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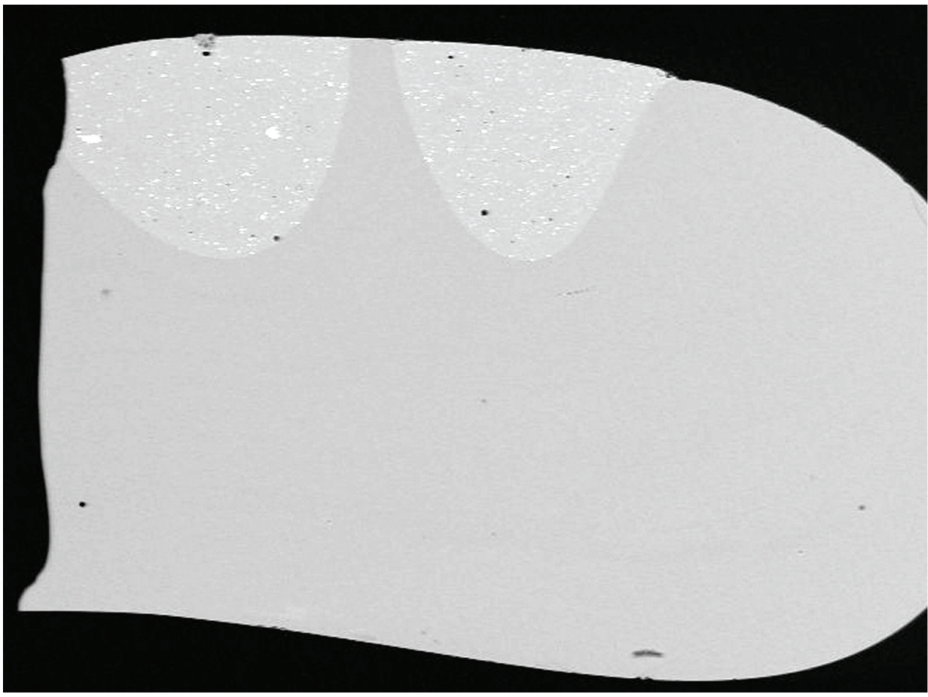
35–39 SOUTH MAIN STREET, CORK, IRELAND
ANALYSIS OF MEDIEVAL GLASS VESSELS

TECHNOLOGY REPORT

Matt Phelps



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35–39 South Main Street, Cork, Ireland

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SUMMARY

Seventeen fragments of glass were excavated from 35–39 Main Street, Cork, Ireland dating approximately to the 11th–12th century. One vessel was a decorated polychrome vessel stylistically similar to two contemporary vessels found from high status sites in France and Italy. Compositional analysis was carried out on the 17 fragments of glass using an SEM with EDS detector. The analysis showed 16 fragments to be ancient glass which fell into three main compositional groups and two sub-groups (Groups 1a, 1b, 2 and 3). For all groups the glass was found to be of a soda-lime-silica type made of natron flux most similar to 1st–3rd century Roman period glass and showing indications of recycling. The groups showed close similarity to Roman blue-green glass, a common glass for vessel manufacture in the Roman period. Colouration was provided by antimony oxide in the opaque white glass and manganese oxide in the purple glass. The colourless glass had increased levels of lead oxide. At least 3 different vessels were identified using typology and composition.

ACKNOWLEDGEMENTS

I would like to thank Clare McCutcheon for offering these samples for research and for allowing us to take samples. Thanks also to Rose Cleary, the Project Manager for the Archaeological site in Cork, for allowing English Heritage involvement in the project. Lastly, acknowledgement has to be made to Sarah Jennings who initiated this project with the preliminary sampling and the sample preparation; sadly she was unable to see this project completed.

ARCHIVE LOCATION

The samples taken for scientific analysis are held by English Heritage, Fort Cumberland, Portsmouth, PO4 9LD. The original glass fragments are in the possession of Rose Cleary, Department of Archaeology, University College, Cork.

DATE OF RESEARCH

2010–2011

CONTACT DETAILS

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INTRODUCTION

Decorated and coloured glass fragments belonging to a number of glass vessels were discovered during excavations in Cork, Ireland. These fragments have been dated stratigraphically to the late 11th – early 12th century. Stylistically these fragments are so far a unique find in Ireland but similar glasses have been discovered at high status sites on mainland Europe (Simon-Hiernard 2001; Whitehouse 2003a; Baumgartner and Krueger 1988). This project will discuss the glass stylistically and in terms of the chemical composition to better understand the provenance and manufacture of the glass. Analysis will be undertaken using SEM-EDS and the results compared to glasses of Roman and early Medieval period origin.

BACKGROUND

The Material

The glass fragments were discovered during excavations of a rich urban site at 35–39 South Main Street in the centre of Cork, Ireland. Site excavations were managed by Rose Cleary and 17 samples were sent to Sarah Jennings at English Heritage for further investigation. A catalogue of the samples is given in Table 5 and Figures 10 –18 (Appendix). The glass fragments are from similar contexts; the foundations, under floor and backyard area of a Hiberno-Norse house. The fragments are dated to the late 11th century – early 12th century from archaeological context (Clare McCutcheon *personal communication*) although this is a *terminus ante quem* and the vessels themselves could be much older. The nature of the fragments indicate more than one vessel, one being of purple/reddish transparent glass with overlaid decoration of opaque white glass (Figure 1).

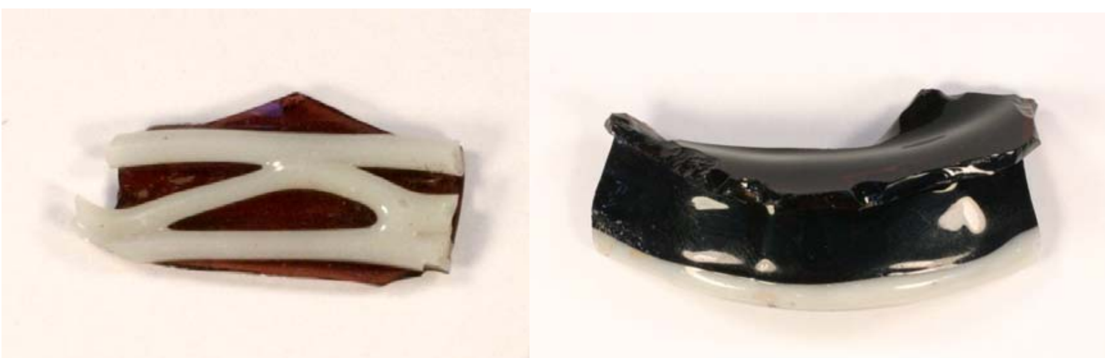

Figure 1. Left, sample CG09, purple/red transparent glass with white overlay. Right, CG01, base piece of possibly the same vessel, purple glass (thickness makes it look darker) with white overlay.

There are nine purple glass fragments; four of these fragments are decorated with one to five lines of opaque white overlay. All the decorated purple fragments probably come from the same vessel. There are three white opaque fragments which do not match the decoration and belong to at least one more vessel (Fig. 15, Appendix). Lastly, there are five fragments of colourless/very pale green glass which belong to another vessel. The colour and decoration of the fragments indicate at least three vessels.

Several similar glasses matching the fragments from Cork have been identified. They are all from central and western Europe (Figure 4) and all date from 10–12th-century contexts. The glass finds have come from high status sites; castles, abbeys, churches and commercial centres (Simon-Hiernard 2001, 72). All the glasses have a coloured transparent main body of the vessel with a number of lines of opaque white glass as decoration, three vessels (Saint-Savin, San Michele and Orleans) also have prunts (Figures 2 and 3). The majority of the glasses are transparent blue and the San Michele glass is transparent green. This differs to the Cork glass which is transparent purple. As yet the location of manufacture of these distinctive glasses is unknown but it is likely to be mainland Europe and Germany has been suggested.

The most complete vessel was found at Saint-Savin Abbey and is now housed at the Musee Sainte-Croix, Poitiers (Simon-Hiernard 2001; Fig. 2) It was discovered in 1866 inside a late 11th century alter and has been contextually dated to the mid 11th century. It is transparent blue, roughly egg shaped, 120mm high and 125mm at widest point with opaque white trailing decoration and prunts (Simon-Hiernard 2001, 72–74; Fig 2). Eighteen fragments of a very similar cup were found at Grotta di San Michele in Olevano, Italy in a 10–11th century context (Whitehouse 2003a, 403). It is also roughly egg shaped, 90mm diameter at the rim and of transparent green glass. The decoration is very similar to the French example.

Figure 2. Image of the Saint-Savin glass vessel held at the Musee Saint-Croix in Poitiers. (http://www.musees-poitiers.org/)

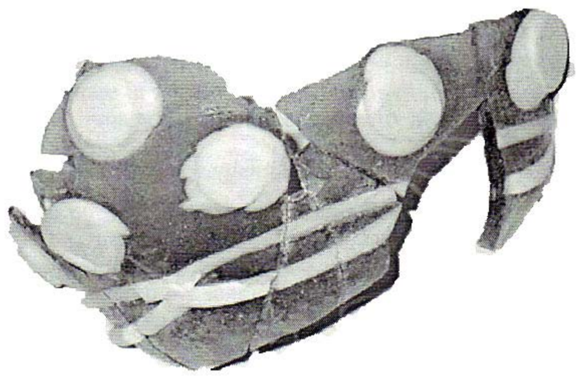

Figure 3. Image of the glass fragment from Grotta di San Michele, Olevano sul Tusciano (Whitehouse 2003a, 406)

Compositional analysis of the white opaque portion of the Saint-Savin glass was carried out using laser ablation ICP-MS (Gratuze *et al* 1997, 35; Table 2). The results indicated a natron glass with antimony as the opacifier. They determined a date of manufacture ranging from the Roman period to no later than the 12th century by looking at a selection of trace elements (cobalt, indium, zinc, lead) (ibid, 36; Simon-Hiernard 2001, 72) and comparing with trace elements in glasses from later periods.

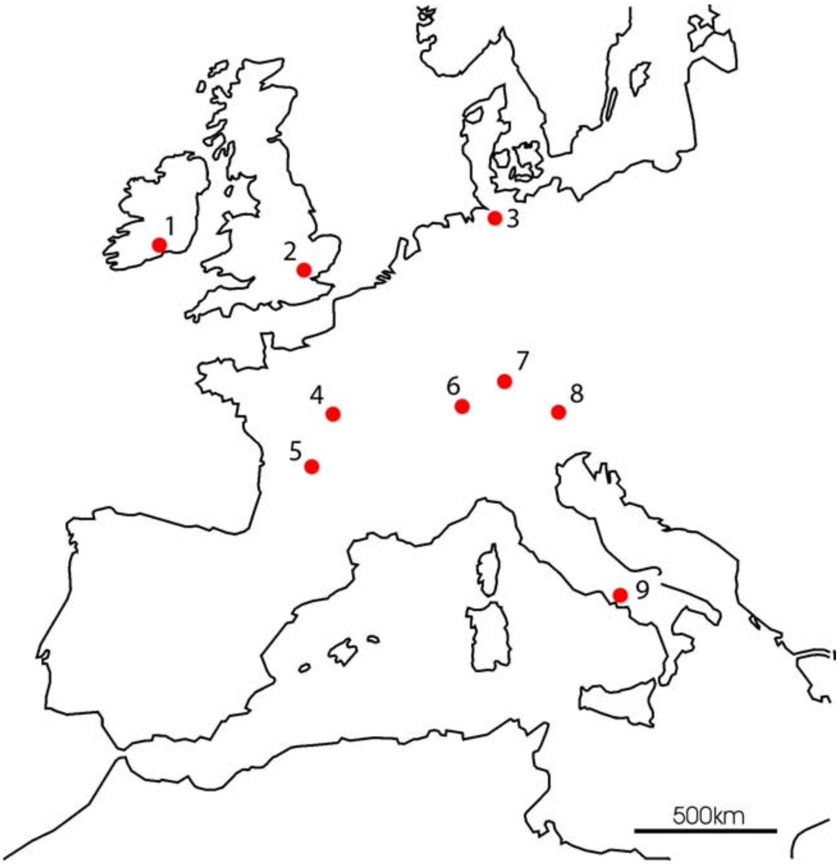

Figure 4. Location of medieval blue glasses decorated with white trailing in Europe. 1. Cork. 2. Waltham Abbey 3. Haithabu (Germany). 4. Orleans. 5. Saint-Savin Abbey. 6. Fullinsdorf (Swizerland). 7. Gammertingen (Germany). 8. Assling (Austria). 9. Grotta di San Michele.

Several other similar fragments have been found across Europe. Blue vessels with white trailing decoration have been found in Orleans (France) (Whitehouse 2003a, 406), Fullinsdorf (Swizerland), Gammertingen and Haithabu (both Germany) and Assling (Austria) (Baumgartner and Krueger 1988, 77–80); all having mid-10th- to mid-12th-century contexts. A similar glass but with reversed colouration was found at Waltham Abbey, Essex. It was a white opaque glass with three dark brown trailed bands found in a 13th century context (Rachel Tyson *personal communication*). Fragment is illustrated in Figure 19 (Appendix) and shows similarity with CG06 in Figure 14.

Background to Roman and Medieval Glass Production

The 10–12th-century glass industry was primarily based on local production using plant ash flux sources (forest glass) but Theophilus notes that the practise of recycling natron based Roman glass continued to occur in the 12th century (Hawthorn and Smith 1979, 59). Cox and Gillies (1986) also found an estimated 700 examples of reused Roman natron glass in 12th-century windows from York Minster. Therefore, while new glass was made in 10–12th century, there was still a significant amount of recycled natron glass in circulation. Natron glass was the dominate flux source from the Roman period to the 10th century, although how much was new production and how much was recycled is debated (Jackson 1996). Thus to understand the range of glasses in the medieval period, it is necessary to understand glass production in the Roman period.

Glass in the Roman period was based on three ingredients; soda, lime and silica. Silica is the main component of glass, often derived from sand, but with a melting temperature of >1700°C; silica on its own melts much too high for glass production (Freestone 2008). Soda is added as a flux which lowers the melting temperature to a manageable ~900°C. There are two main flux sources; minerals sources and plants (Shortland *et al* 2006). Mineral sources are evaporite deposits of sodium salts such as natron or trona. Plant sources are either the ashes of halophytic plants which are high in soda and potash or tree sources such as beech and oak, high in potash, magnesia and calcium. The final ingredient of a glass is lime (calcium oxide). The lime acts as a stabilizer to fix the glass structure preventing the glass dissolving and weathering. In Roman times calcium was a component of the sand and in medieval Northern Europe it was found as a component of the wood ash.

Changes in glass manufacture can be traced through the glass composition. The subject has been dealt with well over the years starting with the pioneering work of Turner (1956) and Sayre and Smith (1961; 1967). Analysis of glasses from the Roman and post-Roman periods has provided a detailed picture of the glass industry and a clear indication of the prevailing glass compositions (Sayre and Smith 1961; 1967; Wedepohl 1997; Brill 1999; Freestone *et al* 2002; Jackson 2005; Silvestri *et al* 2005). Roman glass in the 1st–4th centuries was a soda-lime-silica glass categorised by high soda (16–20%), and low (<1%) potash and magnesia (Brill 1999; Silvestri *et al* 2005) termed low magnesia glass (LMG – Sayre and Smith 1967; Henderson 1988a; 2000). This composition indicated a mineral source such as natron as the flux. Natron sources were produced by evaporation and are known from sites such as Wadi Natrun in Egypt. Natron was the flux for the Roman glass industry (Shortland *et al* 2006). The natron was mixed with sand to provide the silica and the lime content. Lime-rich sands are often found in coastal locations, eg the Belus river mentioned by Pliny (Freestone 2008).

A lack of chemical diversity was noticed in glass analyses from across the Roman Empire (Sayre and Smith 1961). This indicated glass production to be occurring at only a few large-scale primarily locations (Freestone 2005; Freestone *et al* 2002, 259; Figure 5). Large production sites have been found on the Levantine Coast (Gorin-Rosen 2000), Syria-Palestine and Egypt (Nenna *et al* 2000). Large tank furnaces have been found capable of producing 8–9 tonnes of glass from post-Roman sites (Brill 1967) and similar production scales were likely in the Roman period. After production the glass was broken into chunks and exported to secondary workshops (Paynter 2006, 1038). Secondary workshops re-melted the glass chunks and shaped the glass for selling to the local region. This model explained the homogeneity of Roman glass.

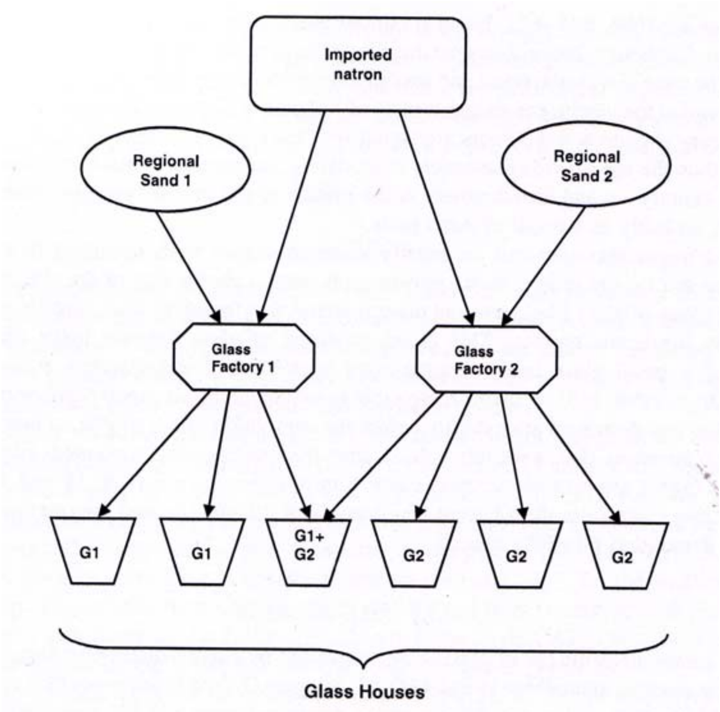

Figure 5. Schematic model of the Roman glass industry (from Freestone et al *2002, 259)*

In the late Roman Empire (5th century onwards) the compositions of glass changed from the standard Roman composition (Freestone *et al* 2000; 2002; Foy *et al* 2003). New glass sorts were identified such as HIMT glass (Freestone 1994) containing high iron, manganese and titania and another was Levantine 1 (Freestone 2000) made from coastal sands that have lower soda, higher lime, alumina and low iron. The changes were due to different sand being used, possibly from a change in the production location (Silvestri *et al* 2005, 810). Anglo-Saxon (5–8th century) period glasses from Britain contain HIMT glass and HIMT glass has been found across Europe (Freestone *et al* 2008). The trade in raw glass continued in the post–Roman period, this has been proven by the discovery of chunks of raw HIMT glass in a post-Roman shipwreck off the coast of France (Whitehouse 2003b, 305).

However, there were signs that all was not well. By looking at the abundance of trace elements associated with colourants (Co, Cu, Zn, Pb, Ag) later Anglo-Saxon glasses (6–8th century) showed increased levels of lead, cobalt, copper and reduced zinc. This indicated glass mixing and recycling with the loss of the more volatile elements (Freestone *et al* 2008). Some glass samples also showed increased amounts of magnesia and potash. Freestone *et al* (2008, 39) interpreted this as the mixing of small amounts of plant ash glass with natron glass to pad out the glass. This may indicate a time where the supplies of raw glass could not meet demands.

In the 8th–9th centuries a 'revolution' (Silvestri *et al* 2005, 798; Henderson 2002, 595; Freestone *et al* 2008, 29) in glass production occurred as natron began to be replaced by plant ash. The resulting compositions were much lower soda but higher potash and magnesia (Sayre and Smith 1967; Silvestri *et al* 2005). Plant ash was provided by trees like beech in northern and western Europe and by halophytic plants like *Salicornia* in the Middle East. This revolution was probably the result of a final cessation of the natron trade from Egypt due to political destabilisation (Shortland *et al* 2006) although analyses have shown that the trade in waste Roman glass (cullet) continued. Analysed glass from 8–9th century Hamwic (Hunter and Heyworth 1998) and York (Jackson 1996) which contained colourant impurities showed continued use of recycled Roman glass. Use of heavily coloured glass in the 8–10th centuries suggested 'increasing dependence upon Roman material' with the glass being salvaged from decaying Roman-buildings (Freestone *et al* 2008, 41). The trade in new raw glass was replaced by a trade in old Roman glass for recycling.

Decolourisers and colourants

Chemical additives were used extensively in ancient glass to modify colour, add opacity and to decolourise glass. Roman glass contained a range of colourants used to colour transparent glass; Fe^{2+} and Fe^{3+} could be manipulated to produce a range of colours from brown, green, blue and yellows; Mn^{3+} for purple; Mn^{2+} for faint yellow; Cu^{2+} for blue glass with a greenish tinge; and Co^{2+} for making a deep blue glass (Mirti *et al* 2000, 221; Pollard and Heron 2008, 158). The different colours and hues were produced by modifying the redox conditions in a furnace, either by controlling the amount of oxygen or by adding reducing agents such as manganese oxide (*ibid*).

Manganese oxide was added to Roman glasses as a decolourant from the 1st century AD (Sayre 1962, 263; Jackson 2005, 763). Most ancient glasses contains iron oxide impurities and manganese acted to oxidise the strongly coloured Fe^{2+} to the less strongly coloured Fe^{3+} reducing its colouring effect (Mirti *et al* 2002, 221; 2000, 366–7). The pale pink of the Mn^{3+} counteracted the pale yellow of the Fe^{3+} making the glass look colourless. Antimony oxide was also used as a decolourant in the early Roman Empire, but declined in use after the 2nd century AD and was replaced by manganese oxide.

Antimony oxide was another material regularly added in Roman times to produce opaque white glass. The addition of antimony oxide resulted in a reaction with the calcium in the glass to produce insoluble crystals of calcium antimonate. These white crystals scattered light to produce opacity (Turner and Rooksby 1961; Henderson 2000). For yellow opaque glass lead oxide (galena) and antimony oxide was added, they combined in the glass to form lead antimonate ($Pb_2Sb_2O_7$). From the 4th century antimony use declined and was replaced with tin compounds (Tite *et al* 2008, 68; Freestone and Bimson 1995, 422). Tin-based opacifiers were used extensively from the

5th to 9th centuries in Anglo-Saxon England (Bayley 2000), early Christian Ireland (Henderson 1988b) and Merovingian Germany (Heck and Hoffman 2000). Tin oxide (SnO_2) produced a white opaque glass and lead stannate ($PbSnO_3$) a yellow opaque glass. The reduction in antimony usage could have been caused by trade route disruptions at the end of the Roman Empire. Studies by Mirti *et al* (2002) found glass containing calcium antimonate in the 9th century and that antimony was certainly present in glass until the end of the 1st millennium AD (*ibid*, 229) although this is most likely through the recycling of Roman opaque glasses and not production of new opaque glass.

AIMS

The aim of this project is to provenance the glass fragments and to better understand the manufacture of the glass. This will rely on a detailed examination of the glass composition and comparing to other known glass types.

METHOD

Sampling was undertaken by Sarah Jennings who removed between 4 and 81mg of glass from each of the 17 samples. Care was taken to remove the minimum of material. Samples were embedded in resin before hand polishing to a 1micron finish using diamond paste to create a polished block. Samples were carbon coated before analysis.

Analysis was carried out using a scanning electron microscope (SEM) with an energy dispersive X-ray spectrometer (EDS). The SEM used was an FEI Inspect F with an Oxford Instruments X-act detector and INCA software for element quantification. The working parameters were set to an accelerating potential of 25kV, a current of 1.2nA, 100s counting time and 10mm working distance. Three representative areas of approximately 300 by 500 microns were taken of each different glass type in each sample to determine the bulk composition. Additional analyses were undertaken of notable inclusions in the glass when present, either spot analysis or much smaller size areas. All of the results are presented as normalised compound weight % with oxygen calculated stoichiometrically for all elements except chlorine which is reported as element wt%.

The elements sought were F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Co, Ni, Cu, Zn, Sb, Sn, Ba and Pb. Calibration of the spectra was performed using a cobalt standard before each session. To ascertain the accuracy of the results, glass reference materials of a similar composition were analysed. The results for Corning glass standards A and B are shown in Table 6 (Appendix) indicating results for relative percentage variation from the known. The maximum variation for the major elements is <5% (Na_2O, MgO, Al_2O_3, SiO_2, CaO); <10% for the minor elements (FeO, MnO, P_2O_5) and <15% for

K_2O; and varying from 9.15% (CuO) to 83.13 (TiO_2) for the minor and trace elements (SO_3, CuO, PbO, Sb_2O_5 TiO). The minimum detection limits for most of the measured elements was 0.1wt% and 0.3wt% for P_2O_5, SnO_2, BaO, Sb_2O_5, PbO and SO_3.

RESULTS

Type of glass?

All of the Cork glass is high soda (~17%) and low magnesia and potash (<1.1) except for CG05. This is indicative of a natron flux source rather than a plant ash. CG05 was found to be a modern glass (see Appendix). The natron glasses are in the Roman tradition and not the wood ash tradition of the medieval period. Complete data for the individual samples is shown in Table 1. For comparison, values have been added for 1st–3rd century Roman (from Binchester, Colchester and Lincoln; Paynter 2006), late and Post-Roman (Foster and Jackson 2009), 8–10th century wood ash glass from Germany (Wedepohl 1997) and the Sainte-Savin glass analysis (Gatuze *et al* 1997; Table 2). Figure 5 is a graph of soda verses magnesia illustrating the natron region (containing the Cork, Roman and Post-Roman natron glasses) and the wood ash region (containing the 8–10th century wood ash glass). All the natron glasses have high soda (~15–20%) and low magnesia (<1.5%). The natron glass from Saint-Savin has a particularly high soda level (~25%). By comparison the wood ash glass contains only <2% soda and 2.5–5% magnesia.

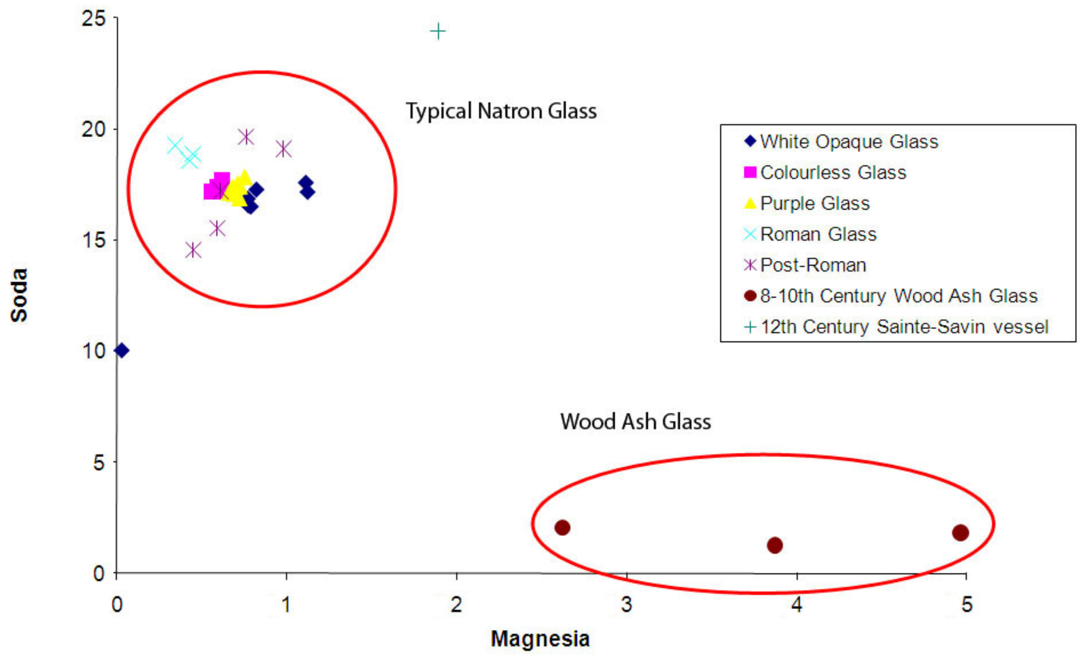

Figure 5. Graph showing soda against magnesia.

Table 1. Results for the Cork glass fragments reported as normalised (to 100%) compound wt% oxides.

Purple Glass

Group	Sample	F	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	FeO	CoO	CuO	ZnO	SnO_2	Sb_2O_5	BaO	PbO
1a	CG01	<0.3	17.8	0.8	2.5	66.2	<0.3	<0.3	1.1	0.8	6.7	0.2	1.9	0.9	<0.1	<0.1	<0.1	<0.3	0.5	<0.3	<0.3
1a	CG02	<0.3	17.6	0.7	2.5	66.5	<0.3	<0.3	1.1	0.7	6.7	0.2	1.9	0.9	<0.1	<0.1	<0.1	<0.3	0.5	<0.3	<0.3
1a	CG03	<0.3	17.1	0.7	2.5	66.4	<0.3	<0.3	1.1	0.8	6.9	0.2	2.0	0.9	<0.1	<0.1	<0.1	<0.3	0.5	<0.3	<0.3
1a	CG04	<0.3	17.4	0.7	2.4	66.3	<0.3	<0.3	1.1	0.8	6.9	0.2	2.0	1.0	<0.1	<0.1	<0.1	<0.3	0.4	<0.3	<0.3
1a	CG06	<0.3	17.1	0.7	2.4	66.4	<0.3	<0.3	1.1	0.8	7.1	<0.1	2.1	0.9	<0.1	<0.1	<0.1	<0.3	0.5	<0.3	<0.3
1a	CG08	<0.3	17.3	0.7	2.4	66.6	<0.3	0.4	1.1	0.7	6.9	0.2	2.0	1.0	<0.1	<0.1	<0.1	<0.3	0.4	<0.3	<0.3
1a	CG09	<0.3	17.4	0.7	2.5	66.2	<0.3	<0.3	1.1	0.8	6.9	0.2	2.0	0.9	<0.1	<0.1	<0.1	<0.3	0.6	<0.3	<0.3
1a	CG10	<0.3	16.9	0.7	2.5	66.6	<0.3	<0.3	1.1	0.8	6.9	<0.1	2.0	0.9	<0.1	<0.1	<0.1	<0.3	0.5	<0.3	<0.3
1a	CG11	<0.3	17.4	0.7	2.5	66.0	<0.3	<0.3	1.1	0.8	6.9	0.2	2.0	0.9	<0.1	<0.1	<0.1	<0.3	0.5	<0.3	<0.3

White Glass

Group	Sample	F	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	FeO	CoO	CuO	ZnO	SnO_2	Sb_2O_5	BaO	PbO
1b	CG01	<0.3	17.3	0.8	2.1	66.5	<0.3	0.4	1.0	0.6	6.2	<0.1	0.3	0.4	<0.1	<0.1	<0.1	<0.3	4.0	<0.3	<0.3
1b	CG06	<0.3	16.6	0.8	2.1	66.7	<0.3	0.5	0.9	0.6	6.7	<0.1	0.2	0.5	<0.1	<0.1	<0.1	<0.3	4.2	<0.3	<0.3
1b	CG09	<0.3	16.9	0.8	2.1	66.7	<0.3	0.4	0.9	0.6	6.5	<0.1	0.2	0.4	<0.1	<0.1	<0.1	<0.3	3.9	<0.3	<0.3
1b	CG10	<0.3	16.5	0.8	2.1	66.9	<0.3	0.4	0.9	0.6	6.6	<0.1	0.2	0.5	<0.1	<0.1	<0.1	<0.3	4.0	<0.3	<0.3
2	CG12	<0.3	17.2	1.1	2.1	67.1	<0.3	0.4	1.1	0.6	6.7	<0.1	0.3	0.4	<0.1	<0.1	<0.1	<0.3	2.7	<0.3	<0.3
2	CG07	<0.3	17.6	1.1	2.1	66.7	<0.3	<0.3	1.0	0.6	6.6	<0.1	0.3	0.5	<0.1	<0.1	<0.1	<0.3	2.7	<0.3	<0.3
Modern	CG05	3.9	9.8	<0.1	7.5	60.8	<0.3	<0.3	<0.1	2.5	4.5	<0.1	<0.1	<0.1	<0.1	<0.1	9.7	<0.3	<0.3	0.6	<0.1

Pale green Glass

Group	Sample	F	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	FeO	CoO	CuO	ZnO	SnO_2	Sb_2O_5	BaO	PbO
3	CG13	<0.3	17.2	0.6	2.4	67.1	<0.3	0.4	1.2	0.7	6.5	<0.1	0.7	0.6	<0.1	<0.1	<0.1	<0.3	0.9	<0.3	1.5
3	CG14	<0.3	17.2	0.6	2.4	66.9	<0.3	<0.3	1.2	0.7	6.6	<0.1	0.7	0.6	<0.1	<0.1	<0.1	<0.3	0.8	<0.3	1.5
3	CG15	<0.3	17.2	0.6	2.4	67.1	<0.3	0.4	1.2	0.8	6.7	0.2	0.7	0.6	<0.1	<0.1	<0.1	<0.3	0.7	<0.3	1.5
3	CG16	<0.3	17.7	0.6	2.3	67.2	<0.3	<0.3	1.1	0.8	6.6	<0.1	0.7	0.7	<0.1	<0.1	<0.1	<0.3	0.6	<0.3	1.2
3	CG17	<0.3	17.4	0.6	2.4	67.1	<0.3	<0.3	1.2	0.8	6.7	0.2	0.7	0.7	<0.1	<0.1	<0.1	<0.3	0.6	<0.3	1.3

Table 2. One analysis of the 12th-century glass from Saint-Savin (Gratuze et al *1997) by ICP-MS.*

11–12th-century White Opaque glass

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	FeO	CoO	NiO	CuO	ZnO	SnO_2	Sb_2O_5	PbO
Saint-Savin	24.40	1.89	2.00	56.80	n.d	n.d	1.80	0.84	6.80	0.12	0.21	1.43	0.05	0.01	0.86	n.d	0.06	2.30	0.27

Table 3. Spot analysis white inclusions found in opaque white glasses. Results as normalised (to 100%) elemental wt% due.

	O	F	Na	Mg	Al	Si	Cl	K	Ca	Ti	Mn	Fe	Zn	Sn	Sb	Ba	
CG01	28.8	<0.3	3.7	0.5	0.3	7.0	0.3	<0.1	14.5	<0.1	<0.1	<0.1	<0.1	<0.3	45.0	<0.3	Calcium Antimonate
CG05	28.2	18.1	4.7	<0.1	3.6	26.8	<0.1	1.8	8.9	<0.1	<0.1	<0.1	6.5	<0.3	0.5	0.6	Zinc/Flouride inclusion

Table 4. Averaged glass values of the different groups. Normalised wt% by oxide.

Groups	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	Cl	K_2O	CaO	TiO_2	MnO	FeO	ZnO	Sb_2O_5	PbO
1a	17.3	0.7	2.4	66.4	0.3	1.1	0.8	6.9	0.2	2.0	0.9	<.01	0.5	<0.3
1b	16.8	0.8	2.1	66.7	0.4	0.9	0.6	6.5	<0.1	0.2	0.5	<.01	4.0	<0.3
2	17.4	1.1	2.1	66.9	0.4	1.1	0.6	6.6	<0.1	0.3	0.5	<.01	2.7	<0.3
3	17.3	0.6	2.4	67.1	0.3	1.2	0.8	6.6	<0.1	0.7	0.7	<.01	0.7	1.4
Modern (CG05)	10.0	<0.1	7.8	63.6	<0.3	<0.1	2.7	4.7	0.3	<0.1	0.1	10.2	<0.3	<0.3

Different Glass Groups

Of the ancient glasses, three main groups and two sub groups are discernable. Table 3 contains average glass results split by group. The different groups are well illustrated in Figures 6, 7 and 9.

Group 1a: this is a purple translucent natron glass. It is characterised by high manganese oxide (~2%; responsible for the purple colour) and increased titania and iron oxide.

Group 1b: this is an opaque white natron glass found in conjunction with Group 1a glass. Very similar to 1a but containing less titania, manganese oxide and iron oxide. It contains ~4% antimony which is used as a white opacifier.

Group 2: this is a second group of opaque white glasses. Similar in composition to 1b but containing lower antimony (2.7%) and has increased levels of magnesia (1.1%).

Group 3: transparent colourless (very pale green) natron glass. The levels of iron oxide and manganese oxide are midway between groups 1a and 1b. 1.4% lead oxide indicates possible mixing with a high lead glass, possibly high lead enamel. For soda, alumina, lime and potash composition is very similar to 1a and 1b.

Group 1a was decorated with group 1b and therefore are found together as one vessel. Group 2 is a slightly different composition of white opaque glass and forms a second vessel. Group 3 is colourless glass and forms a third vessel. Therefore there are at least three ancient vessels in this assemblage.

Differentiating the Glass Groups

Glass compositions can be differentiated by looking at the differences in some of the minor and major elements. Variations in some elements (eg Fe, Ti, Al, Mn, Ca) can indicate different sand sources (Aerts *et al* 2003, 664). Figure 6 is a graph of iron oxide against alumina. As can be seen, the fragments separate out into their different glass groups. Group 1a contains the largest amounts of iron oxide, alumina and also of manganese and titania. Manganese is used as a colouring agent and the raised levels of iron oxide and titania could be due to impurities in the manganese source used. Groups 1b and 2 on the other hand seem to be the cleanest of the glasses with the lowest levels of impurities. Group 3, the colourless glass, has mid-level of manganese oxide, iron oxide and titania which could be from the use of an alternative base glass with slightly higher impurities, such as HIMT glass. The very slight disparity between alumina content could be due to a dilution effect caused by the addition of the various colourants (antimony and manganese oxide) in the different fragments. The Sainte-Savin glass contains higher iron oxide than the Cork glass but similar titania.

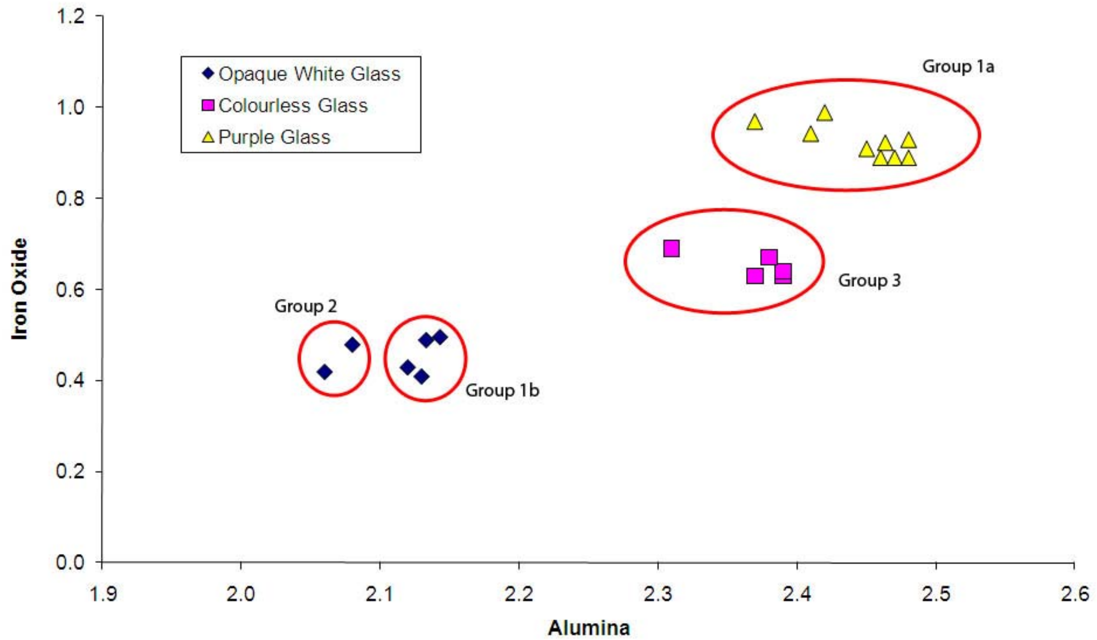

Figure 6. Iron Oxide verses Alumina.

Colourants and Additives

The main colourants and decolourisers used in the Cork glass are antimony and manganese (Figure 7). The opaque white Cork glass contains between 2.6–4.2% antimony oxide, higher than the green and purple glasses that contain <1%. At high magnification white crystals of calcium antimonate 2–15 microns across are visible (Figure 8). Spot analysis (Table 3) confirms these are calcium antimonate. Two opaque white glasses (Group 2) contain less antimony, a level which is similar to the Sainte-Savin vessel. Group 3 contains between 0.6–0.9% manganese oxide possibly due to the use of manganese-rich glass rather than deliberate addition as a decolouriser. The purple glass contains significant amounts of manganese oxide (~2%) which is consistent with its use as a purple colourant. This could have been added to the glass in Roman times or maybe when the vessel was made in the 10–11th century. As well as high manganese, the colourless glass (Group 3) also contains higher than expected levels of lead. Lead compounds have been used to make yellow opaque glasses and have been used in Cameo glasses (Brill 1999) but is not found in these concentrations in colourless glasses. Silvestri suggests that the addition of lead to a glass in amounts over 1000ppm would be to impart 'brilliance' in the glass (Silvestri *et al* 2005, 811) making it more sparkly by increasing its refractive index. But the lead could be from the mixing in of high lead glasses such as enamels (Henderson 1991).

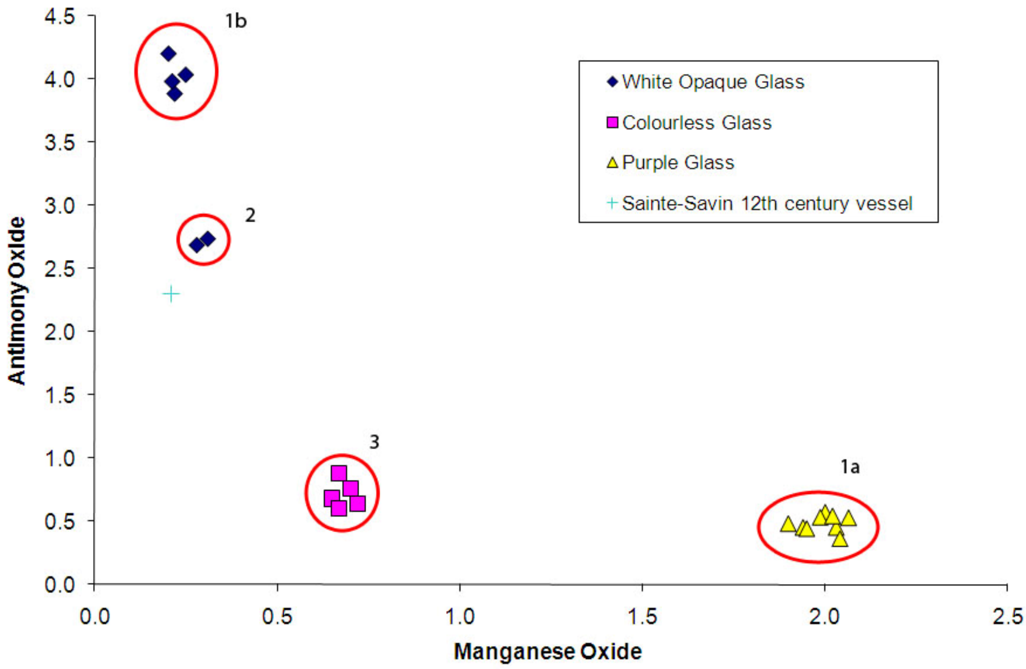

Figure 7. Antimony oxide verses manganese oxide.

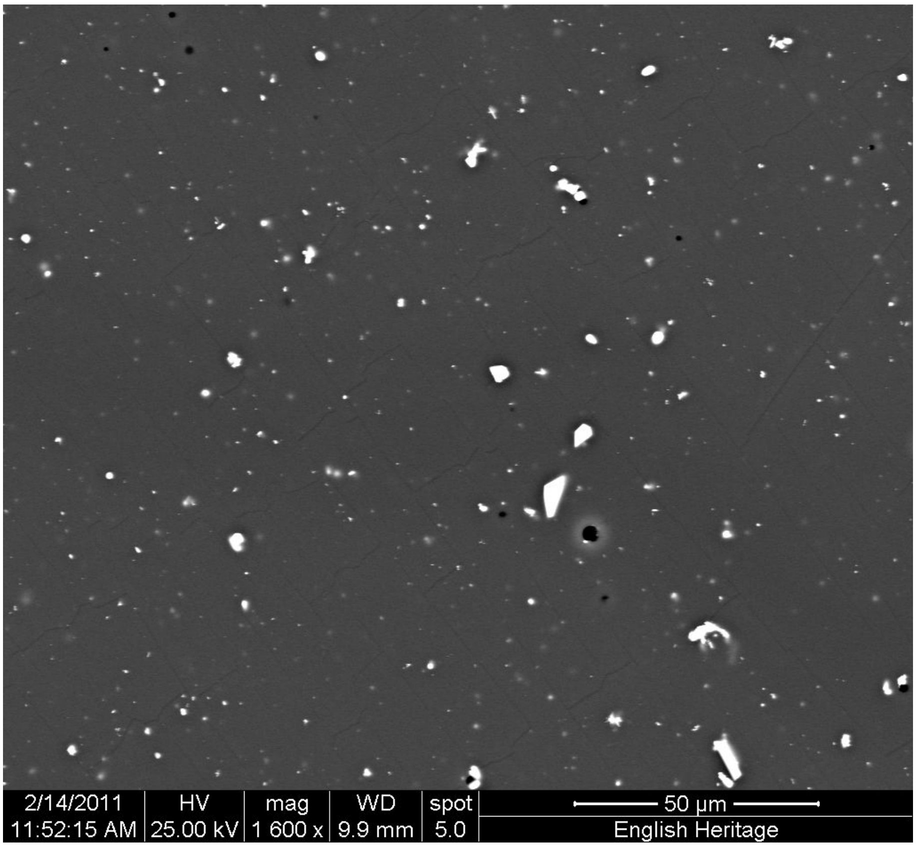

Figure 8. Backscattered SEM image of calcium antimonate crystals in sample CG01.

DISCUSSION

Origin of the Glass?

Fresh natron glass was not made in 10–11th-century Europe, therefore the origin for the Cork glass was through the recycling of Roman or post-Roman glasses and not medieval production. The Cork glass was found to be most similar to 1st–3rd century Roman glass. Of the different groups of Roman glass, Groups 1a, 1b and 3 were found to be most similar to a blue-green glass. Roman glass can be grouped into different types and blue-green glass was a common glass used for vessels and is found throughout the Roman Empire (Jackson 1991; Foster and Jackson 2009). This section will discuss the reasons for these findings.

Antimony: A Roman Additive?

The Cork glass samples contain considerably high levels of antimony; between 2 and 4% for the opaque white glass and 0.4–0.9% in the other fragments. Figure 9 is a graph of soda against antimony comparing the Cork glass against Roman and post-Roman types. While the soda content remains much the same a difference is clearly displayed in the antimony levels between the Roman glass pre–4th century and the glass made after. The Roman and Cork glasses contained antimony oxide levels greater than 0.35%, whilst the post-Roman glasses all contained below 0.2% except for two examples of Anglo-Saxon glass.

Antimony was used regularly in the Roman periods and died out from the 4th century (Tite *et al* 2008, 64). The lack of antimony in glass from after the 4th century is supported by studies of 5–7th-century glass from northern Italy (Salviulo *et al* 2004) and of post-Roman Byzantine glass (Freestone *et al* 2002) among others. The reduction in antimony use could have been due to a lack of supply. Consequently later glasses do not contain antimony as a new additive but only from recycling Roman material. The antimony present in the Cork glass is a strong indicator that the glass is of a 1st–3rd century Roman origin rather than later.

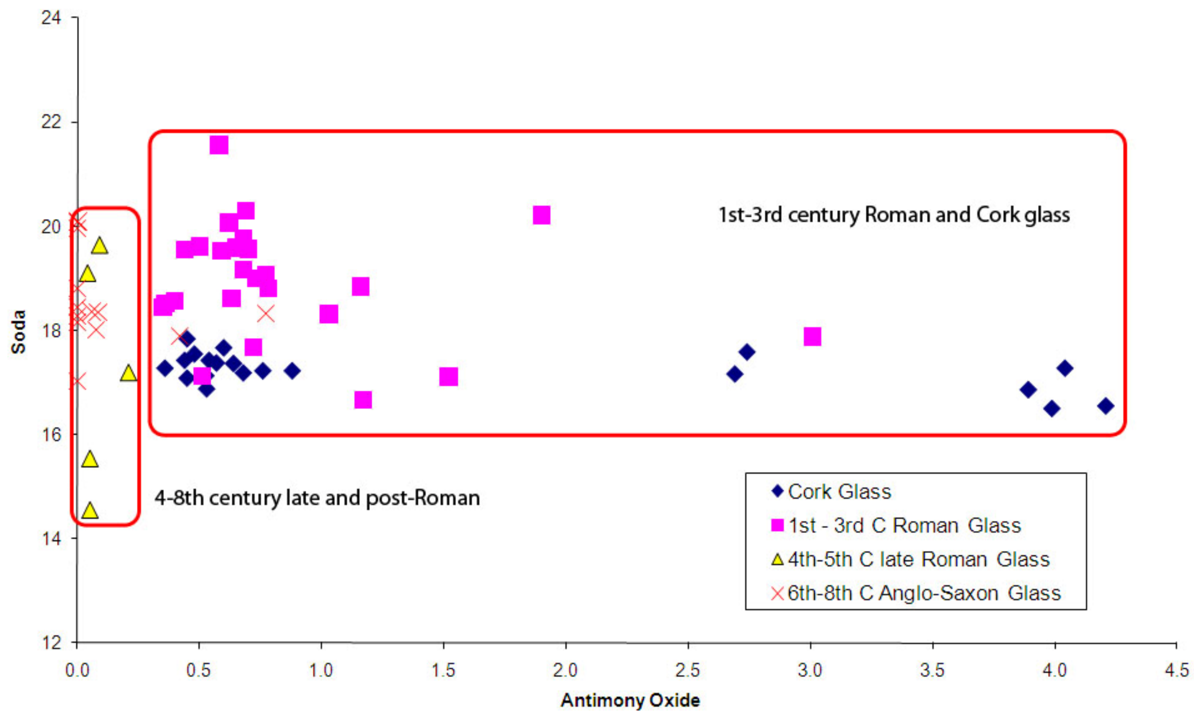

Figure 9. Soda verses antimony. Cork glass compared 1st–3rd century Roman glass (Paynter 2006); average 4th–5th century glass types (Foster and Jackson 2009) and 6th–8th century Anglo-Saxon glass (Freestone et al *2008).*

Group 1 and Blue-Green glass

To find out the base glass used for Group 1 further comparisons were made to Roman and post-Roman glass using TSS (the sum of the squares), a statistical method to measure similarity. The comparison was be made using Group 1b because of possible contamination of 1a by titania and iron oxide mentioned earlier. Quantifying the similarity was accomplished by removing the antimony oxide and re-normalising the data to 100%. There are a number of different glass types in Roman period and they are based on different manufacturing locations, eg Levantine I and II, blue-green, HIMT, Egypt I and II (Freestone 2005; 2006; cf Paynter 2006, Fig 10). Using TTS the glass was compared to different glass types from the 4–5th centuries (Foster and Jackson 2009), results are shown in Table 7 (Appendix). The closest similarity was found to Blue-Green type glass (TSS = 0.67) and the next nearest HIMT 1 (5.82). The test was repeated with 2nd and 3rd century Blue-Green glass from Mancetter and Leicester (Jackson *et al* 1991, 299). An even closer correlation was shown for Mancetter glass (0.28). This indicates the Group 1b glass to have very similar compositions to the Blue-Green glass and therefore was probably used as the base glass for 1b and possibly 1a. Blue-Green glass was a common base glass used for vessels in the Roman period and antimony oxide would have been added to it.

Group 2

Comparing Group 2 to Group 1b, the levels of potash, titania, manganese, lime and alumina are very similar. This would suggest a similar sand source to Group 1b. The only difference between the glasses is the high magnesia (increased by 0.3%) and lower antimony (reduced by ~1.5%). The higher magnesia could possibly be explained by the addition of higher magnesia glass or enamels such as those identified by Henderson (1991, 290) The mixing of glass could reduce the antimony oxide content of the glass, although the antimony content was variable between batches anyway.

Group 3

Comparing Group 3 to Group 1, the levels of lime, alumina, magnesia, silica and potash are again very similar. As with the Group 1a, the only difference is the higher levels of iron oxide, slightly raised titania, and higher manganese oxide. The ratios of manganese oxide to iron oxide are different from Group 1a showing their source to be different. The level of manganese oxide is small and unlikely to have been a deliberate addition. Using TSS (as above but with lead oxide removed before re-normalising) and comparing to the different glass groups the nearest glass type is again found to be Blue-Green glass. For the 4–5th century Blue-Green glass a value of 0.69 is shown, for the Mancetter 2nd century glass a value of 0.56 (Table 7, Appendix). There is, therefore, a similarity between Group 3 glass and the Blue-Green glass as in Group 1.

Indications of recycling

There are a number of indicators of recycling and the Cork glass demonstrates some of them. As glass colours were not always separated perfectly before re-melting, trace amounts of colouring compounds became mixed into the new glass (Jackson *et al* 1996; Mirti *et al* 2000). Work by Henderson on post-Roman glass from Ribe (Denmark), Åhus (Sweden), Borg (Norway) and early Christian sites in Ireland have found higher levels of elements associated with colourants (lead, antimony and tin) when compared to Roman colourless glass (Henderson 1995). Freestone *et al* (2008) similarly found increased elements associated with colourants in 5–6th century Anglo-Saxon vessels and found that in recycled glass, zinc concentrations became depleted but lead content increased to 'several hundred ppm' (*ibid*, 34). That amount of lead is not found in glassmaking sands but only lead-based opaque colourants.

In Group 3 additional amounts of colourant were found. There were significant amounts of lead oxide, this could be explained by mixing of very small amounts of high lead glasses such as those reported by Mass *et al* (1998) or high lead enamels (Henderson 1991) during recycling. Group 3 also contains higher levels of antimony oxide (0.6–0.9%) which is also probably from recycling with antimony containing glasses. Levels of other colourants (Co, Cu, Sn) were below the detection limits.

Another possible indicator of the continued recycling of glass is slightly increased potash and magnesia levels; this could be from the re-melting of the glass in a flux rich environment due to the fuel ash (Paynter 2008). Group 3 also showed increased magnesia and on the whole the magnesia and potash levels of the Cork glass is slightly higher than typical Roman values.

A more obvious indicator of recycling was found in glass by Freestone *et al* (2008) and Cox and Gillies (1986). They observed higher than expected levels of magnesia and potash in analysis of natron glass which they interpreted as the watering down of the natron glass by the addition of wood ash glass. The glass from Cork does not show this.

Similarities with the Saint-Savin glass

The Cork glass fragments and the one analysis of the opaque white glass from the Saint-Savin cup do show similarities. Both are natron glasses and both use antimony as the opacifier. The Saint-Savin glass also shows small amounts of copper, lead and cobalt inferring recycling. It suggests a similar production history using recycled Roman glass but there are significant differences in the compositions to the Cork glass. Their soda contents differs by 7%, silica by 10%, and magnesia and iron oxide by 1%. This is either explained by the different analytical methods (SEM-EDS verses LA-ICP-MS) or that very different glass types were used. The soda content is much higher than normal Roman glasses.

Manufacture of the Glass and Summary

Groups 1a, 1b and 3 are natron glasses and their levels of antimony indicate them to be of a 1^{st}–3^{rd} century Roman rather than later Roman or post-Roman. All three have been found to be most similar to Blue-Green glass, a type of Roman vessel glass found throughout the Empire.

Glass 1a is a Blue-Green recycled glass that has had manganese oxide to act as a purple colourant. Purple colouration can be created using a combination of temperature and reducing conditions in a furnace and was known in the 11^{th}–12^{th} century (Hawthorn and Smith 1979, 58) but it is most likely that the manganese oxide was added during Roman times as manganese was already widely used as a decolourant in glasses. The manganese oxide source was possibly the origin of the increased iron oxide and titania in the glass.

Group 1b is a Blue-Green glass that had antimony oxide added to it in the Roman period to make an opaque white glass. It has been re-melted in the medieval period but had no additional elements were added.

The opaque glass in Group 2 is similar in many respects to the other Blue-Green glasses but contains additional magnesia and less antimony oxide. This indicates either a separate origin from the other glasses or a more varied mixing history with other higher magnesia glass sorts.

Group 3 is another Blue-Green based glass. Manganese oxide could have been added as a decolouriser but this is unlikely. Raised levels of lead oxide and antimony oxide are from mixing with high lead glasses or enamels (Freestone 1991, 46; Brill 1999).

The spread of typologically similar glasses around Europe (Figure 4) and the account of the re-melting of Roman coloured mosaics in France by Theophilus makes the glass most likely produced in Continental Europe, possibly France (Hawthorn and Smith 1979, 59) rather than in Ireland. The Romans never conquered Ireland and therefore a native glass source for recycling would not have been available. The recycling of Roman glass at such a late date indicates that a trade in Roman glass and cullet was operating, either in the stripping of mosaics from temples and abandoned Roman buildings or the digging of Roman waste sites for glass fragments.

CONCLUSION

Glass in the 10–11th century was an expensive and luxury commodity and these highly decorated and coloured vessels would have been particularly prized. The Cork glass fragments are a unique find in Ireland but other similar vessels, such as the Saint-Savin and Grotta di San Michele cups have been found at high status sites such as castles, abbeys, churches and commercial centres around Europe. After 600 years of looting and recycling, Roman glass is very likely to have been expensive, rare and sought after.

The glass fragments recovered at Cork are recycled Roman types made of natron glass most closely resembling Roman period Blue-Green vessel glass and show varying degrees of recycling. The colourants used were antimony oxide for the opaque white and manganese oxide which were both most likely added during the Roman period. The different glass groups indicated the presence of at least three glass vessels.

The manufacturing location of these vessels is most likely continental Europe. Theophilus mentions France as a centre for the re-melting of Roman glass but there is nothing in the composition to link the glass to France. The glass compositions were similar to the Saint-Savin glass but further analysis is needed to investigate similarities to other stylistically similar glasses.

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APPENDIX

Table 5. Catalogue of the samples.

Sample	Site	Context	Find	Description	Context
CG01	04E0371	515B	1	Footed base fragment, purple with opaque white overlay	Organic spread to the rear of the Hiberno-Norse House
CG02	04E0371	559	15	Body fragment, purple	Clay foundation for a pathway associated wit the Hiberno-Norse house
CG03	04E0371	585	52	Body fragment, purple	Organic debris within a Hiberno-Norse house
CG04	04E0371	601	1	Body fragment, purple	Organic spread in backyard area of Hiberno-Norse housing
CG05	04E0371	606C	1	Body fragment, opaque white	Found beneath a timber trackway. Late 11th/early 12th century date expected
CG06	04E0371	621B	1	Rim fragment, purple with five lines of white opaque inlay	Clay floor of a Hiberno-Norse house
CG07	04E0371	621B	2	Body fragment, opaque white	Clay floor of a Hiberno-Norse house
CG08	04E0371	642	6	Body fragment, purple	Organic debris within Hiberno-Norse house
CG09	04E0371	654	1	Body fragment, purple with three lines of white opaque inlay	Possible floor of a Hiberno-Norse house
CG10	04E0371	654	2	Body fragment, purple with one line of white opaque overlay	Possible floor of a Hiberno-Norse house
CG11	04E0371	668	1	Body fragment, purple	Organic debris within a Hiberno-Norse house
CG12	04E0371	668	2	Body fragment, opaque white with purple tip	Organic debris within a Hiberno-Horse house
CG13	04E0371	668	3	Body fragment, very pale-green with bubbles	Organic debris within a Hiberno-Norse house
CG14	04E0371	668	3	Body fragment, very pale-green with bubbles	
CG15	04E0371	668	3	Body fragment, very pale-green with bubbles	
CG16	04E0371	668	3	Body fragment, very pale-green with bubbles	
CG17	04E0371	668	3	Body fragment, very pale-green with bubbles	

Figure 10. CG01

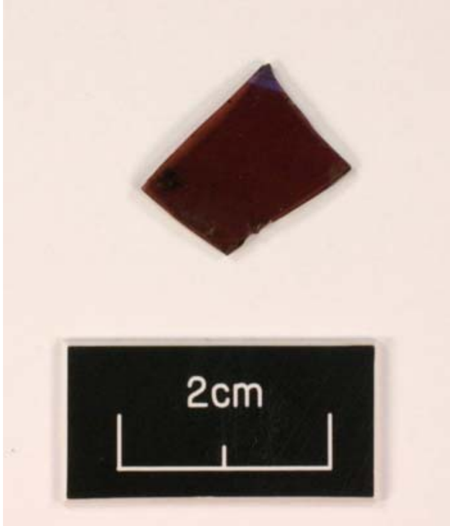


Figure 11. CG03

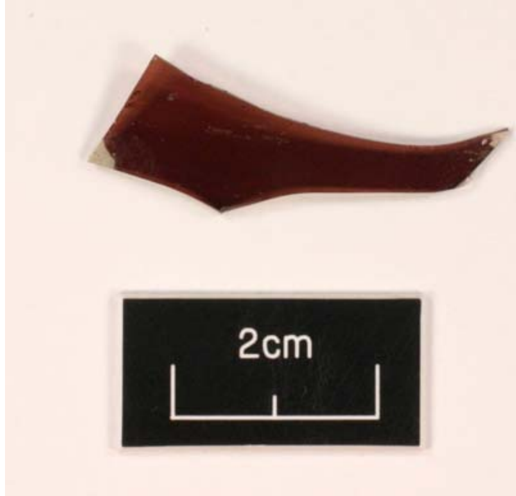


Figure 12. CG04

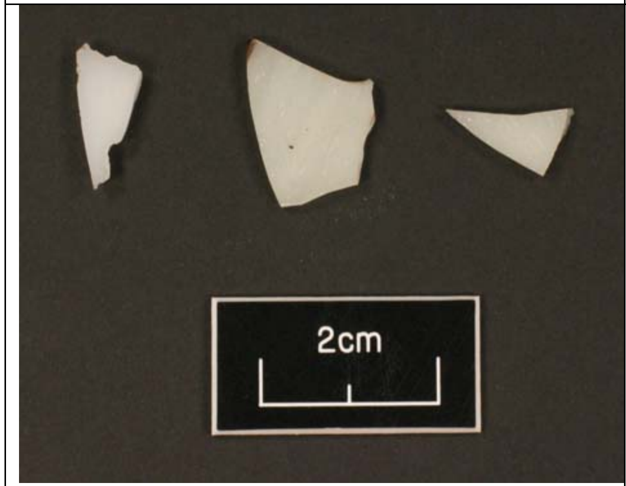


Figure 13. Left to right, CG05, 12 and 07.

Figure 14. CG06.

Figure 15. CG08

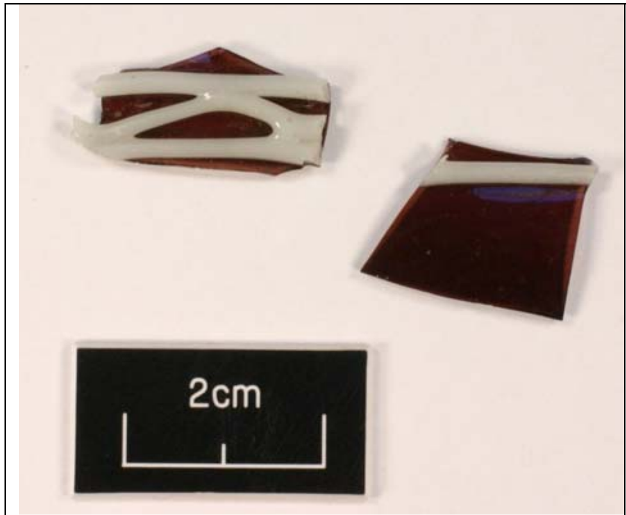
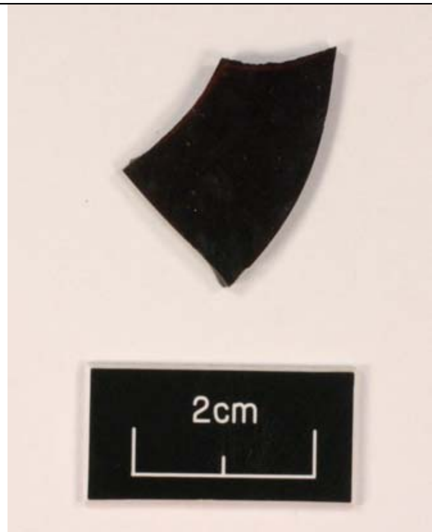
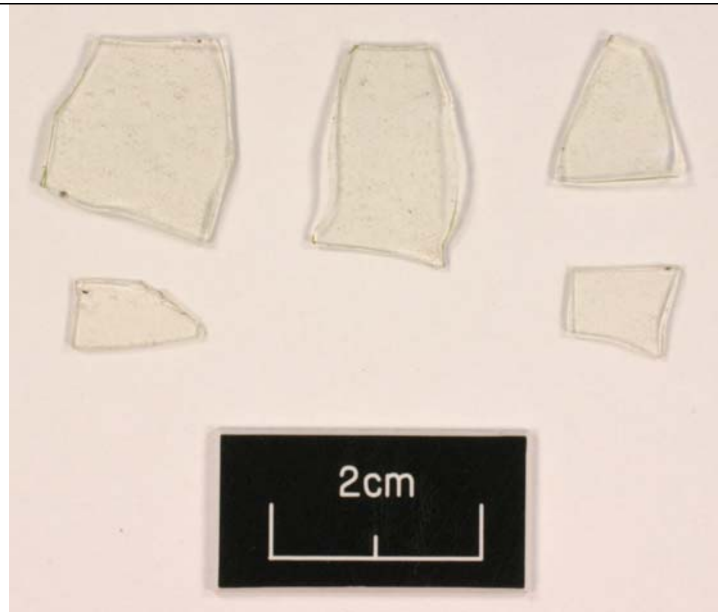
		

Figure 16. CG09 and 10	Figure 17. CG12	Figure 18. CG13, 14, 15, 16 and 17

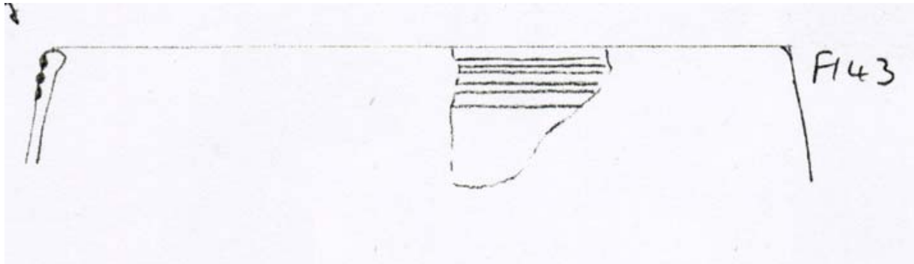


Figure. 19. Rim fragment of a bowl or beaker from a late 13th-century context at Waltham Abbey. White opaque glass with dark brown trailed bands (Rachel Tyson personal communication*)*

Table 6. Standards data for Corning A and Corning B as wt% normalised oxides.

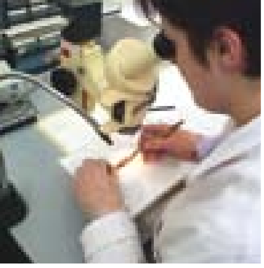
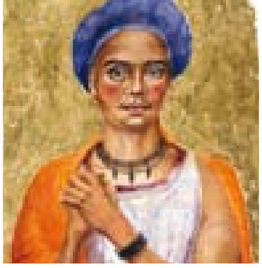
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	FeO	CoO	NiO	CuO	ZnO	Sb_2O_5	PbO
Corning A	14.25	2.63	1.01	66.37	<0.3	<0.3	3.08	5.11	1.00	1.00	1.02	0.13	<0.1	1.25	<0.1	2.13	<0.3
	13.74	2.50	0.96	66.44	<0.3	<0.3	3.11	5.45	1.13	1.15	1.06	0.24	<0.1	1.37	<0.1	1.98	<0.3
	14.08	2.54	0.97	67.08	<0.3	<0.3	3.03	5.27	1.06	1.10	1.04	0.17	<0.1	1.23	<0.1	1.92	<0.3
Average	*14.02*	*2.56*	*0.98*	*66.63*	*<0.3*	*<0.3*	*3.07*	*5.28*	*1.06*	*1.08*	*1.04*	*0.18*	*<0.1*	*1.28*	*<0.1*	*2.01*	*<0.3*
Known	**14.30**	**2.66**	**1.00**	**66.76**	**0.13**	**0.10**	**2.87**	**5.03**	**0.79**	**1.00**	**1.09**	**0.17**	**0.03**	**1.17**	**0.04**	**1.75**	**0.12**
difference	**0.28**	**0.10**	**0.02**	**0.13**	**-**	**-**	**0.20**	**0.25**	**0.27**	**0.08**	**0.05**	**0.01**	**-**	**0.11**	**-**	**0.26**	**-**
relative % diff	1.93	3.88	2.00	0.19	-	-	7.08	4.90	34.60	8.33	4.59	5.88	-	9.69	-	14.86	-
Corning B	16.64	1.04	4.19	61.57	0.79	0.62	1.14	8.90	0.15	0.21	0.34	<0.1	0.11	2.79	0.18	0.38	0.52
	15.98	1.01	4.29	61.56	0.81	0.69	1.22	9.13	0.10	0.29	0.35	<0.1	0.12	2.99	0.16	0.61	0.49
	16.31	0.90	4.25	61.64	0.87	0.71	1.09	8.91	0.16	0.27	0.41	<0.1	0.14	2.93	0.24	0.42	0.43
Average	*16.31*	*0.98*	*4.24*	*61.59*	*0.82*	*0.67*	*1.15*	*8.98*	*0.13*	*0.26*	*0.37*	*<0.1*	*0.12*	*2.90*	*0.19*	*0.47*	*0.48*
Known	**17.00**	**1.03**	**4.36**	**61.52**	**0.82**	**0.50**	**1.00**	**8.56**	**0.79**	**0.25**	**0.34**	**0.05**	**0.10**	**2.66**	**0.19**	**0.46**	**0.61**
difference	0.69	0.05	0.12	0.07	0.00	0.17	0.15	0.42	0.66	0.01	0.03	-	0.02	0.24	0.00	0.01	0.13
relative % diff	4.06	4.53	2.68	0.11	0.00	34.67	15.00	4.91	83.12	2.67	7.84	-	24.58	9.15	0.00	2.17	21.31

Table 7. The sum of the squared differences (TTS) is given between 4-5th century late Roman glasses (Foster and Jackson 2009) and 2st and 3rd Century blue-green glass from Mancetter and Leicester (Jackson et al *1991) and glass Groups 1b and 3 in order to show the degrees of similarity between the glass sorts.*

	Na_2O	MgO	Al_2O_3	K_2O	CaO	TiO_2	MnO	FeO	Sb_2O_5	
HIMT 1	19.11	0.98	2.49	0.50	6.08	0.33	1.71	1.36	0.04	
HIMT 2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
Levantine 1a	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
Levantine 1b	14.56	0.45	2.93	0.82	8.55	0.06	0.10	0.33	0.05	
Blue-green	17.20	0.61	2.59	0.80	7.16	0.08	0.55	0.76	0.21	
Mancetter	17.50	0.54	2.44	0.70	7.09	0.08	0.41	0.48	0.19	
Leicester	18.40	0.55	2.33	0.69	6.43	0.10	0.26	0.66	0.37	
Group 1b (normalised)	17.52	0.82	2.22	0.64	6.75	0.08	0.23	0.48	-	
Group 3 (normalised)	17.58	0.61	2.40	0.76	6.70	0.13	0.69	0.66	0.72	
R^2 Results for Group 1b										**Sum of R^2**
HIMT 1	2.54	0.02	0.07	0.02	0.45	0.06	2.19	0.78		**6.14**
HIMT 2	4.55	0.00	0.00	0.00	0.57	0.00	0.56	0.12		**5.82**
Levantine 1a	3.86	0.05	0.35	0.00	2.88	0.00	1.00	0.00		**8.16**
Levantine 1b	8.74	0.14	0.50	0.03	3.23	0.00	0.02	0.02		**12.69**
Blue-green	0.10	0.05	0.14	0.03	0.17	0.00	0.10	0.08		**0.66**
Mancetter	0.00	0.08	0.05	0.00	0.11	0.00	0.03	0.00		**0.28**
Leicester	0.78	0.07	0.01	0.00	0.10	0.00	0.00	0.03		**1.00**
R^2 Results for Group 3										**Sum of R^2**
HIMT 1	2.33	0.14	0.01	0.07	0.39	0.04	1.04	0.49	0.46	**4.96**
HIMT 2	4.27	0.02	0.02	0.03	0.49	0.00	0.08	0.03	0.40	**5.35**
Levantine 1a	4.14	0.00	0.17	0.03	3.05	0.00	0.29	0.06	0.45	**8.18**
Levantine 1b	9.15	0.03	0.28	0.00	3.41	0.01	0.35	0.11	0.45	**13.77**
Blue-green	0.15	0.00	0.03	0.00	0.21	0.00	0.02	0.01	0.26	**0.69**
Mancetter	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	**0.56**
Leicester	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	**1.06**

CG05 – Modern Glass

Despite the early 12th century date indicated by the context, this fragment does not match any known archaeological glass. It most closely resembles a modern fluoride opal glass. It contains high soda (10%) and has high levels of potash, alumina and some lime but practically no magnesia. It is a white opaque glass which has a more even and 'whiter' white than antimony opacified glass. This is due to the much smaller particle size (0.5-1micron) than calcium antimonate (2-15microns). The opacifier is a zinc and fluoride compound (Table 3). The small particle size of the opacifiers cause poorer data collection, nevertheless the main constituents of the white precipitate are approximately zinc (6%), calcium (9%) and fluoride (18%). A search found no mineral or compound that suited this composition. Zinc is present in the bulk composition of the glass at 10% and possibly also acts as a stabilizer in the glass, 3.9% fluoride is also present in the glass. No additional information could be found on zinc rich glasses.



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