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Glassmaking at Geoy Tepe (Azerbaijan) during the early 2nd millennium BC: a study of blue colourants using PIXE spectrometry

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28.1. Introduction

The site of Geoy Tepe lies in a large flat plain surrounding the modern town of Rezaiyyeh, on the western edge of Lake Urmia in north-western Iran (Fig. 28.1). Ancient settlement seems to have extended over an area of about 0.030 km^2, but the intrusion of modern houses and cemeteries onto its mound limited excavation to just eight widely-scattered trenches (Burton-Brown 1951, pp. 110–120). The final stratigraphy, subdivided into phases M through A, yielded material which, on the basis of a subsequent comparison with the pivotal pottery sequence of Hasanlu (Dyson 1992), has been established as ranging in date from the late 4th to the late 2nd millennium BC.

Our archaeometric interest in Geoy Tepe was stimulated by an observation in the site's excavation report that three glass spacer beads were "coloured blue by a colouring matter which was shown by spectrophotometric evidence to be primarily cobalt." (Burton-Brown 1951: 127, #1604). We had applied the technique of proton-induced x-ray emission (PIXE) spectrometry to compositional analysis of glass on several occasions over the past decade (Fleming & Swann 1987; Fleming & Swann 1988; Swann & Fleming 1990), and knew that our detection limit for CoO could be in the range of 50 to 200 ppm, unless the glass was particularly iron-rich. A recent MASCA study of glass and frit beads from the artefact-rich Tomb B10a.B27 (circa 1800–1600 BC, see Rubinson 1991) at the site of Dinkha Tepe, provided no instance where cobalt was involved in blue colouration. Instead, Dinkha Tepe blue glass was copper-rich (with CuO contents ranging 2.9% to 9.2%), while darker frits contained similar amounts of copper and manganese (McGovern *et al.* 1991). Since Dinkha Tepe is only about 100 km south of Geoy Tepe, this difference in approach to glassmaking seemed surprising, and in need of confirmation.

Tracking down of the whereabouts of material from the Geoy Tepe excavations was not a trivial matter, since it was known to have been divided between at least three museums in England — the Ashmolean in Oxford, the Fitzwilliam in Cambridge, and the Manchester Museum — none of which had any record of glass among their donations. In the Spring of 1992, however, we discovered that the Geoy Tepe glass and frit beads (and many carved from carnelian and soapstone) were in The University Museum at Philadelphia itself, stored in the match boxes and small containers in which they had been presented by Burton-Brown in 1973, but thereafter left uncatalogued. Specifically, we found several packages of unstrung beads which originally were the components of a sizeable necklace for one of the six individuals found in Grave C. This grave contained a pottery bowl of red polished ware which, via stylistic parallels with pottery found at Haftavan, at the northern end of Lake Urmia, dates *c.* 1600–1450 BC. (Haftavan Late VIB: see Edwards 1983, pp. 141–154). Though several groups of beads were recovered from other graves and tombs at Geoy Tepe, the technical discussion here focuses on just those from Grave C.

28.2. Previous studies

Fig. 28.2 shows one cluster of the beads from Grave C, re-strung so as to draw together several of the intact beads that were analysed prior to *The 6th International Conference on PIXE and its Analytical Applications*, held at Waseda University (Japan) in July 1992. The initial findings from that research (Swann *et al.* 1993), can be summarised as follows:

1. that Geoy Tepe blue glass did indeed owe much of its colouration to the presence of cobalt (CoO range, 0.021% to 1.4%) which will have enhanced the effects of a quite modest copper content (CuO range, 0.22% to 3.2%);
2. that lead antimonate was used as a yellow glass colourant at this early date, ahead of its much greater popularity in Egypt during the mid-14th century BC. (Lucas & Harris 1962, 340–344).

To these observations, we can now add that at least one of the beads from Grave C was made from a red glass coloured by copper, and opacified by the presence of antimony (see appendix). The glass colouration "palette" for Geoy Tepe can now be said to have strong similarities to that of Nuzi, several hundred kilometres to the south (Vandiver 1983), though evidence for any technological contacts between these ancient settlements has yet to be established.

That initial research did raise some practical concerns, however, in that almost all the compositional data was obtained through the analysis of just a surface region of each bead. At that time, contamination from the burial medium was not felt to be a significant problem: analysis was always carried out in a region where the bead's colour was apparent, once the pearlescent rind of devitrification which had formed on most of the beads during burial had peeled away. What had not been determined was whether the elements responsible for colouration — together with minor elements that might help to source the mineralogical origins of those colourants — had been at least partially lost during devitrification, despite the good colour retention.

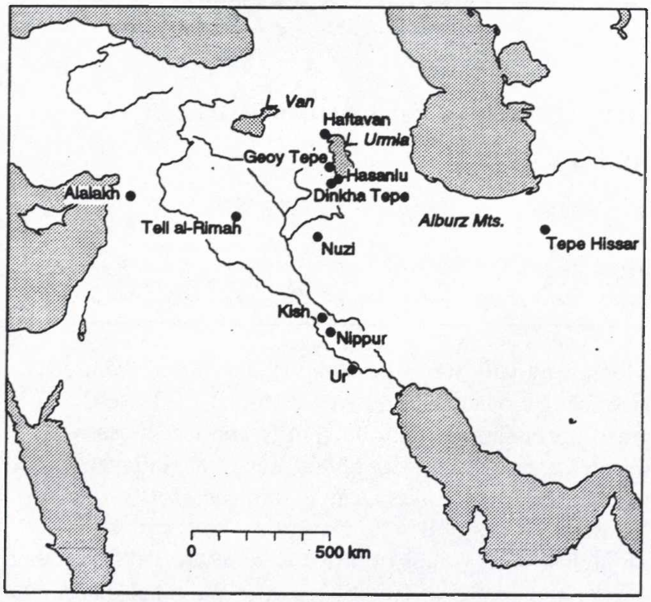


Fig. 28.1: Ancient Mesopotamia: some sites which have yielded glass and faience artifacts. Graphic: B. Scaife and P. Zimmerman, MASCA.

For such studies, proton-induced x-ray emission (PIXE) spectrometry had major advantages over other analytical techniques:

1. a high spatial resolution, down to a 50 µm x 50 µm area, if need be (Fleming and Swann 1988): most of the beads are only about a millimetre across in their annular section;
2. a good detection sensitivity for those elements which are usually introduced by glass colouration (i.e., manganese to antimony [Z, 25 through 51], and for lead [Z, 82]), since the dilution of their concentration by the primary ingredients of glassmaking—sand, soda, and lime—will often reduce the presence of everything else to the 0.5% to 100 ppm range.

PIXE detection limits for glass analysis are reviewed in Table 28.1. The original study was therefore extended to cover some 81 beads in all, including 26 blue ones discussed in detail below.

28.3. Devitrification and trace element patterning

A survey of the whole corpus of beads from Grave C yielded seven fragmented beads which were decidedly blue in their innermost matrix, while retaining that colour to a varying degree on their outer surface. The compositional data for the matrix regions of those beads are given in Table 28.2. Two of those beads — #560,y and #560,w — each retained a hard, iridescent coating of devitrification products over their entire surfaces. The remaining five beads had well exposed surface regions, so it was possible to compare matrix and surface analyses in some detail. The impact of devitrification on many of the primary and minor constituents of these beads is summarised in the bar charts of Figs. 28.3a–3b.

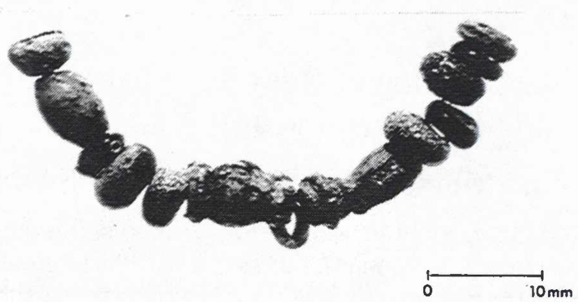


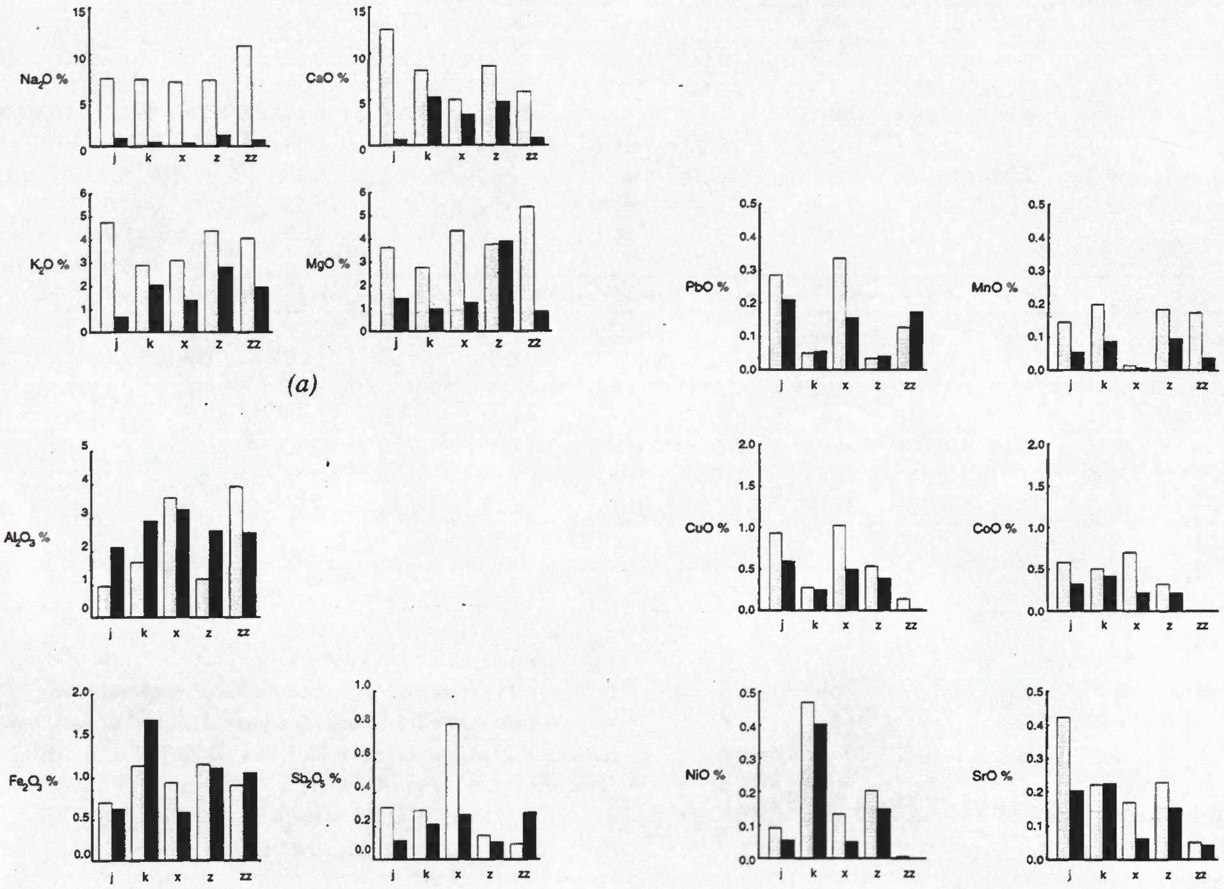
Fig. 28.2: A cluster of variously coloured glass and frit beads from Grave C at Geoy Tepe (now arbitrarily strung). The Museum inventory number (prefixed #73-7-) and the colour of each bead are as follows (left to right): 560, i, h, g, f, and e (all blue), 566 (blue), 560, d (blue), 564 (white), 560, c, b and a (blue), 567 (yellow), 558 (red). Composition of the red bead at end of article.

The near-complete loss of sodium from the surface regions of each bead, together with a partial depletion of potassium, calcium and magnesium (Fig. 28.3a), is in keeping with previous observations on the devitrification of glass, ancient and modern (e.g., Sanderson *et al.* 1984; *Harvey et al.* 1986). The erratic changes observed in aluminium and iron contents (Fig. 28.3b) are perhaps explicable as indicating a certain amount of uptake of these elements from the surrounding burial medium. In support of that idea are some PIXE data of the iridescent surface of two beads for which we have comparable matrix analyses:

Oxide	White frit (ppm)	Blue glass (ppm)
3.8 mg/cm² Al foil		
TiO_2	≤25	≤135
Cr_2O_3	≤17	≤47
MnO	≤15	≤160
5.7 mg/cm² Al foil		
CoO	≤28	≤115
NiO	≤15	≤50
ZnO	≤10	≤40
As_2O_3	≤17	≤20
Ag_2O	≤130	≤250
SnO_2	≤250	≤430
Sb_2O_5	≤470	≤800

Table 28.1: PIXE detection limits as determined for various trace elements in the analysis of a white frit ($SiO_2 \geq 90\%$), and a blue glass coloured by a modest level of copper (CuO, c. 1%). The sand ingredient of glass invariably contains some iron-bearing impurities (Fe_2O_3, c. 1.1% for Geoy Tepe glass). The MnO detection limit is therefore quite dependent upon the iron content in the blue glass, increasing by about 140ppm for each additional 1% Fe_2O_3.

The selective filter array used in the PIXE detection system is italicised. The way in which such filtering improves the detectability of many trace elements in glass is described in Swann and Flemming (1990).



(a)

(b)

(c)

Fig. 28.3: Summary of the effect of surface devitrification on the major, minor and trace elemental contents in five blue glass beads fro Geoy Tepe. All these beads (inv. #73–7–560j, k, x, z, and zz) are fragmented, so the original composition of the glass could be determined from a PIXE analysis of each matrix. See Table 28.2 for full listings. (Graphic: P. Zimmerman, MASCA).

#73–7–560,w	Al_2O_3, 16.8%	Fe_2O_3, 3.37%
#73–7–560,y	Al_2O_3, 13.7%	Fe_2O_3, 5.20%.

These same analyses indicated that, by some mechanism or other, an antimony enrichment of a glass surface also is a possible consequence of devitrification. The superficial Sb_2O_5 levels of 1.23% (#560,w) and 1.20% (#560,y) are significantly above those in the matrices of these beads (0.26% and 0.86%, respectively).

Other minor and trace elements exhibit quite similar patterns of surface depletion (Fig. 28.3c). Losses of about 30% (surface *v.* matrix) seem typical here. Some instances of a small surface enrichment of these elements (e.g. ZnO for #560,x; PbO for #560,k) are illusory, being no more than an indication that they are retained somewhat better than the primary ingredients, particularly sodium. At a secondary level, we can also assume some compositional variability within the matrix of each glass, limiting the reproducibility of all data here to about ±10%.

The interpretation of compositional data obtained by PIXE analysis of the *surface* of the blue glass beads from Geoy Tepe therefore must be treated as providing only semi-quantitative information. For all the bead surfaces that we have studied now, the levels of minor and trace elements, including those more strongly influencing colouration (e.g. CoO, CuO, and MnO: see Fig. 28.4), must represent lower limits of their contents within the matrix of each bead. They may be used to explain the darkness and/or richness of colouration (Sanderson & Hutchings 1987): to say more than that would probably be imprudent.

28.4. Colouration and ore sourcing

If we assume that a high retention of sodium content is indicative of data reliability among the matrix compositions of Geoy Tepe beads listed in Table 28.2, then we can ask whether any of the trace elements might serve as a "fingerprint" for the cobalt ore used. There are many mineralogical forms of cobalt ores, but they can be broadly subdivided into those which are an admixture of cobalt and manganese oxides, and those which are virtually manganese-free (Hurlbut 1971, p. 473). There are mineralised zones of cobaltite — (Co,Fe)AsS — that are intrusive to igneous rocks in the Dashkessan region of Azerbaijan, to the east of Lake Urmia. They might be expected to contain elevated levels of lead, zinc, and nickel. And there are other cobaltite sources further south, near the Iranian city of Kashan (Moorey 1987 196). They may have attracted some attention in antiquity, because they

Ref.	SiO_2	Na_2O	K_2O	MgO	Al_2O_3	CaO	Fe_2O_3	TiO_2	SrO
560,j	64.5	7.44	4.78	3.65	0.96	12.7	0.71	0.025	0.43
560,k	70.1	7.29	2.92	2.79	1.68	8.23	1.16	0.060	0.23
560,x	70.1	7.02	3.14	4.38	3.61	5.04	0.95	0.065	0.17
560,y	65.9	4.34	6.20	4.00	0.71	11.3	1.34	0.023	0.38
560,z	69.3	7.25	4.41	3.79	1.19	8.69	1.17	0.015	0.23
560,zz	66.4	11.0	4.08	5.40	3.94	5.93	0.92	0.050	0.055
560,aa	66.8	7.50	5.41	4.90	2.25	8.19	1.30	0.091	0.16

	CuO	CoO	PbO	MnO	ZnO	NiO	Sb_2O_5	SO_3	Cl_2O
560,j	0.94	0.600	0.290	0.150	0.023	0.094	0.32	0.55	0.98
560,k	0.29	0.510	0.053	0.200	0.900	0.470	0.30	0.85	1.02
560,x	1.04	0.710	0.340	0.017	0.011	0.140	0.81	0.45	0.47
560,y	1.04	0.330	0.540	0.031	0.017	0.089	0.86	1.08	0.90
560,z	0.54	0.330	0.036	0.190	0.350	0.210	0.15	0.39	0.72
560,zz	0.15	0.017	0.130	0.170	0.036	0.010	0.10	0.38	0.66
560,aa	0.65	0.360	0.180	0.036	0.009	0.042	0.45	0.45	0.56

Table 28.2: Compositional data for Geoy Tepe blue glass beads: matrix analyses. Constituents (%, by weight). Typical detection limits for several of these elements are listed in Table 28.1. Reference numbers are abbreviated from University Museum inventory numbers that would read in full as #73–7—.

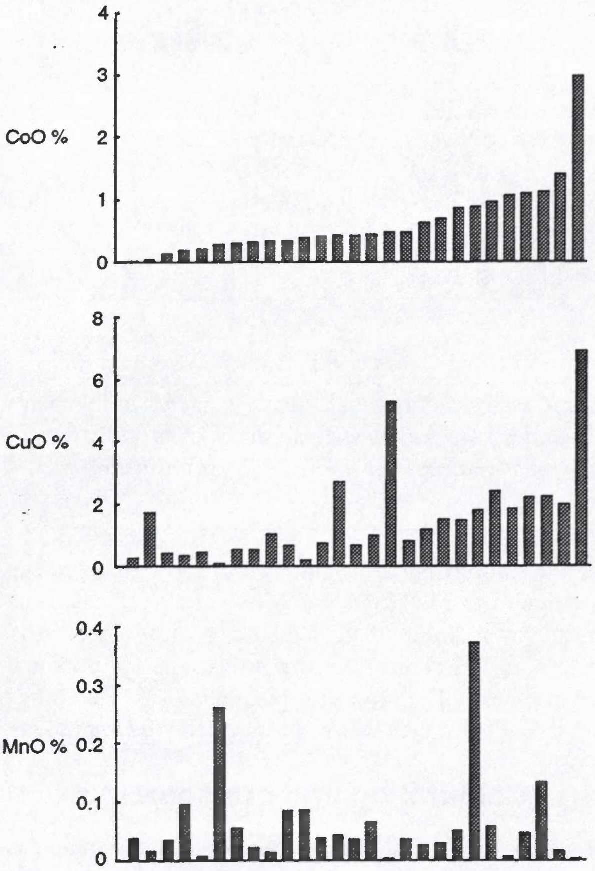


Figure 28.4: PIXE data for the surface analysis of blue beads from Geoy Tepe, for their cobalt, copper and manganese contents. These data are ordered according to ascending CoO content, which ranges 0.044% to 3.0%. (Graphic: L.-A. Bedal, MASCA.) The soda contents for each surface (as a rough measure of the extent of its devitrification) are listed here in the same order:

UM inv. #	Na_2O%	UM inv.#	Na_2O%
560,zz	≤0.76	560,f	2.91
560,y	≤0.51	559,e	≤0.52
560,g	1.52	560,c	≤0.80
560,z	1.31	560,a	1.00
560,x	≤0.48	560,p	≤0.47
560,b	1.42	560,o	≤0.58
560,j	≤0.99	560,n	1.99
560,i	1.01	560,m	≤0.59
566.	≤0.40	559,c	≤0.43
560,aa	≤0.91	560,h	≤0.67
560,k	≤0.56	556.	≤0.49
560,l	≤0.60	559,h	1.33
560,d	1.89	559,f	1.14
559,e	≤0.90		

contain attractive amethyst-pink crystals of erythrite — $Co_3(AsO_4).8H_2O$. They are said to be nickel-free (Garner 1956).

We might therefore have expected a high degree of correlation here between CoO and any of five other oxides determined in our PIXE analysis—MnO, Fe_2O_3, PbO, ZnO, and NiO[1] In practice, those correlations are simply not in evidence (Table 28.3, left-hand column). In fact, a similar correlation study for the CuO content of the glass suggests that the lead content originated from the copper-rich ingredient of the glass mix—most likely, malachite, or chrysocolla—but leaves it quite unclear in what form the manganese and zinc were introduced (also Table 28.3, left). A moderately close linkage between CoO and CuO may reflect some attempt at control of the recipe for darkening of blue colouration, rather than some commonality in their ore source. The cobalt ore used can certainly be said to have been of the manganese-free variety. Beyond that, it would appear that any trace element patterning which might have characterised that ore was thoroughly obscured once the various ingredients of the glass were melted together.

This situation is in marked contrast to what we have observed for cobalt- and copper-coloured blue glass from the famous Egyptian site of el-Amarna. Four sets of compositional data of such glass are given in Table 28.4, and correlation coefficients are included in Table 28.3 (right-hand column). Though the limited number of analyses involved here may exaggerate their statistical significance to

	Geoy Tepe (n=7)[1]			el-Amarna (n=4)[2]		
	CoO	CuO	Fe_2O_3	CoO	CuO	Fe_2O_3
CoO	+1.00	+ 0.63	− 0.26	+1.00	+ 0.53	+ 0.80
CuO	+ 0.63	+1.00	− 0.03	+ 0.53	1.00	+ 0.17
Fe_2O_3	− 0.26	− 0.03	1.00	+ 0.80	+ 0.17	+1.00
PbO	+ 0.24	+ 0.82	+ 0.08	− 0.20	− 0.49	+ 0.43
MnO	− 0.30	− 0.74	− 0.31	+ 0.46	− 0.37	+ 0.85
ZnO	+ 0.13	− 0.53	+ 0.20	+ 0.99	+ 0.54	+ 0.79
Sb_2O_5	+ 0.48	+ 0.81	+ 0.30	− 0.21	+ 0.67	− 0.26
NiO	+ 0.38	− 0.29	+ 0.16	+ 0.99	+ 0.50	+ 0.81

Table 28.3: Correlation coefficients (R-values) which relate the cobalt, copper and iron contents of Geoy Tepe and el-Amarna blue glasses to other minor constituents.
[1] Geoy Tepe, derived from the data of Table 28.2.
[2] el-Amarna; recent technical studies for glass from this site are reported in Kaczmarczyk and Hedges (1983); Vandiver (1991); and McGovern et al. *(1993).*

Ref.	*SiO_2*	*Na_2O*	*K_2O*	*MgO*	*Al_2O_3*	*CaO*	*Fe_2O_3*	*TiO_2*	*SrO*
E 843a	54.0	14.3	0.56	4.20	2.71	10.8	1.01	0.124	0.47
E 843b	57.2	12.8	3.76	2.99	0.68	10.0	0.43	0.054	0.58
E 860a	62.9	11.0	1.08	2.26	1.61	8.3	0.92	0.071	0.37
E 860b	67.5	11.8	1.56	3.93	1.72	7.9	0.58	0.041	0.25
	CuO	*CoO*	*PbO*	*MnO*	*ZnO*	*NiO*	*Sb_2O_5*	*SO_3*	*Cl_2O*
E 843a	2.53	1.160	0.012	0.23	1.300	0.590	3.92	0.31	1.12
E 843b	1.91	0.032	0.043	0.26	0.048	0.016	6.95	0.63	1.57
E 860a	0.46	0.320	2.820	0.31	0.350	0.180	3.45	1.28	1.27
E 860b	0.22	0.310	0.036	0.18	0.370	0.180	0.72	0.57	1.76

Table 28.4: Compositional data for blue glass items from el-Amarna: matrix analyses. Typical detection limits for these elements are listed in Table 28.1. University Museum artefacts: E 843a, rod of glassmaking debris; E 843a, strip of glassmaking debris; E 860a, sidewall of small, multi-banded vessel; and E 860b, rimsherd of small, multi-banded vessel.

some extent, a linkage between CoO and both ZnO and NiO appears quite clear-cut. The cobalt ore also seems to have contributed some iron and some manganese to these blue glasses; but a separate iron source—perhaps just an oxide contaminant of the primary sand ingredient—seems to have provided most of the manganese in this instance (cf. the Geoy Tepe data). Kaczmarczyk concluded that evaporite minerals were the source of Egyptian cobalt.

28.5 Conclusions

Despite the two advantages of PIXE spectrometry that we have exploited here — good spatial resolution and a high sensitivity for trace element detection — we have been able to draw only limited conclusions about the chemistry of glassmaking at Geoy Tepe. Compositional analysis of devitrified surfaces have to be interpreted with great caution, even when good colour retention occurs. A surface enrichment of antimony during the weathering of the glass is surprising, but quite clear-cut. Fortunately, however, we detected no instance here, among the blue glass, of a heavy loss of a specific minor element involved in colouration that was not matched by an overall heavy depletion of elements, major minor, and trace.

Note

1. Perhaps As_2O_3, as a potential indicator of the use of cobaltite ore, should have been included in this list, but its volatility at the typical temperatures of glassmaking may well have made it fugitive. Thus, the fact that no As_2O_3 content was observed above its PIXE detection limit of about 0.014% need not mean that arsenic was not a primary component of the cobalt ore used.

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