# School of History, Archaeology and Religion
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## REPORT ON THE GLASS AND GLASSWORKING DEBRIS FROM THE TARBAT MONASTERY EXCAVATIONS

(Requested by the National Museum of Scotland)

*An assemblage of glass fragments from the Tarbat monastery excavations were analysed by SEM-EDXA. Of the blue glasses, two are modern. The third is a natron-type glass of Roman type which is likely to represent re-use of early material by early medieval craftsmen. The remaining three glasses (all opaque yellow) are unambiguously consistent with early-medieval glass technology. However, it was not possible to establish whether opaque yellow glass was being made at Tarbat, or simply being worked there.*

## Introduction

A small assemblage of glass and glassworking debris from the Tarbat monastery excavations was provided for analysis, the majority of which were assumed to be of early medieval date. This included one glass stud, two vessel fragments (one decorated with a reticella trail), and five fragments of glassworking waste including crucible fragments, cullet and driblets. Unfortunately the reticella fragment could not be sampled for analysis due to its fragility. This is the only assemblage containing glassworking waste from early medieval Scotland. It was hoped that compositional analysis would give further insight into glass production during the period.

## Materials and Methods

A list and brief description of each of the samples analysed is presented in Table 1, and images of the glasses and glassworking waste are presented in Appendix 1.

Small samples were taken, mounted in epoxy resin and polished. They were coated with a thin layer of carbon and examined in the scanning electron microscope (CamScan Maxim). The chemical compositions of the samples were determined using an Oxford Instruments ISIS energy-dispersive x-ray analyser (EDXA) attached to the SEM. Relative analytical accuracy is believed better than ±2% for silica, and ±5% for other elements present in concentrations greater than 10%, but greater for elements present in lower concentrations. Detection limits were 0.2% for most of the components analysed, 0.3% for lead and tin and 0.4%-0.7% for antimony, depending on the glass matrix. Results were taken from an average of three analyses, and were normalised to 100% to improve precision and comparability.

Oxide compositions for the six glasses analysed are presented in Table 2.

## Results

### *Blue glass*

Samples 686 and 1901 are soda-lime-silica glasses, made using a relatively pure source of alkali, as indicated by their low potash and magnesia contents (Table 1). However, they have significant compositional differences which suggest that they originate from different manufacturing traditions. The 18% soda, 2.2% alumina and small but significant amounts of manganese and antimony oxides in the stud 686 are fully consistent with weakly coloured Roman glass which was made between the first and fourth centuries AD. These glasses were decoloured using manganese and antimony oxides (e.g. Jackson 2005). The blue colour of this glass may derive from small amounts of cobalt present in the glass not detectable by EDXA (Freestone *et al.* 2008).

Vessel glass sample 1901 is a particularly pure glass, containing lower levels of iron and aluminium oxides than the other glasses analysed, and is especially distinguished by a lack of chlorine. On the other hand, its lime content of 13.1% is high relative to soda-lime-silica glasses of the first millennium AD. The unusual composition, particularly the low chlorine content, strongly suggests that this soda-lime-silica glass dates to after the introduction of the Leblanc process for the production of synthetic soda in the early nineteenth century and that it is intrusive.

Opaque cullet sample 11/1000 is also unlikely to relate to the early medieval period. It is distinguished by a very high lime content (25.4%) and low soda (1.2%). The chlorine content is also very low (0.2%). Its composition is characteristic of post-medieval glasses of the high-lime low-alkali (HLLA) compositional type, which was in use between the sixteenth and nineteenth centuries (Dungworth *et al.* 2006; Dungworth and Loaring 2009). The alumina and iron oxide contents and the presence of a small amount of phosphate are typical for HLLA glasses (Dungworth and Loaring 2009). No opacifier was observed in this sample, suggesting that its opaque appearance is due to the thickness of the fragment and the presence of bubbles.

Table 1 – The glass and glassworking debris analysed

| Sample | Description | Glass Colour |
|--------|-------------|--------------|
| 686 | Decorated glass stud with opaque white inlay | Transparent blue |
| 25/1385 | Irregular waste trail of glass | Opaque yellow |
| 25/1458 | Irregular driblet of glass | Opaque yellow-olive green |
| 1901 | Vessel glass | Transparent blue |
| 11/1000 | Large fragments of waste glass/cullet | Opaque blue |
| 11/3469 | Heating tray fragment containing glass patches | Opaque yellow |

Table 2 – EDS analyses of Tarbat glass and glassworking waste[1]

| Oxide (wt%)[2] | Sample | | | | | |
|---|---|---|---|---|---|---|
| | 686 | 25/1385 | 25/1458 | 1901 | 11/1000 | 11/3469 |
| $Na_2O$ | 18.0 | 8.1 | 5.5 | 12.1 | 1.2 | 0.0 |
| $MgO$ | 0.7 | 0.4 | 0.3 | 0.3 | 2.0 | 0.3 |
| $Al_2O_3$ | 2.2 | 2.0 | 2.3 | 1.0 | 3.2 | 5.8 |
| $SiO_2$ | 66.9 | 36.7 | 27.9 | 71.3 | 58.5 | 13.2 |
| $P_2O_5$ | 0.1 | b.d. | b.d. | b.d. | 1.7 | 10.2 |
| $SO_3$ | 0.5 | 0.4 | b.d. | 0.6 | 0.6 | 0.5 |
| $Cl$ | 0.6 | 0.6 | 0.5 | b.d. | 0.2 | 0.6 |
| $K_2O$ | 0.6 | 0.5 | 0.4 | 0.4 | 2.8 | b.d. |
| $CaO$ | 6.3 | 3.5 | 2.3 | 13.1 | 25.4 | 4.9 |
| $TiO_2$ | b.d. | b.d. | b.d. | b.d. | 0.3 | 0.6 |
| $MnO$ | 0.6 | 0.2 | 0.2 | 0.1 | 0.2 | b.d. |
| $Fe_2O_3$ | 1.0 | 1.4 | 3.3 | 0.3 | 2.2 | 5.6 |
| $CuO$ | 0.8 | 0.6 | 0.7 | 0.6 | 0.6 | 0.6 |
| $ZnO$ | b.d. | b.d. | 0.2 | b.d. | b.d. | b.d. |
| $SnO_2$ | b.d. | 2.7 | 6.9 | b.d. | 0.4 | 8.8 |
| $Sb_2O_3$ | 0.9 | b.d. | b.d. | b.d. | 0.6 | 1.2 |
| $PbO$ | 0.2 | 42.6 | 49.3 | b.d. | b.d. | 47.0 |

[1]Average of three area analyses normalised to 100 percent; see text for details.
[2]b.d. = below detection. Detection limits were thought to be about 0.2% for most of the elements analysed, although this is marginally higher for lead and tin at about 0.25-0.3% and rises to over 0.5% for antimony in glasses with high calcium. Barium oxide and cobalt oxide were analysed for but not detected.

*Opaque yellow glass*

All of the yellow samples analysed are coloured and opacified with lead-tin oxide, visible in the SEM as small crystals dispersed throughout the glass matrix (Figs. 1 and 2). In all three samples, spot analyses identified these crystals as consisting of approximately 30-35 percent tin oxide and 60-65 percent lead oxide, corresponding to the cubic phase $PbSnO_3$ (Rooksby 1964; Tite *et al.* 2008). It is apparent from the compositions (Table 1) that the two glass trails, 25/1385 and 25/1458, are essentially mixtures of soda-lime-silica glass and a component rich in lead and tin oxides. This is confirmed by the microstructures of the glasses, which are heterogeneous on a coarse scale. For example, Fig. 2 shows large regions rich in lead and tin, with abundant tin oxide crystals, in a matrix which is richer in silica. Tin-oxide opacified yellow glasses, with high lead, are typical of the early medieval period in northwestern Europe (Tite *et al.* 2008).

The yellow deposit on the heating tray, 11/3469, differs from the other samples in terms of its high phosphate and low soda and silica contents. Removal of sodium and deposition of phosphate from the environment is typical of weathering processes observed in some glasses (Freestone *et al.* 1985) and our interpretation is that this yellow material, rich in lead and tin, has resulted from the weathering of an opaque yellow glass similar to those of the trails.
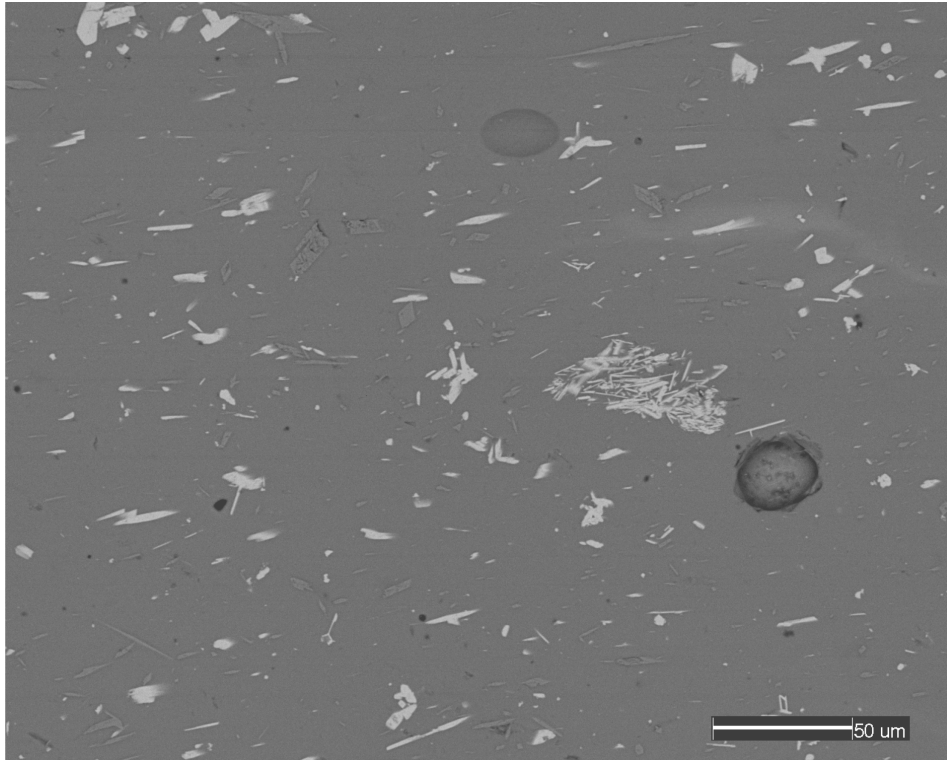
Figure 1 – A backscattered electron image showing crystals of lead-tin oxide dispersed throughout the glass matrix of sample 25/1458.
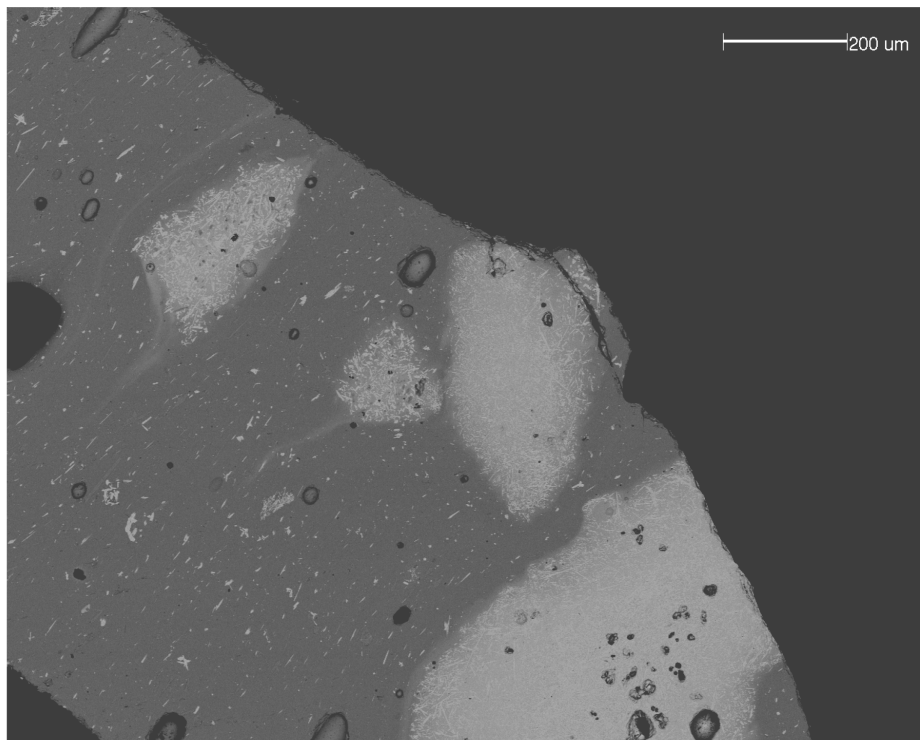


Figure 2 – A backscattered electron image showing crystals of lead-tin oxide dispersed throughout the glass matrix of sample 25/1385. The glass is very heterogeneous, as shown by sub-angular patches of lead-tin oxide opacifier crystals. The glass matrix appears brighter in the crystal-rich regions because it contains much more lead than the darker grey regions.

Table 3 – Comparison of opaque yellow glass from Tarbat to published analyses of contemporary glass from elsewhere

| Oxide (wt%)[1] | Sample | | |
|---|---|---|---|
| | Schleitheim[2] | Dunmisk: 13[3] | Tarbat: 25/1385[4] |
| $Na_2O$ | 7.8 | 9.1 | 8.1 |
| $MgO$ | 0.3 | 0.4 | 0.4 |
| $Al_2O_3$ | 2.9 | 2.2 | 2.0 |
| $SiO_2$ | 33.9 | 43.6 | 36.7 |
| $P_2O_5$ | <0.1 | 2.1 | <0.1 |
| $Cl$ | n.a. | 0.8 | 0.6 |
| $K_2O$ | 0.2 | 1.2 | 0.5 |
| $CaO$ | 2.7 | 2.9 | 3.5 |
| $Fe_2O_3$ | 0.8 | 0.9 | 1.4 |
| $SnO_2$ | 1.7 | 4.7 | 2.7 |
| $Sb_2O_3$ | n.a. | 0.4 | <0.4 |
| $PbO$ | 49.5 | 32.9 | 42.6 |

[1]n.a. = not analysed.
[2]Opaque yellow glass bead from Schleitheim, Switzerland. Mid 7th century Merovingian date (taken from Heck *et al.* 2003).
[3]Opaque yellow crucible glass from Dunmisk Fort, Co. Tyrone, Ireland. Early Christian date (taken from Henderson 1988).
[4]Opaque yellow waste trail of glass from Tarbat (taken from Table 2, this report).

**Discussion**

The results indicate that two of the three blue glasses are post-medieval, so only the stud is of particular interest here. There is now a wide range of evidence in support of models of glass production in the first millennium AD which interpret soda-lime-silica glass to have originated largely in the Levant and Egypt, where it was made from its raw materials on a scale of many tons in large tank furnaces (Freestone 2006). This raw glass was distributed across the Mediterranean and Europe to be remelted and shaped into vessels, windows and other artefacts (Freestone 2003; Freestone and Hughes 2006; Freestone *et al.* 2008).

As indicated above, the composition of the stud is characteristically Roman. Its soda, lime and alumina contents do not match the compositions of primary glass prevalent after the fourth century and the presence of antimony argues for an early date. Roman glass was re-used for inlay and enamelling until as late as the fourteenth century including in the jewellery of Anglo-Saxon Britain (Bimson and Freestone 2000). Given that the design of the stud is characteristically early medieval (Campbell, pers. comm.), this is almost certainly the case here. Compositional parallels to the blue stud may be found from the Dalriadic capital of Dunadd (Henderson 2000a) and from the assemblage at Dunmisk, County Tyrone (Henderson 1988).

The yellow glasses are all opacified and coloured by crystals of lead-tin oxide, or lead stannate ($PbSnO_3$). Glass of this type was used in Europe from the second century BC and continued in use throughout the first millennium AD, and has been interpreted by Henderson to represent the continuity of a Celtic rather than a Roman tradition (Henderson 2000a; Henderson 2000b; Henderson and Ivens 1992). The minor compositional differences between the yellow glasses analysed are probably due to slight variations in the quantities of raw materials used in the glass recipes, combined with the notable heterogeneity of these glasses (Fig. 2).

Heck *et al.* (2003) investigated a crucible and bead (Table 3) of Merovingian date from Schleitheim, Switzerland and found that the yellow glass was prepared in two stages. First, lead-tin yellow pigment was prepared by heating a mixture of the oxides of lead and tin, which reacted with the crucible fabric to form crystals of lead-tin oxide in a lead-silica glass. This was then mixed with a pre-existing soda-lime-silica glass to form the yellow glass used to make beads. A similar process was used in post-medieval Venice to make yellow glass (Moretti and Hreglich 1984) and was probably widely used throughout the medieval period (Tite *et al.* 2008). The sub-angular nature of the aggregates of lead-tin oxide crystals in sample 25/1385 (Fig. 2) suggests that they were directly added to the soda-lime-silica matrix as crushed lumps of a lead-tin-silica material and that the resultant hybrid glass was not heated for long enough to fully disperse them. The duration of heating would have been minimised as lead-tin yellow is unstable, and the yellow glass can readily lose its colour at high temperatures.

The compositions of the soda-lime-silica glasses used to manufacture the yellow glasses cannot be determined accurately as the compositions may reflect contamination from a number of sources. However, the presence of antimony oxide in the relict glass on the heating tray (Table 1: 11/3469) suggests that the re-use of Roman material is a strong possibility.

Sample 11/3469 was the only glass analysed directly from a refractory ceramic. The flat, open shape of this heating tray is paralleled by heating trays associated with potential glass-working debris found elsewhere, for example in early medieval Ireland, although the evidence for glass working is far from unambiguous in many cases, as noted by Henderson and Ivens (1992). It has been suggested that they were only used for softening glass prior to shaping it, as more closed shapes would have been necessary to melt it completely (Henderson and Ivens 1992). No evidence was observed in the SEM of partially-fused primary raw materials that might suggest the making of glass, rather than its manipulation.

Overall, these results provide evidence only for the manipulation of opaque yellow glass at Tarbat. There is no evidence for primary glass making from raw materials and, as the lump of blue cullet is no longer considered early medieval, no evidence to support the manipulation of other colours. The opaque yellow glass appears to have been made using a technique which is closely paralleled in Merovingian Switzerland. We are unable to determine if it was made on site or brought in from elsewhere; the deteriorated condition of the glass on the heating tray limits our ability to speculate here.

This interpretation differs considerably from that previously put forward for glass industrial debris from Dunmisk where it has been suggested that yellow glass was being made directly from its raw materials, including soda, and that the craft activity is a continuation of a specifically Celtic technological tradition (Henderson and Ivens 1992). This difference may relate simply to the character and positions of the sites, but we note the close similarities of the opaque yellows from Dunmisk and Tarbat, and that from Switzerland (Table 3) which strongly suggest a common technology. It may be that the quartz grains upon which so much depends in the interpretation of the crucible deposit from Dunmisk (Henderson 1988; Henderson and Ivens *op. cit.*) are relicts from the production of the lead-tin yellow pigment, rather than the soda-bearing glass.

**Conclusion**

Of the six glasses analysed, only four appear to be early medieval, and we have no evidence for the working of colours other than opaque yellow. The compositions of the glasses are strongly paralleled at Dunadd and Dunmisk, and are interpreted as evidence for an industry based largely on the re-use of soda-lime-silica glass which, at least in part, had its origins in the Roman period. Before the fourth century, opaque yellow glass was largely based upon the use of antimony oxides, and the lead-tin yellow pigment found here is characteristically early medieval. It was produced by adding pre-formed yellow pigment to a soda-lime-silica glass which, in some cases at least, was recycled material. The technique to produce the yellow pigment seems to have been quite widespread and was certainly carried out at Schleitheim in Switzerland (Heck *et al.* 2003) and Dunmisk in Ireland (Henderson and Ivens 1992). However, we are unable to determine if this procedure was undertaken at Tarbat or if the yellow glass was imported. At present the evidence at Tarbat seems to be limited to the hot manipulation of yellow glass.

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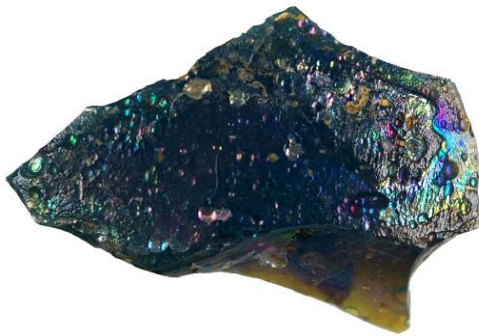
# Appendix 1

5 mm

686

5 mm

1901

2 cm

11/1000

3 cm

11/3469

5 mm

25/1385

1 cm

25/1458