

Egyptian faience glazing by the cementation method part 2: cattle dung ash as a possible source of alkali flux

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Abstract Based on our current awareness, there are three distinct primary sources of alkali flux in the ancient Egyptian faience making: natron, soda rich plant ash and the so-called ‘mixed alkali fluxes’. Whereas the nature and origin of the first two types are identified to some extent, there are more questions regarding mixed alkali fluxes. In an attempt to provide further clarification on the latter source, a series of replication experiments on the production of Egyptian faience by the cementation glazing method were conducted using cattle dung ash as the source of alkali flux. After firing at 980 °C, the appearance of the faience objects, the microstructure and the chemical composition of selected samples obtained using scanning electron microscopy/energy-dispersive spectroscopy (SEM-EDS) were investigated. The discussion has primarily focused on cattle dung ash as the most, or one of the most, available sources of ash in ancient societies and its possible use as a source of alkali flux in the production of Egyptian faience, at least by the cementation glazing method.

Keywords Egyptian faience · Donkey beads · Cattle dung · Qom technique · Cementation glazing · Alkali flux

Introduction

At the present time, it is generally accepted that there are three primary sources of alkali flux in the production of Egyptian faience objects: natron, soda rich plant ash and the so-called ‘mixed alkali fluxes’ (Tite and Shortland

2008, 38–43, 204–205). It should be noted that the term ‘Egyptian faience’ in this paper does not refer only to ancient faience objects produced in Egypt, but rather siliceous ceramics of the ancient world in general. The term is however used to distinguish this material from later tin-glazed majolica type earthenwares made at Faenza which are generally known as ‘faience’.

‘Natron’, in modern mineralogy, is the mineral name denoting the compound sodium carbonate decahydrate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$). However, as an archaeological term, it normally refers to the polyphase evaporite deposits that consist mainly of the carbonates, bicarbonates, chlorides, and sulphates of sodium. Furthermore, this term may be used specifically for evaporite deposits from the Wadi El-Natron or Natroun (Arabic for Natron valley, which is the best known source of natron), located in the desert of the northwestern Nile Delta, some 100 km NW of Cairo (roughly 30° 19′–30° 24′ N, 30° 18′–32° 24′ E) (see Shortland 2004; Shortland et al. 2006). Natron consists mainly of sodium carbonate and sodium bicarbonate and is characterised by very low potash, lime and magnesia content, typically each being less than 0.5 % (Tite and Shortland 2008, 42).

Soda-rich ashes are obtained from burning salt tolerant, halophytic plants of the *Chenopodiaceae* family, growing in desert regions, coastal and salt marshes (Tite et al. 2006). The chemical composition of plant ash does not merely depend on the plant species but also on factors such as the preparation circumstances of the ash, the parts of the plant burnt to ash (i.e. root, stem, leaf and flower), the age of the plant, the season of sampling and the composition of water and soil. Nevertheless, soda-rich ashes generally contain, in addition to soda, significant amounts of potash, magnesia and lime, and the $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios are usually in the range 2.4–11 (Tite and Shortland 2008, 39).

Mixed alkali fluxes can be distinguished by significant potash contents (generally higher than those of soda) and by

This paper is dedicated to the late Dr. Hans E. Wulff who conducted pioneering studies on the cementation glazing process.

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low levels of lime and magnesia (Tite and Shortland 2008, 42). The $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios are typically in the range 0.3–1.5 (Tite and Shortland 2008, 42). Whereas natron and plant ashes have been subject to extensive research studies as sources of alkali fluxes (see e.g. Tite et al. 2006; Shortland et al. 2006; Rehren 2008 and references therein), little is known on the nature, origin and sources of mixed alkali fluxes. The reason behind this obscurity is that in the course of production of ancient vitreous materials, the alkalis and alkali earths are not necessarily taken up in the ratios originally present in the flux. Hence, as discussed in part 1 of this paper (Matin and Matin 2012, 765–6; hereinafter referred to as part 1), the composition of ancient vitreous materials can be significantly different from that of the fluxes from which they were produced. In other words, the oxide ratios as analysed cannot be taken to represent the original flux composition (see Rehren 2008 and references therein). This is particularly true for Egyptian faience glazing by the cementation method, mainly due to the active role of vapour glazing (chlorides glazing mechanism (CGM); see part 1, 770–3) in this process, which intensifies the problem. *Salsola kali* and seaweed are generally suggested as potential sources of mixed alkali fluxes in coastal regions. Other suggested sources include the efflorescent salts from latrine and manurial soils, which consist largely of saltpeter (Brill 1992; Tite and Shortland 2008, 43), as well as the treatment and purification of ashes before use (Tite and Shortland 2008, 42, 145; Tite et al. 2006, 1285).

Cattle dung ash as a source of alkali flux

Cattle dung is not only a rich source of nitrogen and phosphorus but also contains significant amounts of potassium. By today's standards, a cow producing 35 kg milk per day excretes yearly 150 kg nitrogen, 20 kg phosphorus and 80 kg potassium (Enghag 2004, 984). In a series of replication experiments by Matin (2014), it was shown that the glazing of quartz stone by vapour glazing mechanism, and using dung ash as the source of alkali flux, is possible. Moreover, as discussed in part 1, the glazing of faience by the cementation method is heavily reliant on the vapour glazing mechanism. Therefore, the question arises as to whether cattle dung ash could have been used as a source of alkali flux for ancient faience production, at least by the cementation method.

Since the domestication of cattle in the eight millennium BC (Rezende 2007, 3, 6), dung has been a valuable source of

fuel, particularly in dryland areas. In many parts of the world today (for instance India and Northern Pakistan), dung is considered as the main source of domestic fuel (see e.g. Harris 2000). There is much archaeological evidence confirming the use of dung as a source of fuel in ancient societies, for instance in the Near East (see e.g. Albert et al. 2008; Miller 1996; Shahack-Gross and Finkelstein 2008; Shahack-Gross 2011; and references therein) or Indus valley (Madella 1997; Reddy 1999). Cow dung fire is characterised by the release of much more smoke relative to that of wood fire. However, cow dung and wood fires are both capable of releasing a similar amount of heat (Braadbaart et al. 2012, 845). During the firing process, the size and the shape of the pieces of fuel in the fuel bed have an important effect on the rate of combustion. Therefore, the tightly packed structure of cow dung results in slow-burning steady fires, whilst wood produces fast fires. Hence, where a more consistent temperature over longer periods of time is required, it would be more advantageous to use cow dung as the source of fuel (for example, for cooking or heating of dwellings). Moreover, little time and energy is required to collect cow dung compared to that needed to chop and transport wood. Experimental firing of clay figurines in a small dung-fuel kiln has demonstrated that cow dung fire can reach high temperatures; for example, over 1000 °C in 1 h or 1095 °C in 1 h and 20 min (Braadbaart et al. 2012; Lancelotti and Madella 2012; Kenoyer 1994). Most importantly, perhaps, is its ready availability in dryland areas. These factors make dung stand out as an ideal source of fuel for ancient societies, not only for cooking or heating but also for more traditional activities such as pottery firing (Sillar 2000).

The extensive use of dung as a source of fuel means that in practice dung ash had been the most, or at least one of the most, available ashes and hence could have been the most available source of alkali fluxes in ancient societies.

The charcoal question

The belief in the use of charcoal as a raw material used in the production of faience by the cementation glazing method appears to be based entirely upon the observations by Wulff et al. (1968). However, recent studies cast doubt over the validity of this assumption. In part 1, it was shown that the production of faience by the cementation method without the use of charcoal is perfectly possible. More precisely, it was

Table 1 The Qom workshop glazing mixture recipe

Raw materials (wt%)				
Plant ash	Hydrated lime	Quartz powder	Ground charcoal	Copper oxide
34.94	34.94	23.3	5.82	1

Based on the data by Wulff et al. (1968)

Table 2 Chemical composition of raw materials used in the Qom workshop (wt%)

Raw materials	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	MnO	TiO ₂	PO ₄	Total
Quartz powder ^a	90	1	–	2	0.3	5	0.8	0.05	0.05	–	99.2
Plant ash	10	40	6	6	10	2	0.7	0.1	0.1	4	78.9

Stated by Wulff et al. (1968)

^a Mentioned as ‘bead body before glazing’ in the original text

proven that not only does charcoal not act as an essential raw material, but it also can have adverse effects on the glazing process as it generates a reducing atmosphere (see part 1, 768). According to the authors’ personal communications with a few of the elderly individuals involved in the production of faience in Iran in the first half of last century, none confirmed the use of charcoal as a raw material.

In order to address this question, it is worthwhile to have a closer look at the study of Wulff et al. (1968). Table 1 shows the glazing mixture recipe based on the data by Wulff et al. (1968, 100). Table 2 summarises the chemical composition of quartz powder and plant ash given by Wulff et al. (1968), assuming that the chemical composition of ‘bead body before glazing’ is the same as that of quartz powder. No details of the employed analytical technique were given by Wulff and colleagues. In Table 3, row 1, the chemical composition of the glazing powder given by Wulff et al. (1968) is presented. Row 2 shows the calculated chemical composition of the glazing powder, based on the described recipe of Wulff et al. (1968). For this calculation, three main assumptions were made to facilitate discussion: firstly, that the chemical composition given for bead body before glazing by Wulff et al. (1968) is the same as that of quartz powder; secondly, that pure calcium hydrate was used; hence, its chemical formula was used for calculations. This assumption was made mainly because the chemical analysis for calcium hydrate was not given by Wulff et al. (1968). Finally, the chemical composition of charcoal was not taken into account in calculations. Charcoals, depending on their type of wood, generally contain less than 5 % ash (and often less than 2 %). Therefore, since, according to Wulff et al. (1968), only 5.85 % charcoal was present in the recipe, the resulting ash was too small in amount to

have any considerable effect on the final composition of the glaze after firing.

Table 3 indicates that, as expected, there is a significant difference of the SiO₂ and CaO contents between the recipe of Wulff et al. (1968) and the calculated recipe. This is mainly due to the fact that in the calculated recipe, calcium hydrate was assumed to be pure. Moreover, the amounts of PO₄ and K₂O+Na₂O given by Wulff et al. (1968) show a meaningful difference to those of the calculated recipe. This suggests that there could have been a source of phosphates and alkalis in the recipe of Wulff et al. (1968) that was not taken into account. This could have definitely not been charcoal. However, since dung ash is a rich source of phosphates and alkalis, the question arises as to whether it could have been used in the production of faience. Furthermore, noting the considerable resemblance in appearance between ground charcoal and dung ash, there is the possibility that these two had been mistaken by Wulff et al. (1968). It seems that they were aware of some possible inaccuracies in their observations and stated that some aspects of the work were ‘not revealed to us by our reluctant informants’ (Wulff et al. 1968, 107).

As discussed above, experimental studies conducted by Matin (2014) showed the successful glazing of quartz stones using dung ash as the source of alkali flux. This suggests that the use of dung ash in the production of faience by the cementation method is plausible. In an attempt to address this issue, a series of replication experiments were undertaken.

Experimental procedure

Replication experiments by the cementation glazing method were undertaken with three glazing powder recipes using dung ash as the sole source (GP9 and GP10) or the main source

Table 3 Chemical composition of the Qom glazing powder (normalised to 100 %)

Chemical composition (wt%)	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	MnO	TiO ₂	PO ₄	CuO	Na ₂ O+K ₂ O
Stated by Wulff et al. (1968)	43.65	20.3	3.05	20.30	2.03	6.09	1.52	–	–	2.03	1.02	23.35
Calculated composition (based on the described recipe by Wulff et al. (1968))	31.31	18.19	2.69	37.15	4.56	2.38	0.55	0.05	0.05	1.79	1.28	20.88

Table 4 Particle size distribution of raw materials (μm , wt%)

Raw materials	Less than 44	44–88	88–149	149–250
Silica sand (fine)	40	60	–	–
Silica sand (coarse)	10	20	25	45
Feldspar	40	60	–	–
Calcium carbonate	100	–	–	–

(GP11) of alkali flux. Two recipes for the body paste, as well as quartz stones, were used as experimental bodies. Rock quartz pieces were used as comparative indicators for alkali and copper vaporisation (see part 1, 763). After firing the samples at 980 °C, the appearance of the resulting objects was observed with the naked eye and a low-power binocular microscope, and macroscopic evidence was reported. Subsequently, polished sections of the selected objects, through the glaze and into the body, were prepared. In order to determine their microstructures, these polished sections were examined using a LEO scanning electron microscope (LEO1450VP), operated in backscattered electron mode, in which the different phases can be distinguished on the basis of their atomic number contrast.

The chemical composition of the glass and crystal phases present in the glaze were determined using an energy-dispersive spectrometer (EDS) attached to the scanning electron microscopy (SEM), which had been calibrated using appropriate primary standards. The accuracy of the measured data was evaluated against standards of corning glass. For the glass coatings, bulk analysis from three or four areas of each sample was performed, the resulting average analytical totals being normalised to 100 % (analytical totals range from 97.4 to 99.2 wt%). For the white and needle-like crystals, a number of spot analyses were carried out along the lateral line and the average composition was normalised to 100 %. An accelerating voltage of 20 kV and a probe current of 10 nA were used.

Raw materials

Silica sand (fine and coarse) and feldspar were used as raw materials for the faience body paste. Their particle size

distributions are given in Table 4. A large piece of rock quartz was broken into small parts, about 3–4 cm in length, and the resulting pieces were used as quartz objects for glazing. The raw materials for glazing powder mixture were fine silica sand, calcium hydroxide, cattle dung ash and copper scale. The proportions were chosen according to authors' previous unpublished replication experiments as well as the results presented in part 1. Table 5 shows chemical composition of the raw materials obtained by induced coupled plasma atomic emission spectroscopy (ICP-AES, PerkinElmer instrument) at a commercial lab. Appropriate standards (SY4 and BCR-1) were used to check the accuracy of the system. The calcium hydroxide was produced by calcination of calcium carbonate (limestone) at 980 °C. The calcined lime (quick lime) was then moistened and left to dry for 15 days at room temperature. Cattle dung samples were collected from two different rural farms located near Yazd (a city in central Iran, situated near the desert with arid climate at 31° 53' N, 54° 21' E), and Saveh (or Sava, a city located about 100 km southwest of Tehran at 35° 01' N, 50° 21' E, with a cold semi-arid climate). Both farms practice traditional animal husbandry. For preparation of the ashes, cattle dung samples, air dried for 1 month, were placed in an unglazed porcelain pan and heated at 400 °C for 24 h in an electric kiln. The copper scale, obtained from a traditional coppersmith located in Yazd, was used as a source of copper oxide. The copper scale, obtained from a traditional coppersmith located in Yazd, was used as a source of copper oxide. According to the analytical data obtained by atomic absorption spectroscopy at a commercial laboratory, it was found to contain 83.5 wt% CuO, the rest being mainly SiO₂, Al₂O₃, CaO, MgO and L.O.I.

Faience bodies

Two pastes, BR and B2, were used to produce faience bodies. Their recipes and calculated chemical compositions are provided in Tables 6 and 7, respectively. As noted in part 1, the BR sample was used as the reference faience body paste. In an attempt to replicate translucent faience objects (see part 1, 766), the B2 body paste was also used together with the GP11 glazing mixture, which is discussed in the following

Table 5 Chemical composition of raw materials (wt%, normalised to 100 %)

Raw materials	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	S	Cl	P ₂ O ₅
Silica sand	96.89	1.70	0.17	0.05	0.70	0.01	0.03	0.45	na	na	na
Feldspar	73.23	15.42	0.26	0.34	1.43	0.01	4.19	5.12	na	na	na
Quartz stones	99.21	0.20	0.11	0.02	0.25	0.06	0.10	0.05	na	na	na
Lime	2.70	0.19	0.19	0.02	95.18	1.31	0.35	0.06	na	na	na
Cattle dung ash (S), <i>Saveh</i>	51.25	7.25	2.58	0.33	9.95	3.57	3.95	11.58	0.53	4.34	4.67
Cattle dung ash (Y), <i>Yazd</i>	25.17	2.80	1.55	0.15	14.07	6.65	8.63	19.56	0.87	14.26	6.29

na not analysed

Table 6 The recipes of faience bodies (wt%)

Code	BR	B2
Fine silica sand	85	–
Coarse silica sand	–	95
Feldspar	10	–
Serish	5	5

subsection. As a binder and plasticizer, 5 % *Serish* (powdered root tuber of *Asphodelus sphaerocarpus*; see part 1, 765) was used in both the BR and B2 body pastes. *Serish* is the Persian name for the powdered root tuber of *Asphodelus sphaerocarpus*, whose aqueous solution was commonly used as an adhesive in many traditional crafts in Persia, such as bookbinding and textile crafts (Wulff 1966). In addition, its usage in the faience body mixtures of the last century has been pointed out by Yaghoobi (2002). The ash content of *Serish* is only about 5 % at 900 °C. In the BR recipe, 10 % feldspar was used as the alumina source in the body to replicate an impure sand source (see part 1, 765, 775–776). The body raw materials were mixed, and for better homogenisation, the resulting powder mixtures were sieved twice (30 mesh, 590 µm). By the addition of about 30 wt% water to each mixture, a paste was created, which was wedged and kneaded for a few minutes without any further ‘ageing’ of the body paste. The pastes were then formed into bricks in two plastic (epoxy resin) moulds in two thicknesses (40×21×12 and 7.5 mm). The brick-shaped faience bodies were then left to dry at room temperature for 48 h.

Glazing and firing

Replication experiments were undertaken using three glazing mixture recipes (see Table 8). In the GP11 glazing mixture, sodium carbonate was added as an additional source of alkali flux. The ingredients of glazing mixtures were weighed and mixed, and the resulting powders were sieved twice (30 mesh) and placed into unglazed porcelain containers with a porcelain prop in their centre (Fig. 1). The faience bodies (BR and B2) were then buried alongside each other in the middle height of the glazing powder and around the prop. A piece of rock quartz was placed on top of the prop as a relative indicator for alkalis and copper vaporisation, and finally, everything was covered by a container lid. An orifice of 25 mm in diameter had been made in the centre of the container lid, to model the kiln chimney (similar to actual mass production

Table 7 Calculated chemical composition of faience bodies (wt%)

Code	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O
BR	94.5	3.06	0.17	0.07	0.78	0.01	0.45	0.96
B2	96.87	1.7	0.17	0.05	0.71	0.01	0.03	0.46

Table 8 The glazing mixture recipes (wt%)

Experiment code	Silica sand (fine)	Cattle dung ash		Calcium hydrate	Copper scale	Added Na ₂ O ^a
		S	Y			
GP9	11	30	–	56	3	–
GP10	11	–	30	56	3	–
GP11	11	–	30	56	3	2

S collected from Saveh, Y collected from Yazd

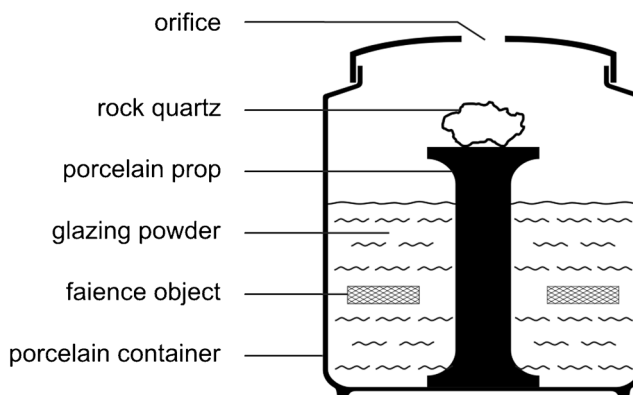
^a Grams added Na₂O/100 g glazing mixture supplied by sodium carbonate, supplied by pure synthetic sodium carbonate

firing) (Wulff et al. 1968, 101). The porcelain containers were placed in an electric kiln, and firing was carried out according to the firing schedule shown in Fig. 2 (with maximum temperature of 980 °C).

Results

GP9

The faience objects glazed by the GP9 mixture were covered by a rich but very wavy and uneven glaze coating. The glaze colour was not turquoise but greenish navy blue. Furthermore, the glaze coating exhibited many holes penetrated to the faience bodies. The reverse sides of the faience objects, where they were rested during firing, were also covered by a rich uneven glaze, and there was no considerable difference observed in the appearance of the underside and upside glaze coatings. The faience objects were surrounded by a very thin (0.5 mm or less) capsule, and there were patches of capsule flakes or glazing mixture, stuck on the glaze coatings (Fig. 3a). The fired glazing mixture was porous, and it crumbled easily when pressed by hand, and hence, it provided for easy and safe removal of buried faience objects. The quartz object glazed by the GP9 mixture exhibited a shiny deep blue glaze coating, showing extensive runners and drips (Fig. 4a).

**Fig. 1** Setting of quartz and faience objects for firing

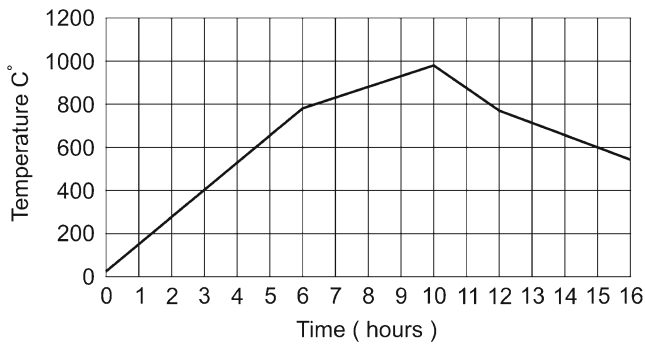


Fig. 2 Firing schedule for faience and quartz objects fired in an electric kiln

GP10

The overall appearances of the faience and quartz objects covered by the GP10 glazing mixture were similar to those glazed by the GP9. However, compared to the GP9 faience objects, those of the GP10 tend to be more blue in colour and have a less green tint (Figs. 3b and 4b). Moreover, less patches of capsule flake or the glazing mixture are observed stuck to the GP10 glazed surface. The SEM photomicrograph (Fig. 5a) shows the very variable thickness of the GP10 glaze, from approximately 10 to more than 150 μm . In the body microstructure, minimal interparticle glass phase is observed, as light grey halos around some quartz particles (darker grey). The buffer layer is more than 1500 μm in thickness but lacks a continuous uniformity and includes several pores. The analytical data obtained by SEM-EDS on the glass phases and the glaze and buffer layers are provided in Table 9 (rows 1 and 2).

GP11

As mentioned above, the GP11 glazing mixture was applied on both the BR and B2 body pastes. The faience objects made from the BR body paste were covered by a rich shiny and smooth turquoise blue

Fig. 3 Faience objects glazed by the GP9 (a), GP10 (b) and GP11 (c and d) glazing mixtures

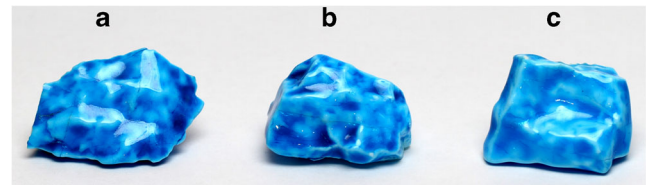
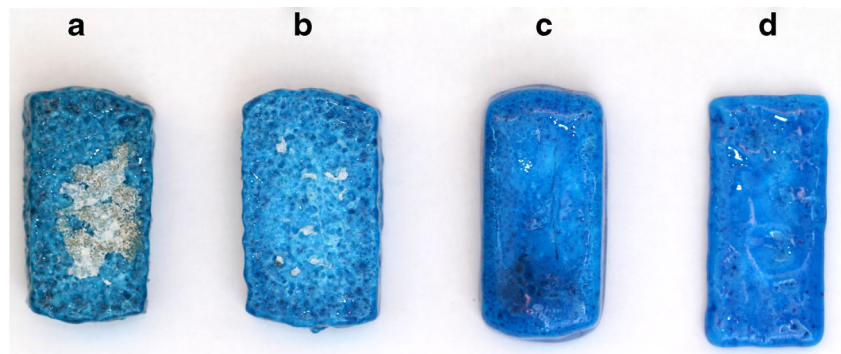


Fig. 4 Quartz objects glazed by the GP9 (a), GP10 (b) and GP11 (c) glazing mixtures

glaze (Fig. 3c). However, on their underside, where they were rested during firing, the glaze coating seemed rough and uneven. No adhesion of the glazing powder to the objects was observed. The sintered glazing powder was porous, and it crumbled easily when pressed by hand. Faience objects were surrounded by a firm capsule (Fig. 6). The quartz object associated with the GP11 glazing mixture was covered by a smooth shiny light turquoise blue coating, including run and drip marks. The SEM image revealed a glaze coating, which is approximately 150 up to 350 μm in thickness, and a well-defined and uniformly distributed buffer layer (about 400 μm ; see Fig. 5b). The SEM image at higher magnifications shows the body quartz particles (dark grey), which are bonded together by sufficient interparticle glass (light grey, Fig. 5c).

As expected (see part 1, 766), the glaze coating on the faience objects made by the B2 body paste was uneven and wavy (Fig. 3d). However, no adhesion of the glazing powder to the faience objects was observed. Optimum sintering was exhibited by the glazing mixture, and it crumbled easily. The thin faience objects (6.5 mm in thickness), which were made by the B2 body paste, were entirely translucent (Fig. 7). However, translucency was not observed on the same faience object made in 12-mm thickness. The cross section of the translucent faience object, in comparison with the reference faience object made by the BR body paste and the GP11 glazing mixture, is shown in Fig. 8. The glaze layer is about 40–100 μm in thickness, and the quartz particles in the body (dark grey) are embedded in a continuous glass matrix (light grey). No obvious and defined

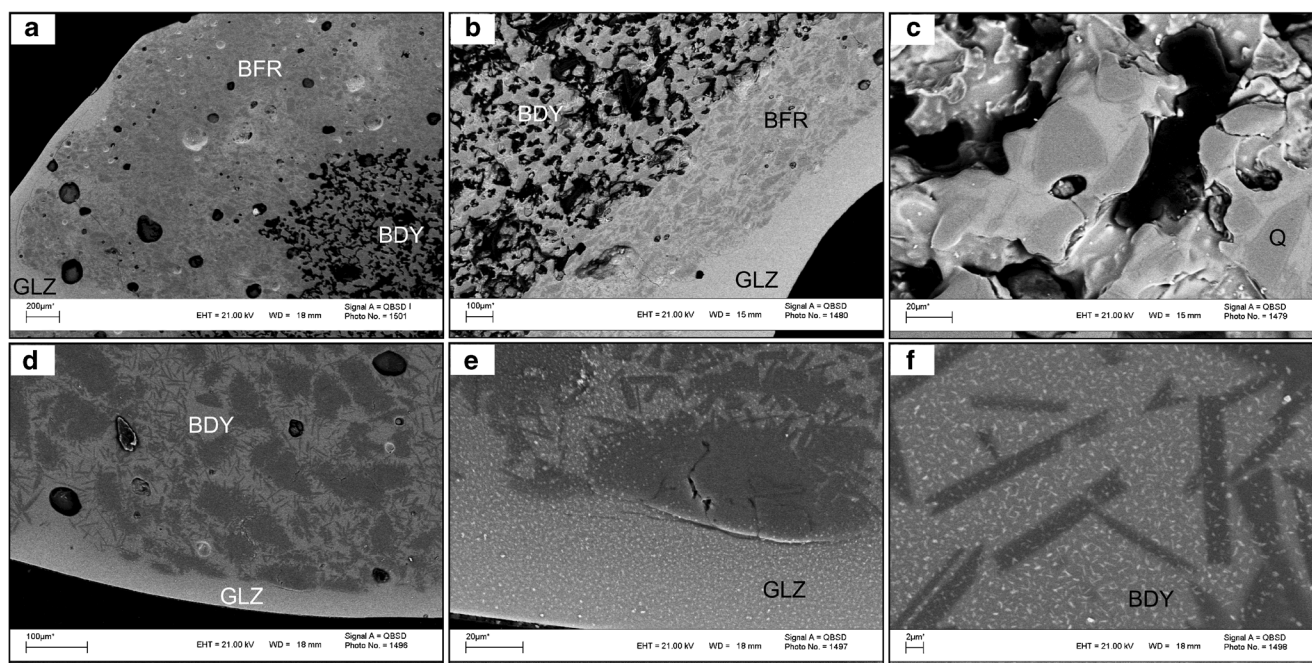


Fig. 5 SEM-BSE images of cross sections through replicated faience samples made by the Y cattle dung ash: **a** glazed by the GP10 glazing mixture; **b, c** glazed by the GP11 glazing mixture on the BR body paste;

d, e, f glazed by the GP11 glazing mixture on the B2 body paste. *BDY* body, *BFR* buffer layer, *GLZ* glaze, *Q* quartz

buffer layer is visible, and the glaze layer has merged into the quartz body, which is bonded together by continuous interparticle glass (Fig. 5d). At higher magnification, grey needle-like crystals, about 15–20 μm in length, are visible in the interparticle glass, and white needle-like crystals, less than 1 μm in length, are observed both in the interparticle glass and the glaze layer (Fig. 5e, f). The analytical data obtained by SEM-EDS on glass phases of the faience objects associated with the GP11 glazing mixture and needle-like crystals (both grey and white crystals) are provided in Tables 9 and 10, respectively. The crystals are essentially copper silicates, but further research is required to provide their exact mineralogical identification.

Discussion

Cattle dung ash as a source of alkali flux in cementation glazing

Cattle dung ash composition may vary according to a variety of factors such as animal diet, species, age, husbandry and environmental conditions (Lancelotti and Madella 2012). In the GP9 and GP10 glazing mixtures, two distinctive samples of cattle dung ash (types S and Y, respectively; see Table 5) were used as the sole source of alkali flux. As demonstrated by the appearance of the objects (Fig. 3a, b) and analytical data (Table 9, rows 1 and 2), despite the considerable difference in the composition

Table 9 EDS analyses of glass phases of faience objects, glazed using the Y cattle dung ash (normalised to 100 %)

Glazing mixture	Faience body paste	Glass phase position	Raw no.	Glass phase composition (wt%)								Na ₂ O/K ₂ O
				SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Cl	CuO	
GP10	BR	Glaze	1	71.1	8.9	0.8	0.3	1.8	2.7	1.3	13.1	0.7
		Buffer	2	78.7	8.4	0.9	0.2	1.7	2.6	1.0	6.5	0.7
GP11	BR	Glaze	3	68.7	1.1	2.1	0.2	3.9	16.0	1.2	6.8	0.2
		Buffer	4	72.7	2.8	1.4	0.1	3.1	15.1	0.9	3.9	0.2
		Body	5	78.8	4.3	0.7	0.1	2.3	11.3	0.6	1.9	0.2
	B2	Glaze	6	73.3	1.6	0.3	0.1	3.9	12.7	1.3	6.8	0.3
		Buffer or body	7	79.8	1.5	0.2	bd	3.2	10.6	1.2	3.5	0.3

bd below detection limits

of the types S and Y ashes, they both contribute significantly in the cementation glazing process. On the basis of the replication experiments carried out, it seems that the main mechanism involved in the cementation glazing process using the GP9 and GP10 mixtures is the CGM (the main characteristics of which are summarised in part 1, 773 (Table 9)). This hypothesis is supported by the evidence as follows:

1. Faience appearance (such as pitted glaze coating with greenish navy blue hues, or similar glaze coatings on the upper and underside of objects; see Fig. 3a, b)
2. Rock quartz appearance (such as greenish navy blue glaze coating including runs and drip marks; see Fig. 4a, b)
3. Faience glaze composition (which is the ‘low alkalis-high copper’ type; see Table 9, row 1)
4. Faience microstructure (a thick and uneven buffer layer and minimal interparticle glaze; see Fig. 5a)

As previously discussed, a concentration of only about 5 wt% of alkali oxides (supplied by carbonates) in the glazing mixture composition is sufficient for a successful cementation glazing at 980 °C (see part 1, 767). However, replication experiments by the GP11 glazing mixture showed that with the contribution of cattle dung ash, an extra 2 wt% Na₂O is sufficient for successful cementation glazing.

In the case of faience objects produced by the cementation method using mixed alkali fluxes, the average Na₂O/K₂O ratios in glass phases generally range from 0.4 to 1.1 (Tite and Shortland 2008, 200–205). As Table 9 shows, the Na₂O/K₂O ratios in the glass phases produced by the GP10 and GP11 are 0.7 and 0.2–0.3, respectively; however, in comparison with the GP10, the absolute percentage of soda in the GP11 is higher. An interesting point is the presence of a higher content of K₂O in the GP11 with the addition of only 2 wt% Na₂O. It seems that the reaction between sodium carbonate and dung ash raises the amount of ‘reactive’ potash, which subsequently contributes to the glass network by the so-called ‘preferential take up of potash’ phenomenon. As previously



Fig. 6 Faience object surrounded by its capsule (BR body paste, glazed by the GP11 glazing mixture)



Fig. 7 Translucent faience object (about 6.5 mm in thickness) produced by the GP11 glazing mixture and the B2 body paste

discussed in the “Introduction” (see also part 1, 764–766), for various reasons, the composition of the glass phases in faience objects can be significantly different from that of the glazing mixture from which they were produced. In the case of glazing by the cementation method, this phenomenon is intensified. It has been repeatedly observed in the cementation glazing replication experiments that the absolute percentages of potash in faience glass phases, in comparison to original glazing mixtures, were markedly increased, and the Na₂O/K₂O ratios were in turn decreased (Tite and Shortland 2008, 51–53 and references therein). The reason behind this phenomenon has never been fully investigated and requires further research.

The details of the contribution of cattle dung ash in the glazing process, and the relevant chemical interactions have not been fully investigated yet. The presence or formation of potassium nitrate in this process seems unlikely. Nevertheless, potassium nitrate, like the fully reactive alkali carbonates, contributes to the cementation glazing process (part 1, 768).

As pointed out in the “Introduction”, the origin and sources of the so-called mixed alkali flux in the production of ancient faience objects has not yet been identified. Replication experiments by the GP11 glazing mixture suggest cattle dung ash as a possible source of mixed alkali flux in the cementation glazing method. That is, particularly, in combination with other alkali flux sources. The use of cattle dung ash in the

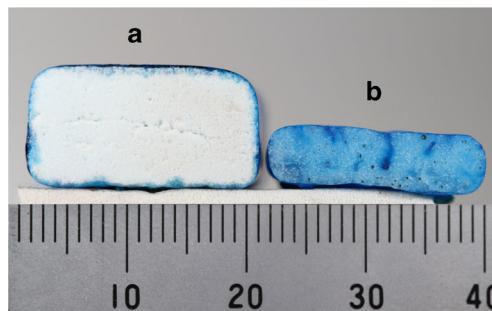


Fig. 8 Cross sections of faience objects produced by the GP11 glazing mixture: BR body paste (a), B2 body paste (b)

Table 10 EDS analyses of needle-like crystals associated with the GP11 glazing mixture and the B2 faience body paste (normalised to 100 %)

Crystal appearance	Fig.no.	Crystal position	Crystal composition (wt%)							
			SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Cl	CuO
Needle-like grey crystals	5d, 5f	Body	87.2	1.6	0.9	0.2	1.4	2.8	1.1	4.8
Needle-like white crystals	5f	Body	82.2	0.7	0.6	0.1	2.5	5.1	1.4	7.4
Needle-like white crystals	5e	Glaze	79.4	2.1	0.4	0.1	3.2	5.6	1.5	7.7

ancient faience glazing by other methods, i.e. application and efflorescence, is a direction for further research. In this context, for instance, the partial dissolving of cattle dung ash in water and recovering of the soluble salts by evaporation could be an interesting possibility.

Microstructural criteria

In part 1 of this paper, the general criteria for determination of the glazing techniques were discussed (part 1, 764). The results of the present study—such as the presence of runs and drip marks both on the quartz and faience objects (Figs. 3c and 4, respectively), or the translucent faience object (Fig. 7) which reveals the presence of extensive interparticle glass in the faience body (Figs. 5d and 8)—suggest, once again, that the generally accepted macroscopic and microstructural criteria should be treated with more caution (see part 1, Sects. 4.5 and 4.6).

The mechanism of capsule formation

The firing shrinkage and mechanism of capsule formation has been extensively discussed in part 1 (773–775). In summary, the CaO/SiO₂ ratio in cementation glazing mixtures is too high to produce a dense sintered mixture at about 1000 °C. Thus, after firing, a friable glazing mixture is achieved which enables an easy removal of objects. However, by decreasing the CaO/SiO₂ ratio, a dense sintered mixture will be obtained in actual practice. In other words, increasing the SiO₂ content in the glazing mixture results in a significant reduction in the melting point of the glazing mixture and hence in the

formation of a dense sintered material. This phenomenon is the main cause of the capsule formation. By diffusion of silica (from the faience body) into the glazing mixture (and the resulting reduction in the CaO/SiO₂ ratio), a layer of dense sintered mixture forms around the object, which is known as a ‘capsule’. After the initial stage of the shrinkage process and the simultaneous formation of the capsule, silica migration continues only through the object’s underside, at the bottom of the capsule. Thus, the base of the capsule is generally thicker than its walls.

The chemical compositions of the capsule and the sintered glazing mixture resulting from the GP11 glazing mixture and the BR faience body paste are provided in Table 11. The significant increase in the SiO₂ and a decrease in the CaO contents in the capsule, compared to those of the sintered glazing mixture, confirm previous investigations regarding the mechanism of the capsule formation (see part 1, 774–775).

Conclusion

The principal aim of this paper has been to consider the possible use of cattle dung ash as the main source, or at least one of the sources, of alkali flux in Egyptian faience glazing by the cementation method. The results of the experimental replication indicate that cattle dung ash, particularly in combination with other sources of alkali flux, could have been used as a source of mixed alkali flux in ancient faience production. This, however, has been proved only for the cementation glazing method. Further research remains to be conducted as to whether cattle dung ash, or its derivatives,

Table 11 Chemical composition of capsule and sintered glazing mixture resulting from the GP11 glazing mixture and the BR faience body paste, obtained by wet chemistry analytical methods

Sample	Chemical composition (wt%)										
	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Cl	CuO	P ₂ O ₅	S	Total ^a
Sintered glazing mixture	21.98	1.46	52.77	2.71	3.94	4.68	6.90	2.79	2.30	0.45	99.98
Capsule	37.46	1.69	44.51	2.23	4.32	3.20	1.23	0.91	1.94	0.19	97.68

^a Fe₂O₃, TiO₂, MnO: not analysed

could have been used in ancient faience production by other glazing techniques.

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