Staffordshire Hoard Research Report 2

The PIXE and PIGE Analysis of Glass Inlays from the Staffordshire Hoard

Andrew Meek

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Information about this report

This report was produced in 2013 as part of Stage 1 of the project, i.e. before fragments were joined and catalogued. The concordance of the K numbers given in the report to the catalogue numbers as they appear in the final publication is as given on the following page. The list also includes the names of the objects as used in the final publication.

The work was carried out in the Accélérateur Grand Louvre d'Analyse Elémentaire, Paris (ALGAE) and the Department of Conservation and Scientific Research in the British Museum.

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The following article was based on this work.

Meek, A. 2016. 'Ion beam analysis of glass inlays from the Staffordshire Anglo-Saxon Hoard', *Journal of Archaeological Science: Reports* 7, 324-9

K number	Catalogue number	Name in publication
82	569	Mount with fantail in silver with geometric niello inlay and gilded borders (part).
137		Hilt-plate
160	187	Hilt-collar in cast silver, of narrow form, with gilded low relief decoration and black niello inlay (part).
182	569	Mount with fantail in silver with geometric niello inlay and gilded borders (part).
242	76	Pommel in cast silver, of cocked-hat form with double sword-rings, with cast interlace and niello inlay and mounts with cloisonné and filigree decoration (part).
291	76	Pommel in cast silver, of cocked-hat form with double sword-rings, with cast interlace and niello inlay and mounts with cloisonné and filigree decoration (part).
304	186	Hilt-collar in cast silver, of narrow form, with gilded low relief decoration and black niello inlay.
310	567	Eye-shaped mount in silver with geometric niello inlay and filigree trim.
347	56	Pommel in gold, of round-back form, with incised decoration inlaid with niello and filigree ornament.
550		Inscribed strip
660	166	Hilt-collar in gold, of high form, with cloisonné decoration.
713	570	Strip-mount in silver with geometric niello inlay and gilded borders (part).
1005	569	Mount with fantail in silver with geometric niello inlay and gilded borders (part).
1021	568	Mount of eye-shaped form in silver with geometric niello inlay (part).
1069	570	Strip-mount in silver with geometric niello inlay and gilded borders (part).
1235	571	Strip-mount in silver with pointed turned ends, geometric niello inlay and a gilded border (part).
1364	187	Hilt-collar in cast silver, of narrow form, with gilded low relief decoration and black niello inlay (part).
1630	569	Mount with fantail in silver with geometric niello inlay and gilded borders (part).

The British Museum

DEPARTMENT OF CONSERVATION AND SCIENTIFIC RESEARCH

The PIXE and PIGE analysis of glass inlays from the Staffordshire Hoard

Science Report PR07444-1

Andrew Meek

Abstract: Glass inlays from six objects from the Staffordshire Hoard have been analysed by proton induced X-ray and gamma ray emission (PIXE and PIGE) at AGLAE, Paris in November 2010. The glasses analysed can be divided into two distinct groups based not only on appearance, but also on their composition.

The opaque blue and white glasses are of a natron-based composition and are very likely to be reused and reworked Roman glass, possibly mosaic tesserae. The opacifiers used in their production are also those expected for Roman glasses. These glasses share some compositional parallels with the opaque glasses analysed from the Sutton Hoo ship burial.

The transparent red glasses have a similar base composition to the opaque glasses, but with elevated potassium and magnesium levels. Pieces in this second group also appear to have originally been natron glass, but with the later addition of what was probably a plant ash. It is likely that this addition was made to extend the amount of glass available to northern European craftsmen (Freestone *et al*. 2008; 42). It is not possible to say whether the natron-based glass was recycled from old objects or was newly imported glass. It is interesting that a transparent red glass from the Sutton Hoo ship burial appears to have a similar composition to that expected for this natron-based glass.

By comparison with the glass vessels analysed by Freestone *et al*. (2008) it is possible to suggest that the transparent red glasses so far analysed in the Staffordshire Hoard were produced during the period 550-700 AD (Evison 2008). This glass type is present on all the objects analysed here, apart from K377, and provides a probable *terminus post quem* for their production.

The discovery of transparent red glasses with a composition associated with Anglo-Saxon vessels suggests that the millefiori were produced by contemporary north-western European, and possibly Anglo-Saxon, glass workers.

CSR Project no. PR07444
Staffordshire Hoard numbers: K370, K377, K674, K1166, K1167, K1226
3 October 2012

Introduction

The Staffordshire Hoard was discovered in July 2009 in a field near Lichfield, Staffordshire, and consists of over 3500 items of Anglo-Saxon origin. The objects fall within a date range from the mid-sixth to early eighth century AD (Dean *et al*. 2010; 145). However, a more specific range has been suggested by Høilund Neilson (2010) of between 600 and 700 AD based on the decorative styles employed on the objects.

In November 2010 objects from the Staffordshire Hoard were taken to the Accélérateur Grand Louvre d'Analyse Elémentaire (AGLAE), Paris, and subjected to compositional analysis by proton induced X-ray and gamma ray emission (PIXE and PIGE). The materials analysed include metals, garnets, glasses and unidentified inlays. This report will focus on the analysis of glass inlays only (for examples of these inlays see Figures 1 and 2).

Figure 1: Apex of sword pyramid K1166. Central inlay is millefiori glass.

Figure 2: Sword pyramid K377. Blue triangles are glass inlays.

Aims

The aims of this project are to identify the chemical composition of a small number of the glass inlays which decorate garnet inlayed pieces and interpret these data to illuminate how, where and when they were produced.

Background

<u>Glass Production</u>

Scientific analysis allows the raw materials used to produce ancient glasses to be identified. To make a stable glass it is necessary to have three major components. These are:

- Silica
  - which forms the glass and is added in the form of sand or quartz pebbles
- Flux
  - which is necessary to allow the glass to melt at temperature achievable in the furnace. It is typically added in the form of sodium- or potassium-rich plant ashes or minerals, or lead salts
- Stabiliser
  - which stabilises the glass structure and compensates for the reduction in stability caused by the addition of a flux. It is normally provided by the calcium-rich impurities present in the plant ashes or by the limestone or shells present in sands. However, in some cases it may constitute a separate addition to the glass melt.

Further ingredients can be added to give the glass colour, remove unwanted colour, or make the glass opaque.

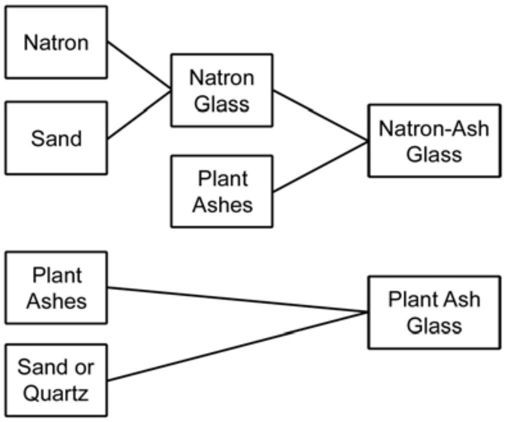

Figure 3: Flowchart of glass production types discussed in the text.

Many previous analytical studies have been undertaken on Anglo-Saxon glass, mostly on relatively small assemblages (e.g. Biek and Bayley 1985; Henderson 1990; Bimson and Freestone 2000; Freestone *et al*. 2008 among others). These studies have focussed on typical Anglo-Saxon glass objects: beads, inlays and vessels. Their results show that the majority of Anglo-Saxon glasses are natron-based. Natron is a sodium-rich evaporate mineral used as a flux in glass production. The use of this type of flux is commonly associated with production in the eastern Mediterranean between the fifth century BC and ninth century AD (see Freestone *et al*. 2000). The use of this type of flux results in glasses with a high soda (Na_2O), low magnesia (MgO), low potash (K_2O) composition and can be differentiated from plant ash glasses which contain higher levels of both magnesia and potash.

It is not believed that the glass used in the production of Anglo-Saxon objects was produced from raw materials (primary production) in north-western Europe (Bimson and Freestone 2000; 134). Instead, it is probable that new glass was either imported from the eastern Mediterranean in the form of raw glass or vessel cullet (broken or waste glass gathered for remelting) during this period or glass, brought into this region during the preceding Roman period, was reused (i.e. used as found) or reworked (i.e. cut into new shapes or melted and formed into new objects).

In their study of Anglo-Saxon vessels from the British Museum Freestone *et al*. (2008) have shown that this reworked glass was not always simply melted to form into vessels (secondary production). At some point during the sixth century AD the composition of glass used in the production of Anglo-Saxon vessels changed from identifiably natron-based to glass with higher and correlated magnesia and potash levels. This glass composition has been shown, by Freestone *et al*. (ibid.; 40), to be the result of adding plant ash-rich material to natron-based glass, not simply a new plant ash-based glass (Figure 3). These additions are thought to have been made to extend the amount of available natron-based glass from the Mediterranean (ibid.; 40).

As noted by Freestone *et al*. (ibid.), plant and wood ashes are highly variable in composition and the glasses they analysed show a consistent ratio of magnesia and potash. This suggests that glass of this natron-ash type was produced by a very limited number of workshops, or perhaps only one, using a consistent source of this ash material (ibid.; 41). They go on to suggest that the rarity of this glass type in other continental contexts may show that it was produced in Britain (ibid.; 42).

Sutton Hoo glass

Figure 4: Shoulder clasp from Sutton Hoo (BM 1939,1010.5).

Figure 5: Square escutcheon from Sutton Hoo hanging bowl (BM 1939,1010.110).

Figure 6: Round escutcheon from Sutton Hoo hanging bowl (BM 1939,1010.110).

The best inlays for comparison with those in the Staffordshire Hoard based on proposed date and appearance, are the glass inlays from the Sutton Hoo ship burial (Figures 4-6) (Bruce-Mitford 1974; Høilund Neilson 2010). The Sutton Hoo ship burial was excavated in 1939 near Woodbridge, Suffolk, and is thought to date, based on coins and historical context, to between 620-5 and 640 AD (Bruce-Mitford 1974; 4). The glass-containing objects from this site have been divided into two groups by Bimson (1978; 427): the first group includes the gold and garnet jewellery, such as the shoulder clasps and purse, which feature Germanic animal style designs and cut millefiori set into gold as if they were precious stones (see Figure 4, or the purse lid, BM 1939,1010.2, for example); secondly, the hanging bowl escutcheons, which contain millefiori imbedded into opaque red glass and are of Celtic design and probably provenance (Figures 5 and 6).

Two analytical studies have been published on a small number of the glass inlays from Sutton Hoo by Bimson (1978) and Bimson and Freestone (2000). Of particular interest to the current study are the transparent red and opaque white and blue glasses, which are summarised and then discussed below (Table 1).

Table 1: Summary of previously published results for glass inlays from Sutton Hoo (see Figures 4-6).

Reference	Glass	Results
Bimson 1978	Transparent red probably from the purse lid	Manganese (MnO) content is 1.21%
Bimson 1978	Opaque white probably from the purse lid	Manganese (MnO) content is 1.18%. Calcium antimonate used as opacifier.
Bimson 1978	Opaque blue probably from the purse lid	Cobalt used as blue colourant.
Bimson 1978	Opaque white from hanging bowl escutcheon	Tin oxide used as opacifier.
Bimson 1978	Transparent blue from hanging bowl escutcheon	Cobalt used as blue colourant.
Bimson and Freestone 2000	Transparent red probably from the purse lid	Natron-based low MgO and K_2O glass. Manganese used as colourant
Bimson and Freestone 2000	Opaque white probably from the purse lid	Relatively high MgO glass. Calcium antimonate used as opacifier.
Bimson and Freestone 2000	Opaque blue probably from the purse lid	Natron-based low MgO glass. Cobalt probably used as colourant. Calcium antimonate used as opacifier. Lead oxide present at ~2%.

Opacifiers

The opaque glasses analysed from Sutton Hoo contain compounds of either antimony (Sb) or tin (Sn) which act as opacifiers. These are the most commonly used opacifiers in ancient glass production (Henderson 2000; 35). Antimony is added to the glass melt and reacts with the calcium already present in the glass to form calcium antimonite crystals which cause opacity (ibid.). Tin oxide crystals, added as the mineral cassiterite, can also produce opacity.

In the first millennium AD calcium antimonate occurs as opacifier in glasses produced in the Mediterranean area, tin oxide rarely occurs except in Northern Europe. During the fourth century AD tin-based opacifiers started to replace antimony-based opacifiers and had almost completely replaced them by the early medieval period (Tite *et al*. 2008; Bimson 1978). The discovery of calcium antimonate in the Sutton Hoo shoulder clasp inlay glasses suggest that they derive from earlier Roman glasses. The use of tin oxide in the hanging bowl inlays suggest that they may have been produced later and in a non-Roman tradition (Bimson 1978).

Bimson (1978; 433) uses the two groups of objects discussed above to investigate this theory further and suggests that the Anglo-Saxon jewellery 'produced by Germanic craftsmen were made using glass derived from Roman sites whereas the craftsmen working in the old Celtic tradition on the hanging bowl escutcheons, used glass containing the new early-medieval opacifiers'.

Colourants

The blue glasses are coloured using cobalt (Co). Cobalt has been used as a glass colourant throughout ancient glass production. Only a very small quantity (~0.05 wt%) is needed to give glass a deep blue colour. Previous analytical studies have attempted to discover the sources of cobalt used by ancient glass producers with varying success (see Gratuze *et al*. 1995 and Henderson 2000; 31 for examples). The amount of cobalt present in the Sutton Hoo glass inlays were below detection and are not presented in the publications and as such it is not possible to comment on the likely sources of the cobalt used as a colourant in these glasses. The opaque blue glass analysed by Bimson and Freestone (2000) contains significant levels of lead oxide. They did not conclude why it is present, but note that it is probably associated with the addition of cobalt or antimony and is also found in Roman opaque blue glasses.

The transparent red glasses are coloured using manganese (Mn). Manganese has been used in ancient glass production as both a decolourant, counteracting the unwanted green tint given by iron impurities in the sand sources used, and as a purple colourant. Bimson (1978; 430) believed that the use of manganese as a red colourant may imply that it is reused Roman glass because manganese red glasses are very rare in Anglo-Saxon contexts.

Glass types

The data presented by Bimson (1978) on some of the inlays from Sutton Hoo is mostly qualitative and limited to the colourants and opacifiers found in these glasses. Consequently it was not possible to suggest what the original major raw materials used in the primary production of the glasses may have been. However, quantitative data from scanning electron microscope-energy dispersive X-ray spectrometry (SEM-EDX) analysis is presented in Bimson and Freestone (2000). The results are for transparent red, opaque blue and opaque white glass from a piece of millefiori thought to have come from the Sutton Hoo purse lid (Table 1).

These results show that the transparent red and opaque blue glasses were produced with a natron-based glass. The white glass contains much higher levels of magnesia (1.8 wt% MgO). However, these levels are also found in some Roman opaque white glasses (see Bimson and Freestone 2000; 132; Henderson 1990; 290). All three of these glass types are therefore very likely to originate from the reworking of Roman glass or the importation of new natron glass from the eastern Mediterranean.

It was hoped that by comparing the glass inlays within objects in the Staffordshire Hoard with these previous studies it would be possible to discern more about when and where they might have been made. This would provide information about the objects themselves and the trading links exploited by their producers.

Methodology

The samples were analysed using a 6 SDH-2 2 MV tandem Pelletron accelerator made by NEC and located in the Centre de recherche et de restauration des musées de France (C2RMF) laboratories at the Louvre (Figure 7). The analyst was Thomas Calligaro (C2RMF). An open 3 MeV proton beam was used for the analysis with a helium flush to aid with the detection of light elements. Two Si(Li) detectors were used: a low energy Si(Li) X-ray detector (1-10 keV) (FWHM ~ 145 eV at 5.9 keV) and a high energy Si(Li) X-ray detector (3-40 keV) with 50 μm aluminium filter (FWHM ~ 152 eV at 5.9 keV). A high-purity germanium detector (HPGe) was used for prompt induced-gamma rays. The beam current used was ~500 pA with an acquisition time of ~ 2 minutes. The beam size used was ~ 50 μm and the scanned area was ~ 300 x 300 μm^2.

The data analysis was performed using GUPIXWIN and TRAUPIXE (Pichon *et al*, NIM B 268 2010 2028-2033) software. The sodium content of the samples was calculated using the 440 keV gamma ray line from PIGE. The PIGE analysis was calibrated with Corning A and BGIRA certified glass. The results are presented as weight percent (wt%) oxide or element in Tables 2 and 3.

Figure 7: The particle accelerator at C2RMF. The beam head and the pectoral cross, from the Staffordshire Hoard can be seen on the left of the picture.

Results and discussion

<u>Introduction</u>

Tables 2 and 3 report the results of the PIXE analyses of glass inlays in the Staffordshire Hoard objects. Figures 7-12 illustrate where the analyses were carried out on each object.

Figure 7: K370 with one of the two sites of analysis marked. Eye 1 is a similar position on the reverse of the piece.

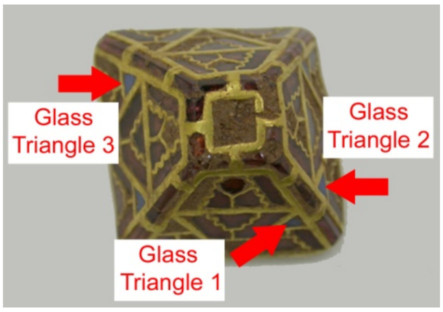

Figure 8: K377 showing the locations of the glass triangles analysed.

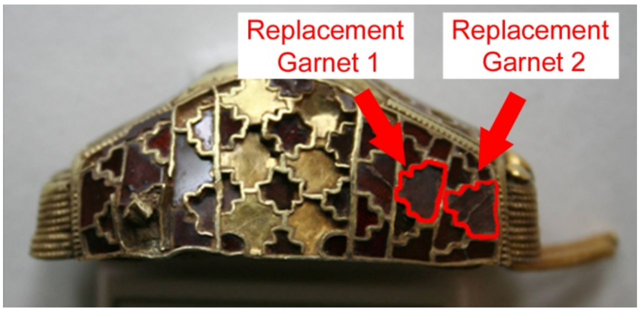

Figure 9: K674 with one of the two areas of glass analysed marked.

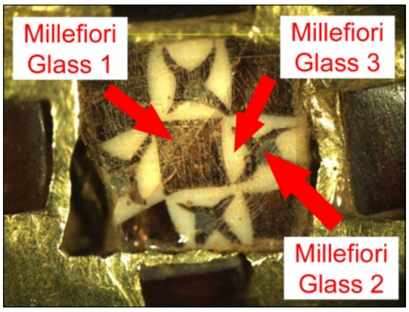

Figure 10: K1166 with the opaque white and transparent red millefiori glass analysed marked.

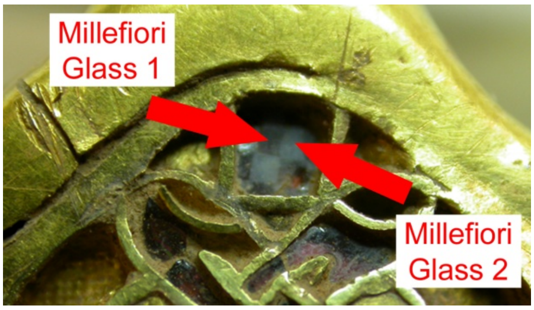

Figure 11: K1167 with the transparent red and white millefiori glass analysed marked.

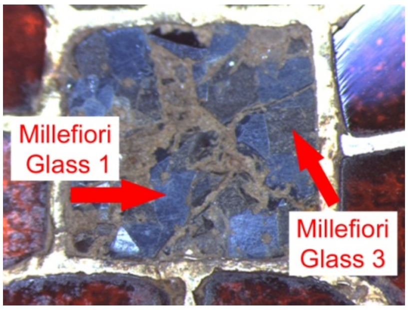

Figure 12: K1226 with the transparent red and blue millefiori glass analysed marked

The levels of soda (Na_2O) reported in Tables 2 and 3 should not be considered as representative of the levels in the body of the glasses analysed. Over time most types of ancient glass deteriorate and the alkalis (soda and potash (K_2O)) leach out from the surface forming a silica-rich layer depleted in alkalis as seen here (Newton and Davison 1989; 136). Almost all of the results for soda in Tables 2 and 3 are considerably lower than those expected for Roman (~10-20 wt%) or unweathered Anglo-Saxon glasses (~14-20 wt%), which otherwise provide the closest compositional parallels (see Freestone *et al*. 2000 and Freestone *et al*. 2008). The soda levels within the glass bodies of the pieces analysed for this study should be expected to be in these ranges.

Analysis no.	Object	Description	Glass colour	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CuO	ZnO	SrO	CoO	NiO	SnO_2	Sb_2O_5	PbO
29nov011	K370	eye 1	Trans. red	4.93	1.42	3.18	74.16	nd	0.56	0.98	0.84	9.84	0.19	2.57	1.10	0.01	0.01	0.11	nd	0.00	nd	nd	nd
29nov012	K370	eye 2	Trans. red	1.09	1.31	3.22	78.85	nd	0.54	0.55	0.78	8.92	0.22	2.83	1.39	0.02	0.00	0.13	nd	0.00	nd	nd	0.02
29nov013	K674	garnet replacement 1	Trans. red	0.49	0.99	4.56	81.08	nd	0.55	1.00	0.57	7.13	0.14	2.05	1.25	0.01	0.00	0.06	nd	0.00	nd	nd	nd
29nov014	K674	garnet replacement 2	Trans. red	0.90	1.00	3.96	81.37	nd	0.51	1.06	0.58	7.20	0.14	2.01	1.16	0.01	0.00	0.06	nd	0.00	nd	nd	nd
29nov016	K377	glass triangle 1	Opaque blue	6.14	0.66	3.38	72.03	nd	nd	0.73	0.98	7.99	nd	0.96	1.35	0.27	0.01	0.06	0.20	0.01	nd	3.38	4.50
29nov017	K377	glass triangle 2	Opaque blue	7.42	0.60	3.18	71.20	nd	nd	0.73	0.89	7.94	nd	0.94	1.26	0.26	0.01	0.06	0.20	0.01	nd	3.39	4.31
29nov018	K377	glass triangle 3	Opaque blue	6.61	0.60	3.25	71.76	nd	nd	0.72	0.99	7.79	nd	0.97	1.32	0.27	0.01	0.06	0.20	0.01	nd	3.52	4.43
29nov026	K1166	millefiori glass 1	Trans. red	12.05	1.88	3.98	66.06	0.27	0.31	0.74	1.60	8.65	0.16	2.95	1.17	0.05	0.01	0.14	nd	0.00	nd	nd	nd
29nov027	K1166	millefiori glass 2	Trans. red	10.80	1.72	5.15	66.57	0.30	0.24	0.74	1.52	7.88	0.20	2.27	1.61	0.11	0.01	0.11	0.03	0.01	nd	0.84	0.80
29nov028	K1166	millefiori glass 3	Opaque white	7.86	0.67	4.16	71.44	nd	0.86	0.59	0.98	11.89	nd	0.39	0.86	0.02	0.01	0.08	nd	nd	nd	20.71	0.03
29nov032	K1167	millefiori glass 1	Trans. red	10.87	1.01	4.73	68.48	nd	nd	0.76	0.73	9.15	0.11	3.09	0.74	0.01	0.00	0.06	nd	nd	nd	nd	0.01
29nov033	K1167	millefiori glass 2	Opaque blue	4.05	0.79	3.96	75.52	nd	0.51	0.82	0.92	8.25	nd	0.94	0.83	0.07	0.01	0.07	0.06	0.00	nd	4.09	2.98
29nov034	K1226	millefiori glass 1	Opaque blue	6.77	0.75	3.46	72.80	nd	0.49	0.78	0.96	7.92	nd	1.03	1.34	0.25	0.01	0.07	0.20	0.01	nd	3.64	3.15
29nov036	K1226	millefiori glass 3	Trans. red	12.64	1.40	3.04	67.96	nd	0.39	0.72	1.10	7.77	0.21	3.13	1.31	0.04	0.01	0.09	nd	0.00	nd	nd	0.07

Table 2: PIXE and PIGE results for glasses from the Staffordshire Hoard organised by object (reported in wt% oxide or element, not normalised, nd=not detected).

Analysis no.	Object	Description	Glass colour	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CuO	ZnO	SrO	CoO	NiO	SnO_2	Sb_2O_5	PbO
29nov016	K377	glass triangle 1	Opaque blue	6.14	0.66	3.38	72.03	nd	nd	0.73	0.98	7.99	nd	0.96	1.35	0.27	0.01	0.06	0.20	0.01	nd	3.38	4.50
29nov017	K377	glass triangle 2	Opaque blue	7.42	0.60	3.18	71.20	nd	nd	0.73	0.89	7.94	nd	0.94	1.26	0.26	0.01	0.06	0.20	0.01	nd	3.39	4.31
29nov018	K377	glass triangle 3	Opaque blue	6.61	0.60	3.25	71.76	nd	nd	0.72	0.99	7.79	nd	0.97	1.32	0.27	0.01	0.06	0.20	0.01	nd	3.52	4.43
29nov033	K1167	millefiori glass 2	Opaque blue	4.05	0.79	3.96	75.52	nd	0.51	0.82	0.92	8.25	nd	0.94	0.83	0.07	0.01	0.07	0.06	0.00	nd	4.09	2.98
29nov034	K1226	millefiori glass 1	Opaque blue	6.77	0.75	3.46	72.80	nd	0.49	0.78	0.96	7.92	nd	1.03	1.34	0.25	0.01	0.07	0.20	0.01	nd	3.64	3.15
		Average	Opaque blue	6.20	0.68	3.44	72.66	nd	0.50	0.76	0.95	7.98	nd	0.97	1.22	0.23	0.01	0.06	0.18	0.01	nd	3.60	3.87
29nov011	K370	eye 1	Trans. red	4.93	1.42	3.18	74.16	nd	0.56	0.98	0.84	9.84	0.19	2.57	1.10	0.01	0.01	0.11	nd	0.00	nd	nd	nd
29nov012	K370	eye 2	Trans. red	1.09	1.31	3.22	78.85	nd	0.54	0.55	0.78	8.92	0.22	2.83	1.39	0.02	0.00	0.13	nd	0.00	nd	nd	0.02
29nov013	K674	garnet replacement 1	Trans. red	0.49	0.99	4.56	81.08	nd	0.55	1.00	0.57	7.13	0.14	2.05	1.25	0.01	0.00	0.06	nd	0.00	nd	nd	nd
29nov014	K674	garnet replacement 2	Trans. red	0.90	1.00	3.96	81.37	nd	0.51	1.06	0.58	7.20	0.14	2.01	1.16	0.01	0.00	0.06	nd	0.00	nd	nd	nd
29nov026	K1166	millefiori glass 1	Trans. red	12.05	1.88	3.98	66.06	0.27	0.31	0.74	1.60	8.65	0.16	2.95	1.17	0.05	0.01	0.14	nd	0.00	nd	nd	nd
29nov027	K1166	millefiori glass 2	Trans. red	10.80	1.72	5.15	66.57	0.30	0.24	0.74	1.52	7.88	0.20	2.27	1.61	0.11	0.01	0.11	0.03	0.01	nd	0.84	0.80
29nov032	K1167	millefiori glass 1	Trans. red	10.87	1.01	4.73	68.48	nd	nd	0.76	0.73	9.15	0.11	3.09	0.74	0.01	0.00	0.06	nd	nd	nd	nd	0.01
29nov036	K1226	millefiori glass 3	Trans. red	12.64	1.40	3.04	67.96	nd	0.39	0.72	1.10	7.77	0.21	3.13	1.31	0.04	0.01	0.09	nd	0.00	nd	nd	0.07
		Average	Red	7.28	1.35	3.92	72.48	0.27	0.44	0.80	0.99	8.27	0.18	2.69	1.24	0.03	0.00	0.10	0.03	0.00	nd	0.84	0.19
29nov028	K1166	millefiori glass 3	Opaque white	7.86	0.67	4.16	71.44	nd	0.86	0.59	0.98	11.89	nd	0.39	0.86	0.02	0.01	0.08	nd	nd	nd	20.71	0.03

Table 3: PIXE and PIGE results for glasses from the Staffordshire Hoard organised by colour (reported in wt% oxide or element, not normalised, nd=not detected).

Three different glass colours were identified and analysed; opaque blue, opaque white and transparent red. The results concerning the colourants and opacifiers of each glass type will be discussed first, followed by the recipes used to produce the glasses.

Blue and white colourants and opacifiers

The opaque blue glasses in objects K377, K1167 and K1226 are coloured with the addition of cobalt and are opacified by antimony (see Tables 2 and 3 and cf. Table 1). They also contain significant levels of lead (3-4.5 wt% PbO). The opaque white glass in object K1166 (Figure 10) is also opacified by antimony.

The discovery of antimony as the opacifier in the Staffordshire Hoard opaque glasses, accompanied by lead in the blue glasses, suggests that, like those in the Sutton Hoo jewellery (see Table 1), they are reworked Roman glasses (Bimson and Freestone 2000). They are different from the opaque glasses used in the Sutton Hoo hanging bowl which are opacified with tin (SnO_2, cassiterite). This is unsurprising as the objects analysed here all fall into the 'jewellery' category, as discussed above, and no hanging bowl escutcheons are found in the Staffordshire Hoard.

The cobalt-rich raw material used to colour the glass blue seems to have introduced nickel (Ni) to the glasses used in objects K1226 and K377 (Figures 8, 12 and 13; Table 3). Nickel is associated with a number of cobalt ores known to have been used in ancient glass production (Gratuze *et al*. 1995). The use of nickel-containing cobalt raw materials is not currently linked to Roman glass production. However, in many previously published studies of Roman glasses the nickel content is not presented, or is below the detection limit of the analytical technique used. There is no correlation between cobalt and alumina (Al_2O_3) or magnesia content and it is therefore not suggested that the cobalt source used was a cobaltiferous alum, as is proposed to have been used in ancient Egyptian glass production by Tite and Shortland (2003) and others. There is also no correlation between cobalt and iron (Fe) or zinc (Zn) and this can discount further possible cobalt sources (Gratuze *et al*. 1995). The presence of nickel suggests a similar source to that used in the late medieval/Renaissance period in Europe, thought to be located in the Erzegibirge Mountains, Germany (ibid.).

The elevated levels of copper in most but not all the blue glasses are probably not directly related to the cobalt-rich raw material used (Figure 14). Copper is another blue-green colourant which may have also been added to the glasses to alter the shade of blue produced. However, its presence is also potential evidence of recycling of different coloured glasses (Freestone *et al*. 2008; 40). As it has already been suggested that these glasses are likely to be recycled Roman glasses, the second of these possibilities seems the more likely.

The three blue glass triangles analysed on object K377 (Figure 8) have almost identical compositions. The glass on this object is therefore very likely to have come from a single piece/melt of blue glass.

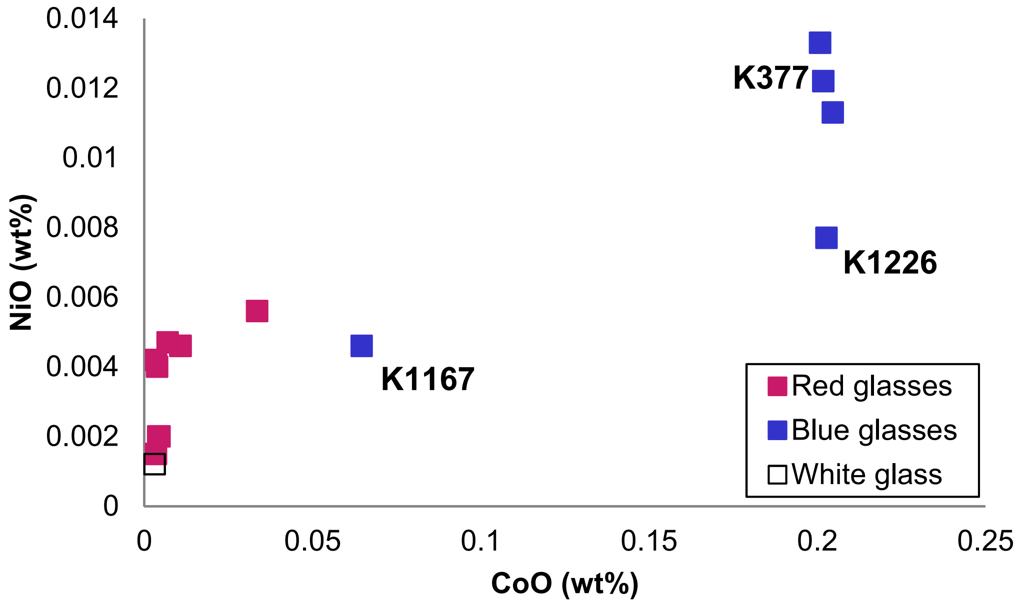

Figure 13: PIXE results for NiO vs. CoO

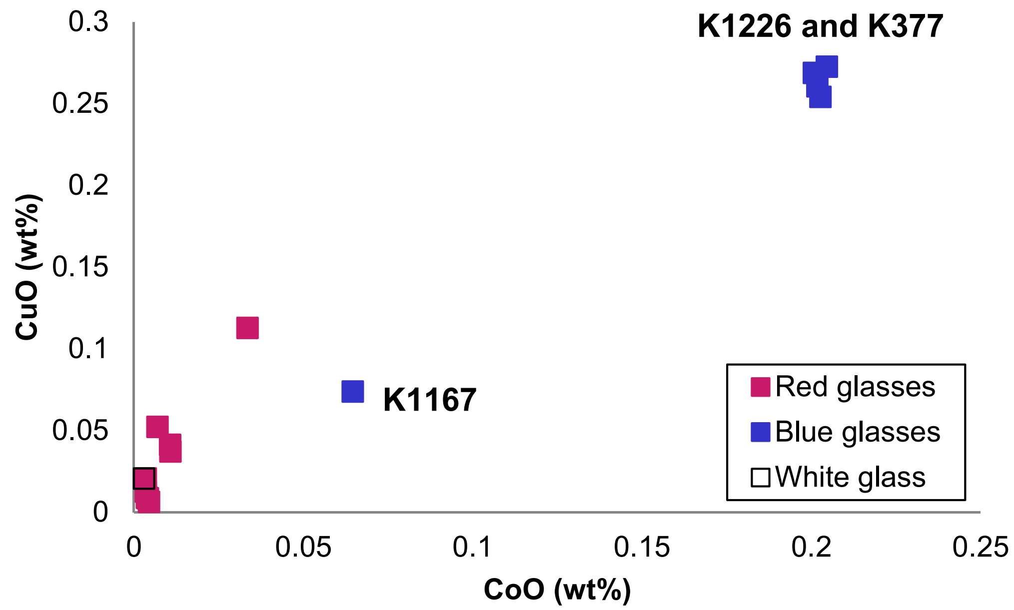

Figure 14: PIXE results for CuO vs. CoO

It is not possible to draw any firm conclusions about the cobalt source used to colour the glass in object K1167. The low levels of cobalt mean that any associated components will be present in such low quantities as to make their detection and correlation very difficult (Figures 13 and 14). Despite the low level of cobalt present in this sample, there is sufficient to produce its blue colouration.

Red colourants

Areas of transparent red glass were analysed on objects K370, K674, K1166, K1167 and K1226 (see Figures 7 and 9-12). Like the Sutton Hoo glasses discussed above these transparent red glasses are coloured using manganese (Table 3). As noted above, manganese can also be used as a decolourant and is added to glasses to neutralise unwanted colours contributed by iron impurities in the raw materials of glass production. However, the levels of manganese oxide (*c.*2-3.3%) added to the Staffordshire Hoard transparent red glasses are in excess of that needed to produce a colourless glass, resulting in a transparent red glass.

Because of their present condition some of these glasses were initially thought to be transparent blue or colourless, but the discovery of such high levels of manganese and lack of significant quantities of cobalt or copper suggest that they were intended to be transparent red (see Bimson 1978; Bimson and Freestone 2000). Similarly coloured glass is found in the Sutton Hoo shoulder clasp millefiori sections (BM 1939,1010.110, Figure 4). Here again it is used in combination with white or blue opaque glass. An approximate virtual reconstruction of the millefiori rectangle in K1226 has been produced using this similarly coloured piece as a model (Figures 15 and 16).

Figure 15: K1226 central with damaged millefiori rectangle (see Figure a).

Figure 16: Virtual reconstruction of K1226. Created using images of similar millefiori from the Sutton Hoo shoulder clasp (BM 1939,1010.110) and by cloning undamaged areas.

The transparent red glasses in objects K370 and K674 may be replacements for lost garnets or have been used in the place of garnets when the objects were first made. In the case of K370 it seems more likely that the latter of these two options is the case, perhaps glass being chosen as it was easier to cut into the small pieces needed (Figure 9). However, in the case of K674 it seems more likely that they are later replacements as there are many other places on this object where garnets were used to fill similar shaped cells.

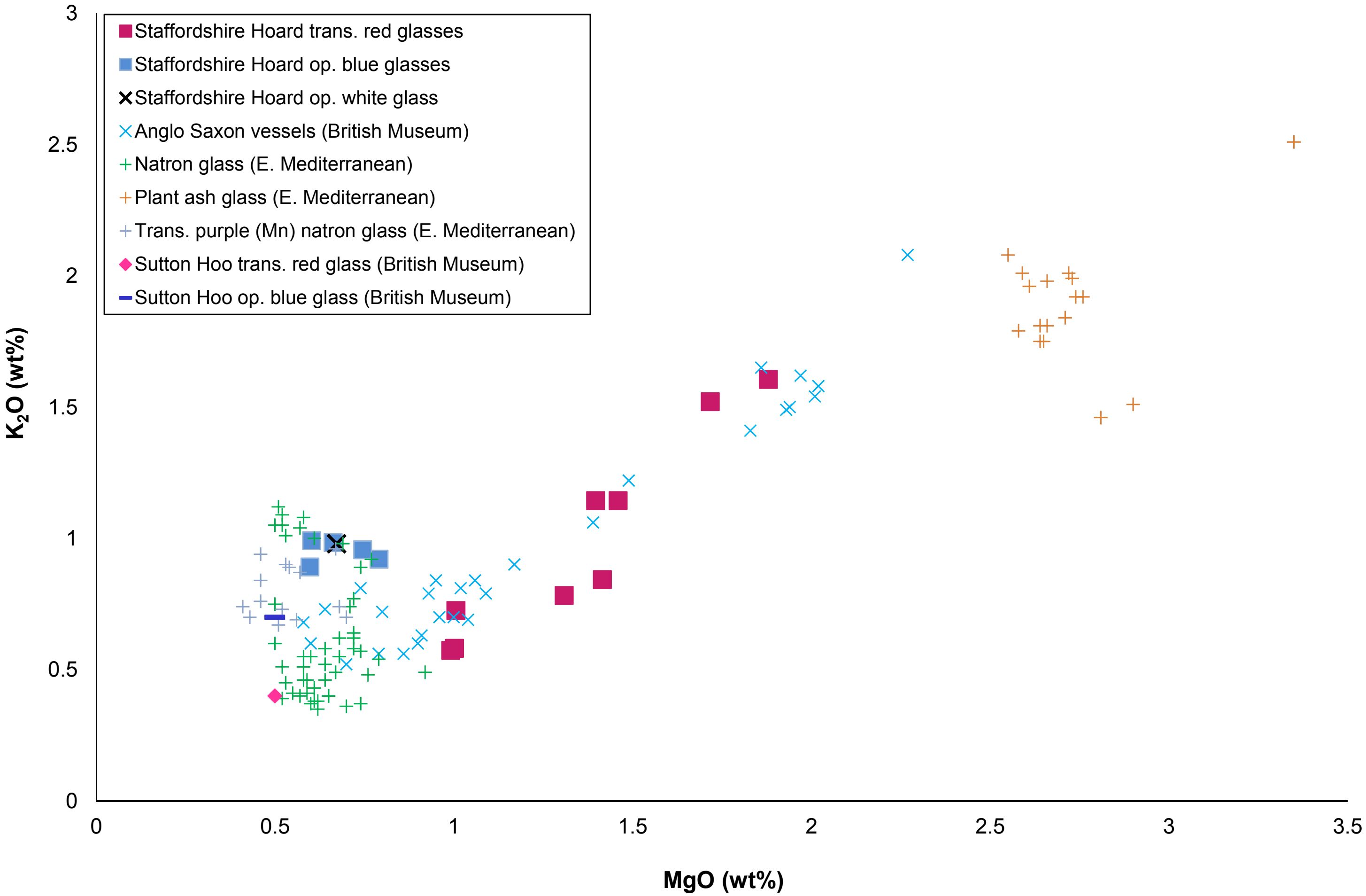

Figure 17: A plot of the PIXE results for K_2O vs. MgO for the Staffordshire Hoard glasses and comparable Anglo-Saxon vessels (Freestone *et al*. 2008), Anglo-Saxon inlays from Sutton Hoo (Bimson and Freestone 2000 [the white glass is not plotted because accurate K_2O levels were not presented in their publication]) and examples of natron glasses from Byzantine sites in Israel (Freestone *et al*. 2000).

Raw materials used in the primary production of the Staffordshire Hoard glasses

The blue and white glasses have relatively low levels of potash (*c*.0.9-1 wt% K_2O) and magnesia (*c*.0.6-0.8 wt% MgO) (Figure 17 cf. other natron glasses shown). This characterises them as having been produced using a mineral source of alkali known as natron (see Background). The opaque blue glass from Sutton Hoo has a similar composition.

The single opaque white glass inlay analysed from the Staffordshire Hoard does not have the elevated magnesia levels seen in the glass inlay analysed from the Sutton Hoo jewellery piece (Table 1; Bimson and Freestone 2000). As already suggested, based on evidence from the opacifiers used, these opaque glasses could either be reused Roman glass, possibly mosaic tesserae, or newly imported natron glass.

The levels of potash and magnesia in the transparent red glasses are more variable than in the blue and white glasses (Table 3). While some contain fairly similar magnesia levels to the other coloured glasses (K674 and K1167), others contain much higher levels (K370, K1226 and K1166). The transparent red glasses are highly correlated for potash and magnesia (Figures 13 and 14). They are also correlated with the transparent red glass from Sutton Hoo (Bimson and Freestone 2000). However, the Sutton Hoo transparent red glass analysed contains much lower levels of these components than those from the present study (Figure 18). If we accept the theory of Freestone *et al*. (2008) discussed above and that the Staffordshire Hoard glasses of this natron-ash compositional type were produced by the addition of a plant-ash material to natron-based glass (see Figure 3), then perhaps it is possible to suggest that the transparent red glass from Sutton Hoo is an example of the natron-based glass used in this process (Figure 3; Figure 18).

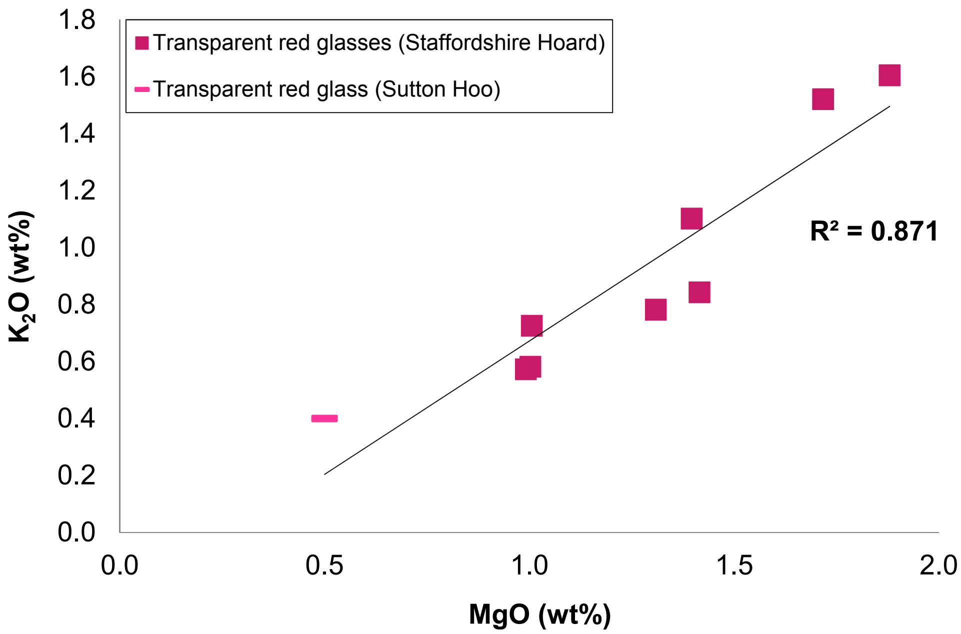

Figure 18: A plot of K_2O vs. MgO composition of transparent red glasses from the Staffordshire Hoard and Sutton Hoo (Bimson and Freestone 2000) (Note: the R2 value corresponds to the level of correlation in the data, an R^2 value of 1 would denote perfect correlation).

The particular glasses analysed by Freestone *et al*. (2008) which have correlated potash and magnesia contents (see Figure 18) all date to between 550 and 700 AD (Evison 2008). This suggests a possible date for the transparent red glasses in the Staffordshire Hoard.

Conclusions and implications

The small number of glasses analysed here can be divided into two clear groups based not only on appearance, but also their composition. The opaque blue and white glasses are of a natron composition and are very likely to be made from reworked (i.e. cut or melted and formed into new shapes) Roman glass, possibly mosaic tesserae. The transparent red glasses have a similar base composition, but with correlated potash and magnesia levels. Pieces in this second group also appear to have started life as natron glass, but with the later addition of what was probably a plant ash. It is likely that this addition was made to extend the amount of glass available to northern European craftsmen (Freestone *et al*. 2008; 42). It is not possible to say whether the natron glass used was recycled from old objects or was newly imported glass. It is very interesting to note that an example of transparent red glass from the Sutton Hoo ship burial assemblage has a similar composition to that expected for the natron glass which was used in this process.

By comparison with the Anglo-Saxon glass vessels analysed by Freestone *et al*. (2008) it was possible to suggest that the transparent red glasses in the Staffordshire Hoard were produced during the period 550-700 AD (Evison 2008). This glass type is present on all the objects analysed here, apart from K377, and provides a probable *terminus post quem* for their production.

The importance of identifying that these transparent red glasses are of a type associated with Anglo-Saxon objects of a particular time period is clear. However, more than this, the analysis indicates that the millefiori containing the transparent red glasses were produced by contemporary, possibly Anglo-Saxon, glass workers. This is the first time that it can be shown that the producers of these objects were not using recycled Roman millefiori, but contemporary, or even Anglo-Saxon produced, millefiori.

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