there is significant weathering and the glass phase is lost almost entirely, or the glass phase survives in an essentially unaltered state. Thus, in those ancient frit samples in which significant glass phase survives, the observed flux contents provide a true measure of the amounts of flux present in the original mixture from which the frit was produced.

On the basis of the above similarities between the microstructures of the ancient and replicate frits, it is suggested that the cakes of Egyptian blue frit were primary, and were produced by firing a mixture of coarse quartz, calcium carbonate, a copper compound, and a few percent of alkali at a temperature up to about 1000 °C. The powder residues could then have been produced by grinding these primary cakes, and the vessels by moulding this powder to the required shape and refiring, again to a temperature up to about 1000 °C.

3.1.2. Green frits

The cakes of green frit are characterised by large areas of interconnected glass containing partially reacted quartz grains, typically up to about 50 µm across, together with crystals of wollastonite, up to about 5 µm across and acicular high temperature polymorphs of silica (Fig. 4a and b). In contrast, the powder residues of green frit consist of isolated fragments of glass containing, again, partially reacted quartz particles, acicular high temperature silica polymorphs and wollastonite crystals (Fig. 4c). The microstructure of the single fragment of a green frit vessel is comparable to that of the cakes consisting, again, of large areas of interconnected glass (Fig. 4d). However, the partially reacted quartz particles (up to about 20 µm across) are smaller than in the cakes, and the overall interconnection appears to have been achieved through the formation of “necks” of glass.

Although a sequence of replicate green frits were not produced in the laboratory, it seems probable that the relationship between the cakes, powder residues and vessels of green frit was similar to that for the equivalent Egyptian blue frits. Thus, the cakes were again the primary product, and would have been ground to produce the powder residues. The powder would then have been moulded to the required shape and refired to produce the vessels, the powder fragments being joined through the formation of “necks” of glass (Fig. 4d).

3.2. New Kingdom Amarna: chemical compositions and raw materials

The bulk chemical compositions of the Egyptian blue and green frits, as determined by EDS, are given in Tables 2 and 3 respectively, and the chemical compositions of surviving glass phase, as determined by WDS, are given in Tables 4 and 5 respectively.

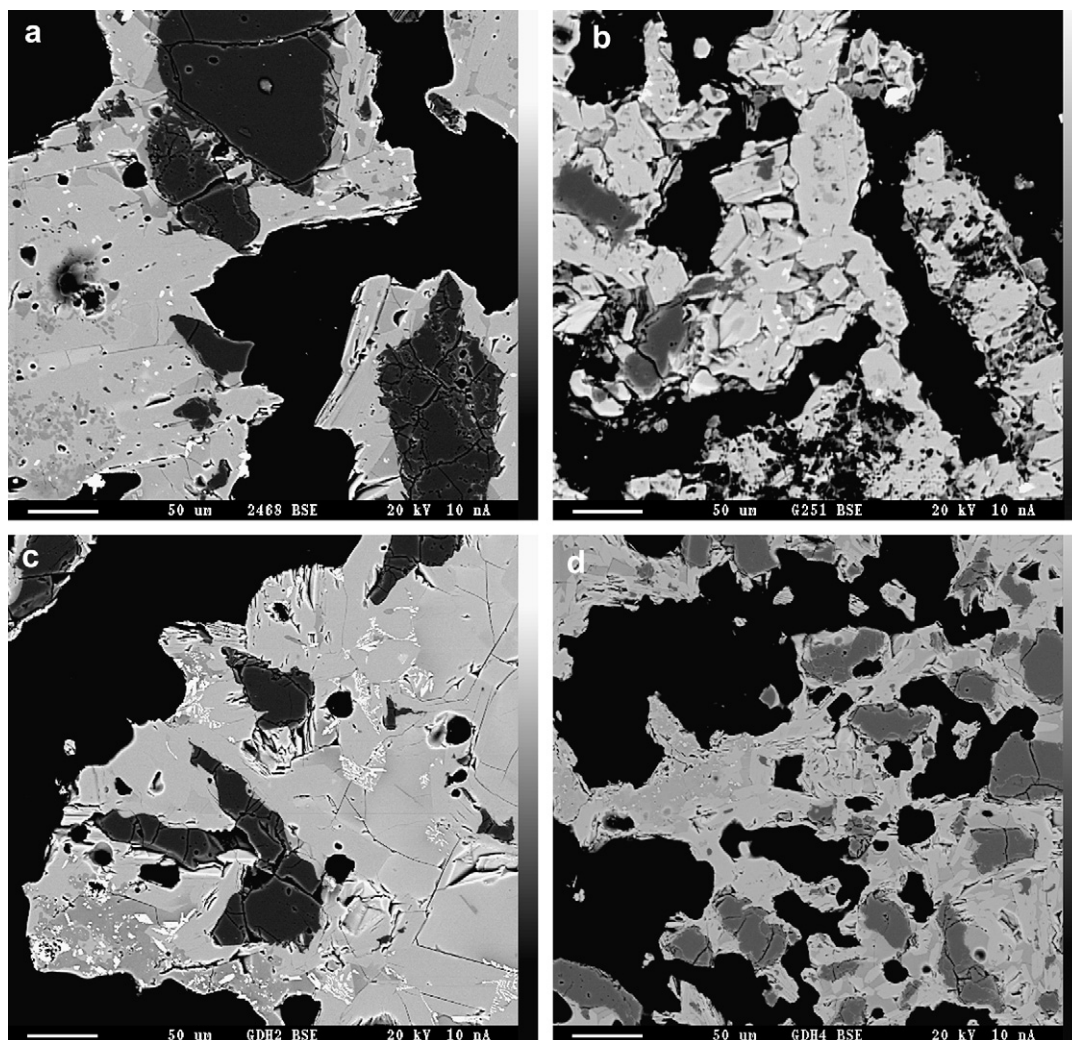


Fig. 1. SEM-BSE photomicrographs of sections through Amarna Egyptian blue frit cakes (a) UCL24684 and (b) UCL25153; and replicate Egyptian blue frit fired at 1000 °C and produced using (c) coarse grained quartz and (d) fine grained quartz. (Grey tone becomes progressively lighter from quartz particles to glass phase to Egyptian blue crystals. Pores are black and unreacted copper oxide is white.)

Also included in Table 2 are the calculated excess percentages of silica, lime and copper oxide, as determined by assuming complete reaction to produce the maximum possible amounts of Egyptian blue crystals (i.e. cuprorivaite, $\text{CaCu-Si}_4\text{O}_{10}$). These data indicate that the Egyptian blue frits always contain excess silica, with the excess for the majority of the frits from Amarna being in the range from 10 to 25%. In addition, the great majority of the frits contain a much smaller excess of lime (less than 4% for uncontaminated Amarna frits), with copper oxide being only very occasionally in excess.

The principal distinguishing feature, as between the Egyptian blue frits and the green frits, is that the bulk copper oxide contents for the Egyptian blue frits are normally greater than the bulk lime contents (CaO/CuO ratios in range 0.6–1.0) whereas the bulk lime contents for the green frits are greater than the bulk copper oxide contents (CaO/CuO ratios greater than 1.8). The exceptions are two Egyptian blue frit residues (AM4 and AM9) which are contaminated by lime from the substrate (CaO/CuO ratios 1.5 and 1.8). Since the lime contents of Egyptian blue frit (11–13% CaO, excluding contaminated

residues AM4 and AM9) and green frit (8–24% CaO) overlap, the change from producing Egyptian blue frit to producing green frit was most probably achieved by reducing the copper oxide content of the mixture.

A further difference is that the green frits (62–83% SiO_2) tend to have higher silica contents than the Egyptian blue frits (61–69% SiO_2). Also, the bulk soda contents extend to higher values in the green frits (up to 6.5% Na_2O) compared to the Egyptian blue frits (up to 4.7% Na_2O). This is in spite of the higher copper oxide contents of the Egyptian blue frit, and therefore, greater contributions to the soda peak from the overlapping copper peak.

3.2.1. Quartz

The two possible sources of quartz used in the production of the frits are crushed quartz pebbles and quartz sand. A potential distinguishing feature is the shape of the particles, crushed quartz particles being angular whereas sand particles are normally rounded. Crushed quartz pebbles are also characterised by high purity (Table 6). In contrast, significant

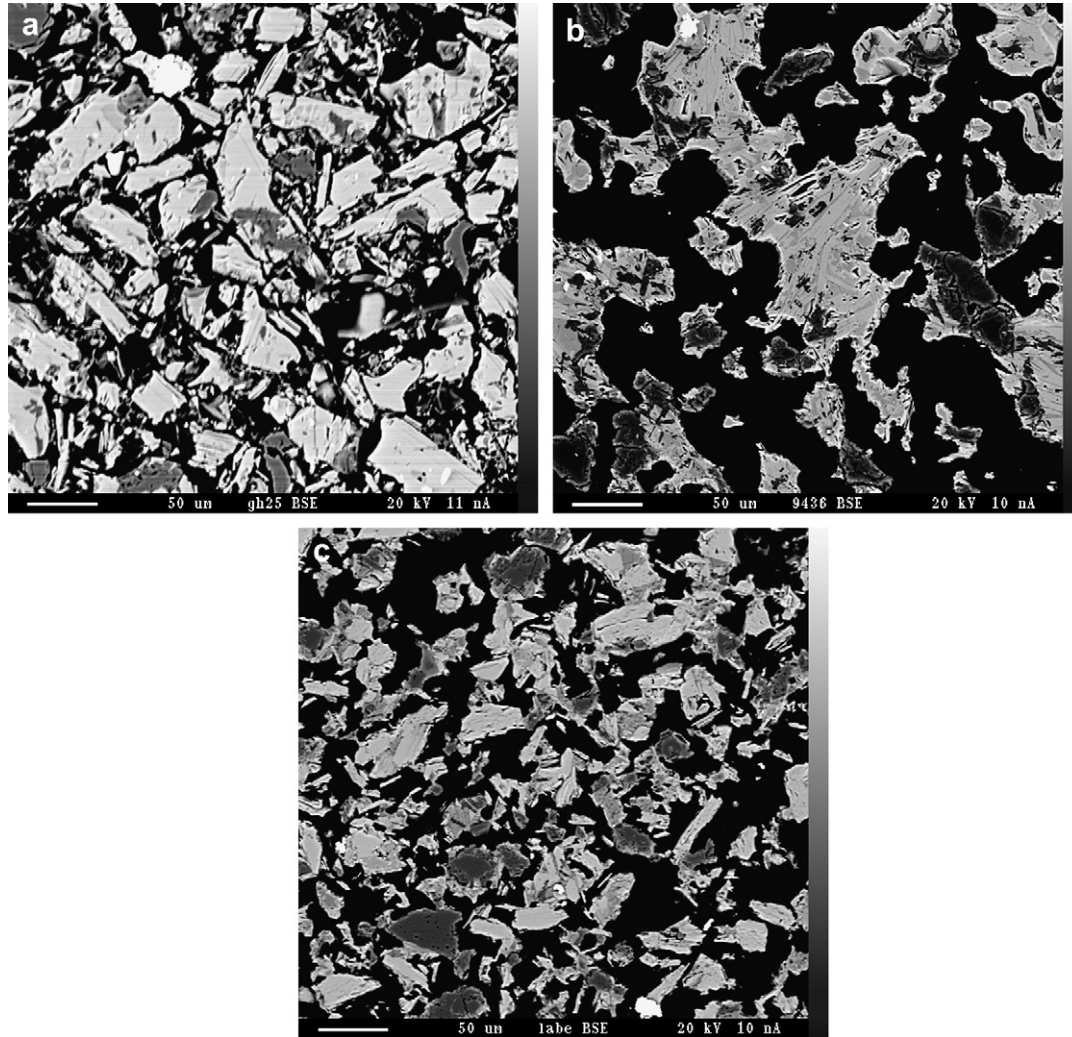


Fig. 2. SEM-BSE photomicrographs of sections through Amarna Egyptian blue powder residues (a) UCL25039 and (b) AM4; and (c) replicate Egyptian blue frit produced by refring ground primary frit based on fine grained quartz to 800 °C. (Grey tone becomes progressively lighter from quartz particles to glass phase to Egyptian blue crystals. Pores are black and unreacted copper oxide is white.)

amounts of limestone or shell fragments, feldspars and iron-titanium oxides can be present in quartz sands, which therefore typically contain measurable amounts of alumina, lime, magnesia, potash, and iron and titanium oxides.

The quartz particles in the Egyptian blue and green frits are rounded and although partially reacted, it seems unlikely that they were originally angular since quartz particles in faience retain their angularity in spite of being embedded in an extensive glass phase (Tite and Shortland, 2003: Figs. 3 and 4). Therefore it seems probably that quartz sand was used in the production of these frits. This conclusion is supported by both the bulk alumina and iron oxide contents (majority 0.3–1.8% Al_2O_3 and 0.3–1.3% FeO, excluding green frit residues AM5, AM6 and AM7 which have been contaminated by the substrate) (Tables 2 and 3), and the observed weak correlation between them ($r^2 = 0.52$, again excluding contaminated residues) (Fig. 5).

3.2.2. Lime

The calcium carbonate used in the production of the frits could either have been added as a separate component, in

the form of crushed limestone or shell, or it could have been incorporated as a component of the sand. The sands available at Amarna, that have been analysed, contain up to about 17% lime (Table 6) which would have been sufficient for the production of the frits.

3.2.3. Copper

The possible sources of the copper used in the production of the frits are a relatively pure copper ore such as malachite, and the scale resulting from the oxidation of copper metal or copper alloy. Since all the Egyptian blue frits and the majority of the green frits contain greater than 0.3% tin oxide (Tables 2 and 3), it is clear that scale from bronze provided the source of the copper, the SnO_2/CuO ratios indicating that up to about 10% tin bronze was normally used. Similarly, Jaksch et al. (1983) and El Goresy (2000) had previously concluded that bronze scale had been used in New Kingdom Egyptian blue and green pigments on the basis of the frequent presence of tin rich phases (i.e. cassiterite (SnO_2) and malayaite (CaSnSiO_5)).

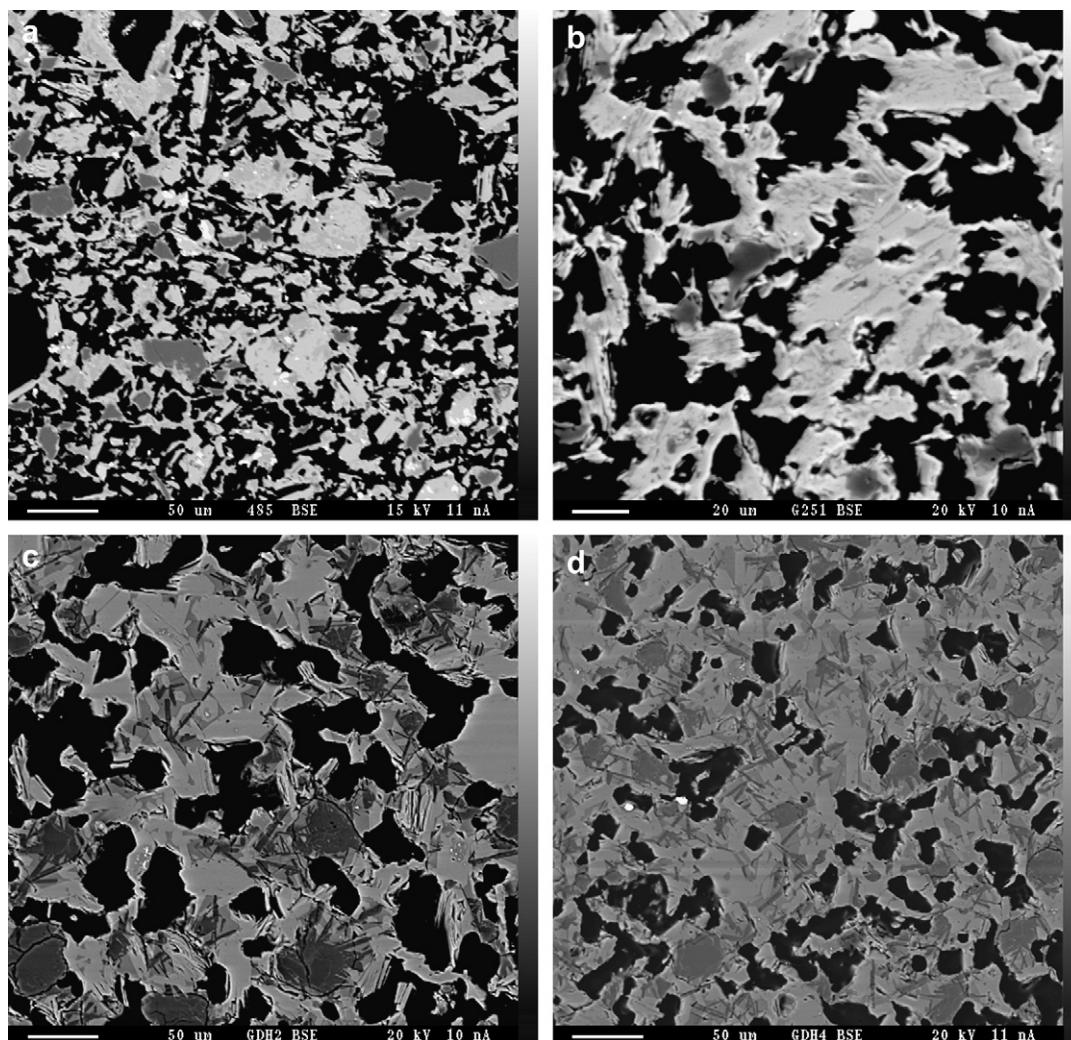


Fig. 3. SEM-BSE photomicrographs of sections through Amarna Egyptian blue frit vessels (a) ASH1893.1-41-485 and (b) UCL25155; and replicate Egyptian blue frit produced by refining ground primary frit based on (c) coarse grained quartz and (d) fine grained quartz to 1000 °C. (Grey tone becomes progressively lighter from quartz particles to glass phase to Egyptian blue crystals. Pores are black and unreacted copper oxide is white.)

3.2.4. Alkali flux

The two possible sources of soda-rich alkali flux used in the production of the frits are the natural evaporite, natron, and soda-rich plant ashes. Natron, the most well known source of which is the Wadi Natrun on the edge of the Western Desert of Egypt, consists predominantly of sodium carbonate and sodium bicarbonate. It, therefore, contains few impurities, and its $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios are typically in the range from 70 to 90, and its $\text{Na}_2\text{O}/\text{MgO}$ ratios in the range from 90 to 130 (Table 7). Soda-rich ashes are derived from salt tolerant, halophytic plants, such as *Salsola soda* and *Anabasis articulata*, growing in coastal, salt marsh and desert regions. The compositions of such ashes are very variable with $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios typically in the range from 3 to 11, and $\text{Na}_2\text{O}/\text{MgO}$ ratios typically in the range from 6 to 25 (Table 7).

The $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios for the glass phase in all the Egyptian blue frits and in more than half the green frits are less than about 6 (Tables 4 and 5), indicating that the source of the alkali flux was almost certainly soda-rich plant ash. However,

the $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios for the glass phase in the remainder of the green frits (in the range from 12 to 27) are higher than normally observed for plant ashes. Plant ashes with ratios in the range 12–15 are perhaps not impossible but ratios of 26–27 seem very unlikely, and are more probably the result of the use of natron. Although the $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios in natron itself are considerably higher (70–90) (Table 7), the ratios in the resulting glass phase will be significantly reduced because of the contribution to the overall potash content from feldspars in the quartz sand. For example, in Roman glass, which was certainly produced using natron, the $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios are typically in the range 20–30 (Freestone et al., 2000).

3.3. Other sites in New Kingdom Egypt

The microstructures of the New Kingdom Egyptian blue and green frits from Karnak, Thebes and Zawiyet Umm el-Rakham are very similar to the microstructures of equivalent frits from Amarna. Thus, when unweathered, the frit cakes

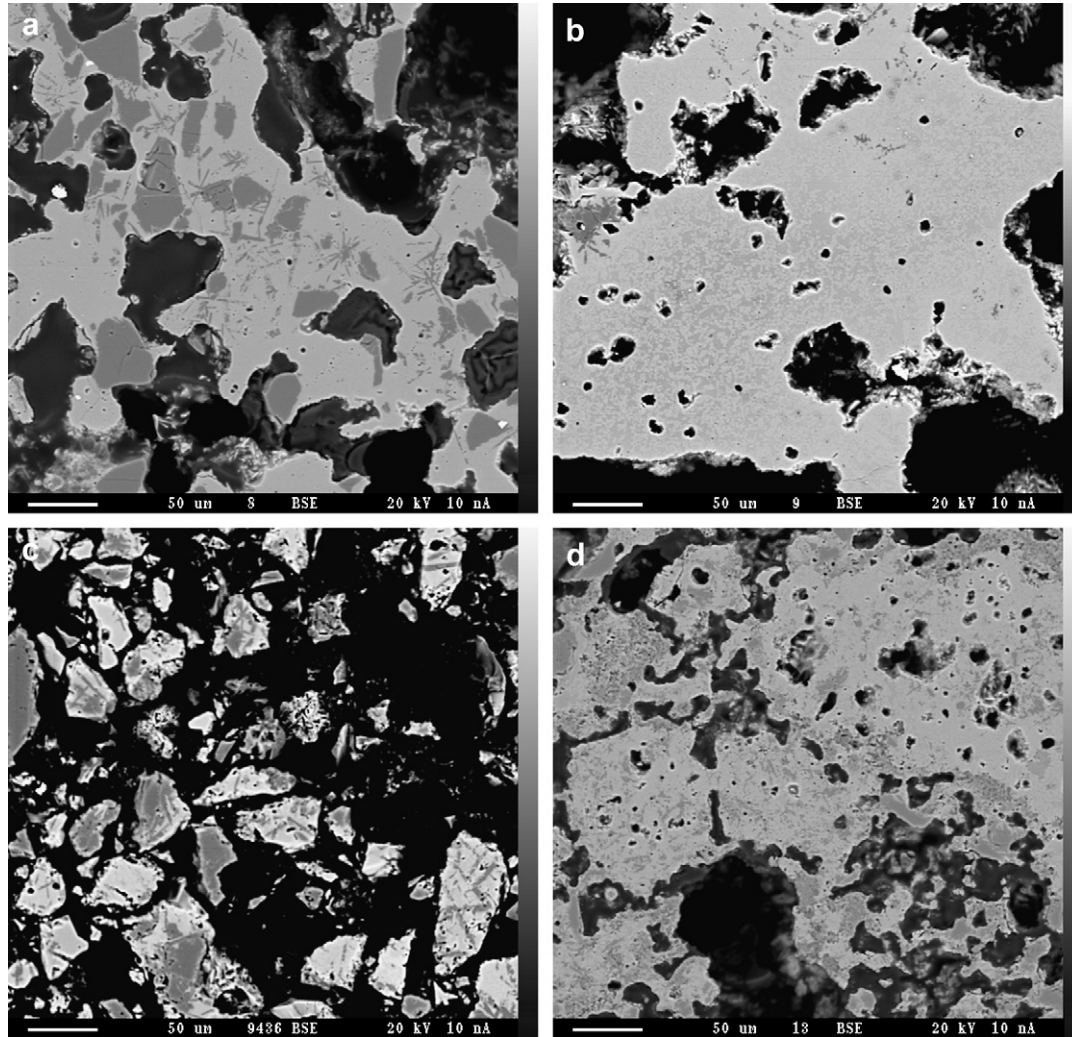


Fig. 4. SEM-BSE photomicrographs of sections through Amarna green (a) frit cake UCL25041, (b) frit cake UCL25044, (c) powder residue AM7, and (d) frit vessel UCL25157. (Grey tone becomes progressively lighter from quartz particles-plus-high temperature silica polymorphs to glass phase to wollastonite crystals which are just visible only in (b). Pores are black.)

of Egyptian blue frit consist of clusters of large Egyptian blue crystals (up to about 150 μm in length) and partially reacted quartz particles bonded together by a glass phase (Fig. 6a), and those of green frit consist of extended areas of glass containing partially reacted quartz, high temperature silica polymorphs and wollastonite (Fig. 6c). In contrast, in the case of the cakes from Zawiyet Umm el-Rakham, the glass phase has been almost entirely lost as a result of weathering so that only the crystalline phases survive (Fig. 6b). Similarly, the single Egyptian blue frit bead from Zawiyet Umm

el-Rakham consists of smaller isolated Egyptian blue crystals (up to about 70 μm in length) and partially reacted quartz particles, without any connecting glass phase which has again been lost through weathering (Fig. 6d). As for the Amarna

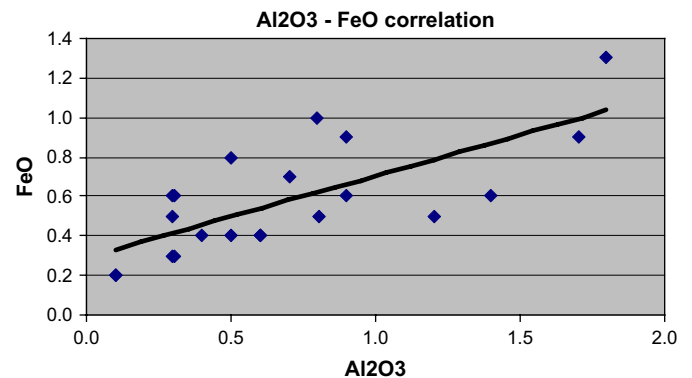


Fig. 5. Plot showing weak correlation ($r^2 = 0.52$) between bulk alumina and iron oxide contents (wt%) for Egyptian blue and green frits from Amarna (excluding green powder residues AM5, AM6 and AM7 that are contaminated by substrate). Absolute errors on data points range from ± 0.03 to ± 0.25 wt%.

Table 6
Chemical compositions of quartz pebbles and sands from Amarna

Material	Code	SiO ₂	Al ₂ O ₃	FeO	TiO ₂	Na ₂ O	K ₂ O	CaO	MgO
Pebbles	1298 ^a	99.83	0.05	0.01	0.01	0.05	bd	0.05	0.01
Pebbles	1299 ^a	99.79	0.05	0.05	0.01	0.05	bd	0.05	0.01
Sand	AM44 ^b	93.61	1.23	0.57	0.15	0.26	0.29	3.68	0.21
Sand	AM43 ^b	76.78	2.37	1.36	0.32	0.81	0.45	17.29	0.61

^a Data from Brill (1999).

^b Data from Hatton (2005).

Table 7
Chemical compositions of soda-rich alkali fluxes

Material	Plant species	Code	Na ₂ O	K ₂ O	CaO	MgO	P ₂ O ₅	SO ₃	Cl	SiO ₂	Al ₂ O ₃	FeO	Na ₂ O/ K ₂ O	Na ₂ O/ MgO
<i>Natron</i>														
Egyptian tomb		655 ^a	50.5	0.55	0.30	0.38	na	7.10	38.88	0.5	0.10	0.14	91.8	132.9
Egyptian tomb		657 ^a	42.7	0.48	0.39	0.42	na	7.37	14.90	2.0	0.61	0.40	89.0	101.7
Egyptian tomb		658 ^a	41.6	0.58	0.42	0.46	na	6.66	9.52	2.0	0.47	0.26	71.7	90.4
<i>Soda-rich plant ashes</i>														
Egypt-Taposiris Magna	<i>Anabasis articulata</i>	WM3 ^b	48.9	4.5	2.0	2.0	2.0	4.2	34.9	0.8	0.5	0.1	10.9	24.5
Egypt-Barnug	<i>Suaeda</i>	WM2 ^b	43.4	6.5	5.2	3.9	5.3	8.2	20.0	5.1	1.5	0.9	6.7	11.2
Levant	<i>Salsola soda</i>	Ashtor ^c	43.0	6.8	3.6	1.8			0.9	3.0			6.4	23.9
Syria-Jabul-SE Aleppo	<i>Arthrocnemum strobilaceum</i>	8 ^d	42.0	5.5	1.6	2.5	0.35				0.17	0.08	7.6	16.8
Syria-NE Damascus	<i>Anabasis syriaca</i>	30 ^d	31.6	6.6	5.3	5.1	0.57				0.22	0.12	4.8	6.2
Syria-25 km N Raqqa	<i>Salsola</i> sp.	15 ^d	33.8	10.2	2.0	2.2	1.51				0.25	0.14	3.3	15.3

^a Data from Brill (1999).

^b Data from Tite et al. (2006).

^c Data from Ashtor and Cevidalli (1983).

^d Data from Barkoudah and Henderson (2006).

Egyptian blue frits, when the glass phase has been almost entirely lost as a result of weathering (Fig. 6b and d), the surviving Egyptian blue crystals and partially reacted quartz particles are similar in abundance, morphology and distribution to those for unweathered samples. The microstructures are again consistent with the frit cakes being the primary product, and the bead being produced by moulding to shape, and refiring the powder obtained by grinding the cakes.

The Egyptian blue frits again tend to be distinguished from the green frits by their lower CaO/CuO ratios, the majority being in range 0.8–1.2 for blue frits whereas the majority are greater than 2 for green frits (Tables 2 and 3). However, because of both loss of material through weathering and possible contamination during burial, the differences in CaO/CuO ratios are less clear-cut than for the Amarna frits.

The rounded quartz particles together with the bulk alumina and iron oxide contents (majority 0.4–1.9% Al₂O₃ and 0.3–1.3 FeO) (Tables 2 and 3) suggest that sand provided the source of the quartz. It is, therefore, again possible that the lime was incorporated with the sand rather than being added as a separate component. The high magnesia contents of the Zawiyet Umm el-Rakham frits (majority 2–6% MgO), compared to the Amarna and Thebes frits (0.3–1.2% MgO and 0.4–0.9% MgO respectively), suggest that the calcium carbonate in the Zawiyet Umm el-Rakham frits was derived from a dolomitic limestone.

The tin oxide contents which are greater than 0.3% for the majority of the frits again indicate that scale from bronze, containing up to about 10% tin, provided the source of the copper. Lead isotope analysis of the Zawiyet Umm el-Rakham frits indicated that the copper used in their production and the copper used for tools and weapons found in Egypt have the same source (Shortland, 2006). As discussed by Stos-Gale et al. (1995), the copper metal used in Egypt appears to have been imported from a number of sources, including possibly Laurion in Greece, and Cyprus.

Where glass phase survives, all but one of the Na₂O/K₂O ratios are less than 10 (Tables 4 and 5), indicating the use of soda-rich plant ash as the source of the alkali flux. The

exception is a green frit from Thebes (BM23188), for which the high Na₂O/K₂O ratio (~35) suggests the use of natron.

3.4. 15th century BC Mesopotamia

As a result of weathering, the glass phase has been lost from all the Egyptian blue frits from Tell Brak and Tell Rimah that have been examined for the present paper. Therefore, in both the frit cakes and the beads, only isolated Egyptian blue crystals and partially reacted quartz particles survive. The cakes (Fig. 7a) differ from the beads (Fig. 7b) in that, in the cakes, the Egyptian blue crystals tend to cluster around the partially reacted quartz particles, and also tend to be larger (up to about 100 μm compared to up to about 50 μm in the beads). As in the case of the frits from Egypt, the microstructures are again consistent with the frit cakes being the primary product, and beads being produced by moulding to shape, and refiring the powder obtained by grinding the cakes.

In spite of the weathering, the bulk copper contents of the Egyptian blue frits are, with one exception, greater than the lime contents (CaO/CuO in the range 0.6–1.1) (Table 2). A distinguishing feature of the Egyptian blue frits from Mesopotamia compared to those from Amarna, Karnak and Thebes, are their high absolute silica contents (70–83% compared to 61–70% SiO₂), and their high excess silica contents (35–80% compared to 11–35% excess SiO₂). Furthermore, the highest silica values are associated with the frit beads rather than the primary cakes. In the study of contemporary Egyptian blue frit beads and other small objects from Ugarit in the Levant, Matoian and Bouquillon (2000) have similarly identified a group with absolute silica contents in the range from about 75 to 90% SiO₂. They suggest that these objects were produced by mixing ground Egyptian blue frit with additional quartz. They further argue that these objects should be regarded as faience coloured by Egyptian blue frit although, in the absence of any evidence for the presence of a glaze, “diluted” Egyptian blue frit would perhaps be a better description.

The rounded quartz particles together with the bulk alumina and iron oxide contents (0.8–4.4% Al₂O₃ and 0.6–1.5 wt%

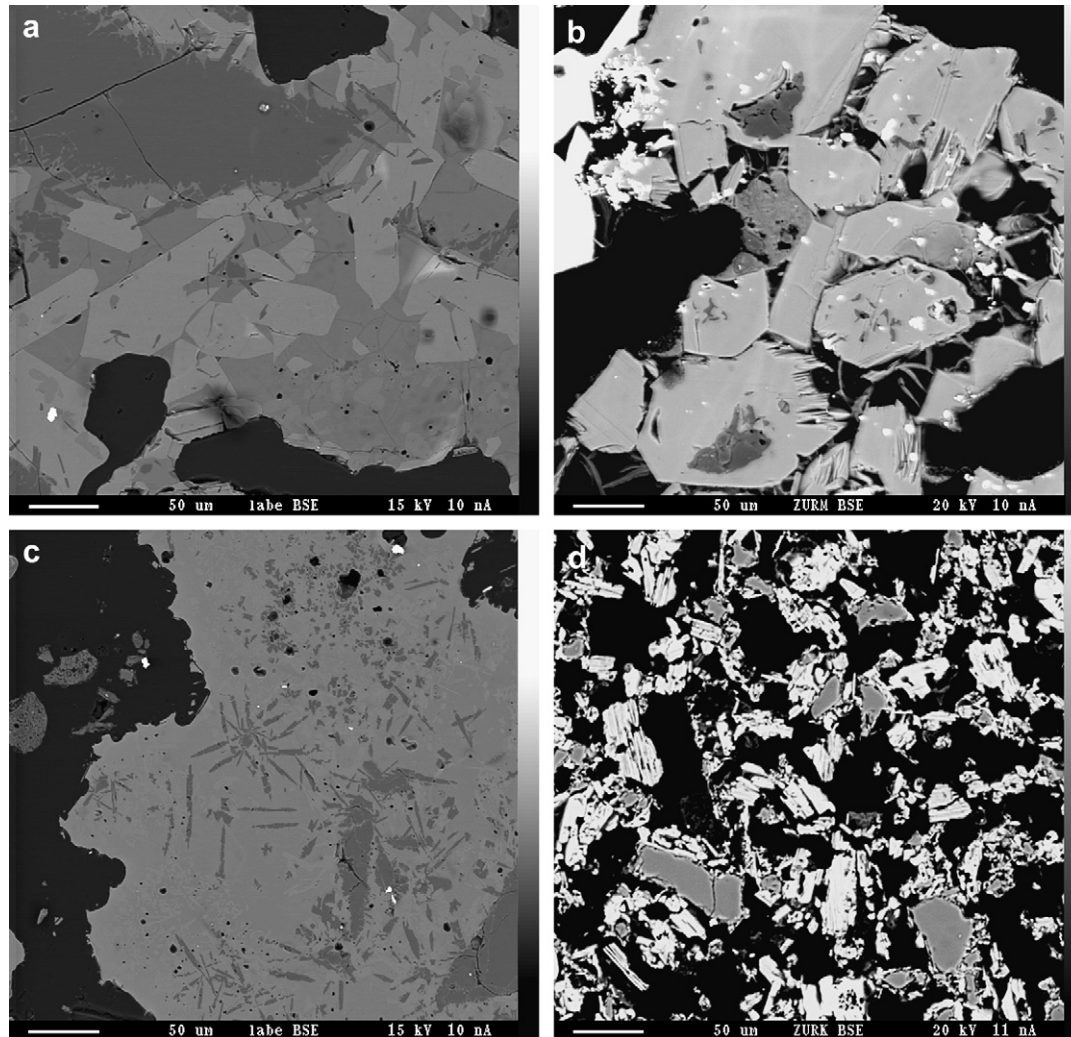


Fig. 6. SEM-BSE photomicrographs of sections through (a) Egyptian blue frit cake from Thebes BM23187, (b) Egyptian blue frit cake from Zawiyet Umm el-Rakham ZURM1S411, (c) green frit cake from Thebes BM23186, and (d) Egyptian blue frit bead from Zawiyet Umm el-Rakham ZURK1000. (For Egyptian blue frit, grey tone becomes progressively lighter from quartz particles to glass phase (only present in (a)) to Egyptian blue crystals, and for green frit, grey tone becomes progressively lighter from quartz particles-plus-high temperature silica polymorphs to glass phase to wollastonite crystals. Pores are black and unreacted copper oxide (present in (b)) is white.)

FeO) (Table 2) suggest that sand again provided the source of the quartz.

In these frits, the majority of tin oxide contents are below or close to the detection limits for tin (about 0.3% SnO₂). Therefore, the source of the copper was probably either copper ore or scale from copper metal, rather than scale from bronze. Lead isotope analysis of the Mesopotamian frits (Hatton, 2005: 60) indicated the use of different sources of copper to those used for the frits from Egypt, Iranian sources being one possibility.

Since a glass phase does not survive in any of these frits, it is not possible to identify the source of the alkali flux, although, on the basis of the flux used for Mesopotamian glass (Shortland and Eremin, 2006), soda-rich plant ash seems most likely.

4. Conclusions

Both Egyptian and Mesopotamian frits were most probably produced using lime-rich quartz sand such that the calcium

carbonate was incorporated with the sand rather than needing to be added as a separate component. The copper for the Egyptian frits was provided by scale from bronze whereas that for the Mesopotamian frits was provided either by scale from copper metal or by copper ore. Also, on the basis of the lead isotope analyses, copper from different sources was exploited in Egypt and Mesopotamia. The alkali flux in both regions was predominantly soda-rich ash produced from burning halophytic plants, but it is possible that, in Egypt, natron was occasionally used for the green frits. A further distinguishing feature of the Egyptian blue frits from Mesopotamia is their higher silica contents, which suggest that, in producing small objects, the Mesopotamian frit was sometimes diluted by mixing it with additional quartz.

Although green frit might have first been produced as a result of the use of a failed recipe for Egyptian blue, it is clear that, from an early stage, green frit was being produced as a distinct pigment (El Goresy et al., 1986). The production

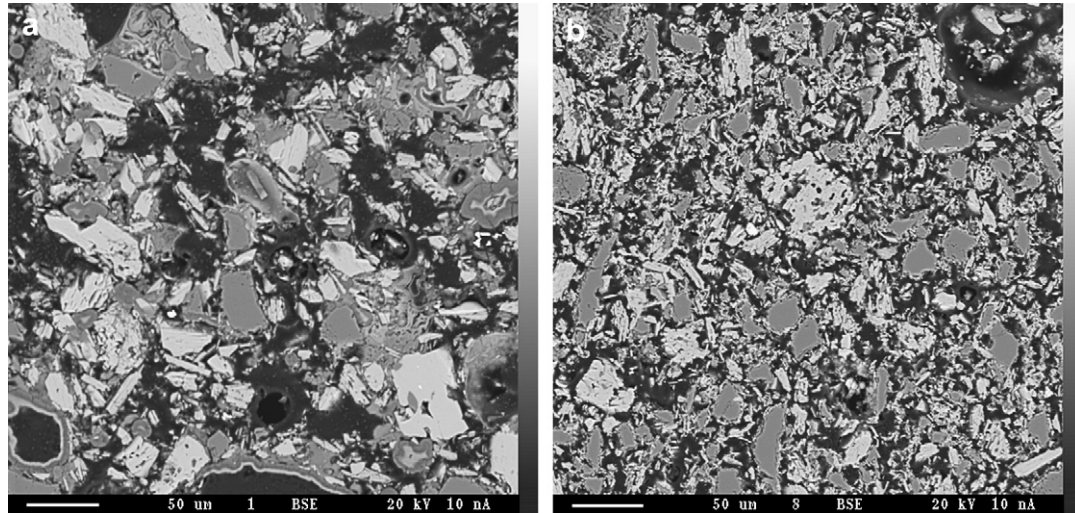


Fig. 7. SEM-BSE photomicrographs of sections through Tell Rimah Egyptian blue frit (a) cake TR4747A and (b) bead TR5572b. (Grey tone becomes lighter from quartz particles to Egyptian blue crystals. No glass phase survives. Pores are black.)

of green frit seems to have involved a reduction in the amount of copper added to the mixture, compared to that added for Egyptian blue frit, and an increase in the amount of alkali flux. For Amarna, the range of lime contents in the Egyptian blue frit (11–13% CaO) was significantly less than that in the green frits (8–24% CaO), which suggests that the quartz sand were more carefully selected for the production of Egyptian blue frit.

The differences in the raw materials used indicate that frit was being produced independently in both Egypt and Mesopotamia in second half of the 2nd millennium BC. In addition, the use of sand containing dolomitic limestone only at el-Rakham indicates that there was definitely more than one, and most probably several, production centres for frits in New Kingdom Egypt.

In terms of the raw materials used, frit production is, in some respects, more closely related to faience production than to glass production. Thus, glass is generally assumed to have been produced using crushed quartz pebbles (Petrie, 1909: 25; Brill, 1970: 109), whereas faience was most probably more frequently produced using quartz sand (Tite et al., 2007). However, on the basis of the bulk compositions of faience, the sand used for faience would have had a lower lime content. In Egypt, scale from bronze provided the copper for both faience and glass whereas, in Mesopotamia, scale from copper metal or a copper ore was normally used (Shortland and Eremin, 2006; Tite et al., 2007). Similarly, soda-rich plant ash was used for faience and glass in both regions.

The microstructural evidence suggests that the powder frit residues were produced by grinding frit cakes which were the primary product, and that the frit vessels and beads were then made by moulding this powder to the required shape, and refiring. However, at Amarna, nothing was found to compare with the ceramic vessels containing a mass of Egyptian blue frit balls that were excavated at the Ptolemaic-Roman period site at Memphis, and therefore, we do not know how the

primary cakes themselves were produced. The excavation of site O45.1 at Amarna by Nicholson during the 1990s exposed five kilns and one working hearth (Kiln 5) (Nicholson, 2007). The microstructures of the fused clay linings as observed in a SEM suggest that parts of Kilns 2 and 3 sometimes reached temperatures as high as 1250 °C (Shortland, 2000: 40; Shortland et al., 2007), which is in excess of the 850–1000 °C and 950–1100 °C firing temperature ranges used in the production of Egyptian blue and green frits respectively. Therefore, it is more likely that Kilns 2 and 3 were used for the working or production of glass than for the production of the primary frit cakes. Kilns 1, 4 and 6 were much less vitrified and could, in principle, have been used to fire frit cakes, as well as faience. However, Kiln 1 is located close to a pottery workshop, and is therefore more likely to have been used for firing pottery, as is Kiln 6 which is similar in form to Kiln 1. Kiln 4 is different in form to Kilns 1 and 6, and therefore, might have been used for firing frit and faience, although there are no obvious signs of the contamination that might have been expected as a result of such firings.

Irrespective of how primary frit cakes were produced, it is clear from the scale of the monuments on which Egyptian blue frit pigment was used that frit was being produced in large quantities. On the basis of laboratory experimentation, Hatton (2005: 186) established that the coverage of Egyptian blue pigment, when mixed with water, was approximately 17.5 cm²/g. He then estimated that the areas covered with Egyptian blue pigment in a typical New Kingdom tomb (Queen Nefertari) and a typical New Kingdom temple (Medinet Habu) at Thebes were 65 m² and 2500 m² respectively. For the tomb, the weight of Egyptian blue pigment required was, therefore, approximately 37 kg which is equivalent to some 160 primary cakes, assuming a cake diameter of 100 mm and thickness of 20 mm, and for the temple, the weight was approximately 1400 kg which is equivalent to some 6300 primary cakes.

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