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THE WEST WINDOW, BEVERLEY MINSTER, BEVERLEY, EAST YORKSHIRE
CHEMICAL ANALYSIS OF THE WINDOW GLASS AND PAINT

TECHNOLOGY REPORT

David Dungworth, Helen Bower, Alison Gilchrist and Roger Wilkes

ARCHAEOLOGICAL SCIENCE

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SUMMARY
This report describes the scientific investigation of stained window glass from Beverley Minster, Yorkshire. The window glass comes from two panels in the west window produced by the John Hardman Company in 1859 and 1865. The glass has undergone conservation treatment at the York Glazier's Trust to deal with several aspects of deterioration, including the degradation of the paint. The chemical analysis of the window glass shows that several different types of glass were used including soda-lime-silica and flint (potassium-lead-silicate) glass. In addition, some of the glass appears to have been made by mixing flint and soda glass (or perhaps just the raw materials for each glass type). Much of the glass displays a chemical complexity which does not seem to be strictly necessary but may reflect the extraordinary lengths that 19th-century glassmakers were forced to go to achieve glass for the Gothic revival. The range of metal oxides detected correlates closely with the colours of the finished glass and agrees with practice described in contemporary texts. The paint shows extensive degradation and in some cases the paint has completely corroded leaving only corrosion products. The chemical composition of the surviving paint is complex and offers no immediately obvious explanation why it has degraded.

ARCHIVE LOCATION
The samples taken for scientific analysis are held by the York Glazier's Trust, 6 Deangate, York, YO1 7JB

DATE OF RESEARCH
2009–2010

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INTRODUCTION

The analysis of fragments of window glass from Beverley Minster forms part of a much larger English Heritage project investigating the chemical composition of window glass produced and used in Britain during the past five centuries. Samples of window glass have been selected from archaeological excavations (including glass production sites) and from historic buildings. These have been analysed to determine their chemical composition. A comparison of the chemical composition with the available dating evidence shows that a series of changes in window glass manufacturing took place during this period. The aim of this research is to provide a technique to date the manufacture of individual panes of glass in historic buildings. This knowledge will allow architects and others to make more informed judgements about which glass to retain and which can be replaced (Clark 2001).

Almost all glass produced in Britain during the medieval period was produced using sand and terrestrial plant ashes (primarily bracken) and has a distinctive potassium-rich composition (Dungworth and Clark 2004). The arrival of French glassmakers in the late 16th century saw a change to a high-lime low-alkali (HLLA) glass. HLLA glass was probably made using sand and the ash of hardwoods (such as oak). This HLLA glass remained in use until the end of the 17th century when it was superseded by a glass made using sand and seaweed (kelp) ash (Dungworth *et al* 2009; Parkes 1823; Watson 1782). This kelp glass dominated the window glass industry until the early part of the 19th century when it was abandoned in favour of glass made using synthetic soda (Cooper 1835; Ure 1844; Muspratt 1860).

Nicholas Leblanc invented a process for the synthesis of soda at the end of the 18th century. Common salt was heated with sulphuric acid to produce sodium sulphate (soda saltcake). The sodium sulphate was then heated with lime and charcoal or coal to produce sodium carbonate. Initially, glass could only be made with sodium carbonate, but glassmakers soon discovered that the sulphate could be used directly if it was combined with charcoal or coal. Glass made for the century or so following the 1830s was a simple soda-lime-silica glass with low levels of impurities (Dungworth 2009).

The early decades of the 20th century saw the development of techniques for automatically drawing glass (Cable 2004; McGrath and Frost 1937) which initially had problems with glass devitrifying. These problems were solved by substituting a small amount of magnesia for lime and virtually all window glass made in Britain since 1930 has contained 2–5% magnesia (Smrcek 2005).

The types of glass used for the manufacture of stained glass windows were more varied than those used for most plain, vernacular glazing. While some coloured glass was simply prepared by adding appropriate colorants (such as cobalt or copper) to the existing glass recipe, some stained glass was made from base glass specially formulated for that purpose. The examination of early 19th-century coloured glass from Margam Castle (Dungworth and Adams 2010) showed that colourless and yellow (silver) stained glass was made from soda-lime-silica glass, while most of the coloured glasses were made from potassium-lead-silicate glass. Bontemps, writing in the 1860s, describes the use of a variety of glass types for the manufactured of coloured window glass (Cable 2008).

The Minster at Beverley was built in the Perpendicular style from the 13th to the 15th centuries. The glass examined here was installed in the west window in the mid-19th century. The glass was the work of John Hardman and Company of Birmingham which was founded in 1838 and began manufacturing stained glass windows in 1844. The upper half of the window (represented here by samples from panel 6d) was made in 1859 and the lower (panel 2a) in 1865. The glass has remained *in situ* since the 1860s but it is now subject to conservation investigation and treatment by York Glaziers Trust. While a visual assessment suggests that the glass is not suffering from any significant corrosion, there is significant paint loss (especially from panel 2a). In addition, the lead came is suffering from fatigue and there is a general loss of structural stability.

The extent of the deterioration of the paint layers in panel 2a is paralleled in other stained glass windows produced by John Hardman in the 19th century. The great West Window at Sherborne Abbey was designed by A W Pugin and produced by Hardmans but has suffered from such advanced pigment loss that it was completely replaced in 1997 (Shepherd 2009, Shepherd 1994–5).

The sampling of glass and paint from the two panels of the west window at Beverley Minster provides the opportunity to compare Hardman glass and paint of almost the same age and exposed to the same environmental conditions but with contrasting degrees of deterioration.

In his study of the stained glass of A W Pugin (who worked with Hardmans in the 1840s), Shepherd discusses the lengths that Pugin, Hardmans and others went to in trying to produce stained glass with much of the character of Gothic stained glass (Shepherd 2009). A wide range of colours was supplied by different glass manufactures; however, not all of these met with the approval of Pugin and others. Suppliers, such as Hartley's of Sunderland, were encouraged to experiment with the batch composition and forming process to produce suitable glass. Pugin and others obtained samples of Gothic glass and had them analysed to provide information for the glass manufacturers. It is possible that some glass manufactured for Pugin, Hardmans, and others may have been deliberately formulated to recreate anachronistic recipes.

Since medieval times, painted detail has been added to stained glass windows using a mixture of a low-melting lead glass and various metal oxides, which is applied and then fired to a sufficient temperature to fuse the glass paint to the substrate glass (Newton and Davison 1989). Many stained glass windows of the mid-19th century have suffered from loss of this painted detail; this deterioration has often been ascribed to the use of borax to lower the melting temperature of the paint, as well as to underfiring of the paint (Harrison 1980, Newton and Davison 1989).

THE GLASS

Thirty-four fragments of window glass from the West Window of Beverley Minster were available for scientific examination. These derived from two separate panels: 2a installed in 1865, and subject to significant deterioration of the black (enamel) paint used to form the decoration, and 6d installed in 1859, and subject to limited deterioration. The glass included clear or colourless glass as well as coloured glasses. In some cases the coloured glass is of uniform colour throughout its thickness ('pot metal'), while in others the colour has been applied as a thin layer to one surface ('flashed'). The pot metals included greens, blues, purples, pinks, and amber/ochre. The flashed glasses were mostly red on colourless glass, although one comprised a peach flashed onto white which had been flashed onto colourless glass.

Figure 1a. Beverley Minster, west window, panel 2a, colour photograph

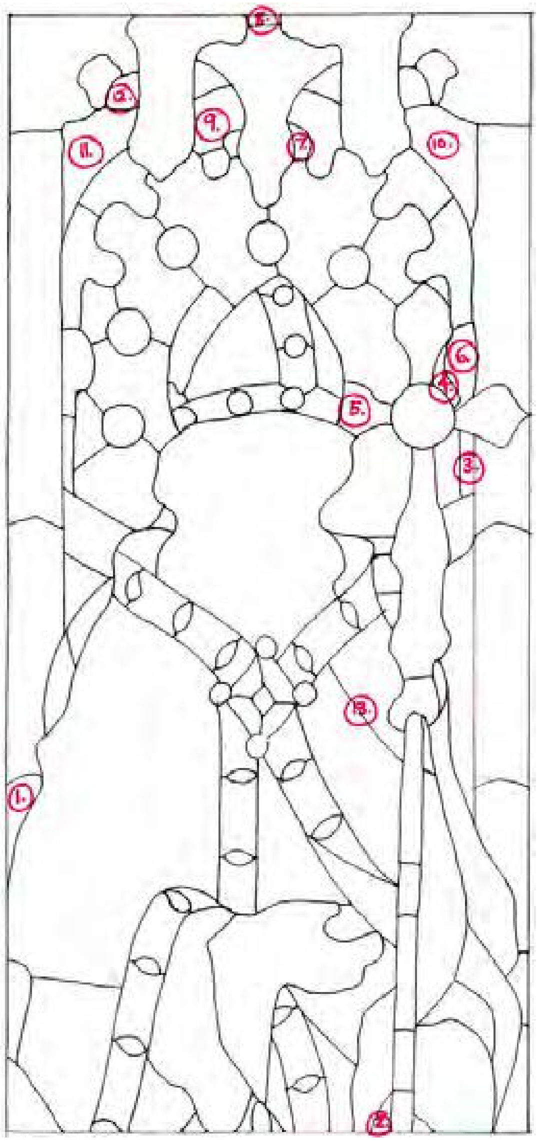

Figure 1b. Beverley Minster, west window, panel 2a, line drawing indicating sample location

Figure 2a. Beverley Minster, west window, panel 6d, colour photograph

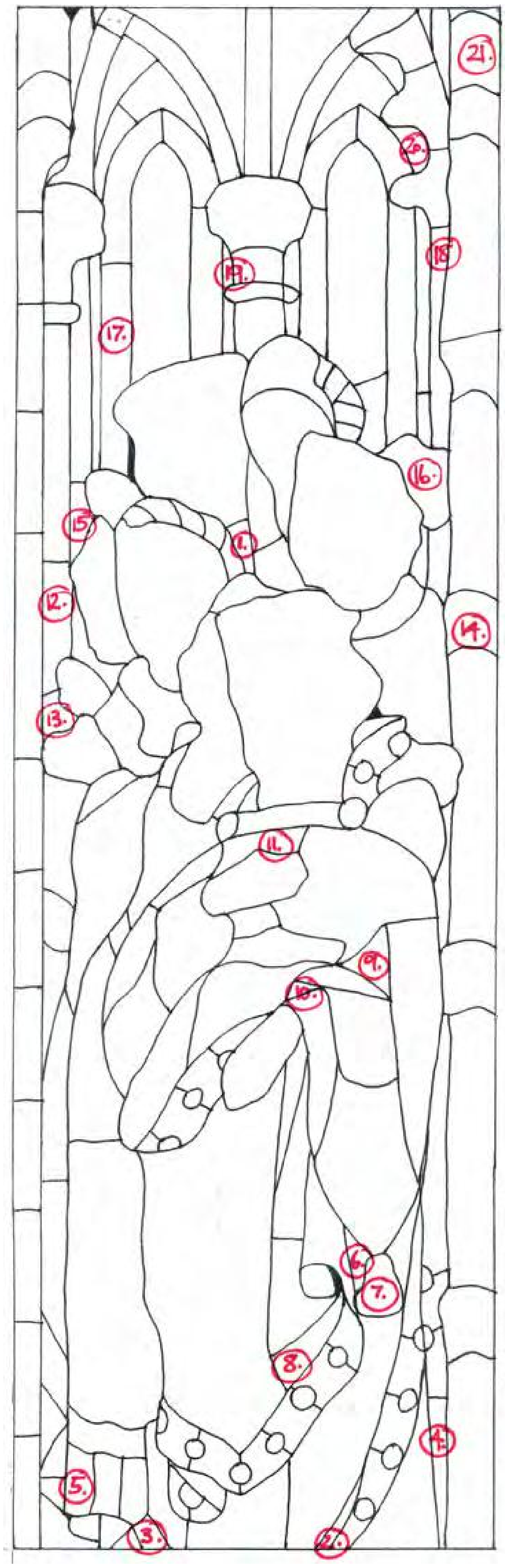

Figure 2b. Beverley Minster, west window, panel 6d, line drawing indicating sample location

Table 1. Description of Beverley Minster West window glass samples (Paint = paint layer visible on sample of glass analysed)

Panel	Sample	Colour	Paint
2a	1	Clear	No
2a	2	Pale blue pot metal	Yes
2a	3	Green pot metal	No
2a	4	Red flash and clear	No
2a	5	Pale green tint	Yes
2a	6	Yellow ochre pot metal	Yes
2a	7	Red flash and clear	Yes
2a	8	Pale green/blue pot metal	No
2a	9	Amber pot metal	Yes
2a	10	Pinky/brown/murray	Yes
2a	11	Pinky/purple pot metal	No
2a	12	Clear	Yes
2a	13	Blue pot metal	Yes
6d	1	Purple pot metal	No
6d	2	Blue (Royal) pot metal	No
6d	3	Peach flash and white	No
6d	4	Red flash and white	No
6d	5	Mid blue pot metal	No
6d	6	Pale green tint	Yes
6d	7	Bright green pot metal	Yes
6d	8	Plum pot metal	Yes
6d	9	Green tint pot metal	Yes
6d	10	Pale blue pot metal	No
6d	11	Pale green pot metal	Yes
6d	12	Mid green pot metal	Yes
6d	13	Purple pot metal	Yes
6d	14	Mid green pot metal	Yes
6d	15	Red flash and white	Yes
6d	16	Purple/violet pot metal	No
6d	17	Pink pot metal	Yes
6d	18	Yellow ochre pot metal	Yes
6d	19	Pale pink pot metal	No
6d	20	Pale purple pot metal	Yes
6d	21	Clear tint	No

METHODS

All of the fragments of glass were mounted in epoxy resin and ground and polished to a 1-micron finish to expose a cross-section through the glass. The samples were inspected using an optical microscope (brightfield and darkfield illumination) to identify corroded and uncorroded regions. Where possible, the samples were analysed using two techniques to determine chemical composition: SEM-EDS and EDXRF. The energy dispersive X-ray spectrometer (EDS) attached to a scanning electron microscope (SEM) provided accurate analyses of a range of elements while the energy dispersive X-ray fluorescence (EDXRF) spectrometer provided improved sensitivity and accuracy for some minor elements (in particular manganese, iron, cobalt, nickel, copper, arsenic, strontium and zirconium) due to improved peak to background ratios.

Table 2. Minimum Detection limits (MDL) and analytical errors for each oxide

	SEM-EDS			EDXRF	
	MDL	Error		MDL	Error
Na_2O	0.1	0.1	V_2O_5	0.02	0.03
MgO	0.1	0.1	Cr_2O_3	0.02	0.03
Al_2O_3	0.1	0.1	MnO	0.02	0.03
SiO_2	0.1	0.2	Fe_2O_3	0.02	0.03
P_2O_5	0.1	0.1	CoO	0.02	0.02
SO_3	0.1	0.1	NiO	0.02	0.03
Cl	0.1	0.1	CuO	0.02	0.01
K_2O	0.1	0.1	ZnO	0.02	0.01
CaO	0.1	0.1	As_2O_3	0.03	0.01
TiO_2	0.1	0.1	SnO_2	0.1	0.05
BaO	0.2	0.1	Sb_2O_5	0.15	0.07
PbO	0.2	0.1	Rb_2O	0.005	0.005
			SrO	0.005	0.005
			ZrO_2	0.005	0.005
			PbO	0.03	0.02

The SEM used was a FEI Inspect F which was operated at 25kV with a beam current of approximately 1.2nA. The X-ray spectra generated by the electron beam were detected using an Oxford Instruments X-act SDD detector. The quantification of detected elements was achieved using the Oxford Instruments INCA software. The EDS spectra were calibrated (optimised) using a cobalt standard. Deconvolution of the X-ray spectra and quantification of elements was improved by profile optimisation and element standardisation using pure elements and compounds (MAC standards). The chemical composition of the samples is presented in this report as stoichiometric oxides with oxide weight percent concentrations based on likely valence states (the exception being chlorine which is expressed as element wt%). The EDXRF used was an EDAX Eagle II which was operated at 40kV with a current of 1mA. The Eagle II was fitted with a glass capillary to focus the X-Ray beam on an area approximately 0.3mm in diameter. While compositional data on thin surface layers could be obtained using the SEM-EDS, the same could not be achieved using the EDXRF. Therefore EDXRF data was only obtained for the bulk glass and not for painted surfaces. The compositional data for Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, Cl, K_2O, CaO, TiO_2 and PbO was obtained exclusively using SEM-EDS. SrO and ZrO_2 data was obtained exclusively using EDXRF. SEM-EDS was not able to reliably detect either of these elements in the Beverley Minster glass, but EDXRF was able to detect these elements in some of the samples. CoO, NiO, As_2O_3, MnO, Fe_2O_3, CuO and PbO data was obtained using both techniques: below 0.25wt% the EDXRF data was more accurate (and precise), above 0.25wt% the SEM-EDS data was more accurate. The accuracy of the quantification of all oxides was checked by analysing a wide range of reference materials (Corning, NIST, DGG and Newton/Pilkington).

RESULTS

The presentation of the results has been separated into two sections: the first deals with the bulk composition of the glass as a whole, the second reports the examination of the black paint applied to the surface of the glass.

The glass

The chemical composition of the glass can be considered in two ways: the overall glass composition/type (ie the range of proportion of silica, alkalis and stabilisers) and the addition of selected elements to produce specific colours (in particular manganese, iron, cobalt and copper). Full data on the chemical composition of the glass can be found in Appendix 1.

The analysed samples from the west window of Beverley Minster can be grouped into a number of different glass types depending on the proportion of major elements (Figures 3 and 4). There are two major categories of glass present: soda-lime-silica, and flint glass. In addition there is a hybrid group with a composition which lies between flint glass and soda-lime-silica glass. One sample (6d1) has a composition which does not match any of the other glass and it is considered below.

The soda-lime-silica glasses were clearly made using pure materials (including a synthetic soda such as that made using the Leblanc process) and can be further divided into two groups: SLS1 with high calcium and SLS2 with low calcium. The flint glasses, besides silica, contain mainly potassium oxide and lead oxide and belong to the same broad type of glass used for the manufacture of some tablewares (Dungworth and Brain 2005; forthcoming). The flint glasses have been divided into Flint1 and Flint2 on the basis of their lead content as well as the concentrations of a range of other oxides. The flint glasses often contain small amounts of phosphorus and this generally correlates with the calcium content of these samples (Figure 5). It is possible that the calcium and phosphorus content of the flint glass is due to use of a small proportion of bone ash in the glass batch.

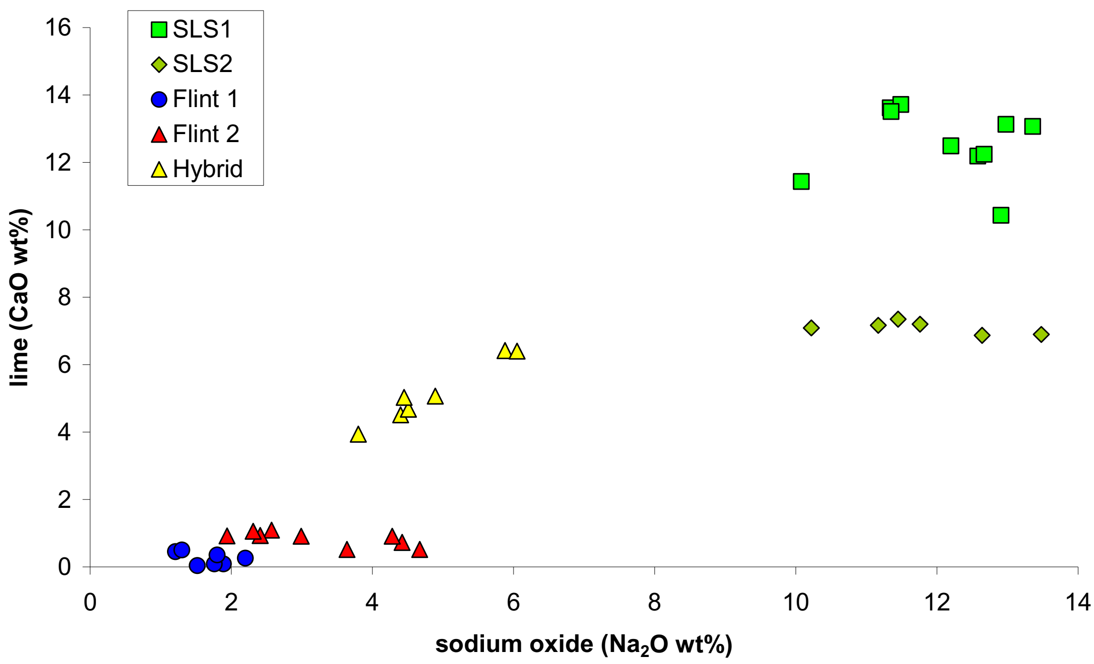

Figure 3. Sodium oxide and lime content of the Beverley Minster window glass (omitting 6d1)

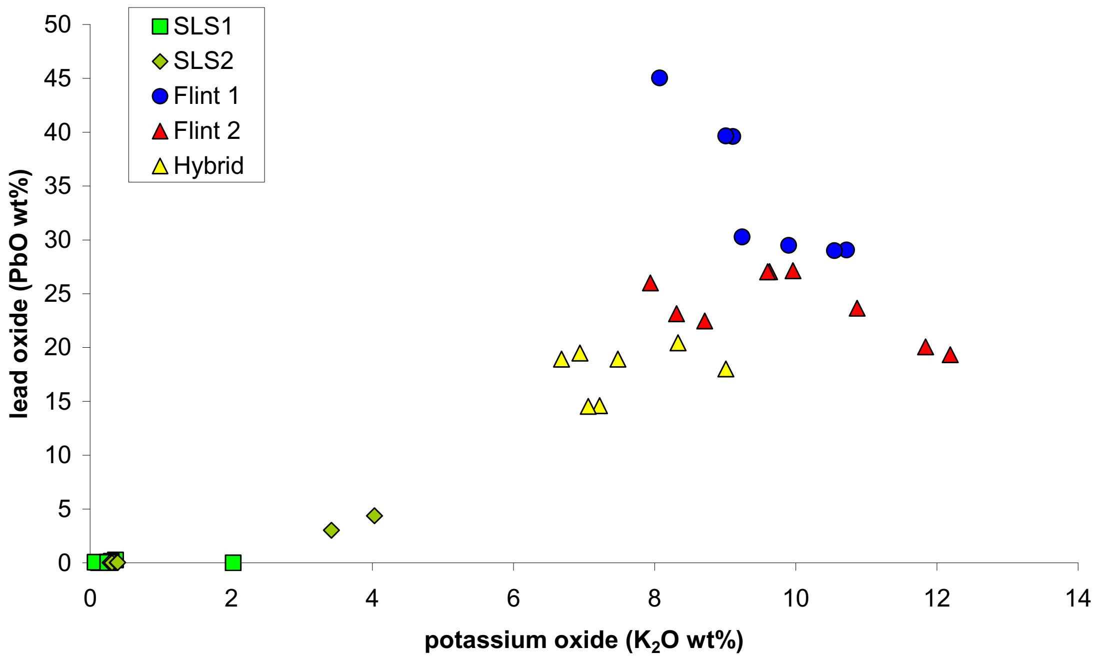

Figure 4. Potassium oxide and lead oxide contents of the Beverley Minster window glass (omitting 6d1)

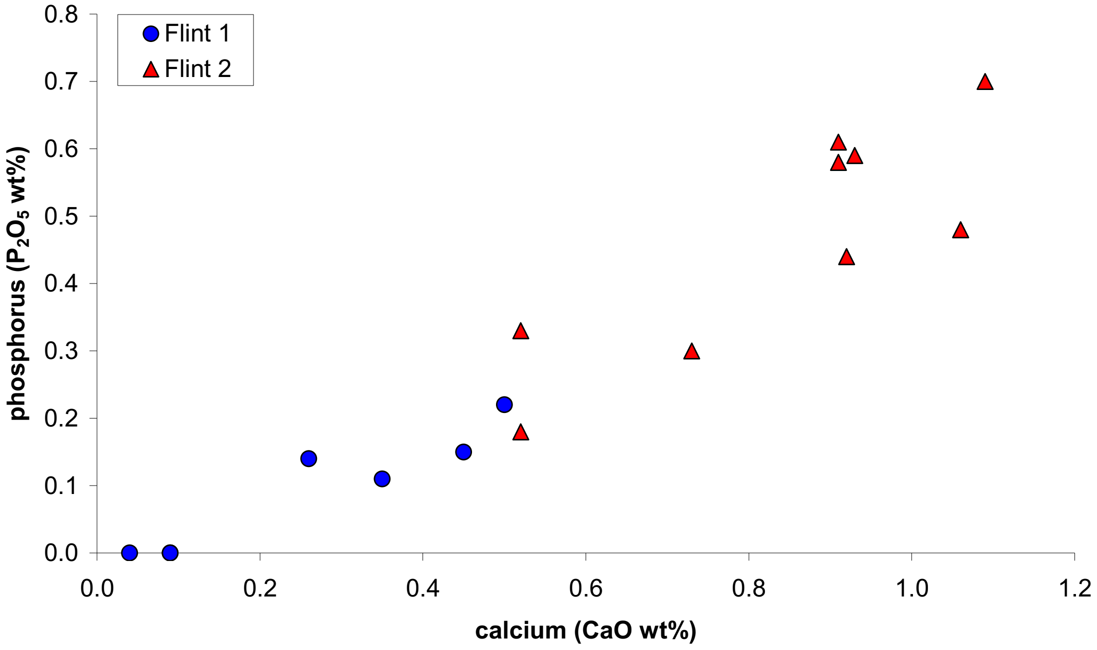

Figure 5. Calcium and phosphorus contents of the flint glass samples

The remaining samples have rather mixed compositions and contain a wide range of elements. The proportions of these elements generally lie between the flint and the soda-lime-silica glasses and this glass type has been labelled Hybrid.

Sample 6d1 has suffered from extensive corrosion at the surfaces (Figure 6). The glass is a potassium-silicate which contains negligible concentrations of any glass stabiliser elements (calcium, magnesium and lead). The low concentrations of any glass stabiliser provide the explanation for the severe corrosion of this sample. The absence of a stabiliser in this sample is curious as the role of calcium (and other divalent elements) in promoting glass stability was well understood by the beginning of the 19th century.

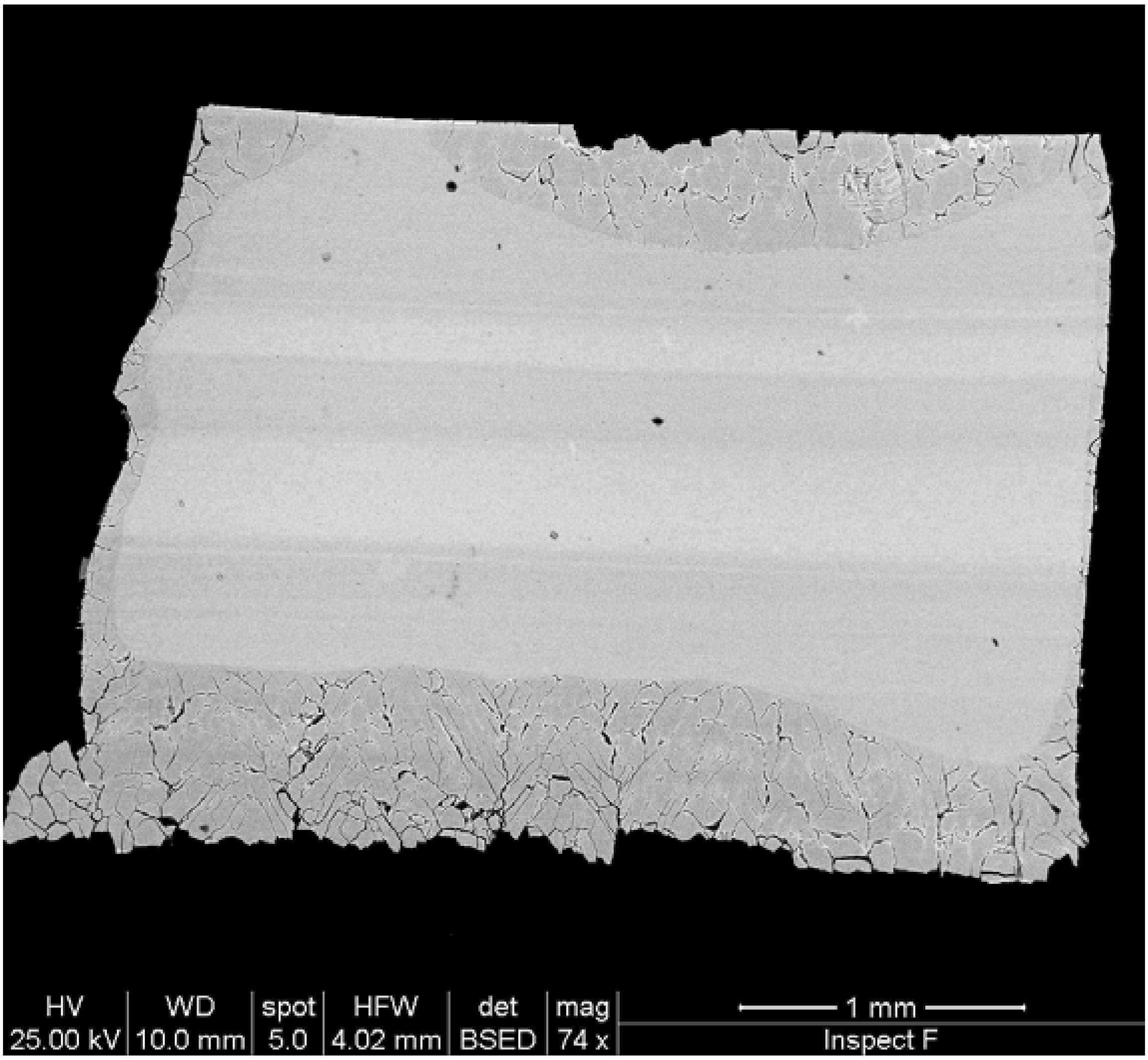

Figure 6. SEM image (back-scattered electron detector) of sample 6d1. The surfaces of the glass have undergone severe corrosion

The Beverley Minster window glass samples include a wide range of colours which were achieved through the deliberate addition of varying amounts of metal oxides (Figure 7). The colourless glasses are generally characterised by low levels of any metal oxides that could give colour. On average the iron oxide content of the colourless glass is 0.22wt% Fe_2O_3, which is consistent with ordinary window glass of the 19th century (Dungworth 2009; Dungworth and Wilkes 2010). Almost all of the coloured glass contains elevated levels of iron oxide and it is likely that this was deliberately added. Iron can give blue, green or even yellow colour to a glass depending on its concentration and oxidation state, and the presence of other metal oxides. The blue glass was usually coloured using small amounts of cobalt, although this was often accompanied by a range of other metals (manganese, iron, copper and nickel). Copper was used to produce blue-green colours in pot metals and was also used to make the thin layers of flashed red glass. In the former case the colour was present as oxides throughout the glass while in the latter case the copper was present as metallic nano-particles in the thin flashed layer. The darker green glass contained higher concentrations of copper than the pale green. In addition, the darker green glass was usually a flint glass while the pale green was usually a soda-lime-silica glass.

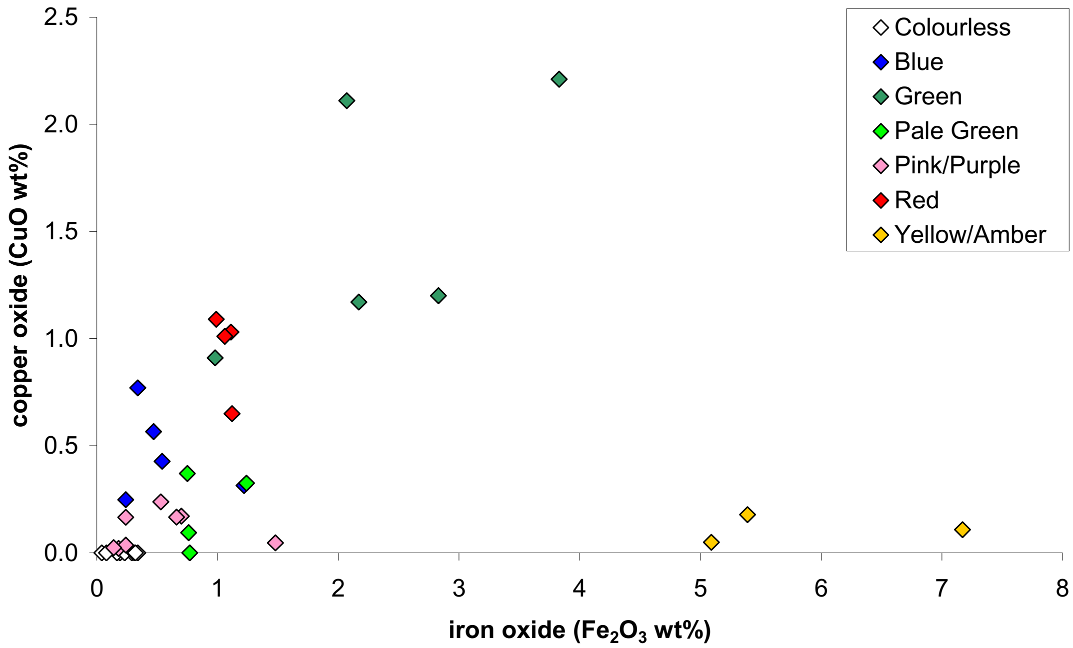

Figure 7. Iron oxide and copper oxide contents of the Beverley Minster window glass

Painted surfaces

The surfaces of many of the fragments of glass are painted with a black material (Table 1). This paint is clearly visible when examined with the SEM as surfaces layers which have a higher average atomic number than the underlying glass (Figure 8). These surfaces are usually 20–30 microns thick and contain a range of crystals, some of which appear to be material that has not entirely reacted while some appears to have crystallised from a melt. Many of the samples show that the paint has undergone varying degrees of corrosion (Figure 9). In some cases the corrosion was so severe that it was not possible to carry out any meaningful chemical analysis of the paint layer.

Where paint could be analysed (see Appendix 2) it was generally composed of silica and lead oxide (Figure 10) with numerous metal oxides (Figure 11). The sum of silica and lead oxide in the paint on panel 2a glass was usually higher (mean 75wt%) than that on 6d (mean 60wt%). The analytical technique used (see above) allows for the detection of boron although the detection level for this element is substantially higher (at least 1wt%) than most other elements sought. Boron was not detected in any of the paint surfaces and so it is unlikely that borax was used in these paints. The low levels of silica and lead oxide in the panel 6d paint is due, at least in part, to the presence of higher concentrations of iron oxide (Figure 11). Panel 2a paint generally contains a wide variety of metal oxides to give the black appearance, while the colour of panel 6d paint was achieved primarily through its iron content, resulting in a reddish-brown appearance in reflected light (Figure 12). Panel 2a contains high levels of cobalt. While cobalt is usually used to give a blue colour to glasses and enamels, at the concentrations seen in this paint the result would be effectively black.

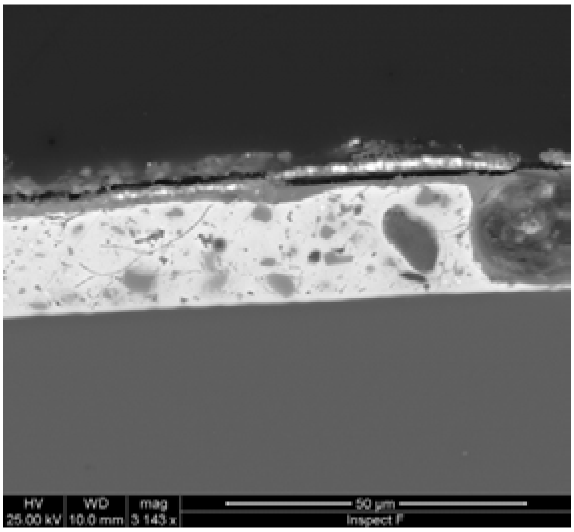

Figure 8. SEM image (back-scattered electron detector) of paint on the surface of 2a5. The paint is the brighter region; the grey area below is the glass

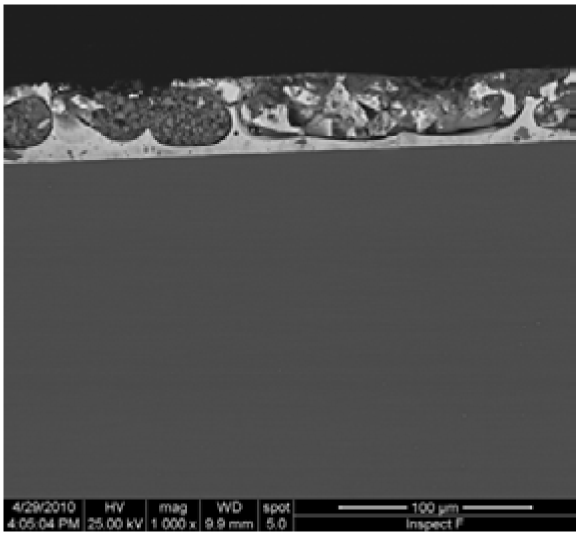

Figure 9. SEM image (back-scattered electron detector) of corroded paint on the surface of 6d15. While some areas of paint seem to have survived most has been severely affected by corrosion

The panel 2a paint can be divided into two groups: the first of which (2a2, 2a5, 2a7 and 2a13) contains chromium, zinc and antimony, while the second group (2a6, 2a9, 2a10 and 2a12) contains no detectable amounts of these oxides. Chromium produces a green colour in glasses and enamels (although at the concentrations seen in these paint samples would have produced a black). Zinc does not normally colour glass and it may have been introduced as an impurity with some other material deliberately added to the paint. Antimony can be used to produce white or yellow colours, however, it is most commonly used to make an opaque glass.

The painted surfaces all contain appreciable concentrations of sodium and potassium but it is far from certain whether either of these two oxides was deliberately added to the raw materials used to make the paint. The concentrations of the two alkalis in the painted surfaces generally correlate with the concentrations of the alkalis in the underlying glass (Figure 13). The detailed study of the painted surfaces on the Margam Castle glass showed that (presumably during the firing process) alkalis diffused from the glass into the paint (and vice versa). The strong correlation between the alkalis in the Beverley Minster glass and associated paint suggests that alkalis were not part of the paint batch.

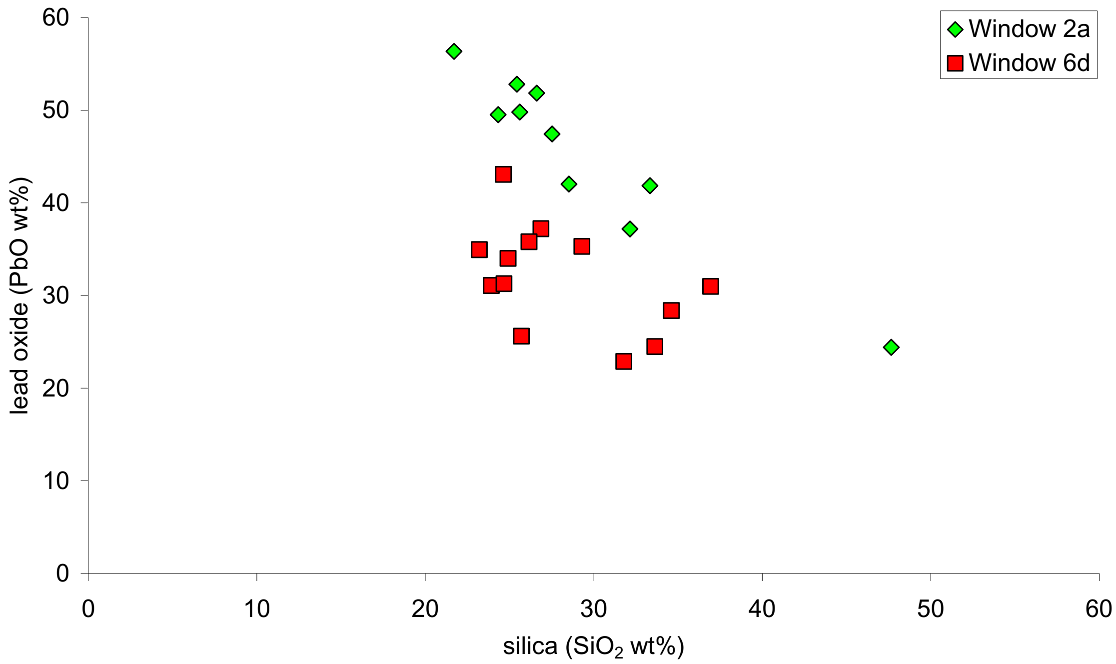

Figure 10. Silica and lead oxide contents of the painted surfaces

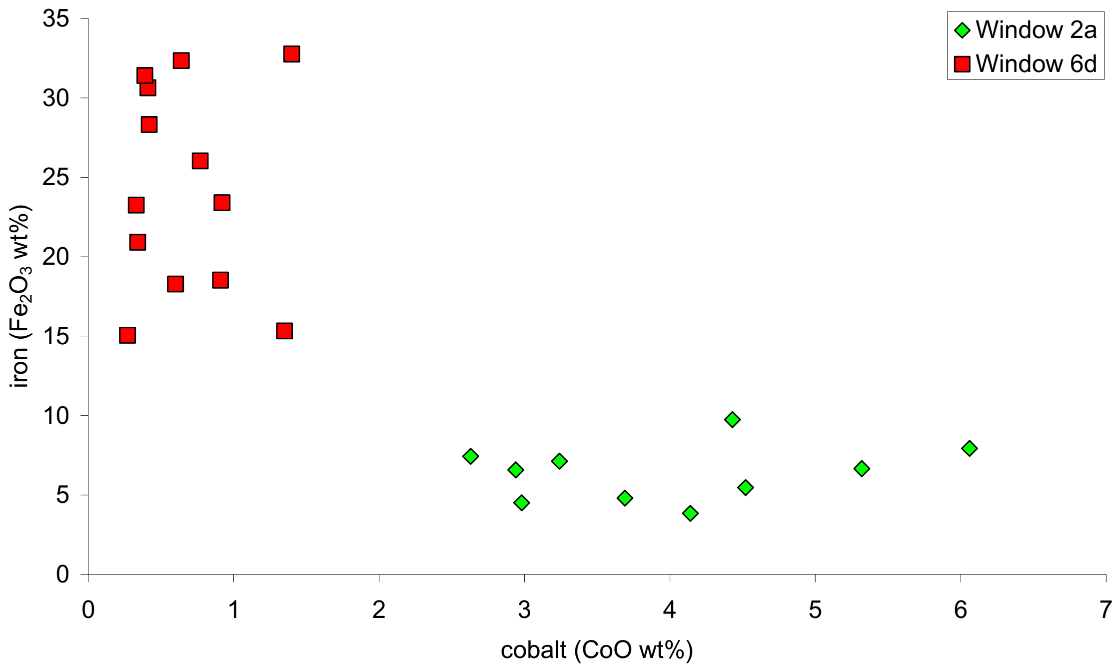

Figure 11. Cobalt and iron oxide contents of the painted surfaces

Figure 13. Panels 2a and 6d seen in reflected light

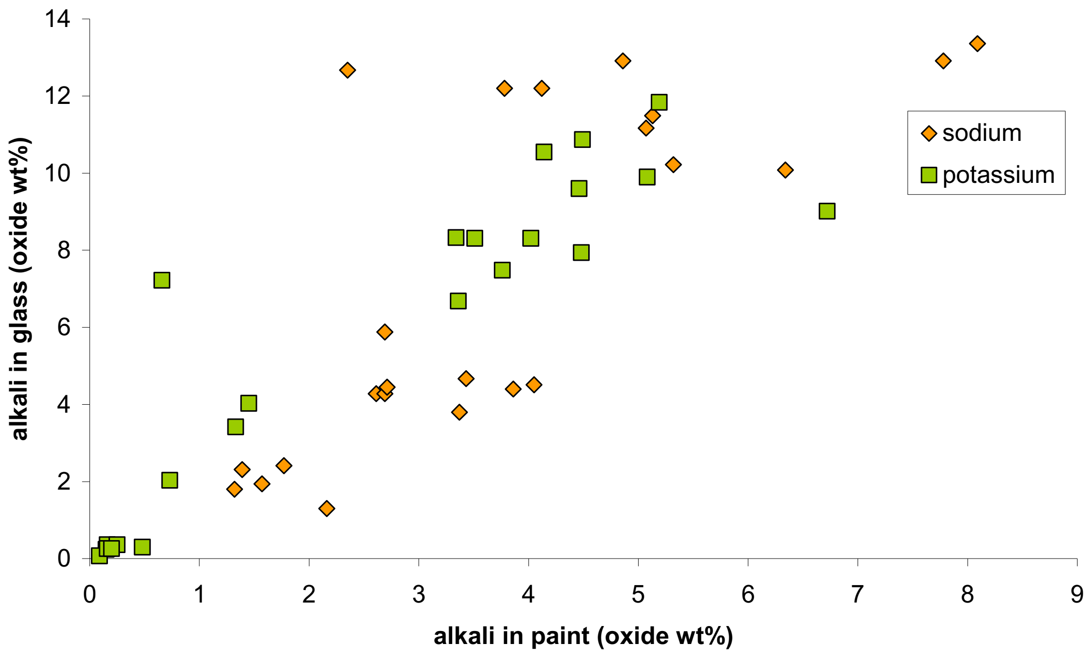

Figure 13. Alkali contents of the painted surfaces compared with the alkali contents of the associated glass

DISCUSSION

The Hardman window glass from Beverley Minster displays a wide range of chemical compositions. This is evident in both the base glass composition as well as the range and concentrations of various metal oxides added to produce particular colour. While plain colourless window glass of the period was made using a simple recipe of sand, soda (sodium carbonate or sodium sulphate) and lime (calcium carbonate), the Beverley Minster glass includes some soda-lime-silica glass but also some flint glass (potassium-lead-silicate glass).

Soda-lime-silica glass

The colourless soda glass (ie SLS1 excluding the coloured glass samples) used by Hardmans has a composition which is virtually indistinguishable from that of plain colourless vernacular glass of the period (Table 4). The only significant difference is the presence of manganese in the Hardman glass. Manganese has long been added to glass in small quantities to reduce the colour produced by iron and this was probably the intention of those who made the Hardman glass. The iron content of this glass was very low however, and it is uncertain whether the manganese would have had an appreciable effect.

Table 4. Chemical composition of some colourless 19th-century flat glass (Sources: 1 = Dungworth and Adams 2010; 2 = Dungworth 2009; 3 = Wilkes and Dungworth 2010; 4 = this report; 5 = Hatton 2004; 6 = Dungworth and Wilkes 2010; 9 = Dungworth 2010)

Site	Source	Date	Na_2O	MgO	Al_2O_3	P_2O_5	SO_3	Cl	K_2O	CaO	MnO	Fe_2O_3	SrO
Margam kelp	1	1834	8.1	5.3	1.6	1.4	0.1	0.6	3.8	11.9	0.07	0.58	0.61
Margam soda	1	1834	10.5	0.1	1.2	<0.2	<0.1	1.0	0.2	16.3	0.14	0.35	0.02
Chatsworth	2	1837–40	14.0	<0.1	0.7	<0.2	0.3	<0.1	<0.1	14.1	<0.02	0.33	0.02
Tower of London	3	1840	11.8	0.3	0.5	<0.2	0.4	<0.1	0.1	14.6	0.05	0.17	0.04
Beverley SLS1 (colourless)	4	1859-65	12.3	0.1	0.7	<0.2	0.5	<0.1	0.2	13.1	0.36	0.25	0.04
Nailsea	5	1830–70	13.1	0.2	0.8	<0.2	0.6	<0.1	0.1	13.6	0.06	0.33	0.02
Wentworth	6	1877	11.9	0.4	0.7	<0.2	0.2	<0.1	0.3	14.3	<0.02	0.28	0.03
Welch Road	7	1894–95	11.4	0.1	1.5	<0.2	0.4	<0.1	0.7	13.4	<0.02	0.25	0.02

The coloured soda-lime-silica glass from Beverley Minster falls into two compositional groups. The first is identical to the colourless SLS1 described above except for the presence of a range of metal oxides used to produce a range of colours (pale green, pink and plum). The second group (SLS2) comprises the red flashed glass and two samples of pale green glass. SLS2 is distinguishable from SLS1 due to the low calcium content of the former. Despite the compositional differences between SLS1 and SLS2 they were both made at the same glasshouse. The red flash SLS2 glass was present on the surface of SLS1 glass and this could only be achieved if both glasses were available in their molten state during forming.

Flint Glass

The flint glass is a potassium-lead-silicate glass with a composition which resembles the flint glass used for the manufacture of tableware. The colourless lead-potassium-silicate glass developed in the late 17th century continued to be used for the manufacture of tablewares into the 19th century. The classic recipe comprised 1 part potash, 2 parts lead oxide and 3 parts sand which would give a glass with a composition comparable with Flint1. Most of the flint glass was used to produce coloured glass and much of this was strongly coloured. Medieval window glass did not make use of lead-based glass in this way but it was used in 1834 at Margam Castle (Dungworth and Adams 2010) and is described by contemporary texts (eg Pellatt 1849, 34; Cable 2008, 255–285). The use of lead-based glasses for the production of windows seems, however, to be restricted to the manufacture of *coloured* window glass.

The Margam Castle coloured flint glass contains fewer impurities compared to the Beverley Minster Hardmans glass. The presence of impurities not normally associated with flint glass is particularly apparent among Flint 2 glass samples. Some of the elements detected in this glass do appear to have been deliberately added rather than simply due to the use of impure raw materials. The correlation between calcium and phosphorus, for example, suggests that a small proportion of bone ash was added to the batch. Bone ash is occasionally mentioned by contemporary sources as an ingredient in the manufacture of opalescent glass (Cable 2008, 408–410).

Hybrid Glass

The final group of glass (Hybrid) contained significant proportions of almost every element found in 19th-century glass. In particular, this glass contains sodium and calcium as well as potassium and lead. The correlation between sodium and calcium is striking and suggests that the glass was made using either a proportion of soda-lime-silica glass cullet or that a complex glass was made by combining all of the raw materials used in the manufacture of soda and flint glass. This hybrid glass contrasts with the glass used at Margam Castle, which tended to be either soda *or* flint glass. Nevertheless, some of recipes given by Bontemps in 1868 (Cable 2008, 255–285) indicate that some coloured window glass was made using a variety of raw materials including soda, lime, potash *and* lead.

Coloured Glass

The Beverley Minster glass includes a wide variety of colours, including red, blue, green, pink and purple. These colours were achieved by the careful addition of selected metal oxides and the control of glass melting conditions. Most of the coloured glass samples can be paralleled with recipes given by Bontemps (Cable 2008, 255–285). Many of the colours rely on the presence of several different metal oxides and this in part appears to reflect the requirements of producing coloured glass for Gothic Revival stained glass windows. The blue glasses are a case in point. While blue glass can be made by simply adding a small amount of cobalt, the Beverley Minster blue glass commonly contains small amounts of manganese, iron, copper and nickel in addition to cobalt. The deliberate addition of these other oxides would moderate the colour of the cobalt-blue glass and may have helped to produce a blue glass that was closer to the medieval originals that the glassmakers were attempting to copy. The cobalt available to medieval glassmakers was an impure material and naturally contained a range of metal oxides such as manganese, iron, copper and nickel. The 19th century glassmakers had pure cobalt available but deliberately added the remaining oxides, possibly on the basis of 19th-century analyses of medieval glass (Shepherd 2009).

Paint

The paint applied to the surface of the Beverley Minster glass contains lead and silica as well as a range of other ingredients. The alkalis in the paint do not appear to have been deliberately added but to have diffused into the paint from the underlying glass during the firing process. Bontemps gives two recipes for the flux used to make paint (Cable 2008, 540). Flux A contains 25 parts lead oxide and 10 parts silica, while Flux B contains 25 parts lead oxide, 12 parts flint glass cullet and 5 parts borax. Both of these recipes would yield a paint containing a much higher proportion of lead than seen in any of the Beverley Minster samples. The silica and lead oxide concentrations in the Beverly Minster paint suggest that silica and lead oxide were mixed in the ratio 2:3, although the severe corrosion seen suggests that this may not be the original composition of the paint. No boron was detected and it is most unlikely that borax (or any other boron compound) was used to make the paint.

The Beverley Minster paint samples from panel 2a contain a very wide variety of metal oxides which at high concentrations would render it black. Contemporary recipes suggest the used of several different metal oxides in varying proportions to achieve grey, black or other colours (Cable 2008, 540–541). For grey, Bontemps recommends burnt umber which would contain manganese and iron (as well as clay minerals). The elevated levels of aluminium in the paint compared to the underlying glass, could derive from clay minerals in a burnt umber, however, the manganese concentrations in the paint samples are somewhat lower than might be expected. For black, Bontemps recommends burnt umber and azure (a hydrated copper carbonate), but none of the paint samples contains copper concentrations as high as those predicted by his recipe. Perhaps the most striking aspect of the paint is the inclusion of such a wide variety of metal oxides: chromium, manganese, iron, cobalt, nickel, copper, zinc and antimony. This suggests that on occasion the glass painters (or their suppliers) added every metal oxide available to them to achieve a desired shade of grey or black. In contrast, the samples from panel 6d show only iron oxide at a much higher level, giving a black appearance in transmitted light but a reddish-brown in reflected light.

The SEM examination of the paint demonstrates that it has deteriorated and in some cases nothing is left but corrosion products. The chemical analysis of the surviving portions, however, has not clearly demonstrated any fundamental shortcoming in the composition of the paint. A study of early lead crystal (Dungworth and Brain 2005) showed that glass with less than 20wt% lead oxide (in the absence of substantial concentrations of calcium or some other glass stabiliser) was chemically unstable. The lead content of all of the Beverley Minster paint samples, however, is in excess of 20wt% PbO. The other oxides present in the paint are all present at reasonable concentrations which cannot be responsible for the degree of deterioration. However, the different extents of deterioration of the paint on the two parts of the window may relate to their different compositions.

As the recipes used to make the paint seem to have been appropriate and cannot be used to explain its deterioration, other explanations must be sought. Two possibilities should be considered: the firing of the paint and the environment it has occupied on the west side of Beverley Minster. If the paint was not fired to a sufficiently high temperature then it would not form a proper glass and so would be susceptible to corrosion. The evidence for diffusion of alkalis from the glass into the paint, however, suggests that the firing was carried out at an appropriate temperature and for a sufficient time. The use of flint glass as a substrate, however, does suggest that relatively low firing temperatures must have been used to avoid this substrate glass softening and deforming in the kiln; this in turn suggests that the glass paints used should have been formulated to melt at a low temperature.

The environment could potentially play a significant role in the deterioration of the paint. The corrosion process depends on the presence of water (Newton and Davison 1989), and given the position of the window on the exposed west face of the Minster, it is very likely that condensation forms on the inner (painted) side in cold weather. It is also possible that the heating systems used in the Minster since the nineteenth century may have accelerated the corrosion process by releasing acidic fumes into the atmosphere.

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APPENDIX I

Chemical composition of the glass

Sample	colour	Type	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	PbO
2a01	colourless	SLS1	13.0	<0.1	0.5	72.0	<0.2	0.4	<0.2	0.1	13.1	0.03
2a02	pale blue	Hybrid	5.9	0.2	0.8	61.5	<0.2	0.3	0.2	7.2	6.4	14.6
2a03	green	Flint 2	4.4	<0.1	0.5	56.6	0.3	<0.2	<0.2	8.7	0.7	22.5
2a04a	colourless base	SLS1	12.6	0.1	0.9	71.9	<0.2	0.5	<0.2	0.3	12.2	<0.2
2a04b	red flash	SLS2	13.5	<0.1	1.7	72.8	<0.2	<0.2	0.2	0.3	6.9	<0.2
2a05	pale green	SLS1	12.2	0.2	1.2	69.8	<0.2	0.4	0.3	0.4	12.5	0.28
2a06	yellow	Hybrid	4.4	0.1	1.0	55.1	<0.2	<0.2	<0.2	7.5	4.5	18.9
2a07a	colourless base	SLS1	12.7	<0.1	0.8	71.8	<0.2	0.5	<0.2	0.2	12.2	<0.2
2a07b	red flash	SLS2	12.6	<0.1	1.3	74.7	<0.2	<0.2	<0.2	0.3	6.9	<0.2
2a08	pale blue-green	Hybrid	6.1	0.2	0.8	61.3	<0.2	0.3	0.2	7.1	6.4	14.5
2a09	amber	Hybrid	4.5	0.2	1.0	53.1	<0.2	0.2	0.2	6.7	4.7	18.9
2a10	murray	Flint 2	4.7	<0.1	0.5	54.3	<0.2	<0.2	<0.2	7.9	0.5	26.0
2a11	pink-purple	Hybrid	4.9	<0.1	0.8	58.5	<0.2	<0.2	0.2	6.9	5.1	19.5
2a12	colourless	SLS1	13.4	<0.1	0.4	71.5	<0.2	0.6	<0.2	<0.1	13.1	<0.2
2a13	blue	Flint 2	4.3	<0.1	0.5	56.4	0.6	<0.2	<0.2	8.3	0.9	23.1
6d01	purple	Ungrouped	0.8	<0.1	1.2	73.9	<0.2	<0.2	0.2	16.0	0.1	5.18
6d02	blue	Flint 2	3.6	<0.1	0.3	56.0	0.3	<0.2	0.2	9.6	0.5	27.1
6d03a	colourless base	Flint 1	1.9	<0.1	0.3	48.2	<0.2	<0.2	<0.2	9.1	0.1	39.6
6d03b	white flash	Flint 1	1.5	<0.1	0.2	42.1	<0.2	<0.2	0.2	8.1	<0.1	45.0
6d03c	colourless flash	Flint 1	1.8	<0.1	0.4	48.3	<0.2	<0.2	0.2	9.0	0.1	39.7
6d04a	colourless base	SLS1	11.3	0.2	0.8	71.7	<0.2	0.5	<0.2	0.3	13.6	0.05
6d04b	red flash	SLS2	11.5	0.1	1.6	74.5	<0.2	<0.2	<0.2	0.4	7.4	<0.2
6d05	blue	Flint 2	2.6	<0.1	0.3	55.3	0.7	<0.2	0.2	10.0	1.1	27.1
6d06	pale green	SLS2	11.2	0.1	1.5	70.9	<0.2	0.5	0.4	3.4	7.2	3.03
6d07	green	Flint 2	1.9	<0.1	0.6	54.4	0.4	<0.2	<0.2	10.9	0.9	23.7
6d08	plum	SLS1	10.1	0.1	0.8	70.6	<0.2	0.4	0.2	2.0	11.4	0.03
6d09	green	Hybrid	4.5	0.3	0.7	58.7	<0.2	0.2	0.2	9.0	5.0	18.0
6d10	pale blue	Flint 2	3.0	<0.1	0.3	61.9	0.6	0.3	0.2	12.2	0.9	19.3
6d11	pale green	SLS2	10.2	<0.1	1.3	69.8	<0.2	0.4	0.4	4.0	7.1	4.37
6d12	green	Flint 2	2.4	<0.1	0.4	58.4	0.6	0.3	0.3	11.8	0.9	20.1
6d13	purple	Flint 1	1.8	<0.1	0.4	53.8	<0.2	<0.2	<0.2	9.9	0.4	29.5
6d14	green	Flint 2	2.3	<0.1	0.4	53.5	0.5	<0.2	0.2	9.6	1.1	27.0
6d15a	colourless base	SLS1	11.5	0.2	0.8	71.2	<0.2	0.5	<0.2	0.3	13.7	0.05
6d15b	red flash	SLS2	11.8	<0.1	1.6	74.4	<0.2	<0.2	<0.2	0.4	7.2	<0.2
6d16	purple	Flint 1	2.2	<0.1	0.3	53.5	<0.2	<0.2	<0.2	9.2	0.3	30.3
6d17	pink	SLS1	12.9	<0.1	0.6	70.8	<0.2	0.7	<0.2	0.3	10.4	<0.2
6d18	yellow	Hybrid	3.8	0.1	1.0	54.4	<0.2	0.3	0.2	8.3	3.9	20.4
6d19	pink	Flint 1	1.2	<0.1	0.4	54.7	<0.2	<0.2	0.2	10.7	0.5	29.1
6d20	pink-purple	Flint 1	1.3	<0.1	0.3	54.8	0.2	<0.2	<0.2	10.6	0.5	29.0
6d21	colourless	SLS1	11.4	0.2	0.8	71.1	<0.2	0.6	<0.2	0.3	13.5	0.03

Chemical composition of the glass (continued)

Sample	Cr_2O_3	MnO	Fe_2O_3	CoO	NiO	CuO	ZnO	As_2O_3	SnO_2	Sb_2O_3	SrO	ZrO_2	BaO
2a01	<0.01	0.10	0.19	<0.02	<0.02	<0.02	<0.02	0.10	<0.2	0.2	0.03	0.01	<0.2
2a02	<0.01	0.58	1.22	0.04	0.02	0.31	<0.02	0.11	<0.2	<0.2	<0.05	0.01	<0.2
2a03	0.02	1.26	2.83	<0.02	<0.02	1.20	<0.02	<0.05	<0.2	<0.2	<0.05	0.01	0.37
2a04a	<0.01	0.37	0.29	<0.02	<0.02	<0.02	<0.02	0.35	<0.2	0.2	0.03	0.00	<0.2
2a04b	<0.1	0.05	0.99	<0.1	<0.1	1.09	<0.1	<0.2	2.2	<0.2	<0.2	<0.2	<0.2
2a05	0.02	1.11	0.76	<0.02	<0.02	0.09	<0.02	0.24	<0.2	<0.2	0.03	0.01	<0.2
2a06	<0.01	2.08	5.39	<0.02	<0.02	0.18	<0.02	0.06	<0.2	<0.2	<0.05	0.00	<0.2
2a07a	<0.01	0.35	0.23	<0.02	<0.02	<0.02	<0.02	0.35	<0.2	0.2	0.03	0.00	<0.2
2a07b	<0.1	0.08	1.12	<0.1	<0.1	0.65	<0.1	<0.2	1.8	<0.2	<0.2	<0.2	<0.2
2a08	<0.01	0.58	1.24	0.04	0.02	0.33	<0.02	0.12	0.2	<0.2	<0.05	0.01	<0.2
2a09	<0.01	2.34	7.17	<0.1	<0.02	0.11	<0.02	0.07	0.3	<0.2	<0.05	0.01	<0.2
2a10	<0.01	2.57	2.36	<0.02	<0.02	0.04	<0.02	<0.05	<0.2	<0.2	<0.05	0.01	0.31
2a11	<0.01	1.61	1.48	<0.02	<0.02	0.05	<0.02	0.09	<0.2	<0.2	<0.05	0.01	<0.2
2a12	<0.01	0.11	0.17	<0.02	<0.02	<0.02	<0.02	0.10	<0.2	0.2	0.03	0.01	<0.2
2a13	<0.01	1.93	0.34	0.03	<0.02	0.77	0.11	0.11	<0.2	<0.2	<0.05	0.01	1.23
6d01	<0.01	1.47	0.24	<0.02	<0.02	0.17	<0.02	<0.05	<0.2	<0.2	<0.05	0.01	<0.2
6d02	<0.01	0.48	0.47	0.03	0.02	0.57	<0.02	<0.05	<0.2	<0.2	<0.05	0.01	<0.2
6d03a	<0.01	0.21	0.04	<0.02	<0.02	<0.02	<0.02	<0.05	<0.2	0.2	<0.05	0.01	<0.2
6d03b	<0.1	0.52	0.17	<0.1	<0.1	<0.1	<0.1	<0.2	<0.2	1.9	<0.2	<0.2	<0.2
6d03c	<0.1	0.23	0.08	<0.1	<0.1	<0.1	<0.1	<0.2	<0.2	0.2	<0.2	<0.2	<0.2
6d04a	<0.01	0.30	0.31	<0.02	<0.02	<0.02	<0.02	0.31	<0.2	<0.2	0.05	0.01	<0.2
6d04b	<0.1	0.11	1.06	<0.1	<0.1	1.01	<0.1	<0.2	1.8	<0.2	<0.2	<0.2	<0.2
6d05	<0.01	0.56	0.54	0.03	0.02	0.43	<0.02	0.18	<0.2	<0.2	<0.05	0.01	<0.2
6d06	<0.01	0.05	0.75	<0.02	<0.02	0.37	<0.02	0.21	<0.2	0.2	<0.05	0.01	<0.2
6d07	0.03	0.43	3.83	0.04	<0.02	2.21	0.04	<0.05	<0.2	<0.2	<0.05	0.01	<0.2
6d08	<0.01	4.02	0.24	<0.02	<0.02	0.04	<0.02	<0.05	<0.2	<0.2	0.02	0.00	<0.2
6d09	<0.01	0.38	0.98	<0.02	<0.02	0.91	<0.02	<0.05	0.4	<0.2	<0.05	0.01	<0.2
6d10	<0.01	0.26	0.24	<0.02	<0.02	0.25	<0.02	<0.05	<0.2	<0.2	<0.05	0.01	<0.2
6d11	<0.01	0.08	0.77	<0.02	<0.02	<0.02	<0.02	0.18	<0.2	0.4	<0.05	0.01	<0.2
6d12	<0.01	0.56	2.17	<0.02	<0.02	1.17	0.03	0.06	<0.2	<0.2	<0.05	0.01	0.31
6d13	<0.01	2.69	0.53	<0.02	<0.02	0.24	<0.02	<0.05	<0.2	<0.2	<0.05	0.01	0.22
6d14	<0.01	0.32	2.07	<0.02	<0.02	2.11	0.05	0.06	<0.2	<0.2	<0.05	0.01	<0.2
6d15a	<0.01	0.29	0.32	<0.02	<0.02	<0.02	<0.02	0.30	<0.2	0.4	0.05	0.01	<0.2
6d15b	<0.1	0.07	1.11	<0.1	<0.1	1.03	<0.1	<0.2	1.8	0.2	<0.2	<0.2	<0.2
6d16	<0.01	3.24	0.14	<0.02	<0.02	0.02	<0.02	<0.05	<0.2	<0.2	<0.05	0.02	<0.2
6d17	<0.01	3.25	0.18	<0.02	<0.02	0.02	<0.02	0.16	<0.2	0.3	0.02	<0.005	<0.2
6d18	<0.01	1.77	5.09	<0.02	<0.02	0.05	<0.02	<0.05	<0.2	<0.2	<0.05	0.01	<0.2
6d19	<0.01	1.69	0.70	<0.02	<0.02	0.17	<0.02	<0.05	<0.2	<0.2	<0.05	0.02	0.32
6d20	<0.01	1.66	0.66	<0.02	<0.02	0.17	<0.02	<0.05	<0.2	<0.2	<0.05	0.01	0.32
6d21	<0.01	0.98	0.34	<0.02	<0.02	<0.02	<0.02	<0.05	<0.2	0.3	0.04	0.01	<0.2

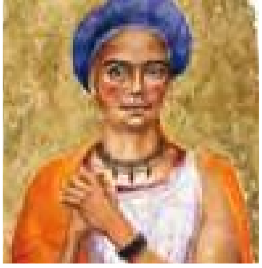
APPENDIX 2

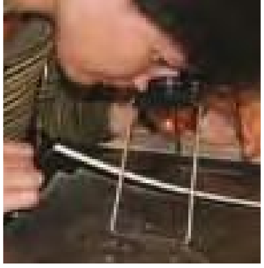
Chemical composition of the paint

Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	PbO
2a02	2.7	0.3	1.1	21.7	0.7	0.3	<0.2	0.7	1.1	56.4
2a05	4.1	0.4	1.4	25.6	0.3	0.2	<0.2	0.3	1.5	49.8
2a05	3.8	0.3	1.3	25.4	0.4	0.4	0.2	0.2	1.6	52.8
2a06	3.9	0.2	1.0	33.3	0.5	0.2	<0.2	3.8	2.5	41.9
2a07	2.4	0.3	1.8	24.3	0.9	0.7	0.4	0.2	2.0	49.5
2a09	4.1	0.4	1.4	32.2	<0.2	0.7	<0.2	3.4	2.7	37.2
2a10	3.4	0.3	1.3	28.5	<0.2	0.6	<0.2	4.5	1.1	42.0
2a12	8.1	0.3	1.0	47.7	<0.2	0.8	<0.2	<0.1	7.5	24.4
2a13	2.7	0.2	1.1	27.5	0.2	0.6	<0.2	4.0	1.1	47.4
2a13	2.6	0.3	0.9	26.6	<0.2	0.8	0.2	3.5	0.9	51.9
6d06	5.1	0.2	2.2	31.8	0.5	0.7	<0.2	1.3	2.6	22.9
6d07	1.6	0.2	2.8	24.9	0.3	0.4	<0.2	4.5	2.7	34.0
6d08	6.3	0.2	2.6	36.9	0.3	0.6	<0.2	0.7	4.8	31.0
6d09	2.7	0.3	2.3	34.6	0.3	0.9	<0.2	6.7	4.3	28.4
6d11	5.3	0.2	2.6	25.7	0.4	0.4	<0.2	1.5	2.4	25.6
6d12	1.8	0.2	2.9	26.9	0.3	0.5	<0.2	5.2	3.1	37.2
6d13	1.3	0.3	2.3	23.2	0.3	0.5	<0.2	5.1	2.6	34.9
6d14	1.4	0.2	1.8	23.9	0.3	0.4	<0.2	4.5	1.7	31.1
6d15	5.1	0.2	3.3	26.2	0.3	0.4	<0.2	0.5	4.3	35.8
6d17	7.8	0.2	3.3	33.6	0.2	0.4	<0.2	0.2	4.1	24.5
6d17	4.9	0.1	2.5	24.7	0.3	0.4	<0.2	0.2	3.1	31.3
6d18	3.4	0.2	3.4	29.3	0.3	0.6	<0.2	3.3	3.8	35.3
6d20	2.2	0.3	2.3	24.6	0.3	0.5	<0.2	4.1	3.1	43.1

Chemical composition of the paint (continued)

Sample	Cr_2O_3	MnO	Fe_2O_3	CoO	NiO	CuO	ZnO	Sb_2O_3	BaO
2a02	1.2	1.0	5.5	4.5	0.2	0.6	1.5	0.3	<0.2
2a05	0.9	2.1	7.1	3.2	0.3	0.5	1.6	0.4	<0.2
2a05	0.6	0.8	4.8	3.7	0.3	0.7	1.8	0.5	0.2
2a06	<0.1	1.9	6.6	2.9	0.1	0.3	<0.1	<0.2	0.2
2a07	0.7	1.0	6.7	5.3	0.4	1.3	1.3	0.6	<0.2
2a09	<0.1	2.4	9.8	4.4	0.3	0.2	<0.1	<0.2	0.3
2a10	<0.1	2.8	7.9	6.1	0.4	<0.1	<0.1	<0.2	0.2
2a12	<0.1	0.9	3.9	4.1	0.3	<0.1	<0.1	<0.2	<0.2
2a13	0.6	1.5	7.4	2.6	0.2	0.3	1.2	0.5	0.2
2a13	0.6	1.0	4.5	3.0	0.2	0.3	1.3	0.6	0.5
6d06	<0.1	0.2	30.6	0.4	<0.1	0.7	<0.1	0.2	<0.2
6d07	<0.1	0.3	26.0	0.8	<0.1	0.7	<0.1	<0.2	<0.2
6d08	<0.1	0.9	15.1	0.3	<0.1	<0.1	<0.1	<0.2	<0.2
6d09	<0.1	0.3	15.3	1.4	<0.1	1.6	0.1	0.2	<0.2
6d11	<0.1	0.8	32.8	1.4	<0.1	0.5	<0.1	<0.2	<0.2
6d12	<0.1	0.2	20.9	0.3	<0.1	0.3	<0.1	<0.2	<0.2
6d13	<0.1	0.3	28.3	0.4	<0.1	0.2	<0.1	<0.2	<0.2
6d14	<0.1	0.2	32.3	0.6	<0.1	1.0	<0.1	<0.2	<0.2
6d15	<0.1	0.1	23.2	0.3	<0.1	<0.1	<0.1	<0.2	<0.2
6d17	<0.1	0.7	23.4	0.9	<0.1	<0.1	<0.1	<0.2	<0.2
6d17	<0.1	0.3	31.4	0.4	<0.1	<0.1	<0.1	<0.2	<0.2
6d18	<0.1	0.4	18.5	0.9	<0.1	<0.1	<0.1	<0.2	<0.2
6d20	<0.1	0.2	18.3	0.6	<0.1	<0.1	<0.1	<0.2	<0.2


ENGLISH HERITAGE RESEARCH DEPARTMENT

English Heritage undertakes and commissions research into the historic environment, and the issues that affect its condition and survival, in order to provide the understanding necessary for informed policy and decision making, for sustainable management, and to promote the widest access, appreciation and enjoyment of our heritage.

The Research Department provides English Heritage with this capacity in the fields of buildings history, archaeology, and landscape history. It brings together seven teams with complementary investigative and analytical skills to provide integrated research expertise across the range of the historic environment. These are:

- *Aerial Survey and Investigation*
- *Archaeological Projects (excavation)*
- *Archaeological Science*
- *Archaeological Survey and Investigation (landscape analysis)*
- *Architectural Investigation*
- *Imaging, Graphics and Survey (including measured and metric survey, and photography)*
- *Survey of London*

The Research Department undertakes a wide range of investigative and analytical projects, and provides quality assurance and management support for externally-commissioned research. We aim for innovative work of the highest quality which will set agendas and standards for the historic environment sector. In support of this, and to build capacity and promote best practice in the sector, we also publish guidance and provide advice and training. We support outreach and education activities and build these in to our projects and programmes wherever possible.

We make the results of our work available through the Research Department Report Series, and through journal publications and monographs. Our publication Research News, which appears three times a year, aims to keep our partners within and outside English Heritage up-to-date with our projects and activities. A full list of Research Department Reports, with abstracts and information on how to obtain copies, may be found on www.english-heritage.org.uk/researchreports

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