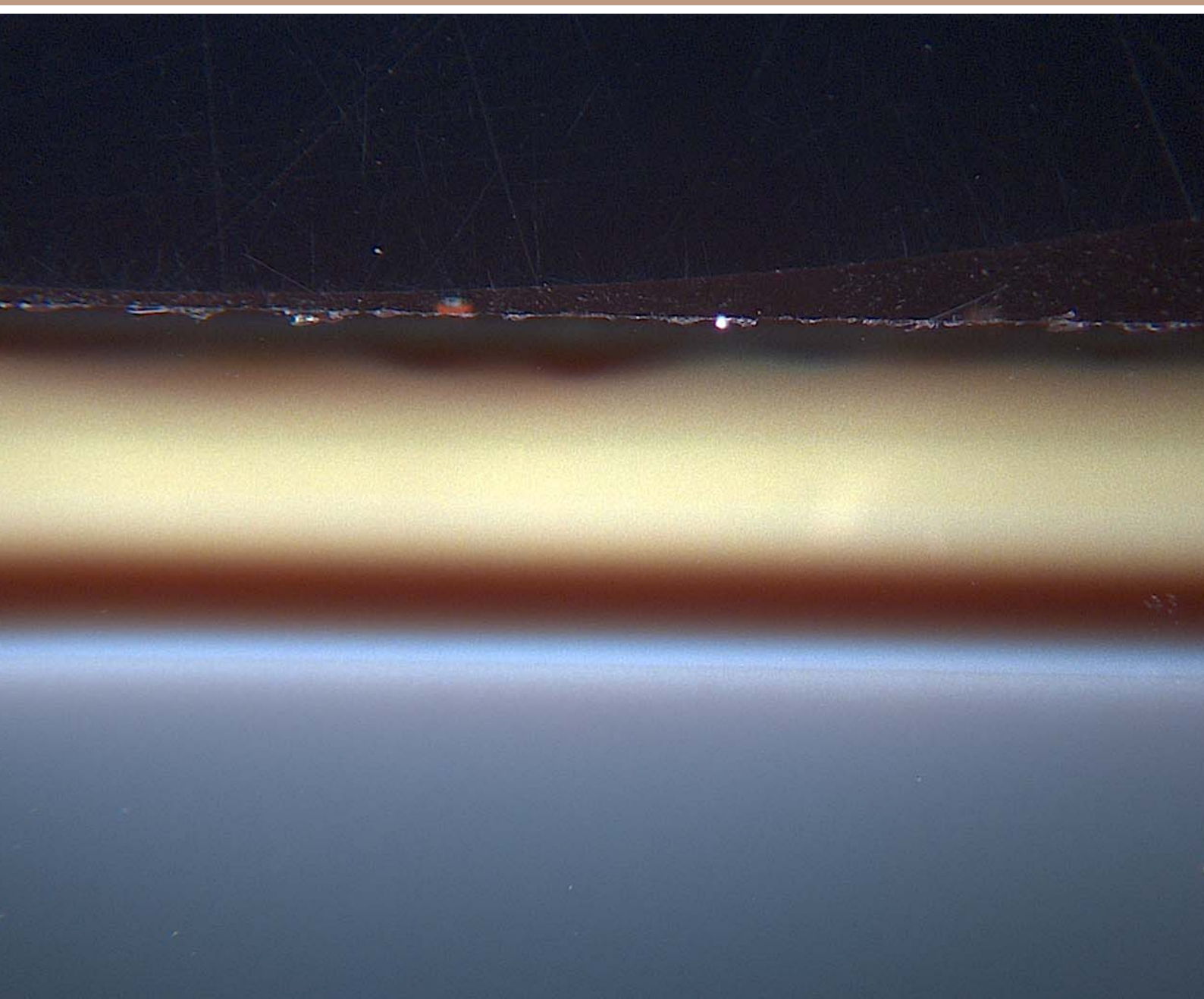


MARGAM CASTLE, PORT TALBOT,
WEST GLAMORGAM
SCIENTIFIC EXAMINATION OF THE
WINDOW GLASS

TECHNOLOGY REPORT

David Dungworth and Alun Adams



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SUMMARY

The scientific examination of fifteen samples of decorated window glass from Margam Castle provides information on glass in use in the 1830s as well as glass used for a repair in 1905. There are two types of colourless glass: the first made using seaweed ash and the second made using a synthetic soda. The contemporary use of both a seaweed glass and a synthetic soda glass is entirely consistent with the period. The seaweed glass was frequently stained yellow, orange or red using silver. The nature of staining has been investigated: silver nano-particles imaged and elemental X-ray linescans obtained through the stained layers. In addition the black painted surfaces layers on the colourless glass have also been investigated. The coloured pot metals are all flint glasses with the addition of specific metals to provide the blue, green or purple colour.

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INTRODUCTION

The analysis of fragments of window glass from Margam Castle forms part of a much larger 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 manufacture of synthetic 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 window glass examined here was obtained from Margam Castle, Port Talbot, West Glamorgan during the restoration of the windows undertaken by the Architectural Glass Centre of Swansea Metropolitan University. The Castle was originally constructed for CRM Talbot between 1827 and 1844 and included decorated heraldic windows in the entrance hall. The painting of this glass was by David Evans of Shrewsbury and it was delivered in 1834. The fortunes of the Talbot family declined in the 20th century and the

Castle was almost derelict when it was acquired by Glamorgan County Council in 1973. The Castle has been extensively restored and is currently listed at Grade I.

THE GLASS

Fifteen fragments of glass were available for scientific examination, including a range of painted colourless glass and coloured pot metal (Table 1). Sixteen of these fragments appear to be from the original design of 1834 while MC15 is from the restoration undertaken in 1905 (probably by Powells of Whitefriars).

Table 1. Description of Margam Castle window glass samples

#	Th (mm)	Colour	Date	Stain
MC01	1.29	colourless	1834	
MC02	1.22	blue	1834	
MC03	1.06	colourless	1834	
MC04	1.26	colourless	1834	Yellow-orange
MC05	1.18	colourless	1834	
MC06	0.95	colourless	1834	Orange-red
MC07	1.81	purple	1834	
MC08	1.65	purple	1834	
MC09	1.10	colourless	1834	
MC10	1.52	green	1834	
MC 11	1.14	colourless	1834	Yellow and red layers
MC 12	1.35	colourless	1834	
MC 13	1.68	blue	1834	
MC 14	1.38	green	1834	
MC 15	1.99	colourless	1905	Yellow
MC 16	1.30	colourless	1834	Both sides (one red, one yellow)
MC 17	1.34	colourless	1834	Both sides (one red, one yellow)

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. None of the Margam Castle samples exhibited any substantial corroded surfaces, however, almost all displayed altered surfaces, either stained or painted. 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 ₂ O	0.1	0.1	V ₂ O ₅	0.02	0.03
MgO	0.1	0.1	Cr ₂ O ₃	0.02	0.03
Al ₂ O ₃	0.1	0.1	MnO	0.02	0.03
SiO ₂	0.1	0.2	Fe ₂ O ₃	0.02	0.03
P ₂ O 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 ₂ O	0.1	0.1	ZnO	0.02	0.01
CaO	0.1	0.1	As ₂ O ₃	0.03	0.01
TiO ₂	0.1	0.1	SnO ₂	0.1	0.05
BaO	0.2	0.1	Sb ₂ O ₅	0.15	0.07
			Rb ₂ O	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 or silver stained glass. The compositional data for Na₂O, MgO, Al₂O₃, SiO₂, P₂O₅, SO₃, Cl, K₂O, CaO, and TiO₂ was obtained exclusively using SEM-EDS. CoO, NiO, As₂O₃, SrO and ZrO₂ data was obtained exclusively using EDXRF. SEM-EDS was not able to reliably detect any of these elements in the Margam glass, but EDXRF was able to detect these elements in some of the samples. MnO, Fe₂O₃ and CuO 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

reference materials (Corning, NIST, DGG and Newton/Pilkington). A number of elements were sought but not detected: vanadium, chromium, zinc, rubidium and barium.

RESULTS

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

The glass

The composition of the glass is rather varied (Tables 3 and 4) but the 1834 samples (MC01–14) can be divided into three major groups: soda-lime glass (MC01, MC03, MC05 and MC09), mixed alkali glass (MC04, MC06, MC11 and MC12), and lead glass (MC02, MC07, MC08, MC10, MC13 and MC14).

Table 3. Major elements in the window glass

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	Cl	K ₂ O	CaO	PbO
MC01	10.55	<0.1	1.20	69.6	<0.1	1.03	0.17	16.20	<0.04
MC02	0.36	<0.1	0.44	48.7	<0.1	0.17	13.79	0.17	33.6
MC03	10.43	0.11	1.19	69.5	<0.1	1.03	0.18	16.38	<0.04
MC04	8.30	5.31	1.49	66.6	1.40	0.52	3.76	11.09	0.05
MC05	10.58	<0.1	1.22	69.6	<0.1	1.01	0.16	16.17	<0.04
MC06	8.59	5.60	1.70	65.8	1.52	0.55	3.92	11.31	<0.04
MC07	0.55	<0.1	0.49	50.3	<0.1	0.17	11.40	0.22	34.0
MC08	0.48	<0.1	0.45	48.4	<0.1	0.17	13.09	0.33	33.3
MC09	12.50	<0.1	1.45	71.0	<0.1	0.34	0.13	13.36	<0.04
MC10	0.29	0.14	0.67	47.6	<0.1	0.13	11.70	0.16	32.3
MC11	8.24	5.24	1.43	66.9	1.34	0.55	3.86	11.42	0.07
MC12	7.29	5.00	1.89	65.2	1.18	0.58	3.70	13.75	<0.04
MC13	0.33	<0.1	0.44	48.7	<0.1	0.17	13.80	0.12	33.6
MC14	0.30	<0.1	0.65	47.5	<0.1	0.13	11.80	0.15	32.2
MC15	7.76	1.69	2.25	68.6	0.16	0.30	1.12	16.56	0.06
MC16	8.44	5.29	1.63	65.9	1.40	0.52	3.84	11.81	<0.04
MC17	8.16	5.05	1.60	65.7	1.34	0.51	3.94	12.09	<0.04

Table 4. *Minor elements in the window glass*

	SO ₃	TiO ₂	MnO	Fe ₂ O ₃	CoO	NiO	CuO	As ₂ O ₃	SrO	ZrO ₂
MC01	<0.1	<0.1	0.13	0.33	<0.02	<0.02	<0.02	<0.04	0.01	<0.005
MC02	0.11	<0.1	0.53	0.39	0.10	0.07	0.07	0.07	<0.1	0.010
MC03	0.14	<0.1	0.13	0.34	<0.02	<0.02	<0.02	<0.04	0.02	0.007
MC04	0.15	<0.1	0.05	0.62	<0.02	<0.02	<0.02	<0.04	0.62	0.027
MC05	<0.1	<0.1	0.14	0.37	<0.02	<0.02	<0.02	<0.04	0.02	<0.005
MC06	<0.1	<0.1	0.05	0.51	<0.02	<0.02	<0.02	<0.04	0.64	0.023
MC07	<0.1	<0.1	1.60	0.41	<0.02	<0.02	0.05	<0.04	<0.1	0.011
MC08	<0.1	<0.1	1.92	0.71	<0.02	<0.02	0.04	<0.04	<0.1	0.010
MC09	0.51	<0.1	0.28	0.13	<0.02	<0.02	<0.02	<0.04	0.03	<0.005
MC10	0.14	<0.1	0.07	4.05	<0.02	<0.02	2.70	<0.04	<0.1	0.010
MC11	0.13	<0.1	0.05	0.58	<0.02	<0.02	<0.02	<0.04	0.62	0.029
MC12	0.15	<0.1	0.11	0.61	<0.02	<0.02	<0.02	<0.04	0.55	0.021
MC13	<0.1	<0.1	0.50	0.44	0.10	0.07	<0.02	0.12	<0.1	0.010
MC14	<0.1	<0.1	0.07	3.95	<0.02	<0.02	2.74	<0.04	<0.1	0.009
MC15	0.27	0.19	0.03	0.64	<0.02	<0.02	<0.02	<0.04	0.12	0.016
MC16	0.10	0.12	0.04	0.59	<0.02	<0.02	<0.02	<0.04	0.63	0.033
MC17	0.18	0.13	0.05	0.79	<0.02	<0.02	<0.02	<0.04	0.59	0.020

Three of the soda-lime glasses (MC01, MC03 and MC05) share almost identical glass compositions and are likely to have been made at the same time and place. These samples have a chemical composition (in particular the absence of phosphorus) which suggests that they were made using synthetic soda. Sample MC09 is similar to the other soda-lime glasses but exhibits some significant differences. It was almost certainly made at a different time and/or place to the other soda-lime glasses. One of the most interesting aspects of its chemical composition is the iron content which is very low compared to most 19th-century window glass (Dungworth 2009). Iron contents as low as that found in MC09 are not commonly seen until the early 20th century. This sample is not, however, closely comparable with the known early 20th century replacement (MC15). Sample MC15 is (on the basis of the style of decoration) attributed to the early 20th-century restoration by Powell. This glass has a rather unusual chemical composition for glass of this period: it contains a relatively low proportion of sodium and a high proportion of calcium compared to ordinary window glass of the period (cf Dungworth 2010a; Turner 1926). This sample also contains a wide range of minor elements and appears rather anachronistic. It is possible that the composition of this glass was specifically formulated for use as a 'staining' glass. All of these soda-lime glasses are essentially colourless (in cross-section a pale green or pale blue-green tint is detectable). All of these samples contain small amounts of manganese which in some cases may have been deliberately added to reduce the colouring effect of the small amount of iron in the glasses.

The mixed alkali samples (MC04, MC06, MC11, MC12, MC16 and MC17) share broadly similar compositions and were almost certainly made using similar raw materials and technologies. This glass contains an appreciable concentration of phosphorus which is often an indicator of the use of an unrefined plant ash the source of alkali. The presence

of relatively high concentrations of strontium in this glass is a strong indicator of the use of kelp (seaweed) as the source of alkali (Dungworth *et al*/2009). The mixed alkali (kelp) glasses contain higher concentrations of iron compared to the colourless soda-lime glasses and have a slightly stronger green or blue-green tint, although they are still essentially colourless. While these glasses contain some manganese, the concentration of this element is so low it would have little or no effect on the colour of the glass and it was probably not added deliberately. Three of the four mixed alkali (kelp) glasses have a silver stain on one surface (see below).

The lead glass samples (MC02, MC07, MC08, MC10, MC13 and MC14) are all strongly coloured pot metals, that is the colour is produced by the presence of metal oxides which were added to the glass while it was molten in the crucible, or 'pot'). The base glass contains silica, potassium oxide and lead oxide with low concentrations of other elements, other than those which appear to have been deliberately added to achieve specific colours. The base glass is broadly similar to that used in the late 18th century for colourless lead crystal vessels (Dungworth and Brain forthcoming) and contemporary flint glass batch recipes (eg Pellatt 1849, 34).

Samples MC02 and MC13 share almost identical compositions and were probably made at the same time and place. The blue colour of this glass appears to have been produced by a suite of elements including manganese, iron, cobalt, nickel and copper. Contemporary sources frequently recommend the use of cobalt to colour glass blue and that the colour can be altered through the addition of small proportions of iron, manganese or nickel. It is possible that this blue glass was prepared using carefully selected proportions of metal oxides, however, it is more likely that the source of cobalt was not chemically pure. Writing in 1860, Bontemps stated that 'before it was recognised that cobalt was a specific metal it was always used in the form of a mineral [zaffre] that also contained nickel and iron' (Cable 2008, 74). Many cobalt ores (eg erythrite) contain significant quantities of a range of metals including manganese, iron, nickel, copper and arsenic.

Samples MC07 and MC08 are both purple but they do not share identical compositions and may have been made at different times and/or places. While the base glass compositions differ significantly, the range of colouring elements and their proportions are very similar. The purple colour of these samples appears to have been achieved essentially with manganese moderated with small amount of iron and copper. Pellatt (1849, 34) recommends 20lbs of manganese for each 6cwt of glass which would give a manganese concentration of 2.9wt% (MnO) which is somewhat higher than that of the Margam purple glass. It is possible that the source of manganese naturally contained a small proportion of iron but Bontemps recommended deliberately adding iron and manganese (in proportions 1:4) to modify the colour (Cable 2008, 266). The copper in this glass was certainly a separate addition (manganese minerals do not usually contain significant proportions of copper) and may have been added to modify the colour.

Samples MCI0 and MCI4 share almost identical compositions and were probably made at the same time and place. The green colour of this glass appears to have been produced by the presence of copper (2.7wt% CuO) and iron (4.0wt% Fe₂O₃). Pellatt recommends adding 12lbs of copper scales and 12lbs of iron ore to 6cwt of glass to achieve an emerald green (Pellatt 1849, 34) which would give a glass with 1.7wt% CuO and 1.7wt% Fe₂O₃. Bontemps recommends the use of iron, copper and chromium for green glass (Cable 2008, 275), although he states that iron and copper may be used on their own (ibid, 276). While chromium was first discovered at the end of the 18th century, its absence from the Margam green glass suggests that chromium was not widely used in glass manufacturing until perhaps the mid 19th century.

Silver stain

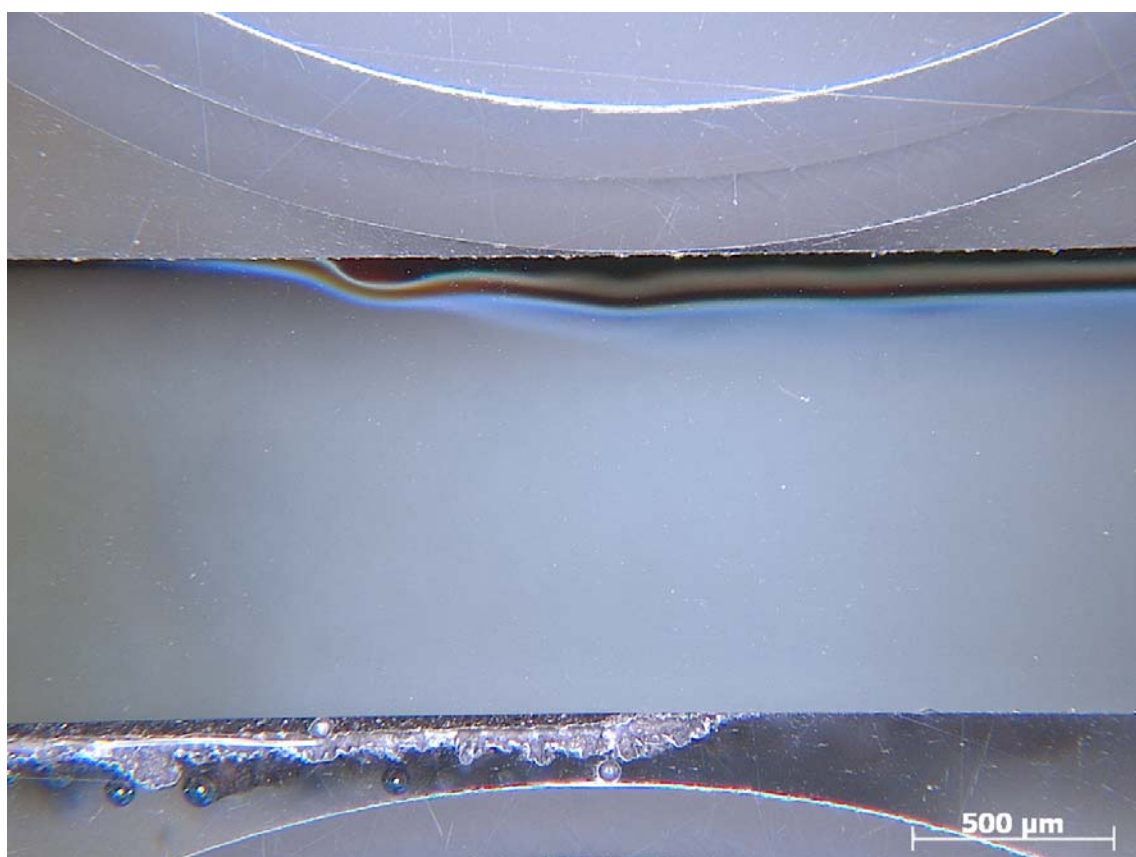


Figure 1. Optical Microscope image of MCI1 (darkfield illumination) showing the yellow-red upper surface

Six samples (five of the kelp glass and the Powell repair) had been treated in such a way as to stain one or more surface of the glass varying shades of yellow, orange or red (Figure 1). The stain was not always applied uniformly: in some cases it was applied to only some parts of the glass. The six stained samples from Margam were examined in detail and large numbers of silver-rich droplets could be detected within the stained

regions (Figure 2). These droplets tend to be spherical, have a higher average atomic number than the glass and are extremely small (<50nm diameter). The small size of these droplets precludes their direct analysis using SEM-EDS as the smallest area from which an X-ray spectrum can be generated is approximately 50 times larger than an individual droplet. Nevertheless, direct examination by other researchers (eg using transmission electron microscopes) of experimentally prepared silver stained glass suggests that these droplets are usually metallic in nature (eg Jembrich-Simbürger *et al* 2002; Pérez-Villar *et al* 2008).

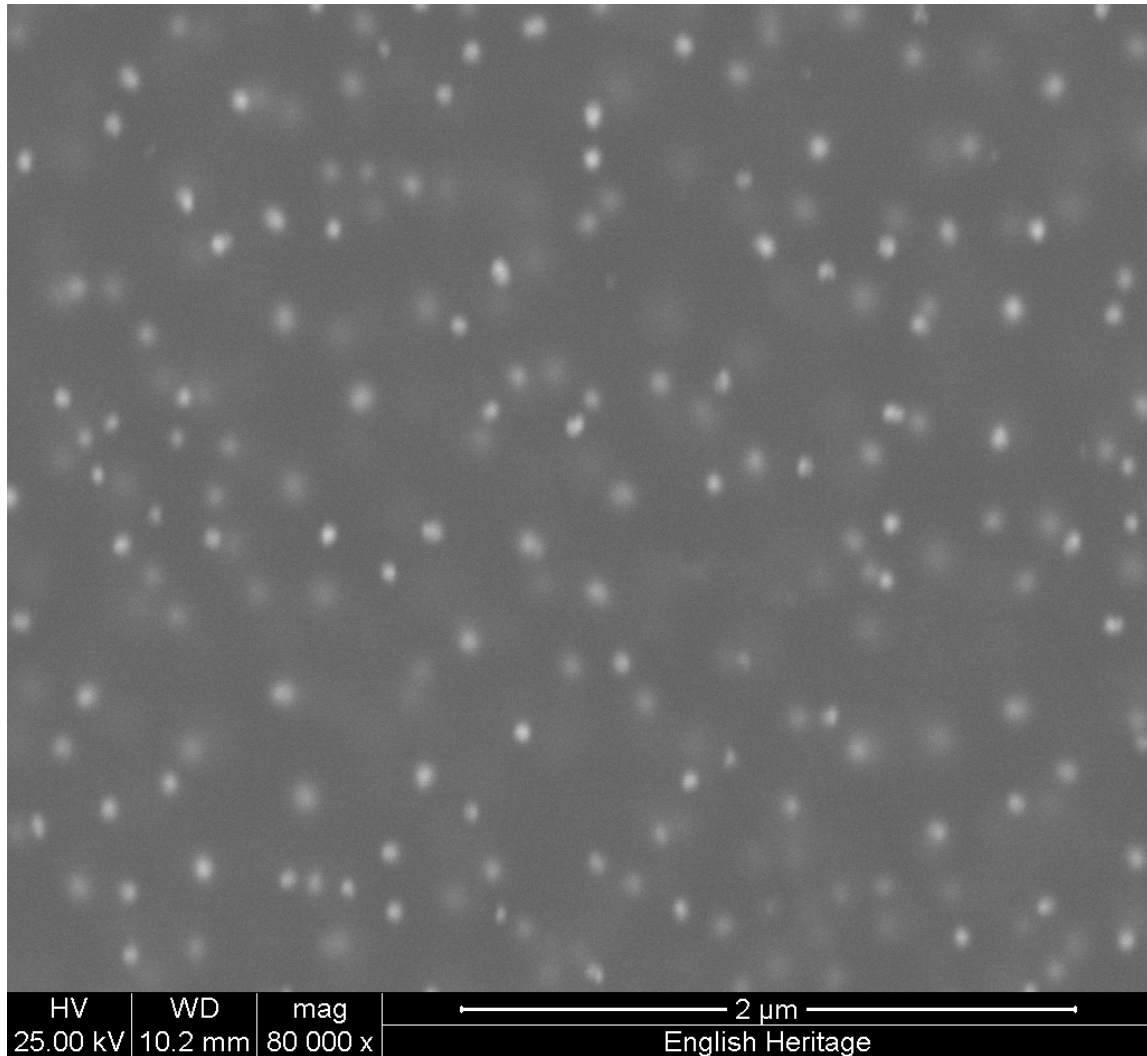


Figure 2. SEM image (back-scattered electron image) of the silver stained region of sample MC11 (the bright droplets are silver-rich)

The production of silver stained glass has traditionally been achieved by applying silver compounds with ochres and/or clays to the surface of the glass. The glass is then heated to produce the colouring effect. Weyl (1976, 410–418) describes four steps in this process:

- 1) ion exchange reaction
- 2) migration of ions
- 3) reduction of silver ions
- 4) crystallisation

The silver compounds at the surface provide the silver ions which move into the glass in an ion exchange mechanism — taking the place of sodium or potassium ions. This process only occurs at the surface of the glass and further movement of silver ions through the glass depends on silver and alkali ions exchanging places (Weyl 1976, 410). The driving force for this process is the concentration of silver ions at the surface and the process is described by Fick's Law (Jemrich-Simbürger *et al*/2002, 321). Silver ions appear to have little effect on the colour of glass and the yellow colour is produced by small droplets of metallic silver. The reduction of silver ions to metallic silver requires electron donors, of which iron (Fe^{2+}) is the most important. The silver atoms must then be able to migrate small distances to form nano-particles. Experimental samples have been prepared where the silver ions were reduced to metallic silver at a sufficiently low temperature ($\sim 100^\circ\text{C}$) to prevent the formation of nano-particles — these glasses did not develop a yellow colour (Weyl 1976, 416). The colouring effect produced by the silver nano-particles is likely to be due to the production of surface plasmon resonance (Pérez-Villar *et al*/2008, 1838) with varying shades of yellow and red possibly produced by variations in nano-particle size as well as the overall abundance of nano-particles in the glass.

A series of SEM-EDS analyses was carried out starting from the outer surface and extending into the glass slightly beyond the visible extent of the silver stain (see Appendix I for full results). Silver was only detected on the stained surfaces and only in regions with the bright droplets (Figures 1 and 2). Most samples of silver stained glass were treated on only one side, however, two samples (MC16 and MC17) were stained on both sides. The silver concentration is highest close to the outer surface of the glass and then gradually decrease (Figure 3). The opposite (unstained) side of several samples was also examined and showed no detectable silver. Most other elements in the glass show no variation associated with the presence of the silver-rich droplets, however, sodium (and to a lesser extent potassium) are depleted in the areas richest in silver (Figure 4). In general the darker, more red the colour, the greater the silver concentration and the greater the thickness of the treated layer.

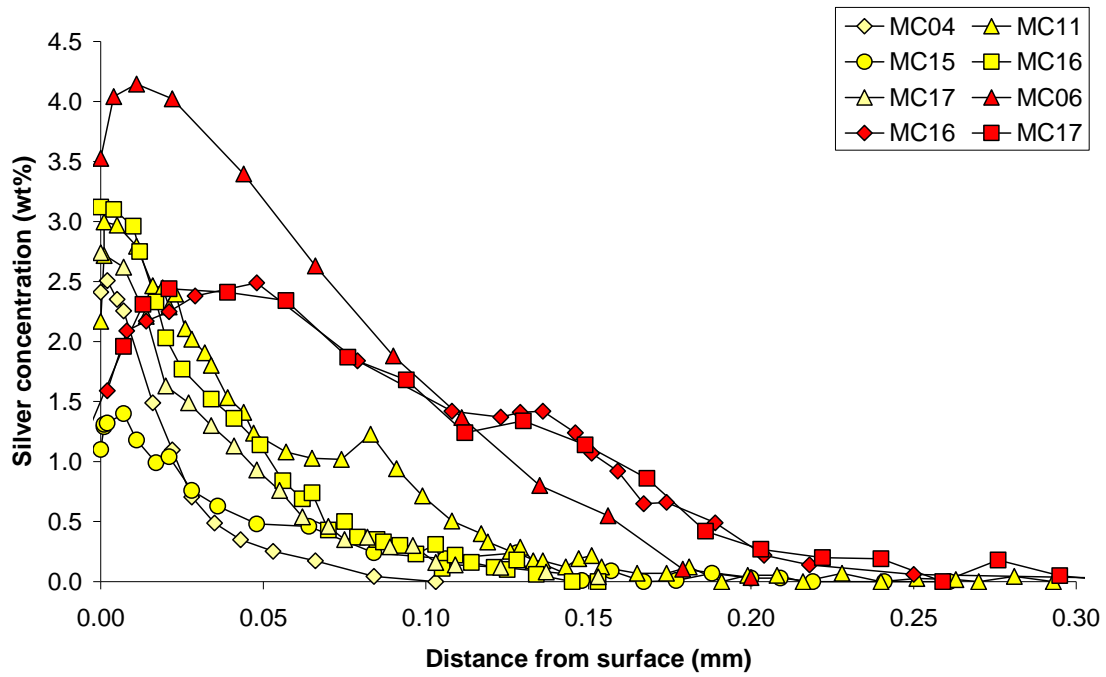


Figure 3. Linescans for silver through the silver stained surface (red symbols = red-orange stain; yellow symbols = yellow stain)

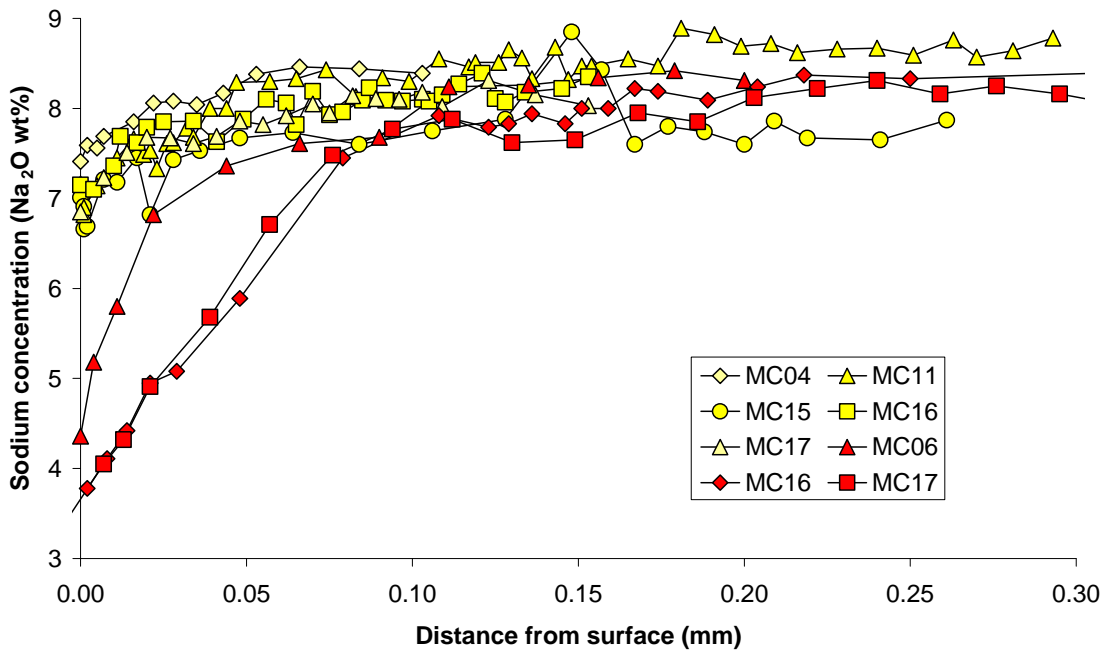


Figure 4. Linescans for sodium through the silver stained surfaces (red symbols = red-orange stain; yellow symbols = yellow stain)

Painted surfaces

The surfaces of many of the fragments of glass are painted with a black material. These are clearly visible when examined with the SEM as surface layers which have a higher average atomic number than the underlying glass (Figure 5). 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. Table 5 gives the average composition of the black paint for each sample. These paints are all lead-based glasses which contain high concentrations of manganese and iron. The manganese and iron are present at sufficient concentrations to render this surface nearly black.

A series of SEM-EDS analyses were undertaken through the black paint and into the glass to a depth of several hundred microns to investigate any interaction between the two layers (see Appendix 2 for full results). This procedure was followed for samples of black paint on both soda-lime glass and mixed alkali (kelp) glass but the results are similar in both cases. Most elements show very little diffusion between the painted surface and the underlying glass (Figures 6 and 7) but the alkalis show a high degree of mobility (Figure 8). The potassium concentration in the black paint is generally higher than in the associated glass, however, Figure 8 shows that the potassium concentration actually rises at the paint-glass boundary before gradually falling. This elevation of potassium at an interface in vitrified materials has previously been observed in the vitrified layers adhering to the interior surface of crucibles (Dungworth 2008). The black paint layers contain sodium (4–7wt% Na₂O) but Figure 8 suggests that most of this may have diffused from the underlying glass. It is likely that the black paint was prepared by mixing an ochre (containing both manganese and iron) with a fairly standard flint glass.

Table 5. Average compositions of the black paint (SEM-EDS analyses only)

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	PbO
MC01	5.8	0.2	1.2	53.6	0.2	0.2	0.1	2.3	1.1	<0.1	3.2	0.9	31.2
MC03	4.7	0.1	1.2	52.3	<0.1	0.4	<0.1	2.3	0.8	<0.1	2.2	0.6	35.4
MC04	4.5	0.3	1.0	47.3	<0.1	0.5	0.2	5.7	0.8	<0.1	7.5	2.0	29.8
MC05	4.8	0.1	0.8	51.0	<0.1	<0.1	<0.1	2.1	1.2	<0.1	4.7	0.7	34.5
MC06	3.2	0.2	0.6	52.0	<0.1	0.3	0.2	5.8	0.5	<0.1	1.4	1.3	34.3
MC09	6.5	0.2	0.8	52.9	0.4	0.7	<0.1	1.5	3.2	<0.1	3.1	1.0	29.8
MC11	4.3	0.1	0.8	49.7	0.2	0.1	0.2	4.8	0.7	<0.1	3.5	1.3	33.4
MC12	4.2	0.4	2.2	54.0	0.3	0.4	<0.1	4.1	1.7	<0.1	1.9	1.0	29.7
MC15	4.3	0.3	1.2	48.7	<0.1	0.3	0.2	5.7	0.8	0.2	5.6	1.5	31.2
MC16	3.7	0.3	0.9	47.6	0.1	0.2	0.4	6.6	0.6	<0.1	4.8	2.3	32.3
MC17	3.7	0.3	0.9	48.3	<0.1	0.1	0.3	6.5	6.5	<0.1	4.3	1.3	33.0

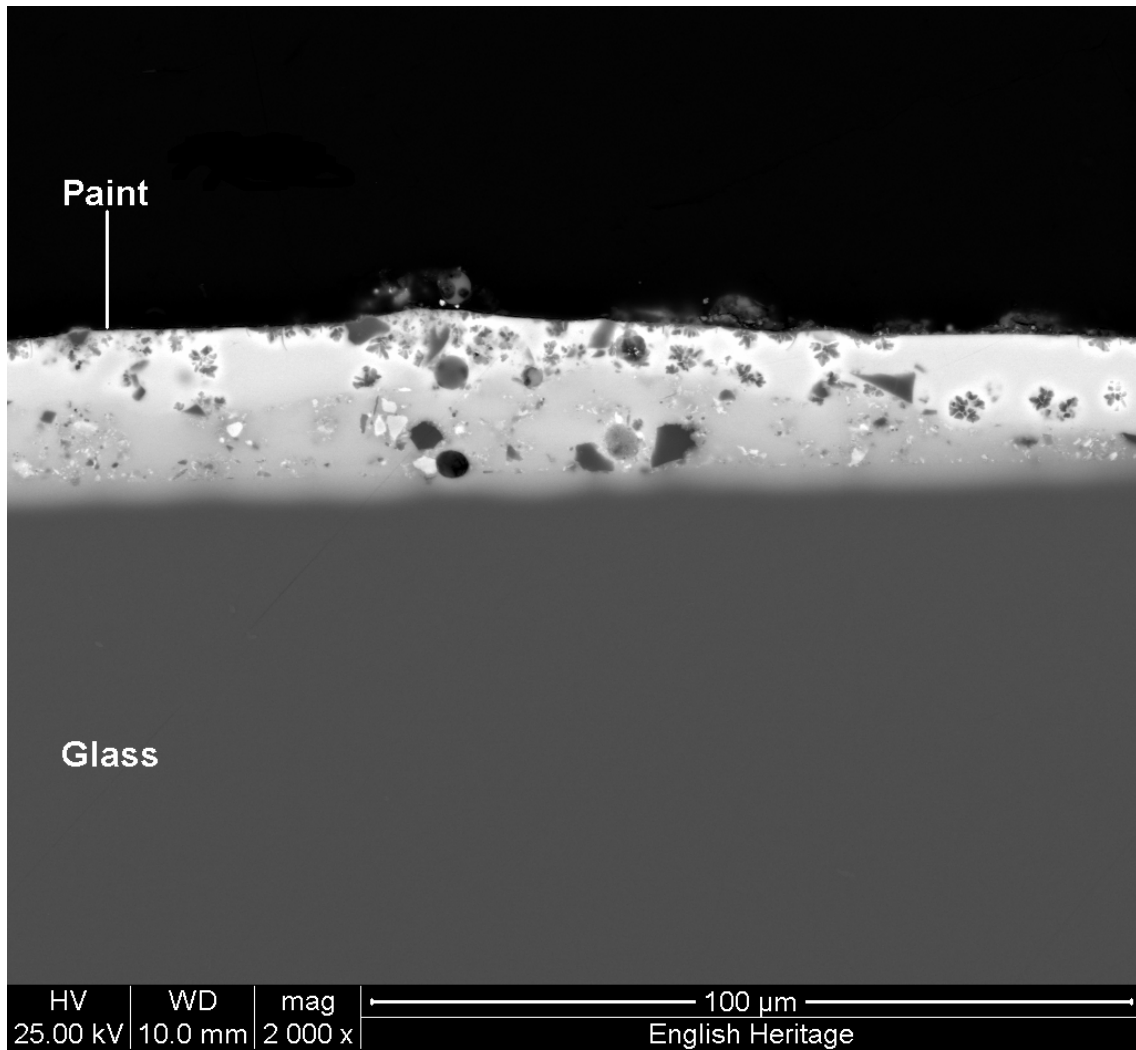


Figure 5. SEM image (back-scattered electron image) of the black paint on the surface of sample MC01

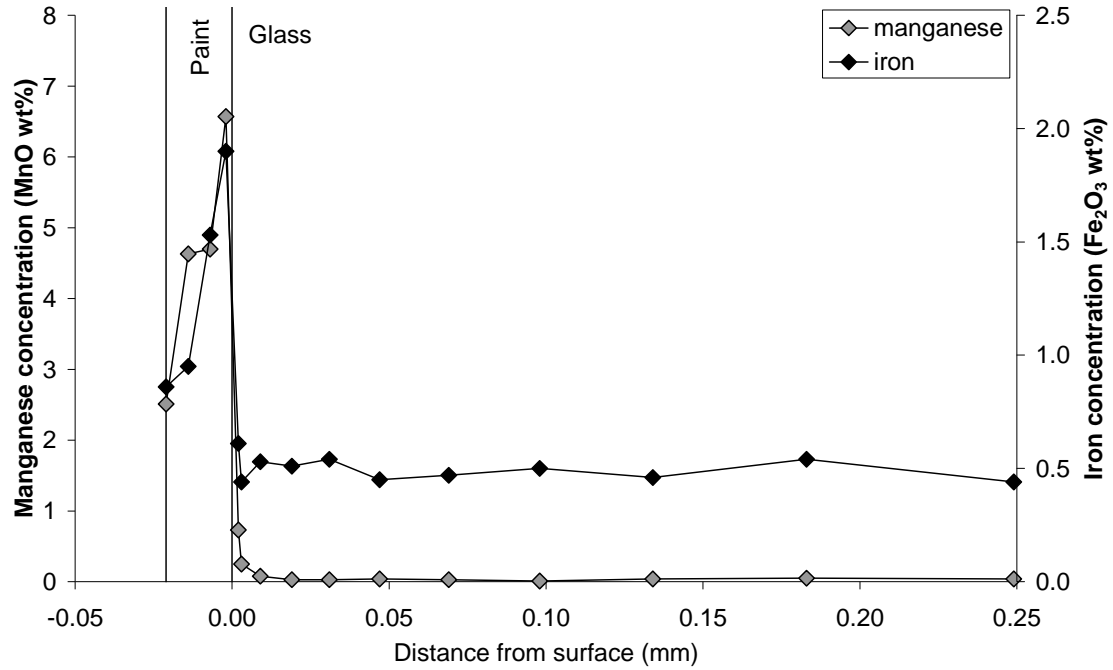


Figure 6. Manganese and iron concentrations within the black paint and underlying glass of sample MC04

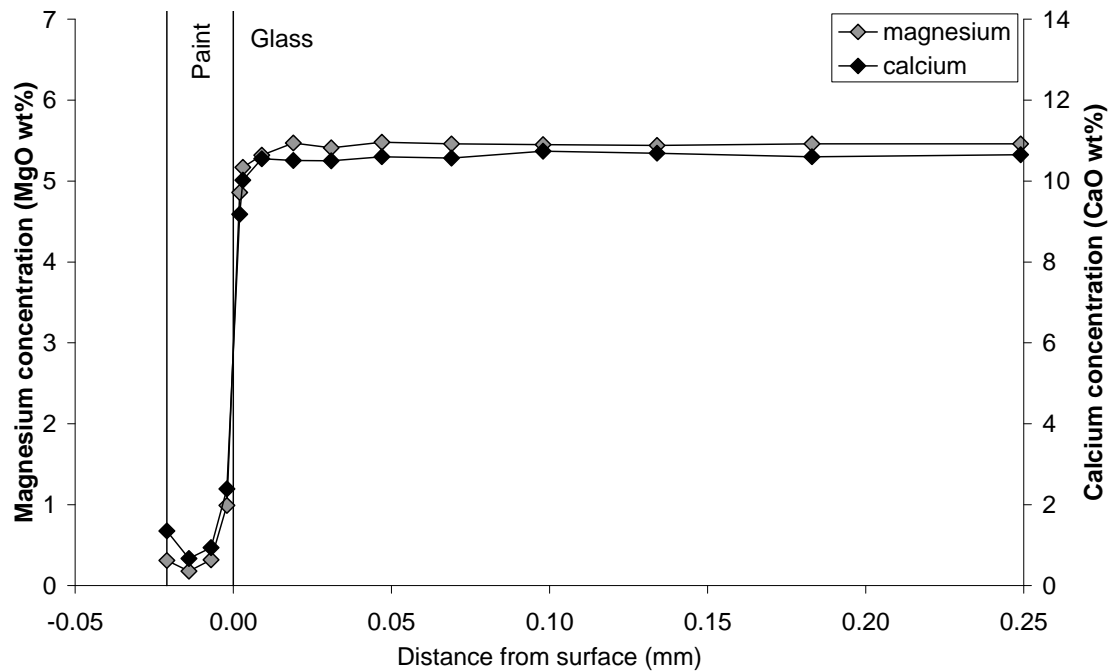


Figure 7. Magnesium and calcium concentrations within the black paint and the underlying glass of sample MC04

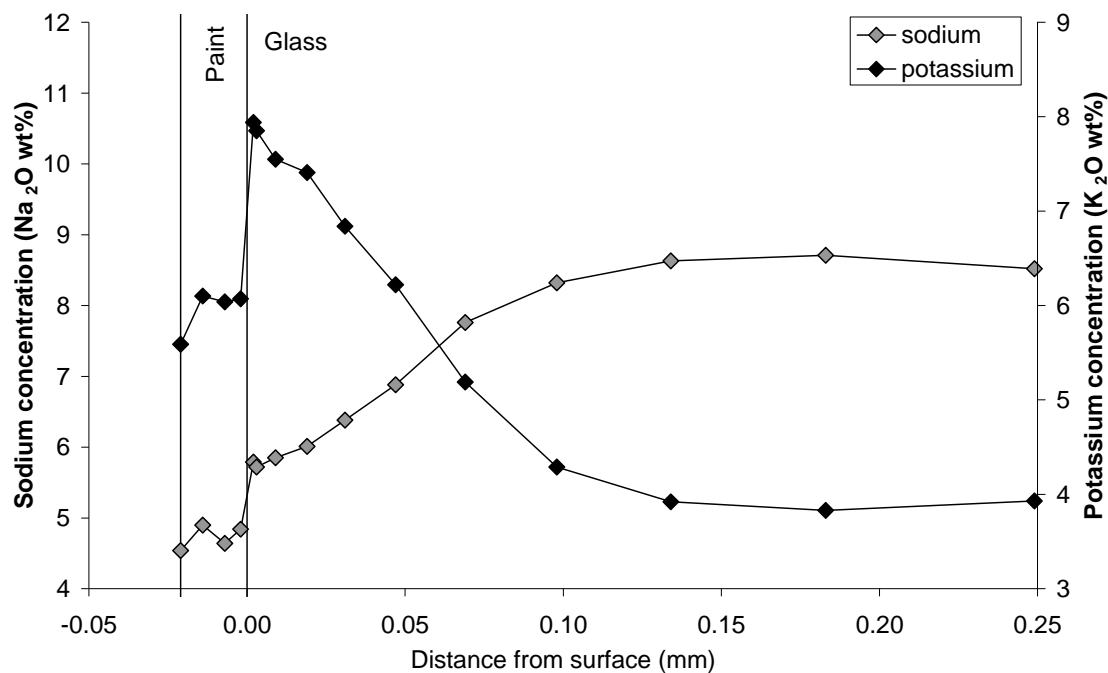


Figure 8. Sodium and potassium concentrations within the black paint and the underlying glass of sample MC04

DISCUSSION

The examination of fifteen fragments of decorated window glass from Margam Castle has provided a great deal of information about the sorts of window glass available in the 1830s and the technologies used to decorate them.

The coloured glass (blue, purple and green) was all coloured by adding suitable metal oxides to the glass while molten: these are usually called pot metals (in this context metal means glass) to distinguish them from colourless glass which was given a colour by staining. The coloured pot metals are all essentially flint glasses which correspond closely to the standard recipe (3 parts sand, 2 parts lead oxide and 1 part potash). The range and proportion of metal oxides present do not always correspond exactly with contemporary written sources, however, such sources often stress that the proportions should be varied to achieve particular shades of a desired colour. The range of metal oxides present in the blue glass are consistent with the use of an impure source of cobalt (zaffre) which naturally contained a range of other metal oxides (manganese, iron, nickel, copper and arsenic). The absence of chromium from the green glass suggests that this metal was not widely used in the glass industry until after 1834.

The colourless Margam glass falls into two compositional groups: a soda-lime glass and a mixed alkali glass. The latter type of glass is well known from previous work and was

made using the ash of seaweed (kelp). This type of glass was first used for the manufacture of windows at the beginning of the 18th century. Historical sources indicate that the use of kelp was rapidly abandoned in the 1830s as synthetic soda manufactured using the Leblanc process became widely available (Chance 1856; Chance 1919; Clow and Clow 1952; Cooper 1835; Muspratt 1860; Ure 1844). The Margam kelp glass represents some of the last glass manufactured in England using that kelp. The composition of the Margam kelp glass is similar to 18th-century examples of kelp glass (Table 6) and suggests that the raw materials and recipe remained largely unchanged from c1700 to the 1830s.

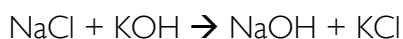
Table 6. Chemical composition of some 18th- and 19th-century flat glass (Sources: 1 = Dungworth and Loaring 2009; 2 = Dungworth 2006; 3 = Dungworth 2007; 4 = Dungworth and Mortimer 2005; 5 = this report; 6 = Dungworth 2009; 7 = Hatton 2004; 8 = Dungworth and Wilkes 2010; 9 = Dungworth 2010 a; 10 = Dungworth 2010b)

Site	Source	Date	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	MnO	Fe ₂ O ₃	SrO
Shaw House 1	1	1700–30	8.3	5.4	2.4	65.5	1.4	0.1	0.7	4.3	10.4	0.04	0.54	0.63
Shaw House 2	1	1700–30	8.3	5.4	3.3	65.2	0.8	0.3	0.6	4.0	10.6	0.06	0.76	0.48
Shaw House 3	1	1700–30	7.2	5.0	1.9	66.5	1.3	0.1	0.7	4.2	11.8	0.04	0.53	0.47
Shaw House 4	1	1700–30	9.4	5.4	3.1	66.2	0.7	0.3	0.5	4.3	8.7	0.05	0.69	0.41
Shaw House 5	1	1700–30	7.6	5.2	2.8	66.7	0.9	0.3	0.5	4.1	10.7	0.06	0.61	0.46
Silkstone	2	1700–30	7.8	5.6	2.1	63.9	1.4	0.1	0.8	4.3	10.7	0.09	1.02	0.37
St Thomas St	3	1710–60	7.4	5.1	3.4	67.5	0.9	0.3	0.6	4.5	10.5	0.06	0.71	0.41
Cheese Lane	4	1710–1810	7.8	5.4	3.0	66.8	1.2	0.2	0.3	4.2	10.0	<0.02	0.82	0.41
Margam kelp	5	1834	8.1	5.3	1.6	66.1	1.4	0.1	0.6	3.8	11.9	0.07	0.58	0.61
Margam soda	5	1834	10.5	0.1	1.2	69.6	<0.1	<0.1	1.0	0.2	16.3	0.14	0.35	0.02
Chatsworth	6	1837–40	14.0	<0.1	0.7	70.3	<0.1	0.3	<0.1	<0.1	14.1	<0.02	0.33	0.02
Nailsea	7	1830–70	13.1	0.2	0.8	68.9	<0.1	0.6	<0.1	0.1	13.6	0.06	0.33	0.02
Wentworth	8	1877	11.9	0.4	0.7	71.5	<0.1	0.2	<0.1	0.3	14.3	<0.02	0.28	0.03
Welch Road	9	1894–95	11.4	0.1	1.5	72.2	<0.1	0.4	<0.1	0.7	13.4	<0.02	0.25	0.02
Fort Cumberland	10	1940	14.3	2.9	0.3	72.5	<0.1	0.3	<0.1	<0.1	9.4	<0.02	0.13	0.01

The soda-lime glass used at Margam (leaving aside MC09) is characterised by low concentrations of impurities (in particular phosphorus) suggesting that it was manufactured using a synthetic soda rather than a plant ash. The best-known example of synthetic soda in this period is that obtained using the Leblanc process. This was developed in France at the end of the 18th century but only introduced into Britain in the 1830s. Common salt (sodium chloride) was treated with sulphuric acid to yield sodium sulphate. As sodium sulphate reacts with silica rather slowly, the sulphate was heated with carbon and calcium carbonate to produce sodium carbonate. Glassmakers gradually learnt to use the sulphate directly, however, by adding carbon with the sulphate to the glass batch.

This composition of the Margam soda-lime glass, however, does not correspond closely to other soda-lime window glass of the 19th century (Table 6) and was probably not made with Leblanc soda or sodium sulphate. The Margam glass contains relatively high

concentrations of chlorine compared to other 19th-century soda-lime glasses. In the late 18th and early 19th centuries sodium chloride was (with varying degrees of efficiency) converted into sodium carbonate using potash and a double decomposition process (Clow and Clow 1952, 95–97; Parkes 1823, 208). A solution of wood ashes (rich in potassium) was prepared and sodium chloride added to this. The resulting reactions produced potassium chloride which would tend to crystallise leaving a sodium-rich solution from which soda could be extracted by heating.



If the proportion of potash to salt was slightly too high, not all of the potassium would crystallise as potassium chloride, and the end product would contain both soda and potash. If the proportion of potash to salt was too low then the end product would contain both soda and sodium chloride. The use of soda prepared using this double decomposition process appears to have been preferred by plate glass manufacturers (Parkes 1823, 209) even after Leblanc soda became available (Brayley 1846). The high chlorine content of the Margam soda-lime glass indicates that it was probably manufactured using a soda obtained from common salt by double decomposition with potash.

The presence of both a kelp-based glass and a synthetic soda glass in the Margam window glass assemblage is entirely consistent with its manufacture during a period in which the use of kelp was being abandoned in favour of synthetic soda. The presence of both types of glass may, however, be related to the ways in which they were used. While the Margam soda-lime glass was decorated only with black paint, three out of the four kelp glasses were stained yellow, orange or red with silver (and also painted black). The fourth sample of kelp glass had no silver stain but this could be explained due to the small size of the fragment and the fact that the silver stain was not applied uniformly to all such glass (Figure 1). It appears, therefore that the kelp glass was deliberately selected for silver staining, while the soda-lime glass was selected for glass which was not stained.

Writing in 1860, Bontemps described the difficulties in obtaining a high-quality silver stain,

When I set up the manufacture of painted glass at Choisy-le-Roi in 1829 under the direction of Mr Edward Jones, the glass I made would only yield a pale yellow and glasses obtained from other works in the normal way of trade likewise gave only a very pale yellow. Mr Jones attributed this to a lack of hardness in our glass and by making a harder glass, that is with less alkali we did succeed in making a rather darker tint but it was still far from that desired. Mr Jones kept showing me a fragment of English glass half of which was stained on only one surface to give a deep orange-yellow. This glass was hard but I recognised from its greenish tint that, like all window glass then made in England, it had been made with raw soda (*kelp*) as flux. I assumed that this material must be able to affect the tint given by the silver. It would have been difficult to obtain some raw soda and it would have been necessary to set up a fritting furnace even though the result was not certain. If this soda were to give the desired result, it must, no doubt be due to one of its constituents. In addition to the sulphate and a little sodium carbonate, the raw soda contained the following: some sea salt, potash, alumina, iron

oxide. Not knowing which of these constituents was likely to be responsible for the effect desired, I presumed that the sodium chloride, with its well known affinity for silver, was likely to have the major role. I therefore made a batch with a considerable content of silver chloride whilst also remembering to add the other constituents mentioned above. The first melt, which I kept a hard [low alkali] one, made a glass which coated on only one side, yielded as deep an orange as the best of the English window glasses.

(Cable 2008, 274)

It seems, therefore, that the colourless glass employed at Margam was either a soda-lime glass (manufactured from soda obtained using double decomposition soda) which was used as a colourless glass, or a kelp glass which was deliberately selected for yellow staining because it took a stronger colour than other types of plain glass. Given the experiments carried out by Bontemps it is not immediately obvious which property of kelp glass made it better suited to taking a silver stain. Weyl suggests that 'under proper conditions silver stain can be applied to all silicate glasses . . . minor constituents, such as FeO, play the important role and . . . the glass composition is not of great influence' (Weyl 1974, 41). It is possible, therefore, that synthetic soda glass, with its emphasis on an absence of colour (achieved through a low iron content), would have been capable of admitting silver ions but lacked sufficient Fe²⁺ to allow the reduction of silver ions to metallic silver.

Sample MC15 (an example of the Powell 1905 repair) has a chemical composition which does not closely correspond to any early 20th-century plain glass: it contains relatively little sodium, but high concentrations of calcium and a wide range of minor elements. This glass may have been specially formulated (along the same lines as Bontemps) for use as a glass suitable for silver staining.

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APPENDIX I

Linescan through silver stained surface of MC04

Distance (mm)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	Fe ₂ O ₃	AgO
0.000	7.41	5.06	1.48	64.4	1.60	0.35	0.75	3.41	10.48	0.46	2.77
0.002	7.59	5.08	1.48	65.5	1.48	0.2	0.73	3.66	10.95	0.44	2.88
0.005	7.56	5.37	1.45	65.3	1.45	0.17	0.76	3.71	10.74	0.48	2.70
0.007	7.69	5.35	1.45	65.4	1.40	0.24	0.77	3.70	10.83	0.58	2.59
0.016	7.85	5.23	1.51	65.7	1.46	0.12	0.79	3.79	10.93	0.51	1.71
0.022	8.06	5.43	1.40	66.5	1.38	0.23	0.74	3.91	11.00	0.48	1.26
0.028	8.08	5.25	1.51	66.3	1.45	0.23	0.75	3.91	10.98	0.53	0.81
0.035	8.04	5.35	1.53	66.1	1.50	0.22	0.74	3.99	10.97	0.49	0.56
0.043	8.17	5.38	1.45	66.3	1.63	0.16	0.73	3.95	10.87	0.52	0.40
0.053	8.38	5.37	1.44	66.0	1.59	0.17	0.77	3.94	10.91	0.51	0.29
0.066	8.46	5.34	1.49	66.6	1.33	0.17	0.74	3.95	10.98	0.47	0.20
0.084	8.44	5.24	1.52	66.3	1.56	0.18	0.79	4.00	10.95	0.50	<0.2
0.103	8.39	5.42	1.48	66.4	1.51	0.21	0.78	3.89	11.06	0.49	<0.2

Linescan through silver stained surface of MC06

Distance (mm)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	Fe ₂ O ₃	AgO
0.000	4.57	5.04	1.49	65.2	1.44	0.12	0.70	6.05	10.66	0.51	4.24
0.004	5.22	5.31	1.64	63.2	1.54	0.13	0.71	5.47	11.68	0.45	4.67
0.011	5.87	5.14	1.63	63.4	1.44	0.13	0.75	4.91	11.46	0.49	4.82
0.022	6.82	5.28	1.56	63.4	1.59	0.10	0.77	4.03	11.38	0.49	4.62
0.044	7.37	5.38	1.60	63.5	1.57	0.13	0.73	3.88	11.44	0.46	3.91
0.066	7.65	5.34	1.70	64.3	1.53	0.11	0.77	3.93	11.20	0.47	3.03
0.090	7.69	5.42	1.59	64.7	1.62	0.13	0.77	4.10	11.41	0.44	2.16
0.111	8.25	5.55	1.68	64.4	1.51	0.08	0.74	4.24	11.41	0.51	1.57
0.135	8.29	5.53	1.70	64.9	1.56	0.16	0.77	4.11	11.57	0.47	0.92
0.156	8.36	5.41	1.61	65.3	1.52	0.27	0.75	4.21	11.46	0.47	0.63
0.179	8.44	5.47	1.72	65.7	1.43	0.13	0.81	4.18	11.57	0.50	<0.2
0.200	8.36	5.51	1.73	65.5	1.66	0.13	0.77	4.27	11.60	0.47	<0.2

Linescan through silver stained surface of MCI I

Distance (mm)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	Fe ₂ O ₃	AgO
0.000	7.37	5.70	2.14	65.1	2.50	0.45	0.81	3.08	9.39	0.88	2.56
0.001	6.88	5.65	1.65	65.9	1.64	0.24	0.79	3.21	10.29	0.55	3.15
0.001	6.91	5.40	1.43	65.9	1.48	0.16	0.73	3.41	10.62	0.50	3.45
0.005	7.17	5.30	1.42	65.4	1.47	0.21	0.78	3.55	10.77	0.45	3.42
0.011	7.45	5.35	1.47	65.5	1.46	0.16	0.68	3.64	10.62	0.48	3.21
0.016	7.67	5.39	1.51	65.6	1.37	0.18	0.74	3.60	10.64	0.43	2.84
0.019	7.50	5.42	1.51	65.3	1.60	0.21	0.73	3.73	10.76	0.45	2.82
0.021	7.57	5.29	1.52	65.9	1.48	0.17	0.73	3.64	10.58	0.51	2.64
0.023	7.37	5.39	1.42	65.7	1.43	0.19	0.72	3.74	10.72	0.50	2.77
0.026	7.67	5.39	1.42	65.7	1.51	0.28	0.76	3.61	10.69	0.47	2.44
0.028	7.62	5.25	1.57	65.9	1.48	0.19	0.77	3.81	10.59	0.47	2.32
0.032	7.78	5.34	1.48	65.9	1.40	0.29	0.73	3.75	10.67	0.47	2.19
0.034	7.72	5.33	1.46	65.9	1.51	0.21	0.75	3.84	10.74	0.45	2.08
0.039	8.02	5.27	1.45	66.1	1.52	0.19	0.73	3.73	10.67	0.54	1.77
0.044	8.01	5.39	1.48	66.1	1.50	0.18	0.76	3.71	10.70	0.50	1.62
0.047	8.32	5.43	1.53	66.1	1.48	0.18	0.76	3.78	10.44	0.50	1.43
0.057	8.35	5.35	1.61	66.1	1.48	0.25	0.78	3.74	10.63	0.48	1.25
0.065	8.35	5.59	1.41	66.2	1.46	0.16	0.74	3.78	10.66	0.49	1.18
0.074	8.41	5.48	1.42	66.3	1.54	0.22	0.74	3.69	10.55	0.46	1.17
0.083	8.16	5.26	1.44	66.3	1.44	0.26	0.76	3.79	10.64	0.54	1.42
0.091	8.36	5.51	1.47	66.3	1.47	0.20	0.74	3.82	10.55	0.48	1.08
0.099	8.33	5.36	1.51	66.5	1.62	0.22	0.71	3.86	10.63	0.42	0.82
0.108	8.59	5.51	1.53	66.5	1.51	0.16	0.73	3.82	10.61	0.45	0.58
0.117	8.46	5.51	1.44	66.7	1.54	0.21	0.71	3.87	10.66	0.45	0.46
0.119	8.55	5.42	1.50	66.8	1.56	0.10	0.73	3.86	10.63	0.47	0.38
0.126	8.56	5.49	1.54	66.61	1.50	0.23	0.79	3.91	10.55	0.52	0.29
0.129	8.70	5.47	1.48	66.8	1.46	0.23	0.72	3.78	10.60	0.43	0.33
0.133	8.58	5.37	1.58	66.7	1.48	0.19	0.75	3.82	10.73	0.54	0.20
0.136	8.34	5.47	1.53	67.0	1.52	0.15	0.73	3.82	10.80	0.41	0.20
0.143	8.70	5.46	1.44	66.7	1.43	0.21	0.72	3.93	10.75	0.49	0.14
0.147	8.36	5.35	1.61	66.9	1.51	0.23	0.75	3.86	10.69	0.50	0.22
0.151	8.53	5.57	1.50	66.7	1.48	0.20	0.77	3.77	10.70	0.48	0.25
0.154	8.51	5.62	1.48	66.7	1.71	0.17	0.74	3.85	10.64	0.41	<0.2
0.165	8.55	5.47	1.64	66.9	1.51	0.11	0.73	3.87	10.59	0.50	<0.2
0.174	8.51	5.45	1.56	67.0	1.48	0.13	0.77	3.85	10.65	0.47	<0.2
0.181	8.89	5.58	1.57	66.5	1.47	0.14	0.78	3.86	10.55	0.47	<0.2
0.191	8.88	5.50	1.46	66.9	1.49	0.17	0.77	3.84	10.50	0.44	<0.2
0.199	8.73	5.59	1.44	66.9	1.57	0.13	0.72	3.76	10.70	0.44	<0.2
0.208	8.74	5.61	1.46	67.0	1.49	0.14	0.74	3.73	10.63	0.43	<0.2
0.216	8.69	5.43	1.60	66.9	1.47	0.19	0.78	3.78	10.72	0.45	<0.2
0.228	8.73	5.37	1.51	66.9	1.53	0.19	0.71	3.89	10.64	0.48	<0.2
0.240	8.65	5.46	1.51	66.8	1.49	0.23	0.76	3.84	10.72	0.49	<0.2
0.251	8.63	5.44	1.53	67.0	1.46	0.22	0.73	3.87	10.64	0.46	<0.2
0.263	8.75	5.54	1.48	66.9	1.48	0.20	0.75	3.88	10.55	0.48	<0.2
0.270	8.58	5.40	1.57	67.1	1.48	0.21	0.75	3.86	10.59	0.43	<0.2
0.281	8.71	5.47	1.55	66.9	1.44	<0.1	0.78	3.79	10.76	0.48	<0.2
0.293	8.81	5.48	1.48	66.7	1.58	0.25	0.74	3.89	10.58	0.44	<0.2

Linescan through silver stained surface of MCI5

Distance (mm)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	AgO
0.000	7.04	1.60	2.51	66.5	0.15	0.52	0.48	1.31	17.19	0.24	0.80	1.11
0.001	6.69	1.70	2.50	66.7	0.23	0.53	0.52	1.25	17.62	0.22	0.73	1.30
0.001	6.94	1.78	2.46	66.7	0.22	0.36	0.44	1.28	17.55	0.14	0.62	1.32
0.002	6.72	1.75	2.46	67.1	0.22	0.38	0.49	1.24	17.71	0.14	0.64	1.33
0.007	7.24	1.84	2.44	66.3	0.22	0.40	0.48	1.23	17.40	0.27	0.62	1.41
0.011	7.21	1.73	2.35	66.8	0.30	0.45	0.44	1.25	17.64	0.27	0.69	1.19
0.017	7.48	1.81	2.32	67.1	0.17	0.38	0.46	1.26	17.56	0.19	0.59	0.99
0.021	6.85	1.75	2.37	67.6	0.21	0.46	0.45	1.28	17.29	0.16	0.69	1.04
0.028	7.47	1.68	2.33	67.8	0.26	0.35	0.47	1.27	17.25	0.19	0.59	0.76
0.036	7.56	1.77	2.40	67.2	0.18	0.50	0.44	1.17	17.52	0.21	0.68	0.63
0.048	7.70	1.74	2.38	67.0	0.26	0.39	0.41	1.26	17.55	0.18	0.68	0.48
0.064	7.76	1.68	2.48	67.8	0.21	0.32	0.36	1.19	17.21	0.18	0.63	0.46
0.084	7.63	1.77	2.39	68.4	0.27	0.32	0.35	1.27	17.02	0.11	0.64	0.24
0.106	7.78	1.69	2.33	67.8	0.22	0.36	0.41	1.26	17.16	0.26	0.63	<0.2
0.128	7.92	1.61	2.34	67.6	0.14	0.44	0.51	1.22	17.05	0.27	0.63	0.24
0.148	8.87	1.03	9.48	65.6	0.12	0.31	0.28	1.88	11.41	0.35	0.48	<0.2
0.157	8.46	1.35	7.67	66.5	0.14	0.32	0.32	1.70	12.76	0.29	0.52	<0.2
0.167	7.63	1.75	2.64	67.4	0.20	0.44	0.42	1.21	17.29	0.20	0.62	<0.2
0.177	7.84	1.90	2.47	67.6	0.19	0.42	0.45	1.24	17.28	0.23	0.64	<0.2
0.188	7.77	1.81	2.38	67.8	0.13	0.38	0.42	1.25	17.40	0.31	0.67	<0.2
0.200	7.63	1.81	2.44	67.0	0.24	0.39	0.45	1.28	17.58	0.23	0.68	<0.2
0.209	7.89	1.87	2.41	67.1	0.16	0.47	0.40	1.32	17.41	0.14	0.66	<0.2
0.219	7.71	1.74	2.46	67.3	0.30	0.39	0.46	1.24	17.54	0.22	0.61	<0.2
0.241	7.69	1.72	2.45	67.5	0.21	0.38	0.46	1.30	17.49	0.23	0.59	<0.2
0.261	7.90	1.85	2.51	67.2	0.29	0.34	0.44	1.31	17.63	0.19	0.59	<0.2

Linescan through paint and red silver stained surface of MCI 6
 (<0mm = paint, >0mm = glass)

Distance (mm)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	MnO	Fe ₂ O ₃	AgO	PbO
-0.033	3.59	0.58	1.08	49.68	0.36	0.51	0.72	6.69	0.81	3.36	2.45	1.03	29.62
-0.028	3.74	0.25	0.95	46.32	0.12	0.23	0.64	7.10	0.61	6.24	3.69	1.14	29.13
-0.022	3.63	0.18	0.87	47.64	<0.1	<0.1	0.48	7.02	0.54	4.45	1.58	1.09	32.53
-0.016	3.61	0.15	0.84	46.09	<0.1	0.25	0.45	7.21	0.55	5.29	1.63	1.25	32.18
-0.011	3.53	0.15	0.86	47.16	<0.1	0.31	0.48	7.10	0.54	4.71	1.51	1.16	32.08
-0.005	3.55	0.24	0.91	47.71	<0.1	0.20	0.47	7.11	0.75	6.63	1.85	1.17	29.21
-0.002	3.33	0.37	1.03	47.71	<0.1	0.35	0.46	7.38	1.27	7.36	1.97	1.27	27.40
0.002	3.81	4.55	1.56	60.64	1.32	<0.1	0.74	8.74	10.24	1.06	0.72	1.60	4.92
0.008	4.14	5.03	1.61	63.74	1.42	0.10	0.70	8.69	11.81	0.13	0.56	2.10	<0.1
0.014	4.45	5.28	1.56	63.39	1.38	0.18	0.74	8.63	11.60	<0.1	0.47	2.19	0.19
0.021	4.99	5.18	1.64	63.50	1.45	0.11	0.73	8.18	11.62	<0.1	0.47	2.27	0.11
0.029	5.12	5.13	1.55	63.81	1.57	0.24	0.72	7.58	11.64	<0.1	0.53	2.40	<0.1
0.048	5.93	5.22	1.63	64.24	1.43	<0.1	0.72	6.17	11.72	<0.1	0.45	2.51	<0.1
0.079	7.51	5.35	1.65	64.42	1.48	0.17	0.75	4.54	11.76	<0.1	0.44	1.85	<0.1
0.108	7.98	5.20	1.63	64.74	1.63	0.07	0.77	4.22	11.87	<0.1	0.48	1.43	<0.1
0.123	7.85	5.26	1.68	64.73	1.57	0.23	0.73	4.04	11.95	<0.1	0.50	1.38	<0.1
0.129	7.89	5.16	1.67	65.28	1.51	<0.1	0.80	4.21	11.98	<0.1	0.50	1.42	<0.1
0.136	8.00	5.18	1.66	65.22	1.59	0.10	0.75	4.09	11.87	<0.1	0.49	1.43	<0.1
0.146	7.88	5.29	1.69	65.15	1.45	0.10	0.69	4.18	11.77	<0.1	0.49	1.25	<0.1
0.151	8.06	5.25	1.60	65.09	1.44	0.20	0.76	4.16	11.96	<0.1	0.57	1.08	0.15
0.159	8.06	5.16	1.59	65.33	1.52	0.12	0.79	4.17	12.00	<0.1	0.49	0.93	<0.1
0.167	8.28	5.31	1.64	65.38	1.65	0.24	0.68	4.19	11.87	<0.1	0.52	0.65	<0.1
0.174	8.25	5.32	1.64	65.28	1.54	0.19	0.76	4.25	11.95	<0.1	0.50	0.66	<0.1
0.189	8.15	5.30	1.65	65.16	1.51	0.18	0.74	4.14	12.00	<0.1	0.50	0.49	<0.1
0.204	8.30	5.34	1.62	66.09	1.63	<0.1	0.74	4.18	12.01	<0.1	0.48	0.22	<0.1
0.218	8.43	5.39	1.57	66.13	1.61	0.29	0.74	4.13	12.22	<0.1	0.53	<0.2	<0.1
0.250	8.39	5.40	1.59	65.79	1.37	0.14	0.69	4.20	12.15	<0.1	0.49	<0.2	<0.1
0.351	8.50	5.31	1.65	66.00	1.46	0.15	0.75	4.14	12.13	<0.1	0.53	<0.2	<0.1
0.402	8.45	5.25	1.67	65.55	1.39	0.15	0.77	4.19	12.07	<0.1	0.50	<0.2	<0.1

Linescan through yellow silver stained surface of MCI 6

Distance (mm)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	Fe ₂ O ₃	AgO
0.000	7.27	5.03	1.58	64.35	1.55	0.23	0.77	3.77	11.64	0.64	3.17
0.004	7.16	5.27	1.68	64.11	1.50	<0.1	0.76	3.75	12.08	0.48	3.13
0.010	7.38	5.16	1.59	64.25	1.52	0.16	0.80	3.83	11.86	0.47	2.97
0.012	7.75	5.10	1.59	64.35	1.49	0.11	0.69	3.85	11.86	0.45	2.77
0.017	7.67	5.07	1.67	64.61	1.49	0.13	0.73	3.83	11.92	0.52	2.34
0.020	7.82	5.08	1.71	64.73	1.44	0.21	0.81	3.87	11.83	0.47	2.04
0.025	7.90	5.23	1.57	64.64	1.60	0.15	0.70	3.99	11.92	0.51	1.78
0.034	7.92	5.23	1.66	64.91	1.60	0.12	0.73	3.95	11.86	0.49	1.53
0.041	7.69	5.18	1.53	65.15	1.47	0.24	0.74	4.17	11.96	0.48	1.37
0.049	7.98	5.17	1.59	65.22	1.37	0.11	0.75	4.12	12.08	0.46	1.16
0.056	8.16	5.22	1.65	65.04	1.47	0.22	0.77	4.13	11.99	0.50	0.85
0.062	8.09	5.14	1.67	65.25	1.59	0.11	0.80	4.22	11.93	0.52	0.69
0.065	7.88	5.24	1.61	65.58	1.44	0.11	0.71	4.14	12.01	0.54	0.75
0.070	8.25	5.28	1.69	65.25	1.46	0.19	0.78	4.08	12.08	0.51	0.43
0.075	7.99	5.22	1.65	65.37	1.48	0.18	0.79	4.22	12.08	0.51	0.50
0.079	8.03	5.21	1.65	65.42	1.58	0.20	0.75	4.20	12.10	0.48	0.37
0.085	8.16	5.28	1.61	65.45	1.58	<0.1	0.81	4.16	11.96	0.54	0.35
0.087	8.28	5.22	1.67	65.50	1.47	0.15	0.69	4.15	12.06	0.47	0.33
0.092	8.18	5.23	1.64	65.57	1.51	0.16	0.73	4.18	12.05	0.45	0.30
0.097	8.20	5.27	1.73	65.45	1.48	0.06	0.80	4.14	12.15	0.49	0.23
0.103	8.17	5.15	1.71	65.54	1.40	0.13	0.72	4.23	12.11	0.52	0.31
0.105	8.15	5.37	1.62	65.57	1.53	0.11	0.79	4.19	12.01	0.54	<0.2
0.109	8.23	5.40	1.61	65.51	1.37	0.12	0.72	4.21	12.11	0.49	0.22
0.114	8.32	5.19	1.63	65.55	1.48	0.17	0.70	4.20	12.05	0.53	<0.2
0.121	8.42	5.20	1.60	65.52	1.44	0.15	0.75	4.18	12.09	0.53	<0.2
0.125	8.17	5.38	1.62	65.67	1.46	0.13	0.77	4.21	12.06	0.44	<0.2
0.128	8.19	5.30	1.63	65.49	1.51	0.15	0.79	4.17	12.07	0.52	<0.2
0.134	8.28	5.19	1.64	65.74	1.46	<0.1	0.74	4.26	12.12	0.46	<0.2
0.145	8.32	5.02	1.61	65.89	1.40	0.22	0.75	4.15	12.18	0.47	<0.2
0.153	8.41	5.27	1.52	65.38	1.49	0.23	0.80	4.25	12.09	0.56	<0.2

Linescan through paint and red silver stained surface of MCI7
 (<0mm = paint, >0mm = glass)

Distance (mm)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	MnO	Fe ₂ O ₃	AgO	PbO
-0.028	3.89	0.40	0.78	48.23	<0.1	0.24	0.39	6.98	0.55	3.40	0.84	1.01	33.29
-0.021	3.69	0.08	0.75	46.84	0.20	0.30	0.42	6.86	0.74	4.24	1.03	1.15	33.69
-0.014	3.62	0.32	0.99	47.21	<0.1	<0.1	0.44	7.04	0.73	5.09	1.35	1.15	32.03
-0.007	3.57	0.19	1.22	47.06	<0.1	0.19	0.64	7.02	0.72	5.61	1.54	1.24	30.99
-0.003	3.51	0.42	0.98	47.56	<0.1	0.10	0.53	7.20	1.26	6.06	1.49	1.32	29.49
0.007	4.07	4.93	1.58	62.68	1.41	0.24	0.73	8.80	11.13	0.23	0.49	1.97	1.75
0.013	4.34	5.23	1.58	63.64	1.44	0.10	0.70	8.59	11.50	<0.1	0.50	2.32	<0.1
0.021	4.91	5.15	1.59	63.61	1.52	<0.1	0.76	7.86	11.41	<0.1	0.52	2.44	<0.1
0.039	5.72	5.20	1.63	63.80	1.54	0.16	0.73	6.69	11.57	<0.1	0.47	2.43	<0.1
0.057	6.75	5.23	1.65	64.41	1.42	0.15	0.71	5.14	11.66	<0.1	0.47	2.35	<0.1
0.076	7.50	5.26	1.66	64.78	1.32	0.16	0.78	4.47	11.68	<0.1	0.52	1.87	<0.1
0.094	7.83	5.18	1.69	64.82	1.54	<0.1	0.71	4.11	11.78	<0.1	0.55	1.69	<0.1
0.112	7.95	5.22	1.69	64.76	1.52	0.12	0.74	4.21	11.99	<0.1	0.45	1.25	<0.1
0.13	7.66	5.23	1.56	65.06	1.49	0.24	0.79	4.15	11.92	<0.1	0.51	1.35	<0.1
0.149	7.67	5.37	1.59	65.26	1.55	0.13	0.72	4.12	11.85	<0.1	0.57	1.14	<0.1
0.168	8.00	5.22	1.66	65.13	1.49	0.17	0.72	4.15	12.06	<0.1	0.47	0.87	<0.1
0.186	7.88	5.15	1.68	65.53	1.53	0.22	0.75	4.20	12.11	<0.1	0.47	0.42	<0.1
0.203	8.16	5.29	1.71	65.42	1.42	0.18	0.76	4.13	11.98	<0.1	0.56	0.27	<0.1
0.222	8.28	5.28	1.69	65.46	1.49	0.12	0.73	4.13	12.01	<0.1	0.57	0.20	<0.1
0.24	8.37	5.20	1.74	65.35	1.42	0.19	0.79	4.20	11.97	<0.1	0.51	<0.2	<0.1
0.259	8.20	5.29	1.72	65.41	1.38	0.24	0.75	4.16	12.08	<0.1	0.60	<0.2	<0.1
0.276	8.33	5.45	1.60	65.29	1.58	0.20	0.73	4.16	11.89	<0.1	0.56	<0.2	<0.1
0.295	8.19	5.16	1.73	65.60	1.60	<0.1	0.78	4.15	12.15	<0.1	0.49	<0.2	<0.1
0.314	8.12	5.26	1.64	65.81	1.48	<0.1	0.77	4.21	12.01	<0.1	0.54	<0.2	<0.1
0.332	8.30	5.26	1.66	65.63	1.50	<0.1	0.75	4.18	11.96	<0.1	0.52	<0.2	<0.1
0.351	8.31	5.24	1.63	65.58	1.55	0.12	0.73	4.19	12.08	<0.1	0.50	<0.2	<0.1
0.368	8.36	5.24	1.51	65.79	1.44	0.10	0.77	4.22	12.03	<0.1	0.51	<0.2	<0.1
0.387	8.32	5.27	1.66	65.42	1.60	0.16	0.76	4.21	12.10	<0.1	0.48	<0.2	<0.1

Linescan through yellow silver stained surface of MCI7

Distance (mm)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	Fe ₂ O ₃	AgO
0.000	6.90	4.92	1.64	63.81	1.40	0.13	0.70	3.98	13.29	0.48	2.76
0.007	7.30	5.15	1.65	64.24	1.56	0.17	0.76	3.98	12.12	0.43	2.65
0.014	7.51	5.11	1.58	64.54	1.38	0.19	0.77	4.05	12.16	0.49	2.21
0.020	7.73	5.12	1.47	64.92	1.40	0.16	0.81	4.13	12.16	0.47	1.64
0.027	7.69	5.12	1.63	64.97	1.44	0.23	0.75	4.06	12.14	0.46	1.49
0.034	7.66	5.24	1.66	65.06	1.39	0.19	0.71	4.20	12.15	0.43	1.31
0.041	7.72	5.18	1.68	65.32	1.50	0.12	0.75	4.06	12.10	0.43	1.13
0.048	7.93	5.15	1.65	65.12	1.56	<0.1	0.78	4.07	12.19	0.52	0.94
0.055	7.90	5.29	1.63	65.34	1.45	0.14	0.78	4.15	12.03	0.53	0.77
0.062	8.02	5.23	1.71	65.27	1.59	<0.1	0.78	4.17	12.11	0.51	0.55
0.070	8.15	5.11	1.64	65.40	1.31	0.10	0.82	4.21	12.28	0.51	0.47
0.075	8.05	5.27	1.67	65.37	1.53	<0.1	0.72	4.30	12.05	0.59	0.35
0.082	8.18	5.15	1.67	65.42	1.51	<0.1	0.72	4.17	12.19	0.52	0.37
0.089	8.12	5.22	1.59	65.53	1.43	0.21	0.80	4.18	12.09	0.53	0.29
0.096	8.14	5.22	1.73	65.35	1.58	0.14	0.75	4.04	12.22	0.52	0.30
0.103	8.25	5.21	1.68	65.38	1.58	0.11	0.80	4.16	12.13	0.54	<0.2
0.109	8.08	5.22	1.70	65.64	1.41	0.14	0.79	4.11	12.22	0.55	<0.2
0.123	8.36	5.10	1.71	65.43	1.41	0.18	0.71	4.32	12.14	0.52	<0.2
0.137	8.20	5.32	1.64	65.44	1.56	<0.1	0.77	4.17	12.25	0.51	<0.2
0.153	8.07	5.30	1.70	65.58	1.49	0.14	0.76	4.18	12.21	0.52	<0.2

APPENDIX 2

Linescan through black paint of sample MC04 (<0mm = paint, >0mm = glass)

Distance (mm)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	MnO	Fe ₂ O ₃	PbO
-0.021	4.54	0.31	0.88	49.8	<0.1	0.12	0.27	5.59	1.35	2.51	0.86	32.88
-0.014	4.90	0.18	0.78	48.9	<0.1	0.16	0.23	6.10	0.67	4.63	0.95	31.77
-0.007	4.64	0.32	1.06	49.8	<0.1	0.34	0.25	6.04	0.94	4.70	1.53	29.88
-0.002	4.84	0.99	1.35	51.3	0.26	0.77	0.35	6.07	2.39	6.57	1.90	22.61
0.002	5.79	4.86	1.44	62.2	1.33	0.31	0.65	7.94	9.18	0.73	0.61	4.70
0.003	5.72	5.17	1.48	64.8	1.50	0.25	0.72	7.85	10.02	0.25	0.44	1.50
0.009	5.85	5.32	1.49	66.2	1.51	0.17	0.72	7.55	10.55	0.08	0.53	<0.1
0.019	6.01	5.47	1.45	66.1	1.57	0.18	0.72	7.41	10.51	0.03	0.51	<0.1
0.031	6.38	5.41	1.45	66.1	1.55	0.21	0.71	6.84	10.50	0.03	0.54	<0.1
0.047	6.88	5.48	1.51	66.2	1.55	0.10	0.75	6.22	10.60	0.04	0.45	<0.1
0.069	7.76	5.46	1.60	66.2	1.46	0.19	0.72	5.19	10.57	0.03	0.47	<0.1
0.098	8.32	5.45	1.58	66.7	1.60	0.14	0.80	4.29	10.74	0.01	0.50	<0.1
0.134	8.63	5.44	1.55	66.6	1.43	0.11	0.76	3.92	10.69	0.04	0.46	<0.1
0.183	8.71	5.46	1.45	66.1	1.50	0.25	0.75	3.83	10.60	0.05	0.54	<0.1
0.249	8.52	5.46	1.57	66.7	1.60	0.22	0.71	3.93	10.65	0.04	0.44	<0.1

Linescan through black paint of sample MC09 (<0mm = paint, >0mm = glass)

Distance (mm)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	Cl	K ₂ O	CaO	MnO	Fe ₂ O ₃	PbO
-0.012	5.05	<0.1	0.39	53.9	0.23	0.23	1.25	1.05	0.15	0.44	37.44
-0.009	4.87	0.14	0.39	54.9	<0.1	0.16	1.26	1.14	0.39	0.25	36.80
-0.008	6.05	0.18	0.53	53.3	0.56	0.20	1.52	2.64	2.82	0.68	31.23
-0.004	7.59	0.27	1.19	52.8	1.20	0.22	1.98	5.33	5.55	1.09	22.18
-0.001	9.17	0.12	1.37	65.0	0.76	0.50	2.46	11.57	1.03	0.28	7.09
0.001	9.77	<0.1	1.46	70.2	0.61	0.48	2.61	13.78	0.40	0.20	0.91
0.004	10.30	<0.1	1.39	70.3	0.75	0.46	2.59	13.69	0.34	0.16	<0.1
0.007	10.06	0.19	1.45	70.4	0.62	0.49	2.56	13.57	0.33	0.11	<0.1
0.012	10.21	<0.1	1.48	70.3	0.63	0.47	2.37	13.59	0.31	0.13	0.15
0.020	10.52	<0.1	1.53	70.5	0.64	0.47	2.17	13.67	0.29	0.18	<0.1
0.023	10.71	<0.1	1.49	70.4	0.67	0.47	2.07	13.48	0.25	0.17	<0.1
0.026	10.49	<0.1	1.54	70.4	0.67	0.44	1.90	13.56	0.30	0.13	<0.1
0.031	10.75	<0.1	1.48	70.7	0.76	0.47	1.71	13.57	0.30	0.19	<0.1
0.034	10.74	<0.1	1.56	70.5	0.61	0.46	1.67	13.57	0.36	0.14	<0.1
0.040	10.93	<0.1	1.48	70.4	0.71	0.46	1.52	13.58	0.26	0.18	<0.1
0.045	10.70	<0.1	1.46	70.6	0.71	0.48	1.28	13.73	0.30	0.13	<0.1
0.056	11.86	<0.1	1.50	71.0	0.61	0.49	0.82	13.65	0.30	0.09	<0.1
0.062	11.61	<0.1	1.55	70.7	0.71	0.48	0.70	13.71	0.32	0.19	<0.1
0.072	12.25	<0.1	1.47	70.4	0.76	0.49	0.52	13.57	0.30	0.17	<0.1
0.082	12.30	<0.1	1.46	70.9	0.63	0.54	0.34	13.55	0.26	0.09	<0.1
0.112	12.26	<0.1	1.45	70.4	0.68	0.48	0.24	13.59	0.37	0.15	<0.1
0.125	12.51	<0.1	1.58	70.7	0.73	0.51	0.19	13.58	0.26	0.13	<0.1
0.146	12.64	<0.1	1.39	70.6	0.64	0.48	0.24	13.50	0.30	0.14	<0.1



ENGLISH HERITAGE RESEARCH DEPARTMENT

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