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# ST GREGORY'S MINSTER, KIRKDALE, NORTH YORKSHIRE
# ANALYSIS OF A GLASS ROD

TECHNOLOGY REPORT

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ARCHAEOLOGICAL SCIENCE

ENGLISH HERITAGE

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Research Department Report Series 18-2009

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## SUMMARY

A small fragment of a weathered glass rod from St Gregory's Minster, Kirkdale, North Yorkshire, believed to be early medieval in date, was analysed using SEM-EDS. The compositional information indicated that the rod was originally of colourless glass decorated with trails of yellow and white, which was then twisted. Similar material was recovered during English Heritage excavations at Whitby Abbey in 2002 and a comparison of the glass fragments will be included in the forthcoming Research Department report on the Whitby material.

## ARCHIVE LOCATION

Mounted SEM sample will be retained at English Heritage, Fort Cumberland, Portsmouth.

## DATE OF RESEARCH

2009

## CONTACT DETAILS

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# INTRODUCTION

A small fragment of a weathered glass rod (diameter ~ 2.5mm) from excavations at St Gregory's Minster, Kirkdale, North Yorkshire, was analysed using SEM-EDS. Similar material was recovered during English Heritage excavations at Whitby Abbey in 2002. On the basis of the style of the fragment, and the date of comparable material, it is thought to be early medieval. The fragment was made from a rod of glass, which was nearly colourless save for a slight blue-green tint. A trail of opaque yellow glass had been applied on one side, and an opaque white trail to the other, before the rod was twisted to produce *reticella* effect (Watts *et al*. 1997, 51-52).

The purpose of analysis was:

1. To confirm the original colours of the glass and the colourants used.
2. To establish the likely date of the glass.
3. To allow comparison with the Whitby glass fragments once these have been analysed, in order to investigate potential links between Kirkdale and the glassworking activity at Whitby.

# METHODS

A small fragment of the rod (approximately 2mm long) was removed, mounted in epoxy resin and polished to a 0.25 micron finish, so that the cross section of the rod could be examined. High magnification images of the glass microstructure were obtained using an FEI scanning electron microscope using back-scattered electron imaging, which shows areas with different compositions as different shades on a greyscale. At the same time, areas of the sample were analysed using an attached energy dispersive spectrometer (EDS) with Oxford ISIS software. The spectrometer was calibrated with cobalt and the accuracy and precision checked by analysing standards of known composition, including Corning Standard A (Brill 1999). A beam voltage of 25kV and a beam spot size number 5 were used.

# RESULTS

The captions for Figures 1-3 explain the structural details visible in the nearly colourless glass rod and applied coloured glass trails using the SEM. The SEM-EDS analytical results for the rod and both trails are given in Table 1.

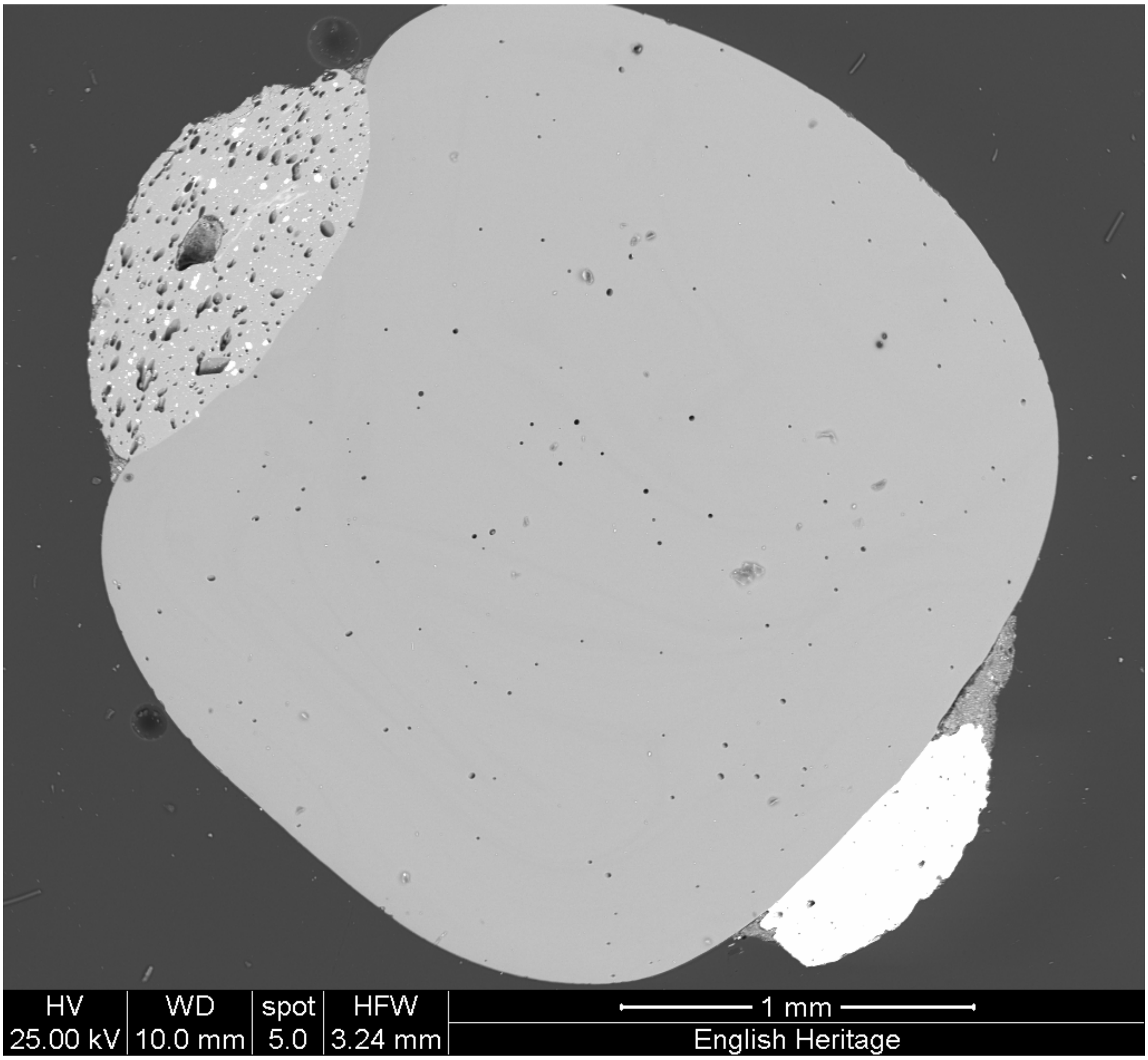



*Figure 1 shows a cross section of the colourless glass rod (mid-grey circle) using back-scattered electron imaging. The protrusion on the bottom right is the yellow glass trail, which appears white in this image because it contains a high concentration of lead. The protrusion on the top left (appearing light grey) is the white trail. The black spots are bubbles in the glass.*

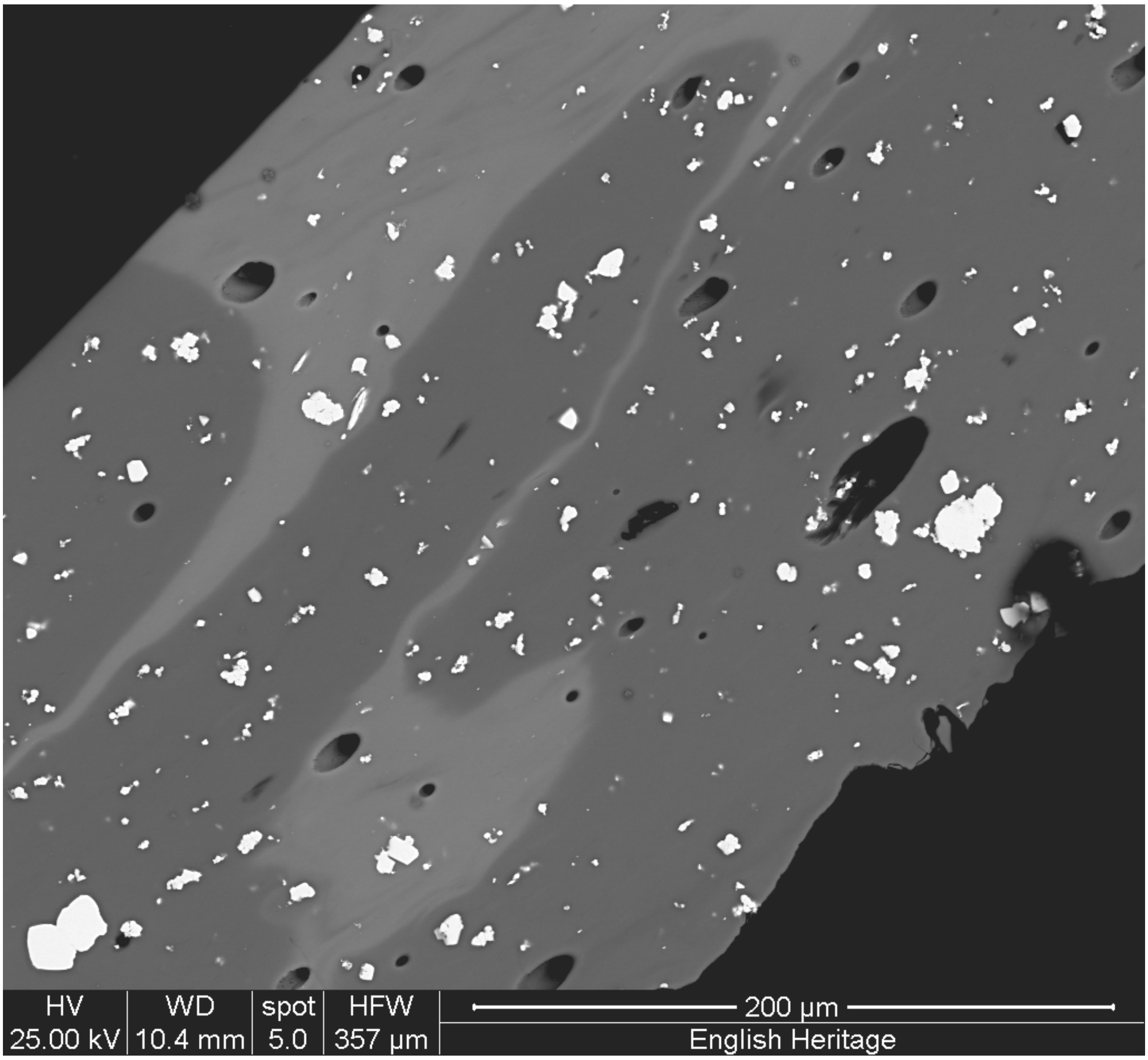



*Figure 2 shows part of the yellow trail at higher magnification. The white patches are crystals of yellow lead stannate ($PbSnO_3$). The glass is heterogeneous – the lighter grey areas contain more lead oxide than the darker grey areas.*

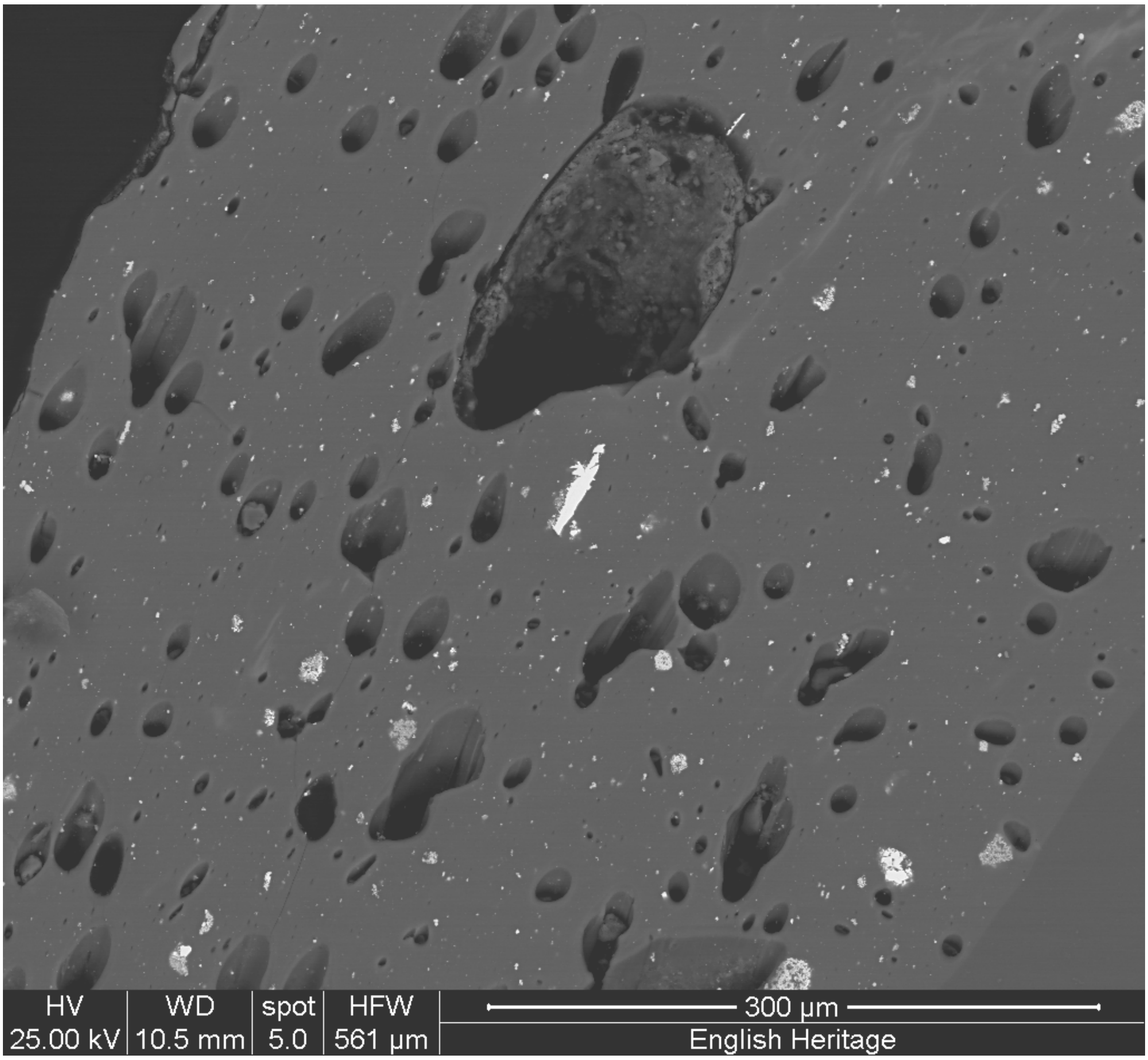



*Figure 3 shows the white trail at higher magnification, with tin oxide ($SnO_2$) crystals (appearing white in the image) in a glass matrix (mid-grey) with numerous elongated bubbles (black).*

Table 1: SEM-EDS analyses of the different parts of the Kirkdale glass rod: Y = yellow, C= colourless, W = white, (normalised). bd = below detection limit.

| Area | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | Cl | $K_2O$ | CaO | $TiO_2$ | MnO | FeO | CuO | ZnO | $SnO_2$ | PbO |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Y dark matrix | 10.03 | 0.61 | 2.46 | 45.82 | bd | bd | 0.60 | 0.90 | 4.35 | 0.18 | 0.31 | 0.81 | 0.22 | 0.12 | 0.95 | 32.64 |
| Y bulk | 9.92 | 0.62 | 2.41 | 43.09 | bd | bd | 0.54 | 0.79 | 4.16 | 0.14 | 0.30 | 0.87 | 0.22 | bd | 2.23 | 34.71 |
| C bulk | 16.79 | 0.86 | 2.64 | 68.58 | 0.10 | 0.25 | 0.84 | 1.03 | 7.35 | 0.12 | 0.62 | 0.83 | bd | bd | bd | 0.24 |
| C bulk | 16.64 | 0.80 | 2.60 | 68.54 | bd | 0.29 | 0.97 | 0.96 | 7.41 | 0.14 | 0.55 | 0.75 | bd | bd | bd | 0.25 |
| C bulk | 16.69 | 0.85 | 2.56 | 68.40 | 0.11 | 0.27 | 0.95 | 0.97 | 7.34 | 0.16 | 0.58 | 0.83 | bd | bd | bd | 0.24 |
| W bulk | 15.23 | 0.96 | 2.39 | 67.92 | bd | 0.44 | 1.12 | 0.58 | 6.78 | bd | 0.43 | 0.87 | bd | bd | 1.69 | 1.23 |

## DISCUSSION

The nearly colourless glass forming the main rod is a soda-lime-silicate with low levels of magnesia and potash (Table 1), characteristic of glass made with a mineral source of alkali, such as the evaporite natron. So-called natron glass is typical of the great majority of glass found in England from the late Iron Age through the Roman and early medieval periods (Freestone *et al.* 2008; Sanderson *et al.* 1998). The raw materials for glass production were carefully selected because low levels of naturally present impurities, such as iron compounds, could impart a strong colour to the glass produced. In colourless glass, oxides of manganese or antimony are often added to counteract this effect; the glass in the Kirkdale rod is decolourised with manganese oxide although a slight blue-green tinge persists from the small quantities of iron oxide unintentionally incorporated into it.

Although some archaeological evidence from England (Jackson *et al.* 2003) and elsewhere in Europe (Wedepohl *et al.* 2001) has been interpreted as waste from the manufacture of natron glass from raw materials in the earlier centuries of the Roman period, this is counteracted by a substantial body of evidence that indicates that much of the natron glass circulating the Roman Empire was produced at a small number of large-scale production centres. The centres producing glass in the 1st to 3rd centuries AD have yet to be identified but likely locations for the furnaces making the glass common in the late Roman and Byzantine / early medieval periods are in the Levant and Egypt, near to the major sources of natron as well as suitable sources of sand (Freestone *et al.* 2008). Chunks of the glass were then transported to numerous glass workshops across the Empire where the glass was worked into different objects (secondary production).

Natron glass of early medieval / Anglo-Saxon date from sites in England has a similar composition to that from elsewhere, indicating that glass is still likely to have been produced on a large scale in a few centres and then transported widely. There is also evidence to suggest increased recycling (Freestone *et al.* 2008). The glass from which the Kirkdale rod is made is compositionally very similar to the later Anglo-Saxon vessel glass from Hamwic (8th / 9th centuries) (Sanderson *et al.* 1998). The coloured trails on the *reticella* decoration featuring on the Hamwic glass was nearly always opaque yellow or white. Henderson (1998) analysed the opaque yellow and white glass forming such decoration and found that the opacifiers were similarly tin oxide for the white glass and lead stannate for the yellow. Although some lead oxide was detected in the white Hamwic glass, the ratios of lead oxide to tin oxide were considerably higher in the yellow glass. The distribution of this type of decoration on glass is discussed in more detail by Heyworth and Hunter (1998, 37-38). A turquoise blue rod with opaque white trails was also found at Glastonbury Abbey, where the evidence of glassworking is thought to be of similar date (Bayley 2000).

Glass is made opaque by adding something to it that will scatter light as it passes through. One of the most effective ways of opacifying glass is to cause numerous tiny crystals to form throughout. The type and size of the crystals will influence the level of opacity and also the glass colour. These crystals can be seen in the SEM images of the coloured trails (Figures 1-3) and the analyses identified the colourants; the opaque white trail was coloured by tin oxide ($SnO_2$) and the opaque yellow one by lead stannate ($PbSnO_3$). The type of opacifiers used in glass varies chronologically. Calcium antimonate was used from a very early date to make white glass, and continued to be used in Roman glass throughout the Empire. Tin compounds were used to opacify glass in some areas of Northern Europe around the 2nd to 1st century BC (Tite *et al.* 2008) but their use did not become widespread until later, from about the 4th century AD. Tin oxide was used to give a white colour and lead stannate for a yellow colour. It is not uncommon however for white glass, opacified with tin oxide, to nevertheless contain a substantial amount of lead oxide as well, but in solution in the glass rather than as part of the opacifying crystals. Therefore both the composition of the bulk glass and the type of opacifiers used strongly suggest an 8th / 9th century date for this fragment.

## CONCLUSIONS

This nearly colourless glass rod originally has trails of opaque white and yellow. The nearly colourless glass is a natron type, decolourised with manganese. The yellow glass was opacified with lead stannate. The white glass was opacified with tin oxide. The glass has a composition and form typical of around the 8th / 9th centuries.

## REFERENCES

Bayley, J (2000) Saxon glassworking at Glastonbury Abbey, in J Price (ed) *Glass in Britain and Ireland AD 350-1100*, London: British Museum (Occasional Paper 127), 161-188 and 204.

Freestone, I C, Hughes, M J and Stapleton, C P 2008, 'The composition and production of Anglo-Saxon glass', in Evison, V I *Catalogue of Anglo-Saxon Glass in the British Museum*. London: British Museum, 29-46.

Jackson, CM, Joyner, L, Booth, CA, Day, PM, Wager, E C W, Kilikoglou, V 2003, 'Roman glass-making at Coppergate, York? The nature of production'. *Archaeometry* 45 (3), 435-456.

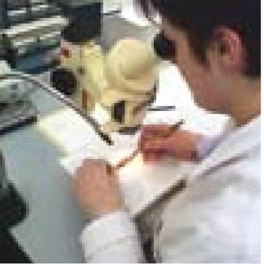
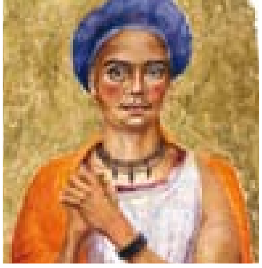
Henderson, J 1998 'Appendix Three. Electron microprobe analysis of the Hamwic glass' in Hunter, J R and Heyworth, M P *The Hamwic Glass*. CBA Research Report 116, 97.

Sanderson, D C W, Hunter, J R, Warren, S E and Heyworth, MP 1998 'Appendix two. Scientific analysis of the Hamwic glass' in Hunter, J R and Heyworth, M P *The Hamwic Glass.* CBA Research Report 116, 71-96.

Tite, M, Pradell, T and Shortland, A 2008 'Discovery, production and use of tin-based opacifiers in ancient glass, enamels and glazes: a reassessment'. *Archaeometry* 50 (1), 67-84.

Watts, L, Rahtz, P, Okasha, E, Bradley, S A J and Higgitt, J 1997 'Kirkdale – the inscriptions'. *Medieval Archaeology* 41, 51-99.

Wedepohl, K H, Gaitzsch, W, Follmann-Sculz, A B 2001 'Glassmaking and glassworking in six Roman factories in the Hambach Forest, Germany' in *Annales du 15e Congrès de l'Association Internationale pour l'Histoire du Verre*. Amsterdam: AIHV, 56-61.



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