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Vauxhall, London: the scientific examination of glass and glassworking materials from the late seventeenth century glasshouse

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Summary

The late 17th-century glasshouse at Vauxhall was excavated by archaeologists from the Museum of London in the 1980s. The recent monograph on the site contains some information from scientific examination of the glass and glassworking materials. This report contains all the available information, including some unpublished data. A range of glass and glassworking materials (eg crucibles) from the site was examined using scientific techniques. The SEM-EDS and XRF analyses show that some of the data (chemical composition) previously acquired using ICPS (and reported in the monograph) is inaccurate. The examination of some materials (the crucibles and the 'frit') using SEM-EDS allowed chemical composition to be compared to microstructure (eg glass-crucible interaction). This approach demonstrates that the 'frit' identified by Tyler and Willmott is devitrified glass.

Keywords

Glass
Post-medieval

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Introduction

This report provides results obtained from the scientific examination of glass vessels and glass working debris from the site of the late 17th-century glasshouse at Vauxhall, London. The site was excavated by the Museum of London in 1989 (that is prior to PPG16) and, due to the importance of the site, English Heritage subsequently provided funds for post-excavation work, including some scientific analyses, and publication. During 2004 further scientific work was undertaken on samples of glass and glass working material from the site but most of these results were not incorporated into the final published report (Tyler and Willmott 2005). The published site report contains a section entitled 'The ICPS analysis of the glass' (Tyler and Willmott 2005, 74–8), which is attributed to Caroline Jackson and Nick Walsh with David Dungworth. This section was not written by the named authors and they were not consulted about the use of their names as authors. This present report aims to correct some of the errors in the published site report, and make the full range of data publicly available.

Assessing the quality of the published ICPS data

The published report contains chemical compositional data for 94 samples of glass and glass waste; the analyses were undertaken by Nick Walsh, Royal Holloway and Bedford New College, University of London, using Inductively Coupled Plasma Spectrography (ICPS, Tyler and Willmott 2005, 74–8). Unfortunately, there are grounds for doubting the accuracy of the results; this is recognised in the published report (Tyler and Willmott 2005, 74). ICPS is usually conducted on samples in aqueous solutions and for the analysis of silica-rich materials (including glasses) samples must be treated with hydrofluoric acid to remove the silica. Therefore, it is not possible to obtain a determination of the silica content of the sample and, for silica-rich materials, the analysed total will always fall short of 100w%. This failure of analysed totals to reach 100wt% means that it is not easy to detect analytical problems, such as the low levels of lead discussed below. There are no indications that any reference materials (that is glasses of known composition) were included in the batch of analysed samples which could have acted as a means of assessing accuracy.

The published chemical compositions are mostly clearly in error for lead. Three samples {95}, {97} and {98} contain very low levels of all elements except potassium and lead and so are likely to be lead-potash glasses (cf Brain and Dungworth 2005, 25). The lead levels for these samples are reported as 68,950, 65,507 and 65,981ppm (respectively), but should be in the region of 200,000 to 400,000ppm (Dungworth and Brain 2005, 29–30). The determination of lead concentration by ICPS for samples rich in lead is not accurate (Nick Walsh *personal communication*) and, with hindsight, it would have been helpful if the analyst had been warned that some samples might be lead-rich.

In order to assess the quality of the published compositional data, samples were analysed using energy dispersive X-ray fluorescence (EDXRF) and an energy dispersive spectrometer attached to a scanning electron microscope (SEM-EDS). Further details of these techniques can be found elsewhere (for example, Dungworth 2003; Dungworth and Clark 2005; Dungworth and Brain 2005). In 91 cases, sufficient

powdered sample remained after ICPS analysis to allow EDXRF analysis. The results (see appendix 1) were quantified using a fundamental parameters method and calibrated against a range of certified reference materials (Corning, DLH, NIST, etc). In 27 cases, samples of the original glass artefacts or glass working residues remained; these were re-sampled (for details of sample preparation see Dungworth 2003) and analysed using SEM-EDS. The results (see Appendix 2) were calibrated against certified reference materials (see Figure 1 and Table 1). The SEM-EDS and EDXRF analyses gave analysed totals in the range 95–102wt% but have been normalised to 100wt%. In 22 cases, samples were analysed by both EDXRF and SEM-EDS; the compositional data for these samples are in very close agreement with each other.

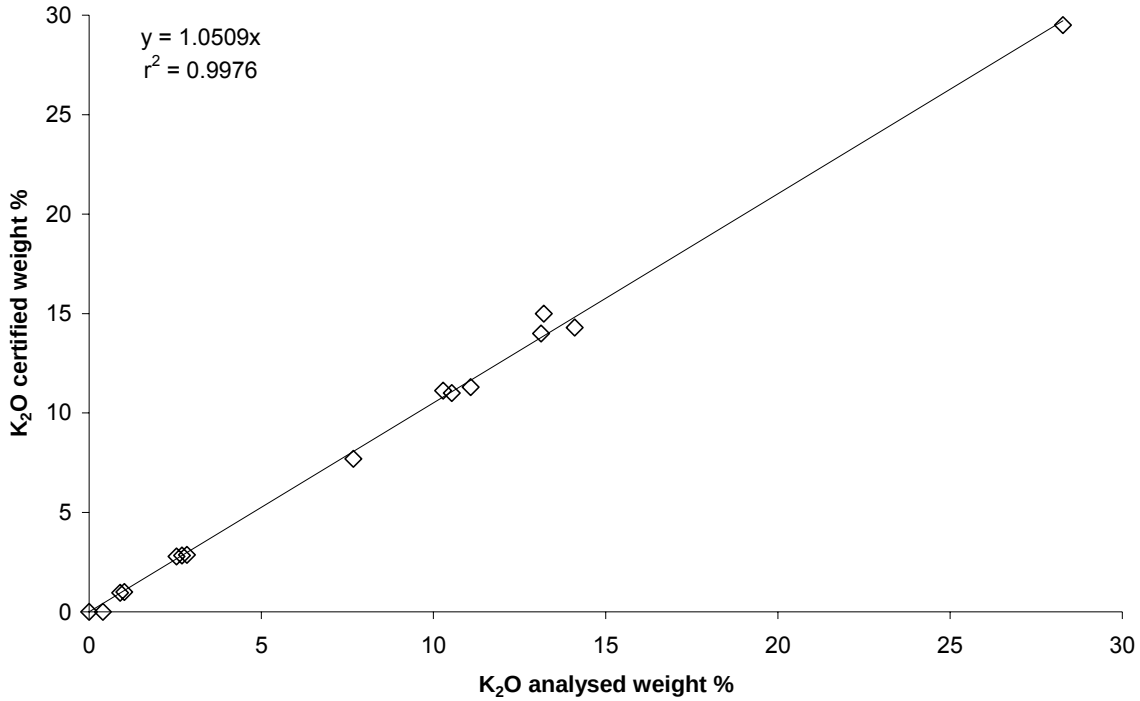


Figure 1. Plot of analysed potash (K_2O) content against certified potash content for the reference materials used to calibrate SEM-EDS analyses. (The straight line is the least-squares best fit line which passes through the origin and where the slope = y)

The compositions of the Vauxhall samples determined using SEM-EDS and EDXRF have been compared with the compositions determined by ICPS (Table 2; Figures 2–5). For many oxides the correlation coefficients are sufficiently high (r^2 >0.9) to be confident that the ICPS data are reliable (Figures 2 and 3). The magnesia and potash (Figure 4) contents as determined by ICPS are poorly correlated with the contents as determined by EDXRF or SEM-EDS and it is likely that the ICPS data is unreliable.

Table 1. Standard errors and detection limits (all in weight %) for the SEM-EDS and EDXRF analyses listed in Appendices 1 and 2

	SEM-EDS		EDXRF	
	Standard error	**Detection limit**	**Standard error**	**Detection limit**
Na_2O	0.1	0.2	0.5	0.5
MgO	0.1	0.1	0.5	0.5
Al_2O_3	0.1	0.1	0.5	0.1
SiO_2	0.3	0.1	0.5	0.1
P_2O_5	0.1	0.2	0.3	0.2
SO_3	0.1	0.2	0.2	0.2
Cl	0.1	0.2	0.2	0.2
K_2O	0.1	0.1	0.1	0.1
CaO	0.1	0.1	0.1	0.1
TiO_2	0.1	0.1	0.1	0.1
MnO	0.1	0.1	0.1	0.1
Fe_2O_3	0.1	0.1	0.1	0.1
PbO	0.1	0.2	0.1	0.1
SrO	0.1	0.5	0.01	0.01

Table 2. Correlation coefficients for oxide composition as determined by ICPS and EDXRF (82 samples, excludes the samples with more than 7.5wt% PbO as well as samples {69}, {72} and {90})

oxide	**r^2**
Na_2O	0.9077
MgO	0.3420
Al_2O_3	0.8929
P_2O_5	0.9793
K_2O	0.4955
CaO	0.9585
TiO_2	0.7452
MnO	0.9518
Fe_2O_3	0.9446
PbO	0.9826
SrO	0.6087

It is not apparent why the ICPS analyses of some oxides appear to be reliable while others are unreliable. Baxter *et al* (2005) encountered similar problems with two sets of ICPS analyses of the same samples; the second set of analyses carried out using the same instrument in the same laboratory but several years later. The lead oxide contents are strongly correlated up to approximately 7.5wt% (Figure 5) but above this level the contents as determined by ICPS are too low. The SEM-EDS and EDXRF analyses confirm that samples {95}, {97} and {98} have compositions typical of late 17th-century colourless lead glass (Dungworth and Brain 2005).

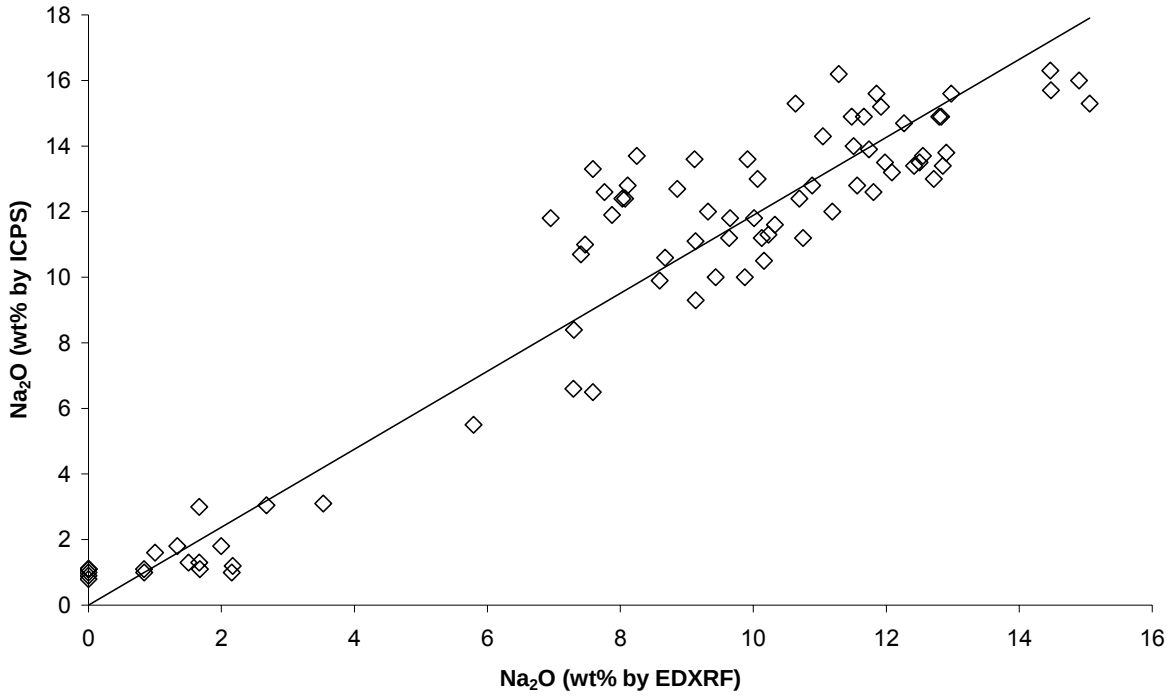


Figure 2. Soda (Na_2O) content of 82 samples analysed by EDXRF and ICPS

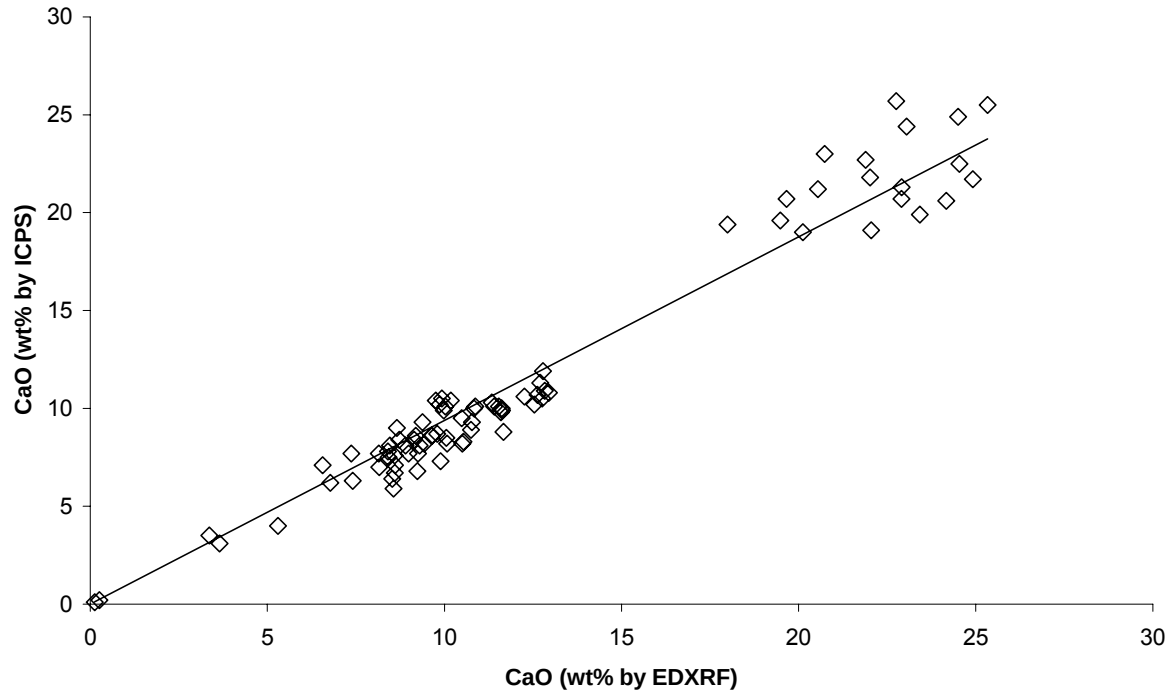


Figure 3. Lime (CaO) content of 82 samples analysed by EDXRF and ICPS

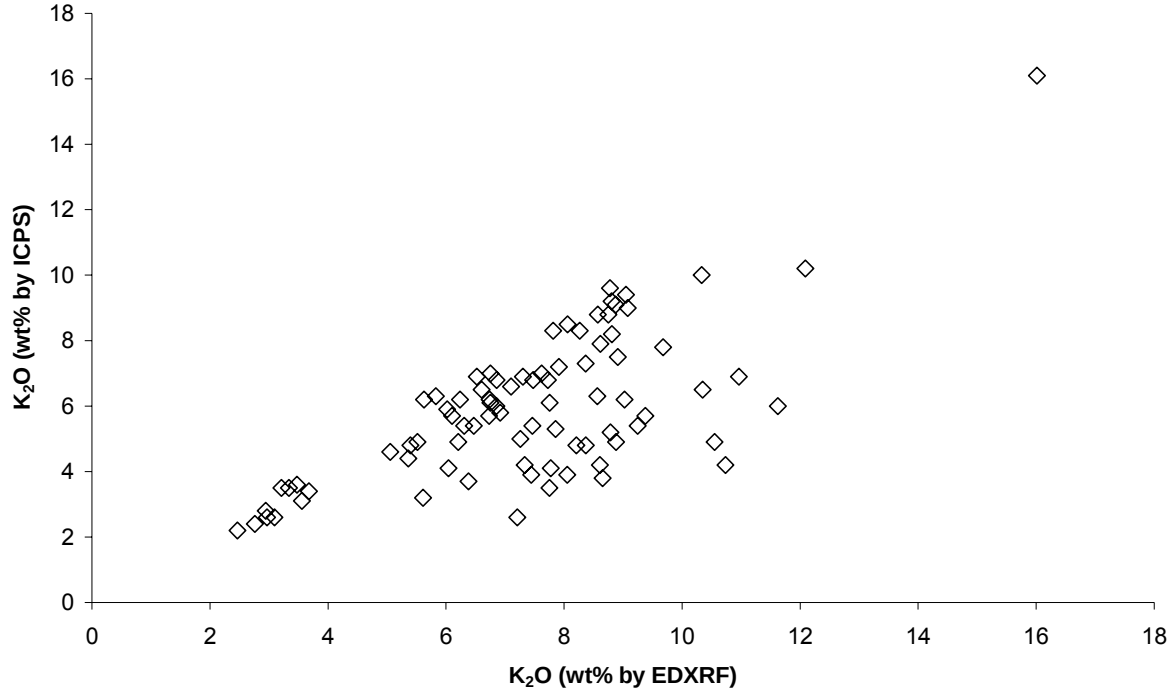


Figure 4. Potash (K_2O) content of 82 samples analysed by EDXRF and ICPS

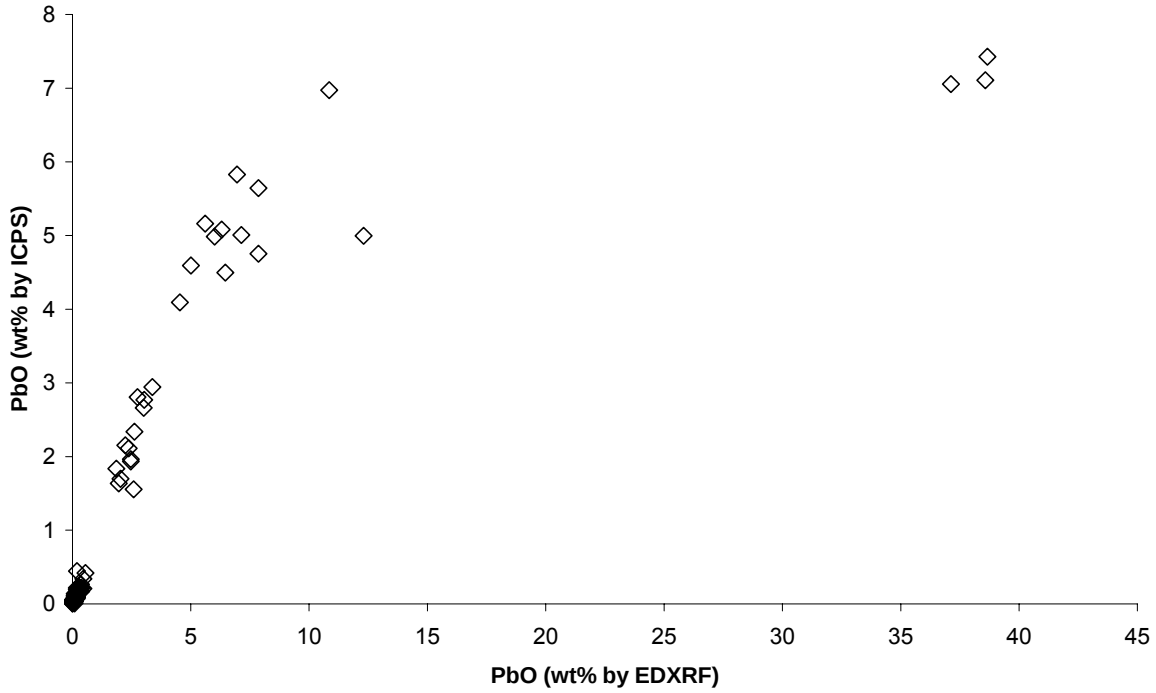


Figure 5. Lead oxide (PbO) content of 82 samples analysed by EDXRF and ICPS

The careful examination of the analytical data obtained by each method shows that there are additional problems with three samples: {69}, {72} and {90}. The published ICPS analysis of sample {69} shows consistently higher concentrations of all oxides compared to the EDXRF analysis (Table 3). The ICPS results for samples {72} and {90} show consistently lower concentrations of all oxides compared to the SEM-EDS analyses (Table 3). The reasons for this are not immediately apparent.

Table 3. ICPS, EDXRF and SEM-EDS results for samples {69}, {72} and {90} in weight %

	{69}		**{72}**		**{90}**	
	ICPS	**EDXRF**	**ICPS**	**SEM-EDS**	**ICPS**	**SEM-EDS**
Na_2O	6.06	1.6	0.72	1.2	6.67	12.7
MgO	6.06	2.6	0.92	2.0	1.83	3.7
Al_2O_3	6.42	4.4	1.21	2.4	0.94	1.4
SiO_2	NA	64.0	NA	62.1	NA	61.0
P_2O_5	4.13	3.5	0.85	1.8	0.18	0.2
SO_3	NA	0.2	NA	0.2	NA	0.2
Cl	NA	0.7	NA	0.3	NA	0.6
K_2O	6.80	3.0	2.60	5.0	2.66	5.1
CaO	38.17	17.8	11.27	23.7	5.84	11.7
TiO_2	0.53	0.3	0.08	0.2	0.06	0.1
MnO	1.38	0.7	0.09	0.1	0.41	0.7
Fe_2O_3	2.08	1.0	0.47	1.0	0.94	0.4
PbO	0.45	0.2	0.0004	<0.2	0.09	2.2

Discussion of the chemical compositions of the glass working waste

The discussion of the chemical composition of the glass working waste (and the following section on the composition of the glass artefacts) uses the EDXRF data and the SEM-EDS data given in appendices 1 and 2. For the 22 samples which could be analysed by both methods, the SEM-EDS data has been used in preference to the EDXRF data (due to improved accuracy and detection limits).

There are a wide range of contemporary and modern terms used to classify post-medieval glass. Contemporary post-medieval terms include, 'crystal', 'ordinary' and 'green'. These terms are not used here, as the basis for identification is frequently unclear. Modern reports often use terms such as 'soda glass', 'potash glass' or 'lead glass' without reference to any analyses to define chemical composition. It is to be suspected that such attributions are based on the visual qualities of the glass, eg colour and weathering. Recent research (De Raedt *et al* 1998; Dungworth and Brain 2005; Dungworth and Cromwell forthcoming) has shown that the visual appearance of a glass does not always simply correlate with chemical composition. The recent increase in the number of chemical analyses of post-medieval glasses has shown that glasses were made with a broad range of soda to potash ratios. Those with roughly equal proportions of soda and potash are called mixed alkali glasses. There is, however, no sharp distinction between soda glass and mixed alkali glass. For the purposes of this report, the boundary between soda and mixed alkali glass is arrived at after a consideration of the distribution of soda and potash contents (Figure 6).

The Vauxhall glasshouse produced several different types of glass (Table 4; Figures 6–9): soda glass, mixed alkali glass and high-lime low-alkali glass. In addition six samples of glass working waste do not belong to any of these three groups (here called miscellaneous). The two 'experimental test-pots', which were recovered from modern dumps, contain glasses with compositions that are not typical of the 17th century (see below).

Table 4. Glass working waste samples belong to each compositional group

	soda	**mixed alkali**	**high-lime low-alkali**	**miscellaneous**
Samples	4	42	8	6
Sample numbers	{39}, {48}, {52}, {70}	{1}, {2}, {3}, {5}, {7}, {8}, {9}, {10}, {11}, {12}, {15}, {16}, {18}, {20}, {21}, {22}, {23}, {24}, {25}, {26}, {27}, {28}, {29}, {47}, {49}, {50}, {53}, {54}, {55}, {56}, {57}, {58}, {59}, {60}, {61}, {62}, {63}, {64}, {67}, {68}, {74}, {81}	{17}, {19}, {41}, {42}, {43}, {44}, {45}, {51}, {99}, {100}	{4}, {6}, {30}, {31}, {46}, {61}

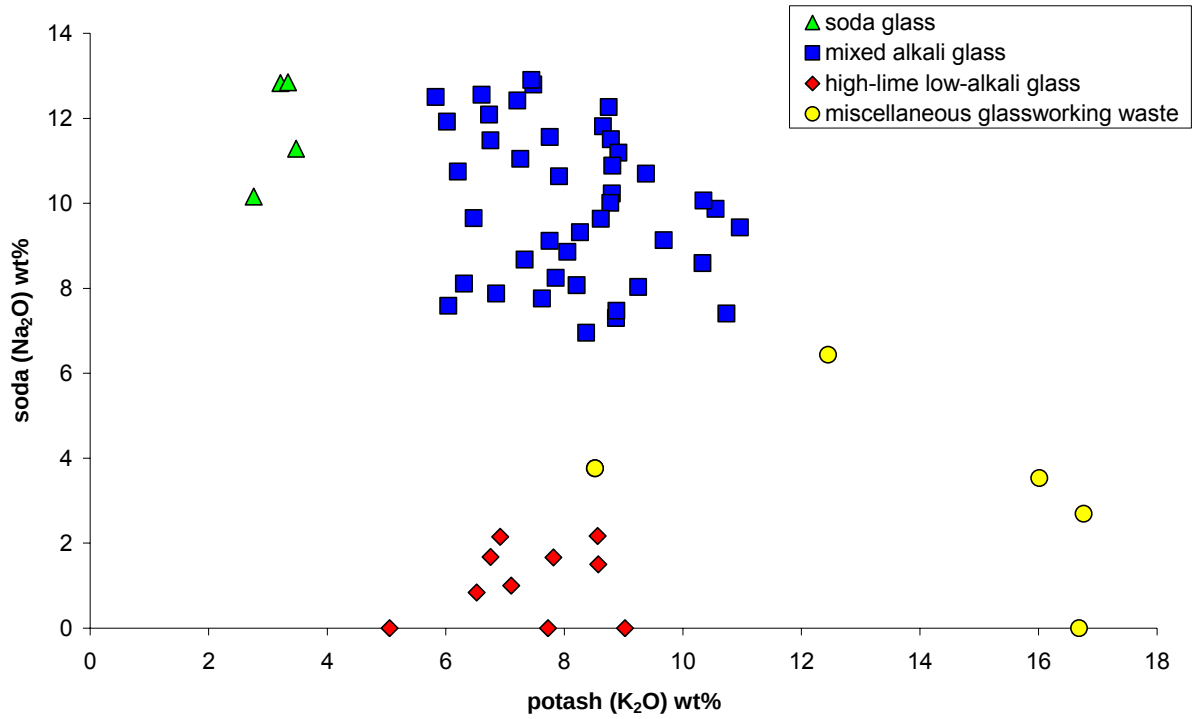


Figure 6. Plot of potash and soda contents of the glass working waste from Vauxhall (62 samples, SEM-EDS and EDXRF data, excludes the two experimental test-pots)

Soda Glass

Four samples (7% of the analysed glass working samples) are sufficiently rich in soda and low in potash (more than three times as much soda as potash) to be described as soda glasses (Figure 6 and Table 5), but most other oxides are present in levels similar to the mixed alkali glass (Table 6).

Table 5. Mean and standard deviation of the weight % composition of the soda glass manufactured at Vauxhall (4 samples, EDXRF data)

oxide	mean	sd
Na_2O	11.8	1.3
MgO	3.1	0.4
Al_2O_3	1.5	0.1
SiO_2	67.4	1.3
P_2O_5	0.4	<0.1
SO_3	<0.2	
Cl	0.6	0.1
K_2O	3.2	0.3
CaO	9.9	0.2
TiO_2	0.1	<0.1
MnO	1.2	0.2
Fe_2O_3	0.6	0.1
PbO	0.1	0.1
SrO	0.07	0.02

The composition of the soda glass manufactured at Vauxhall is similar to *vitrum blanchum* Venetian glass (Verità 1985) but can be distinguished by the higher levels of iron oxide and manganese oxide (a phenomenon common to most *façon de venise* glass, cf De Raedt *et al* 1998). The iron would derive from raw materials and the manganese would have been deliberately added in an attempt to counteract the colouring effect of the iron. The closest parallel for the composition of the soda glass manufactured at Vauxhall can be found among some of the early 17th-century soda glass manufactured at Broad Street, London (Mortimer 1995). The flux used to manufacture this soda glass was probably imported soda-rich plant ash such as *Salicornia* (Cable 2001; Godfrey 1975; Verità 1985).

Mixed Alkali Glass

Forty-two samples (70% of the analysed glass working waste) contain soda and potash in roughly equal proportions (Figure 6, the soda to potash ratio varies from 0.7 to 2.1) and can be described as mixed alkali glasses (De Raedt *et al* 1998; Henderson 2005). The manufacture of mixed alkali glasses is known at the contemporary glasshouse at Silkstone, South Yorkshire (Dungworth & Cromwell forthcoming) and the 18th-century glasshouse at Cheese Lane, Bristol (Dungworth and Mortimer 2005; Mortimer and Dungworth in Jackson 2005).

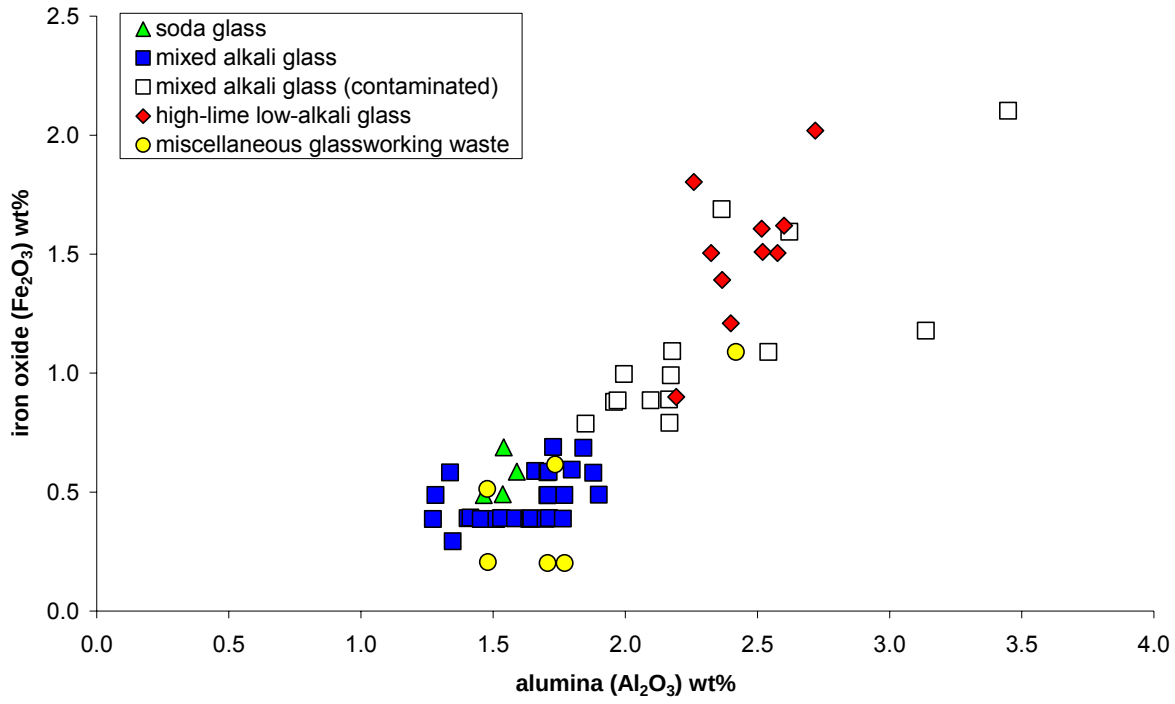


Figure 7. Plot of alumina and iron oxide contents of the glass working waste from Vauxhall (62 samples, SEM-EDS and EDXRF data, excludes the two experimental test-pots)

Figure 7 shows the alumina and iron oxide contents of the mixed alkali glasses divided into two groups. The first group (dark blue squares) consists of a fairly tight cluster around 1.6wt% alumina and 0.5wt% iron oxide (Table 6). The second, rather diffuse group (white squares) contains elevated levels of these oxides (and slightly elevated levels of titania). These oxides are likely to have derived from reactions with the crucibles and/or the fuel ash (cf Dungworth & Mortimer 2005, figure 6). A high

proportion of the samples of contaminated mixed alkali glass come from glass adhering to crucibles. The detailed study of the interaction between two crucibles and their adhering glass (see below) confirms that alumina, iron oxide, titania and silica all tend to migrate from the crucible into the adhering glass. It is important that such mechanisms are considered carefully when attempting to determine the composition(s) of the glass manufactured through the analysis of fragments of discarded waste.

The relatively high strontium oxide content (>0.2wt%) of some mixed alkali glasses from other glasshouses (eg Cheese Lane and Silkstone phase 1) suggests that these were manufactured using seaweed ash (kelp) as a flux. The use of seaweed for the manufacture of mixed alkali glass at Silkstone and Bristol has been confirmed by the measurement of strontium isotopes present in these glasses (Patrick Degryse *personal communication*). The Vauxhall mixed alkali glass, however, contains relatively low levels of strontium oxide (Table 6) and it is unlikely that kelp was used.

Table 6. Mean and standard deviation of the weight % composition of two groups of mixed alkali glass manufactured at Vauxhall (28 and 14 samples respectively, SEM-EDS and EDXRF data)

	mixed alkali (dark blue squares in Figure 7)		**mixed alkali (contaminated) (white squares in Figure 7)**	
	mean	**sd**	**mean**	**sd**
Na_2O	10.9	1.4	8.2	0.9
MgO	2.3	0.6	1.6	0.3
Al_2O_3	1.6	0.2	2.3	0.5
SiO_2	63.6	2.2	65.2	2.2
P_2O_5	0.3	0.1	0.3	0.1
SO_3	<0.2		<0.2	
Cl	0.5	0.1	0.3	0.2
K_2O	8.1	1.5	8.1	1.1
CaO	9.5	1.4	10.3	1.8
TiO_2	0.1	<0.1	0.2	0.1
MnO	0.9	0.1	1.0	0.2
Fe_2O_3	0.5	0.1	1.1	0.4
PbO	1.7	2.1	1.3	1.8
SrO	0.06	0.02	0.07	0.02

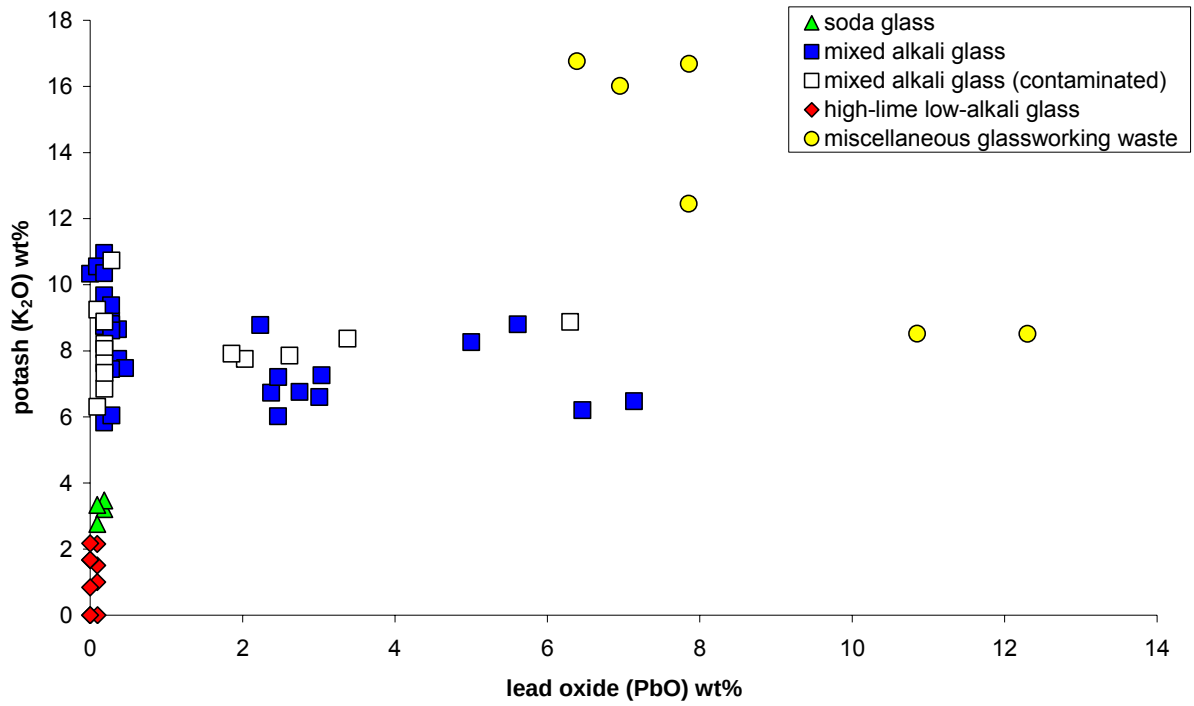


Figure 8. Plot of lead oxide and potash contents of the glass working waste from Vauxhall (62 samples, SEM-EDS and EDXRF data, excludes the two experimental test-pots)

The mixed alkali glass from Vauxhall can be divided into three groups on the basis of the lead oxide content (Figure 8). The first and largest group (26 out of 42 samples) contains up to 0.5wt% lead oxide. The second group (11 samples) contains 2–4wt% lead oxide and the third group (5 samples) contains 4–8wt% lead oxide. Except for the lead content, there are no significant differences in the compositions of these three groups. It is not certain how these glasses came to contain lead oxide. Traditional European plant ash glasses (both the potash-rich northern tradition and the soda-rich southern tradition) contain very low levels of lead oxide. Lead oxide was deliberately used in large proportions to make colourless glasses from the 1670s (Dungworth and Brain 2005). Mixed alkali glasses produced at both Silkstone (Dungworth 2003) and Cheese Lane (Mortimer and Dungworth in Jackson 2005), like many of the samples of Vauxhall mixed alkali glass, contain moderate levels of lead oxide (~1wt%). Minor amounts of lead oxide in 18th-century alkali glasses have aso been noted by Brill and Hanson (1976) and Kunicki-Golfinger *et al* (2000). It is possible that lead was incorporated into some mixed alkali glass through the use of cullet which contained some lead crystal, however, comparable lead content is not seen in high-lime low-alkali glasses (see below). An alternative explanation could be the use of lead vessels for the purification (lixiviation) of plant ashes used as fluxes (cf Brill and Hanson 1976, 223).

High-Lime Low-Alkali (HLLA) Glass

Ten samples (17% of the analysed glass working waste) contain high levels of lime and low levels of soda and potash (Figures 6 and 9; Table 7) and can be described as high-lime low-alkali glasses (cf Mortimer 1991). The earliest HLLA glasses are found in the late medieval period, at the forest glasshouses of Germany (Wedepohl 1997) and France (Barrera and Velde 1989). Some finished HLLA glass window glass of this period has been found in Britain (Newton and Fuchs 1988) but the manufacture of HLLA glass in Britain starts in the late 16th century with the arrival of immigrant glassworkers (Dungworth & Clark 2005).

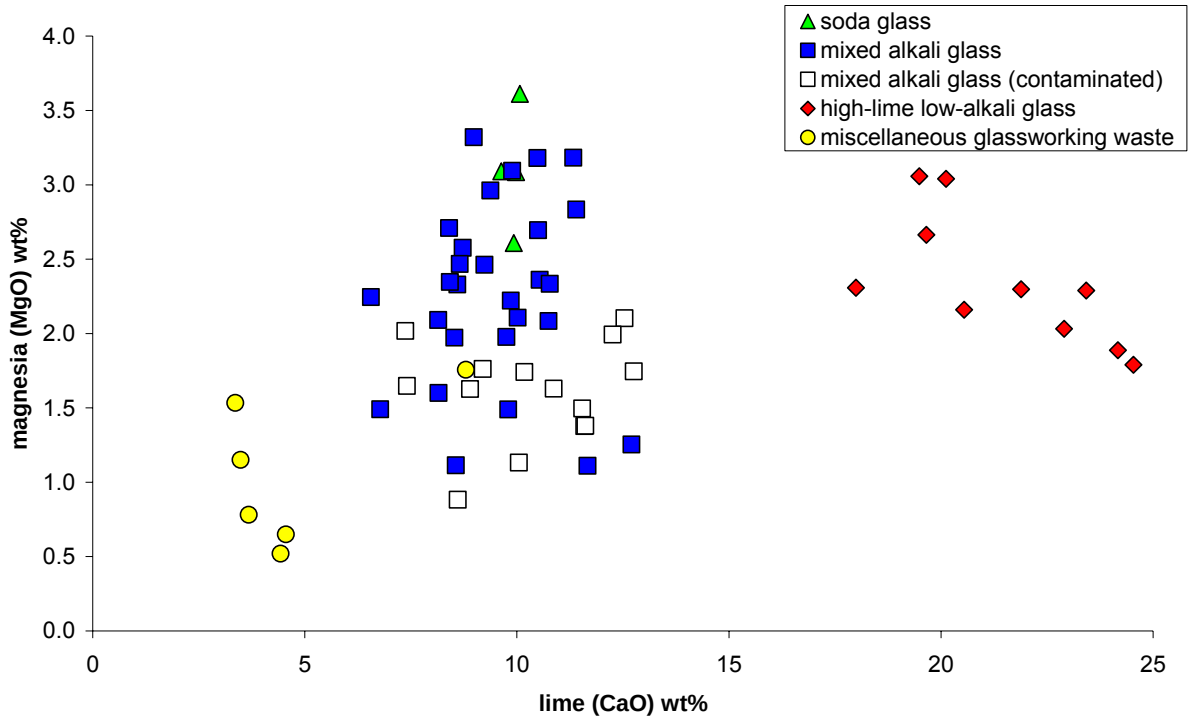


Figure 9. Plot of lime and magnesia contents of the glass working waste from Vauxhall (62 samples, SEM-EDS and EDXRF data, excludes the two experimental test-pots)

The composition of the Vauxhall HLLA glass (eg relatively high levels of phosphorus and manganese) suggests the use of a plant ash flux, possibly oak (Jackson *et al* 2005). Later HLLA glasses (from *c* 1700 onwards) appear to have been made using an increasing proportion of cheap fluxes, especially waste products of other industries (eg slag). During the 17th century, HLLA glass was used to produce window, vessel and bottle glass (Bayley *et al* forthcoming; Dungworth and Cromwell forthcoming; Paynter and Doonan 2003). After the development of lead crystal in the 1670s, HLLA glass was largely restricted to the manufacture of window and bottle glass (Dungworth & Brain 2005). The use of HLLA glass for the manufacture of window glass appears to have discontinued *c* 1700 (Bayley *et al* forthcoming; Dungworth 2006 and forthcoming a). HLLA glass continued to be used for the manufacture of bottles until the end of the 19th century.

Table 7. Mean and standard deviation of the weight % composition of the HLLA glass manufactured at Vauxhall (10 samples, SEM-EDS and EDXRF data)

oxide	mean	sd
Na_2O	1.1	0.9
MgO	2.4	0.4
Al_2O_3	2.4	0.2
SiO_2	60.7	1.6
P_2O_5	2.4	0.3
SO_3	0.2	0.2
Cl	<0.2	
K_2O	7.4	1.2
CaO	21.5	2.2
TiO_2	0.2	<0.1
MnO	0.2	<0.1
Fe_2O_3	1.5	0.3
PbO	<0.1	
SrO	0.07	0.02

Miscellaneous Glasses

The remaining six samples ({4}, {6], {30], {31], {46] and {66]) have chemical compositions which do not match any of the other compositional groups from Vauxhall. These sample contain some of the highest levels of lead (Figure 8) but these are still substantially lower than contemporary lead crystal glasses (Brain and Dungworth 2005). In addition, these samples contain appreciable amounts of a range of oxides associated with mixed alkali glasses (soda, magnesia, lime, etc) which are largely absent from true lead crystal. Nevertheless, it is possible that some of these miscellaneous glasses were attempts to imitate early lead crystal. It is striking that samples {30}, {31} and {66} contain very high levels of potash (16–17wt%) which are rare in English post-medieval glasses, except for the earliest phase of lead crystal glass manufactured in the 1670s (Group 1, Dungworth and Brain 2005).

'Experimental Test-Pots'

The glass in the two 'experimental test-pots' ({14} and {71}) have unusual compositions that do not match any of the glass working waste from the site. The potash and soda levels are broadly similar to the other glasses from Vauxhall but the levels of lime, magnesia, strontium, phosphate and manganese are extremely low. This glass would not have been successful due to the lack of a stabiliser (in particular lime) which would have lead to 'crizzling' (cf Tyler and Willmott 2005, fig 46). These 'experimental test-pots' were recovered from modern dumping contexts (Tyler and Willmott 2005, 46) and so might have no direct connection with the late 17th-century glasshouse. The lack of association is strengthened by the petrographic examination; 'experimental test-pot' {14} was made using different raw materials compared to the ordinary crucibles and had probably been exposed to a lower temperature.

Discussion of the composition of the analysed glass artefacts

The remaining 30 analysed samples were taken from 17 vessels, 6 wine bottles, 5 fragments of plate glass, 1 bull's eye from crown glass, and 1 ?moil ({82} whose composition does not match any of the glass working waste from the site).

Vessels

The 17 samples of vessel glass included items believed to have been manufactured at Vauxhall (Tyler and Willmott 2005, 68–74). Each item is considered briefly below (the G numbers are from the published glass catalogue).

G10 {87} Goblet with a mould-blown ladder stem, described as an English product of the early 17th century (Tyler and Willmott 2005, 69). This is a mixed alkali glass with a remarkably high manganese content and it is most unlikely that it was manufactured at Vauxhall. This result agrees with Tyler and Willmott (2005).

G13 {89} A pedestal bowl, described as probably an early 17th-century import (Tyler and Willmott 2005, 69). This is a mixed alkali glass with a composition that is subtly but significantly different from that produced at Vauxhall (eg the manganese is too low). This result agrees with Tyler and Willmott (2005).

G15 {90} The spout of a jug or posset distorted by heat, described as possibly cullet. (Tyler and Willmott 2005, 69). This is a mixed alkali glass with a composition that is subtly but significantly different from that of Vauxhall (eg the magnesia is too high). This result agrees with Tyler and Willmott (2005).

G46 {72} Cylindrical phial. It is believed that this vessel was (probably) a product of the Vauxhall glasshouse (Tyler and Willmott 2005, 73). This is a HLLA glass within the compositional limits of the HLLA glass produced at Vauxhall. This result agrees with Tyler and Willmott (2005).

G49 {88} Globular phial. It is believed that this vessel was (probably) a product of the Vauxhall glasshouse (Tyler and Willmott 2005, 73). This is a HLLA glass within the compositional limits of the HLLA glass produced at Vauxhall. This result agrees with Tyler and Willmott (2005).

G52 {86} Goblet. It is believed that this item was (probably) a product of the Vauxhall glasshouse (Tyler and Willmott 2005, 73). This is a mixed alkali glass with a composition which does not match the glass produced at Vauxhall: it contains low levels of lime, iron and manganese. This result contradicts Tyler and Willmott (2005).

G53 {84} Goblet. It is believed that this item was (probably) a product of the Vauxhall glasshouse (Tyler and Willmott 2005, 74). This is a mixed alkali glass with a composition which matches the glass produced at Vauxhall. This result agrees with Tyler and Willmott (2005).

G54 {85} Goblet. It is believed to be (probably) a product of the Vauxhall glasshouse (Tyler and Willmott 2005, 74). This is a mixed alkali glass with a composition which matches the glass produced at Vauxhall. This result agrees with Tyler and Willmott (2005).

G56 {83} Uncertain vessel type. It is believed that this item was (probably) a product of the Vauxhall glasshouse (Tyler and Willmott 2005, 74). This is a mixed alkali glass with a composition which matches the glass produced at Vauxhall. This result agrees with Tyler and Willmott (2005).

G57 {93} Flask or bottle. It is believed that this item was (probably) a product of the Vauxhall glasshouse (Tyler and Willmott 2005, 74). This is a mixed alkali glass with a composition which is subtly but significantly different from that produced at Vauxhall (the manganese composition is too high). This result contradicts Tyler and Willmott (2005).

G58 {92} A flask or decanter. It is believed that this item was (probably) a product of the Vauxhall glasshouse (Tyler and Willmott 2005, 74). This is a soda glass with a composition which does not match the glass produced at Vauxhall (the magnesia is too high and the potash too low). This result contradicts Tyler and Willmott (2005). The composition matches that of Venetian 'standard' glass (Verità 1985).

G59 {91} Uncertain vessel type. It is believed that this item was (probably) a product of the Vauxhall glasshouse (Tyler and Willmott 2005, 74). This is a soda glass almost identical in composition to G58 and was not made at Vauxhall. This result contradicts Tyler and Willmott (2005).

G62 {98} A beaker, described as a lead glass. It is believed that this item was not a product of the Vauxhall glasshouse (Tyler and Willmott 2005, 74). This is a lead glass of Dungworth and Brain (2005) Group 3; produced from the 1680s onwards, but not at Vauxhall. This result agrees with Tyler and Willmott (2005).

G64 {95} A goblet, described as a lead glass. It is believed that this item was not a product of the Vauxhall glasshouse (Tyler and Willmott 2005, 74). This is a lead glass of Dungworth and Brain (2005) Group 3; produced from the 1680s onwards, but not at Vauxhall. This result agrees with Tyler and Willmott (2005).

G65 {94} A goblet, described as a lead glass (Tyler and Willmott 2005, 69. It is believed that this item was not a product of the Vauxhall glasshouse (Tyler and Willmott 2005, 69). This is a mixed glass with a composition which does not match the glass produced at Vauxhall (the magnesia, lime, manganese and iron are too low). The very low levels of magnesia and lime might have arisen due to the use of purified (lixivated) plant ashes and would make the glass prone to 'crizzling' (cf Tyler and Willmott 2005). The chemical analysis contradicts the identification of this as a lead glass but agrees with the suggestion that the vessel was not made at Vauxhall.

G66 {97} A flask or bottle, described as a lead glass. It is believed that this item was not a product of the Vauxhall glasshouse (Tyler and Willmott 2005, 69). This is a lead glass of Dungworth and Brain (2005) Group 3; produced from the 1680s onwards, but not at Vauxhall. This result agrees with Tyler and Willmott (2005).

G67 {96} A beaker or tumbler, described as a lead glass. It is believed that this item was not a product of the Vauxhall glasshouse (Tyler and Willmott 2005, 69). This is a mixed alkali glass with a composition which matches the glass produced at Vauxhall. The chemical analysis contradicts the identification of this as a lead glass and the suggestion that the vessel was made at Vauxhall.

The analysis of vessel glass shows that many vessels have compositions which match the glasses produced at Vauxhall. Four out of the nine analysed vessels originally believed to have been made at Vauxhall, however, have compositions which do not match the glass working waste. In addition, one out of the eight analysed vessels assumed not to have been made at Vauxhall has a composition which does match the glass working waste and so could have been made at Vauxhall. The analysis of five vessels described as 'lead glass' (presumably on the basis of visual appearance and apparent density) shows that only three are true lead glasses (cf Dungworth and Brain 2005).

Wine bottles

Samples were taken from six shaft-and-globe wine bottles; a type whose manufacture is dated to *c* 1650 to *c* 1680. All six samples are HLLA glasses with compositions within the range of the glass working waste from Vauxhall and were almost certainly products of the glasshouse. This agrees with Tyler and Willmott (2005).

Plate glass

Five fragments of plate glass were analysed; Tyler and Willmott suggest that these samples 'have lower iron and alumina levels [than the working waste], suggesting a provenance elsewhere' (2005, 51) and propose that it was cullet. The plate glass samples actually have compositions that correspond very closely to Vauxhall working waste: two are similar to the soda glass and three to the mixed alkali glass. The iron oxide and alumina contents of the plate glass samples are low but are not outside the range of compositions for the working waste. Therefore, it is possible that this plate glass was made at John Baker's glasshouse. Indeed, one of the tenants at Vauxhall was John Bellingham who held patents for the manufacture of plate glass and glass for coach and sash windows (Tyler and Willmott 2005, 9). The fact that the plate glass fragments recovered at Vauxhall do not have polished and finished surfaces strengthens the idea that these are not cullet but were produced nearby.

Samples {37}, {40} and {82}

The last three samples include two for which there is no contextual or typological information and one which was described as a ?moil but which does not match the composition of the glass working waste from the site.

Examination of the crucibles

Two samples of crucible ({1} and {8}) were subject to petrographic examination (Tyler and Willmott 2005, 47, 64–67). This showed that they had been hand-made using two clays with crushed flint or quartz and confirmed that they had been exposed to a high temperature. Merrett, writing in 1662, states that the crucibles used for making 'green glass are made of Non-such clay, mixed with another clay brought from Worcestershire, which bears the fire better than that of Nonsuch' (Cable 2001, 304).

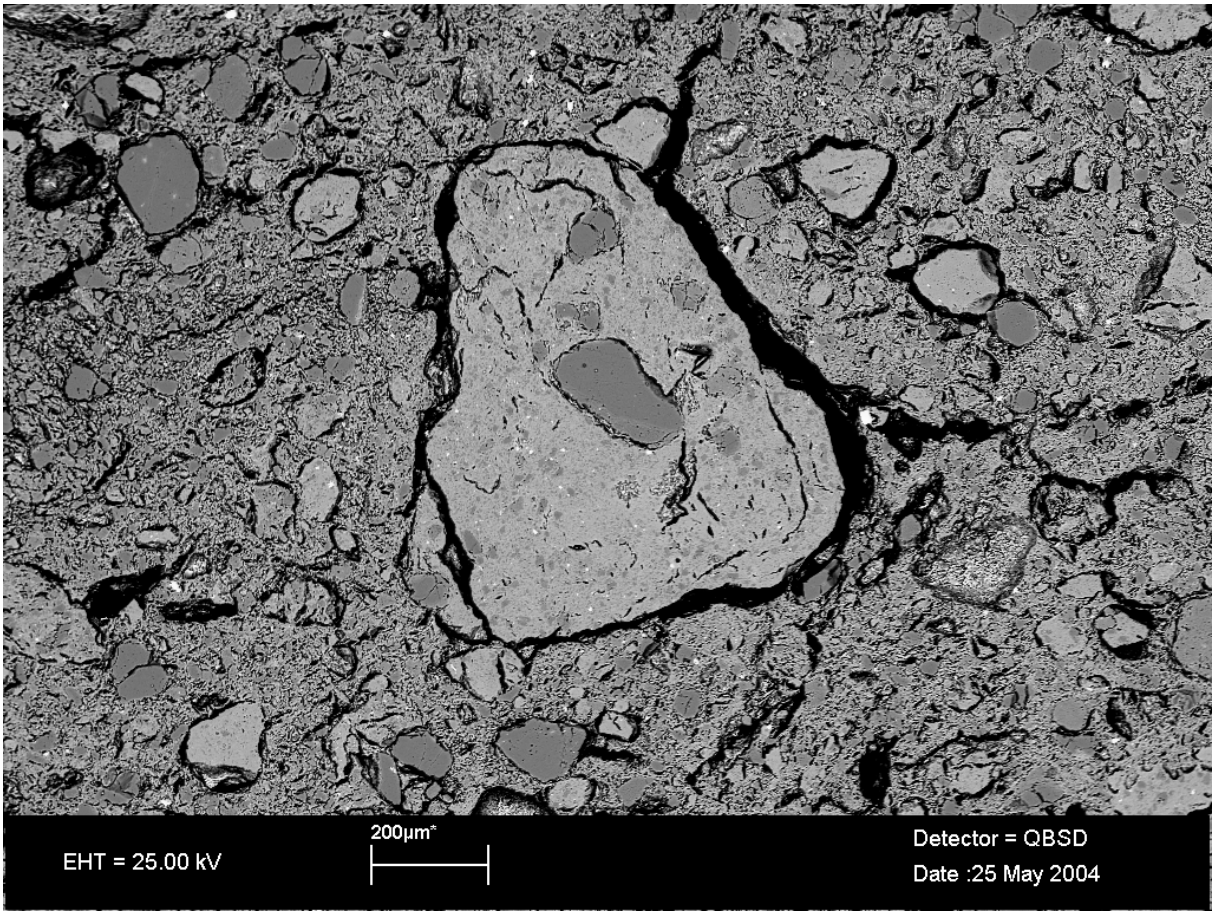


Figure 10. SEM photograph (back scattered electron detector) of crucible {2} showing clay pellet (region in the centre surrounded by shrinkage cracks), silica polymorph inclusions (dark grey) and porosity (black)

Two samples of crucible ({2} and {16}) were examined and analysed with the SEM. The microstructure of the clay fabric of the crucible shows many of the features observed petrographically, such as silica polymorph inclusions, clay pellets and porosity (Figure 10). The term silica polymorph is used here to cover all minerals with the formula SiO_2. Most samples were analysed using SEM-EDS which is not capable of distinguishing between the different silica polymorphs (quartz, cristobalite, tridymite, etc). The pellets appear to be more heavily vitrified than the surrounding ceramic indicating that they had been heavily fired prior to the forming of the crucible. This suggests that they are re-used old crucibles, ie 'grog' (cf Powell *et al* 1883).

The chemical composition of the crucibles was determined using SEM-EDS; the bulk composition was determined by analysing large areas (~5mm^2) away from the surfaces where the crucible had been attacked by glass or other materials which will have altered the chemical composition of the interior and exterior surfaces. In

addition, the grog particles and small areas of the ceramic matrix avoiding grog (typically 0.1mm^2 areas) were analysed (Table 8).

Table 8. Chemical composition of crucibles (SEM-EDS analyses, average of 4 analyses for each region)

	{2}			{16}		
Area	**Bulk**	**Ceramic**	**Grog**	**Bulk**	**Ceramic**	**Grog**
Na_2O	0.1	<0.1	<0.1	0.2	0.1	<0.1
MgO	0.4	0.4	0.4	0.5	0.4	0.3
Al_2O_3	26.3	25.0	29.9	25.1	25.0	23.2
SiO_2	67.7	69.4	65.2	69.1	69.5	72.2
P_2O_5	0.1	0.2	0.1	0.1	0.1	0.2
SO_3	0.1	0.1	<0.1	0.1	<0.1	<0.1
Cl	0.1	0.1	<0.1	<0.1	<0.1	<0.1
K_2O	0.9	0.8	0.7	0.7	0.7	0.5
CaO	0.7	0.7	0.3	0.4	0.4	0.4
TiO_2	1.5	1.3	1.5	1.5	1.5	1.5
Fe_2O_3	2.1	2.0	1.8	2.2	2.3	1.8

The grog within each crucible tends to be of a slightly different chemical composition compared to the ceramic matrix, however, the differences are not consistent for the crucibles analysed (see table 9). In crucible {2}, the clay pellets have lower levels of lime (but the potash levels are similar to the ceramic matrix), while in crucible {16} the clay pellets have low levels of potash (but the lime levels are similar to the ceramic matrix). The differences in chemical composition between the clay pellets and the ceramic matrix are relatively slight compared to the differences between the two crucibles and are extremely slight when compared to contemporary crucibles from other glasshouses (Table 9). It is possible that the variations in chemical composition are simply a reflection of the varied nature of the raw materials. The bulk composition of the Vauxhall crucibles is broadly similar those of other post-medieval glasshouses (Table 9) but the closest similarities are with Stourbridge fireclays. Further research is needed on the composition of glassmaking crucibles in order to understand where the glass makers obtained their clays (Crossley 1998, 221).

Table 9. Average composition of post-medieval glassmaking crucibles (Sources: Bristol = Dungworth and Mortimer 2005; Blakelock et al *forthcoming; Silkstone = Dungworth 2003; June Hill = Dungworth forthcoming b; Shinrone = O'Brien* et al *2005; Stourbridge = Edwards 1927; Evers 1921)*

	Vauxhall	Bristol	Silkstone	June Hill	Shinrone	Stourbridge
Na_2O	0.1	<0.2	<0.2	0.2	<0.2	0.5
MgO	0.5	0.4	0.2	0.5	0.4	0.4
Al_2O_3	25.7	22.0	16.6	23.4	22.4	27.7
SiO_2	68.4	73.7	78.0	70.4	71.2	67.7
K_2O	0.8	0.7	1.5	1.6	2.0	0.4
CaO	0.6	0.2	0.1	0.4	0.4	0.4
TiO_2	1.5	1.2	1.0	1.6	2.4	1.0
Fe_2O_3	2.2	1.6	1.0	1.6	0.8	1.8

Both the ceramic matrix (and the pellets) contain small crystals of mullite ($3Al_2O_3.2SiO_2$, Figure 11). The mullite is likely to have formed as a result of the degradation of kaolinite in the clay, a reaction which normally occurs at temperatures above 1200°C (Eramo 2005).

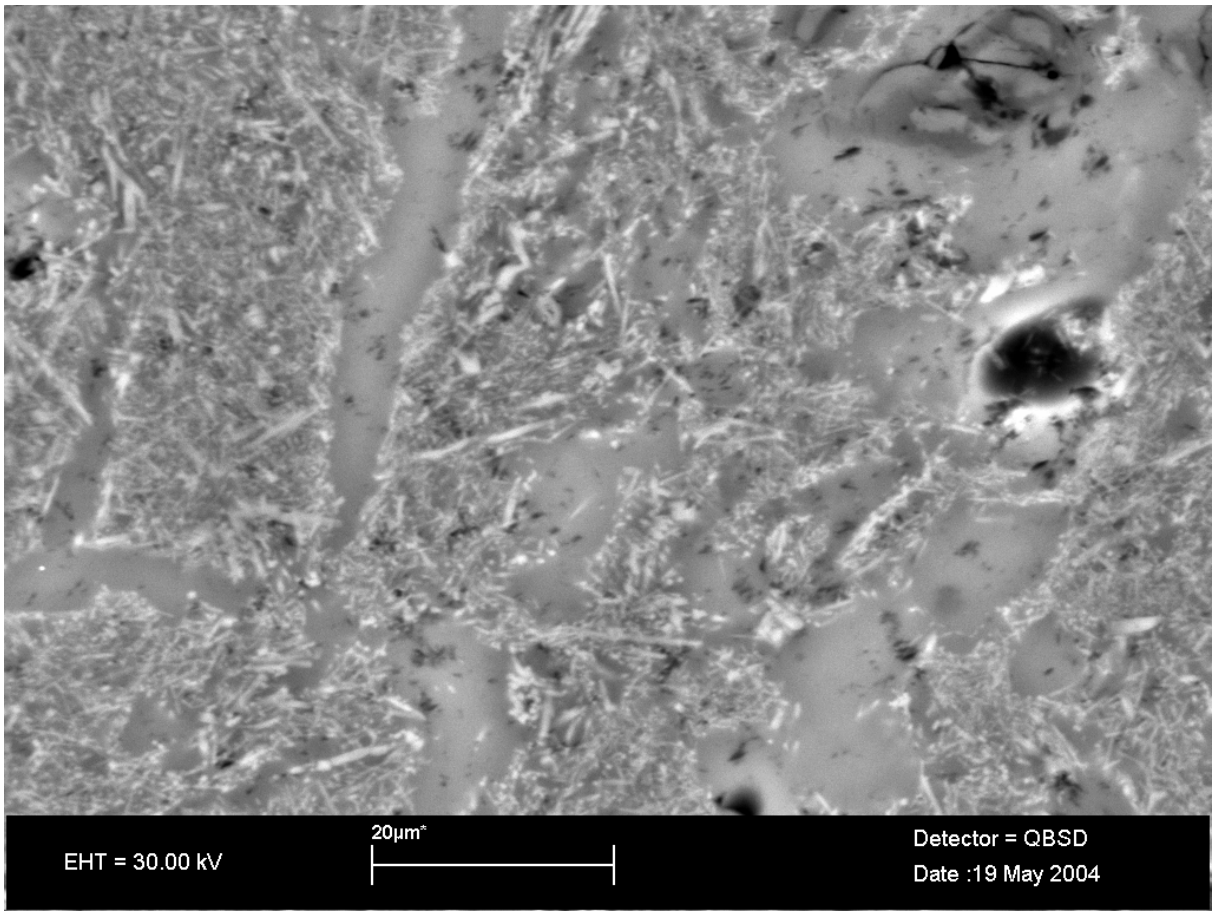


Figure 11. High magnification SEM photo (back scattered electron detector) of crucible {16} showing small crystals of mullite (the bright needle-like crystals)

Figures 12 and 18 show the glass adhering to the interior surfaces of the two crucibles. The chemical composition of the adhering glass is not homogenous but varies with distance from the ceramic-glass interface. In addition, there are differences between the two samples. Crucible {2} has a mineral phase which has crystallised within the 'interaction zone' (Figure 12). Crucible {16} shows a distinct vitreous 'interaction zone' between the ceramic of the crucible and the adhering glass with no crystal phases visible (Figure 18; cf Dungworth 2003, figure 10). The SEM was used to examine the changes in the concentrations of various oxides through the ceramic-glass interface, including elemental X-ray maps and by quantitatively analysing a series of areas arranged perpendicular though to the interface through the crucible and the adhering glass (Appendices 3–4).

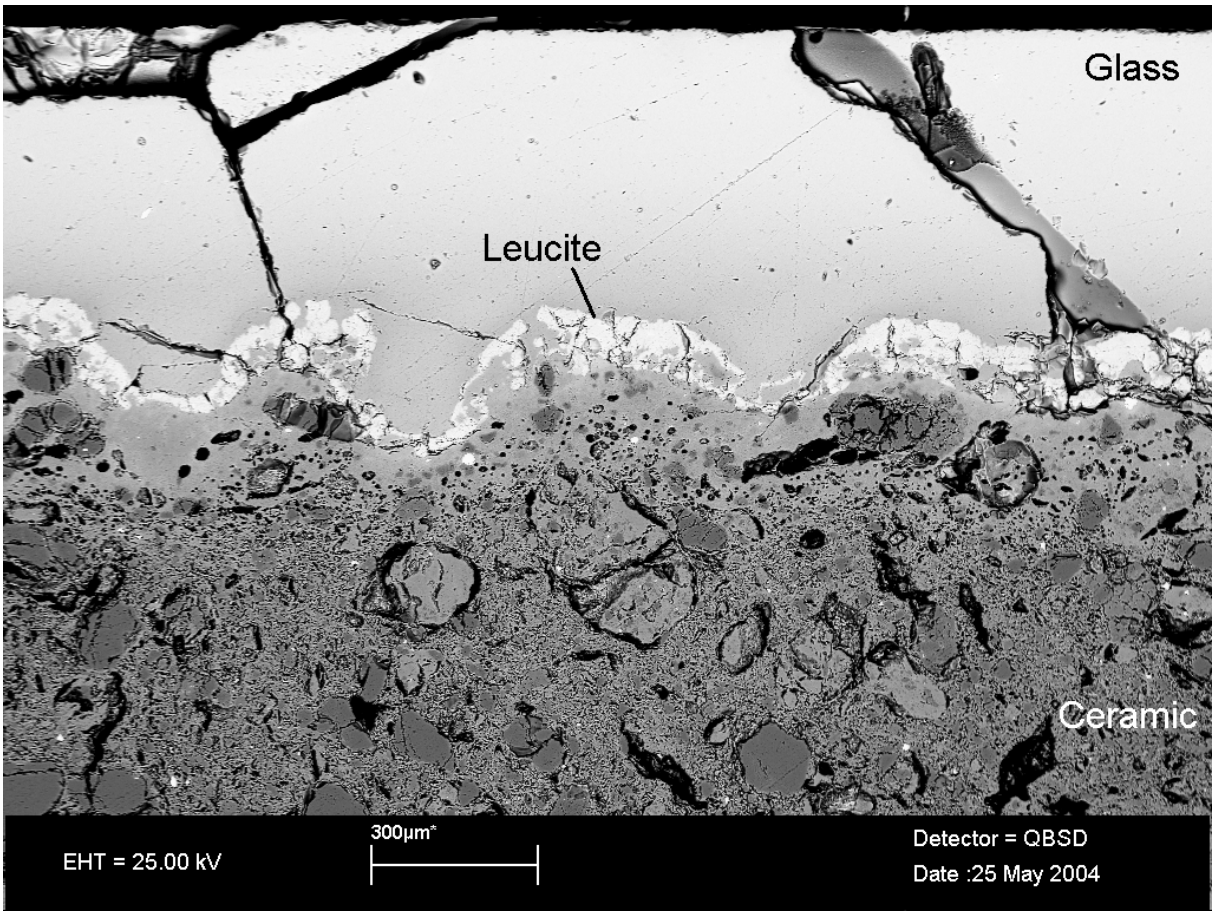
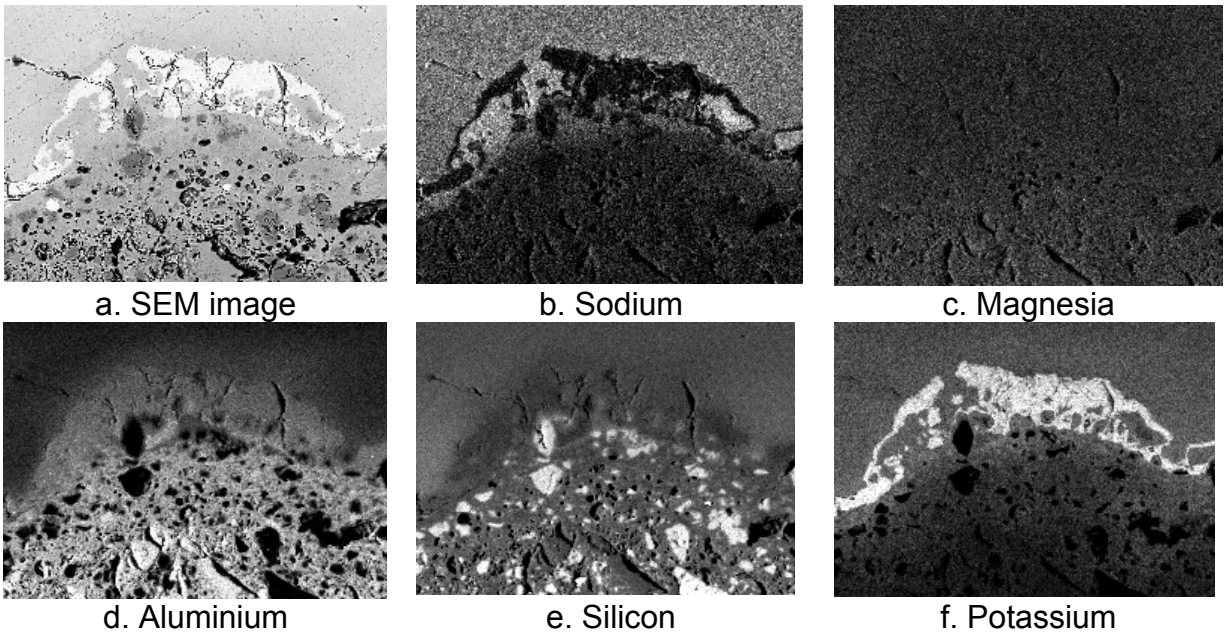


Figure 12. SEM image (back scattered electron detector) of crucible {2}



a. SEM image b. Sodium c. Magnesia

d. Aluminium e. Silicon f. Potassium

Figure 13. A series of elemental X-ray maps of the leucite crystals and surrounding area (centre of Figure 12) adhering to the interior surface of crucible {2}

The X-ray maps (Figure 13) and Linescans of the ceramic fabric of crucible {2} and its adhering glass (Figures 14–17) show that the reactions between glass and ceramic were complex. The composition of adhering glass varies with distance from the glass-ceramic interface. This variation is further complicated by the presence of crystals within the 'interaction zone'.

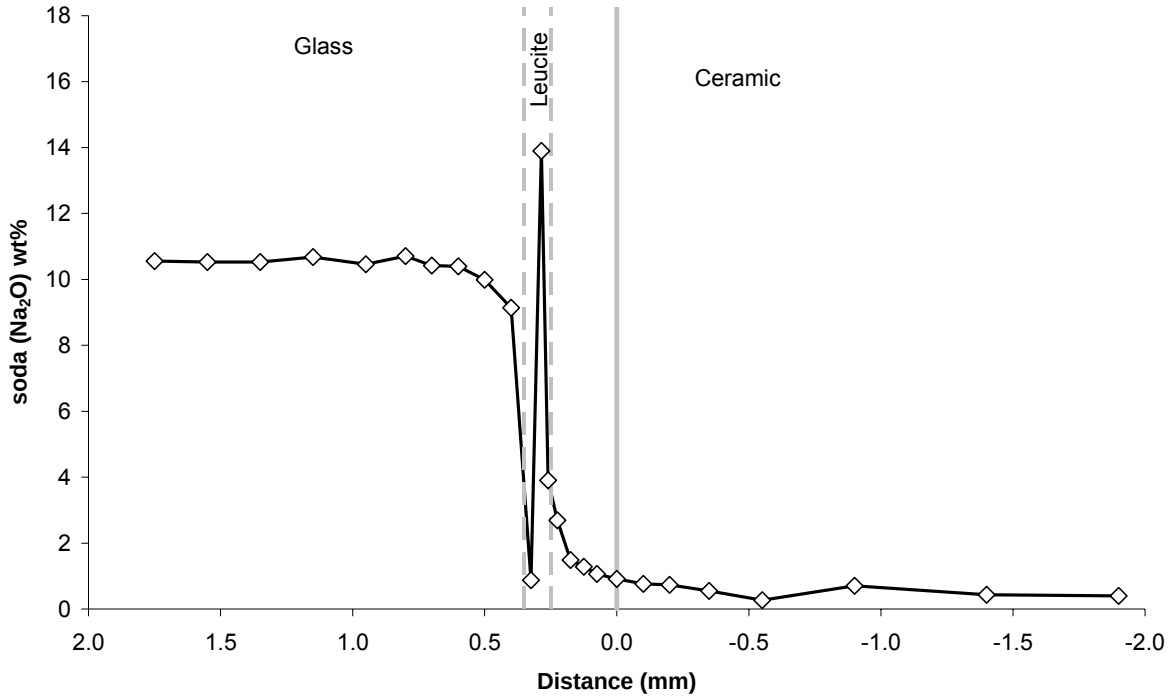


Figure 14. Plot showing changes in soda content through the adhering glass and into crucible {2}.

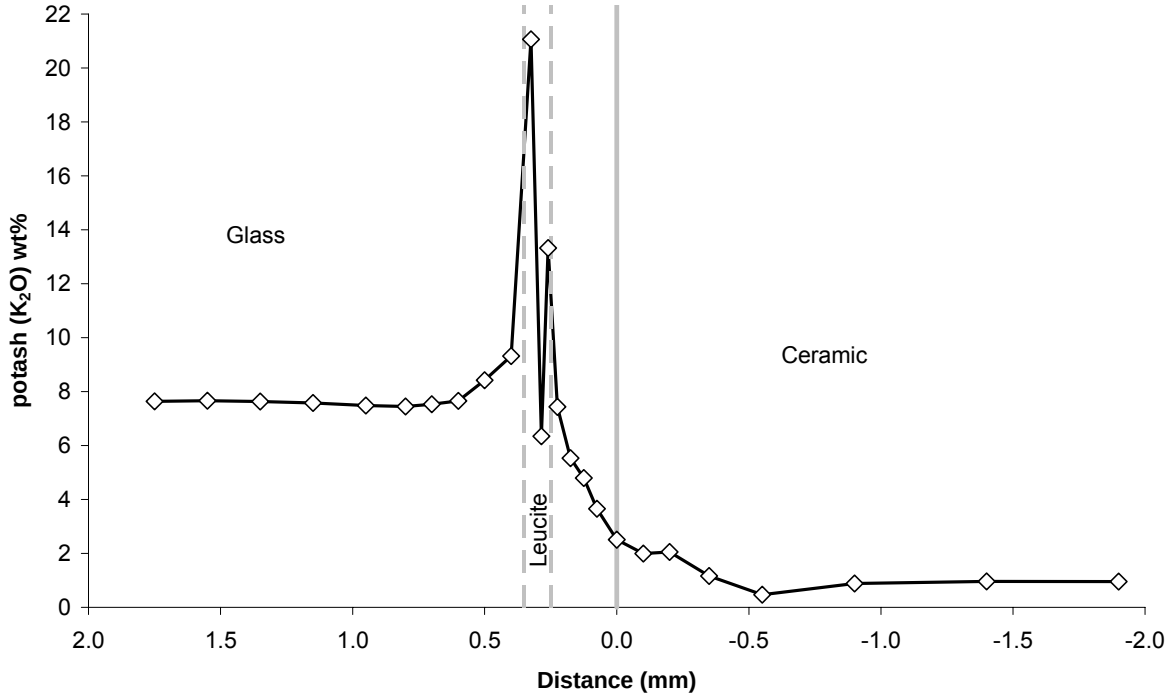


Figure 15. Plot showing changes in potash content through the adhering glass and into crucible {2}

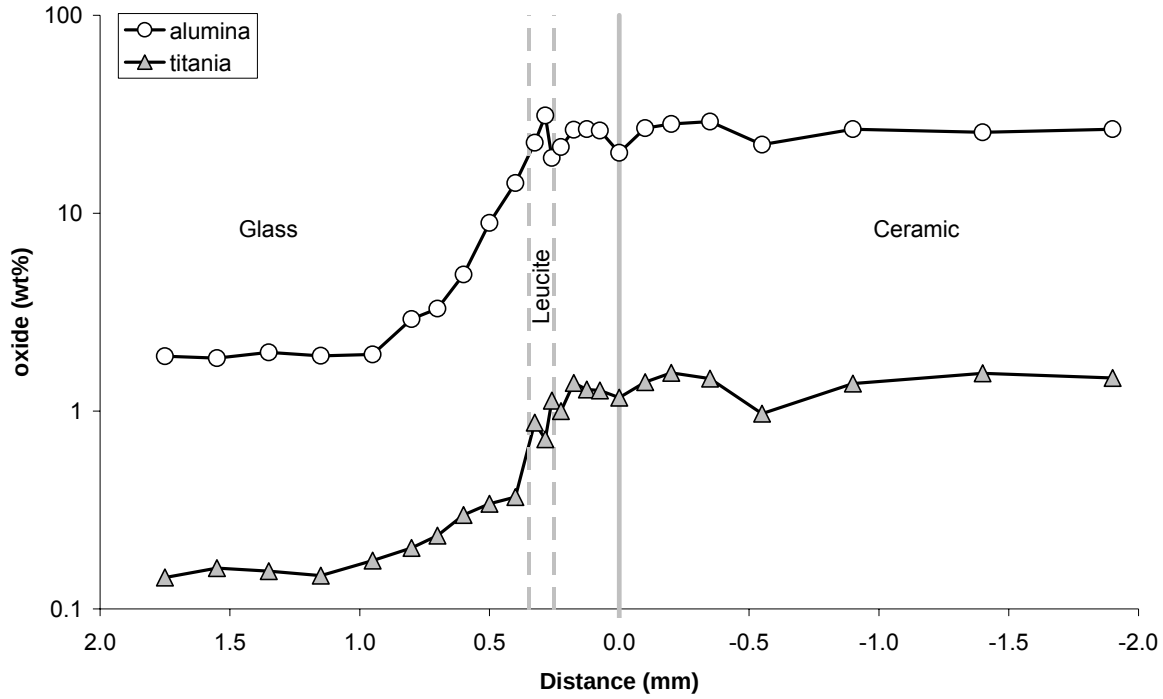


Figure 16. Plot showing changes in alumina and titania contents through the adhering glass and into crucible {2}.

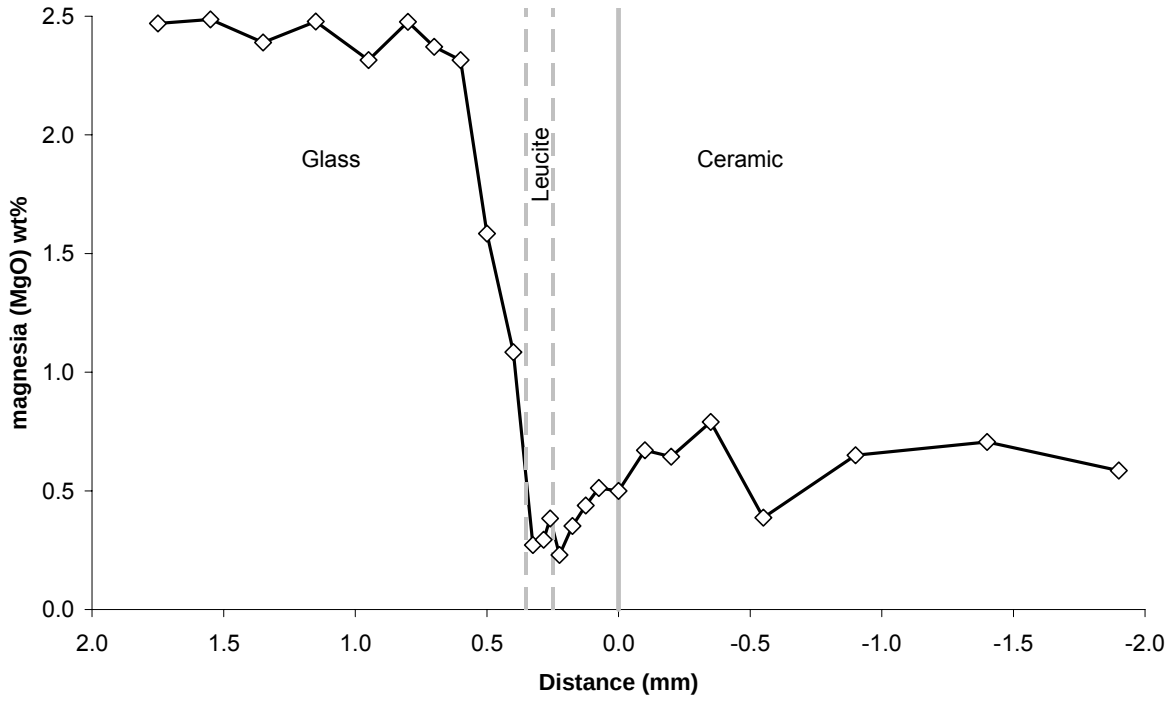


Figure 17. Plot showing changes in magnesia content through the adhering glass and into crucible {2}.

When viewing compositional trends from the glass to the ceramic (from left to right in Figures 14–17) the glass-forming elements decline (Figures 14, 15 and 17) while the ceramic elements increase (Figure 16). Soda and potash clearly penetrate into the ceramic fabric of the crucible up to a depth of 0.5mm while alumina and titania from the crucible penetrate up to 1mm into the adhering glass.

Figures 12 and 13 show the presence of euhedral crystals within the interaction zone between the ceramic and adhering glass. The SEM-EDS analyses show that these are leucite, $Al_2O_3.K_2O.4SiO_2$, which forms at temperatures between 1100º and 1300°C (Levin *et al* 1956, Fig 811; Perera and Trautman 2005). It is likely that it would act as a relatively stable viscous 'reaction product interlayer' (Lee and Zhang 1999, 79) which would help to impede further corrosion of the ceramic by the glass. The dark areas within the leucite are a sodium-aluminium-silicate (probably $Al_2O_3.Na_2O.4SiO_2$).

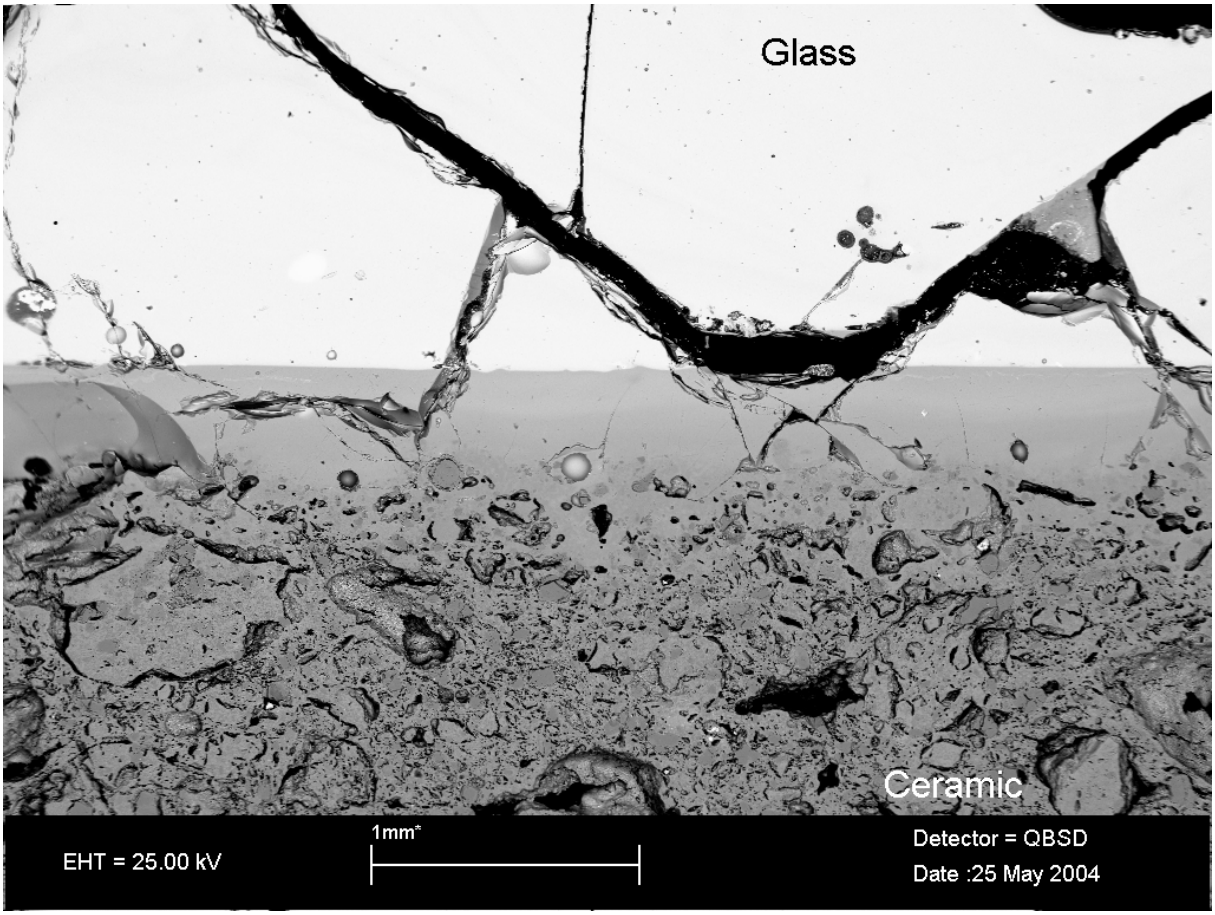


Figure 18. SEM photograph (back scattered electron detector) of crucible {16} with interaction zone and adhering glass

The examination of crucible {16} found no euhedral crystals at the interface between the ceramic and the glass but did show two distinct layers of adhering glass (Figure 18) similar to the crucibles from Silkstone (Dungworth 2003, figures 10 and 12). Nevertheless, many of the trends in the compositions of individual elements are similar to those outlined above for crucible {2}: the glass tends to penetrate into the crucible (Figures 19 and 20) and the crucible tends to dissolve into the glass (Figure 21). The innermost layer of glass is likely to be a 'reaction product interlayer' (Lee and Zhang 1999; Cable 1994) and is not the remains of 'glazing' the interior surface of the crucible prior to use. In reviewing *post-mortem* studies of modern glassmaking refractories, Cable notes: 'It frequently happens, as here, that there is a thin interfacial layer considerably different from either the bulk glass on one side or the glassy phase of the refractory on the other. Its properties have a crucial role in governing refractory corrosion' (Cable 1994, 294).

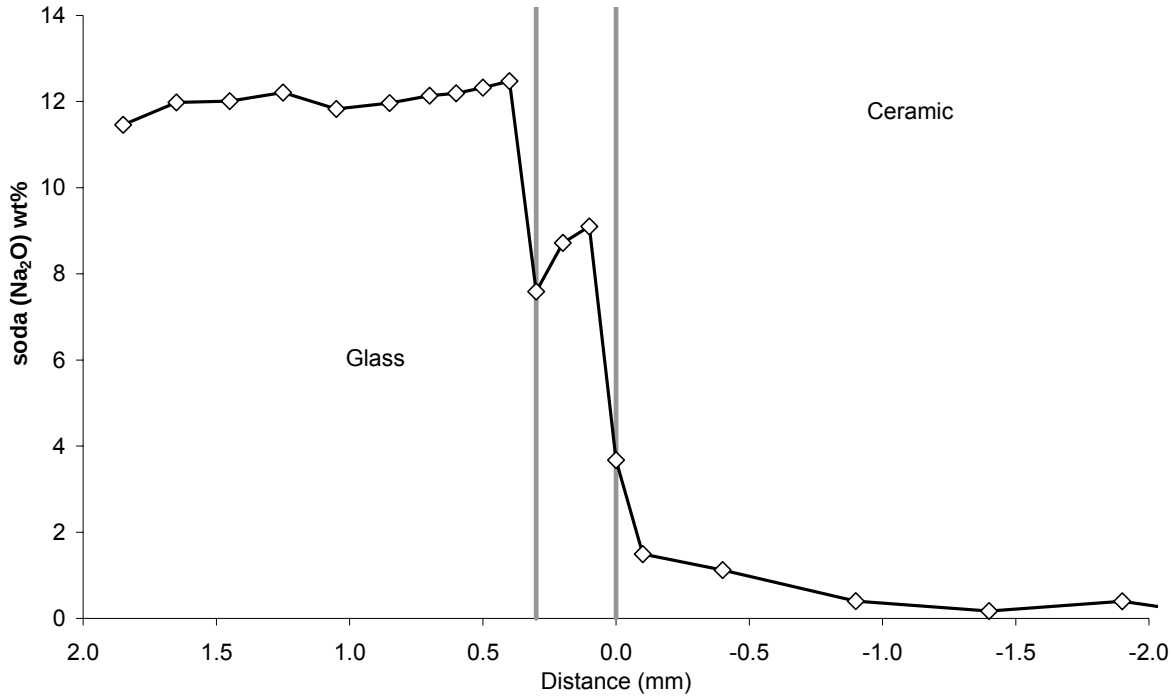


Figure 19. Plot showing changes in soda through the adhering glass and into crucible {16}

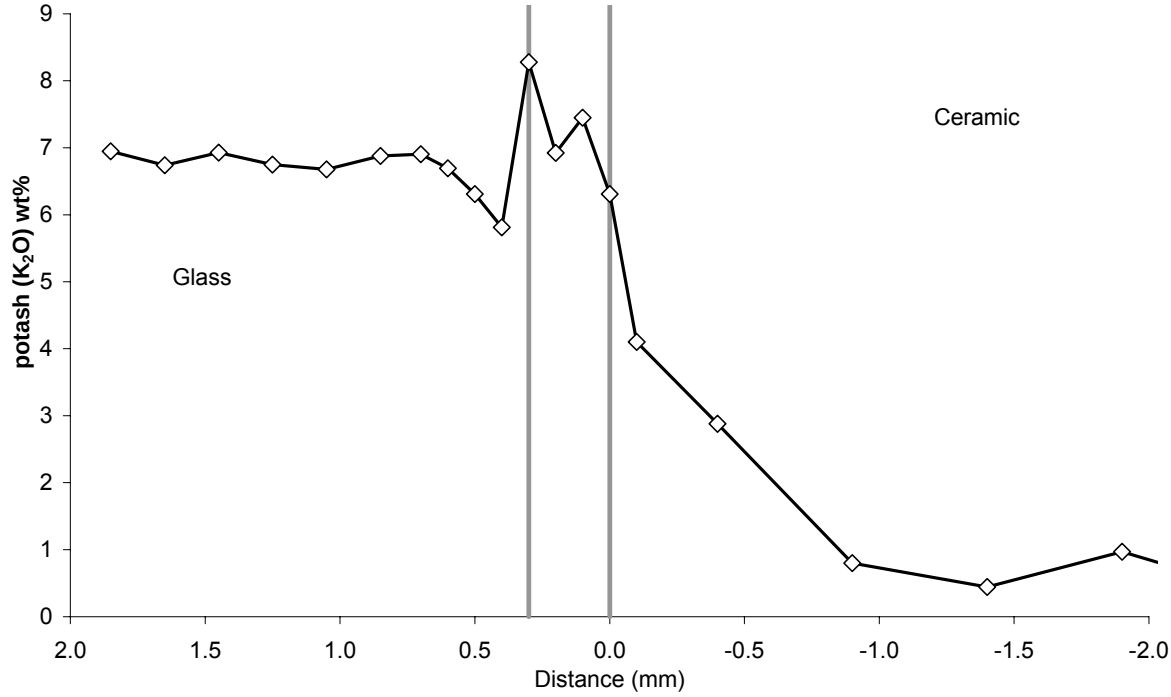


Figure 20. Plot showing changes in potash through the adhering glass and into crucible {16}

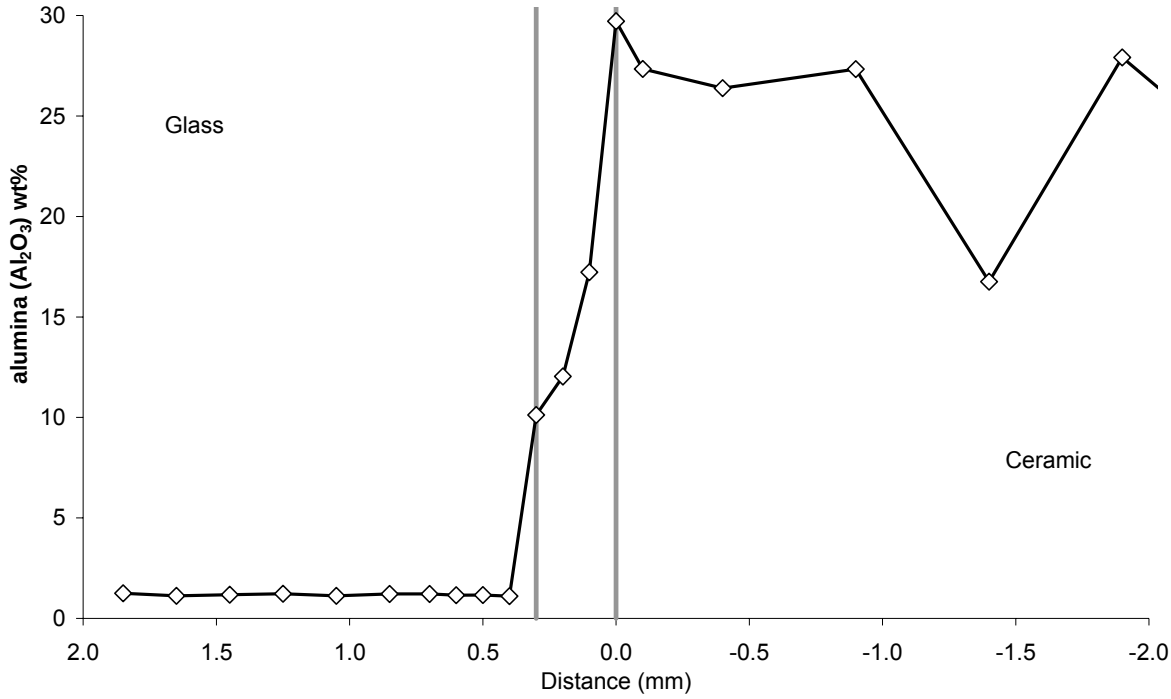


Figure 21. Plot showing changes in alumina through the adhering glass and into crucible {16}

Data on the chemical composition of the glass adhering to crucibles {2} and {16} have been obtained into two distinct ways: by EDXRF analysis of the powdered samples left after the ICPS analysis (see appendix 1) and by SEM-EDS analysis of larger fresh samples taken from the crucibles (see appendix 2). The results show consistent differences: the EDXRF analyses indicate higher levels of those oxides which derive from the crucible (alumina, silica, titania and iron oxide). These differences reflect the way in which the powdered samples used for the ICPS and EDXRF analysis were obtained. ICPS requires 100mg of powdered material which would equal approximately 4mm^3. Therefore, these powdered samples are likely to include material from the zone where glass and ceramic have reacted together. The glass adhering to the interior surfaces of the crucibles provides information about the compositions of the glass(es) that were manufactured but it is clear that such glass would have reacted with, and been contaminated by, the ceramic fabric of the crucible. Such samples need to be analysed using a technique (such as SEM-EDS) where chemical analyses of discrete areas and spots can be linked to microstructure.

The ‘Frit’

One of the glass working residues recovered from the backfill [299] of the glass furnace is described as ‘frit’ (Tyler and Willmott 2005, 42). The ‘frit’ is described as a unique find, however, the identification is erroneous — the ‘frit’ is actually devitrified glass.

Frit is a term used by numerous writers from the 12th to the 19th centuries to describe a material produced during glassmaking (Hawthorne and Smith 1979, 52–3; Smith and Gnudi 1990, 127–8; Hoover and Hoover 1950, 587; Cable 2001, 66–7, 297, 330; Cable 2003; Cossons 1972). Frit was produced by mixing raw materials (sand and plant ashes) and then heating them but not melting them. The frit was then crushed (and usually mixed with cullet) and melted at a higher temperature. Fritting allowed reactions to start between the sand and plant ashes used; alkali and alkali earth carbonates would tend to react with silica to form silicates, liberating carbon dioxide in the process. It is possible that this two stage process (fritting and then melting) was more fuel efficient than a single melting stage. In addition, it may have helped to minimise the formation of bubbles in the glass. Fritting appears to have been abandoned in the 1830s as plant ash flues were replaced by synthetic soda (Muspratt 1860, 205).

Tyler and Willmott (2005, 42) describe the frit as a light purple crystalline material with a greener base. Their identification of this material as frit is based on the observation that it ({99} and {100}) has the same chemical composition as the HLLA glass produced at Vauxhall, and that when heated it formed a green glass (Tyler and Willmott 2005, Fig 39). It is undeniable that samples {99} and {100} have chemical compositions within the range of the HLLA glass produced at Vauxhall, however, this does not prove that the material is frit. The sample of the ‘frit’ that was melted is reported as containing, ‘. . . opaque white patches [that] are caused by a lack of stirring of the batch’ (Tyler and Willmott 2005, 43). Unfortunately, Tyler and Willmott do not publish any images of the microstructure of the ‘frit’ in support of their interpretation. Samples {99} and {100} have been examined in some detail (see below). This demonstrates that the material is *not* frit, but is devitrified glass. It is likely that the opaque white patches reported by Tyler and Willmott are actually crystals that have precipitated from the melt (ie evidence for devitrification).

The fritting process involves the heating of the plant ash and sand at a temperature high enough to start reactions but not so high as to cause melting. It is usually assumed that this temperature would be around 700–800ºC. It is likely, therefore, that the microstructure of frit would consist of partially reacted silica grains (most of which would be 0.25–0.5mm in size, Boswell 1918) and some silicates in a relatively silica-poor matrix (cf Paul 1990, 158–63). This matrix would have a composition comparable with that of the plant ash used, and the nature of the silicates would vary depending on fritting temperature and duration as well as the composition of the plant ash.

The examination of samples {99} and {100} with a scanning electron microscope (Figures 22 and 23) shows that they both have similar microstructures: they consist of two or three crystalline phases in a glassy matrix. Samples {99} and {100} both contain a calcium silicate and a calcium phosphate. In addition, sample {100} contains a silica-rich phase (the dark grey crystals in Figure 23). Chemical analyses

were undertaken of several examples of each phase using SEM-EDS in spot mode (Appendix 5). These results are less than ideal as some of the phases were approximately the same size as the interaction volume of the beam in spot mode and so some of the elements detected may actually be in the surrounding matrix rather than the phase in question. Nevertheless the spot analyses suggest that the calcium silicate is wollastonite ($CaO.SiO_2$) and that the calcium phosphate is whitlockite ($3CaO.P_2O_5$). The third phase in sample {100} is rich in silica and also contains some lime, but the analysed totals fall significantly short of 100wt%. XRD analysis of sample {100} indicated the presence of α-wollastonite and whitlockite but it has not been possible to identify the third, silica-rich phase. Mixtures of silica and lime will form wollastonite above 1400ºC but mixtures including alkali sulphates will produce wollastonite at temperatures as low as 850ºC (Paul 1990, 163).

The crystalline phases present in samples {99} and {100} are less than 100 microns in size: the wollastonite and the silica polymorphs are usually under 50 microns and the whitlockite crystals are under 20 microns. All of the crystals are euhedral (the boundaries are clear and often straight) which suggests that they crystallised from a melt.

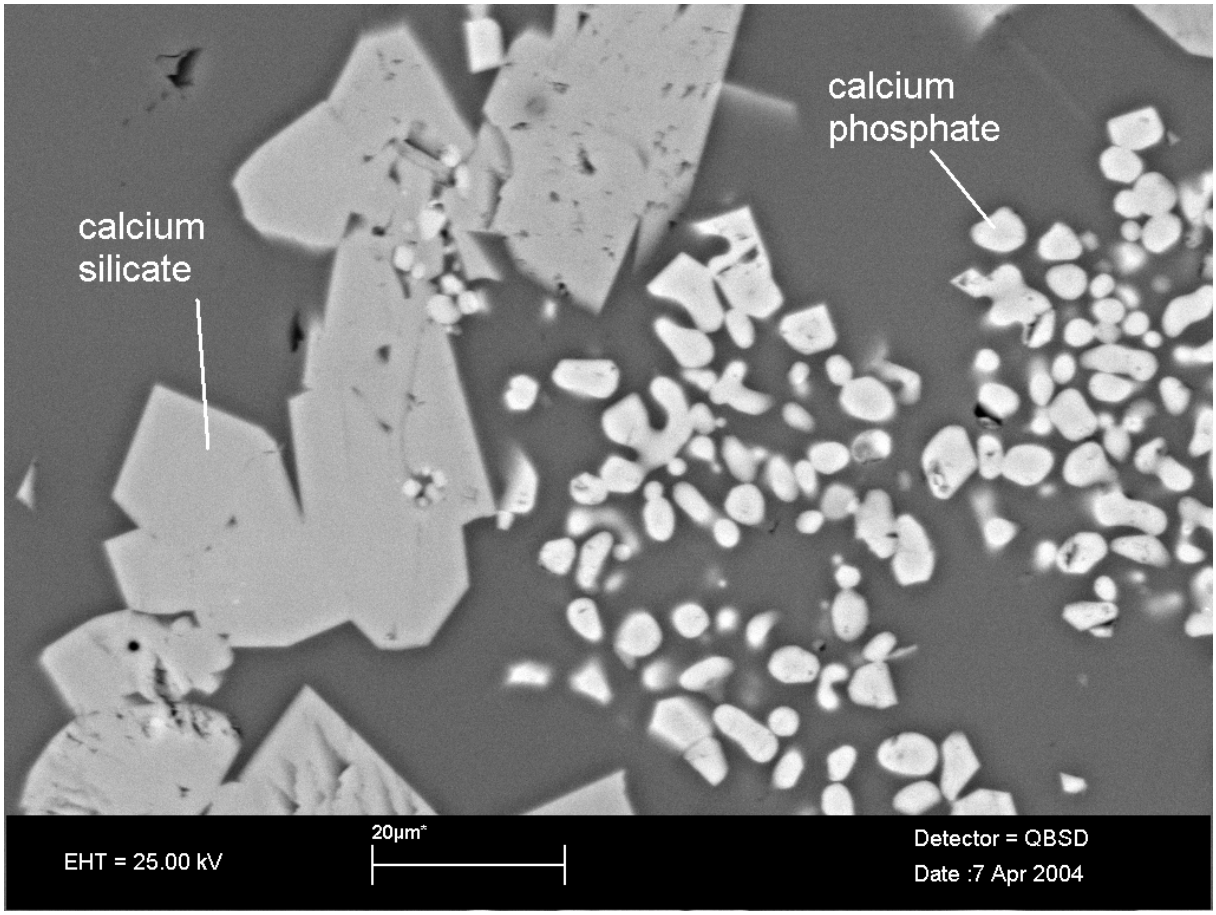


Figure 22. High magnification SEM photo (back scattered electron detector) of {99}

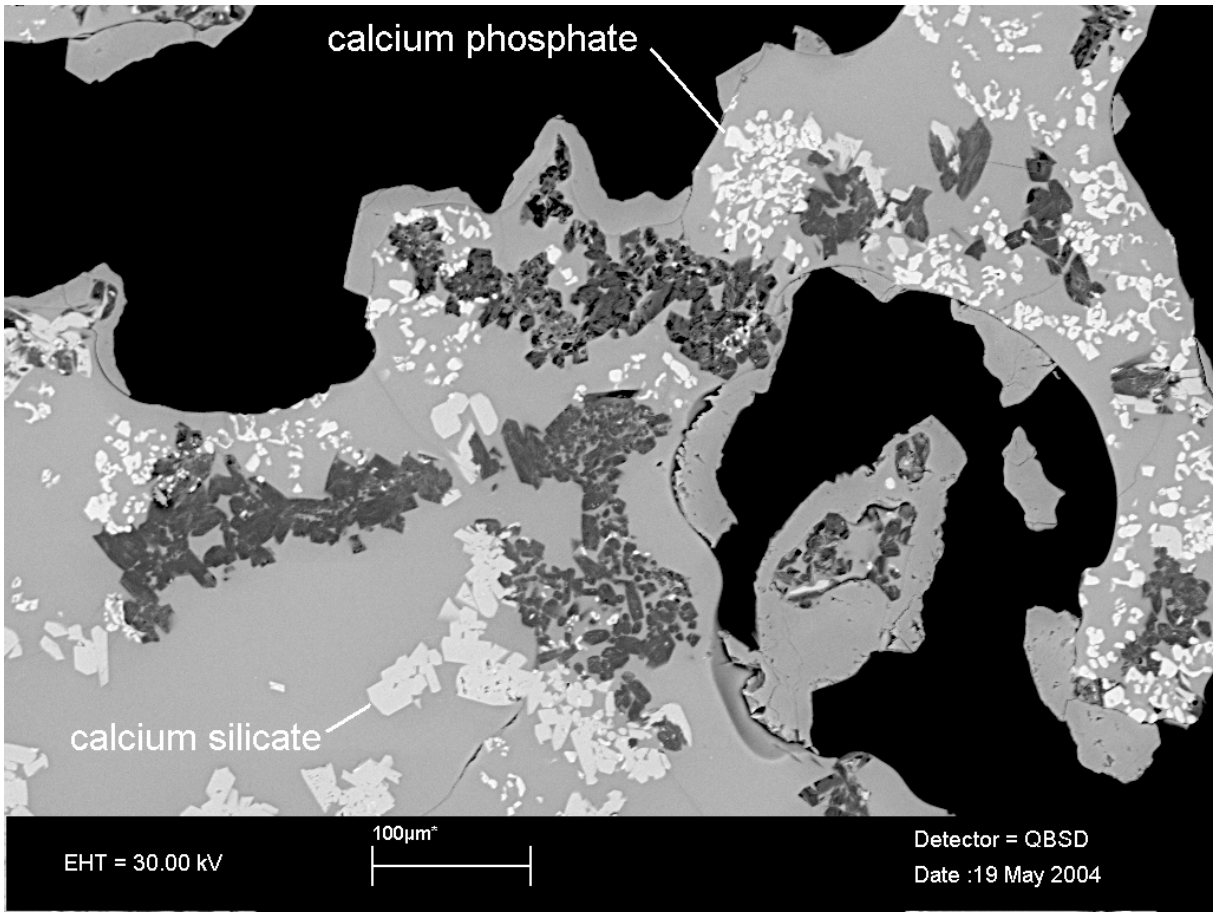


Figure 23. High magnification SEM photo (back scattered electron detector) of {100}

The microstructures of samples {99} and {100} is not what would be expected of fritting: the shape and size of the various crystals suggests they all crystallised from a molten glass and there are no eroded (partially-reacted) silica grains in an alkali-rich matrix. The microstructure is, however, what would be expected for a devitrified glass: 'All glasses are capable of undergoing the change to the crystalline state when kept for a sufficient time at a suitable temperature. The process which then takes place is known as "devitrification," and sometimes gives rise to serious manufacturing difficulties' (Rosenhain 1919, 2). The chemical composition of a glass has a strong influence on its ease of devitrification and nature of the crystals that form. Studies of devitrification (eg Kitaigorodsky 1929; Parmelee and Monack 1929) have shown that devitrified glass commonly contains high temperature silica polymorphs (tridymite and cristobalite) and wollastonite. Kitaigorodsky concluded that low concentrations of alkalis and high concentrations of alkali earths increase the likelihood of devitrification, 'glasses containing more than 11 per cent of CaO with an alkali content not exceeding 14 per cent have a high crystallising capacity' (Kitaigorodsky 1929, 229).

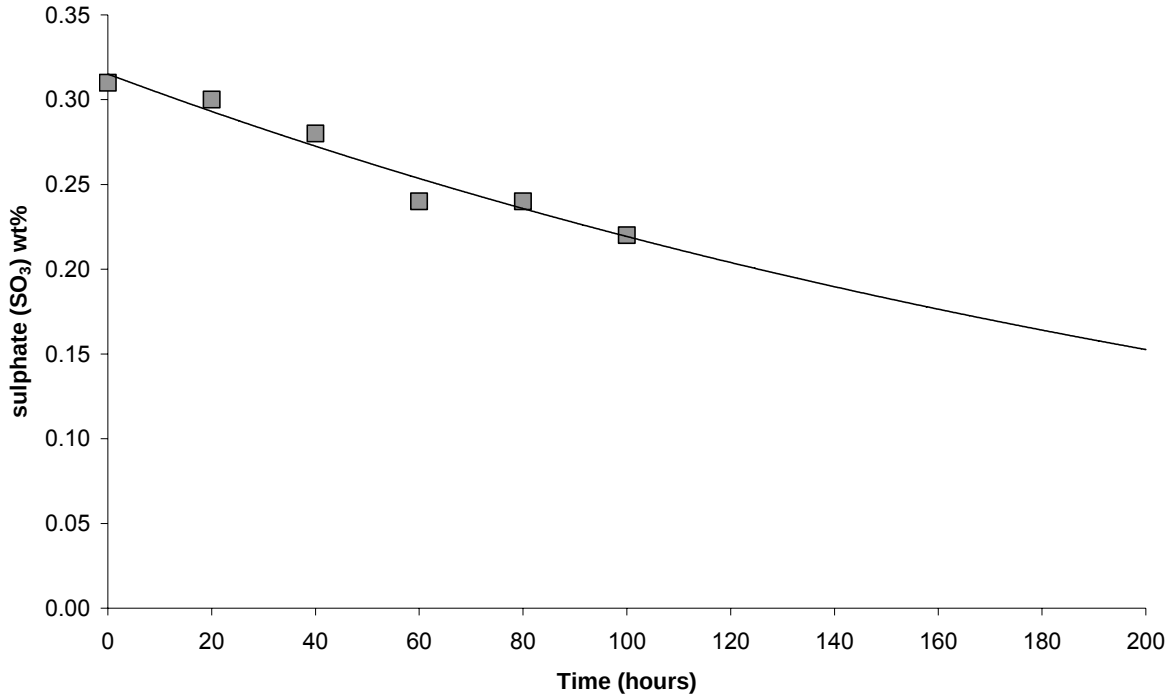


Figure 24. Sulphate concentration in a soda-lime-silica glass at 1300ºC (after Preston et al *1936)*

The SEM-EDS analyses of samples {99} and {100} showed the absence of sulphur even though the other Vauxhall HLLA glass waste samples contained sulphur (average = 0.2wt% SO_3). A study of the volatilisation of sulphate from soda-lime-silicate glasses (Preston *et al* 1936) showed that sulphate loss was fastest at higher temperatures and that the loss rate decreased with time (Figure 24). The absence of sulphate in sample {99} and {100} can be explained as a result of it having been held at a high temperature for a long period of time.

Samples {99} and {100} have chemical compositions which are almost identical to the HLLA glass production waste from Vauxhall. The microstructure of the samples does not conform to what would be expected of frit. The composition, size, shape and distribution of the crystals identified in samples {99} and {100} all point to them having formed from a molten glass. The devitrified microstructure of the samples almost certainly arose as a result of very slow cooling of glass. The context from which these samples were recovered (the backfill of the fire trench) would provide the perfect environment for slow cooling.

Conclusions

The scientific examination of samples of glass and glass working waste from Vauxhall has provided insights into glassmaking practices of the late 17th century as well as demonstrating the limitations of some modern scientific techniques.

In summary, the scientific examination of material from the site has confirmed that three different types of glass were manufactured on site. The most abundant glass type among the analysed glass working samples was mixed alkali glass. This was possibly manufactured using the ashes of a soda-rich coastal plant such as plants of the genus *Salicornia*. In contemporary terms, this was probably an 'ordinary' glass. It is certain that some of this mixed alkali glass was used to produce drinking glasses (goblets). It is possible that this glass was also used to produce plate glass used make mirrors and some windows (eg coach windows and sash windows). The glasshouse was managed in 1681 by John Bellingham who, in 1685, obtained a patent for the manufacture of glass for sash windows and coach windows (Tyler and Willmott 2005, 9). Tyler and Willmott (2005, 9) claim that there was no evidence for the manufacture of plate glass at Vauxhall, but the presence of unpolished plate glass on site would be compatible with production. It is not always easy to identify the products of a glasshouse from an archaeological assemblage. This is particularly true when the production process does not leave diagnostic forms of waste; the manufacture of flat glass (crown or broad window glass, and plate glass) may leave virtually no diagnostic waste material.

Soda glass was also manufactured at Vauxhall, which was of a similar composition to the mixed alkali glass but contained much lower levels of potash. This glass would have been called either 'crystal' or 'ordinary' and was presumably used to make drinking vessels. The third glass type manufactured was a high-lime low-alkali glass (a 'green glass') which was used for the manufacture of wine bottles and phials. Tyler and Willmott (2005, 60) argue the green glass bottles were the primary product of the glasshouse, but it is likely that the glasshouse manufactured a range of items, and the choice of products may have varied over time.

The examination of two crucibles suggests that they did not use the same clay sources as the glasshouse sites which have been studied to date. It is possible that the clay used was Stourbridge fireclay with the addition of 'grog'. The microstructure of the crucibles shows they had been exposed to temperatures in excess of 1200°C.

The material described in the excavation report as frit is not frit — it is devitrified glass.

The success of ICPS analysis to determine the chemical composition of the glass and glass working wastes at Vauxhall has been limited. It is likely that there was insufficient dialogue between archaeologists and scientists and this has resulted in a number of serious errors and misunderstandings. The data is not always of a high standard and the interpretation is often inadequate or inaccurate.

While no technique used for determining chemical composition is free from problems, ICPS of silicate materials is especially vulnerable to errors as the analysed totals never add up to 100wt% (cf Paynter 2006). Where ICPS is employed, it is essential that suitable standard reference materials are included to help identify systematic

errors. ICPS is a technique which has the ability to detect minute concentrations of almost all elements in a sample, however, the suite of elements selected for ICPS analysis of the Vauxhall samples is significantly under-used. The published report contains data on 22 different elements or oxides but only seven are discussed. It is not clear why the other elements were included in the ICPS analysis. A further drawback of ICPS is that it requires powdered samples so it is difficult to compare composition with microstructure, especially where this varies through a sample (eg glass adhering to crucibles). The scientific technique employed for this report (SEM-EDS) does not suffer from all these drawbacks, though it lacks the low detection limits of ICPS.

Assessing the composition of the glass produced at a site by analysing archaeological residues must consider site formation processes and glassmaking technologies. It is likely that most of the residues recovered from archaeological excavations were either deliberately discarded or could not be easily reused. It cannot be assumed that an excavated assemblage of glassworking waste accurately and completely represents the historic glassworking activities. This point is acknowledged in principle by Tyler and Willmott (2005, 60) but is not sufficiently engaged with when interpreting the scientific data.

In the glasshouses glass would regularly be sampled as it underwent melting and refining. This usually consisted of gathering a small amount of glass (a ‘proof’) on an iron rod (Pellatt 1968, 48). This could be inspected to see if bubbles or other defects were present and to assess the viscosity and suitability for working (by watching how quickly it would fall off the iron). The chemical composition of such ‘pulls, runs, and droplets’ might differ in small but significant ways from the final glass, especially where the glass had not yet completely melted or been refined.

Glass adhering to the interior surfaces of crucibles can provide information about the composition of the glass manufactured on site, but only if the layers of glass are thick. The glass close to the crucible will have reacted with the crucible and contain elevated levels of those oxides that are most abundant in the crucible (silica, alumina and titania). This contaminated layer of glass can be as little as 0.3mm or more than 1mm thick. The variation in thickness could reflect the ‘working age’ of the crucible; the thicker the contaminated layer the longer the working age. Given the variable thickness of the contaminated layer, it is essential that chemical analysis be undertaken in conjunction with the use of scanning electron microscope rather than a technique which relies on powdered samples (such as ICPS).

Where a process did not work well, a batch of material might be deliberately thrown away. This might arise where the raw materials employed were unexpectedly of a much poorer quality than had been expected. A much more common occurrence appears to be where a crucible failed in the furnace. In this case the glass inside would flow out of the crack and into the fire and flues (Pellatt 1968, 55). This was seen as exceedingly dangerous as the molten glass could extinguish the fire and then solidify to form a hard mass, thus putting the furnace out of operation for days or weeks at a time (Marson 1918, 45–46). The standard response in such cases was the swift emptying of the remaining contents of the crucible. While some of this ‘pot-metal’ might be retained for later use, it was more important to prevent the glass flowing into the fire (Powell *et al* 1883, 34). The material from post-medieval glass working sites includes substantial proportions of vitreous material that has fallen into

the fire and flues and remained there for days, weeks, or months. Pot-metal which falls into the fire and flues can mix with fuel ash, glass gall and other waste materials. This material will remain at elevated temperatures for long periods and so the more volatile components will be depleted and the glass will tend to devitrify.

The application of scientific techniques, such as chemical analysis, has the potential to shed considerable light on glass manufacturing processes. However, success requires dialogue between archaeologists and scientists. Selecting samples for analysis, the choice of scientific techniques and the interpretation of results requires a good understanding of glassmaking processes, the archaeological record (including stratigraphy, site formation processes and the identification of glass working residues), and techniques of scientific analysis.

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Appendix 1: Composition of samples determined by EDXRF

#	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	PbO	SrO
1	7.9	1.7	1.9	65.5	0.4	0.2	0.5	6.9	12.8	0.1	1.2	0.8	0.2	0.10
2	8.9	1.5	2.1	64.8	0.4	<0.2	0.4	8.1	11.5	0.1	1.2	0.9	0.2	0.08
3	8.1	1.4	2.2	65.1	0.4	0.2	0.5	8.2	11.6	0.2	1.2	0.8	0.2	0.09
4	3.8	0.5	1.5	68.7	<0.2	0.2	<0.2	8.5	4.4	0.1	0.9	0.5	10.9	0.02
5	8.0	2.0	2.0	63.9	0.3	<0.2	<0.2	9.2	12.3	0.1	1.2	0.9	0.1	0.11
6	3.8	0.6	1.7	65.6	0.6	0.4	0.2	8.5	4.6	0.1	0.9	0.6	12.3	0.03
7	7.6	1.3	1.8	67.7	0.5	0.0	0.5	6.0	12.7	0.1	1.0	0.6	0.3	0.09
8	9.1	2.1	2.0	61.9	0.3	<0.2	0.2	7.8	12.5	0.2	1.0	0.9	2.0	0.07
9	8.2	1.6	2.5	63.5	0.3	<0.2	0.4	7.9	10.9	0.2	0.9	1.1	2.6	0.06
10	10.6	1.7	3.1	61.9	0.3	<0.2	0.2	7.9	10.2	0.2	0.9	1.2	1.9	0.06
11	9.7	2.4	1.4	60.1	0.4	0.3	0.5	6.5	10.5	0.1	0.8	0.4	7.1	0.05
12	12.4	2.1	1.9	61.0	0.3	<0.2	0.3	7.2	10.7	0.1	0.9	0.6	2.5	0.07
14	5.8	<0.5	2.6	76.0	<0.2	<0.2	0.3	12.1	0.1	0.1	<0.1	0.4	2.6	0.01
15	11.0	1.1	1.3	61.9	0.3	0.3	0.5	7.3	11.7	0.1	1.0	0.5	3.0	0.06
16	11.5	2.3	1.3	62.0	0.2	0.2	0.5	6.8	10.8	0.1	0.9	0.6	2.7	0.06
17	1.5	2.2	2.6	60.2	2.4	<0.2	<0.2	8.6	20.5	0.2	0.2	1.5	0.1	0.08
18	8.1	1.1	2.2	68.9	0.3	<0.2	0.4	6.3	10.1	0.2	1.2	1.1	0.1	0.07
19	2.2	1.9	2.4	58.3	2.0	0.3	<0.2	6.9	24.2	0.2	0.2	1.4	0.1	0.06
20	7.8	1.4	2.2	66.2	0.4	<0.2	0.4	7.6	11.6	0.1	1.2	1.0	0.2	0.07
21	12.8	1.6	1.6	65.6	0.2	<0.2	0.6	7.5	8.2	0.1	1.0	0.4	0.5	0.07
22	8.7	1.6	3.4	68.0	0.3	<0.2	<0.2	7.3	7.4	0.2	0.8	2.1	0.2	0.05
23	7.4	1.6	2.2	66.2	0.3	<0.2	0.4	10.7	8.9	0.1	1.0	0.9	0.3	0.06
24	7.0	1.8	2.4	64.8	0.3	<0.2	0.2	8.4	9.2	0.2	0.8	1.7	3.4	0.05
25	7.5	0.9	2.6	68.1	0.2	<0.2	0.4	8.9	8.6	0.2	0.9	1.6	0.2	0.05
26	9.3	1.5	1.7	64.8	0.4	0.2	0.5	8.3	6.8	0.1	1.0	0.6	5.0	0.02
27	11.2	2.0	1.7	65.2	0.2	<0.2	0.5	8.9	8.5	0.1	0.9	0.5	0.3	0.05
28	11.6	1.1	1.5	66.8	0.3	<0.2	0.6	7.8	8.6	0.1	1.0	0.4	0.4	0.04
29	9.6	1.5	1.8	65.5	0.3	<0.2	0.4	8.6	9.8	0.1	1.3	0.7	0.3	0.05
30	<0.5	0.8	1.5	68.7	0.4	<0.2	<0.2	16.7	3.7	<0.1	0.2	0.2	7.9	0.01
31	3.5	1.5	1.7	66.0	0.5	<0.2	<0.2	16.0	3.4	<0.1	0.2	0.2	7.0	0.01
32	9.9	1.7	1.5	66.0	0.2	<0.2	0.5	9.0	9.1	0.1	1.1	0.4	0.4	0.05
33	11.7	2.1	1.2	65.6	0.2	0.2	0.7	3.6	12.8	0.1	0.9	0.5	0.5	0.06
34	11.9	2.1	1.2	66.1	0.3	<0.2	0.6	3.1	12.6	0.1	1.3	0.5	0.3	0.08
35	9.1	1.9	1.1	61.3	0.3	0.3	0.4	9.1	9.3	0.1	0.8	0.4	6.0	0.02
36	11.7	2.6	1.5	63.8	0.2	<0.2	0.5	8.4	9.6	0.1	1.0	0.4	0.3	0.07
37	12.0	2.1	1.2	65.6	0.2	0.2	0.6	3.0	12.9	0.1	1.0	0.5	0.6	0.08
39	10.2	3.6	1.5	68.9	0.4	<0.2	0.7	2.8	10.1	0.1	1.0	0.7	0.1	0.04
40	<0.5	2.0	2.6	60.1	2.1	0.3	<0.2	5.4	24.9	0.2	0.3	1.9	0.1	0.06
41	1.0	2.0	2.3	60.0	2.4	<0.2	<0.2	7.1	22.9	0.2	0.3	1.5	0.1	0.05
42	<0.5	2.3	2.5	59.0	2.4	0.4	0.2	7.7	23.4	0.2	0.2	1.6	0.1	0.04
43	<0.5	1.8	2.7	61.0	2.1	0.3	<0.2	5.1	24.5	0.2	0.3	2.0	<0.1	0.07
44	1.7	3.1	2.5	61.5	2.6	0.2	0.2	6.8	19.5	0.2	0.2	1.5	<0.1	0.07
45	0.8	2.3	2.4	62.0	2.2	0.3	<0.2	6.5	21.9	0.2	0.2	1.2	<0.1	0.07
46	6.4	1.8	2.4	57.7	0.5	<0.2	0.2	12.5	8.8	0.1	0.7	1.1	7.9	0.03
47	7.3	2.0	2.0	63.5	0.4	<0.2	0.2	8.9	7.4	0.1	0.6	1.0	6.3	0.05
48	12.8	3.1	1.6	66.4	0.4	<0.2	0.6	3.3	9.6	0.1	1.3	0.6	0.1	0.09
49	10.0	2.2	1.7	66.2	0.3	<0.2	0.4	8.8	6.6	0.1	0.8	0.7	2.2	0.04
50	10.9	2.3	1.7	65.3	0.3	<0.2	0.5	8.8	8.4	0.1	0.9	0.6	0.3	0.08
51	1.7	3.0	2.2	61.5	2.0	0.4	0.0	7.8	20.1	0.2	0.2	0.9	<0.1	0.11
52	11.3	2.6	1.5	68.1	0.4	<0.2	0.6	3.5	9.9	0.1	1.3	0.5	0.2	0.07
53	12.3	2.6	1.7	63.7	0.2	<0.2	0.5	8.7	8.7	0.1	0.9	0.4	0.2	0.05
54	8.6	2.8	1.6	63.3	0.3	<0.2	0.3	10.3	11.4	0.1	0.8	0.4	<0.1	0.07

#	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	PbO	SrO
55	11.9	3.2	1.5	61.3	0.4	<0.2	0.5	6.0	11.3	0.1	0.8	0.4	2.5	0.08
56	10.7	3.1	1.3	60.1	0.4	<0.2	0.5	6.2	9.9	<0.1	0.8	0.3	6.5	0.06
57	12.1	2.7	1.3	61.9	0.4	<0.2	0.5	6.7	10.5	0.1	0.8	0.4	2.4	0.06
58	11.5	2.7	1.7	64.4	0.2	<0.2	0.5	8.8	8.4	0.1	0.9	0.5	0.3	0.08
59	12.9	2.3	1.6	64.5	0.2	<0.2	0.6	7.4	8.6	0.1	1.0	0.4	0.3	0.07
60	10.7	2.5	1.7	63.8	0.2	<0.2	0.5	9.4	9.2	0.1	1.0	0.6	0.3	0.07
61	9.1	2.1	1.9	64.5	0.4	<0.2	0.4	9.7	10.0	0.1	1.1	0.5	0.2	0.06
62	9.9	3.3	1.8	63.4	0.3	<0.2	0.4	10.6	9.0	0.1	0.8	0.4	0.1	0.05
63	9.4	2.0	1.7	63.8	0.4	<0.2	0.3	11.0	9.8	0.1	1.0	0.4	0.2	0.06
64	12.5	2.2	1.8	65.0	0.4	<0.2	0.6	5.8	9.9	0.1	1.0	0.5	0.2	0.09
66	2.7	1.2	1.8	66.7	0.4	0.2	<0.2	16.8	3.5	<0.1	0.2	0.2	6.4	0.01
67	12.6	3.2	1.5	60.1	0.5	0.3	0.5	6.6	10.5	0.1	0.9	0.4	3.0	0.05
68	10.2	3.0	1.4	59.6	0.4	<0.2	0.4	8.8	9.4	0.1	0.7	0.4	5.6	0.04
69	2.7	3.3	2.8	60.6	2.3	<0.2	0.4	3.7	22.0	0.3	0.8	1.0	0.2	0.05
70	12.8	3.1	1.5	66.3	0.4	<0.2	0.6	3.2	10.0	0.1	1.3	0.5	0.2	0.09
71	7.6	1.8	2.4	73.6	<0.2	<0.2	0.2	11.6	0.3	0.1	<0.1	0.4	2.0	0.01
73	1.7	3.0	2.4	59.1	2.5	0.3	0.2	8.1	20.7	0.2	0.2	1.4	0.1	0.04
74	11.8	2.1	1.6	65.0	0.3	<0.2	0.5	8.7	8.1	0.1	1.0	0.4	0.4	0.05
75	<0.5	2.4	2.7	60.8	2.3	0.3	<0.2	7.3	22.0	0.2	0.3	1.5	<0.1	0.05
77	2.0	2.8	2.4	59.8	2.1	0.3	0.2	5.6	23.0	0.2	0.3	1.2	<0.1	0.07
78	1.3	2.8	2.4	60.8	2.1	0.2	0.2	5.6	22.8	0.2	0.2	1.2	<0.1	0.06
79	<0.5	2.3	2.5	58.9	2.1	0.3	<0.2	6.2	25.3	0.2	0.3	1.7	0.1	0.06
80	<0.5	2.5	2.3	59.2	2.4	0.3	<0.2	6.9	24.5	0.2	0.3	1.4	<0.1	0.05
81	10.1	2.5	1.7	64.4	0.3	0.0	0.5	10.3	8.7	0.1	0.9	0.5	0.2	0.05
82	14.5	3.2	1.5	64.6	0.4	0.2	0.6	2.9	10.8	0.1	0.8	0.3	0.2	0.08
83	12.7	2.6	1.7	63.6	0.2	<0.2	0.5	8.6	8.5	0.1	0.9	0.4	0.3	0.05
85	15.1	2.3	1.4	63.7	0.2	<0.2	0.6	5.5	9.3	0.1	1.0	0.5	0.4	0.06
86	14.5	1.4	1.3	70.1	0.2	0.3	0.6	5.4	5.3	0.1	0.5	0.3	<0.1	0.05
87	7.3	2.8	1.7	66.3	1.2	<0.2	0.4	7.8	8.6	0.2	2.9	0.8	0.1	0.05
88	0.8	2.7	2.4	60.3	2.3	<0.2	<0.2	6.7	22.9	0.2	0.3	1.3	0.1	0.07
92	14.9	3.8	1.4	63.4	0.4	0.2	0.6	2.5	11.6	0.1	0.6	0.4	0.1	0.10
93	10.1	2.1	1.6	62.7	0.4	0.2	0.4	6.1	9.4	0.1	1.8	0.6	4.5	0.04
94	13.0	0.9	1.4	72.2	<0.2	<0.2	0.6	7.5	3.6	<0.1	0.4	0.2	0.1	0.04
95	<0.5	<0.5	0.4	50.8	<0.2	0.3	<0.2	9.8	0.0	<0.1	<0.1	0.1	38.7	<0.01
96	10.3	3.1	1.4	63.6	0.2	0.2	0.4	6.4	12.8	0.1	1.0	0.4	0.2	0.10
97	<0.5	<0.5	0.5	53.3	<0.2	0.3	<0.2	8.4	0.3	<0.1	0.1	0.1	37.1	<0.01
98	<0.5	<0.5	0.5	52.4	<0.2	<0.2	<0.2	8.4	0.0	<0.1	<0.1	0.1	38.6	<0.01
99	<0.5	2.3	2.6	63.7	2.3	<0.2	<0.2	9.0	18.0	0.2	0.2	1.6	<0.1	0.04
100	2.2	2.7	2.3	59.3	3.2	<0.2	<0.2	8.6	19.7	0.2	0.2	1.8	<0.1	0.06

Appendix 2: Composition of samples determined by SEM-EDS

#	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	PbO
2	10.6	2.5	1.9	62.9	0.4	<0.2	0.5	7.7	11.5	0.1	1.2	0.7	<0.2
16	12.0	3.0	1.2	60.4	0.3	0.2	0.6	6.8	10.9	0.1	0.9	0.4	3.2
66	2.3	1.1	1.2	66.1	0.2	<0.2	0.2	17.3	3.5	0.1	0.3	0.2	7.5
72	1.2	2.0	2.4	62.1	1.8	0.2	0.3	5.0	23.7	0.2	0.1	1.0	<0.2
74	11.9	2.3	1.3	66.1	0.3	0.2	0.5	8.2	7.9	<0.1	0.9	0.4	<0.2
77	1.4	2.6	2.7	59.4	2.2	0.3	0.2	5.5	23.9	0.2	0.2	1.4	<0.2
78	0.8	2.4	2.9	58.8	2.3	0.4	<0.2	6.7	23.8	0.2	0.3	1.4	<0.2
79	0.6	2.2	2.7	58.8	2.2	0.3	<0.2	6.1	25.1	0.2	0.2	1.6	<0.2
80	1.0	2.4	2.8	57.8	2.5	0.4	0.2	6.6	24.2	0.2	0.4	1.5	<0.2
81	11.5	2.8	1.4	64.7	0.2	0.2	0.5	9.5	7.9	<0.1	0.8	0.5	<0.2
83	12.9	2.7	1.5	64.3	0.2	0.2	0.5	8.3	8.2	0.1	0.7	0.4	<0.2
84	11.5	2.8	1.2	67.0	0.3	0.2	0.6	5.7	9.5	<0.1	0.7	0.5	<0.2
85	14.6	2.5	1.3	65.2	0.2	0.2	0.6	5.3	8.7	<0.1	1.0	0.4	<0.2
86	15.4	1.5	0.9	70.5	0.2	0.3	0.6	5.0	4.7	0.1	0.5	0.3	<0.2
87	7.3	2.9	1.7	65.9	1.2	0.2	0.4	7.7	8.5	0.3	3.1	0.8	<0.2
88	1.0	2.6	2.6	59.7	2.5	<0.2	0.2	6.4	23.1	0.2	0.3	1.4	<0.2
89	12.1	2.9	1.2	63.3	0.3	0.2	0.5	6.5	12.1	<0.1	0.5	0.4	<0.2
90	12.7	3.7	1.4	61.0	0.2	0.2	0.6	5.1	11.7	0.1	0.7	0.4	2.2
91	14.6	3.7	1.3	64.4	0.3	0.3	0.7	2.3	11.4	0.1	0.6	0.3	<0.2
92	14.9	3.8	1.3	64.3	0.2	0.4	0.7	2.4	11.1	<0.1	0.6	0.3	<0.2
94	14.5	1.0	1.1	71.3	0.3	0.2	0.7	7.1	3.2	<0.1	0.4	0.2	<0.2
95	<0.2	<0.1	0.4	52.5	<0.2	<0.2	<0.2	10.7	0.0	<0.1	<0.1	<0.1	36.4
96	10.0	3.3	1.0	65.5	0.3	0.3	0.5	5.0	12.6	0.1	1.0	0.4	<0.2
97	<0.2	<0.1	0.3	54.1	<0.2	<0.2	<0.2	9.3	0.0	<0.1	<0.1	<0.1	36.3
98	<0.2	<0.1	0.3	54.4	<0.2	<0.2	<0.2	9.0	0.0	<0.1	<0.1	<0.1	36.3
99	0.6	2.5	2.6	61.1	3.2	<0.2	<0.2	7.9	20.2	0.2	0.2	1.5	<0.2
100	1.4	2.5	2.6	62.9	2.0	<0.2	<0.2	9.2	17.3	0.3	0.2	1.6	<0.2

Appendix 3: SEM-EDS Analyses of crucible {2} and its adhering glass

Distance (mm)	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3
1.75	10.6	2.5	1.9	62.6	0.4	<0.2	0.5	7.6	11.5	0.1	1.2	0.7
1.55	10.5	2.5	1.9	62.5	0.4	0.2	0.5	7.7	11.5	0.2	1.3	0.7
1.35	10.5	2.4	2.0	62.6	0.5	0.2	0.5	7.6	11.2	0.2	1.3	0.7
1.15	10.7	2.5	1.9	62.6	0.4	0.2	0.5	7.6	11.4	0.1	1.2	0.7
0.95	10.5	2.3	1.9	62.9	0.4	0.2	0.5	7.5	11.2	0.2	1.4	0.7
0.80	10.7	2.5	2.9	63.1	0.4	0.2	0.5	7.4	9.7	0.2	1.3	0.9
0.70	10.4	2.4	3.3	63.5	0.4	0.2	0.5	7.5	9.3	0.2	1.1	1.0
0.60	10.4	2.3	4.9	63.4	0.2	0.2	0.4	7.7	7.9	0.3	1.0	1.0
0.50	10.0	1.6	8.9	63.0	0.2	<0.2	0.3	8.4	5.3	0.3	0.7	1.0
0.40	9.1	1.1	14.2	61.9	<0.2	<0.2	0.3	9.3	2.5	0.4	0.3	0.9
0.33	0.9	0.3	22.7	53.6	<0.2	<0.2	<0.1	21.1	<0.1	0.9	<0.1	0.6
0.29	13.9	0.3	31.2	46.9	<0.2	<0.2	0.1	6.3	0.2	0.7	<0.1	0.4
0.26	3.9	0.4	19.0	60.4	<0.2	<0.2	0.1	13.3	0.2	1.1	<0.1	1.5
0.23	2.7	0.2	21.6	66.5	<0.2	<0.2	0.1	7.4	<0.1	1.0	<0.1	0.4
0.18	1.5	0.4	26.4	64.0	<0.2	<0.2	0.1	5.5	<0.1	1.4	<0.1	0.7
0.13	1.3	0.4	26.6	64.4	<0.2	<0.2	0.1	4.8	<0.1	1.3	<0.1	1.2
0.08	1.1	0.5	26.2	65.6	<0.2	<0.2	0.1	3.7	0.1	1.3	<0.1	1.5
0.00	0.9	0.5	20.2	72.8	<0.2	<0.2	0.1	2.5	0.5	1.2	<0.1	1.2
-0.10	0.8	0.7	26.9	65.1	<0.2	0.4	0.1	2.0	0.9	1.4	<0.1	1.7
-0.20	0.7	0.6	28.2	64.5	<0.2	<0.2	0.1	2.1	0.5	1.6	<0.1	1.7
-0.35	0.6	0.8	29.0	62.9	<0.2	0.7	0.1	1.2	1.4	1.5	<0.1	2.0
-0.55	0.3	0.4	22.2	72.2	<0.2	0.5	0.0	0.5	1.1	1.0	<0.1	1.9
-0.90	0.7	0.7	26.6	65.8	<0.2	0.4	0.3	0.9	1.3	1.4	<0.1	2.0
-1.40	0.4	0.7	25.6	66.2	<0.2	0.6	0.1	1.0	1.7	1.6	<0.1	2.0
-1.90	0.4	0.6	26.6	64.6	<0.2	0.8	0.2	1.0	2.2	1.5	<0.1	2.2

Appendix 4: SEM-EDS analyses of crucible {16} and its adhering glass

Distance (mm)	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	PbO
1.85	11.5	3.0	1.2	60.5	0.3	0.3	0.6	6.9	11.0	0.1	0.8	0.4	3.2
1.65	12.0	3.1	1.1	60.5	0.2	0.2	0.5	6.7	10.9	0.1	0.9	0.4	3.2
1.45	12.0	2.9	1.2	60.4	0.2	0.2	0.6	6.9	10.8	0.1	1.0	0.3	3.4
1.25	12.2	3.0	1.2	60.7	0.3	0.2	0.6	6.7	10.8	0.0	0.9	0.4	3.1
1.05	11.8	2.9	1.1	60.7	0.3	0.3	0.6	6.7	11.0	0.1	0.9	0.4	3.2
0.85	12.0	3.0	1.2	60.3	0.3	0.3	0.6	6.9	10.9	0.1	0.9	0.3	3.2
0.70	12.1	2.9	1.2	60.5	0.2	0.2	0.6	6.9	11.0	0.1	0.9	0.4	3.0
0.60	12.2	2.9	1.2	60.6	0.3	0.2	0.5	6.7	10.9	0.1	0.9	0.5	3.0
0.50	12.3	3.0	1.2	60.7	0.3	0.2	0.6	6.3	10.9	0.1	1.0	0.4	3.1
0.40	12.5	2.9	1.1	60.9	0.3	0.3	0.5	5.8	11.2	0.1	0.9	0.4	3.1
0.30	7.6	1.8	10.1	64.6	0.3	0.2	<0.1	8.3	5.1	0.4	0.6	0.9	0.2
0.20	8.7	1.9	12.0	61.6	0.2	0.2	0.1	6.9	6.2	0.5	0.5	0.9	0.2
0.10	9.1	0.6	17.2	60.0	<0.2	0.4	0.5	7.5	2.7	0.7	0.2	0.8	0.2
0.00	3.7	0.2	29.7	57.8	<0.2	<0.2	0.1	6.3	<0.1	1.6	<0.1	0.5	<0.1
-0.10	1.5	0.2	27.3	62.9	0.2	<0.2	<0.1	4.1	<0.1	1.7	<0.1	2.1	<0.1
-0.40	1.1	0.2	26.4	66.5	<0.2	<0.2	<0.1	2.9	<0.1	1.4	<0.1	1.4	<0.1
-0.90	0.4	0.4	27.3	66.9	<0.2	<0.2	<0.1	0.8	0.4	1.5	<0.1	2.1	<0.1
-1.40	0.2	0.4	16.8	79.0	0.2	<0.2	<0.1	0.4	0.3	1.1	<0.1	1.5	<0.1
-1.90	0.4	0.4	27.9	63.4	<0.2	<0.2	0.1	1.0	0.6	2.2	<0.1	3.8	<0.1
-2.15	0.2	0.5	25.1	69.1	<0.2	<0.2	<0.1	0.7	0.4	1.5	<0.1	2.2	<0.1

Appendix 5: SEM-EDS analysis of samples {99} and {100} (the 'frit')

Sample	Area	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Total
99	CS	<0.1	0.7	0.2	49.3	<0.2	<0.1	47.4	<0.1	0.2	0.2	98.0
99	CS	<0.1	0.6	0.2	50.6	<0.2	<0.1	48.5	<0.1	0.2	0.2	100.6
99	CS	<0.1	0.6	0.2	49.7	<0.2	<0.1	47.7	<0.1	0.2	0.2	98.6
99	CS	<0.1	0.9	0.2	49.8	<0.2	<0.1	47.3	<0.1	0.2	0.2	98.6
99	CP	1.2	2.4	0.2	0.7	42.7	1.2	48.6	<0.1	<0.1	0.1	97.1
99	CP	1.4	2.3	0.1	0.5	42.1	1.1	47.3	<0.1	<0.1	<0.1	94.7
99	CP	1.4	2.4	0.1	0.6	44.0	1.1	48.9	<0.1	<0.1	0.2	98.7
99	CP	1.4	2.4	0.1	0.7	43.7	1.2	48.8	<0.1	<0.1	0.1	98.4
99	matrix	1.6	3.4	3.3	67.5	0.7	11.8	5.5	0.3	0.3	2.3	96.7
99	matrix	1.5	3.3	3.4	66.9	0.8	11.7	6.2	0.4	0.2	2.2	96.7
99	matrix	1.6	3.1	3.3	65.9	0.9	11.6	6.4	0.4	0.2	2.2	95.8
100	CS	<0.1	1.0	0.2	49.9	<0.2	<0.1	46.9	<0.1	0.3	0.2	98.6
100	CS	<0.1	1.0	0.2	50.6	<0.2	<0.1	47.3	<0.1	0.3	0.1	99.4
100	CP	1.5	2.6	0.1	1.5	43.4	1.7	47.5	<0.1	<0.1	0.3	98.7
100	CP	1.4	2.5	0.1	0.7	43.6	1.3	48.5	<0.1	<0.1	0.1	98.4
100	CP	1.4	2.6	0.2	0.7	43.6	1.3	48.6	<0.1	<0.1	0.1	98.4
100	matrix	2.0	4.2	3.8	65.0	1.1	13.0	5.1	0.4	0.3	3.0	97.9
100	matrix	1.8	3.3	5.6	63.9	0.7	13.2	4.8	0.6	0.3	3.6	97.9
100	matrix	2.0	3.7	4.0	65.4	0.9	13.1	5.0	0.5	0.3	3.0	97.9
100	S?	<0.1	0.0	0.2	63.2	<0.2	0.1	16.7	<0.1	<0.1	0.2	80.3
100	S?	<0.1	0.2	0.2	70.4	<0.2	0.1	9.5	<0.1	0.2	0.2	80.8
100	S?	<0.1	0.1	0.2	67.9	<0.2	0.1	11.5	<0.1	0.1	0.4	80.4

CS = calcium silicate; CP = calcium phosphate; S? = silica-rich phase