



The use of technical ceramics in early Egyptian glass-making



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ABSTRACT

We present a detailed description of the layered structure developing in the walls of Egyptian Late Bronze Age glass-making vessels, and in similar vessels successfully replicated in laboratory experiments. The analyses show that this layered discolouration and change in ceramic composition is due to the interaction of the glass batch with the vessel during firing. The formation of this visually striking and easy to recognise pattern is due to the chloride content of primary glass batches and does not occur in vessels used to re-melt existing glass. Thus, we argue that these discolourations can be used as a reliable and easy field guide to identify glassmaking waste among Late Bronze Age ceramic assemblages, hopefully increasing the currently very small number of identified LBA glassmaking workshops.

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1. Introduction

Direct archaeological evidence for the production of raw glass during the Late Bronze Age is very limited, despite the abundance of glass objects from this period excavated from Mesopotamia, the Levant, Egypt, Cyprus, Crete, mainland Greece and southern Italy. This is partly due to the inconspicuous nature of glass-making waste and the lack of sufficient diagnostic criteria how to identify primary glass-making archaeologically, and partly due to the relative scarcity of excavations targeting workshop and industrial areas, compared to the more commonly excavated cemeteries, palaces and temple areas.

Current knowledge is that LBA primary glass-making at the Egyptian sites of Qantir and Amarna took place in ceramic vessels including re-used domestic pottery in Qantir (Rehren and Pusch, 2005; Pusch and Rehren, 2007a,b) and purpose-built crucibles in Qantir and Amarna (Rehren, 1997; Nicholson et al., 1997; Rehren and Pusch, 1997), fusing the raw materials at temperatures of around 900–1100 °C. This produced first so-called semi-finished, that is incompletely molten and uncoloured glass (Smirniou and

Rehren, 2011), and in a second step intensely coloured cylindrical glass ingots which were then passed on to secondary workshops (e.g. Pulak, 2008) for the production of finished objects, while the used vessels and crucibles were discarded. Apart from these vessels and crucibles, and small amounts of semi-finished glass, hardly any other waste was produced in the process. So far, semi-finished glass has only been reported from Qantir (Pusch and Rehren, 2007a, 149–51) and Amarna (Smirniou and Rehren, 2011). However, it may have been overlooked elsewhere, as it is easily confused with glassy faience or white glass, and rarely present in significant quantities. Therefore, the archaeologically much more visible and abundant crucible fragments are potentially the most important indicators of Bronze Age glass-making. They can, however, also be used for the re-melting of existing glass. The simple presence of crucibles with glass attached is therefore not sufficient to demonstrate glass-making; this paper aims to present clear criteria to recognize glass-making vessels.

Fragments of crucibles and ‘glassy slag’ that point to primary glass production have been excavated at the New Kingdom sites of Amarna (Petrie, 1894; Nicholson, 1996), Malkata, Lisht, and Qantir (Fig. 1). The finds from Qantir–Pi-Ramesse have been comprehensively studied and form our reference point for primary glass-making during the later Ramesside period (Rehren and Pusch,

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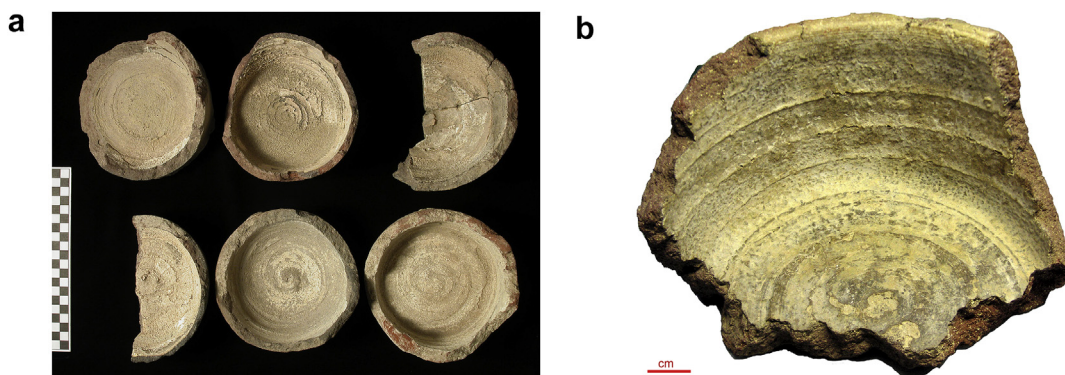


Fig. 1. a: Collection of crucibles from Qantir – Pi-Ramesse. b: Crucible fragment from the site of Amarna.

2005; Pusch and Rehren, 2007a; Schoer and Rehren, 2007). Industrial waste associated with glassmaking excavated by Nicholson in the 1990s at the site of Amarna, and a well-contextualized find of one semi-finished glass fragment (TA22) from the site O45.1 are pointing to primary glass production at Amarna (Nicholson, 2007: 109). A recent study of finds from Amarna also identified semi-finished glass among the finds from Petrie's excavations, representing direct evidence that glass was being made at Amarna from its raw materials (Smirniou and Rehren, 2011).

This paper now examines crucible fragments from Amarna and Lisht, comparing them with fragments from Qantir as well as with crucibles from experimental studies replicating LBA glass-making (Merkel, 2006; Merkel and Rehren, 2007). The aims of this paper are (a) to document the various distinctive layers and zones of discolouration found on the archaeological and experimental crucible fragments, (b) to show that the causal explanations already proposed for the formation of these layers and discolourations for Qantir (Schoer and Rehren, 2007; Merkel and Rehren, 2007) and for Merkel's experiments (Merkel, 2006; Merkel and Rehren, 2007) can be applied also to the material from Amarna and Lisht, and finally (c) to demonstrate how the diagnostic features for glass-making that have been identified by detailed microscopic, macroscopic and geochemical analysis can be used to identify archaeological remains of possible LBA glass-making sites elsewhere.

1.1. Crucibles for glass-making

Coloured glass can be made in a one-step process fusing together the necessary raw materials (Turner, 1954, 443T; Jackson et al., 1998). However, practical considerations such as the volume of unreacted batch material or crushed semi-finished glass relative to the volume of the crucibles and the thickness of the finished glass ingots (Pusch and Rehren, 2007a,b, 153; Merkel and Rehren, 2007, 217, Fig. 26), textual indications from Mesopotamian cuneiform tablets from the 1st millennium BC (Brill, 1970), even though they should be interpreted with some caution (Nicholson, 2007: 117), and the archaeological evidence from Qantir (Rehren and Pusch, 2007) and Amarna (Nicholson, 2007: 129; Smirniou and Rehren, 2011) all point to a process where there were at least two stages in LBA primary glass production.

According to the evidence from Qantir, the raw materials were first mixed in ceramic reaction vessels (in Pi-Ramesse, re-used ovoid beer jars were used for this step) and fired at relatively low temperatures to make semi-finished glass rich in residual quartz, intermediate newly-formed crystals, and porosity (first stage); that frothy semi-finished glass was then crushed and mixed with a colourant and possibly minor amounts of additional flux in purpose-built ceramic crucibles that were fired at somewhat higher

temperatures to produce well-fused coloured glass ingots virtually free of residual quartz, intermediate crystals and bubbles (second stage). Prior to their use, the reaction vessels and the cylindrical crucibles from Qantir were coated on their inside with a mm-thick layer of mostly lime ('parting layer'; Fig. 2) to separate the glass from the ceramic, thus facilitating the removal of the glass from the crucible and preventing contamination of the glass batch by ceramic material (Turner, 1954; Rehren, 1997; Rehren and Pusch, 2005; Pusch and Rehren, 2007a; Schoer and Rehren, 2007; Merkel and Rehren, 2007). The crucible fragments from Amarna (Nicholson, 2007: 123) and Lisht also demonstrate this lime-rich parting layer, first identified and analysed by Turner (1954) on finds from Amarna, on the inner surfaces of the vessels. In addition, some of the ceramic fragments showed a unique pink discolouration of the inner half of the wall fragments (Fig. 3).

1.2. Glass-making in ceramic vessels

Experiments testing the glass-making model developed by Rehren and Pusch (2005) provided a better understanding of the parting layer and its role, examined how the raw materials and the glass melt react with the ceramic vessels, and replicated the pink discolouration that can be found on glass-making crucibles, but not on those used for re-melting existing glass (Merkel and Rehren, 2007). The main points that came out from these experiments are:

- The parting layer does not act completely as a barrier between the batch and the ceramic. Compounds such as soda, chlorides and lime do transfer between the ceramic and glass.
- The presence of significant amounts of salt (NaCl, above 10 to 20 wt%) in the glass batch affects the appearance of the ceramic, leading to its discolouration near the parting layer interface.
- The absence or presence of salt in the batch is responsible for the development of a layered structure on the crucibles during use, including the **parting layer (PL)**, **buff ceramic (Buff)**, **pink discolouration (Pink)**, and **unaltered ceramic (Ceramic)**. In some cases all layers appear, while in other cases some of the layers might not be present.

In some archaeological finds from Qantir and Amarna, a layer of bottle-green glass has been identified between the pink discolouration and the buff ceramic (Rehren, 1997). The experimental work showed that the buff ceramic layer and the pink discoloured ceramic zone only formed in the presence of significant amounts of chlorides in the batch. Thus, the presence of a discolouration zone in archaeological ceramics should indicate the presence of large amounts (equal to about 10–20 wt %) of chlorides in the crucible charge. The presence of such amounts of chlorides is thought to be

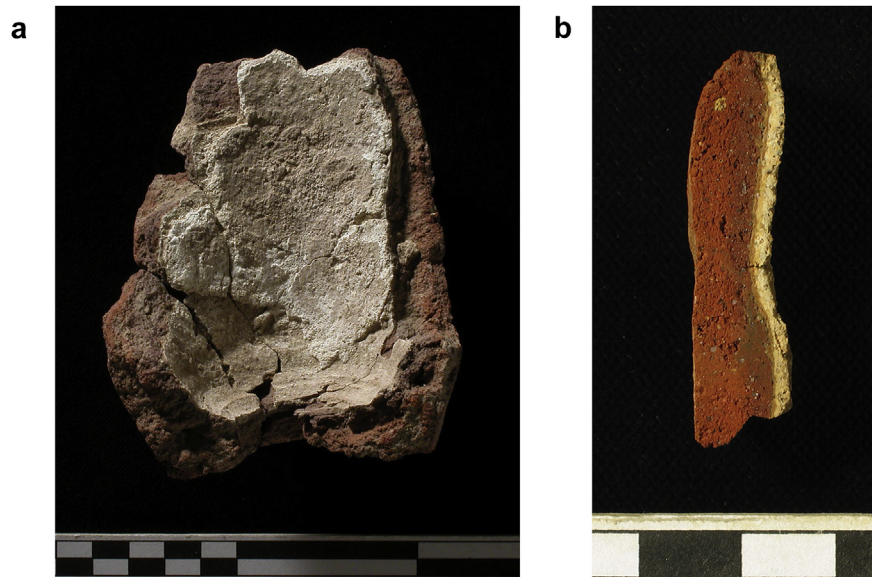


Fig. 2. a: Reaction vessel from Qantir with PL and semi-finished glass; b: Cross section through reaction vessel, showing the PL.

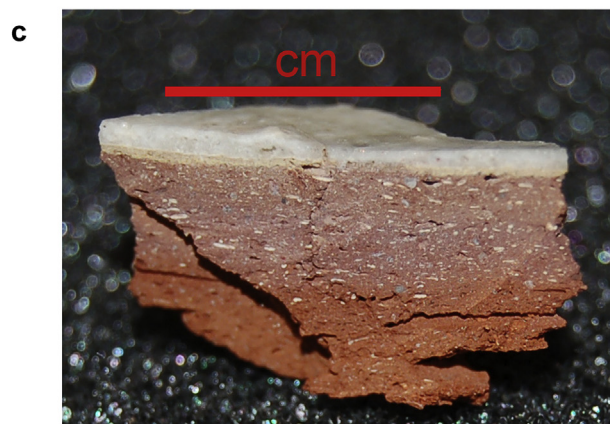
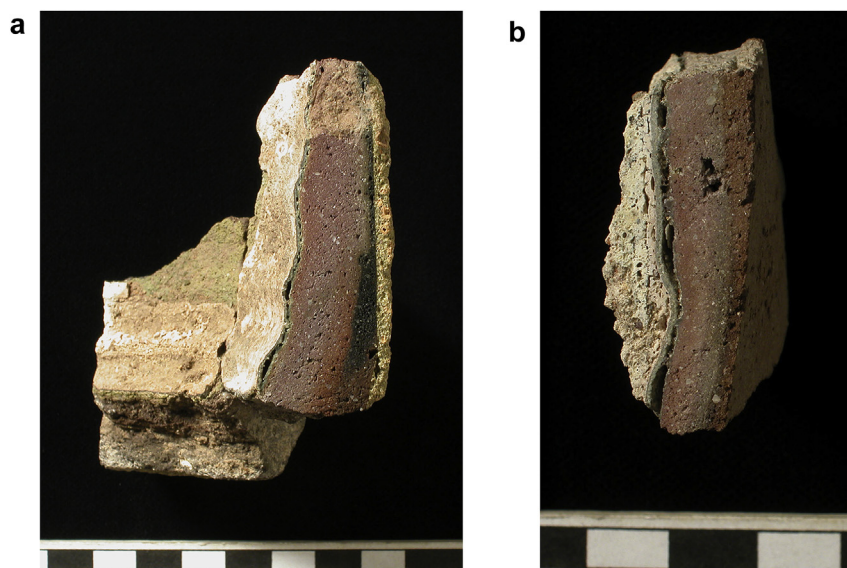


Fig. 3. a: Some of the fragments show a unique discolouration. a and b: Crucibles from Qantir with PL; c: Crucible sample L3 from Lisht.

typical of raw materials for glass making, particularly plant ash (Brill, 1999), but not of pre-existing glass; hence, the presence of a discolouration layer would indicate primary glass-making, as opposed to the re-melting of existing glass. With this paper we provide a detailed material characterisation of these layers to facilitate the recognition of glass-making vessels elsewhere. It is hoped that this will lead to the identification of further LBA glass-making sites, particularly in Mesopotamia where evidence of glass-making is completely lacking, despite the general assumption that glass-making was invented there.

2. Samples

Here we present data from a total of nineteen samples. Four are experimental and five are archaeological samples from Qantir for which we know (experimental) or are confident (archaeological) whether they are directly related to glass making, or only served for glass melting. These nine samples are followed by ten samples from Amarna (7) and Lisht (3) in an attempt to explore whether the diagnostic features on the latter provide sufficient proof of primary glass production in those sites, too.

The crucible fragments studied in this paper share a zoned structure (Table 1) as a result of their use at high temperatures.

2.1. Merkel's experimental samples

The experiments of Steven Merkel were designed to test the influence of glass-making operations on the ceramic vessels in which these operations took place. The vessels for these experiments were ash trays procured in Qantir and thought to have been produced locally using Nile silt similar to the Nile silt used to produce vessels in New Kingdom Pi-Ramesse. Four experiments simulated glass-making, by firing weighed-in quantities of raw materials (glass-making grade quartz powder and carbonates of sodium, potassium, calcium and magnesium) with or without added salt (sodium chloride) creating semi-finished glass, while five experiments tested the behaviour of the semi-finished glass during re-melting and colouration, and the effect this had on the crucibles; again, some had salt added at this stage, others not (Merkel and Rehren, 2007).

Two of the Merkel samples (M1, M3) were taken from the first stage of the glass-making process: M1, which had 20 wt% salt added

to the batch, developed both a buff zone and a pink discolouration, while M3, with no additional salt, demonstrates only a zone of highly vitrified ceramic. The other two samples (M2, M4) were taken from vessels used for re-melting semi-finished glass to produce coloured ingots: M2 had glass attached on unchanged ceramic, while M4, which had again 20 wt% salt added to the semi-finished glass, developed both a buff zone and a layer with pink discolouration.

2.2. Samples from Qantir

Two types of ceramic container have been identified for glass-making at Qantir: reaction vessels (RG) and cylindrical crucibles (GT). The reaction vessels consist of ordinary domestic pottery mostly of ovoid shape utilized for the production of semi-finished glass. The cylindrical crucibles are purpose-made open containers mostly for the production of coloured glass ingots, but were apparently also used for primary glass making. Both types have on the inner walls a lime-rich parting layer of varying thickness, ranging in colour from white to grey to yellowish. A buff zone and interface glass can be seen in both types. Finally a distinct pink discolouration can be seen in many of the fragments, both from reaction vessels and the cylindrical crucibles. The samples selected for further analysis are from three reaction vessels and two cylindrical crucibles:

We should note that both RG and GT samples in this study had semi-finished glass attached (apart from reaction vessel Q4 that had no glass attached on the ceramic). About 30% of the crucible fragments found in Qantir had semi-finished glass attached suggesting that not only reaction vessels but a large part of the crucibles were used for primary glass production as well (Pusch and Rehren, 2007a: 138; see for example find GT 008 in Pusch and Rehren, 2007b: 186–7, or GT 051, Pusch and Rehren 2007a: 77). Both crucible fragments in this study (Q1 and Q5) had a layer of semi-finished glass still attached suggesting their use in the first stage of glass-making.

2.3. Samples from Amarna

There are several groups of technical ceramics from Amarna at the UCL Petrie Museum of Egyptian Archaeology; from these we selected those which have a clear link to glass-making with glass still attached on most of them:

- Crucible fragments with no signs of any layered structure. Some of them have traces of a parting layer, however no buff zone nor any discolouration of the ceramic. One sample was taken for further study.
- Crucible fragments with parting layer, with signs of buff layer, or with interface glass beneath the parting layer. One fragment also shows significant depth of pink discolouration. Six samples were taken for further study.

The samples from the site of Amarna are:

AM2: no buff zone or any layered structure other than glass directly attached on unchanged ceramic.

AM1, AM3, AM4, AM5, AM6, AM7: with a layered structure, a combination of: glass, parting layer, buff zone, interface glass, pink discolouration, unchanged ceramic.

2.4. Samples from Lisht

Numerous crucible fragments have been found at the site of Lisht. Most are fragments with coloured glass attached on an unchanged ceramic fabric, with some exhibiting a layered structure

Table 1

Analysed samples of glass-making ceramic. PL: Parting Layer; BottleGlass: Bottle-green glass; Buff: Buff ceramic; Pink: Pink discolouration; Ceramic: unaltered ceramic.

Number-site	Acc#	Glass	Layers/Zones
AM1 – Amarna	UC47513	Co-blue	PL//Buff//Ceramic
AM2 – Amarna	UC47510	Co-blue	Ceramic
AM3 – Amarna	UC47522	Co-blue	PL//BottleGlass//Ceramic
AM4 – Amarna	UC47528	Co-blue	PL//Buff//Pink//Ceramic
AM5 – Amarna	67,827	Co-blue	PL//Buff//Ceramic
AM6 – Amarna	UC47515	Co-blue	PL//Buff//Ceramic
AM7 – Amarna	UC25248	Co-blue	PL//Buff//Ceramic
L1 – Lisht	G17a	Cu-blue	Buff//Ceramic
L2 – Lisht	11.151.514	Cu-blue	PL//Buff//Ceramic
L3 – Lisht	15.3.1062	White	PL//Buff//Pink//Ceramic
Q1 – Qantir	GT080	Semi-finished	PL//BottleGlass//Ceramic
Q2 – Qantir	RG071	Semi-finished	PL//Buff//Pink//Ceramic
Q3 – Qantir	RG064	Semi-finished	PL//Buff//Pink//Ceramic
Q4 – Qantir	RG061	No glass	PL//BottleGlass//Pink//Ceramic
Q5 – Qantir	GT394	Semi-finished	PL//Buff//Pink//Ceramic
M1 – Merkel	AT2	Semi-finished	PL//Buff//Pink//Ceramic
M2 – Merkel	AT7	Cu-blue	Ceramic
M3 – Merkel	AT8	Semi-finished	PL//vitrified cer//Ceramic
M4 – Merkel	AT9	Cu-blue	Buff//Pink//Ceramic

M1	→ from first-stage process, with additional salt:	buff zone and pink discolouration
M3	→ from first-stage process:	only a highly vitrified ceramic zone
M2	→ from second-stage process:	no layered structure
M4	→ from second-stage process, with additional salt:	buff zone and pink discolouration

Q2-RG; Q3-RG; Q5-GT	→ with parting layer, buff zone and pink discolouration
Q1-GT	→ with parting layer and interface glass
Q4-RG	→ with parting layer, buff zone, interface glass and pink discolouration

including a parting layer, a buff zone and at least one fragment showing an area of pink discolouration. We analysed samples from three crucible fragments currently housed at the Metropolitan Museum of Art in New York. L1 and L2 have remains of glass, a parting layer, a buff area of ceramic over unchanged fabric, while L3 has remains of glass, parting layer, a buff zone, a layer of pink discolouration and a deep zone of unchanged fabric. The glass of all samples has a typical Egyptian LBA composition (Smirniou, 2012).

3. Analytical approach

Cross-sections of approximately 2–4 cm were cut from the samples and embedded into epoxy resin mounts, ground and polished to expose the sequence of layers for investigation using reflected light and electron microscopy.

All samples were photographed in plane (ppl) and crossed polarised light (xpl) at magnifications from 5× to 50×, focussing on the various layers and their interfaces.

Following carbon-coating of the exposed surfaces, a Hitachi S3400N scanning electron microscope with Oxford Instrument energy-dispersive spectrometer (SEM-EDS) was used to observe the samples at magnification from 25× to 2000× and to examine details of the various layers.

Finally a JEOL JXA 8600 electron-probe micro-analyser with wavelength dispersive spectrometry was used to determine the chemical composition of the samples. Analyses were conducted at ×800 magnification and large mineral inclusions were avoided. A series of equidistant analyses were done along the line, reaching more than 100 small areas for each sample; an average composition of multiple small areas for each layer is presented. Based on the analyses of standard reference material most values are within 5% relative of the given values. Only for alumina – with an absolute value of less than 1% – is JEOL out by about 15% compared to the given values (Table 2).

4. Results

4.1. Experimental

Merkel's experiments had shown that the sequence of buff and discoloured pink zones within the ceramic formed only in the presence of rock salt in the batch (samples M1 from first stage of

Table 2
Comparison of EPMA analyses of Corning Glass A to the published values (Brill, 1999).

	SiO ₂	Na ₂ O	CaO	K ₂ O	MgO	Al ₂ O ₃	TiO ₂	Sb ₂ O ₅
CorningA	66.75	14.59	5.06	2.97	2.73	0.86	0.79	1.70
Given	66.56	14.52	5.30	2.93	2.81	1.01	0.80	1.72
δ abs	0.19	0.07	0.24	0.04	0.08	0.16	0.01	0.02
δ rel (%)	0.28	0.49	4.55	1.26	2.85	15.35	0.88	1.40

glassmaking and M4 from re-melting glass, both with additional salt) (Merkel and Rehren, 2007). Our analyses now demonstrate that the lime from the parting layer migrates into the underlying ceramic, resulting in a buff ceramic layer high in lime (Fig. 4) and with elevated contents of Cl. Beneath this, the pink ceramic layer demonstrates no chemical difference to the unchanged ceramic body (Fig. 5a and b). Lime from the parting layer seems to be mobilised by the chloride phase and then absorbed by the ceramic which is directly adjacent, resulting in a content of CaO of around 2 times more than in the non-reacted ceramic further in the interior. This buff layer, although high in lime, remains distinctly ceramic in composition with elevated contents of alumina and iron oxide, but also elevated contents of Cl.

In contrast, sample M2 was used to re-melt semi-finished glass (second-stage process) with the typical glass batch but no additional salt; here, no buff zone or pink discolouration was formed. As also seen in other experiments (Merkel and Rehren, 2007), the absence of additional salt in the batch resulted in the absence of the buff zone and the pink discolouration. However, our analyses show that even with the absence of additional salt there is some movement of the lime from the parting layer towards the ceramic resulting in a thin more vitrified area. This interface area between the glass and the ceramic (GL/C) is characterized mostly by high lime content, elevated chlorine and sulphate, and levels of alumina, titania and iron oxide that are more typical of ceramics.

4.2. Qantir crucible samples

Two of the reaction vessels (Q2, Q3) and one crucible (Q5) from Pi-Ramesse demonstrated the layered structure exactly as seen at some of the vessels created during Merkel's experiments: a lime-rich parting layer between the glass and the ceramic, followed by a creamy buff ceramic area, a pink discolouration and then the

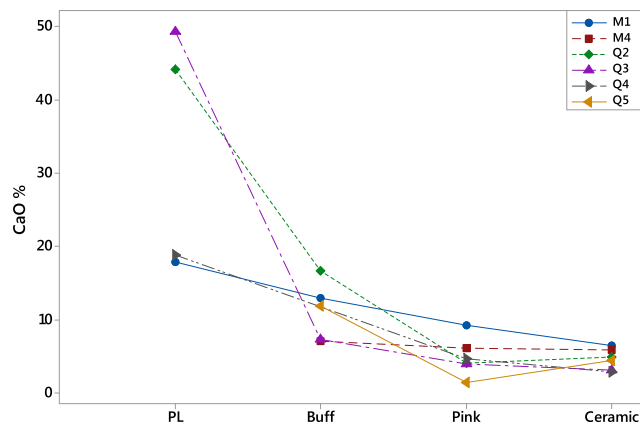


Fig. 4. CaO content of the various layers of Merkel's and Qantir samples.

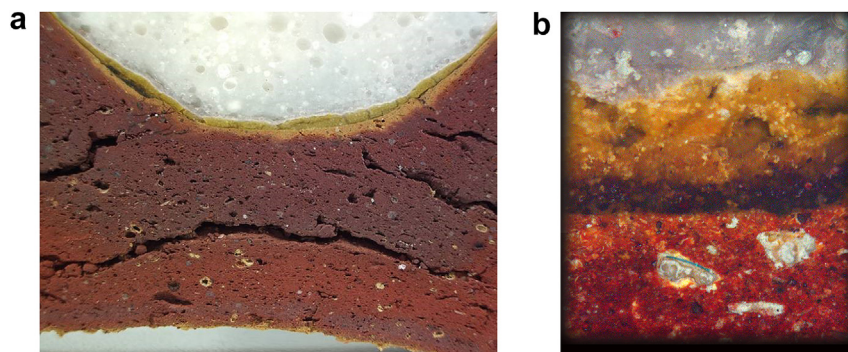


Fig. 5. a: Close-up of crucible M1 (Ashtray 2, Merkel, 2006), b: Collage of reflected light images of sample M1.

unchanged ceramic body.

One reaction vessel (Q4) demonstrated in addition a bottle-green glass interface between the parting layer and the ceramic with a pink discolouration, but no formation of any buff ceramic area, while crucible (Q1) also formed the bottle-green glass interface layer between the parting layer and the ceramic, but with neither pink discolouration nor buff area. It is important to note that most reaction vessels excavated at Qantir have the pink discolouration, while only very few crucibles do.

The analyses show that the buff ceramic area is rich in lime, soda and chlorine compared to the unchanged ceramic. The bottle-green glass interface (BG) demonstrates high soda contents and high chlorine, slightly elevated lime contents but not as high as the buff area, as well as elevated alumina, titania and iron oxide closer to the levels of the ceramic, as first described by Rehren (1997). The pink discolouration layer shows the same chemical composition as the unchanged ceramic.

4.3. Amarna crucible samples

Seven crucible fragments from the site of Amarna were studied, all with dark blue glass attached on their inside. All but one exhibited a layered structure similar to Merkel's experimental vessels and to Qantir's reaction vessels and cylindrical crucibles. The one exception (AM2) featured only finished cobalt blue glass directly attached on unchanged ceramic body. One sample (AM4) demonstrated a parting layer followed by the formation of a buff ceramic area and pink discolouration (Fig. 6). One sample (AM3) had a parting layer followed by a bottle-green glass interface between the parting layer and the unchanged ceramic body (Fig. 7). The four remaining samples (AM1, AM5, AM6, AM7) have a parting layer and a buff ceramic area directly followed by the unchanged ceramic fabric.

All ceramics have unusually high contents of soda, much higher than the ceramic bodies from Qantir and Merkel's experiments, and much higher than the standard Nile silt (Hancock et al., 1986).

The bottle-green glass interface resembles the composition of those seen on Qantir's glassmaking ceramics with high soda, alumina, titania and iron oxide, and elevated chlorine and lime contents. The buff ceramic area shows high lime contents, most likely migrated from the parting layer. Chlorine and sulphur show a continuous increase from the buff zone to the outer surface of the ceramic fabric. The pink discolouration layer exhibits no chemical difference to the unchanged ceramic body.

4.4. Lisht crucible samples

Three crucible fragments were examined from the site of Lisht.

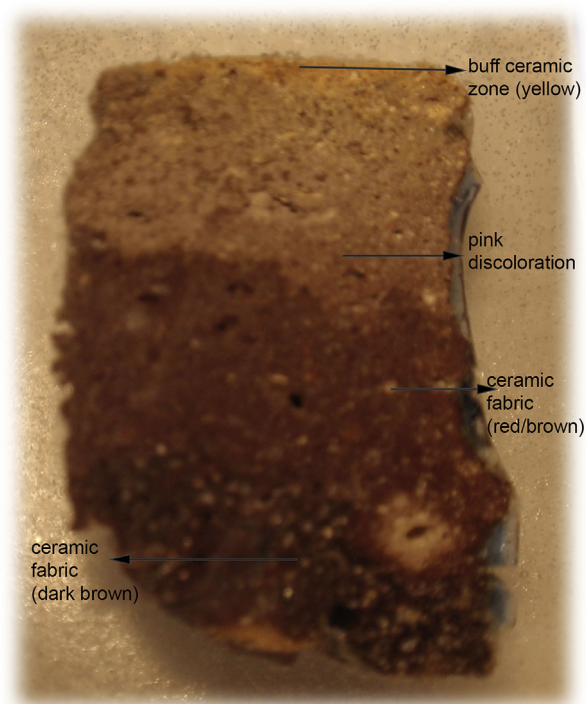


Fig. 6. One sample (AM4) demonstrated the formation of a buff ceramic area and pink discolouration.

Sample L1 has no parting layer present but a well fused finished light blue glass. There is a buff zone formed between the glass and the unchanged ceramic suggesting that most probably there had initially been a parting layer present since high lime is required for the formation of the buff area within the ceramic. The buff zone of sample L1 does not demonstrate a particularly high lime content as we saw at the experimental glassmaking vessels and the other archaeological samples with a buff layer present. It is very probable that the lime responsible for the formation of the buff zone to have been completely absorbed. The buff zone shows high levels of soda, higher contents of chlorine, low contents of iron oxide, and lower levels of alumina than the ceramic fabric which lies below the buff zone. In contrast, sample L2 has several layers underneath the light blue glass matrix: yellow parting layer, a buff ceramic zone, and ceramic fabric. Sample L3 is a crucible wall fragment with buff zone and a deep pink discolouration between the buff zone and the unaltered ceramic (Figs. 3 and 9), and some traces of a powdery parting layer sitting underneath the well-fused white opaque glass.

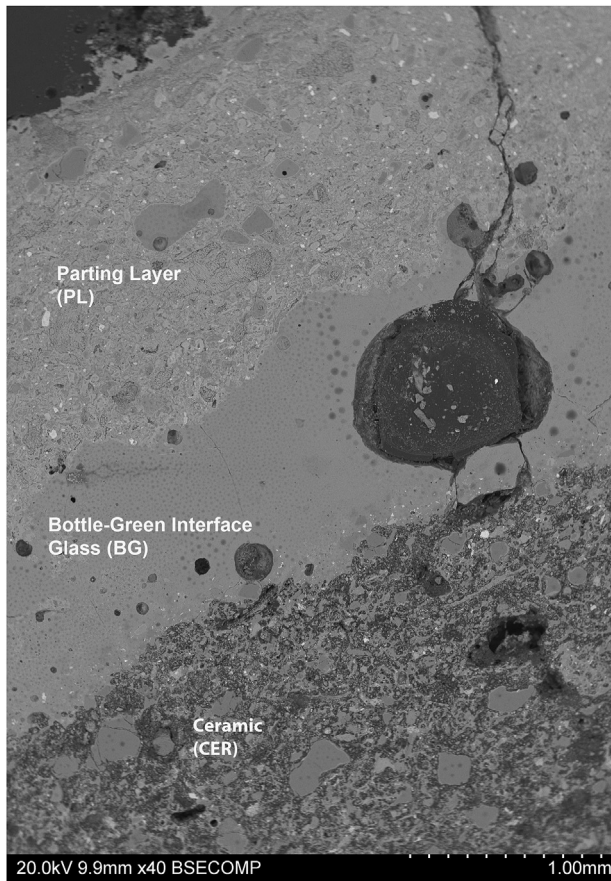


Fig. 7. SEM image of sample AM3 (Amarna-UC47522).

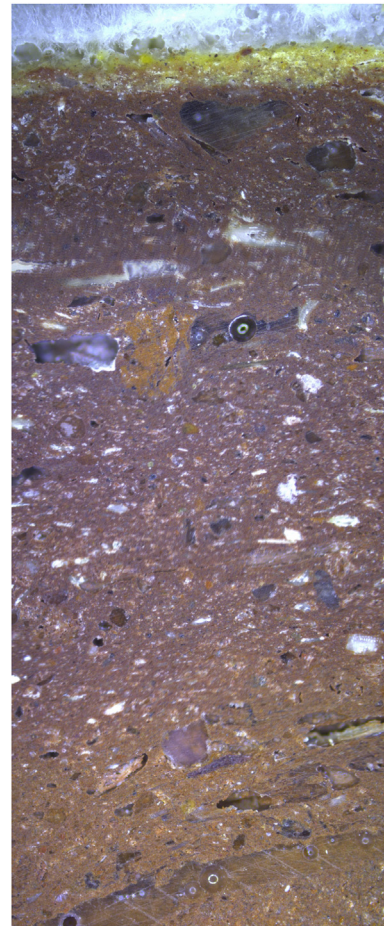


Fig. 9. Detailed image of sample L3 (Lisht-15.3.1062).

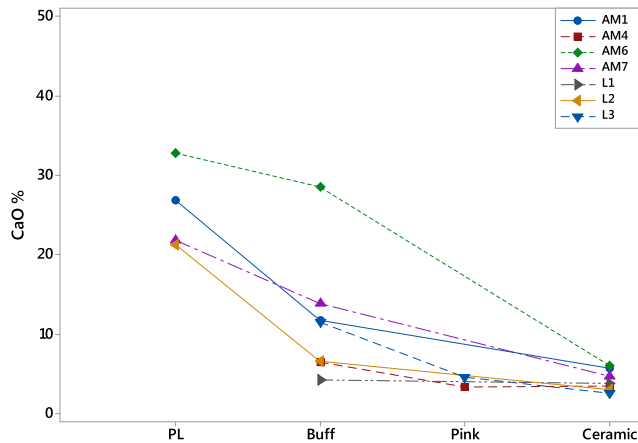


Fig. 8. CaO contents of the various layers of the Amarna and Lisht samples.

The chemical composition of the buff area of samples L2 and L3 is similar to the ones seen in the crucibles from Merkel's experiments, as well as from Qantir and Amarna: it has a high lime content (Fig. 8) probably from the parting layer, typical alumina, titania and iron oxide as of a ceramic composition and also it shows high chlorine content, two to almost three times higher than the levels in the ceramic. However, all the Lisht ceramics have high levels of soda, atypical than what is expected from Nile silt and very similar to the high soda contents of the Amarna crucibles and different to the experimental samples.

The pink discolouration area shows an elevated lime content compared to the unchanged ceramic, most probably demonstrating the effect from the parting layer. The lime is around half or less than the buff zone, but twice the levels of the unchanged ceramic. The iron oxide, alumina, and titania contents are very similar to the levels of the unchanged red ceramic. There are elevated soda levels throughout the ceramic from the buff area, to the discoloured and the unchanged ceramic body. Chlorine is much higher from the red ceramic, and even slightly higher than the buff zone suggesting the presence of additional salts in the batch.

5. Discussion

5.1. Ceramic

The glass crucibles from Qantir, Amarna and Lisht share some common characteristics. They all have an open form and a cylindrical shape; they have thick walls of around 1.0–1.8 cm, a rather coarse fabric made of local Nile silt clay, and when the bases survive they seem to be mostly flat. Glass is still attached to the inner walls of most of the crucible fragments, sometimes only as small patches, and sometimes more comprehensively (Fig. 10) and a lime-rich coating has been applied between the ceramic and the glass.

All crucibles are made from a low calcareous ferruginous clay with CaO levels ranging from 2.5 to 6.1% (Table 3), very typical of the Nile silt that most Egyptian pottery was made of. Elevated contents of phosphorus and normal levels of soda are demonstrated at the Qantir samples. Amarna and Lisht demonstrate



Fig. 10. Crucible fragment from Lisht with thick layer of glass.

and titanium oxides, along with voids from the burnt-out organic temper are seen throughout the ceramic body.

The ceramic of the Reaction Vessels, so far only known from Qantir, is systematically less vitrified, indicating a lower firing temperature (Rehren and Pusch, 2005). Accordingly, the ceramic matrix is predominantly brick red, and more akin to the vitrification stage NV to V of Tite and Maniatis (1975). Since the bulk chemical composition of both vessel types is the same, based on Nile Silt with only minor amounts of non-plastic and fibrous organic inclusions, we assume that the different vitrification levels represent different firing temperatures (Rehren and Pusch, 2005).

5.2. Parting layer

The majority of the crucibles from Amarna, Qantir and Lisht have a lime-rich coating which formed a physical barrier and allowed the easy release of the final glass ingot from the ceramic. In most of the samples the parting layer is still present. Only one

Table 3

Chemical composition of the ceramic body of all samples by EPMA in wt%.

			SiO ₂	Na ₂ O	CaO	K ₂ O	MgO	Al ₂ O ₃	FeO	TiO ₂	SO ₃	Cl	P ₂ O ₅
Amarna	AM1	Mean	54.2	12.8	5.75	0.73	1.90	14.30	6.71	1.50	0.45	1.26	0.20
		Std dev	0.7	0.6	1.0	0.1	0.2	1.1	0.3	0.09	0.08	0.07	0.05
	AM2	Mean	62.6	8.1	2.61	0.83	1.92	12.30	5.86	1.24	0.49	0.62	0.40
		Std dev	6.8	2.1	1.0	0.2	0.3	2.1	0.9	0.20	0.05	0.10	0.29
	AM3	Mean	58.8	6.5	4.69	2.00	2.40	13.90	6.94	1.19	1.04	0.99	0.86
		Std dev	3.3	0.8	0.6	0.3	0.2	1.3	0.5	0.14	0.12	0.20	0.31
	AM4	Mean	57.8	10.0	3.53	1.43	2.52	14.10	6.66	1.28	0.86	0.86	0.72
		Std dev	2.3	0.8	0.7	0.1	0.4	1.9	1.0	0.08	0.23	0.09	0.22
	AM5	Mean	57.7	8.6	4.84	0.68	1.99	16.00	6.90	1.48	0.39	0.50	0.62
		Std dev	1.7	1.1	1.3	0.1	0.3	1.1	0.7	0.19	0.05	0.13	0.10
	AM6	Mean	55.0	8.5	6.12	2.33	2.62	14.00	6.83	1.11	1.34	0.78	0.86
		Std dev	0.8	0.4	0.5	0.0	0.2	0.8	0.4	0.05	0.35	0.02	0.20
	AM7	Mean	56.1	8.7	4.75	0.93	2.34	15.10	8.05	1.91	0.60	0.54	0.64
		Std dev	3.0	0.7	0.2	0.1	0.3	1.3	2.0	0.28	0.27	0.19	0.26
Lisht	L1	Mean	63.7	6.7	3.87	1.68	2.05	13.40	6.23	1.18	0.22	0.29	0.36
		Std dev	1.87	1.69	0.53	0.17	0.10	2.24	0.90	0.23	0.11	0.08	0.14
	L2	Mean	54.5	9.8	3.07	3.26	1.55	18.40	5.65	1.12	1.04	0.58	0.76
		Std dev	2.24	0.56	0.62	0.30	0.07	1.09	0.60	0.42	0.24	0.09	0.11
	L3	Mean	54.7	7.7	2.58	3.12	2.31	15.70	8.06	2.43	1.72	0.52	0.75
		Std dev	2.1	0.7	0.2	0.3	0.2	0.6	1.4	1.78	0.21	0.13	0.08
Qantir	Q1	Mean	61.9	1.9	2.94	4.71	1.89	17.00	7.34	0.93	0.06	0.16	0.85
		Std dev	0.7	0.2	0.9	3.0	0.5	1.1	1.6	0.22	0.02	0.07	0.33
	Q2	Mean	57.4	2.6	4.94	2.67	2.36	18.10	8.29	1.49	0.10	0.23	1.43
		Std dev	1.3	0.1	0.6	0.2	0.2	0.4	0.1	0.06	0.03	0.05	0.30
	Q3	Mean	58.5	2.1	3.13	3.02	2.49	18.00	9.02	1.37	0.07	0.79	0.83
		Std dev	0.1	0.1	0.5	0.1	0.1	0.2	0.2	0.13	0.01	0.20	0.20
	Q4	Mean	57.5	6.8	2.89	2.81	1.56	17.60	7.30	1.19	0.52	0.38	0.98
		Std dev	1.8	1.1	0.3	1.2	0.3	0.5	0.7	0.1	0.2	0.1	0.1
	Q5	Mean	58.2	4.4	4.42	3.81	2.90	16.10	7.12	1.23	0.18	0.38	0.84
		Std dev	2.8	0.5	1.3	0.4	1.7	1.2	0.7	0.17	0.05	0.06	0.23
Merkel	M1	Mean	57.0	3.6	6.50	1.81	2.69	17.80	7.90	1.32	0.06	0.47	0.39
		Std dev	1.3	0.9	0.4	0.6	0.1	0.6	0.5	0.27	0.01	0.11	0.05
	M2	Mean	58.0	2.2	6.38	1.78	2.94	16.60	9.14	1.54	0.07	0.23	0.55
		Std dev	0.9	0.8	0.6	0.4	0.2	0.9	0.6	0.17	0.01	0.02	0.24
	M3	Mean	56.9	3.4	5.95	1.21	2.96	17.60	8.47	1.64	0.16	0.45	0.58
		Std dev	2.3	1.6	0.8	0.4	0.8	1.4	1.7	0.20	0.13	0.24	0.29
	M4	Mean	58.0	4.0	5.84	2.03	2.48	15.90	8.24	1.43	0.08	0.91	0.48
		Std dev	2.9	0.3	1.0	0.3	0.3	1.3	0.8	0.27	0.04	0.24	0.29

higher levels of soda than what is expected from Nile silt (Hancock et al., 1986), while most Amarna samples have lower potash contents.

The microstructure of the fabric of the crucibles has also some similarities. The ceramic matrix is mostly vitrified, probably equating to the V+ to TV stage of Tite and Maniatis (1975), which suggests either high operating temperatures (or long duration of firing) or successive uses of the ceramics. Inclusions of quartz, iron

example (Amarna's AM2) had most probably no lime-rich coating applied to the ceramic before firing, since there is no effect on the ceramic from a previously applied parting layer, such as an area in the ceramic with unusually high lime. Separation of glass from the ceramic must have been difficult because of this absence of the parting layer; this is indicated by the fact that glass is still attached to the ceramic, and there are marks of chiselling on the glass.

There are three examples (Amarna's AM4 and Lisht's L1 and L3)

Table 5
Chemical composition of the buff ceramic zone of all samples by EPMA in wt%.

			SiO ₂	Na ₂ O	CaO	K ₂ O	MgO	Al ₂ O ₃	FeO	TiO ₂	SO ₃	Cl	P ₂ O ₅
Amarna	AM1	Mean	53.6	11.6	11.8	0.65	2.18	11.8	5.64	1.25	0.25	1.03	0.08
		Std dev	3.6	0.5	4.1	0.1	0.2	0.2	0.2	0.14	0.03	0.01	0.01
	AM4	Mean	55.9	6.7	6.5	1.28	3.20	15.2	6.42	1.21	0.66	0.58	2.08
		Std dev	0.7	0.2	0.5	0.1	0.9	0.0	0.8	0.31	0.14	0.04	1.50
	AM6	Mean	42.3	5.7	18.5	0.66	2.76	13.3	8.00	2.30	3.65	1.02	1.43
		Std dev	0.8	0.6	1.0	0.1	0.6	1.3	1.9	1.24	0.71	0.24	0.66
AM7	Mean	57.7	14.3	13.9	0.49	3.94	5.0	1.33	0.23	0.29	0.99	0.15	
	Std dev	0.8	1.6	1.8	0.0	0.7	0.1	0.4	0.09	0.02	0.15	0.05	
Lisht	L1	Mean	64.8	12.8	4.3	2.16	2.18	8.5	2.71	0.47	0.42	0.70	0.41
		Std dev	4.1	0.9	0.7	0.2	0.6	1.2	0.9	0.26	0.07	0.10	0.03
	L2	Mean	49.9	11.2	6.6	2.58	2.17	15.9	6.55	1.10	1.62	1.65	0.44
		Std dev	1.1	0.6	3.0	0.9	0.1	1.0	0.6	0.14	0.26	0.35	0.39
	L3	Mean	58.9	11.1	11.6	2.08	3.06	6.0	2.79	0.94	1.07	1.01	1.17
		Std dev	7.3	2.3	1.5	0.5	0.5	5.5	2.6	1.23	1.00	0.17	0.55
Qantir	Q2	Mean	48.5	4.7	16.7	3.15	2.42	14.3	7.09	0.94	0.18	0.43	1.3
		Std dev	4.2	0.0	4.8	0.3	0.3	1.3	0.6	0.12	0.07	0.06	0.45
	Q3	Mean	54.0	6.0	7.3	4.27	1.91	15.2	6.93	1.02	0.92	1.01	1.01
		Std dev	1.4	1.3	3.0	0.1	0.1	0.6	0.5	0.06	0.49	0.45	0.25
	Q5	Mean	51.2	5.5	11.8	1.52	2.65	15.2	8.45	1.37	0.62	0.54	0.72
		Std dev	3.0	0.8	4.0	0.3	0.2	1.5	0.5	0.34	0.14	0.06	0.07
Merkel	M1	Mean	52.7	3.3	12.9	0.42	2.92	15.7	8.73	1.61	0.07	0.98	0.35
		Std dev	0.2	0.2	0.7	0.1	0.1	0.8	0.4	0.24	0.00	0.03	0.05
	M4	Mean	54.4	4.1	7.0	2.07	3.28	17.3	8.27	1.29	0.17	0.89	0.64
		Std dev	0.9	0.2	0.7	0.3	0.4	0.4	0.4	0.08	0.03	0.17	0.24

Table 6
Chemical composition of the interface glass by EPMA in wt%.

			SiO ₂	Na ₂ O	CaO	K ₂ O	MgO	Al ₂ O ₃	FeO	TiO ₂	SO ₃	Cl	P ₂ O ₅
Amarna	AM3	Mean	52.5	14.5	6.54	1.77	2.67	11.44	6.72	1.52	0.36	1.37	0.12
		Std dev	1.8	0.6	0.4	0.0	0.4	0.9	0.8	0.21	0.15	0.23	0.03
Qantir	Q1	Mean	57.5	9.9	3.52	3.87	2.55	15.01	4.81	1.07	0.28	0.35	0.77
		Std dev	1.7	0.9	1.4	0.5	0.5	2.0	1.1	0.23	0.05	0.17	0.12
	Q4	Mean	55.2	15.2	4.71	1.82	1.63	11.37	5.84	0.86	0.61	1.48	0.23
		Std dev	1.3	1.1	0.7	0.5	0.2	0.1	0.4	0.03	0.11	0.17	0.02

(Amarna's AM4, Lisht's L3, Qantir's Q2, Q3, Q4 and Q5) developed this pinkish discolouration zone on the ceramic area. As Merkel's experimental work (2006) has shown, the formation of this pinkish zone also is dependent on the presence of chlorides in the charge and the presence of the lime-rich parting layer. The changes that are incurred by the salts are restricted to the colour of the ceramic and do not affect the chemical composition (Table 7), unlike the buff layer. Only the first small areas of the pink discolouration layer demonstrate a significant reduction in alumina and iron oxide levels, a slightly reduced content of soda and elevated levels of

silica. Subsequent areas deeper into that layer do not demonstrate any significant difference in chemical composition to that of brown unchanged ceramic nor any discontinuity at the region where we observe the change of colour.

6. Conclusion

The experimental work (Merkel, 2006; Merkel and Rehren, 2007) has demonstrated that discolouration pattern on Nile silt vessels visually matching the archaeological samples from Qantir

Table 7
Chemical composition of the pink discolouration layer by EPMA in wt%.

			SiO ₂	Na ₂ O	CaO	K ₂ O	MgO	Al ₂ O ₃	FeO	TiO ₂	SO ₃	Cl	P ₂ O ₅
Amarna	AM4	Mean	56.8	9.5	3.40	1.26	2.42	16.5	6.72	1.16	0.66	0.66	0.77
		Std dev	3.6	0.9	0.4	0.1	0.7	0.5	1.7	0.23	0.14	0.20	0.31
Lisht	L3	Mean	51.5	9.0	4.58	2.18	2.75	16.6	7.58	1.18	1.94	1.37	0.86
		Std dev	0.7	0.3	0.7	0.1	0.2	0.1	0.2	0.08	0.14	0.20	0.18
Qantir	Q2	Mean	63.8	2.0	4.02	2.73	1.81	14.8	7.68	1.08	0.12	0.33	1.35
		Std dev	2.6	0.2	0.6	0.3	0.2	1.3	0.6	0.15	0.01	0.05	0.18
	Q3	Mean	60.6	2.2	3.91	3.06	2.15	15.9	8.19	1.26	0.11	0.88	1.31
		Std dev	0.5	0.5	0.1	0.6	0.2	0.8	0.2	0.05	0.02	0.16	0.18
	Q4	Mean	59.3	5.8	4.65	2.90	1.75	16.1	6.61	1.16	0.36	0.5	0.53
		Std dev	3.6	1.1	0.3	0.1	0.3	1.9	0.7	0.08	0.17	0.10	0.31
Q5	Mean	62.2	8.6	1.40	1.42	0.70	15.9	6.29	0.98	0.76	0.69	0.91	
	Std dev	2.8	0.5	0.8	0.3	0.5	0.9	1.2	0.24	0.10	0.07	0.09	
Merkel	M1	Mean	56.8	4.0	9.25	0.39	2.81	15.9	8.04	1.43	0.06	0.63	0.36
		Std dev	5.0	0.7	0.6	0.1	0.2	2.3	1.2	0.35	0.01	0.03	0.06
	M4	Mean	55.1	3.9	6.10	1.97	3.07	15.9	9.85	1.66	0.13	1.14	0.61
		Std dev	3.9	0.3	0.6	0.4	0.5	1.6	2.2	0.46	0.04	0.18	0.18

(Fig. 11), Amarna and Lisht can be reproduced by adding substantial amounts of chlorides to the glass batch fired in those vessels. Our analyses have shown that these layered sequences are also compositionally very similar to each other, even if there are differences in detail among individual samples. We argue that they form from the reaction of mobilised compounds from the batch and the parting layer (primarily sodium and calcium carbonate and chloride) with the ceramic of the vessels at the operating temperatures typical for glass-making. Significantly, these visually distinct layers within the ceramic body do not form when there is no or only little sodium chloride present in the batch, and therefore only limited migration of lime occurs from the parting layer into the underlying ceramic. These discolourations have not been seen in any other Bronze Age vessel fragments; the closest parallel is from Iron Age vessels used in Sardis for the parting of gold and silver using a chlorine-rich matrix at elevated temperatures (Ramage and Craddock, 2000), but below those estimated for the glass-making vessels. We believe therefore that it is safe to suggest that this layered structure provides a diagnostic criterion for ceramic vessels and crucibles used in glassmaking, and argue that the necessary chloride compound in the batch was part of the plant ash used.

The Qantir samples in the present study comprise of both types of containers, reaction vessels and cylindrical crucibles, selecting those that we believe have been used to produce semi-finished glass during primary glass production. It is noticeable that most reaction vessels excavated on the site do have these layers, while the cylindrical crucibles with coloured glass attached, unlike the samples in our study, do not display such a layered structure (Pusch and Rehren, 2007a,b). Assuming that the layered structure is characteristic for glass-making vessels but does not form in glass-melting vessels, this strong pattern indicates that at Qantir, glass-making regularly took place in ovoid beer jars as well as in some cylindrical vessels, while the majority of the cylindrical vessels were used for colouration and the production of ready ingots.

The Amarna and the Lisht samples are all from cylindrical crucibles that exhibit these layers, even though the glass still attached is coloured finished glass in all cases. Also the Amarna and Lisht samples do exhibit unusually high soda contents. It is very possible

that in these two sites the same crucibles could have been used both for the first and second stage of glass production, especially as no reaction vessels similar to the ones found in Qantir have been found in these two sites.

On balance, the combination of experimental and analytical work to re-create and characterise the unique zoned structure of New Kingdom glassmaking vessels provides adequate indication that these reaction vessels and crucibles have been used for primary glass production, while acknowledging that the precise mode of operation may have varied somewhat within and between individual workshops. It is known (Pulak, 2008) that LBA glass was traded as glass ingots without their crucible moulds, which instead were discarded at or near to the production site. The identification of layered crucible or vessel fragments as described in this paper therefore provides a sufficient field-suitable indication of glass making, and we hope that this will help locate glass-making sites in areas such as Mesopotamia where they have not yet been identified.

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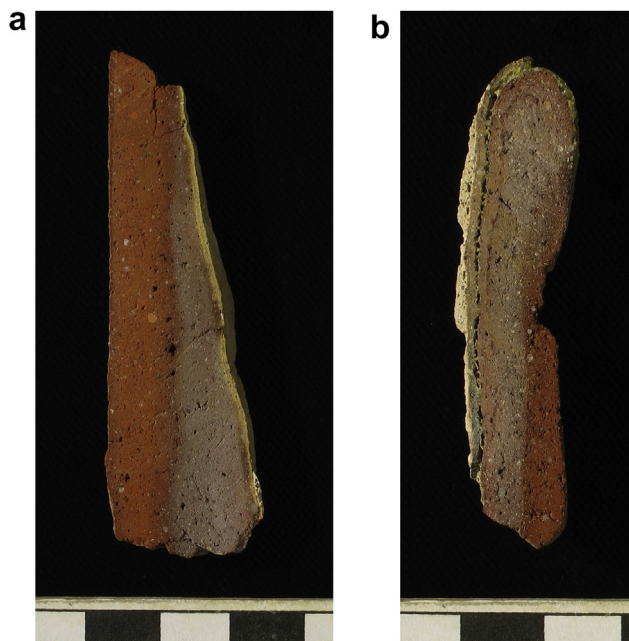


Fig. 11. a, b: Cross sections through two reaction vessels from Qantir, showing pink discolouration and parting layer.

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