# THE BYZANTINE SHOPS AT SARDIS

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with contributions by

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# APPENDIX 2
# METAL AND FRIT PROCESSING: ANALYSIS OF CERAMIC CRUCIBLE RESIDUES

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The manufacturing debris from the Shops consisted in part of residues contained in ceramic crucibles. Six samples of these residues and a sample taken from a fragment of blue frit were analyzed at the Conservation Analytical Laboratory, Smithsonian Institution, Washington D.C.[1] From a detailed study of the variations in composition and microstructure of the residues and the frit, it was possible to reconstruct a set of activities appropriate to the manufacture of jewelry and other small decorative objects. These activities consisted of metallurgical and ceramic processes such as melting and the manufacture of decorative material for inlays.

**Methods of Analysis** **Tables 1 and 2**

The samples were very small, most submillimeter in size, and included frit, slag, dross, and concretions. The samples were first examined with a low-power optical microscope capable of continuous increases in magnification from 7–240x in order to judge the degree of heterogeneity in the materials and to observe fine details such as particle size, particle alignment and porosity. Scanning electron microscopy was employed to characterize microstructure with simultaneous energy dispersive X-ray analysis in order to identify those elements present in concentrations of one percent or more (Table 1). The relative heights of the peaks in the X-ray spectrum were compared to one another and to standards to obtain estimates of the relative amounts of the elements detected. The elements are reported in the order of decreasing peak heights and are uncorrected for effects of atomic number, absorption and efflorescence. An element having a peak about ten percent of the height of the tallest peak is considered a minor constituent. Emission spectroscopy was carried out on a blue frit, BS TS 1, to determine if the colorant was derived from brass scale, and the frit was reheated to determine its sintering temperature (Table 2). X-ray diffraction was used to identify Egyptian blue (Table 2).

**Electrum**

Analyses of the residue in Crucible 4 (P67.7:7289 from E 5, Fig. 249) were the most useful in identifying a specific process. Two samples were analyzed.

BS TS 6 was a low density, silvery, highly porous dross-like material of variable composition. The sample was taken from the upper edge of a glassy residue. In one area of this sample there was a prominent gold peak in the X-ray spectrum with other minor peaks from iron, calcium, silicon and potassium, indicating

1. The samples were taken at Sardis in 1986 and 1987 by J. A. Scott and were made available to the Smithsonian laboratory through the gracious permission of the Ministry of Culture of the Republic of Turkey. We are grateful to the field director, Crawford H. Greenewalt, Jr. for his help and interest and to Teoman Yalçınkaya for forwarding the material to the U.S.

Further analyses are contemplated and the results may be expanded in a forthcoming article. The editors are grateful to Goodway and Vandiver for permitting the preliminary results to appear in this volume. The editors join the authors in gratitude to Edward Sayre for helpful comments and to Harold Westley, who carried out the emission spectroscopy.

Table 1 Results of Crucible Residue Analyses

**Energy Dispersive X-ray Analysis**

BS TS 1 Blue frit which retains shape and circumferential spiral throwing ridges of a ceramic crucible. Sample of lighter blue part of frit.
*Major*: Si, Cu, Ca
*Minor*: Fe, Al, S, Na, K, Cl, Ti

BS TS 2 Sulfur yellow residue from Crucible 5, a shallow bowl with out-folded rim.
*Major*: S, Fe
*Minor*: Ca, Si, K, Al, Cu, Mg, Na

BS TS 3 Two residue samples with brass slag and corrosion products from Crucible 1, a straight-sided ceramic vessel.
Sample 1, brass slag
*Major*: Cu, Si, Zn, Sn
*Minor*: S, Ca, Al, Fe, Mg
Sample 2, copper chloride corrosion product
*Major*: Cu, Cl
*Minor*: Ca, Si

BS TS 4 Bubbly gray slag residue from interior near bottom of Crucible 2, a straight-sided ceramic vessel.
Sample 1
*Major*: Si, Al, Fe, Au
*Minor*: K, Ca, As, Ti
Sample 2, droplet of lead metal coated with lead corrosion product
*Major*: Pb
*Minor*: Sb or Ca

BS TS 5 Friable, brown sample from near rim of Crucible 2.
*Major*: Fe, Si
*Minor*: K, Al
**X-ray diffraction** identified quartz and mica.
**Microstructure** indicates presence of fired clay.

BS TS 6 Dross from Crucible 4, P67.7:7298, bowl with pouring spout. Sample taken from upper edge of glassy residue.
Sample 1
*Major*: Au, Fe, Ca
*Minor*: Si, K
Sample 2
Major: Si, Mg, Ca
Minor: Zn, Fe

BS TS 7 Pool of residue in base of Crucible 4.
Sample 1, possibly dross from melting electrum
*Major*: Si, Ag, Au, K
*Minor*: Ca, Al
Sample 2
*Major*: Fe, Mn
*Minor*: Si, K, Ca
Sample 3, silicious slag
Si, Ca, Al, Fe, K, Zn

Table 2 Emission Spectroscopy and X-Ray Defraction Analysis of BS TS 1, Egyptian Blue

**Emission Spectroscopy:**
*Major* (≥ 10%): Ca, Si
*Minor (1–10%)*: Al, Cu (about 1%), K, Mg, Na
*Faint Trace (0.001–0.01%)*: Ba, Cr, Fe (about 0.02%), Mn, Pb (about 0.03%), Sn (about 0.0007%), Ti, Zn (about 0.03%)
*Very Faint Trace*: Ag, As, Au, B

**X-ray diffraction peaks which identify Egyptian blue:**

| | | | | | | |
|---|---|---|---|---|---|---|
| 7.63/40 | 3.78/90 | 3.29/100 | 3/19/50 | 3.05/40 | 3.00/90 | 2.62/40 |
| 2.58/40 | 2.32/30 | 2.13/10 | 1197/20 | 1.89/15 | 1/83/60 | |
| 1.784/40 | 1.704/40 | 1.603/40 | 1.483/10 | 1.336/25 | | |

*Phases present*: Quartz, very minor Cristobalite

that this dross was associated with the melting of gold. In another area of the sample silicon, magnesium, calcium, zinc and iron were detected.

BS TS 7 was taken from the thick pool of residue in the bottom of the same crucible. The dross contained silicon, silver, gold, potassium, calcium and a small amount of aluminum and, in addition, black particles containing iron and manganese with similar peak intensities. In some areas of this dross the calcium peak intensity was highest.

Since the glassy residue in this crucible contained gold in substantial amounts in some regions and silver was detected in amounts above one percent, but lead was not detected, this crucible was likely to have been used for melting electrum. The absence of lead in this residue indicates that this vessel is not a cupel and was not used for refining.

### Sulfur

The analysis of BS TS 2 from Crucible 5, also from E 5, suggests the possibility that niello was being produced in this Shop. Crucible 5 is an open bowl of the same type as Fig. 251 with which it was found and which also contains a bubbled residue that has not yet been analyzed. BS TS 2 is a fine, compacted pale yellow powder which consists of sulfur, iron, calcium, silicon, potassium, aluminum, copper, magnesium and a trace of sodium, with the major constituents being sulfur and iron. Most of the particles were submicrometer in size with agglomerates in the twenty micrometer range. This powder was homogeneous in both composition and microstructure. It spread easily as a pigment when applied to a streak plate as a chalk.

Sulfur was found in quantity in this and other Shops but its presence in a crucible and in the context of the other samples, which clearly showed metallurgical activity, suggests the possibility that the sulfur was a raw material for making niello to be used as an inlay. All the necessary materials for making niello were found in Shop E 5.

Oddy and La Niece analyzed a gold buckle from Asia Minor dated to about A.D. 350 (in the British Museum AF333) which contained 86 percent gold, 12.5 percent silver and 1.5 percent copper, i.e. electrum.[2] This buckle is inlaid with niello. Oddy, Bimson and La Niece published an analysis of the niello from this buckle. This niello was mixed gold and silver sulfide, which they believed was made from electrum.[3] Earlier niellos were a copper sulfide when used on a bronze or brass, and a silver sulfide when used on silver. Mixed sulfides of silver and copper have not been dated earlier than the sixth century, and no occurrence of lead sulfide has been found from prior to that time.[4] Thus, the niello that might have been produced with the sulfur found in Crucible 5 would logically be a mixed gold and silver sulfide and, in fact, Crucible 4 offered evidence that electrum, rather than silver, was available for this purpose. The data cited above suggests that niello of electrum would be set into a precious metal, not into brass.

2. W. A. Oddy, S. La Niece, "Byzantine Gold Coins and Jewellery: A Study of Gold Contents," *Gold Bulletin* 19:1 (1986) 19–27.
3. W. A. Oddy, M. Bimson, S. La Niece, "The Composition of Niello Decoration on Gold, Silver and Bronze in the Antique and Medieval Periods," *Studies in Conservation* 28 (1983) 29–35.
4. Ibid.

**Lead**

BS TS 4 was taken from near the bottom of Crucible 2 (from E 10, Fig. 371). The sample is of a high porosity gray slag which contained silicon, aluminum, iron, zinc, potassium and calcium, with minor amounts of arsenic and titanium. The iron and zinc peaks were similar in height. Metallurgical activity is indicated but its nature is unclear.

BS TS 5 is a soft, friable, somewhat compacted brown powder from near the rim of the same crucible. This sample, which looks like dross, contained iron and silicon which had peaks of similar intensity, and potassium and aluminum in minor amounts. This is a heterogeneous material. Other phases present included quartz, clay and mica, probably as impurities.

The dross from Crucible 2 (in BS TS 4) contained a droplet of solid metal covered with what appeared to be a thin layer of lead carbonate corrosion product. The solid metal in this droplet was lead. Antimony or calcium may also have been present in a minor amount, but which one could not be confirmed by energy dispersive X-ray analysis, as their peaks overlap.

Metallic lead might have been used in several ways; for example, in brass alloys to promote easier casting, in solders, or for refining gold by cupellation. The melting of lead which contained no other major metallic element suggests that pure lead was being remelted for cupellation.

**Brass**

BS TS 3 was taken from the residue in Crucible 1 (Fig. 370) which is of the same type as Crucible 2 but is misshapen from heat. The two crucibles were found together in Shop E 10. Two parts of BS TS 3 were analyzed. One was a hard, reddish, glasslike slag with a granular surface structure. Entrained, rounded pores were present in cross section. Some white salts and dirt adhered to the surface. The interior composition included copper, silicon, zinc, tin, sulfur, calcium, aluminum, iron, and a trace of magnesium. The greenish part of a mixed red and green sample contained copper, chlorine, calcium and silicon. It was probably a corrosion product, since the reddish part of this sample was the same as that given above. There was a minor black phase which was not identified.

This sample was slag of a copper, zinc, tin alloy with perhaps a minor amount of iron. The fluxes consisted of silicon, calcium, aluminum, sulfur and perhaps iron. The microstructure and composition were consistent with metallurgical activity. Slag with a large amount of copper and minor amounts of zinc and iron is evidence of molten brass. The analytical results are consistent with the alloying of copper with calamine (a zinc carbonate) or the remelting of scrap, which was more likely to have been the case. Iron was a commonplace impurity in early brass and could have come from the copper ore or been incorporated during processing.

There is considerable heterogeneity in the composition of this slag, which might indicate multiple use of the crucible for remelting small amounts of metal derived from different sources. The crucible could not be examined for signs of layering of the slag, melting or other reactions. The high silicon, calcium, and aluminum content might indicate a process for the consolidation of impurities but there was not the usual high porosity characteristic of dross. Smelting of such small amounts of metal in a crucible is unlikely.

The color of brass varies with the amount of zinc present in the composition. If brass contains enough zinc, the color of the clean, polished metal is golden rather than coppery red. If less than ten percent of zinc is homogeneously distributed throughout copper, the alloy maintains the red color inherent in copper. The color of the metal may have been exploited by the producers of copper alloy jewelry although this has not been demonstrated by the few analyses published to date.

However, gilded items were found in the Shops and in other Early Byzantine contexts at Sardis. A crucible found in the colonnade in front of Shop W 7 (P72.9: 8911, Fig. 109) contains a lead slag with droplets of gold which suggested a residue of small scale gilding when analyzed in the field by A. P. Lins.[5] A low-zinc red brass would have been more easily fire gilded than a more highly alloyed copper.[6] Gilding by the application of a gold amalgam (mixture of gold and mercury) and heating to drive off the mercury became common about the third century A.D.[7] To be successfully gilded, copper alloy ought to be free of lead. Unfortunately the gilded copper alloy items from the Shops and from contemporary contexts at Sardis have not been analyzed. They include a brooch with glass paste inlay from Shop E 6

5. *Sardis* M8 no. 958.

6. W. A. Oddy, "Scientific Dating of the San Marco Horses," *MASCA Journal* 2 (1962) 46.

7. Ibid.

(J73.2:8222, Fig. 283).[8] A brass lamp in the form of a lion (M67.4:7291, Figs. 232, 233, from Shop E 5) was found to be free of lead but contains a very high proportion of zinc which would have created a gold color without gilding. X-ray fluorescence performed at the Maden Tetik ve Arama Enstitusu in Ankara showed zinc at 22.78 percent and lead at 0.40 percent. A second analysis of the same sample made by J. M. Schultz at the University of Delaware showed copper to zinc ratios of 22:10 and 18:9 in two runs on the same sample. Lead was not observed and hence was not present in a large concentration.[9]

**Blue Frit**

BS TS 1 was taken from a piece of glassy material which bears the interior shape and wheelmarks of a ceramic container. It was found on the floor of E 6. The fragment shows a sharp demarcation of light to darker blue; the sample was taken from the light area. It is a grayish blue frit with considerable porosity. Angular to subangular quartz particles, about 0.1 mm. in diameter, composed about eighty volume-percent of this sample. These were sintered together with heterogeneous blue particles consisting of a mixture of silicon, copper and calcium with minor amounts of iron, aluminum, sulfur, sodium, potassium, chlorine and titanium. The blue regions consisted of crystals of Egyptian blue, identified by X-ray diffraction, in a glassy matrix. There was also a minor fraction (five volume-percent or less) of red to black particles which were rich in iron, some of which looked like a porous slag and some like small bits of over-fired clay, perhaps from a crucible.

Exclusive of the slag and clay inclusions, the sample is a fritted mixture of ground quartz and blue glass, which contains crystals of Egyptian blue and a small amount of clay. The grayish-blue material at first impression had the appearance of a cobalt aluminate spinel but in fact was colored by the crystals of Egyptian blue and by blue glass containing copper and iron which had been fluxed with both sodium and potassium. No cobalt was detected in this sample by energy dispersive X-ray analysis and only a faint trace was found by emission spectroscopy. Semi-quantitative emission spectroscopy of selected blue particles determined that the copper was not added in the form of brass scale or other alloy. The ratios to copper of tin (0.0007), zinc (0.03), lead (0.03) or iron (0.02) clearly showed insufficient amounts of these other elements to have originated in an intentional alloy with copper. Faint traces (about 0.001–0.01 weight percent) of silver, arsenic, gold, boron, chromium, cobalt, and manganese were also detected but in too small a concentration to affect the color.

Opacity was promoted by a well-dispersed clay addition, which might have been intentional or not. The presence of aluminum, titanium and iron in the glassy part of the mixture are indicators of clay. The fact that the clay is fairly homogeneous throughout the glassy phase suggests that the clay may also have been an intentional addition, yet it is not inconceivable that the clay was introduced adventitiously in a multiple stage process of fritting and grinding.

There was more iron present than can be explained by the addition of clay alone. Iron in some form was probably an intentional addition. The effect of the clay and iron was to produce a grayish, opaque blue, rather than a bright turquoise blue. Multiple fluxes, sodium and potassium, may have been used to promote the formation of glass in what is known as the mixed-alkali effect, the glass then acting as a medium from which the Egyptian blue crystals could precipitate during prolonged heating. Both chlorine and sulfur were also present, suggesting that salts rather than ash may have been the source of the flux.

To produce this fine-particled, opaque, grayish-blue colorant required sustained heat treatment in the range of 800–1000° C. Reheating the frit produced sintering at 850° C, which represents the minimum heating temperature required for cohesion of the frit. There is a slight indication of cristobalite in the X-ray diffraction pattern which would indicate a multiple firing process.

The sample is not suitable as a pigment; if ground to finer particle sizes it becomes bluish white. Neither is this frit suitable for reheating to a glass because of the large amount of quartz present. The frit is suitable for use as an inlay in jewelry such as the brooches found in the Shops (Figs. 283, 338) and elsewhere at Sardis which are decorated with white and yellow as well as blue frits.[10]

8. *Sardis* M8 no. 685. Other objects of the period showing traces of gilding are ibid. nos. 727, 761, 802. A menorah fragment, no. 610, may have been gilded, p. 20. No. 727, an earring, was in a mixed burial context but is dated Early Byzantine on the basis of style.

9. Crawford, "Lion," 292 presents the summary of the analytical results from which these remarks are drawn. The report of the analysts has not been reviewed. Both analyses were done in 1972.

10. *Sardis* M8 nos. 684–687, also a buckle, no. 699. Copper alloy lock plates were also inlaid, possibly with frit although none is

## CONCLUSIONS

These results all point to small-scale metalworking. Several practices appropriate to jewelry making were identified from the residues found in four crucibles. They include such routine metal processing as alloying and remelting. There was also a possibility of refining and circumstantial evidence of fire gilding. Several metals and alloys were clearly present: lead, brass and electrum. One decorative material, the blue frit, was used and another, niello, might have been. The inlaying of both these materials are similar processes that require reheating at a temperature lower than the melting point of the metal into which they are to be set. There is no evidence among these samples for the smelting of metal or of iron working. Although iron was detected in the elemental analyses of the crucible residues, iron is a nearly ubiquitous and often helpful element in fluxing slags of many different metals. None of the samples examined were typical of iron smelting, blacksmith's scale or the like.

While the evidence of the crucibles and their residues leaves little doubt that jewelry and other small decorative metal objects were being produced or repaired, a jeweler's shop cannot be reconstructed. Rather, these results present an alternative hypothesis as to the activities in several Shops or the suggestion that more than one craft was practiced. Further technical studies should compare pieces of jewelry and other finished objects with these analyses. These preliminary results are presented in part to demonstrate the amount of information to be extracted from small samples of residue—had it been possible to analyze all the material at the time of excavation a great deal more would be known about Early Byzantine crafts at Sardis.

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preserved, ibid. no. 381, here Fig. 356 and no. 380 from HoB. A similar brooch (J79.1:8939) was found at MMS/S, *BASOR* 249, 8, fig. 10.