Ancient Monuments Laboratory
Report 53/89

ANALYSIS OF WINDOW GLASS FROM WEST HILL, ULEY, GLOUCESTERSHIRE.

Michael Heyworth BA(Hons) MA MIFA

Ancient Monuments Laboratory Report 53/89

ANALYSIS OF WINDOW GLASS FROM WEST HILL, ULEY, GLOUCESTERSHIRE.

Michael Heyworth BA(Hons) MA MIFA

Summary

A small number of window glass fragments from the Romano-British ritual complex at West Hill, Uley, were analysed. All the fragments were shown to be soda-lime-silica glass. Typological study had shown that some fragments were of post-Roman date and these fragments were compositionally distinct from the Roman fragments. The post-Roman fragments were all of identical compositon and may come from the same window pane. Some of these fragments had red streaking in the glass and the composition indicated that they were copper ruby glass.

Author's address :-

Michael Heyworth BA(Hons) MA MIFA

Ancient Monuments Laboratory
English Heritage
23 Savile Row
London
W1X 2HE

ANALYSIS OF WINDOW GLASS FROM WEST HILL, ULEY, GLOUCESTERSHIRE

Introduction

A number of small fragments of window glass were found during excavations at the Romano-British ritual complex on West Hill. These were divided into two groups, based on visual examination by Dr Jennifer Price, with one group of Roman date and the other post-Roman. It was hoped that chemical analysis would confirm the two groups as compositionally distinct and provide further information on the nature of the glass in each group.

The Glass

The twenty-three fragments of window glass found at West Hill all come from blown panes which have been cylinder-blown, cut open and flattened and are unlikely to pre-date the third/fourth century (Price forthcoming).

Thirteen fragments were from either colourless, green/colourless or light blue/green panes which are commonly found on late Roman sites. Nine of these fragments were included in the analytical programme, four were excluded as they were too small for destructive sampling. The fragments analysed were mainly found in the destruction levels over Building XIV which were dated to the late fourth or early fifth centuries AD. This building was a rectangular timber framed domestic structure.

The remaining ten fragments were found in the same area of the site, ie above Building XIV. However they were a much darker blue-green colour than that usually found in Romano-British window glass. Four fragments had red streaks in the glass metal which is very rare in Romano-British window glass. The only other examples come from Atworth, a late Roman villa site in Wiltshire, and the Roman towns of Wroxeter and Silchester, however none of these fragments come from secure Roman contexts (Price forthcoming). Red streaking is more common in fragments of early medieval window glass in Britain, for example at Monkwearmouth and Jarrow (Cramp 1970) and at Winchester (Hunter & Biddle forthcoming). It is also found in vessel glass of the same period, such as that from Southampton (Hunter & Heyworth forthcoming). These glass fragments may therefore date to the seventh to ninth centuries AD and could possibly have been associated with a stone church.

Analytical Method

The analyses were undertaken using inductively coupled plasma atomic emission spectrometry (ICPS). The ICPS technique is becoming increasingly widely used in the analysis of archaeological materials (see Heyworth et al 1988) as it has a number of advantages over other analytical techniques. In particular, it gives compositional data for a wide range of elements at the major, minor and trace levels (Thompson and Walsh 1986). This is especially important for the analysis of glass where major and minor elements determine the general type of glass and minor and trace elements have an important influence on its colour. In the present programme data was obtained for 32 oxides and elements: Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, MnO, Pb, Sb, Ba, Co, Cr, Cu, Li, Nb, Ni, Sc, Sr, V, Y, Zn, Zr, La, Ce, Nd, Sm, Eu, Dy, Yb and SiO_2. The figure for silica was obtained by difference as the silica is removed in the sample preparation procedure.

Samples of glass for analysis were cut from the glass fragments, using a low speed diamond blade saw, and milled to a fine powder. A powdered sample of 100 mg was then evaporated to dryness with perchloric and hydrofluoric acid, and the residue dissolved in hydrochloric acid and distilled water before diluting to a standard solution strength. The sample preparation and ICPS analysis was undertaken in the Department of Geology at Royal Holloway and Bedford New College, University of London, under the supervision of Dr J.N.Walsh.

The ICPS analysis was carried out using a Philips polychromator ICPS system calibrated for quantitative analysis with multi-element rock standards. The glass solutions were run through the system twice, the first time the majority of major, minor and trace elements were measured, and the second time the solution was diluted to 10% of its original strength to obtain the soda figures. The soda level in the glass is outside the calibration range of the instrument at the original solution strength and the dilution was necessary to maintain a linear calibration for the soda signal. Multi-element rock standards were analysed at regular intervals during the analytical run to allow for correction of any short-term fluctuations in the system. Three glass substandards were also analysed to check the ICPS calibration.

Nineteen of the fragments of window glass from the site were analysed. The full compositional data is listed in Table 1, together with relevant information on the archaeological context in which the glass was found, and the site phase to which it belonged, and a description of the glass colour and any streaking found within the glass.

Analytical Results

All the glass is of the durable, soda-lime-silica type, though there are some variations in the levels of the main oxides which indicates differences in the raw materials used, or possibly even in the recipes used to make the glass.

The nine fragments of Roman date, which are a variety of lightly tinted translucent colours ranging from colourless to light blue-green, have a mixture of compositions. The three colourless fragments (nos. 6436, 6630 and 7583) have very similar compositions and may be part of the same pane. These glasses contain higher levels of antimony, about 0.07%, though at this level it is unlikely to have been effective as a decolourant and may be present in the glass due to the use of cullet. Three other fragments (nos. 3957, 6414 and 8125) contain no antimony but have particularly high manganese levels, about 0.9%. The manganese level does not correlate with increased levels in other oxides/elements which may suggest that manganese was added separately, and deliberately, to these glasses, presumably to act as a decolouriser. Very few analyses of Romano-British window glass have been undertaken, however analysis of window glass from Roman Caerleon (Cole 1966) also showed the use of manganese as a decolouriser, though the glass was dated to the first/second century AD (Boon 1966), rather earlier than that from Uley.

The ten fragments of post-Roman date form a tight compositional group and probably all come from the same window pane. They can be distinguished from the Roman fragments on the basis of much higher iron, potash, lead and copper contents. This suggests that different raw materials were used in the production of the post-Roman batch.

The red streaks in the post-Roman glass are likely to be caused by the presence of discrete coloured particles in the glass. These are probably crystals of cuprous oxide and/or metallic copper which are held in suspension in the glass. The crystals are present due to the precipitation of the copper out of solution when the glass melt has become supersaturated at the heat treatment temperature (Paul 1982). This type of coloured glass is known as copper ruby glass, in this case with a copper content of about 0.5%.

In the production of a copper ruby glass a batch containing copper, together with a reducing agent, is melted in reducing conditions. The melt initially shows the blue colour characteristic of cupric (Cu^{++}) ions, but as the melting proceeds, and the furnace atmosphere becomes more reducing, the colour changes to become almost colourless (cuprous Cu^{+} ions). By subsequent heat treatment commonly known as 'striking', at a temperature somewhere between the annealing and the softening temperature, the ruby colour is developed (Paul 1982). There has been much discussion over the state of the copper in a ruby glass but recent work (eg Debnath and Das 1986) has shown that it is likely to be in the form of metallic copper. In the Uley glass the presence of lead at levels of about 0.8% may have facilitated the initial solution of the copper and the subsequent precipitation of the red crystals by lowering the temperature necessary for the striking to take place (Guido et al 1984). The relatively high iron level of about 1.4% may have assisted in the process by acting as a reducing agent, though these levels are not sufficient on their own. Much has been made in the literature of the need to have tin in a copper ruby glass to act as the reducing agent (eg Duran et al 1984), however this does not necessarily seem to be correct (Freestone pers comm). The ICPS analyses do not include a measurement of tin, but XRF analysis did not detect the presence of any tin in the Uley glass. The apparent lack of a suitable reducing agent in the glass composition is therefore significant and may indicate the use of carbon in the glassmaking process, probably as plant material.

It is unlikely that the ancient glassmakers were attempting to produce a streaked glass, and the deliberate addition to the glass batch of copper probably indicates that they were attempting to produce a coloured glass. As copper ruby glasses are colourless when first made it is possible they were attempting to produce a colourless glass but it seems unlikely that they would add copper to a glass to achieve this. If they intended to produce a colourless glass then it is more likely that they would have added a decolouriser such as manganese to the base glass. Copper in glass is usually associated with a blue colour, though in the presence of lead it usually produces a turquoise-green colour, and it may be that this is what was intended, but the presence of higher than usual levels of lead and iron caused the glass to 'strike' unexpectedly, though this is unlikely without the presence of a stronger reducing agent. Another possibility is that they were attempting to produce a red glass. Modern experiments to produce an opaque red glass have shown it to be a difficult process. Attempts by Michael Cable often resulted in red streaks in the glass, which could develop either during initial cooling, or on reheating in an attempt to 'strike' the colour (Brighton and Newton 1986). It is possible that ancient glassmakers reduced the level of copper to attempt to produce a paler red colour and it got to a level where it would 'strike' in some areas of the glass while adjacent areas would remain relatively colourless. However the lack of any known examples of pure (ie not streaked) red copper ruby glasses of similar date suggest this alternative may be unlikely.

To an extent, given their lack of understanding of the chemistry of the glassmaking process, ancient glassmakers would have been at the mercy of the raw materials available to them and the impurities they contained (Newton 1978). However in the production of the post-Roman window glass from Uley there was probably a deliberate attempt to produce a coloured glass by the addition to the glass batch of copper. The lead could have been added to make the glass colour a more turquoise-green. As the glass was to be coloured there would have been less worry about impurities in the raw materials and a lower grade sand may have been used which contained more iron. The attempt to produce a coloured glass would have relied on control over the thermodynamics of the redox system and in this case the control was not adequate to produce an evenly coloured glass.

Red streaking in glass is known from other early medieval sites such as Southampton, Repton and Winchester and ICPS analyses of fragments from these sites have also shown relatively high levels of copper and lead in these glasses. However further work will be needed to compare the compositions of these glasses before any generalisations can be made.

Conclusion

The two groups of window glass defined by visual inspection are compositionally distinct, though all the fragments are of the same basic type of glass. There was some variation in the composition of the Roman window glass fragments, with evidence for the use of manganese as a decolouriser in some fragments. The post-Roman window fragments were all identical in composition and may originally have been part of the same window pane.

The post-Roman window glass can be described as copper ruby glass, where the red streaks in the glass are probably caused by the precipitation of metallic copper out of solution, possibly facilitated by the presence of lead. The copper and lead were clearly added deliberately to the glass batch. It is likely that the ancient glassmakers were attempting to produce a coloured window glass, however they did not have an adequate control over the glassmaking process to achieve this end.

Acknowledgements

I am grateful to Leo Biek, Justine Bayley, Michael Cable, Ian Freestone and Julian Henderson for discussions and suggestions during the course of this work.

References

Boon,G., 1966 "Roman window glass from Wales", Journal of Glass Studies VIII, 41-5.

Brighton,T. and Newton,R., 1986 "William Peckitt's red glasses", Stained Glass Quarterly 81, 213-220.

Cole,H., 1966 "Analyses and discussion of the Caerleon window glass", Journal of Glass Studies VIII, 46-7.

Cramp,R., 1970 "Decorated window-glass and millefiori from Monkwearmouth", Antiquaries Journal 50, 327-335.

Debnath,R. and Das,S.K., 1986 "Photo-luminescence and the structure of colour centers in the copper-ruby glass", in Collected Papers of the 14th International Congress on Glass, 1986, New Delhi, India, Volume 1, 220-6.

Duran,A., Fernandez-Navarro,J.M., Garcia Sole,J. and Agullo-Lopez,F., 1984, "Study of the colouring process in copper ruby glass by optical and ESR spectroscopy", Journal of Materials Science 19, 1468-76.

Guido,M., Henderson,J., Cable,M., Bayley,J. and Biek,L., 1984 "A Bronze Age glass bead from Wilsford, Wiltshire: Barrow G.42 in the Lake Group", Proceedings of the Prehistoric Society 50, 245-254.

Heyworth,M.P., Hunter,J.R., Warren,S.E. and Walsh,J.N., 1988 "The analysis of archaeological materials using inductively coupled plasma spectrometry", in Science and Archaeology, Glasgow 1987: Proceedings of a conference on the application of scientific techniques to archaeology, Glasgow, September 1987, edited by E.A.Slater and J.O.Tate, BAR British Series 196, pp.27-40.

Hunter,J.R. and Biddle,M., forthcoming "Early medieval window glass", in The Craft Industries, Art and Daily Life in Early Winchester, edited by M.Biddle, Winchester Studies Volume 7.2.

Hunter,J.R. and Heyworth,M.P., forthcoming "The Glass from Hamwic", in Southampton Finds, Volume II: The Glass and Copper Alloys, edited by A.D.Morton.

Newton,R.G., 1978 "Colouring agents used by medieval glassmakers", Glass Technology 19, 59-60.

Paul,A., 1982 Chemistry of Glasses. Chapman & Hall, London.

Price,J., forthcoming "The glass", in The Uley Shrines - excavation of a ritual complex on West Hill, Uley, Gloucestershire: 1977-79, by A.Woodward and P.Leach.

Thompson,M. and Walsh,J.N., 1983 A Handbook of Inductively Coupled Plasma Spectrometry, Blackie & Sons Ltd., Glasgow.

Table 1

ICPS data

The glass samples were analysed using inductively coupled plasma atomic emission spectrometry (ICPS) and data was obtained for 31 oxides/elements. The data from each analysis is divided into the major and minor oxides (listed as oxide weight percentages), minor elements (listed as weight percentages) and trace elements (listed as parts per million). The figure for silica is obtained by subtracting the total figure of the measured oxides/elements from 100%. Consequently the sum of the concentrations, including silica, is always exactly 100%.

The data is listed together with information on the fragment number, the site context in which it was found, the phase of the site to which it belonged, fragment colour and the presence/absence of red streaking in the glass. The glass colours are coded as follows:

Colour code

B/G - Blue/Green
G/C - Green/Colourless
C - Colourless

Uley Roman blown window glass

Number	3957	6179	6414	6436	6630	7251	7412	7583	8125
Al_2O_3 (%)	2.12	2.47	2.32	2.11	2.07	2.37	2.16	2.00	2.99
Fe_2O_3 (%)	.59	.30	.53	.44	.42	.51	.57	.41	.36
MgO (%)	.74	.46	.67	.54	.53	.58	.81	.51	.59
CaO (%)	5.92	7.30	6.64	5.91	5.79	7.71	5.73	5.61	8.50
Na_2O (%)	20.9	14.3	20.0	18.1	18.2	16.8	18.8	17.9	15.0
K_2O (%)	.62	.51	.82	.45	.43	.73	.64	.53	.41
TiO_2 (%)	.13	.08	.11	.10	.09	.09	.13	.09	.08
P_2O_5 (%)	.07	.14	.08	.06	.06	.14	.08	.06	.08
MnO (%)	.91	.22	.87	.15	.12	.37	.49	.12	.90
Pb (%)	.02	.01	.02	.05	.04	.03	.04	.04	.01
Sb (%)	.01	.00	.00	.06	.07	.04	.04	.07	.00
Ba (ppm)	305	219	273	173	167	222	203	161	757
Co (ppm)	9	7	8	7	6	9	8	6	9
Cr (ppm)	20	14	18	14	13	17	18	13	16
Cu (ppm)	102	13	85	130	106	107	123	105	31
Li (ppm)	8	4	7	7	7	9	8	5	4
Nb (ppm)	2	1	3	1	2	2	2	1	2
Ni (ppm)	19	13	17	16	16	16	18	16	19
Sc (ppm)	2	1	2	1	1	2	2	1	1
Sr (ppm)	448	386	422	414	414	405	413	400	509
V (ppm)	22	13	20	13	13	18	21	12	20
Y (ppm)	8	8	8	7	7	8	8	7	10
Zn (ppm)	31	13	31	28	29	30	45	28	14
Zr (ppm)	55	32	46	46	46	49	69	44	36
La (ppm)	14	13	13	13	13	13	14	14	12
Ce (ppm)	17	15	17	16	16	17	16	16	17
Nd (ppm)	11	9	11	10	11	11	11	10	10
Sm (ppm)	1.8	1.4	1.8	1.5	1.7	1.8	1.7	1.7	1.7
Eu (ppm)	0.3	0.3	0.4	0.3	0.3	0.3	0.3	0.3	0.3
Dy (ppm)	1.9	1.1	1.6	0.9	1.0	1.4	1.3	1.0	1.8
Yb (ppm)	0.7	0.6	0.8	0.6	0.7	0.7	0.7	0.6	0.8
SiO_2 (%)	67.9	74.1	67.8	72.0	72.1	70.6	70.4	72.6	70.9
Context	511	310	1100	1100	1100	410	1191	1191	1218
Site Phase	7a	7	7–8	7–8	7–8	7	5d–6b	5d–6b	5d
Colour	G/C	B/G	G/C	C	C	B/G	G/C	C	B/G
Streaked?	–	–	–	–	–	–	–	–	–

Uley post-Roman blown window glass

Number		6398	6400	6412	6443	6455	6622	7066	7152	7218	7344
Al_2O_3	(%)	2.54	2.54	2.52	2.46	2.47	2.50	2.44	2.44	2.48	2.44
Fe_2O_3	(%)	1.46	1.46	1.45	1.42	1.39	1.40	1.38	1.39	1.40	1.39
MgO	(%)	.72	.72	.71	.69	.69	.70	.69	.68	.70	.69
CaO	(%)	7.14	7.15	7.14	6.98	6.89	6.94	6.83	6.83	6.93	6.88
Na_2O	(%)	15.1	16.3	15.6	15.1	14.9	15.4	14.9	14.9	15.4	15.7
K_2O	(%)	1.35	1.23	1.18	1.20	1.21	1.20	1.17	1.17	1.18	1.17
TiO_2	(%)	.11	.12	.11	.11	.09	.10	.09	.10	.09	.10
P_2O_5	(%)	.18	.20	.20	.19	.17	.18	.16	.18	.17	.18
MnO	(%)	.49	.49	.49	.48	.48	.49	.48	.48	.49	.49
Pb	(%)	.83	.82	.83	.80	.81	.83	.81	.82	.83	.82
Sb	(%)	.09	.10	.10	.09	.09	.10	.10	.10	.10	.10
Ba	(ppm)	269	266	264	258	259	262	256	257	260	257
Co	(ppm)	23	23	24	23	23	24	23	23	24	23
Cr	(ppm)	19	20	19	19	18	18	18	18	18	18
Cu	(ppm)	5370	5350	5280	5180	5170	5300	5170	5190	5250	5180
Li	(ppm)	14	13	13	13	13	13	13	13	14	13
Nb	(ppm)	1	2	1	2	2	2	2	1	1	1
Ni	(ppm)	27	27	26	26	25	28	25	23	25	26
Sc	(ppm)	2	2	2	2	1	2	1	2	2	2
Sr	(ppm)	417	414	412	401	404	410	401	403	409	403
V	(ppm)	24	24	23	23	22	22	22	22	22	23
Y	(ppm)	9	9	9	8	9	9	9	9	9	9
Zn	(ppm)	146	146	145	145	147	144	141	143	143	143
Zr	(ppm)	54	56	54	42	38	39	32	37	39	37
La	(ppm)	14	15	14	14	14	14	14	14	14	14
Ce	(ppm)	17	18	18	19	18	19	18	18	18	19
Nd	(ppm)	11	11	11	12	11	12	12	11	12	12
Sm	(ppm)	1.8	1.8	1.8	1.9	1.7	1.7	1.8	1.6	1.8	2.0
Eu	(ppm)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Dy	(ppm)	1.3	1.4	1.4	1.3	1.4	1.4	1.3	1.3	1.4	1.5
Yb	(ppm)	0.8	0.8	0.8	0.7	0.7	0.8	0.7	0.7	0.8	0.8
SiO_2	(%)	69.4	68.3	69.0	69.8	70.3	69.5	70.4	70.3	69.6	69.5
Context		1100	1100	1100	1100	1100	1100	1191	1191	1191	1191
Site Phase		7–8	7–8	7–8	7–8	7–8	7–8	5d–6b	5d–6b	5d–6b	5d–6b
Colour		B/G	B/G	B/G	B/G	B/G	B/G	B/G	B/G	B/G	B/G
Streaked?		Y	–	–	Y	Y	–	–	Y	–	–