Notes on the chemical analysis of the first available fragment

6th September 2010

A small fragment of the badly-affected glass became available in March 2010 as a result of environmental factors exacerbating some pre-existing damage.

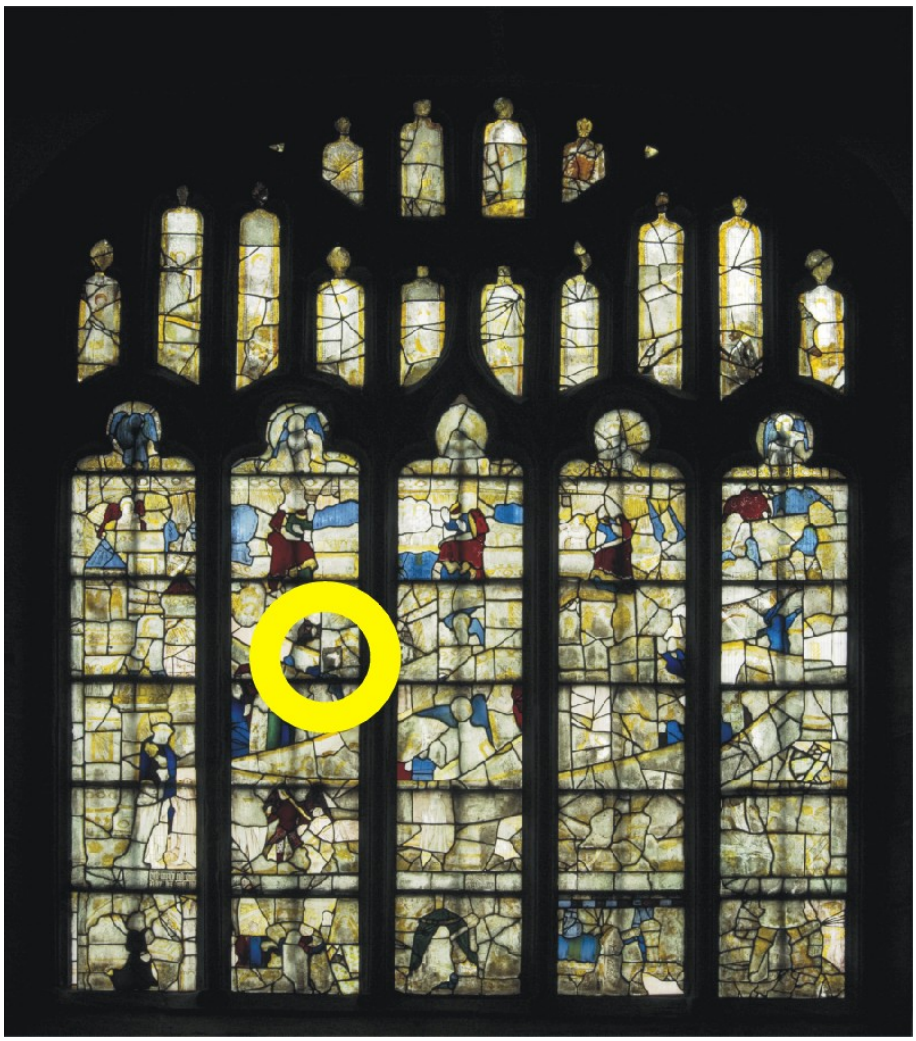

Figure 1: the East Window of the Savile Chapel at Thornhill parish church, showing the location of the fragment which was analysed *(photograph: English Heritage)*

The fragment came from the centre-left lancet, from the panel just above mid height, indicated by the yellow circle in Figure 1. A pre-existing hole in the window had deteriorated since the recent recording of the window by English Heritage. In Figure 2 below one can see the precise location of the fragment at the top right of the hole.

Figure 2: Detail from the photograph by English Heritage (left) and the same area photographed after the fragment had become detached

Margaret West succeeded (in spite of the very small size of the sample) in providing qualitative analyses of the surface and duplicate quantitative analyses of the sample bulk.

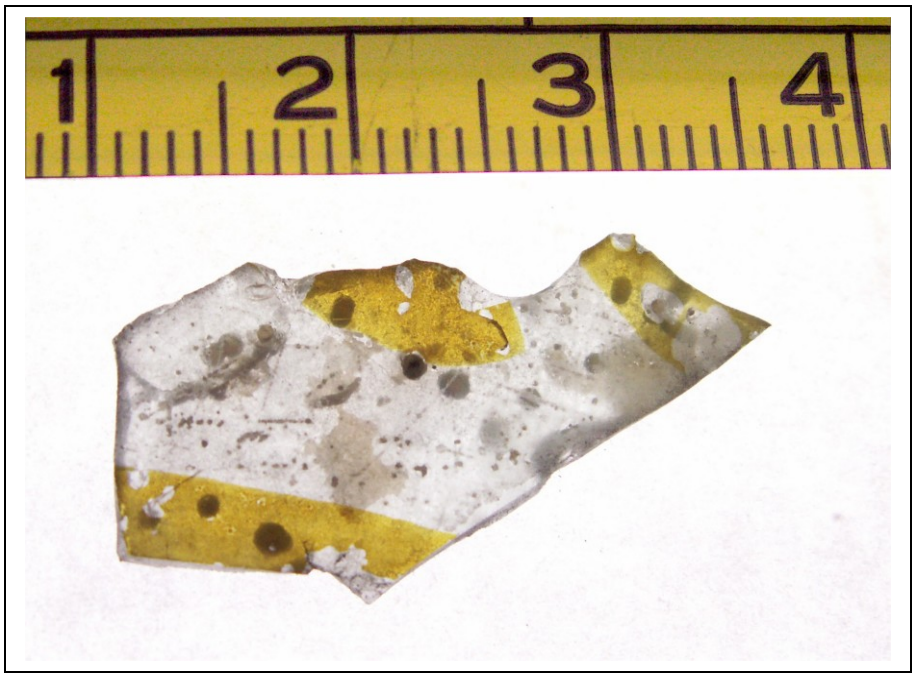

Figure 3: Fragment of glass which became available for chemical analysis

Semi-qualitative surface analysis of the stained and the clear parts of the surface indicated as expected that the major colouring element in the yellow stain was silver oxide. Chloride was detected at around 0.6% by weight.

Of particular interest in view of the evident vulnerability of much of the window was the quantitative analysis. For this purpose the fragment was divided into two portions, one consisting of the clear portion and the other consisting of the part bearing silver stain.

The sample was cleaned in an ultrasonic bath to remove debris held in the pitted sites then ground and fused with lithium tetraborate for quantitative analysis. The oxides quoted are those stable at the fusion temperature of 1100°C. Loss on ignition was 0.82%.

	100615	100606
SiO2	53.3	52.8
K2O	13.6	13.1
Na2O	2.1	1.8
MgO	7.6	7.7
CaO	16.0	15.6
SrO	0.10	0.06
BaO	0.01	0.18
ZnO	0.10	0.06
Al2O3	1.2	1.4
Fe2O3	0.60	0.48
P2O5	3.6	3.8
Mn3O4	1.7	1.8
TiO2	0.10	0.08
SO3	0.20	0.28

Table 1: Duplicate analyses carried out on the available glass fragment (values given are % by weight)

The duplicate analyses given in Table 1 are in remarkably good agreement given the very small mass of glass available and the unusually high dilution necessary to produce beads large enough for the X-ray technique employed.

It is clear that the silica content of 52% is significantly low compared with the value of 72% typically encountered in modern durable glasses. This gives grounds for saying that the atypically severe deterioration of the interior surface of the glass has happened because chemically this glass is of a vulnerable composition rather than because of any unusually severe environmental conditions.

The alkali present is predominantly potassium oxide (13%) with only a small amount of sodium oxide (2%). Coupled with the significant level of phosphorus in the glass (4%) we conclude that this glass is of the type made in a northern European forest glasshouse, rather than glass imported from Mediterranean sources.

It is helpful to use the technique recommended by the late Professor Roy Newton to compare this glass with other less sensitive glass compositions. He expressed the glass compositions in molar rather than mass proportions, to focus attention on the molecular structure of the glass. Silica (SiO_2) is the familiar network former, but oxides such as those of iron and aluminium (Fe_2O_3 and Al_2O_3) would in tandem with the alkalis present (K_2O and Na_2O)

strengthen the molecular network against attack. His "SiO_2" parameter thus incorporates the iron and aluminium oxides together with an equivalent amount of the alkali. Alkali content remaining after this piece of arithmetic was combined under the title "R_2O", and the divalent alkaline earths (mainly CaO and MgO) were lumped together as "RO". Thus the structurally significant compositional factors were made three in number - a welcome simplification which aids comparisons.

Neglecting any minor constituents, these three parameters must total 100 moles per cent. Traditionally such data is plotted on a triangular diagram, but most people find such diagrams hard to interpret. Newton pointed out that a familiar rectangular plot can be used in the same way, the scale for the third constituent forming diagonal lines across the graph. Figure 4 is constructed in this way.

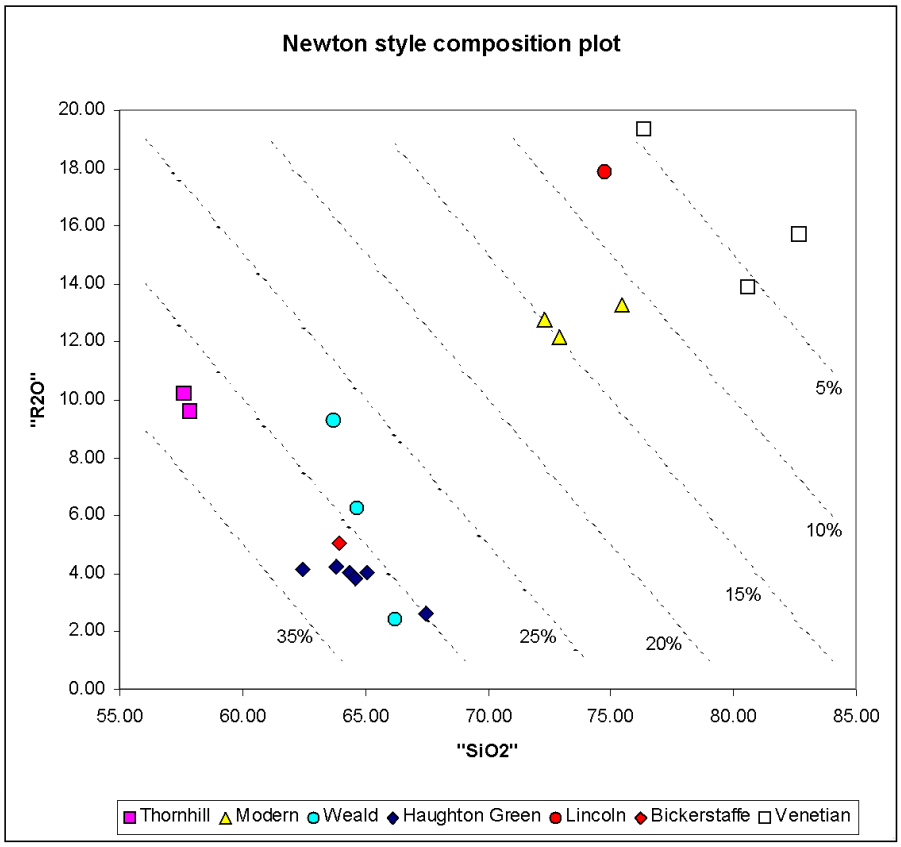

Figure 4: Newton-style plot of the Thornhill analytical data, compared with modern glasses and a selection of archaeological and museum glasses

Although the fragment analysed had quite a high level of lime and magnesia (similar to those found in the 17th century window glass from Haughton Green and the late 16th century glass from Bickerstaffe) the silica content is below the threshold Newton identified as marking a profound change in vulnerability to water attack. So the Thornhill glass is vulnerable by reason of its low silica content.

Venetian glass of the 16th and 17th centuries, and façon de Venise glass of the 17th century are known to give durability problems in the context of museum collections. For these glasses the silica content is quite high, but the high alkali content and the low proportion of alkaline earths seriously compromise the durability. In between these two extremes lie the modern glass compositions with enough of the alkaline earths to stabilise them, and the Wealden and the Lancashire glasses which have lower silica levels but high levels of alkaline earths.

From the conservation point of view, the experience of the Thornhill window underlines the importance of the threshold level of silica in the glass, and assists in assessing ancient glasses for which chemical analytical data are available. The use of portable XRF facilities to provide non-destructive analysis in situ should be encouraged in this regard.