DEVELOPMENTS IN THE SECOND AND EARLIER FIRST MILLENNIA BC

THE RAW MATERIALS OF EARLY GLASSES: THE IMPLICATIONS OF NEW LA-ICPMS ANALYSES

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INTRODUCTION

The first man-made glass was produced in Mesopotamia and Egypt around 1500 BC (Nicholson 1993; Lillyquist and Brill 1993). It is probable that while the earliest production was in Mesopotamia, Egypt was producing glass within 100 years of its invention (Shortland 2000). Glass in this period was a prestige product and extensively 'traded' in a system of competitive gift-giving between neighbouring rulers and between the rulers and their satellite states. Since glass plays an important role in this exchange, the ability to trace individual glass objects back to the place where the glass of which they are made was first produced would add significantly to our knowledge of the economies and political systems of the period.

Unfortunately, provenancing this glass to its production site has proved to be more difficult than might have been expected at first sight since even under quite precise analysis, they all appear very similar. Glass of this period contains three main raw components: silica in the form of quartzite pebbles, a soda-rich plant ash and almost always a colorant (Turner 1956a; 1956b; Henderson 1985). To these deliberately added components there is the potential for accidental contaminants while manufacturing the glass, for example clay from the partial melting of crucibles, copper and bronze from tools and stirrers, and old glass from the reuse of these tools or vessels. No success has yet been achieved with the provenancing of the silica component of the glass. What little progress that has so far been made has been by looking at the colorants. For example, it is probable that most of the cobalt blue glass comes from Egypt since it contains a colorant sourced to Egypt (Kaczmarczyk 1986; Shortland and Tite 2000) (however, see Reade et al. this volume, for another opinion on cobalt colorants). Some success has also been achieved with the source of antimonate opacifiers for white and yellow (Shortland 2002) and with lead isotopes on lead antimonate glasses (Lilquist and Brill 1993; Shortland et al. 2000). Other evidence has so far proved elusive.

This paper examines the third major component of the raw materials of the glass – the plant ash – in an attempt to distinguish glass manufactured in Egypt and that found in Mesopotamia. It then discusses briefly the use of copper colorant for the production of blue glasses.

SAMPLES AND METHODOLOGY

A collection of some 300 samples of early glass, mostly from Egypt and Mesopotamia has been assembled at Oxford. This paper concentrates on a subset of these samples from the sites of Malkata and Amarna in Egypt, both thought to be glassmaking sites in the 14th century BC (Nicholson 1995a; Nicholson and Jackson 1998; Nolte 1968; Keller 1983). These glasses are compared to glass from the site of Tell Brak in Syria, which is also likely to have been a glassmaking site (Oates et al. 1998; Henderson 1998).

The glasses from these three sites were analysed by SEM-WDS and LA-ICPMS following methodologies outlined in the appendix and elsewhere (Henderson 1988; Shortland 2002). The two techniques gave the possibility of analysing 23 elements by SEM-WDS, mostly major and minor elements and 57 by LA-ICPMS, mostly minor and trace elements. Since some of the elements were analysed by both techniques, a total of 64 different elements could be worked with (fig. 1).

RESULTS

In a colourless glass, of the 64 elements that can be analysed, 34 elements are commonly found to be above the lowest limits of detection using these techniques (fig. 1). A colourless glass should have only two raw materials: quartzite pebbles and a plant ash. Analysis of the quartzite pebbles has shown that they are a very pure form of silica contributing no significant amount of any other element to the glass (unpublished analysis by the author; Brill 1999a; Brill 1999b). Given that the quartzite pebbles therefore bring only one element (silicon) to the glass, then the remaining 33 elements must come from the plant ash or...
one of the possible sources of chance contamination. This is obvious for many of the major elements, for example Na, K, Mg, Ca, etc. and it has been realized for some time that ratios of these elements might give some indication as to the type of plant ash that might have been used (Lilyquist and Brill 1993; Turner 1956a; Turner 1956b; Weyl 1951), however the interpretation of the other minor and trace elements has not been attempted. In addition to the fact that these 33 elements seem to be present in the plant ash, further conclusions can be derived from the fact that some of the elements correlate with each other. Figure 2 shows a graph of Al against Fe for all colours of Egyptian glass except cobalt blue. As can be seen, there is a strong correlation between these two elements. This is true for a total of 10 different elements: Al, Ti, V, Fe, Y, Zr, Nb, La, Ce, Pr and Nd – all are correlated to a greater or lesser extent. Furthermore, it is important to note that these elements are often those that might be associated with a clay. To test whether these correlations might be derived from clay being incorporated in the glass a graph of AlO₃ against (FeO+TiO₂) was plotted for the Cu blue glasses from Egypt (Fig. 3). These components correlated well, and when the trendline of the correlation was extended it passed through the values of Nile silt, the local clay. This suggests that the presence of these elements in the glass might be related to the influence, in some form or other, of Nile silt. However, it should be noted that not all the elements correlate so well, suggesting that, if Nile silt is involved, at least some of the elements must be fractionating relative to each other.

**Interpretation**

*Plant ash and clay*

If Nile silt is involved, the question then arises as to how it is being incorporated into the glass. The first possibility is that it is derived from accidental contamination from the crucible. Excavations at the glass workshops at Amarna have shown that the vessels associated with glassmaking and glassworking on this site are made from Nile silt (Nicholson 1995b; Petrie 1894; Shortland and Tite 2000). It is possible that partial melting of the crucible in glassmaking leads to a Nile silt signature contaminating the glass. However, the amount of contamination required to produce this pattern would lead to a significant reduction and weakening of the crucible, probably too much to be a likely solution. The second possibility is that the clay was deliberately added, for some unknown purpose. This is possible, but again unlikely. The third and most likely solution is that the clay is somehow incorporated into the batch with the plant ash. This might be because the plant has been growing on the clay and taken up its chemical signature, or it might be that when the plant was burnt, the collecting of the ash incorporated some of the underlying clay into the ash; possibly both are a factor.

If these correlations represent clay contamination of the glass, then whatever way the clay has become incorporated, it would most probably be derived from the area around which the glass was made. Therefore if glasses are made in different areas then it is possible that different clays, with different chemical signatures, might be involved. If these different clay signatures were distinguishable, then there might be the potential to provenance the glasses. To test this, more plots of the Egyptian glasses were drawn and compared to Mesopotamian glasses from Tell Brak. In many cases the two trendlines were indistinguishable, since the clays of the two areas often have quite similar ratios. However, for some elements there is a significant difference in the element ratios. The best example of this is shown in Figure 4, where Ti is plotted against Fe for copper – and cobalt-coloured glass from Egypt and copper-coloured glasses from Tell Brak. As can be seen, all the Egyptian glasses lie on a tight line, trending towards the Nile silt values (Nile silt trendlines are shown, the actual points lying well off the field of the graph). This seems to indicate that the Egyptian copper and cobalt glasses have similar signatures and possibly similar clays. However, the Mesopotamian glasses (plus two of the Egyptian glasses) are distinctly different falling well below the trend of the others. The trendline for Tell Beydar clay (a source local to Tell Brak) is shown on the graph, and this also falls below the Egyptian values, however the fit of the Tell Brak values to the trendline is not very good. As always, further data are required to confirm the reality of this suggested pattern, but it seems that there is the potential to distinguish differences in the minor and trace element compositions of Egyptian and Mesopotamian glasses, differences that may be linked to the presence of local clay contamination in the glass.

**Colorants:** copper blue

Colorants in the glasses also show correlations between different elements. This has been demonstrated for yellow glasses, for example, where it has been observed that not only are the yellow glasses higher in the two elements, Pb and Sb, that make up the antimonate opacifier in the glass, but also in accidentally incorporated additional elements including Zn, As, Ag, Cd, Ba and perhaps Cr, Mo and Bi. Some of these elements are associated with the antimony component of the opacifier and have helped to trace the source of the antimony in these glasses to the Caucasus.
FIG. 2 Plot LA-ICPMS analyses of Al (%) against Fe (ppm) for Egyptian glasses of all colours except Co blue.

FIG. 3 Plot SEM-WDS analyses of Al₂O₃ (%) against (FeO+TiO₂) (%) for Egyptian copper glasses (squares) with the trendline of this plot. Analysis of Nile silt (diamonds) for comparison.

FIG. 4 Plot LA-ICPMS analyses of Ti (ppm) against Fe (ppm) for Egyptian glasses compared to Tell Brak glasses. The trendlines are for the Nile silt and Tell Beydar clays which lie off the plot area.
(Shortland 2002). In the same way, it is possible to look for elements that may be incorporated in the glass when copper is added as a colorant. The most important of these in Egyptian glasses is tin which, when present, is usually in a ratio of about 1:10 with the copper, indicating that the colorant used was bronze or bronze scrap (Kaczmarczyk and Hedges 1983; Shortland 2000; Turner 1956b). The new analyses of Egyptian copper blue glasses have suggested that in some cases traces of As and Pb might also be included in the bronze, but this is still to be confirmed by further analyses. Of the 26 copper blue glasses from Egypt analysed in this study, 19 contained significant tin, indicative of a bronze colorant being used. Forty or so analyses of copper blue glasses from Mesopotamia were available, either from this study or previously published data (Brill 1999a; Brill 1999b; Henderson 1998; Oates et al. 1998). Although a small number of these glasses were analysed by SEM-EDS and therefore had high detection limits for tin, none of them contained detectable amounts of the element. This seems to suggest that in Mesopotamia a copper or copper compound was used as the colorant in contrast to Egypt where this was used less than 25% of the time, the majority being colour by bronze or bronze scrap. Some difference in the procedures for using colorants are therefore evident between the two areas.

CONCLUSIONS

To conclude, this study of 14th-century BC glasses from Egypt and Mesopotamia has concentrated on looking at elements that might have thought to be associated with the plant ash component of the glass. It seems that of the 34 elements that are detectable in the glasses, ten of them appear to be correlated with each other to a greater or lesser extent. Some of the ratios of these correlated elements appear to be related to the ratios of the same elements in clays that were used in the crucibles and occur locally to the sites where these glasses are thought to be made. The most likely explanation for the occurrence of this clay signature in the glass is that the clay was somehow incorporated into the glass batch with the plant ash, either because the plant had taken on the chemical characteristics of the ground in which it grew, or because it was burnt on a clay surface and some of that clay was incorporated into the plant ash when it was collected up. Either way, there seems to be detectable differences in some of these elements between Egyptian and Mesopotamian glasses, suggesting that, with further analysis, there is a potential to provenance. Similarly, the colorant used in copper-coloured glasses appears to be different between the two areas. In Mesopotamia, no tin has yet been identified in the glasses suggesting a copper colorant was used. However, in Egypt over 75% of the copper blue glasses analysed were found to contain tin, suggesting that in Egypt the norm was to use a colorant based on bronze or bronze scrap. Further work on the analysis of these ancient glasses and particularly on the composition and production of plant ashes is necessary for further progress to be made.

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APPENDIX

Microprobe analyses were conducted on polished sections through the samples which were examined in the Cambridge Microscan 9 microprobe in the Department of Earth Sciences, Oxford. The chemical compositions of the glasses were determined using the attached wavelength dispersive spectrometer following the methodology laid down by Norman Charney and Julian Henderson (Henderson 1988). Regular runs on a Corning glass standard were used to check for machine drift. LA-ICPMS analysis was conducted at the NERC facility at the University of Kingston, Surrey. The widest range of elements, routinely measured at the facility was included, amounting to some 57 elements in all. Each time a new block was put into the sample chamber, two gas blanks (each of five runs) and two analyses each of standards NIST610 and NIST612 (each of three runs) were completed with a rastering laser. Each analysis of an unknown was the mean of three runs. Results were calibrated by using 46Ca as an internal standard and standardising it against the CaO values obtained by WDS microprobe. An ablation volume correction factor was therefore obtained and applied to the other elements. LLD values (lowest level of detection) were obtained using the gas blank and NIST610 results.

REFERENCES

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