

# ST MICHAEL'S AND ALL ANGELS CHURCH, THORNHILL, DEWSBURY, WEST YORKSHIRE

## SCIENTIFIC EXAMINATION OF STAINED WINDOW GLASS

### TECHNOLOGY REPORT

David Dungworth, Jonathon Cooke, Ruth Cooke, Richard Jaques and David Martlew



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## SUMMARY

The chemical composition of a selection of window glass from Thornhill parish church was investigated in order to contribute to its conservation. The window glass includes examples of 15th-century stained/painted medieval window glass which has suffered from significant degrees of deterioration. The conservation treatment of these windows is being funded by English Heritage. Several different potential causes for the deterioration of the historic window have been advanced. The investigation included the chemical analysis of 55 panes of glass carried out *in situ* using a portable x-ray fluorescence (pXRF) spectrometer. In addition, five samples recovered from a 15th-century tomb were analysed using both pXRF and laboratory-based instruments. The glass includes both medieval forest glass and later high-lime low-alkali (HLLA) glass. The pXRF data could be used to identify the type of glass even where the result was affected by surface corrosion. The SEM-EDS data indicates that much of both the Forest glass and HLLA glass at Thornhill contains a very low molar proportion of SiO<sub>2</sub> which renders it unstable and susceptible to significant deterioration.

## ACKNOWLEDGEMENTS

We would like to thank Brian Pearson, the project manager of the Church of St. Michael and All Angels, for providing access to the windows

## ARCHIVE LOCATION

The fragments of glass from tomb are held by Jonathan and Ruth Cooke. The mounted and polished samples from these fragments are archived by English Heritage at Fort Cumberland. The East window of the Savile Chapel (nll), which has been removed for display within the Church will shortly be mounted within an environmentally controlled environment

## DATE OF RESEARCH

2010–2011

## CONTACT DETAILS

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## INTRODUCTION

St Michael's and All Angels' Church, Thornhill, Dewsbury, West Yorkshire (LB 340710) contains significant 15th-century details. A window on the north side of the Savile chapel has the name Thome Savill and the date 1447 (restored 1972). The east window of the chapel (Figure 1) has the name Wiliam Sayvile and the date 1493. All four Savile chapel windows are believed to have been produced in York in the 15th century and were restored in the 1870s by Burlison and Grylls as part of the reordering of the church by the architect G E Street. The chancel East window bears the tree of Jesse and is dated 1499 (considerably restored in the 19th century). Some of the 15th-century glass (especially in the east window of the Savile chapel) is in poor condition and much of the pictorial information is no longer discernible (Figure 1). Newton previously noted the severe corrosion phenomena among some of the glass at Thornhill (Newton 1974).



*Figure 1. The East window of the Savile chapel (nll)*

English Heritage has funded a range of conservation work on elements of St Michael's and All Angels' Church which includes the recent removal of the east window (nll) and its display within the Church, the introduction of a replacement window based on tracings prepared in 1877 by the conservators Burlison and Grylls, the conservation of windows to the north wall of the Chapel and the conservation of the Sir George Savile monument dating from 1614.

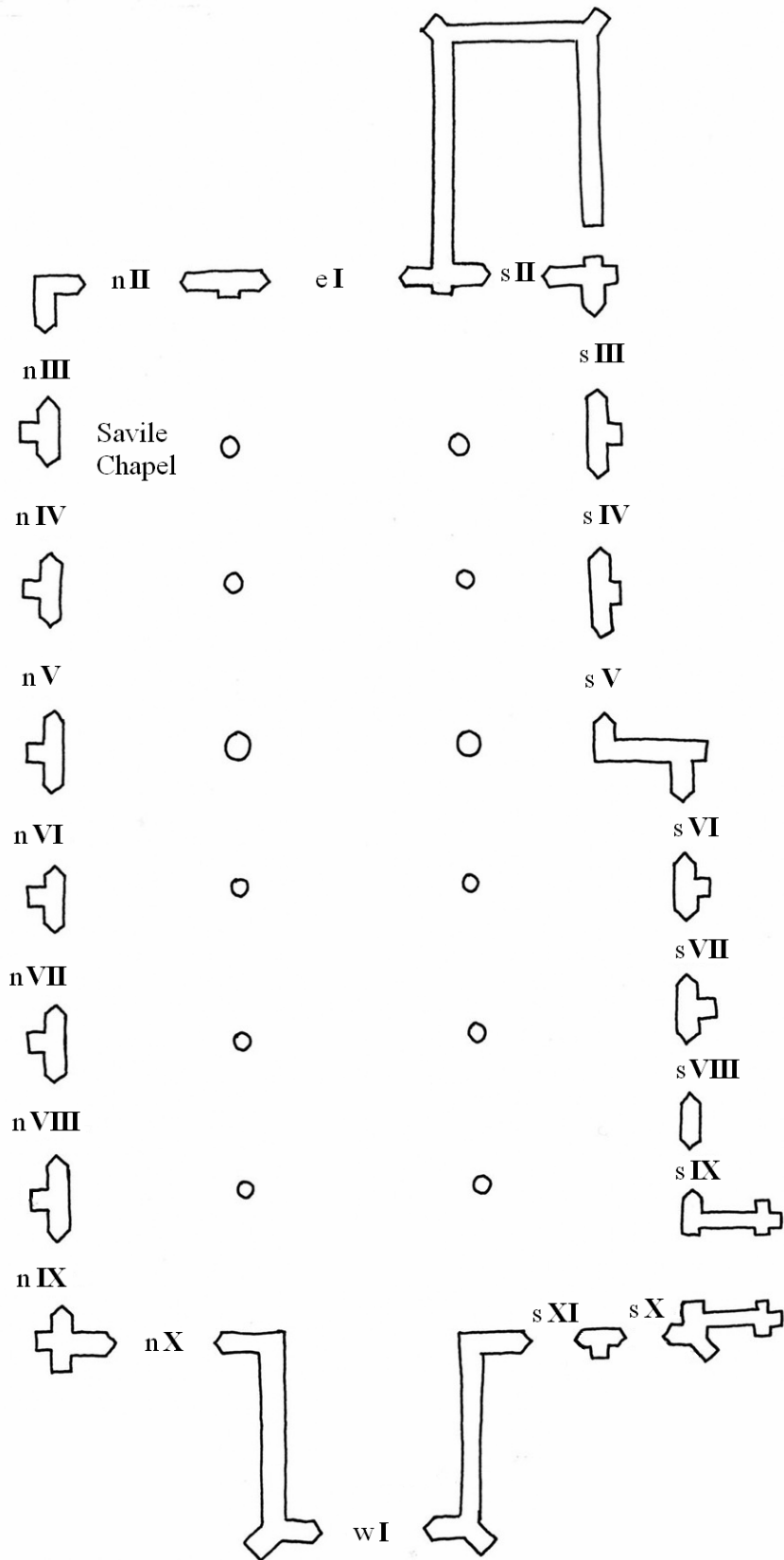


Figure 2. Sketch plan of Thornhill showing the identification of the windows

## THE COMPOSITION AND DURABILITY OF HISTORIC WINDOW GLASS

The deterioration of historic window glass is a major concern among conservation bodies world wide (eg Collonges 1977; Newton and Davison 1996; Römich 2006). Significant heritage assets, in particular European cathedrals and churches, include extensive areas of decorated window glass, some of which was created over a millennium ago. While many of these windows have deteriorated over the centuries, increasing research has contributed to a better understanding of both the nature of historic glass and the causes of deterioration.

Glass corrosion is a complex phenomenon with multiple causes not all of which are fully understood. The corrosion of glass is clearly determined by both intrinsic factors (the nature of the glass itself) and extrinsic factors (the environment the glass was exposed to). Both intrinsic and extrinsic factors are summarised below.

### The composition of historic window glass

*Table 1. Typical composition of different types of historic window glass (Dungworth 2011)*

Phase	1	2a	2b	3	4a	4b	5a	5b
Start		c1567	c1600	c1700	c1835	c1870	c1930	c1960
End	c1567	c1600	c1700	c1835	c1870	c1930	c1960	
Na <sub>2</sub> O	2.5±0.3	1.4±0.7	2.4±1.4	7.9±0.7	12.7±0.9	12.9±2.1	13.9±0.5	13.3±0.4
MgO	7.3±0.7	3.4±0.5	3.0±0.7	5.3±0.3	0.2±0.1	0.2±0.2	2.8±0.2	3.8±0.2
Al <sub>2</sub> O <sub>3</sub>	1.6±0.5	2.8±1.0	3.0±1.3	2.6±0.6	0.6±0.1	1.2±0.3	0.9±0.6	1.3±0.2
SiO <sub>2</sub>	55.8±2.5	60.4±1.8	60.9±2.0	66.5±1.4	70.8±1.2	71.9±0.4	72.2±0.7	72.2±0.5
SO <sub>3</sub>	0.3±0.1	0.2±0.1	0.4±0.2	0.2±0.1	0.4±0.1	0.4±0.2	0.4±0.2	0.2±0.1
Cl	0.4±0.2	0.3±0.2	0.2±0.1	0.6±0.1	0.1±0.1	<0.1	<0.1	<0.1
P <sub>2</sub> O <sub>5</sub>	3.2±0.4	2.1±0.2	2.1±0.6	1.1±0.2	<0.2	<0.2	<0.2	<0.2
K <sub>2</sub> O	11.4±1.5	5.6±1.6	5.1±1.9	4.2±0.2	0.1±0.1	0.5±0.2	0.1±0.1	0.6±0.1
CaO	15.3±1.6	21.5±1.9	21.1±1.7	10.4±1.0	14.0±0.8	12.9±1.6	9.7±0.8	8.3±0.6
MnO	1.26±0.30	0.94±0.37	0.24±0.20	<0.10	<0.10	<0.10	<0.10	<0.10
Fe <sub>2</sub> O <sub>3</sub>	0.65±0.13	1.01±0.20	1.31±0.29	0.71±0.14	0.22±0.06	0.21±0.06	0.13±0.03	0.12±0.01
As <sub>2</sub> O <sub>3</sub>	<0.20	<0.20	<0.20	<0.20	0.22±0.16	<0.20	<0.20	<0.20
SrO	0.07±0.01	0.09±0.02	0.07±0.01	0.45±0.10	0.03±0.01	0.02±0.01	0.01±0.01	0.01±0.01

The analysis of a large number of samples of historic window glass from archaeological and architectural contexts, as well as material from window glass production sites, has enabled the detection of distinct chronological phases of glass composition for England (Dungworth 2011). Each phase can be characterised by a fairly uniform glass composition which can be easily distinguished from glass of other phases (Table 1). In phase 1 (covering the medieval period to the late 16th century) glass was made using the ash of bracken/fern (plus sand) which yielded a potassium-rich product. From the late 16th century until the end of the 17th century window glass was made using a variety of plant

ashes which produced a glass with a high calcium content (phase 2). The window glass of the 18th century (phase 3) was made using seaweed which gave a mixed alkali glass (with significant quantities of strontium — see Dungworth *et al*/2009). From the 1830s onwards (phases 4 and 5) glass was made using pure sodium carbonate and chalk or limestone (see Dungworth 2011 for further details). The chemical composition of English glass appears to be an indication of the period of its manufacture. The English chronology may not be directly applicable elsewhere, and the situation in England may be complicated where imported glass was used (eg Dungworth and Girbal 2011).

### **Intrinsic factors in glass deterioration**

Glasses are materials which lack long range, periodic atomic arrangement (Shelby 2005, 3) and all historic window glass has been based on the use of silica (the network former). The high melting temperature of silica has meant that other materials (network modifiers) have been added to lower the melting temperature. The type and proportion of other materials have a significant effect on the intrinsic durability of the glass and its ability to withstand corrosion (Doremus 1979).

Traditional glass manufacture was an essentially artisanal activity with the selection of raw materials, recipes and technologies determined in large part by inherited customs. The demand for colourless glass and the development of material processing technologies allowed the formulation of more complex glasses using a variety of raw materials (eg Dungworth and Brain 2009). The use of refined alkalis revealed the necessity of including a proportion of calcium in the batch of raw materials (eg Pellatt 1849); however, the deliberate use of so-called glass network stabilisers (a range of divalent cations can act as network stabilisers) was approached empirically and it was some years before models of the atomic structure of glasses were sufficiently sophisticated to explain the role of network stabilisers (Zacharisen 1932).

It has long been appreciated that some archaeological and historic glass has undergone significant deterioration (eg Brewster 1863; Fowler 1880) and more recent investigations have investigated the relationship between glass composition and durability/corrosion. The quantity of medieval glass that survives within European ecclesiastical monuments (and its often poor condition) has ensured that the durability of this glass has received most attention (eg Collonges 1977; Cox *et al* 1979; Gentaz *et al* 2011; Gillies and Cox 1988a; 1988b; Gorbushina and Palinska 1999; Newton 1982; Newton and Davison 1996; Perez y Jorba *et al* 1980; Raw 1955; Römich 2006; Schreiner *et al* 1999; Scott 1932; Woisetschläger *et al* 2000; Wolff 2000). Throughout northern Europe glass was manufactured in the medieval period using forest plants and sand. The chemical analysis of numerous specimens of glass has shown that this glass is a potassium-calcium-silicate glass with a range of minor components (such as magnesium, aluminium and phosphorus) that derive from the impure sands and plant ashes used (Barrera and Velde 1989; Cox *et al* 1979; Dungworth and Clark 2004; Dungworth and Paynter 2010; Freestone *et al* 2010; Wedepohl 1997). While glass with an excessive proportion of alkali (network modifier)



or an inadequate concentration of alkali earth (network stabiliser) will tend to have poor durability, El-Shamy (1973) proposed that a more significant criterion was the proportion of network former ( $\text{SiO}_2$ ). El-Shamy found that glasses with less than 66 molar%  $\text{SiO}_2$  were more susceptible to significant weathering. Cox *et al* (1979) provided data on English medieval window glass (Figure 3) which demonstrated that where the molar proportion of network former ( $\text{SiO}_2$  plus other minor components such as  $\text{Al}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ ) was less than 60%, the glass tended to corrode to a greater or lesser degree (Figure 3).

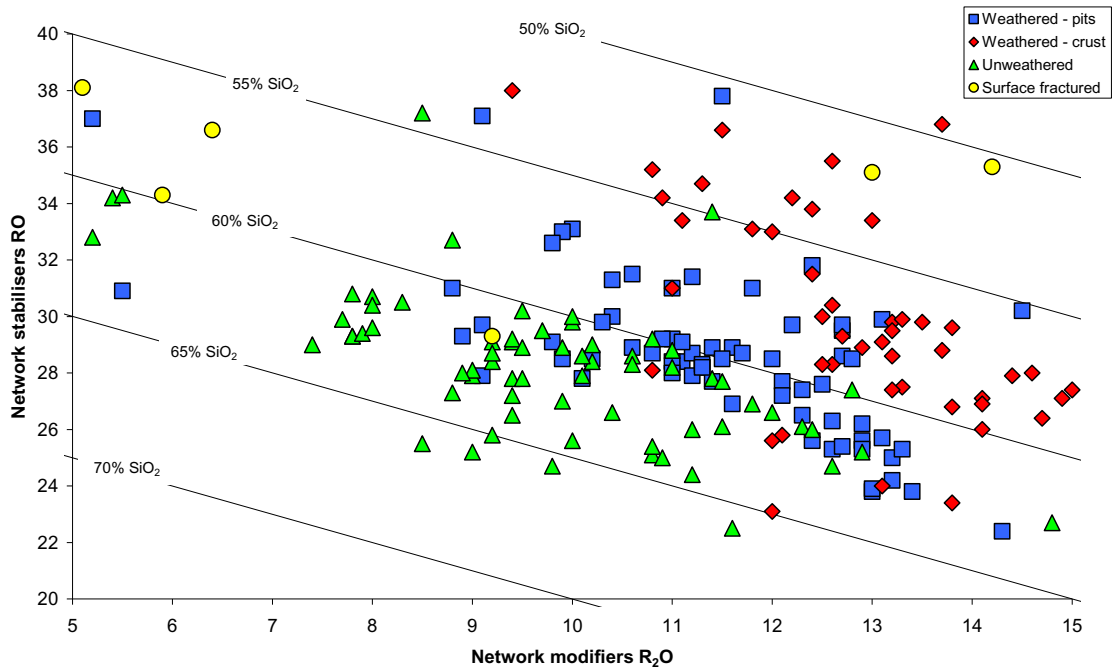


Figure 3. Composition of medieval window glass (molar %) compared to the degree of weathering (after Cox *et al* 1979)

### Extrinsic factors in glass deterioration

The environment that a silica-based glass is exposed to will have a significant effect on the rate and nature of any deterioration. The presence of water and the pH of this water are perhaps the most significant extrinsic factors which affect glass corrosion (Douglas and El-Shamy 1967). In acidic or neutral aqueous solutions glasses will undergo *selective dissolution* (leaching) but in alkaline solutions will undergo *congruent dissolution*. Selective dissolution takes place through an *ion exchange mechanism* — alkali and alkali earth ions within the glass migrate to the surface to form a variety of compounds while aqueous species take their place in the glass (see Conradt 2008 for a recent summary of the various theories and experimental data relating to the exact nature of the aqueous species involved). This leads to the formation of a layer at the surface which contains relatively high concentrations of (mostly molecular) water and silica. Depending on the

nature of the local environment at the surface of the glass, the alkali and alkali earth ions will form sulphates or carbonates. Where these compounds are soluble, they will tend to be removed; but if of low solubility they will tend to accumulate. The preponderance of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and syngenite ( $\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$ ) at the surface of corroded medieval window glass has long been noted (Geilmann 1960; Gillies and Cox 1988a; Lefèvre *et al* 1988; Raw 1955; Scott 1932) and has led to the suggestion that sulphur dioxide in the atmosphere has played a significant role in the corrosion of some historic glass (Fitz *et al* 1984; Newton 1979). The preponderance of sulphate salts at the surface of weathered glass may simply reflect the low solubility of these compounds. The depletion of alkalis and alkali earth elements from the glass (and their replacement by aqueous species) will produce a weathered surface which is rich in silica and water. Congruent dissolution sees the removal of the entire glass network; this is mostly accompanied by the formation of pits in the glass surface. Congruent dissolution will (at varying rates) affect all glass types.

Water plays an important role in the deterioration of glass and, in the context of historic windows, can derive from several sources. The exterior surface of a window may be exposed to varying degrees of precipitation, while moisture may condense on any surface (but especially the interior surface). Condensation may be influenced by the surface roughness of the glass which may in turn vary depending on the technique used to form the glass (eg crown or broad glass). In addition, airborne particulates may accumulate on the surface of glass (especially the exterior surface, but also the interior surface depending on the nature of heating and ventilation systems) and these can attract condensation. Gases within the atmosphere may react directly with components of the glass to form *neocrystallisations* (Munier *et al* 2002b).

The presence of thin aqueous films on the surface of glass will occur periodically depending on the immediate environment (precipitation, condensation, etc). Atmospheric gases will tend to make these aqueous films acidic which will encourage selective dissolution. As alkali and alkali earth ions are brought to the surface the pH of the aqueous film will rise which will encourage congruent dissolution (pitting). Congruent dissolution may be inhibited, however, where the weathered (alkali-depleted) layer is stable as this reduces the diffusion of a variety of ionic species. If precipitation and condensation vary with time, then the surface layers will tend to move through cycles of high and low relative humidity. During periods of low RH the weathered layer may undergo cracking and become dislodged and so expose new areas of glass to further corrosion during the next period of high RH. The replacement of alkali ions by hydrogen ions (or other positively charged aqueous species) will tend to reduce the volume of the weathered layer compared to the unaltered glass which can lead to cracking.

The role of micro-organisms in the deterioration of historic glass remains under-researched (Gorbushina and Palinska 1999; Mellor 1924; Perez y Jorba *et al* 1980). Lichens, bacteria, algae and fungi have all been noted on the surface of corroded medieval window glass. These micro-organisms will promote condensation and the retention of

moisture at the surface; they may also change the pH of the surface water and may promote the deposition of heavy metals such as iron and manganese.

## AIMS AND OBJECTIVES

The chemical analysis of some of the historic glass within St Michael's and All Angels' Church, Thornhill was undertaken to provide insights into the nature of the glass and its deterioration and to test the effectiveness of portable X-Ray Fluorescence (pXRF). It was hoped that information gathered using several analytical techniques (in particular pXRF) could provide insights into the current condition of the window glass. The chemical characterisation of the glass could also contribute to understanding why some has undergone such severe deterioration. It was hoped that this improved understanding would provide the sound evidence base for conservation decisions on the extant glass (retention, removal, treatment, replacement, etc, cf Clark 2001).

The primary research objective was to determine the nature of the glass in key windows (especially in the Savile chapel). At the time the analysis was carried out the glass was *in situ* therefore pXRF offered the only viable means to determine its chemical composition. Five samples from a 15th-century alabaster table tomb in the Savile chapel (believed to be that of Sir John Savile) provided the opportunity to compare pXRF data (*in situ* analysis) with SEM-EDS data (lab-based analysis) for the same samples.

## METHODS

The pXRF instrument used was a Niton XL3t which was operated following procedures developed during the *in situ* analysis of historic window glass at Walmer Castle (see Dungworth and Girbal 2011 for further details). The Niton XL3t is not capable of reporting the sodium content of any analysed material. The detection limits for light elements ( $Z = 12-17$ ) was improved by flushing the instrument with helium. It is anticipated that the results for light elements ( $Z = 12-22$ ) will be affected to some degree by surface corrosion (cf Dungworth and Girbal 2011). The five detached samples were also analysed using an energy dispersive x-ray spectrometer attached to a scanning electron microscope (see Dungworth 2009a for further details). These samples were prepared in the usual way to allow the observation of polished cross-sections and the analysis of uncorroded glass.

## RESULTS

### Analysis of the five fragments of window glass from the Savile tomb

The five fragments of window glass previously recovered during the conservation of the tomb in the Savile chapel (Figure 4) were analysed first using pXRF (Table 2) and then with SEM-EDS (Table 3).

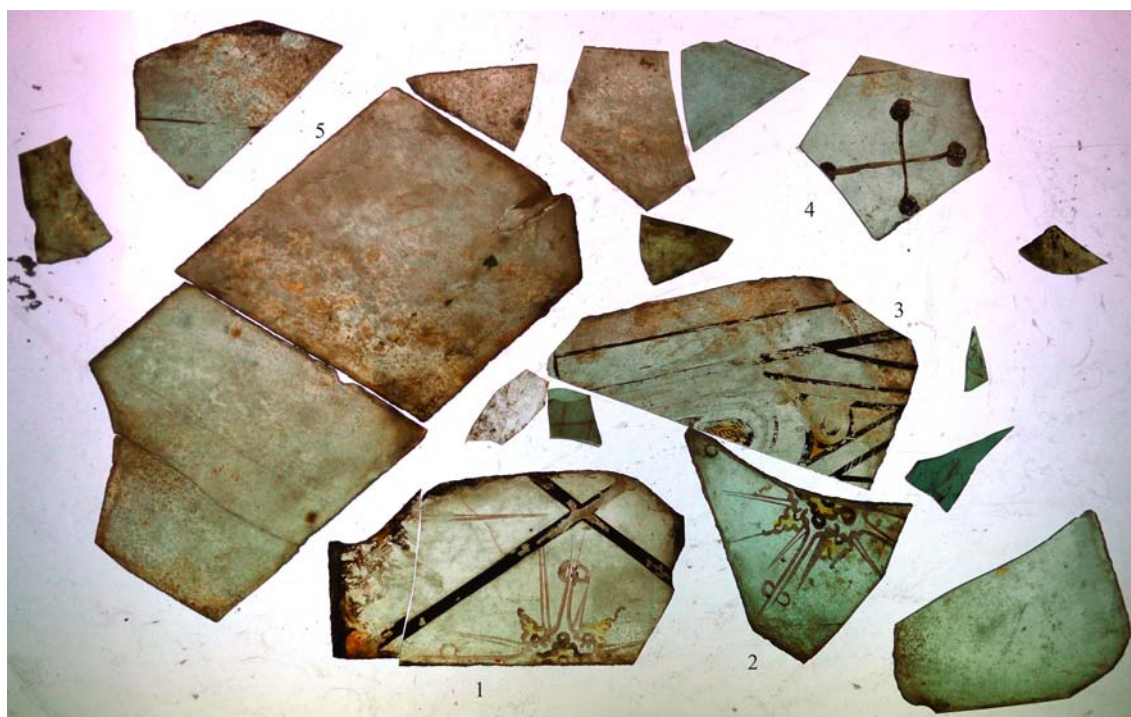


Figure 4. Fragments of glass recovered from Tomb

Table 2. Chemical composition of the five tomb samples as determined by pXRF

	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>
T1	nr	3.6	1.7	54.8	3.4	1.6	0.59	8.5	25.9	0.31	1.32	0.38
T2	nr	8.7	2.9	53.7	2.7	2.0	0.49	12.6	13.0	0.19	1.55	0.62
T3	nr	3.3	3.1	51.4	2.4	3.4	0.88	7.3	21.7	0.35	1.25	0.62
T4	nr	1.9	6.5	51.6	3.5	2.2	0.65	9.2	20.1	0.36	1.72	0.81
T5	nr	3.1	3.3	48.0	1.9	4.2	0.81	5.5	23.6	0.42	0.72	0.70

Table 3. Chemical composition of the five tomb samples as determined by SEM-EDS

	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>
T1	2.8	3.8	1.1	53.3	3.9	0.31	0.50	5.0	26.0	0.14	1.32	0.36
T2	2.2	6.8	1.4	56.1	2.9	0.23	0.36	10.3	15.6	0.09	1.57	0.47
T3	3.4	4.1	1.3	53.3	3.9	0.17	0.67	4.9	25.0	0.12	1.29	0.52
T4	2.1	3.9	4.0	49.5	3.9	0.06	0.47	7.0	25.0	0.14	2.00	0.56
T5	2.8	3.3	1.7	58.1	2.8	0.52	0.46	3.3	24.0	0.38	0.77	0.54

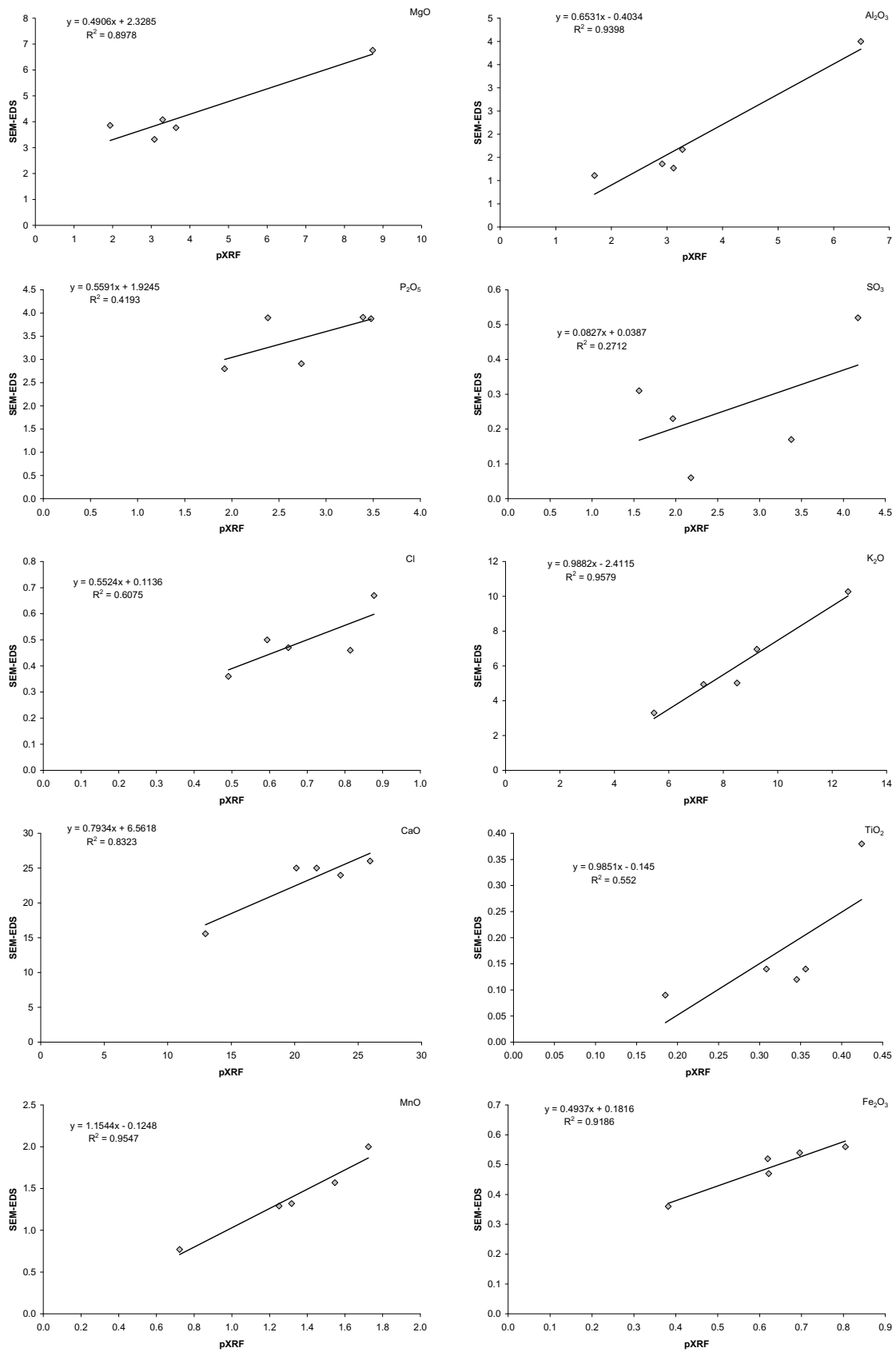


Figure 5. Comparison of chemical analysis (pXRF and SEM-EDS)

A comparison of the data obtained from these five fragments using pXRF and SEM-EDS (Figure 5) suggests that the pXRF data provides a useful indication of the relative concentration of most oxides in the glass. The reported concentrations obtained with the pXRF were in most cases slightly higher than those obtained with SEM-EDS. In some cases this is likely to be a result of the window glass thickness being less than the effective x-ray penetration (cf Dungworth and Girbal 2011). The oxide which showed the most significant differences when analysed by pXRF and SEM-EDS was sulphur trioxide which was present up to 0.5wt% in the glass (SEM-EDS) but *in situ* pXRF detected up to 4wt% SO<sub>3</sub>. Such high concentrations of sulphur in the pXRF measurements probably result from the presence of sulphur-containing compounds at the surface of the glass.

The composition (as determined by both SEM-EDS and pXRF data) of the window glass samples from the tomb shows that one (T2) is a forest glass while the others are high-lime low-alkali (HLLA) glasses. T2 was certainly made before the manufacture of forest glass was superseded by HLLA glass in the late 16th century (Dungworth and Clark 2004). The magnesium content of this glass is sufficiently high to leave little doubt that this glass was manufactured in England (cf Dungworth and Paynter 2011). The remaining HLLA glass samples *could* have been manufactured prior to the late 16th century but in which case they would have been manufactured in France or Germany. If manufactured in England, they would have been produced after c1567. All five samples from the tomb contain sufficient iron to give them a noticeable green tint (Figure 4). These samples also contain manganese and while the deliberate addition of manganese in order to reduce the colouring effect of iron was understood, it is likely that the manganese in these samples of window glass was an unconscious inclusion derived from the plant ash used.

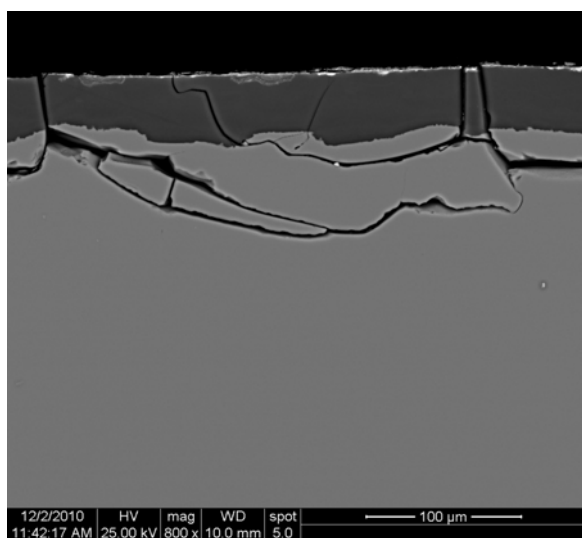


Figure 6. SEM image (back-scattered electron detector) of T1 showing the surface corrosion and underlying uncorroded glass

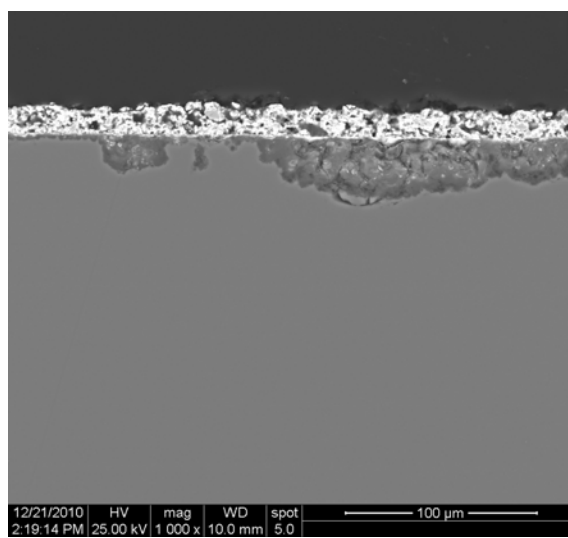


Figure 7. SEM image (back-scattered electron detector) of T3 showing the surface paint, corroded layer and underlying uncorroded glass

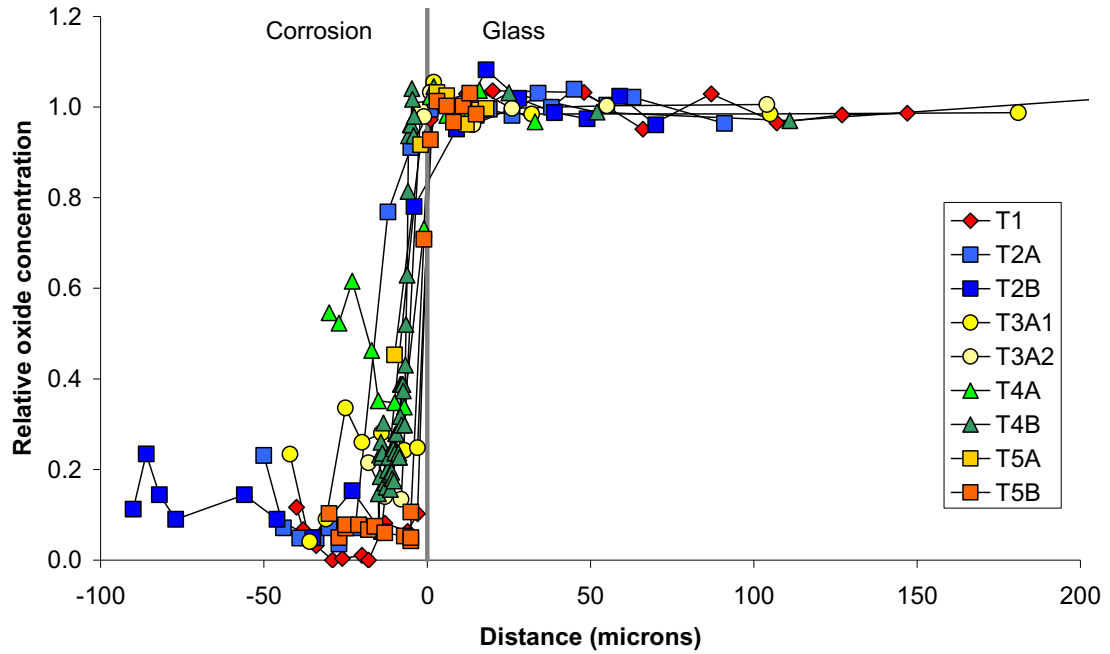


Figure 8. Linescans for sodium (relative concentration) through the glass and surface corrosion of the tomb samples

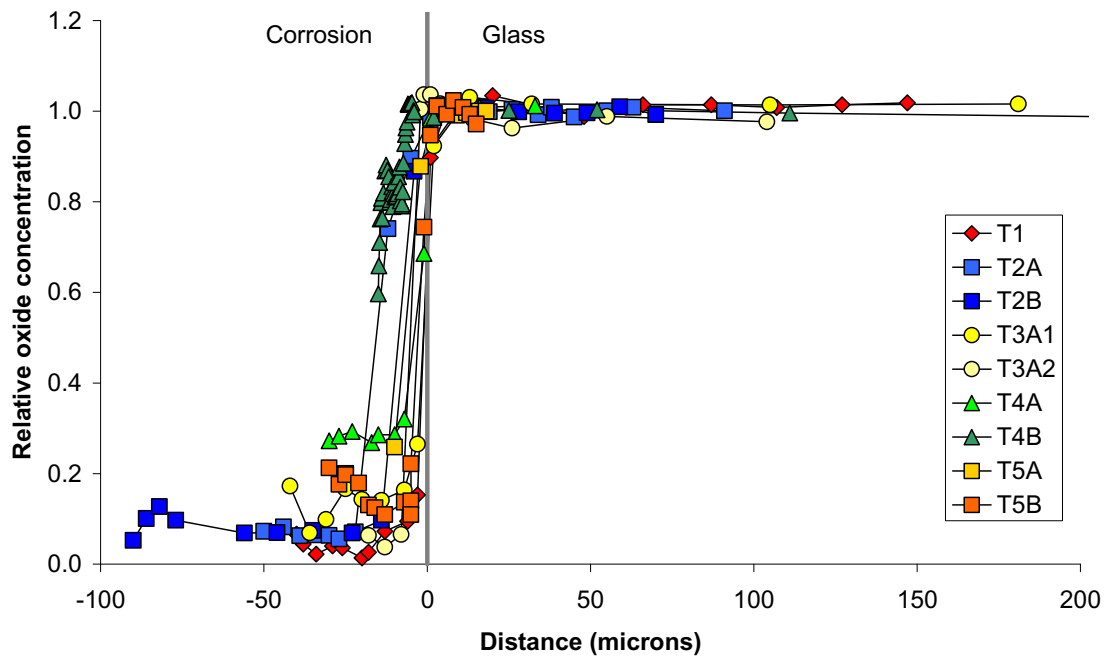


Figure 9. Linescans for potassium (relative concentration) through the glass and surface corrosion of the tomb samples

In order to provide further detail on the relationship between the pXRF and SEM-EDS data, and potentially shed light on the nature of surface corrosion, the five tomb samples

were subject to a series of SEM-EDS analyses through the corroded surfaces into the underlying uncorroded glass (Figure 6). In order to facilitate comparisons between different fragments of glass of different compositions the analyses (which are reproduced in full in appendix 1) were re-calculated as a factor of the composition of the uncorroded glass (glass = 1; if the relative concentration >1 the oxide is more concentrated in the corroded surface layer).

The corroded nature of the surface of the glass is most apparent in the concentration of alkalis (Figures 8 and 9) and calcium (Figure 10). The loss of alkalis (and to a lesser extent calcium) from the surface layers of glass, and their replacement by a variety of ionic species derived from water is well known (Newton and Davison 1996, 136–140). The exact ionic species involved and the mechanisms for their diffusion, however, are not fully understood. The analytical techniques available during the investigation of the Thornhill glass were not capable of identifying such ions.

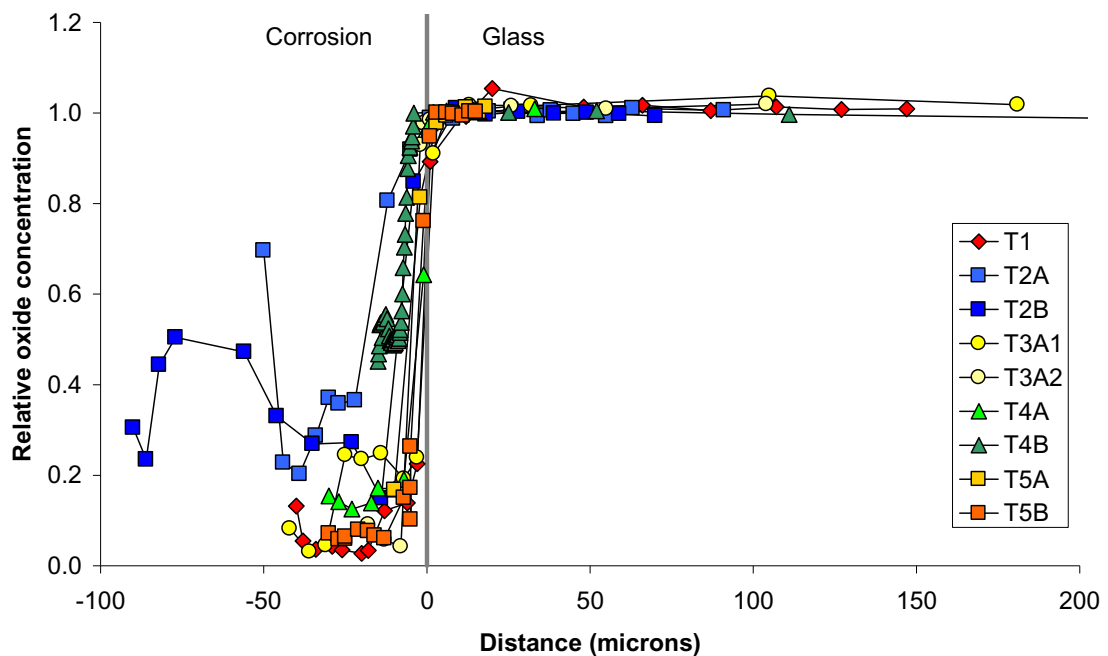


Figure 10. Linescans for calcium (relative concentration) through the glass and surface corrosion of the tomb samples



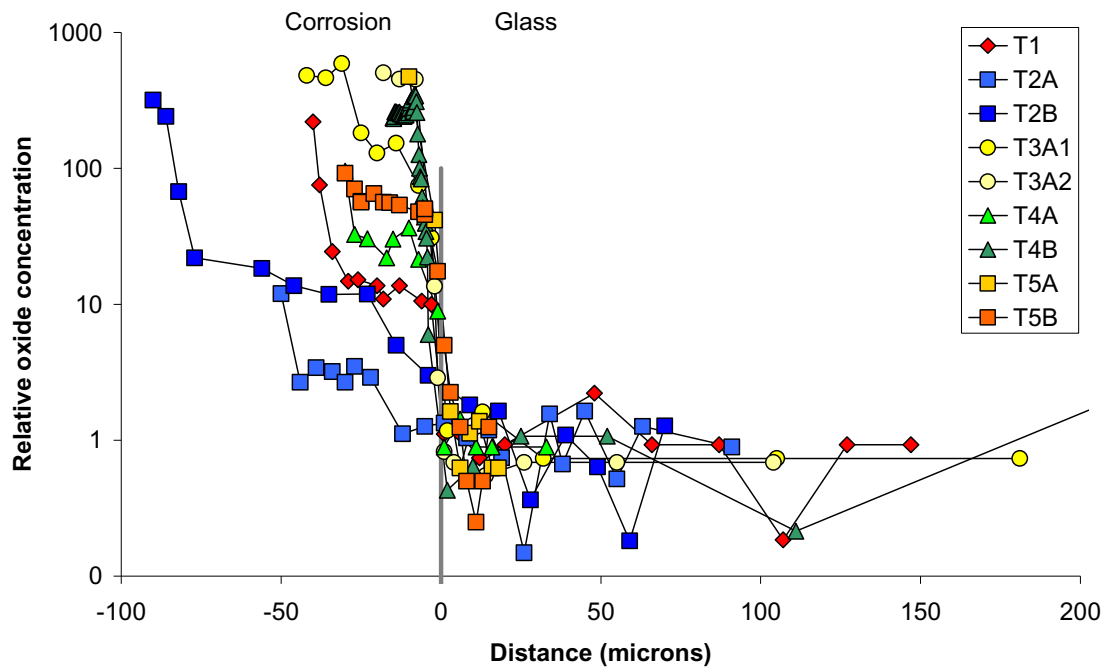


Figure 11. Linescans for lead (relative concentration) through the glass and surface layers of the tomb samples

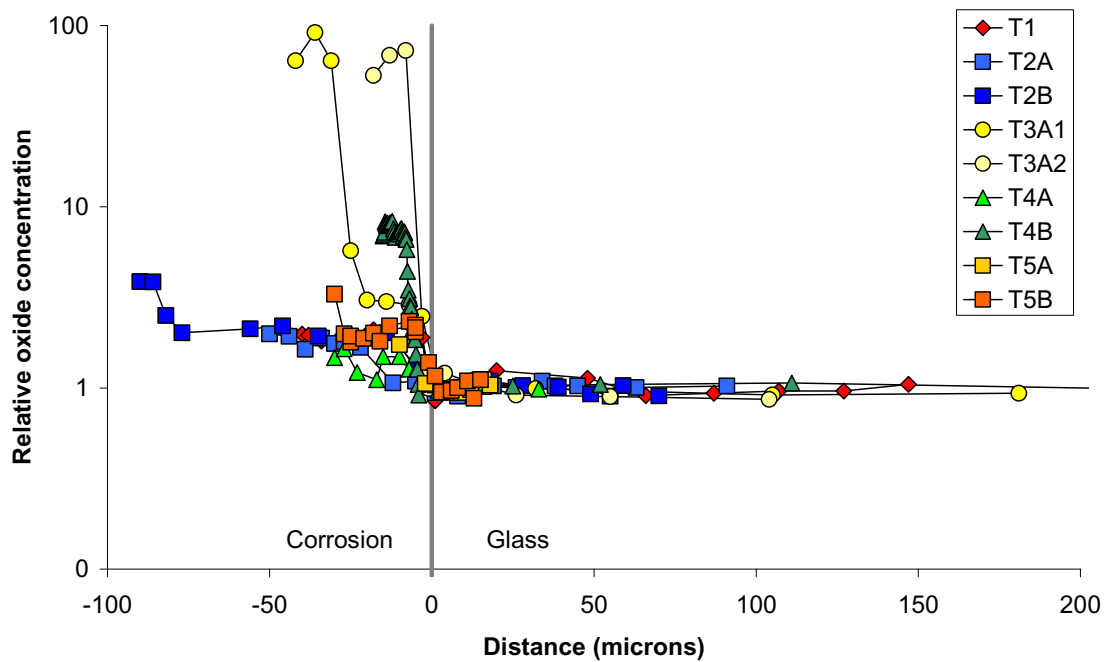
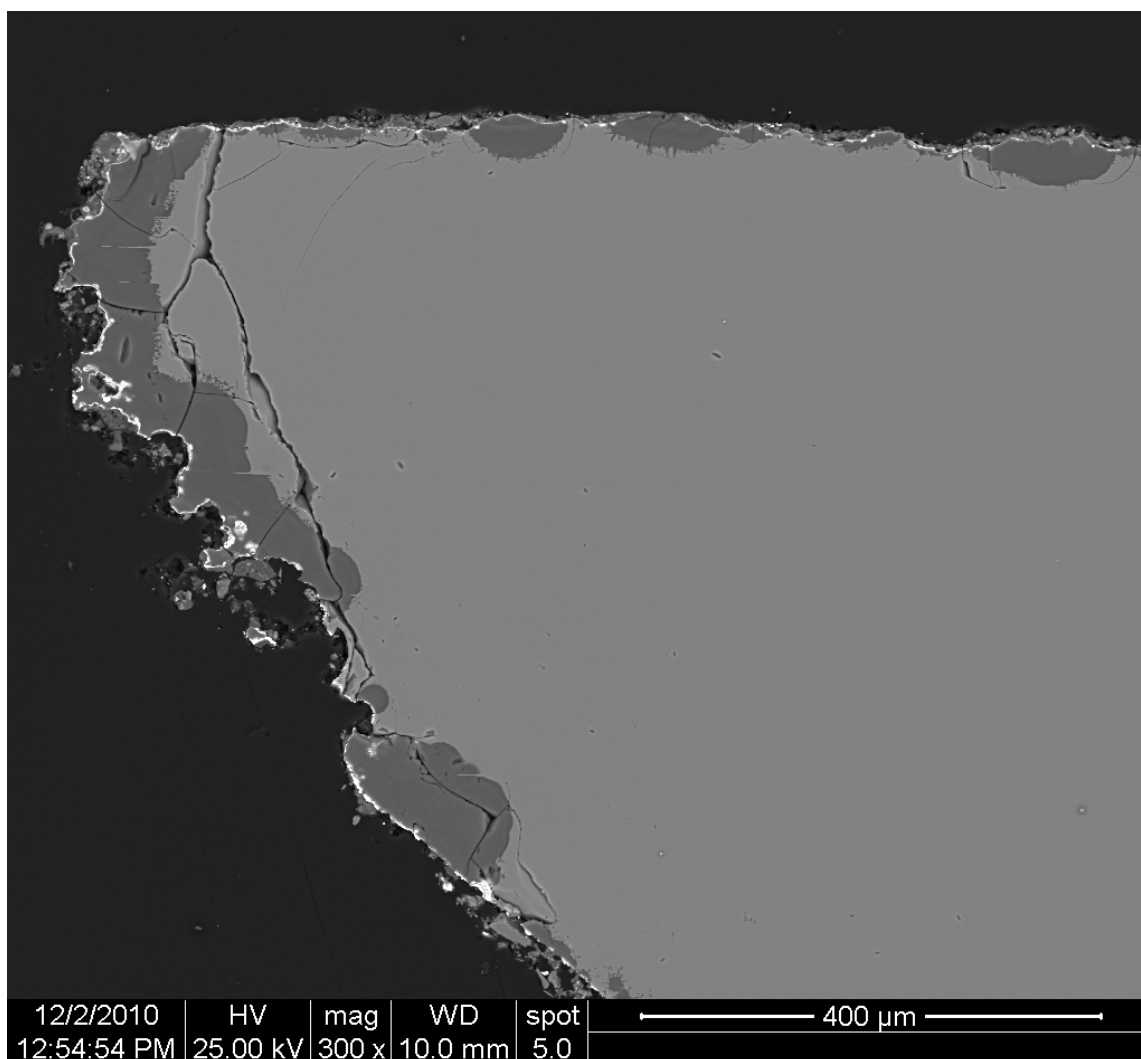


Figure 12. Linescans for iron (relative concentration) through the glass and surface layers of the tomb samples

The identification of corrosion, and the characterisation of changes in chemical composition through such surface layers, is complicated to some extent by the presence

of painted decoration at the surface (Figure 7) which is rich in iron and lead (Figures 11 and 12). While sample T3 had a surface layer with a composition which matched previously examined black glass paint (Dungworth and Adams 2010) the other samples showed more ambiguous results. These often had surface layers which were thinner and with less enrichment of iron and lead. It is likely that in most of these cases the surface layers actually represent surface dirt and corrosion from other components of the window. The windows include iron and lead fittings which have undergone varying degrees of corrosion. The iron and lead corrosion products are likely to have been at least partially soluble in water which will have promoted their transport across the surface of the glass. This mechanism is the most likely explanation for the presence of iron- and lead-rich layers on the edges of glass which would have been encased in window lead (Figure 13).



*Figure 13. SEM image (back-scattered electron detector) of T1 showing the iron- and lead-rich surface layers (and corroded layers) on both an original surface as well as the side of the glass*

The differences between the chemical compositions of the corroded surfaces of the glass and the uncorroded cores (Figures 8–12) are significant. These differences are sufficient to explain the discrepancies between the apparent composition of the tomb samples as determined by pXRF and the actual glass composition as determined by SEM-EDS (Tables 2–3, Figure 5).

### Analysis of the *in situ* window glass

Fifty-five panes of glass were analysed *in situ* using pXRF at Thornhill. The results are provided in Appendix 1 (the locations of the windows are shown in Figure 2). The comparison of the pXRF and SEM-EDS results for the additional five samples from the tomb (Tables 2 and 3, Figure 5) suggests that pXRF results are not as accurate as those obtained by SEM-EDS; light elements (Mg to P) will be affected by surface corrosion and/or adhering dirt. Some heavier elements may be detected due to the corrosion of associated window fittings and may not give an accurate indication of the chemical composition of the glass. Despite these caveats, the pXRF results appear to provide considerable information on the nature of the *in situ* glass.

Forty-eight of the panes contain significant proportions of potassium and phosphorus (Figure 14) suggesting that these were manufactured using terrestrial plant ashes (Barrera and Velde 1989; Brill 1999; Dungworth 2011; Dungworth and Clark 2004; Dungworth and Paynter 2010; Jackson *et al* 2005).

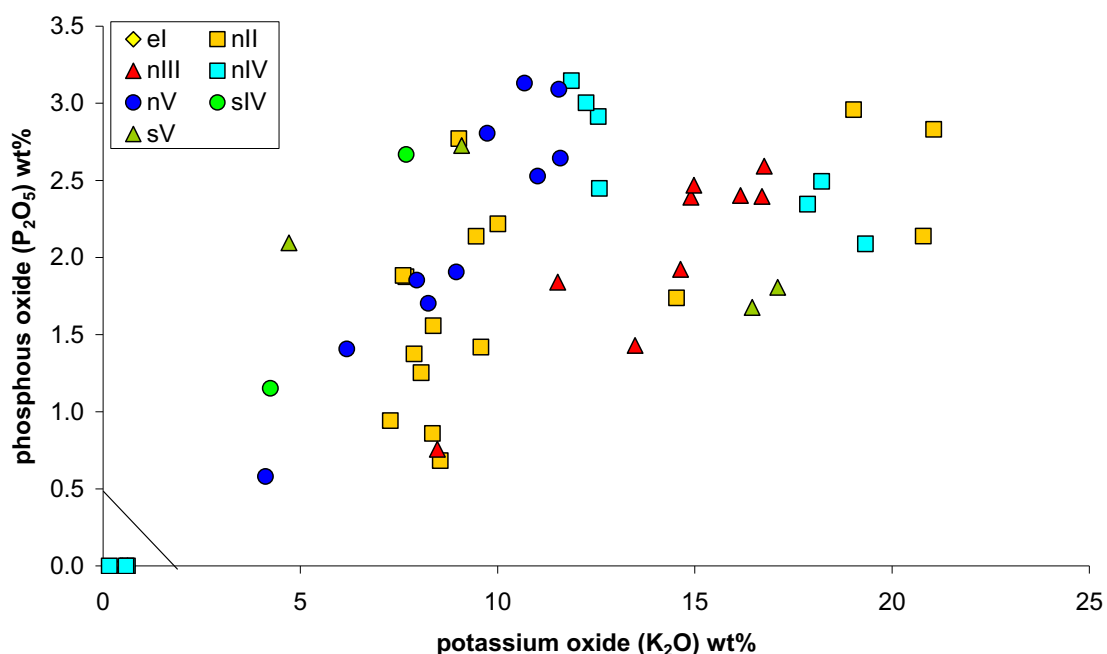


Figure 14. Potassium and phosphorus content of the window glass (pXRF)

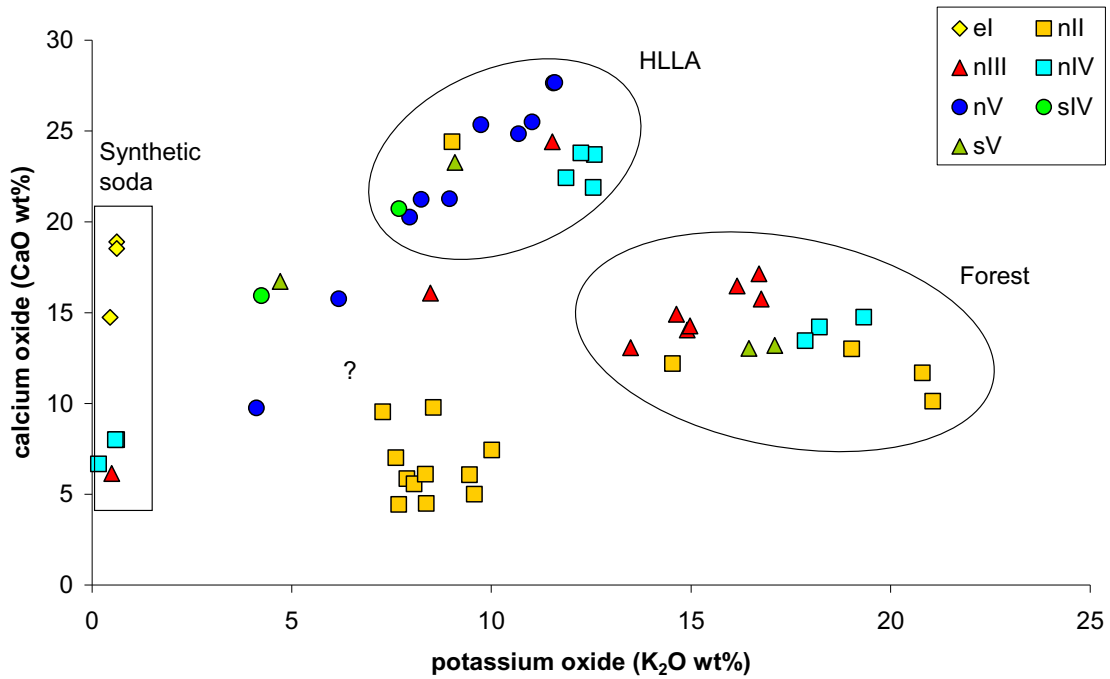


Figure 15. Potassium and calcium content of the window glass (pXRF)

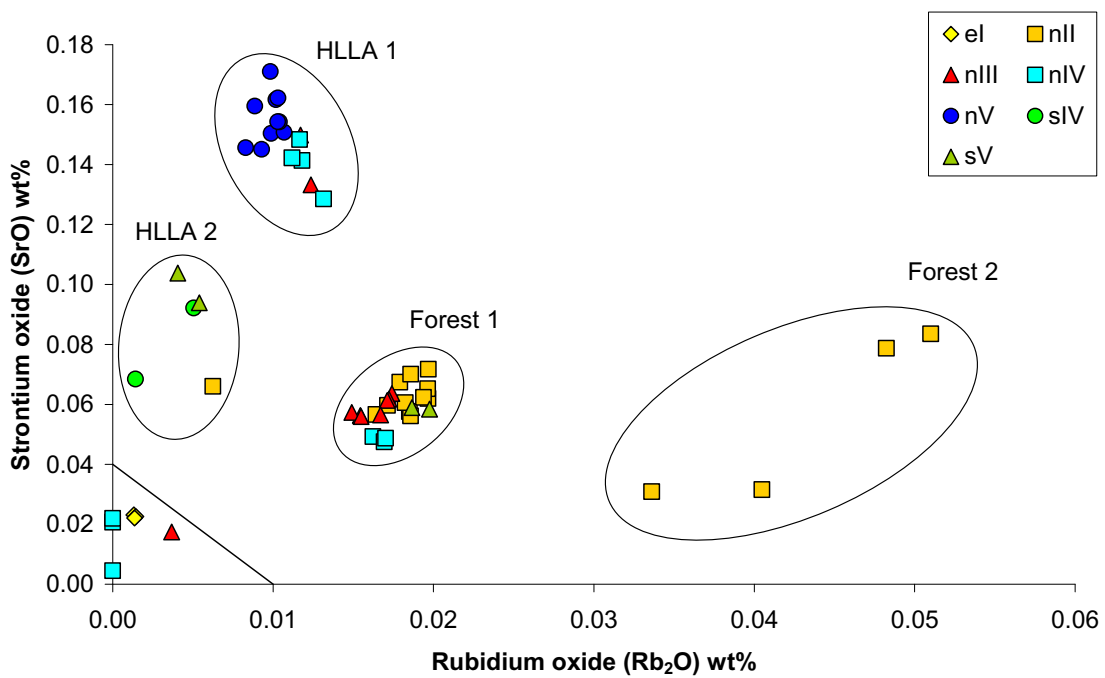


Figure 16. Rubidium and strontium content of the window glass (pXRF)

The composition of the glass in these panes indicates that they were all probably manufactured before the 18th century (when kelp became the preferred source of alkali for window glass). There were two different types of window glass commonly employed before the 18th century: high-lime low-alkali (HLLA) and forest glass (Dungworth 2011).

Distinguishing between these two glass types is unproblematic where fully quantitative data is available: HLLA is characterised by lower magnesium, potassium and calcium compared to forest glass. The Thornhill pXRF data, however, is limited by the corroded surfaces present on some of the glass. While some can be tentatively identified as Forest glass and some as HLLA glass (Figure 15), some panes have apparent compositions which do not readily conform to Forest or HLLA glass. These panes have potassium concentrations that are too low for Forest glass but calcium contents that are too low for HLLA glass. In most cases, the analysis of these samples showed anomalously high levels of sulphur (5–18wt% SO<sub>3</sub>) suggesting that corrosion and surface dirt are responsible for the anomalous results.

A careful examination of a wide range of elements (see Appendix 1) allowed all of the glass to be assigned to six compositional groups. The limited effect of surface dirt and corrosion on selected heavy elements (eg rubidium and strontium, see Figure 16) enabled the initial identification of these compositional groups (Table 4).

Table 4. Average composition of the six glass types at Thornhill (pXRF)

	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	Rb <sub>2</sub> O	SrO	ZrO <sub>2</sub>
Forest 1	2.7	1.3	55.5	1.8	12.8	11.0	0.2	1.3	0.6	0.018	0.059	0.008
Forest 2	3.1	1.7	58.5	2.3	17.6	10.0	0.2	0.9	1.1	0.043	0.056	0.010
HLLA 1	1.8	3.5	49.0	2.2	10.0	22.0	0.3	1.9	0.7	0.011	0.150	0.015
HLLA 2	1.8	1.8	50.7	2.3	6.9	20.2	0.3	1.0	1.2	0.004	0.085	0.016
Leblanc	<1.0	3.3	57.7	<0.5	0.5	14.6	0.2	0.2	1.3	0.002	0.021	0.010
Drawn sheet	2.6	1.1	68.1	<0.5	0.5	7.6	0.1	<0.1	0.1	0.000	0.016	0.022

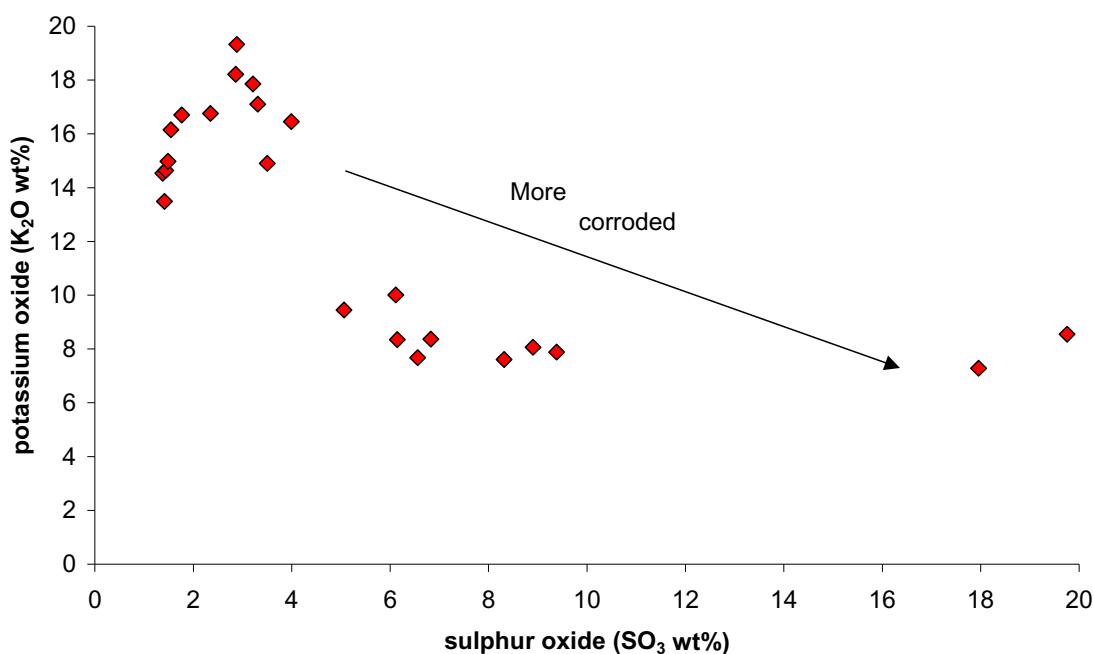


Figure 17. Sulphur and potassium content of the Forest 1 glass (pXRF)

Twenty-two panes have been assigned to **Forest 1** glass group. Thirteen of these panes have compositions which are clearly forest glass: they contain high levels of potassium (>10wt% K<sub>2</sub>O) and magnesium (>2.5wt% MgO). The remaining nine panes have low potassium, phosphorus and lime, and magnesium was not detected. The likelihood that the apparent composition of the latter panes has been affected by corrosion and/or surface dirt is confirmed by a comparison of the sulphur and potassium concentrations (Figure 17). All Forest 1 panes are colourless (actually pale green or pale blue-green). Forest glass was produced in England between the 13th century (and possibly earlier) and the late 16th century (Dungworth and Clark 2004).

Four panes have been assigned to **Forest 2** glass group. Three of these have very high potassium concentrations (19–21wt% K<sub>2</sub>O) and are clearly forest glasses. All four Forest 2 glasses are deliberately coloured (one red and three blue). The red pane contains elevated levels of copper which is often found in red glasses (eg Dungworth and Adams 2011). The red colour produced by copper is so strong that a very thin layer of red glass was usually applied to a colourless base glass. Two of the blue panes contain cobalt (as well as nickel and copper) which would be responsible for the colour. The third blue pane contains no cobalt but does contain copper. In this case the copper is probably found throughout the glass (and not restricted to a surface layer). The characteristics of the Forest 2 glass (colour and chemical composition) suggest that it was not obtained from the same source as the Forest 1 glass. It is possible that this glass was produced in continental Europe rather than England.

Sixteen panes have been assigned to **HLLA 1** glass group. Most of these panes have compositions which clearly indicate that they are HLLA glass, however, a few have apparent compositions which appear to have been affected by surface corrosion and/or adhering dirt. All HLLA 1 glass is colourless (actually pale green or pale blue-green). HLLA glass was produced in Germany from the 14th century (Wedepohl 1997) and France from the 16th century (Barrera and Velde 1989), however, it was not produced in England until the late 16th century (Dungworth and Clark 2004). Five panes have been assigned to **HLLA 2** glass group. Four of these are colourless and one is blue.

The panes with low phosphorus and potassium are likely to have been made using synthetic soda after the introduction of the Leblanc process in the 1830s (Dungworth 2011). Three panes have compositions (~2.6wt% MgO and low Fe<sub>2</sub>O<sub>3</sub> and CaO) which suggest they were manufactured after c1930 and have been assigned to **Mech** glass group. Three of the remaining panes have compositions (low MgO, high CaO and presence of As<sub>2</sub>O<sub>3</sub> and MnO) which conform to window glass manufactured between c1830 and c1930 and have been assigned to **Leblanc** glass group. The last pane has an unusual composition (eg chromium and vanadium) for which there is no exact parallel but it probably belongs to the same group.

## Window eI

The three panes of glass from **eI** have all been assigned to the **Leblanc** glass group. These panes were produced between c1830 and c1930. They do not represent medieval glazing and are presumably later repairs and replacements. The apparent iron concentrations in these panes are significantly higher than most contemporary Leblanc glass (Dungworth 2011). It is possible that this glass was carefully manufactured to achieve a tint that matched the glass which it replaced (cf Dungworth *et al*/2010).

## Window nII

Ten panes of glass from **nII** have been assigned to **Forest 1** glass group (all colourless). All of these panes represent glazing first installed before the late 16th century. Four of the remaining panes (all deliberately coloured glass) belong to **Forest 2** glass group. The last pane (also coloured) has been assigned to **HLLA 2** glass group. Although the colourless and coloured glass would have been obtained from two separate sources (probably English and continental, respectively), it is possible that both were installed at the same time. The use of colourless glass and coloured glass from two distinct sources in the same window at York Minster has been noted by Freestone *et al* (2010). A combination of Forest and HLLA glass (the former from either English or continental producers, but the latter imported) is entirely consistent with a 15th century date for this window.

## Window nIII

The ten panes from **nIII** include seven **Forest 1**, two **HLLA 1** and one probable **Leblanc** glass. Both the Forest 1 and the HLLA 1 panes are colourless and it is possible that the latter represent a later (although pre-18th-century) repair/replacement.

## Window nIV

The ten panes from **nIV** include three **Forest 1**, four **HLLA 1** and three **Drawn sheet** glass. Both the Forest 1 and the HLLA 1 panes are colourless and it is possible that the latter represent a later (although pre-18th-century) repair/replacement. The Drawn sheet glass panes (**nIV-02**, **nIV-10** and **nIV-12**) appear to represent repair/replacement which took place after c1930.

## Window nV

All ten panes from **nV** have been assigned to **HLLA 1** glass group. There are several explanations for the absence of Forest glass from **nV**, however, there is insufficient data to determine which is the correct explanation. If it is assumed that the HLLA 1 glass (all of

which is colourless) was produced in England then it was produced after c1567 and represents later repair/replacement. On the other hand, if it is assumed that the HLLA 1 was produced on the continent it could have been manufactured as early as the 14th century and so could represent original glazing.

### Window sIV

The two panes from sIV are both colourless HLLA 2 glass. The two panes do not share sufficiently similar compositions to suggest that both panes were obtained from the same source.

### Window sV

The four panes from sV include two Forest 1 and two HLLA 2 glass, all of which are colourless. The two Forest 1 panes share almost identical compositions and it is likely that they were both manufactured at the same time and place and then installed at the same time (before the late 16th century). The two HLLA 2 panes also share similar compositions with each other (and so are probably contemporary and from the same source), however, they could have been manufactured at any time up to the end of the 17th century.

## DISCUSSION

The analysis of the Thornhill glass suggests that there are significant proportions of both forest glass and HLLA glass. Both types are known to have been manufactured at the time the Savile Chapel windows were installed (15th century); however, if any of the HLLA glass is original, it must have been imported from mainland Europe, as HLLA production did not start in England until the late 16th century (Dungworth and Clark 2004). The composition of the single fragment of Forest glass analysed using SEM-EDS is entirely consistent with it being of English manufacture (Dungworth and Paynter 2010). Unfortunately the pXRF data for the windows is insufficiently accurate and precise (especially due to surface corrosion) to allow any definite statements to be made about its likely provenance. It is noteworthy that the pXRF identified two Forest glasses based on trace elements and that one of these comprised all of the coloured Forest glass while the other was made up of glass which was not deliberately coloured. It is tempting to see the former as indigenous glass and the latter as imports (cf Marks 1991, 265).

The work of Cox *et al* (1979) indicated that medieval glass with a low molar proportion of SiO<sub>2</sub> was more susceptible to deterioration. It is not possible to analyse the Thornhill pXRF data in the same way, however, as the technique was not able to indicate the concentration of sodium. In addition, the surface corrosion on many of these samples has



produced an apparent chemical composition which will be significantly different from the actual glass composition. The SEM-EDS data obtained from the five tomb samples is of a sufficient standard to allow the calculation and plotting of molar proportions (Figure 18). Figure 18 also shows the molar proportions of RO and R<sub>2</sub>O for a range of historic window glasses, while Figure 19 shows the R<sub>2</sub>O:RO ratio plotted against SiO<sub>2</sub>.

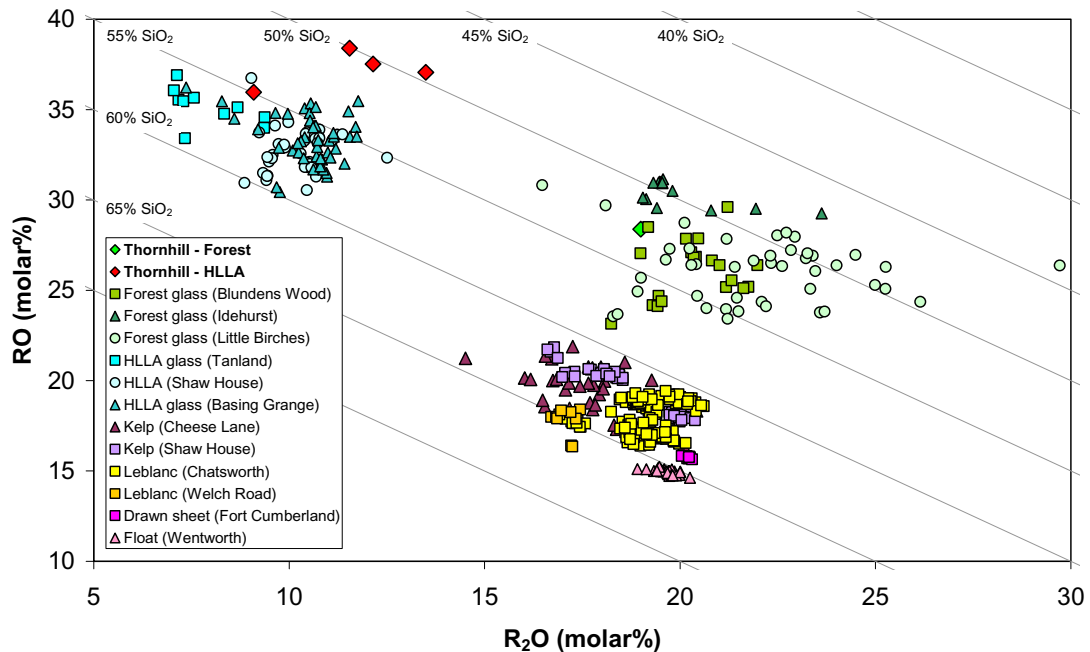


Figure 18. Composition of medieval and later window glass (molar %) (Sources: Dungworth and Clark 2004; Dungworth and Loaring 2009; Dungworth 2010a; Dungworth 2010b; Dungworth 2010c; Dungworth and Mortimer 2007; Dungworth and Paynter 2011; Wilkes and Dungworth 2010; Mortimer 1991)

Most medieval Forest glasses have 16.9–25.5mol% R<sub>2</sub>O, 22.3–31.3mol% RO and 46.6–57.4mol% SiO<sub>2</sub>, while the later HLLA glasses have 7.9–12.4mol% R<sub>2</sub>O, 30.4–36.1mol% RO and 53.7–59.5mol% SiO<sub>2</sub>. Both glass types show considerable compositional variation that is typical of artisanal glasses made using plant ashes. The state of preservation of HLLA glasses is often markedly better than forest glasses — a phenomenon which might be explained in part by the slightly higher proportion of silica (on average). Nevertheless, the durability of some HLLA may also be improved by their relatively low R<sub>2</sub>O:RO ratio (typically 0.3 compared to 0.8 in Forest glass). Kelp and Leblanc window glasses usually have 16.5–20.5mol% R<sub>2</sub>O, 16.5–21.5mol% RO and 60.5–65.0mol% SiO<sub>2</sub>. In terms of R<sub>2</sub>O, RO and SiO<sub>2</sub>, there are few differences between kelp and the earliest synthetic soda window glasses (Leblanc). It is only with the reformulation of window glass recipes following the introduction of Drawn sheet from c1930 that the proportion of RO drops to 15–16mol% and the proportion of SiO<sub>2</sub> increases to 64–66mol%.

The five Thornhill samples analysed using SEM-EDS include a single pane of Forest glass, which has a composition that conforms to most English Forest glass (Dungworth and Paynter 2011). The silica concentration is low (52.6mol%) and this glass would be as susceptible to deterioration as most English medieval window glass. Of the four HLLA samples, one has a molar composition comparable with most HLLA glass, however, three have unusually low proportions of SiO<sub>2</sub> (Figures 18 and 19). These panes would be much more susceptible to corrosion than other HLLA glasses.

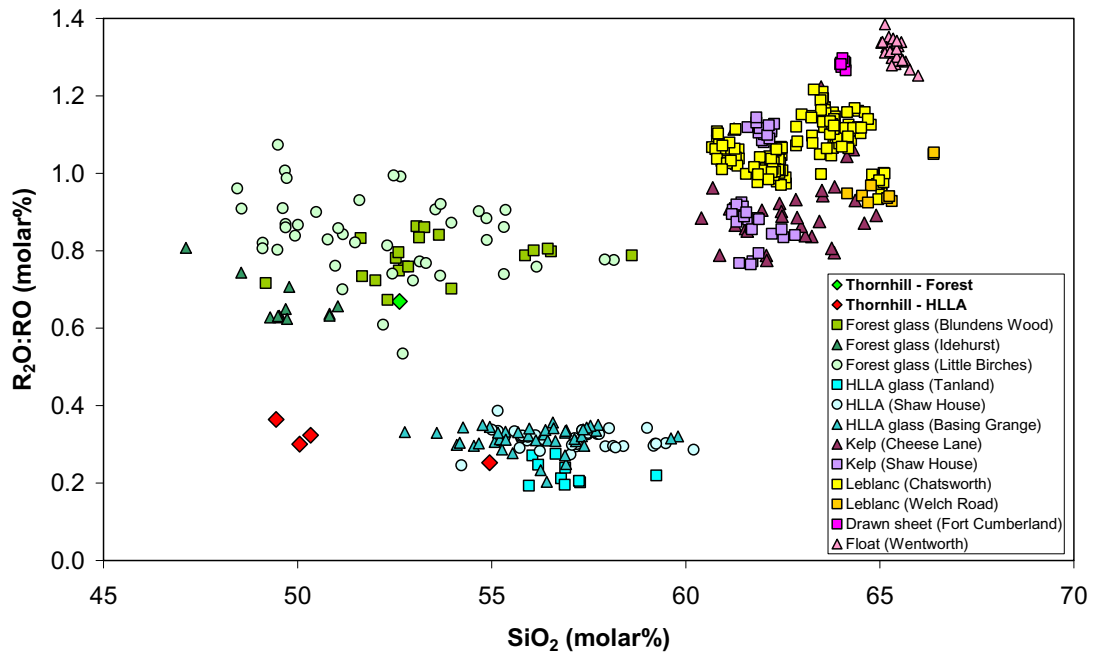


Figure 19. Composition of medieval and later window glass (molar %) (Sources: see caption for Figure 18)

The concentrations of sulphur on the interior surfaces of the *in situ* panes at Thornhill (detected using pXRF) vary from nil to almost 20wt% (SO<sub>3</sub>, Figure 20). This contrasts with the measurement of sulphur on carefully prepared samples analysed using laboratory-based techniques (Dungworth 2011). Normally, historic window glass contains up to 1wt% SO<sub>3</sub> and only eight of the Thornhill panes contain such low sulphur. The analysis of the samples from the tomb using pXRF (Table 2) and SEM-EDS (Table 3) demonstrates that the sulphur is present primarily at the surface of the glass (Figure 21). The SEM-EDS analyses carried out through the thickness of the prepared samples showed that the uncorroded glass contained < 1wt% SO<sub>3</sub> but concentrations at the surface were usually significantly higher (Figure 21); however, none of these samples showed sulphur concentrations as high as those indicated by pXRF.

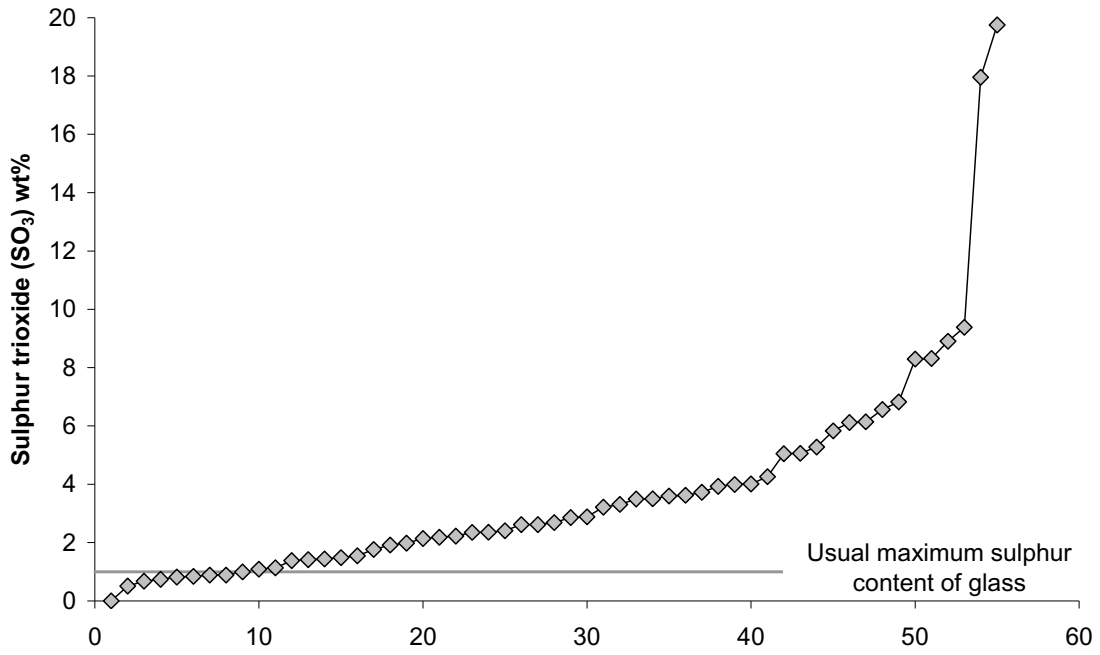


Figure 20. Sulphur (SO<sub>3</sub>) concentrations detected on the interior surfaces of the glass (rank order)

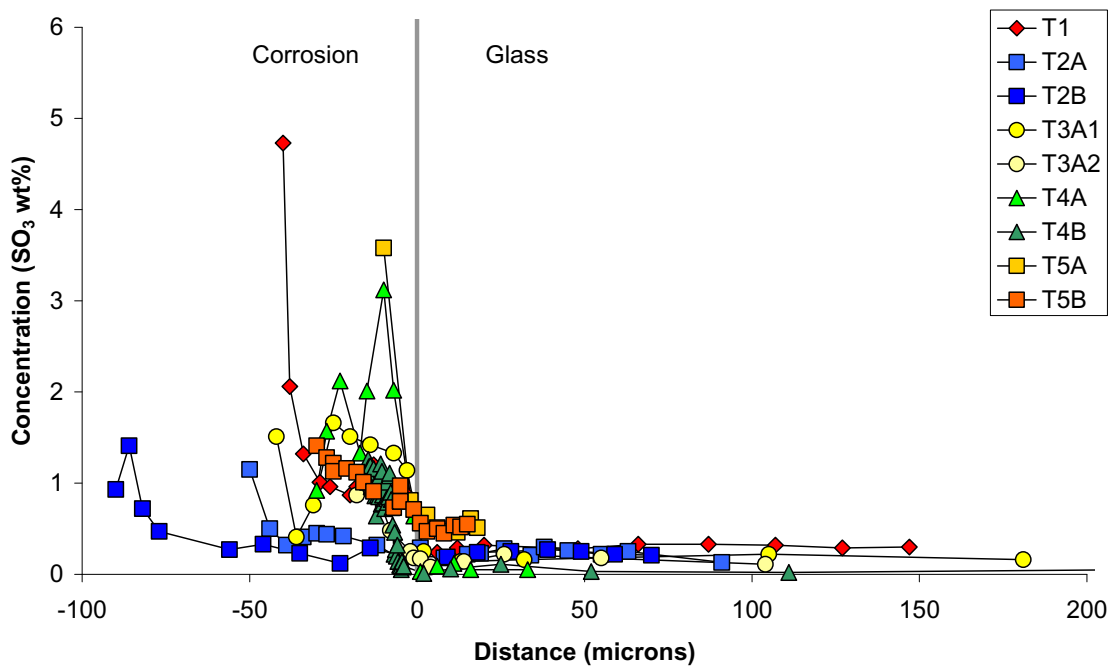


Figure 21. Linescans for sulphur (wt% concentration) through the glass and surface layers of the tomb samples

The levels of sulphur detected using pXRF analysis of *in situ* panes are very high (0–20wt%) compared to the SEM-EDS analysis of the five panes from the Savile tomb (0–5wt%). It is likely that these differences reflect the varied environmental exposure histories of the different glasses: the *in situ* window glasses have been exposed to the atmosphere for several centuries while those from the tomb have been protected from the atmosphere for some time.

Despite the uncertainty about the origin of the sulphur on the surface of the Thornhill glass and its possible role in the deterioration of the glass, the average sulphur content of the glass varies from window to window in ways which can be linked to the relative condition of the extant glass (Table 5). The lowest sulphur concentrations are found on the east window, however only three panes were analysed and all of these were 19th-century (or later) replacements (all fairly durable soda-lime-silica glasses). The highest sulphur levels were consistently found in **nII** (the East window of the Savile chapel).

*Table 5. Mean sulphur (SO<sub>3</sub>) concentrations detected (pXRF) on the interior surfaces of the glass*

Window	mean	sd
el	0.9	±0.1
nII	6.7	±5.6
nIII	2.0	±1.2
nIV	1.8	±1.0
s	3.4	±1.7

## CONCLUSIONS

The scientific analysis of a selection of the Thornhill window glass was undertaken to test the viability of pXRF as a means of characterising historic window glass *in situ*, and to provide information to assist with the formulation of a sustainable conservation solution to the serious deterioration of some of the glass.

The five tomb samples showed a fairly good correlation between chemical composition as determined by pXRF and SEM-EDS. Although these five samples have not been *in situ* for some years and so have been exposed to a different environment, they do suggest that pXRF does provide a reliable indication of the chemical composition of historic window glass.

The pXRF analysis of 55 panes showed that 16 panes (most of which come from **nII**) have *apparent* chemical compositions which do not match any previously known historic window glass (Dungworth 2011). These panes were also those with the highest sulphur readings and it is concluded that corrosion phenomena have distorted the chemical composition as determined by pXRF. The remaining 39 panes could all easily be assigned to four major glass types: Forest, HLLA, Leblanc and Drawn sheet. A comparison of trace

element concentrations in all samples allowed the 16 corroded panes to be assigned to one of the glass types.

The forest glass is unlikely to have been manufactured before the end of the 16th century and most probably represents the composition of glass originally installed in the 15th century. The trace elements (especially rubidium and strontium) in this glass formed two compositional clusters suggesting two batches or sources (Forest 1 and Forest 2). It is striking that all of the Forest 1 panes are not deliberately coloured while all of the Forest 2 panes are coloured (red or blue).

The HLLA glass could have been manufactured as early as the 14th century or as late as the 18th century. If any of the HLLA glass is original then it would have been manufactured in mainland Europe and imported, as English production of HLLA glass is unknown before the late 16th century. The use of HLLA glass for the manufacture of windows came to an end at the beginning of the 18th century in England but may have continued up to the end of the 18th century in mainland Europe. The HLLA glass could be divided into two sub-groups (HLLA 1 and HLLA 2) based on the concentration of a range of trace elements.

Previous research has established that the intrinsic durability of glass can be most effectively evaluated by considering the  $R_2O:RO:SiO_2$  molar composition, in particular where  $SiO_2 < 50\text{mol}\%$  glass will be susceptible to deterioration. The pXRF analysis of *in situ* panes at Thornhill could not be used to assess the  $R_2O:RO:SiO_2$  molar composition of the glass because the technique lacked the necessary accuracy (and soda could not be determined). The SEM-EDS analysis of the five samples from the Savile tomb, however, could be used to determine their  $R_2O:RO:SiO_2$  molar composition. Three of these glasses are characterised by low levels of  $SiO_2$  compared to contemporary glass of the same basic type. It can be concluded, therefore, that at least some of the Thornhill glass is intrinsically unstable. This conclusion supports the removal of window **n11** and its replacement.

## RECOMMENDATIONS FOR FURTHER WORK

The significant deterioration of much of the window glass in the Savile Chapel at Thornhill is likely to be due to the intrinsic instability of this glass. The exact mechanisms which have led to the deterioration of this glass remain unclear and should be investigated further. The removal and conservation of **n11** provides an excellent opportunity to take small samples of glass which can be studied using SEM-EDS. This will shed further light on the nature of the glass most susceptible to deterioration and allow the investigation of the deterioration process through the analysis of cross-sections through the weathered surfaces.

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APPENDIX I. PXRF RESULTS (W = WINDOW; P = PANE)

W	P	Type	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	CoO	NiO	CuO	As <sub>2</sub> O <sub>3</sub>	Rb <sub>2</sub> O	SrO	ZrO <sub>2</sub>	
el	01	cls	Leblanc	<1.0	2.7	64.5	<0.5	0.8	0.4	0.6	18.9	0.17	<0.02	0.23	0.97	<0.01	<0.01	<0.02	0.16	0.001	0.023	0.008
el	02	cls	Leblanc	<1.0	3.0	63.6	<0.5	0.9	0.5	0.6	18.5	0.16	<0.02	0.22	0.95	<0.01	<0.01	<0.02	0.16	0.001	0.022	0.008
el	03	cls	Leblanc	<1.0	2.1	58.7	<0.5	1.1	0.3	0.5	14.7	0.14	<0.02	0.23	1.72	<0.01	<0.01	<0.02	0.18	0.001	0.023	0.009
nll	01	cls	Forest I	<1.0	0.8	58.4	1.3	9.1	1.0	8.0	5.7	0.28	<0.02	1.14	0.61	<0.01	<0.01	<0.02	<0.02	0.019	0.057	0.007
nll	02	cls	Forest I	<1.0	0.9	68.7	1.9	6.6	0.7	7.7	4.4	0.26	<0.02	1.22	0.62	<0.01	<0.01	<0.02	<0.02	0.020	0.062	0.006
nll	03	cls	Forest I	<1.0	1.6	63.8	2.1	5.1	0.6	9.5	6.1	0.28	<0.02	1.13	0.62	<0.01	<0.01	<0.02	<0.02	0.018	0.061	0.008
nll	04	cls	Forest I	2.5	0.9	57.3	1.7	1.4	0.3	14.5	12.2	0.20	<0.02	1.25	0.54	<0.01	<0.01	<0.02	<0.02	0.016	0.057	0.008
nll	05	cls	Forest I	<1.0	0.0	40.9	0.7	19.8	1.8	8.6	9.8	0.22	<0.02	1.01	0.56	<0.01	<0.01	<0.02	0.02	0.020	0.065	0.009
nll	06	cls	Forest I	<1.0	1.2	68.4	1.6	6.8	1.3	8.4	4.5	0.29	<0.02	1.11	0.58	<0.01	<0.01	<0.02	<0.02	0.019	0.062	0.007
nll	07	cls	Forest I	<1.0	1.1	56.3	1.9	8.3	0.3	7.6	7.0	0.24	<0.02	1.21	0.56	<0.01	<0.01	<0.02	0.02	0.018	0.067	0.007
nll	08	cls	Forest I	<1.0	1.5	66.1	2.2	6.1	0.5	10.0	7.4	0.24	<0.02	1.32	0.58	<0.01	<0.01	<0.02	<0.02	0.020	0.072	0.009
nll	09	cls	Forest I	<1.0	0.4	63.2	0.9	6.1	0.7	8.4	6.1	0.24	<0.02	1.17	0.54	<0.01	<0.01	<0.02	<0.02	0.017	0.060	0.008
nll	10	cls	Forest I	<1.0	0.7	50.8	0.9	18.0	1.3	7.3	9.5	0.25	<0.02	1.16	0.53	<0.01	<0.01	<0.02	<0.02	0.019	0.070	0.007
nll	11	blue	HLLA 2	4.1	1.9	54.6	2.8	0.8	0.6	9.0	24.4	0.29	<0.02	1.03	0.65	0.07	<0.01	0.04	<0.02	0.006	0.066	0.018
nll	12	red	Forest 2	<1.0	1.5	54.9	1.4	5.0	1.2	9.6	5.0	0.28	<0.02	0.68	1.20	<0.01	<0.01	0.39	<0.02	0.048	0.079	0.008
nll	13	blue	Forest 2	7.6	1.5	57.5	3.0	0.7	0.6	19.0	13.0	0.16	<0.02	1.07	0.57	0.13	0.09	0.09	<0.02	0.034	0.031	0.013
nll	14	blue	Forest 2	4.8	1.2	67.8	2.1	2.4	0.5	20.8	11.7	0.14	<0.02	1.18	0.76	0.18	0.13	0.12	0.02	0.040	0.032	0.011
nll	15	blue	Forest 2	<1.0	2.6	53.8	2.8	3.7	0.5	21.1	10.1	0.22	<0.02	0.82	1.70	<0.01	<0.01	0.27	<0.02	0.051	0.084	0.008
nlll	01	cls	Forest I	5.9	1.8	54.2	2.4	3.5	0.3	14.9	14.0	0.19	<0.02	1.55	0.63	<0.01	<0.01	<0.02	<0.02	0.017	0.064	0.009
nlll	02	cls	HLLA 1	<1.0	1.3	69.2	0.8	4.0	0.4	8.5	16.1	0.28	<0.02	2.02	0.40	<0.01	<0.01	<0.02	0.03	0.012	0.133	0.017
nlll	03	cls	HLLA 1	1.9	2.9	49.1	1.8	2.6	0.5	11.5	24.4	0.34	<0.02	1.76	0.42	<0.01	<0.01	<0.02	0.02	0.012	0.150	0.017
nlll	04	cls	Forest I	5.1	1.5	52.2	2.4	1.8	0.4	16.7	17.1	0.21	<0.02	1.37	0.69	<0.01	<0.01	<0.02	<0.02	0.015	0.056	0.008
nlll	05	cls	Forest I	6.0	1.5	50.6	2.4	1.5	0.3	16.2	16.5	0.20	<0.02	1.46	0.48	<0.01	<0.01	<0.02	<0.02	0.015	0.057	0.009
nlll	06	cls	Forest I	3.7	1.9	48.0	1.9	1.4	0.4	14.6	14.9	0.19	<0.02	1.36	0.55	<0.01	<0.01	<0.02	0.05	0.015	0.056	0.009
nlll	07	cls	Forest I	3.8	1.5	51.4	2.5	1.5	0.3	15.0	14.3	0.19	<0.02	1.58	0.52	<0.01	<0.01	<0.02	<0.02	0.017	0.062	0.009
nlll	08	cls	Forest I	7.1	1.5	54.7	2.6	2.3	0.4	16.8	15.7	0.23	<0.02	1.55	0.52	<0.01	<0.01	<0.02	<0.02	0.017	0.061	0.010
nlll	09	cls?	Leblanc	<1.0	5.4	43.9	<0.5	<0.2	0.2	0.5	6.1	0.23	0.49	0.31	1.74	0.19	<0.01	<0.02	0.27	0.004	0.017	0.014
nlll	10	cls	Forest I	2.5	1.4	47.8	1.4	1.4	0.3	13.5	13.1	0.19	<0.02	1.38	0.96	<0.01	<0.01	<0.02	0.05	0.017	0.056	0.010

W	P	Type	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	CoO	NiO	CuO	As <sub>2</sub> O <sub>3</sub>	Rb <sub>2</sub> O	SrO	ZrO <sub>2</sub>	
nIV	01	cls	Forest I	6.4	1.4	54.1	2.5	2.9	0.6	18.2	14.2	0.15	<0.02	1.37	0.51	<0.01	<0.01	<0.02	<0.02	0.016	0.049	0.008
nIV	02	cls	Drawn	2.5	1.2	68.8	<0.5	0.7	0.1	0.6	8.0	0.06	<0.02	0.00	0.12	<0.01	<0.01	<0.02	<0.02	0.000	0.021	0.019
nIV	03	cls	HLLA I	2.6	4.5	50.0	2.9	1.1	0.3	12.6	21.9	0.26	<0.02	2.05	0.45	<0.01	<0.01	<0.02	<0.02	0.013	0.129	0.018
nIV	05	cls	Forest I	4.1	1.5	55.3	2.1	2.9	0.4	19.3	14.8	0.17	<0.02	1.33	0.44	<0.01	<0.01	<0.02	<0.02	0.017	0.048	0.008
nIV	06	cls	HLLA I	2.2	4.0	50.2	2.4	2.0	0.4	12.6	23.7	0.32	<0.02	2.01	0.52	<0.01	<0.01	<0.02	<0.02	0.012	0.141	0.018
nIV	07	cls	HLLA I	3.3	5.3	53.7	3.1	2.1	0.3	11.9	22.4	0.30	<0.02	1.92	0.59	<0.01	<0.01	<0.02	<0.02	0.012	0.148	0.020
nIV	08	cls	Forest I	5.5	1.7	53.2	2.3	3.2	0.5	17.9	13.4	0.16	<0.02	1.40	0.47	<0.01	<0.01	<0.02	0.02	0.017	0.049	0.008
nIV	09	cls	HLLA I	2.9	4.9	51.8	3.0	1.9	0.4	12.2	23.8	0.32	<0.02	1.88	0.57	<0.01	<0.01	<0.02	<0.02	0.011	0.142	0.018
nIV	10	cls	Drawn	2.2	0.9	67.5	<0.5	0.5	0.1	0.6	8.0	0.05	<0.02	<0.02	0.11	<0.01	<0.01	<0.02	<0.02	0.000	0.022	0.018
nIV	12	cls	Drawn	2.9	1.2	68.1	<0.5	0.9	0.1	0.2	6.7	0.08	<0.02	<0.02	0.12	<0.01	<0.01	<0.02	<0.02	0.000	0.004	0.030
nV	01	cls	HLLA I	2.7	4.7	45.7	2.5	3.6	0.4	11.0	25.5	0.32	<0.02	1.87	0.78	<0.01	<0.01	<0.02	0.04	0.010	0.150	0.015
nV	02	cls	HLLA I	<1.0	2.9	50.6	1.9	3.9	0.5	9.0	21.3	0.31	<0.02	1.78	0.67	<0.01	<0.01	<0.02	0.03	0.009	0.145	0.013
nV	03	cls	HLLA I	4.3	5.6	50.0	3.1	2.7	0.6	10.7	24.8	0.28	<0.02	2.04	0.76	<0.01	<0.01	<0.02	<0.02	0.011	0.151	0.015
nV	04	cls	HLLA I	2.7	3.8	43.8	2.8	3.6	0.8	9.7	25.3	0.29	<0.02	2.24	0.58	<0.01	<0.01	<0.02	<0.02	0.010	0.171	0.013
nV	05	cls	HLLA I	<1.0	1.9	38.0	1.7	5.3	0.6	8.2	21.2	0.28	<0.02	1.97	1.01	<0.01	<0.01	<0.02	0.03	0.010	0.162	0.011
nV	06	cls	HLLA I	3.2	5.6	53.1	3.1	2.2	0.5	11.6	27.7	0.32	<0.02	2.05	0.74	<0.01	<0.01	<0.02	<0.02	0.010	0.154	0.015
nV	07	cls	HLLA I	<1.0	2.4	44.3	1.9	2.4	0.8	8.0	20.3	0.26	<0.02	1.84	0.52	<0.01	<0.01	<0.02	0.04	0.009	0.160	0.010
nV	08	cls	HLLA I	<1.0	0.9	32.9	0.6	8.3	1.5	4.1	9.7	0.29	<0.02	1.32	2.43	<0.01	<0.01	<0.02	0.18	0.008	0.146	0.011
nV	09	cls	HLLA I	2.4	4.3	43.8	2.6	2.6	0.8	11.6	27.7	0.31	<0.02	2.00	0.80	<0.01	<0.01	<0.02	<0.02	0.010	0.154	0.016
nV	10	cls	HLLA I	<1.0	1.7	58.1	1.4	3.5	0.5	6.2	15.8	0.38	<0.02	1.69	0.52	<0.01	<0.01	<0.02	0.04	0.010	0.162	0.013
s4	01	cls	HLLA 2	<1.0	2.0	44.6	1.2	2.2	0.7	4.2	15.9	0.17	<0.02	0.53	2.62	<0.01	<0.01	0.05	0.19	0.001	0.068	0.016
s4	02	cls	HLLA 2	2.5	2.7	50.6	2.7	5.8	1.0	7.7	20.7	0.30	<0.02	1.04	0.55	<0.01	<0.01	<0.02	0.03	0.005	0.092	0.020
s5	01	cls	Forest I	5.3	2.3	48.8	1.8	3.3	0.9	17.1	13.2	0.17	<0.02	1.49	0.57	<0.01	<0.01	<0.02	<0.02	0.020	0.058	0.008
s5	02	cls	Forest I	4.1	2.1	54.7	1.7	4.0	0.4	16.5	13.0	0.20	<0.02	1.44	0.86	<0.01	<0.01	<0.02	0.04	0.019	0.059	0.008
s5	03	cls	HLLA 2	2.5	1.2	51.6	2.7	1.0	0.5	9.1	23.3	0.29	<0.02	1.19	0.91	<0.01	<0.01	<0.02	0.04	0.005	0.094	0.012
s5	04	cls	HLLA 2	<1.0	1.2	52.3	2.1	4.3	1.2	4.7	16.7	0.41	<0.02	1.09	1.07	<0.01	<0.01	<0.02	0.05	0.004	0.104	0.011

cls = colourless, Leblanc = glass made after introduction of Leblanc soda (c1830–c1930); Drawn = drawn sheet glass produced after mechanisation (>1930)



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