Historical Technology, Materials and Conservation

SEM and Microanalysis

Edited by Nigel Meeks, Caroline Cartwright, Andrew Meek and Aude Mongiatti

Archetype Publications

in association with

The British Museum
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Iron Age glass beads from Carthage

Katherine Eremin, Patrick Degryse, Nathaniel Erb-Satullo, Monica Ganio, Joseph Greene, Andrew Shortland, Marc Walton and Lawrence Stager

ABSTRACT A large number of glass beads were found within urns containing the cremated remains of children and occasionally animals from the Carthage Tophet, dating to the eighth to fourth century BC. The glass beads were analysed to determine their composition and microstructure to identify the alkali source used and assist with determining the likely provenance of the beads. The main analytical technique used was scanning electron microscopy with energy dispersive microanalysis with additional techniques including X-ray diffraction and Raman spectroscopy to more closely characterise the individual phases and matrix glass. This paper concentrates on the most common bead types, which were characterised by high iron contents and high levels of crystalline phases, including magnetic, hematite, wollastonite, nepheline and barium sulphate. The glass was extremely vesicular and contained remnants quartz and (rarely) feldspar. Many samples showed extensive alteration, evident from both the microstructure and composition. These beads represent some of the earliest natron glass known from a firm context, although absolute dates are lacking. The most likely scenario for the manufacture of these beads is local production from imported glass, which was probably coloured locally with iron-rich metallurgical waste.

KEYWORDS Carthage, glass, analysis, Iron Age

Introduction

Excavations in the 'Precinct of Tanit', the so-called 'Tophet' of Carthage, Tunisia, by the American Schools of Oriental Research (ASOR) Punic Project between 1976 and 1979 under the direction of L E Stager yielded cremated remains of human infants, and in some cases young ovicaprids (sheep/goat) and birds, buried in cinerary urns often surmounted by carved stone markers, some of which bear Phoenician inscriptions [1-4]. The excavated materials and records are currently housed at the Semitic Museum, Harvard University. The excavation is now being prepared for publication and the first comprehensive scientific analysis of the finds is being undertaken in conjunction with this.

The Carthage Tophet is a complex burial site consisting of a large number of cremation urns. The nature of the burials remains hotly debated - some authors favour child sacrifice [3] whilst others reject this in favour of normal infant mortality [5]. Use of the Tophet is believed to have spanned the period from the very earliest days of Carthage in the eighth century BC through to 146 BC, when ancient Carthage was destroyed by the Romans.

This paper concentrates on the glass artefacts found in the urns, which include rare monochrome blue glass beads, small numbers of blue and white eye beads, some red beads with white and yellow spots and large numbers of black and brownish beads. These later assemblages can be divided into simple black ring beads, eye beads with a triangular black core and black and white eyes, and small beads with a mottled, brownish or dark brown-black color. Chronologically, the urns, and hence the glass beads enclosed in these, span several phases of use of the Tophet, although most glass beads date to the sixth to fourth century BC (Table 1). Since the alkali source used for glass production in the ancient Mediterranean changed from plant ash to natron during the first millennium BC [6], analysis was undertaken to determine whether these are plant ash or natron glass. It was not possible to sample the monochrome blue beads or the blue and white eye beads due to their rarity and completeness but samples were obtained from the black, mottled and dark beads, as these included large numbers of broken fragments and identical multiples.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Dating BC</th>
<th>No. of urns</th>
<th>Glass beads</th>
</tr>
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<td>1-3</td>
<td>8th to 7th</td>
<td>69</td>
<td>Monochrome blue (rare)</td>
</tr>
<tr>
<td>4-6</td>
<td>6th to 5th</td>
<td>238</td>
<td>Monochrome blue (rare), black ring, black eye bead, small mottled, small dark, blue and white eye beads (rare)</td>
</tr>
<tr>
<td>6+</td>
<td>4th</td>
<td>136</td>
<td>Blue and white eye beads (rare), red spotted, black ring, small mottled, small dark</td>
</tr>
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</table>
Table 2 SEM-EDX data for mounted beads: in order to identify each bead, the sample number consists of the mm number with a unique letter as in some cases several beads share a registration number. Typology of beads: S – small, BR – black, BEB – black core for eye bead, RS – red spotted, BLK – fragments, SRO – small rounded.

<table>
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<th>Al</th>
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<th>FeO</th>
<th>MnO</th>
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<td>RS</td>
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<td>0.3</td>
<td>0.8</td>
<td>67.4</td>
<td>0.3</td>
<td>1.0</td>
<td>0.2</td>
<td>5.8</td>
<td>0.1</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Methodology

Selected beads were sampled and mounted in resin for examination by scanning electron microscopy with energy dispersive microanalysis (SEM-EDX), X-ray diffraction (XRD) and Raman spectroscopy. The samples were polished with successively finer grades of abrasive papers (240, 320, 400 and 600 grade) and finished with polishing using 6 µm and 1 µm monocrystalline diamond suspension. The mounted, polished samples were carbon coated for SEM-EDX analysis. In all cases, the samples contained a full cross-section from the surface to interior of the beads selected. This ensured that analysis was undertaken on the least altered interior glass. The SEM analysis was undertaken with a JEOL JSM-640LV scanning electron microscope operated at 20 kV in high vacuum mode. Samples were imaged using a four quadrant backscattered electron detector (BSE) to examine altered and pristine glass and individual phases, and the phases and glass matrix were analysed using an Inca X-sight Oxford Instruments energy dispersive detector. Raman spectroscopy used a Bruker Senterra dispersive Raman microscope with an Olympus BX51M microscope and 785 nm, 633 nm and 532 nm lasers. The microscope has x20, x50 and x100 objectives, with laser spot sizes approximately 5, 2 and 1 µm respectively and the instrument is controlled via OPUS software version 5.5. XRD was performed with a Bruker D8 Multipurpose Diffractometer. Samples were collected over a 2θ range of 30° to 90° using Cu Kα radiation at 40 kV and 40 mA. The primary X-ray beam was collimated to approximately 0.5 mm with a monocular and the diffracted X-rays detected with a GADDS detector. Polished mounted samples were examined with a polarising microscope under incident light.
Results

SEM examination indicated a variety of microstructures in the beads, which can be divided into original features and those that can be attributed largely to alteration, as discussed below. The compositional information from SEM-EDX is summarised in Table 2. A number of beads share the same field number, hence in the table individual beads are denoted by the urn number and a sequential alphanumeric identifier with the field number given in the adjacent column. Beads with the same urn and field number were found together and are visually extremely similar; these are distinguished only by A, B, C etc.

Black glass: ring and eye beads

Visual examination shows that the black glass beads were formed by wrapping thin strands of glass around a core; these strands are clearly defined by trails of bubbles. The core is still present in many beads and has a yellow appearance. SEM-EDX analysis and imaging shows it is calcite-rich clay with many angular quartz particles and occasional feldspar. The black glass is characterised by varying amounts of crystalline phases, bubbles, and an inhomogeneous glass matrix. In all instances, the black colour results from high to extremely high levels of iron in the glass matrix, which itself is characterised by high soda and lime and low magnesia and potash (almost always less than 0.5 wt% oxide). Several samples have an extremely streaky appearance in the BSE images due to variations in the iron content of the matrix glass.

The main phases present are iron oxides (magnetite, hematite and probably wustite) and wollastonite. The iron oxides occur in a range of morphologies and sizes, from fine equant crystals to coarse dendritic segregations. Remarkably, the dendrites of wustite as seen in the glass are typical for the remains (slag) of iron metallurgy. Wollastonite occurs as small elongated crystals, often in clusters, and frequently nucleated around fine crystals of iron oxide. Again, wollastonite is a phase not uncommon in metal slag. The glass matrix contains some rounded quartz (100-200 μm in size) with rare feldspars (both finely pure sodium and plagioclase feldspar occurring). In some instances, the rounded quartz has an irregular outline due to dissolution into the glass matrix and is surrounded by shrinkage cracks. Many beads contain aggregates of iron oxides and wollastonite both within the glass matrix and as discrete inclusions surrounded by a separate glass phase, as seen in bead 5933C, shown in Figures 1 and 2. Analysis of the distinct glass in the inclusion in Figure 2 revealed higher levels of aluminia and iron and lower levels of silica than the main glass (see below).

The black glass beads analysed span the full chronological range, from Phase 4 to Phase 7 (i.e. the fifth to the sixth century BC) and include both black ring beads and the triangular black cores of black and white eye beads. However, ring beads dominate both the urn assemblage and the samples analysed. The composition of the unaltered black glasses was denoted glass type A and is remarkably consistent over this period, as shown in Table 2, with the exception of a heavily altered eye bead and the glass in the inclusion shown in Figure 2. The glass from the inclusion is very similar to that in some mottled beads, glass type B, discussed below. The altered glass in the eye bead is similar to altered glass, termed glass C, in some mottled beads and small dark beads as discussed below. The high level of alteration of the eye-bead glass is apparent in the microstructure seen in the SEM, varying from coherent, uniform altered surfaces depleted in soda extending 100 to 100 μm into the glass to thicker, irregular alteration zones comprised of multiple lamellae depleted in soda and potash and with concentrations of heavier elements.

Although more data are required, it appears that beads within a particular urn are closer in composition than those from different wos of the same date. This may indicate that beads were produced in small batches and each urn contains a distinct batch. This does not necessarily mean that the beads were produced specifically for the burials, but does imply that they were at least acquired together. There was no significant compositional difference between different typologies within an urn, i.e. between black ring beads and the black triangular cores to black and white eye beads. Although the white layers in the eyes were too altered for quantitative analysis, SEM revealed abundant particles of calcium antimonate indicating an original white glass.

Black glass coloured by high levels of iron has been discussed by Moretti and Gratuze [7], Gratuze [8], and Vanden Linden et al. [9]. In all cases, the authors discuss the compositions but not the microstructure of the glass. Moretti and Gratuze [7] and Gratuze [8] discussed black glass from
a number of Late Bronze Age/Early Iron Age to Roman sites, attributing the colour to iron in all examples. In contrast, Van der Linden et al. [9] divided Roman period black glass into dark green, dark purple and dark brown and attributed the colour to high levels of iron, manganese and the ferri-sulphide (Fe²⁺,Fe³⁺) chromophore respectively. In the samples studied here, the colour can be attributed solely to the presence of high levels of iron. For the Roman examples, Moretti and Gratuzé [7] suggested that iron oxide was added in European workshops to raw glass imported from the Eastern Mediterranean, since the black Roman glass was a typical Roman natron-based glass apart from a high percentage of Fe₂O₃ (5.3–8.3 wt%) and MnO (0.1–1.1 wt%). The Iron Age black glass presented by Gratuzé [8] was also a natron glass but with much higher Fe₂O₃ contents (10–25 wt%) and lower Al₂O₃ (<2 wt%) and CaO than the Roman glass. Some Bronze Age examples had higher levels of potash and magnesia and were probably produced from plant ash but were otherwise similar to the Iron Age examples [8]. In this study, black glass type A had much lower levels of alumina and lower levels of magnesia and potash than the Roman glass presented by Moretti and Gratuzé [7] or Van der Linden et al. [9]. However the iron levels of this black glass type A are lower than in the Iron Age or Bronze Age examples studied by Gratuzé [8]. This seems to be a distinct compositional variant of the black iron-rich glass.

**Small dark beads**

The small dark beads can be subdivided into dark black-brown and mottled (brown-green-red) varieties. All are significantly smaller and more rounded in shape than the more open ring beads. They were again formed by wrapping a strand of glass around a core, which is similar in composition to that used for the black glass, but examination suggests use of a single thicker glass strand.

This glass exhibits two different microstructures: S1 has a high percentage of crystalline magnetite, hematite, wollastonite and barium sulphate. A typical microstructure is shown in Figure 3 for bead 58268 and occurs in both dark and mottled examples. Magnetite occurs mainly as blocky, equant grains whilst hematite occurs as ‘fancy’ networks of fine grains. The surrounding glass matrix is extremely deteriorated, exhibiting fine lamellar and/or leathery alteration and extensive cracking. Some beads also contain abundant barium sulphate, which occurs both in large spherical voids and as fine spherical inclusions in the glass. The barium sulphate contains significant strontium in all instances and occurs in both large voids and as micro-spheres throughout the glass, suggesting it could be primary rather than a secondary alteration product.

A set of mottled beads from urn 3187 exhibits the alternative structure: S2, with fewer crystalline phases and little or no barium sulphate, as shown in Figure 4 for bead 3187C. These are generally better preserved, although with thick, irregular surface alteration zones with multiple compositional lamellae. Magnetite dominates and occurs as large dendritic masses and fine equant grains. Although the morphology of the dendritic iron oxide in SEM and polished section light microscopy (shown in detail in Figure 5 for bead 3187C) is suggestive of wuestite, only magnetite was identified in both the Roman and XRD spectra.

In the highly crystalline beads, alteration of the glass matrix is reflected in the composition, termed glass C in Table 2, which is highly variable and characterised by very low levels of alkali and silica and high levels of iron and alumina. In contrast, the less altered beads from urn 3187 retain high levels of soda and the glass composition is distinguished from black glass A mainly by higher iron and alumina with resultant lower silica. This glass composition was termed glass B. A compositionally similar glass occurs as rare islands in the heavily altered matrix of bead 5826A. One of these islands of unaltered glass is shown in Figure 6 and the glass composition given in Table 2 (denoted S1 inclusion).

**Other coloured beads**

Two other samples were obtained for SEM-EDX analysis: a fragment of a dark blue to black glass bead from phase 2 urn, bead 5967A, eighth to seventh century BC, and a red bead decorated with white and yellow spots from a phase 6/7 urn, bead 5965A, fourth century BC. The compositions are shown in Table 2. Both are again natron glasses, with very low levels of magnesium and potassium and fairly high levels of iron. The red spotted beads have higher levels of alumina than either black glass type A or the early phase 2 bead and the colour can be attributed to
the presence of significant copper, presumably present in the reduced form. The decoration on the spotted beads is extremely deteriorated but analysis indicates lead antimonate in the yellow areas and calcium antimonate in the white areas.

Discussion

The high levels of iron and the dendritic nature of the iron oxide minerals in the glass beads, the latter typical for iron metallurgy waste, suggest that iron slag was used to deliberately colour and/or form the black and mottled glass beads. In the absence of primary glass-working evidence from Iron Age Carthage, it seems likely that the beads were either imported or produced locally from scrap glass and/or imported raw glass. This imported material is unlikely to have been iron-rich (since such high iron glasses are unusual), suggesting the possibility of local addition of iron as a colourant during local bead production. Evidence of iron working has been discovered at a number of sites within Carthage, most notably at the Byrsa [10] and the Massouda [11, 12] and significant amounts of iron-working debris occur within the current port [13]. Industrial scale iron working appears to have been ongoing by the late seventh century and continued into the fifth century BC [11, 12]. There is some debate as to whether actual iron smelting occurred at Carthage rather than simply iron smithing of raw metal imported and shaped into usable objects [10, 11, 12, 14, 15]. Regardless, the current evidence indicates that metal slag was abundant and metalworking was an important industry in Punic Carthage.

Use of iron ores, iron salts or metallurgical slags to colour Iron Age black glass has been proposed by Gratuzo [8]. If metal slag was used, the composition would contain contributions from the fuel ash and furnace or crucible lining as well as the ore itself. Use of an iron slag seems most likely. Iron ores can have appreciable silica, phosphorus and lime depending on geological setting but are unlikely to have high levels of soda. Although some alkalis will be inherited from the fuel ash and/or clays used in the furnace or crucible it is again unlikely that very high levels of soda would be inherited. The presence of a soda-rich glass in all types of beads therefore suggests that the slag was not used directly to make a glass but was instead added to an existing natron glass to achieve a very dark green to black glass.

There is little evidence of glass working from ancient Carthage compared to that for metalworking. The most abundant evidence for glass working at a single site comes from the Roman cemetery which dates to the second-seventh century AD [16, 17]. Glass in general is somewhat lacking in the excavation reports compared to other materials, as discussed by Docter and Sonneveld [18]. They attributed the fally small amount of glass found at the settlement sites to deliberate recycling and garbage collection. The extant Punic glass finds from settlement sites included vessel fragments, beads and wasters, and covered a range of dates from the late eighth to the fifth century BC. None of the glass described was black in colour. The wasters come from the Middle Punic levels, around 480 to 425 BC, and provide the first definitive evidence for the production of glass on site in Carthage [18]. The beads are dominated by ring beads with some eye beads and rare face beads. This is reminiscent of the assemblage from the Tophet where the majority of the beads are flattened, more spherical ring types of eye beads are rare. The colour of the beads and in particular the wasters is very different from that of the beads analysed here and unfortunately no analytical data are yet available. The one glass find with published analysis is from the Bir Massouda and is deteriorated soda-lime glass or glaze coloured with antimony [12].

The importance of the glass assemblage from the Tophet increases when one considers the paucity of glass finds of similar date from other sites. A number of features combine to suggest the possibility of local manufacture, the most convincing being the use of high levels of iron as a colourant in conjunction with the presence of industrial scale iron working in Carthage at a similar period to the likely date of the glass. It is probably no coincidence that the black and mottled glass beads span the sixth to the fourth century BC and the iron working installations are attributed to similar dates. Other factors suggestive of local manufacture, possibly specifically for burial, are the fairly low quality of the glass, the very large numbers of beads, the limited typologies and the apparent lack of similar beads from settlement sites. Local production does not necessarily imply primary glass production at Carthage. It is possible, and perhaps more likely, that iron waste was added as a deliberate colourant to imported and/or recycled cullet. Ongoing trace element and isotopic analysis may differentiate between these two options. The current data suggest local
production of a small range of dark beads using metallurgical waste as the colourant. The groups differ mainly in the density of phases and levels of iron in the matrix glass and are hence believed to have a common origin.

Conclusions

Study of the common varieties of glass beads from the Carthage Tophet showed that these were all natron glass coloured with high levels of iron. The glass composition and presence of abundant iron oxides within the glass suggest the use of metallurgical waste from iron working. Excavations have demonstrated the presence of iron-working installations and large amounts of iron-working waste at a number of sites in Punic Carthage. It is proposed that the beads may have been produced locally using iron slags from the nearby iron-working installations as a colourant.

Acknowledgements

We would like to thank Adam Aja, Semitic Museum, Harvard University, Richard Newman, Museum of Fine Arts, Boston, and Scott Speakman, Massachusetts Institute of Technology for assistance with this project.

References


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