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Rhynie, A Powerful Place of Pictland

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APPENDIX 1:
SCIENTIFIC ANALYSIS OF GLASS FROM TAP O' NOTH AND THE CRAW STANE COMPLEX

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Method

Limited elemental analysis was carried out. The very small and unpolished samples did not allow for detailed examination of the nature of inclusions and colourants, though these potentially could give some valuable information about composition of the glass.

The glass was sampled using the method devised by Bronk and Freestone (2001), which employs a re-usable diamond-coated file, the edge of which is scored across a small section of the surface of the object to produce fine glass flakes. All sampling was carried out under a low-powered optical microscope and the flakes were collected from the file itself, and also as loose pieces collected onto a polyester film sheet. These were picked up by pressing an adhesive carbon tab mounted on an SEM stub onto the fragments, while pressing down onto the polyester sheet to make the microscopic flakes lie as flat as possible. The stubs were then carbon coated.

The fragments could be examined thoroughly by a combination of both secondary (SEI) and back-scattered electron (BSE) images in the Scanning electron microscope (SEM); the two images when viewed in tandem allowed the selection of a flat, clean surface, not shadowed by other pieces (SEI image) and with a lack of surface abnormalities or corrosion (BSE image). At least five measurements were taken from each sample, where possible from different flakes or different areas on a flake and from as large an area free from contamination or corrosion as possible. The protocol devised by Bronk and Freestone (2001) requires analyses to be as close to 100 per cent as achievable; in practice the analyses fell within 90–110 per cent. The overall percentage totals varied due to surface irregularities and variation in orientation of the flakes towards the primary beam and the detector. All the totals were normalised to 100 per cent so they could be compared to one another and to other results. As with Bronk and Freestone's initial study, the standard deviation for the flakes was slightly greater than that for polished samples; but also as with the polished samples, the largest errors occurred in sodium, possibly due to its volatility, and lead, antimony and tin, probably due to uneven dispersal of these metal compounds within the glass matrix, especially when used as colourants.

TAP		Na2O	MgO	Al2O3	SiO2	P2O5	SO2	Cl	K2O	CaO	TiO2	MnO	FeO	CoO	CuO	SnO2	Sb2O5	PbO	PbO
1124	green block	15.23	0.52	2.33	68.58	0.11	0.2	1.08	0.71	7.12	0.09	0.53	0.84	0	1.56	0.01	0	0.19	1.3
1603	blue bead	17.25	0.64	2.42	68.48	0.07	0.45	0.83	0.71	6.33	0.12	0.46	0.94	0.06	0.59	0.03	0.05	2.13	0.33
1701	blue bead	18.33	0.93	2.38	66.01	0.06	0.45	0.84	0.72	7.64	0.16	1.07	1.06	0.08	0.28	0.03	0	0.17	0.17
1701R	red decoration	14.69	1.18	2.27	53.37	0.09	0.06	0.07	1.09	6.44	0.05	0.65	2.04	0.03	2.67	0.68	4.81	0.02	9.15
1701W	white decoration	15.96	0.82	2.18	62.7	0.01	0.38	0.07	2.54	6.94	0.11	1.24	0.67	0	0.34	0	1.97	0	3.57
1702	turquoise bead	16.56	0.64	2.37	65.54	0.12	0.37	0.88	0.69	6.38	0.11	0.39	0.76	0	2	0.17	0.16	1.29	2.81
15008	vessel fragment	18.37	0.57	2.23	69.41	0	0.41	0.96	0.63	6.07	0.09	0.36	0.47	0	0.25	0	0.04	0.55	0.11

Table A1.1
Summary of Tap o' Noth glass composition

Results

Tap o' Noth

All the beads were of a mineral soda-lime-silica composition (Table A1.1), and base glass compositions (achieved by normalising lighter and glass forming elements to 100%) indicate that most of the glass was similar to glass made from a combination of both manganese and antimony decoloured Roman glass, typically circulating in the Roman Imperial period (Freestone 2015a & b), which Jackson and Paynter (2016) have shown constitutes the majority of naturally coloured glass circulating near the northern frontier by the 4th century AD.

SF 1124: green glass block

This appears to be a block or tessera of Roman glass. These were imported into Britain as convenient sized lumps of coloured glass during the Roman period where they were often re-used to form enamels and inlays. Later tesserae, probably looted from Roman buildings, continued to be traded into northern Europe during the early medieval period as primary raw glass became more difficult to obtain (Crocco et al 2021: 15). The base composition of this glass is very similar to Roman glass made from a mixture of antimony and manganese decolourised glass cullet (Freestone 2015a: 32, 34), with the deep green colour obtained by the addition of copper and lead in an oxidising environment; the quantities of these oxides as colourants in the glass fit well with dark green tesserae analysed by Crocco et al (2021: 15). Heck and Hoffmann (2002: 72) state that tin oxide was the most common opacifying agent used in the early medieval period; its absence here points to a Roman coloured glass.

SF1702: turquoise/green glass bead

The base composition of this glass is also similar to Roman glass made from a mixture of manganese and antimony decoloured glass, as seen by the levels of several constituents including alumina, lime, antimony and manganese oxides (Freestone 2015a: 32). Copper seems largely responsible for the colour, but it is likely this was originally added to a near colourless glass as gun metal (copper/tin/zinc alloy) as tin and zinc quantities are roughly proportional to 8% tin oxide and 8.5% zinc oxide of the added copper oxide. Antimony oxide is present in quite large quantities, and this, in conjunction with slightly elevated lime levels imply further deliberate addition to opacify the glass.

SF1701: crumb bead

The base composition of the blue glass has similarities to Roman manganese glass, thought to be manufactured from Egyptian sand; the higher ratio of soda to silica also indicates an Egyptian provenance. However, the quantities of titanium, iron and manganese suggest similarities to glass produced from the 4th to 7th centuries, related to HIMT glasses, also from Egypt (Freestone & Stapleton 2015). The presence of some lead and antimony and zinc suggests a level of recycling. The glass is a deep rich blue colour formed by the addition of small amounts of cobalt.

The coloured decorative elements show some unusual qualities, which could infer glass cullet was being coloured at a more local level to use for the decorative surface inclusions as there are some elements present in unusual quantities.

The additional red glass is coloured by the inclusion of copper and lead, used in relatively low quantities, as for Roman and Anglo-Saxon red glass. However, there is a large amount of tin present, in far higher proportions than would be expected for colouring glass (Heck et al 2003; Barfod et al 2022: 17), the addition of which may be due to the lead being added in the form of a lead/tin alloy, as the two metals were often combined to form pewter objects or solders. Tin, unlike lead, was not necessary for the coloration of red glass; however, Barfod et al (2022: 18), in their study of beads from Ribe (derived from Frankish and Merovingian glass cullet, in turn derived from Roman glass (2022: 5)), believe that 'moderate Pb and Sn concentration combined with low Sb concentrations also indicate Pb stannate as the opacifying agent for red beads', and so could indicate the very deliberate addition of this combination of lead and tin to form the red glass decoration in this bead.

Zinc was also present and also not necessary in contributing to the main composition or colour of the glass, and this could have been incorporated with the copper by using brass, or gun metal (possibly also contributing to the addition of some of the tin present); and if leaded copper alloys were added they could also contribute some additional lead. This could mean that raw materials in the form of copper, lead or their oxides were not available to those colouring the glass, but there was enough knowledge to understand that certain lead alloys and copper alloys, if added, would contain the correct elements needed to form the red glass. Heck and Hoffmann's analysis and experiments show the addition of metal alloys was probably used to produce coloured Merovingian beads (2002: 75) and believe that 'the composition of early medieval copper alloys can be found in the composition of the glass beads'.

The red glass also contains elevated levels of elements contained in clays (eg magnesium, iron, potassium); these could have been incorporated during the secondary process of colouring the leaded glass by heating in a clay crucible (absorption of clay minerals is a phenomenon noted for red and yellow leaded glasses where 'the chemically aggressive nature of the crucible charge against the ceramic, . . . is almost exclusively based on the corrosive action of lead oxide' (Heck et al 2002, 38; Davis and Freestone for red glass 2018: 121–2)). Any ash added or absorbed during this process, possibly to maintain a reducing atmosphere, would also lead to increased potash in the glass matrix (Freestone and Stapleton 2015; Freestone 2015a: 30).

The decorative white glass has a lower amount of lead and tin present, but in similar proportions to the red glass, so may have been coloured using a similar lead/tin alloy in the same workshop. Although tin and lead were often used together to form a yellow colourant, Heck et al (2003) have evidence that where less lead was used, the intention was to produce a white coloured rather than yellow coloured glass. Heating to high temperatures results in the dissociation of lead stannate crystals leading to white rather than yellow coloration. High levels of potash are also present in the white glass, possibly from ash mixed in during secondary working.

Both these coloured additions appear to be made from manganese decolourised glass rather than a recycled mixture of different glass types (Freestone 2015b: 252); it is possible imported Roman tesserae were used to produce the colours.

It was not possible to obtain a sample of the light blue decoration; the colour suggests that the element responsible for the colour was copper rather than cobalt.

SF1603: BLUE BEAD

This bead appears to have a base Roman glass composition where both manganese and antimony decolourised glasses have been remelted together, probably as cullet. Further recycling is indicated by the relatively high level of titanium from recycled Egyptian glass produced in the 'late antique'/early medieval period (Barfod 2022: 8, 21).

Both traces of cobalt and a small amount of copper are present which would colour the bead blue. The presence of antimony (probably combined with lime) might originally have been present to opacify the original glass, especially if the bead was formed from Roman tesserae, but SEM analysis shows there is an absence of calcium antimonate crystals in this bead which would have made the glass opaque rather than translucent. This suggests relatively clear cullet was mixed with opaque blue tesserae modifying the composition and appearance of the glass (Barfod et al 2022: 22). The formation of calcium antimonate crystals within glass is complex, depending on a number of factors (Barfod et al 2022: 20), and Barfod et al conclude that 5–7% lime in combination with antimony oxide with concentrations below 2.5% were not conducive to the extensive formation of calcium antimonate crystals, which seems to be the case for this glass bead.

SF15008: VESSEL GLASS

This has a composition similar to many clear or pale coloured Roman vessel glass type compositions, where both manganese and antimony decoloured glasses have been mixed together.

The Craw Stane Complex

SF161337: YELLOW–GREEN LUMP

This is a muddy green coloured lump of glass with a streaky surface where the colourant has not been fully mixed into the base glass. Its composition largely resembles a Roman glass using a mix of both manganese and antimony decoloured glass from different original sources. The colour is not particularly bright and is probably coloured by a combination of minor element oxides including iron, copper and lead. Antimony in combination with calcium probably contributed to the opacity of the glass.

SF1884: WHITE GLASS ROD

This is a section of white glass rod; its pitted surface has picked up a reddish colour from the surrounding soil giving it a pink appearance. The composition looks predominantly Roman; it has slightly higher lime and antimony oxide levels, which have probably contributed to its opacity and colour.

SF161507: GREEN GLASS ROD

This appears to be a Roman glass made from a mixture of manganese and antimony decoloured glass. However, it has large amounts of additional oxides which have formed the deep green colour. The quantities of lead and copper present are often seen in the production of opaque red glass made under reducing conditions; however, if lead/copper coloured glass is heated in air, it will produce a green colour. There is also a significant quantity of iron present which could also have contributed to the final colour. It is impossible to say whether this rod was originally derived from a remelted red tessera, but that is a possibility considering the proportions of the additional lead, copper and antimony.

Craw Stane		Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_2	Cl	K_2O	CaO	TiO_2	MnO	FeO	CoO	CuO	SnO_2	Sb_2O_5	PbO
1884	white rod	17.05	0.55	2.49	70.34	0.1	0.24	0.97	0.97	6.53	0.1	0.35	0.32	0.05	0.22	0	0.77	0.17
161337	green piece	18.21	0.58	2.52	68.81	0.08	0.26	1.01	0.56	6.21	0.13	0.4	0.43	0.05	0.23	0	0.39	0.89
161507	green rod	13.86	0.56	2.62	58.92	0.07	0.06	0.73	0.73	5.46	1	0.32	1.06	0	3.9	0.24	0.31	11.3

Table A1.2
Summary of Craw Stane Complex glass composition