Ancient Monuments Lab Report No 4184

Examination and analysis of some glass beads from Dunadd, Argyll

Justine Bayley

March 1984

Fifteen whole or fragmentary beads were submitted for examination. They were examined at up to 45x magnification and were also analysed by energy dispersive x-ray fluorescence (XRF). The analytical results are not fully quantitative but in order to allow comparisons to be made between beads of differing size, shape and surface texture the peak heights recorded for individual elements were normalised by dividing them by the corresponding silicon peak height. Silicon is the best standardizing element to choose as it is present as a major component in all glass and, to a first approximation, the proportion of silicon in any glass is roughly constent. The normalised peak heights are given in the table below.

Descriptions of individual beads (Numbers used are SF Nos)

1. Translucent blue glass with bubbles. Bead probably wound.

6. Translucent blue glass. The bead was not originally part of a segmented bead; the ends are original though now chipped in places.

9. Turquoise and white reticella bead. Bichrome glass rods were prepared by laying three parallel trails of opaque white glass along a thicker rod of transparent turquoise glass, marvering them and twisting (and stretching?) the resulting rod (see fig 1). Two of these rods, one with an S-twist and the other with a Z-twist were then fused side by side, a length of this double rod was removed and bent round into a ring which was further marvered to give the bead its final shape.

13. Translucent blue glass with some bubbles. Near the surface are greenish looking streaks due to the inclusion of a small amount of opaque yellow glass (a few distinct yellow particles can be seen).

29. Turquoise, white and yellow glass bead. A plain transparent turquoise bead had a single S-twisted turquoise and white rod (like those used to make SF9)

marvered into its surface. A blob of opaque yellow glass was then applied but not marvered. It appears to be a deliberate addition as it has partly sunk into the underlying turquoise glass (see Fig 2).

54. Transparent turquoise glass with some bubbles. This is part of a segmented bead at least three segments long.

65. Translucent blue glass with some bubbles. No decoration is visible on this fragment.

80. Translucent turquoise glass with some bubbles. Wound bead.

128. Transparent colourless glass and translucent blue glass imperfectly mixed together.

129. Wound bead of dull opaque red glass with streaks which look dark but are actually of clear colourless glass.

371. Opaque yellowish green glass with applied wave of opaque yellow glass which is badly weathered and mostly lost.

402. Translucent blue glass; very bubbly.

500. Translucent blue glass with some bubbles with a marvered trail of opaque yellowish white.

524. Translucent blue glass with some bubbles.

1032. Blue and white reticella bead. A double rod of Z and S-twisted rods of the same pattern as in SF9 was made of translucent blue and opaque white glass. This composite rod was then spiralled round a plain blue glass bead about five times and the whole marvered, giving an all over herringbone effect.

Discussion of the analytical results

The blue glass in both the monochrome beads (SF 1, 6, 65, 128, 402, 524) and in the polychrome ones (SF 13, 500, 1032) ones its colour to the presence of cobalt (Co). This is a very powerful colourant for glass so only very small quantities are needed to produce an intense colour. It is difficult to detect at these low levels as its XRF peak overlaps with the minor iron peak (which is universally present) which explains the uncertainties recorded in the table of results. An extreme example is SF13 where cobalt was not detectable though probably present together with far more iron (Fe) than in the other blue beads. Though copper (Cu) was detected in all the blue beads it was present at far lower levels than in the turquoise glass (where it is the main colourant) and probably does not contribute to the blue colour seen. The blue glasses all contain traces of antimony (Sb) or tin (Sn) which are somewhat unexpected. At these low levels they have no opacifying effect and any decolourising effect of the antimony would be nullified by the blue of the cobalt.

One further element detected in two of the blue beads (SF 146) is nickel (Ni). It is not normally found in ancient glass so its presence here in considerable quantities requires some comment. Cobalt and nickel minerals tend to be found together in nature so it is not surprising that the beads containing nickel also contain cobalt; one of them (SF 6) also contains far more cobalt than any of the other beads, a much higher level than is usually found in ancient blue glass.

The presence of nickel could be interpreted either as the use of a cobalt source rich in nickel or as the accidental selection of the wrong mineral from a mixed ore body. Only further analyses of similar beads will show whether nickel is a normal component of Scottish or Irish beads * (see below, p.4); it is not found in Roman or Anglo-Saxon blue beads in England. Julian Henderson (pers. comm.) has found nickel in only three beads, all of early iron age date. Two blue ones come from Vače in Carniola (N Yugoslavia) or one 'black' one from Hallstatt in Austria (which contained no cobalt.

As noted above, the turquoise glass is coloured by copper in its cupric form. The only other colour to contain more than a trace of copper is the opaque red glass where the copper is in the reduced, cuprous form. This bead also contains large amounts of iron which contribute to the dull red colour; it is in fact the only bead (with the exception of SF 13) where the iron: manganese (Mn) ratio varies significantly from 3:1. This could be taken as indicating the use of a common, manganese decolourised base glass with specific additional colourants for most of the beads. This suggestion of a single source of base glass is supported by the titanium (Ti) figures which are uniformly low. This suggests all the glass was made from sand (silica) which contained only traces of titania. SF 13 appears to be made from a completely different, antimony-decolourised high iron glass, though the opaque yellow streaks in it appear to be lead-tin yellow. As tin and antimony are thought of as being used in two different glass-making traditions this poses problems, unless antimony-decolourised scrap glass was being re-used by a glassworker of the alternative school.

In general opacity seems to be due to the presence of tin compounds, though in some cases traces of antimony make unambiguous interpretation of the results impossible.

The colour of the white glass (in SF 9, 29B and 1032) is probably due to the presence of tin oxide; as usual, these glasses contain virtually no lead. On the other hand the yellow glasses (SF 29A and 371) are coloured by lead-tin oxide and the glass contains a considerable amount of lead. This is true of both the yellowish green and the true yellow glass in SF 371; the former colour is really a greenish base glass with yellow opacity added. The green tinge is probably due to the iron with perhaps some contribution from the copper, which gives a green colour in high lead glass in contrast to the turquoise colour it produces in low lead or lead-free glass. The final opaque colour is the yellowish-white trail on SF 500. Both visually and analytically this is an intermediate colour with both white and yellow particles visible in the glass. It may be an example of an overheated yellow as lead-tin oxide is unstable above 900°C, breaking down gradually to give (white) tin oxide.

The other element appearing in the Table is zinc (Zn). This almost certainly got into the glass together with the copper as a copper alloy rather than the pure metal was used as colourant.

⊛ Warner + Meighan did not ~~detect~~ appreciable amounts of nickel in any of the beads they analysed. (Dating Irish Glass Beads by Chemical Analysis in Irish Antiquity: Essays + Studies presented to Prof. M.J. O'Kelly (1981) ed D. Ó Corráin)

Table: Analytical results.

XRF peak heights normalised to silicon.

S.F. No.	Ti	Mn	Fe	Co	Ni	Cu	Zn	Pb	Sn	Sb	Colour
1	?	.22	.65	+	.22	.45	.11	.34	-	.07	Blue
6	.06	.27	.76	.3	.14	.32	?	.39	-	.13	Blue
9	?	.10	.22	-	-	.14	-	.12	.06	.05	Turquoise & White
13	?	.28	3.97	-	-	.26	-	3.10	.09	.26	Blue (+ Yellow)
29 A	-	.39	1.26	-	-	.86	-	15.03	.21	-	Mainly Yellow
B	.06	.22	.68	-	-	.46	-	.29	.03	.05	Mainly Turquoise & White
54	-	?	.38	-	-	1.86	.58	.81	-	-	Turquoise
65	-	.22	.70	?	-	.17	-	.15	-	-	Blue
80	-	.12	.30	-	-	1.31	.48	.72	-	-	Turquoise
128	.11	.30	.86	+	-	.18	-	.53	.07	-	Blue
129	?	.39	2.55	-	-	.94	.17	.47	.09	.07	Dull Red
371 A	.12	.45	1.41	-	-	.16	?	9.85	.19	-	Mainly Green
B	.09	.49	1.50	-	-	-	-	11.50	.22	-	Green & Yellow
402	?	.20	.59	+	-	.23	-	.31	.05?	.10	Blue
500	?	.18	.52	+	-	.38	-	1.22	.19	.08	Blue & Yellowish White
524	-	.32	.68	+	-	.35	-	.35	-	.09	Blue
1032	?	.15	.40	?	-	.12	-	.14	.10	-	Blue & White

NOTES:- + = Element detected.

? = Uncertain signal.

A & B refer to different areas on polychrome beads.

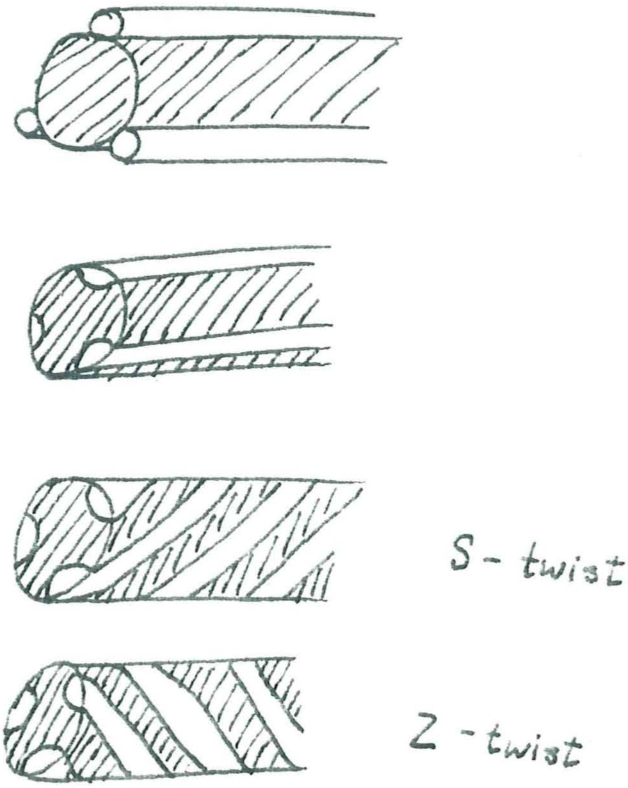

Fig. 1

Fig. 2