# *A RED OPAQUE GLASS FROM SARDIS AND SOME THOUGHTS ON RED OPAQUES IN GENERAL*

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THE PIECE of red opaque cullet which prompted the writing of this article was recovered from a room belonging to a series of Lydian domestic buildings excavated at Sardis between 1982 and 1986. These houses are located near the foot of an enormous building, the "Colossal Lydian Structure," presumed to be a fortification. Both the houses and the Structure were destroyed, apparently deliberately, and brick from the upper part of the Structure was dumped over the ruins of the houses, thus preserving their contents more or less intact. Pottery from the floors of the houses and from beneath the fallen brick (including two Attic black figure cups, Corinthian aryballoi, and local pottery) as well as a radiocarbon date suggest that the destruction occurred about 550 B.C., probably during the capture of the city by Cyrus the Great between 547 and 542 B.C.[1]

Most of the rooms excavated so far are domestic in character, containing hearths, kitchen pottery, loom weights, and other household artifacts. One room, however, contained about 4.8 kg of the red glass cullet discussed here, as well as 0.5 kg of transparent yellow-brown cullet, a few finished glass objects such as "melon beads" made of segments of different colored glasses, and tools including an iron saw and tweezers. Unlike the purely domestic areas, this room had been ransacked after the destruction, probably to salvage its more valuable contents; the cullet and tools were found in the churned-up backfill of the room. Furnishings of the room in-

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1. Cullet was first recovered in a probe dug in 1982, and the workshop was more fully exposed in 1986. Results of these excavations are published by C. H. Greenewalt, Jr., D. G. Sullivan, C. Ratte, and T. N. Howe, "The Sardis Campaigns of 1981 and 1982," *Bulletin of the American Schools of Oriental Research*, Supplement 23, 1985, pp. 73–77; C. H. Greenewalt, Jr., N. D. Cahill, and M. L. Rautman, "The Sardis Campaign of 1984," *BASOR*, Supplement 24, 1987; N. H. Ramage, "Two New Attic Cups and the Siege of Sardis," *American Journal of Archaeology*, v. 90, 1986, pp. 419–424; and C. H. Greenewalt, Jr., N. D. Cahill, H. Dedeoglu, and P. Herrmann, "The Sardis Campaign of 1986," *BASOR*, Supplement 26 (forthcoming). Fragments of cullet were inventoried as G86.7/9362 and exported for analysis with the permission of Turkish authorities. The largest fragment recovered measures ca. 12 × 9 × 7 cm; most of the fragments average ca. 3–10 cm in greatest dimension. Further inquiries about this material should be addressed to Prof. C. H. Greenewalt, Department of Classics, University of California, Berkeley, California 94720.

cluded two stepped benches or platforms, the uses of which are still uncertain. No trace of a furnace or hearth was found, although one could have been located in an adjoining room. But even without a furnace, the discovery of cullet and tools identifies this room as part of a glass workshop. It is not yet certain whether the workshop belonged to one of the houses or was a separate unit, since its entrance has not been exposed. If the workshop was not part of a house, however, it seems at least to have operated within a domestic context, rather than belonging to an industrial district. Further exploration of the area is planned for future seasons, although most of the room has now been exposed.

A sample of one of the chunks of cullet has been chemically analyzed and examined in the laboratory. The parent object is irregularly shaped and measures about 4 cm in greatest dimension. The glass has a strong, fairly bright, red opaque color and is quite homogeneous except for a surface zone of greenish color measuring approximately 1.5–3.5 mm in thickness. This surface zone has the same appearance as weathering products usually observed on ancient red opaque glasses. The object immediately brings to mind chunks of red opaque cullet from Nimrud and Persepolis. Among the ancient red opaques known to us, these seem to be closest in date and appearance to the Sardis finds.[2]

Cullet is expected to be found near either of two types of factories: those where glass was manufactured from raw materials, and those where it was resoftened and fashioned into objects. In ancient times, these two types of factories were sometimes one and the same, or situated very close to one another, but frequently cullet was manufactured in one place and transported over considerable distances before it was formed into objects. Consequently, cullet somehow lost in transit is occasionally found along trade routes connecting places where the two types of glassmaking were carried out.[3] It is not yet known which set of circumstances applies to the Sardis finds.

*The Chemistry and History of Red Opaque Glasses*

Normally when copper is present in a glass, it is in the form of individual cupric ($Cu^{++}$) ions and confers a blue transparent color. In this oxidized form, the ions are dispersed individually throughout the glass and behave in the same way as does a dye (or copper sulfate) dissolved in water. Only when the glass melt is very strongly reduced, either by internal reducing agents or by control of the atmosphere above the glass (or preferably by a combination of both), will the copper be reduced to the cuprous ($Cu^{+}$) ion. In this chemically reduced state, copper can precipitate out as minute, bright red crystals of cuprous oxide ($Cu_2O$).[4] The naturally occurring mineral form of cuprous oxide is cuprite, which has the same red color. We have run X-ray diffraction patterns of numerous examples

2. Ordinarily, we hesitate to publish studies of individual objects of this sort. However, because so much of our present knowledge of red opaques is unpublished and because the subject often seems to be somewhat misunderstood, this seems a good opportunity to offer some thoughts on red opaques in general.

3. A few sites are known where glass definitely was resoftened from cullet and made into objects. The 4th-century factory at Jalame in western Galilee is perhaps the best known. (Robert H. Brill, "Scientific Investigations of the Jalame Glass and Related Finds" in *Excavations at Jalame, Site of a Glass Factory in Late Roman Palestine*," ed. Gladys D. Weinberg, University of Missouri Press, chapter 9. In press.) Several sites are known where cullet lost in transit has been recovered. The 11th-century shipwreck at Serçe Liman is perhaps the best known of these. (George F. Bass, "An 11th-Century Shipwreck at Serçe Liman, Turkey," *International Journal of Nautical Archaeology*, v. 7, 1982, pp. 119–132.) Among the excavated ancient glass factories known to the authors (there are fewer than a dozen), some probably were locations where glass was actually made from scratch, starting with raw materials. However, most of the excavated evidence that has been preserved appears to be remains of processes connected with the forming of objects.

4. It is sometimes remarked that red opaques owe their color to red ferric oxide. We cannot rule out the possibility that such glasses could exist, but are inclined to doubt it. X-ray diffraction patterns we have run of numerous red opaque glasses, and microscopic examinations of the same, have never shown the presence of any iron oxide phases. Neither have we been able to produce red opaque colors in oxidized glasses containing much iron and no copper. Certain types of ancient reddish faience are colored with $Fe_2O_3$ because hematite was present in the faience body before the material was even heated. There is no connection between that color and the color of red opaque glasses. The ruby glasses in medieval stained glass windows were also colored by cuprous oxide, but a somewhat different technology was involved.

of ancient red and orange opaque glasses. They invariably contain cuprite and sometimes metallic copper, but nothing else which would affect the color, only minor amounts of the usual devitrification products or occasional batch stones.

The red opaques are difficult to work with, not only because it is necessary to establish strong reducing conditions while the glass is being melted, but also because the same conditions have to be maintained during the entire time the hot glass is being worked at higher temperatures. Tiny crystals of cuprous oxide will dissolve quickly if the surrounding glass melt becomes oxidized. Hence, if a molten red opaque glass comes in contact with air, even momentarily, the surface may lose its red color.[5] The effects of partial oxidation are clearly evident under magnification. For example, small air bubbles in red opaques are often surrounded by envelopes of green transparent glass in which oxygen dissolved from the bubbles has taken the cuprite crystals back into solution. Dark-colored streaks in the red glass can be seen to be cords of partially oxidized green transparent glass wound in during gathering or stirred in by uneven mixing. These cords, incidentally, can be very useful for reconstructing the methods by which artifacts were formed.

In most cases, the particles of cuprous oxide are so small that they can barely be seen under microscopic magnification up to about 100X.[6] Occasionally, however, when the crystals have been allowed to grow for a longer time, they generate dendritic formations which, in extreme cases, can be large enough to be seen by the unaided eye. Often, minute crystals of metallic copper, formed by the further reduction of cuprous oxide, can also be found among the red crystals. Sometimes one also finds minute globules of metallic copper, lead, or copper alloyed with other metals.[7] If crystallites of copper are carefully grown still larger, they produce aventurine glasses which have a distinctive caramel opaque color with glistening flecks of metallic copper. Aventurines, however, did not appear until the 18th century.

If the cuprite crystallites are suspended in a colorless glass matrix, the glass itself will take on the same bright blood-red color of the crystals. On the other hand, if the matrix glass contains other colorants and has, for example, the aqua or greenish color due to iron impurities, then the bright red color of the crystals is modified to a brick red or muddy brownish color. It is as if one were looking at a bright red object through a pair of green-tinted sunglasses. The same muddying effect will be produced if much dissolved copper, with its attendant blue or green transparent color, remains unprecipitated in the matrix glass.

Consequently, the first trick that glassmakers in ancient times had to master in order to produce red opaques was establishing and maintaining a strong reducing environment. Furthermore, the closer they came to complete reduction of the copper (to maximize the yield of the red phase and to minimize the color remaining in the matrix) and the closer they came to decolorizing the iron (or melting a glass free of iron), the brighter the resulting red color would be. They appear to have mastered the first trick early in the history of glassmaking because examples of red opaques and their brick-colored variants are found among Mesopotamian and Egyptian glasses of the 14th and 13th centuries B.C. Red opaques were not really common in that period, but examples are known. The latter trick (coinciding perhaps with the introduction of lead) appears to have been mastered at least in some instances by the 9th–6th centuries B.C.

The Mesopotamian cuneiform glassmaking texts have a lot to say about glassmaking in general and about red opaques in particular.[8] The sections

5. In synthesizing an ancient red opaque, we once poured the molten glass from a crucible and found the resulting ribbon to be red inside but green transparent on the outside where it had contacted the air for some 5–10 seconds.

6. Robert H. Brill, "The Scientific Investigation of Ancient Glasses," *Proceedings of the VIIIth International Congress on Glass, London*, Sheffield, England: The Society of Glass Technology, 1968, pp. 47–68.

7. Robert H. Brill and Sheldon Moll, "The Electron-Beam Probe Microanalysis of Ancient Glass," *Recent Advances in Conservation, Rome, 1961*, London: Butterworth, 1963, pp. 145–151.

8. Robert H. Brill, "The Chemical Interpretation of the

describing the preparation of red opaques specify the use of copper, closed containers, smoky fires, long firing times, and the need for cooling the glass while still within the kiln. Moreover, they describe ritual processes which suggest the difficulty and perhaps somewhat chancy nature of the processes.

Analyses of several red opaques representative of those of different periods and places are presented in Table 1. These have been selected from some 30 red opaques, most of them unpublished, analyzed over the years by The Corning Museum of Glass. All are colored with copper, with the cuprous oxide levels ranging from about 5% to 15%.[9] Except for the Sardis specimen, it can be seen that all the glasses were prepared by adding the copper-containing ingredient to a soda-lime base glass. This is apparent if one estimates the reduced compositions of the glasses, that is to say, the relative proportions of $SiO_2$, $Na_2O$, and CaO are about the same as those in other colors of glass from the corresponding periods and places of manufacture. From our experience, this was generally the case. The copper-containing ingredient (and also the lead-containing ingredient, if used) could have been added to the base glass at various stages: to the batch, to crushed cullet, during fritting, or (less likely) to a melt.

In addition, antimony is almost always present. One wonders if that was because it happened to be a common additive to luxury glasses anyway (serving as a fining agent or decolorizer) or because it served some specific function in the chemistry of melting red opaques. It could, for example, have served very well as an internal reducing agent or as a redox buffer while the glass was being cooled; or, perhaps, despite the need for maintaining reducing conditions, the antimony might nonetheless somehow have partially decolorized the iron, thus helping to produce a brighter red color.

Interestingly, the iron values are not generally higher than for glasses of other colors from the same periods and places. (Nos. 199 and 706, and the Kenchreai glasses are exceptions. Also, virtually all Byzantine tesserae have higher irons.) In fact, iron would be expected to behave as a good reducing agent for cupric copper in red opaques, just as it was for gold and silver in dichroic glasses used for diatreta.

The presence of two other metallic oxides, those of lead and tin, deserves special comment because both are believed to be beneficial to the formation of the red colorant. The presence of lead in substantial quantities was undoubtedly intentional, but whether or not that of the tin was intentional is open to question. (See below.) The late Harrison P. Hood used to remark that the benefit of lead may be related to the steepness of the solubility curve of cuprite in lead glasses or to keeping the cuprous copper from becoming oxidized. Lead would also be of considerable help in that high-lead glasses are less susceptible to devitrification than soda-lime glasses. Hence, if long heat treatments are used, the red color of a high-lead glass is less likely than that of a soda-lime to become diluted by devitrification phases.

The earliest red opaques we have analyzed, those from Tell el Amarna, do not contain lead. Neither does another Egyptian glass, the inlay head in Table 1 (No. 3223). This is tentatively dated to the 7th–5th centuries B.C., but it could possibly be contemporaneous with the Amarna glasses. Based on the relatively few examples we have analyzed so far, it appears that by about the 9th century B.C., glassmakers in Iran had learned that the presence of lead helps in the formation of the red color. Analyses of two red opaques from Hasanlu, one a bead and the other from one of the Hasanlu beakers,[10] both dating from about 850 B.C., show that they contain 6.99% and 3.2% PbO. By the 6th–3rd centuries B.C., at least some Egyptian red opaques and their orange variants contained considerably

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Texts," in *Glass and Glassmaking in Ancient Mesopotamia*, D. Barag, R. H. Brill, A. L. Oppenheim, and A. von Saldern, Corning, N.Y.: The Corning Museum of Glass, 1971.

9. The total copper is reported as cuprous oxide, but it is possible that some of it was present as dissolved cupric oxide and/or metallic copper.

10. Axel von Saldern, "Mosaic Glass from Hasanlu, Marlik, and Tell al-Rimah," *Journal of Glass Studies*, v. 8, 1966, pp. 9–25; and Brill [note 8].

TABLE 1

| | | *Sardis chunk* 3222 | *Amarna cane* 3355 | *Egypt inlay head* 3223 | *Hasanlu mosaic beaker* 706 | *Hasanlu fragment* 5420 | *Persepolis chunk* 198 | *Persepolis flat slab* 199 |
|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | Δ | ~75.9 | ~62.2 | ~56.6 | ~53.3 | ~52.3 | ~55.3 | ~53.7 |
| $Na_2O$ | a | 0.36 | 16.9 | 15.6 | 15.4 | 12.9 | 10.1 | 15.0 |
| CaO | a | 4.21 | 7.11 | 6.99 | 4.79 | 2.51 | 1.82 | 3.54 |
| $K_2O$ | a | 0.45 | 1.61 | 2.25 | 2.69 | 0.99 | 0.37 | 1.18 |
| MgO | a | 0.79 | 3.23 | 3.88 | 3.28 | 1.15 | 0.31 | 2.40 |
| $Al_2O_3$ | a | 0.63 | 1.21 | 0.64 | 1.53 | 0.80 | 0.53 | 1.26 |
| $Fe_2O_3$ | a | 0.37 | 1.25 | 0.35 | 2.39 | 0.38 | 0.64 | 3.43 |
| $TiO_2$ | | 0.03 | 0.10 | 0.13 | 0.10 | 0.03 | 0.02 | 0.05 |
| $Sb_2O_5$ | a | 3.78 | 0.35 | 1.08 | 2.00 | 1.81 | 3.74 | 2.94 |
| MnO | a | 0.001 | 0.057 | .02 | 0.020 | 0.01 | 0.001 | 0.001 |
| $Cu_2O$ | a | 13.4 | 5.18 | 11.6 | 11.1 | 19.3 | 15.8 | 8.01 |
| CoO | | nf | nf | nf | nf | nf | 0.01 | <0.01 |
| $SnO_2$ | | 0.001 | 0.20 | 0.80 | 0.5 | 0.005 | 0.02 | 0.005 |
| $Ag_2O$ | | 0.002 | <0.001 | 0.003 | 0.001 | 0.005 | 0.03 | 0.01 |
| PbO | a | 0.002 | 0.001 | 0.02 | 2.83 | 6.99 | 11.0 | 8.36 |
| BaO | | 0.001 | <0.01 | <0.01 | <0.01 | 0.01 | 0.01 | 0.01 |
| SrO | | 0.02 | 0.08 | 0.04 | 0.02 | 0.01 | 0.01 | 0.02 |
| $Li_2O$ | | <0.001 | nf | nf | 0.001 | 0.005 | nf | nf |
| $B_2O_3$ | | 0.02 | 0.01 | 0.02 | 0.02 | 0.20 | 0.30 | 0.01 |
| $V_2O_5$ | | nf | nf | nf | nf | <0.005 | <0.005 | 0.005 |
| NiO | | 0.005 | nf | nf | 0.05 | 0.01 | 0.01 | 0.01 |
| ZnO | | 0.037 | 0.0087 | 0.010 | 0.012 | 0.011 | 0.011 | 0.088 |
| $ZrO_2$ | | <0.01 | nf | nf | nf | <0.01 | nf | nf |
| $Bi_2O_3$ | | 0.005 | nf | nf | nf | nf | 0.001 | 0.001 |
| $P_2O_5$ | c | ——— | 0.49 | ——— | ——— | ——— | "Trace" | "Trace" |
| Other Expt.: | | Pb-1109 d = 2.23g/cc | thin-section | Pb-1316 | Pb-411 | Pb-2138 | Pb-463 | Pb-464 |

Sought but not found: $Rb_2O$, $Cr_2O_3$, $As_2O_5$; except 1059 = 0.01 $Rb_2O$; 5420 = 0.60 $As_2O_5$, and 706 = trace $As_2O_5$

greater levels of lead, judging from a series of figurines we found to be heavily leaded.[11] The red opaque glass inlays from Nimrud, dating from the 7th century B.C., also have high lead contents, with four samples ranging from 9.32 to 23.1% PbO.[12] Two pieces of red opaque glass from Persepolis which we have analyzed, dated to the 5th century B.C., have lead contents of 8.36% and 11.0% PbO.[13] Therefore, we know that by about the 7th century B.C., the makers of glasses found in Iraq, Iran, and Egypt were—in at least some instances—taking advantage of the benefits of lead when preparing their red opaques.

From about this time onward, most of the red opaque glasses of the Western World can be expected to contain levels of lead which, if not substantial, at least correspond to intentional addition.

11. Robert H. Brill, I. Lynus Barnes, and Barbara Adams, "Lead Isotopes in Some Ancient Egyptian Objects," *Recent Advances in Science and Technology of Materials*, v. 3, New York and London: Plenum Press, 1974, pp. 9–27. See also "Sample Descriptions."

12. Jeffery J. Orchard and Robert H. Brill, "Some Miniature Glass Plaques from Fort Shalmaneser, Nimrud. Part I: Description and a Restoration; Part II: Laboratory Studies," *Iraq*, v. 40, Spring 1978, pp. 23–39.

13. Frederick R. Matson, "Analyses of Various Substances," in *Persepolis*, by E. F. Schmidt, University of Chicago Press, 1957, v. 2, pp. 127–132.

TABLE 1 (*cont.*)

| | | *Nimrud cullet* | *Nimrud inlays (mean of 4)* | *Hellenistic bowl* | *Egypt* wedjet-*eye (e. microprobe)* | *Tara Hill cullet* | *Kenchreai opus sectile (mean of 9)* | *St. Demetrius tessera* | *San Clemente tessera* | *Orissa bead* |
|---|---|---|---|---|---|---|---|---|---|---|
| | | *200* | *3230 series* | *5040* | *3255* | *3224* | *970 & 3060 series* | *2373* | *2745* | *1063* |
| $SiO_2$ | Δ | ~47.6 | ~47.7 | ~45.0 | 58.15 | ~44.0 | ~64.2 | ~54.0 | ~58.8 | ~70.7 |
| $Na_2O$ | a | 9.00 | 9.68 | 10.1 | 12.8 | 9.43 | 13.6 | 15.8 | 15.1 | 3.21 |
| CaO | a | 4.70 | 3.60 | 6.63 | 7.26 | 6.03 | 8.11 | 7.53 | 7.41 | 3.28 |
| $K_2O$ | a | 1.52 | 1.09 | 0.53 | 2.02 | 0.68 | 2.36 | 1.42 | 1.37 | 6.28 |
| MgO | a | 2.64 | 2.14 | 0.60 | 2.04 | 0.62 | 3.33 | 1.21 | 1.40 | 3.01 |
| $Al_2O_3$ | a | 0.81 | 0.97 | 1.83 | 1.60 | 1.39 | 1.62 | 2.17 | 2.48 | 5.56 |
| $Fe_2O_3$ | a | 0.54 | 0.47 | 0.88 | 1.46 | 0.47 | 1.62 | 2.42 | 2.69 | 2.39 |
| $TiO_2$ | | 0.10 | 0.11 | 0.08 | ——— | 0.10 | 0.21 | 0.15 | 0.15 | 0.20 |
| $Sb_2O_5$ | a | 2.20 | 4.26 | 1.03 | 0.42 | 1.60 | nf | 0.01 | 0.23 | nf |
| MnO | a | 0.018 | 0.02 | 0.58 | 0.30 | 0.34 | 0.46 | 1.15 | 0.61 | 0.32 |
| $Cu_2O$ | a | 11.3 | 13.1 | 7.54 | 2.25 | 10.2 | 2.91 | 2.99 | 2.04 | 4.94 |
| CoO | | nf | nf | 0.01 | ——— | nf | nf | 0.01 | nf | nf |
| $SnO_2$ | | 0.005 | ~0.25 | 0.01 | ——— | 0.08 | ~0.6 | 1.02 | 0.39 | 0.005 |
| $Ag_2O$ | | 0.02 | 0.02 | 0.01 | ——— | 0.008 | 0.01 | 0.002 | 0.001 | 0.001 |
| PbO | a | 21.8 | 16.5 | 25.1 | 11.5 | 24.9 | 1.09 | 9.16 | 6.25 | 0.03 |
| BaO | | nf | 0.01 | 0.01 | ——— | 0.01 | 0.09 | 0.05 | 0.05 | ——— |
| SrO | | 0.02 | 0.02 | 0.02 | ——— | 0.02 | 0.28 | 0.05 | 0.08 | ——— |
| $Li_2O$ | | 0.005 | 0.003 | nf | ——— | nf | nf | 0.002 | 0.005 | ——— |
| $B_2O_3$ | | 0.02 | 0.03 | 0.03 | ——— | 0.02 | 0.08 | 0.02 | 0.03 | 0.01 |
| $V_2O_5$ | | nf | nf | nf | ——— | nf | nf | 0.005 | 0.005 | nf |
| NiO | | 0.01 | 0.01 | 0.01 | ——— | nf | nf | 0.08 | 0.008 | nf |
| ZnO | | 0.039 | 0.017 | 0.034 | ——— | 0.066 | nf | 0.72 | 0.20 | 0.025 |
| $ZrO_2$ | | nf | nf | nf | ——— | nf | ——— | <0.01 | <0.01 | <0.01 |
| $Bi_2O_3$ | | nf | nf | nf | ——— | nf | nf | nf | nf | nf |
| $P_2O_5$ | c | ——— | 0.05 | ——— | ——— | ——— | ——— | ——— | 0.72 | ——— |
| | | Pb-90 | | | Pb-171 | Pb-174 | Pb-465–69 | | | |

There will be some exceptions, and some contain much more lead than others, but unleaded red opaques can be regarded as unusual. We believe this generalization can safely be applied to Hellenistic glass, Roman glass, and all of the red, orange, and brownish opaque glass tesserae in Byzantine and more westerly mosaics.[14] The Kenchreai *opus sectile* glasses in Table 1, nine of which average only 1.09% PbO, are the lowest-leaded red opaques we have encountered among such glasses. Notable exclusions to this rule are some of the familiar Indian red beads, which are seemingly ubiquitous throughout Southeast Asia, India itself, and East Africa. An example we believe to have been made in India (No. 1063 in Table 1) contains only a trace of lead.[15]

It can be decidedly dangerous to generalize about the compositions of red opaques on the basis of a single analysis. In the case of the *opus sectile* glasses from Kenchreai,[16] one would not get into

14. Unpublished analyses of The Corning Museum of Glass laboratory.

15. Robert H. Brill, "Chemical Analyses of Some Early Indian Glasses," *Archaeometry of Glass, Archaeometry Session of the XIVth International Congress on Glass, New Delhi, 1986*, Calcutta: Indian Ceramic Society, 1987, Section I, pp. 1–25; E. Edwards McKinnon and Robert H. Brill, "Chemical Analyses of Some Glasses from Sumatra," *ibid.*, Section II, pp. 1–14.

16. Robert H. Brill, "Scientific Studies of the Panel Materi-

trouble. The mean values for $Cu_2O$ and PbO in nine examples of red opaques from Kenchreai are, respectively, 2.91% and 1.09%. (See Table 1.) The ranges of the same two oxides are 2.19–2.94% and 0.76–1.47%, about what is to be expected for a 4th-century factory which maintained good control of its compositions. On the other hand, the mean of the four red opaque inlays from Nimrud are 13.1% $Cu_2O$ and 16.5% PbO, with ranges of 10.8–19.9% and 9.32–23.1%. Time and again we have seen groups of early glasses from a single factory which had consistent compositions in its base glasses but widely varying compositions in its colorants and opacifiers. This is due, at least in part, to the frequent remelting and mixing involved in the production of red, yellow, and white opaques and their variants.

When studying the history of glassmaking, one must resist the temptation to oversimplify by adopting too many magic moments and believing that they revolutionized technology simultaneously wherever glass was being made. It is an all too common mistake. Different people did things in different ways, and whether or not they changed their ways depended upon cultural factors as well as upon practicality. There is more than passing evidence which suggests that established traditions and older ways of doing things sometimes persisted for many decades, or even centuries, within a region alongside others where newer ways or materials had been introduced. In fact, the red opaque from Sardis discussed below exemplifies the need to avoid simplicism in studying early technologies.[17]

In most ancient colored glass containing copper (both the red opaques and blue transparent glasses), the copper is usually accompanied by tin and sometimes by lead or zinc. The reason is that copper seems not generally to have been added to glass in the form of copper metal. In fact, that would have been a difficult way to color the glass. Instead, copper was introduced in the form of some substance which would dissolve more readily in the glass melt. We believe that copper, bronze, or brass scale from metallurgical workshops was usually used—or else the glassmaker simply heated some scrap metal in his own furnace until it oxidized.[18] An oxide scale can be crushed and then dissolved quite readily in a glass melt. Thus, the analysis of an ancient copper-containing glass often reflects the composition of bronze alloys in local use where the glass was made—or in the case of later glasses, sometimes the brass.[19] For example, the two tesserae (Nos. 2373 and 2745) appear to have been colored by brass derivatives. An interesting variant of this effect is found in the two red opaques from Hasanlu (Nos. 706 and 5420 in Table 1). No. 5420 contains about 0.6% $As_2O_5$ and only a spectrographic trace of tin. The metal from which its colorant came might have been an arsenical bronze containing 3–4% arsenic. No. 706, from the inlay beaker, apparently was colored with a derivative of a tin bronze containing traces of arsenic from the original copper ore. The same Hasanlu glasses show another curious effect. Upon reheating small chips of the unweathered red opaque glass approximately to their softening points, vigorous outgas-

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als" in *Kenchreai, Eastern Port of Corinth*, by L. Ibrahim, R. Scranton, and R. Brill, Leiden, the Netherlands: E. J. Brill, 1976, pp. 225–255.

17. On something of a tangent, there are intriguing comparisons to be made among three of the red opaques listed in Table 1: No. 3223, an Egyptian inlay head probably dating to the 7th–5th centuries B.C. (but possibly earlier); No. 706, one of the Hasanlu fused mosaic beakers, ca. 850 B.C.; and No. 198, a chunk of glass from Persepolis, 5th century B.C. The Hasanlu beaker is a low-leaded glass containing 2.83% PbO, while the Egyptian head contains only a trace ~0.02% of lead. Subtracting out the additives (normalizing $SiO_2$ + $Na_2O$ + CaO + $K_2O$ + MgO + $Al_2O_3$ to 100%) yields very similar natron-type base glass compositions. Lead-isotope analyses of the lead in both glasses (even though the lead in the inlay head is only a trace impurity) show that the leads are nearly identical isotopically. Moreover they are of a type found in other Mesopotamian and Iranian artifacts and in later Egyptian glasses. The Persepolis glass, a plant-ash type, contains 11.0% PbO, and its lead is an isotopic match with the others.

18. At the Herat glass factory in Afghanistan in 1977, this is exactly the way the glassmakers added copper to their glasses as a blue colorant.

19. See, for example, Robert H. Brill, Stephen S. C. Tong, I. Lynus Barnes, Emile C. Joel, and Martin J. Murtagh, "Laboratory Studies of Some European Artifacts Excavated on San Salvador Island," *Proceedings, First San Salvador Conference, Columbus and His World*, College Center of the Finger Lakes, Bahamian Field Station, 1987, pp. 247–292; and Brill [note 3].

sing took place and the glasses frothed up. Clearly, either they were saturated with dissolved gases (at much higher concentrations than ordinary glasses) or else rapid and extensive redox reactions occurred.

Another point of technological interest arises here. The presence of tin has traditionally been thought to aid in the development of red opaque colors. It is possible that this fact was discovered in ancient times, but it is more likely that the presence of tin was just fortuitous, having been introduced through colorants derived from bronzes. In fact, in our own experimental melts, we had just as good luck preparing red opaques without tin, regardless of what other variables were introduced.[20]

*Experimental Melts*

As alluded to above, there is also a bright orange opaque variant of the red opaques. Examples are found among Egyptian glasses from the 6th century B.C. onward (and probably earlier), among Hellenistic and Roman glasses, and, in abundance, among Byzantine mosaic tesserae. The color often shades toward a bright orangy yellow and, less commonly, toward a reddish orange.

The chemical compositions of the red and orange opaques seem to be indistinguishable, and the orange glasses we have analyzed are heavily leaded. The two most probable explanations of the color difference between the glasses are either that the orange glasses contain finer-grained particles of $Cu_2O$ or that the crystallites in the two glasses have different morphologies. (Another possibility might be the coprecipitation of other metals or metalloids in the colorant phase.) In any event, the visible spectrum of cuprous oxide is known to be complex and to contain both yellow and red continua as well as a series of yellow peaks.

Over the years, one of the authors (R.H.B.) has carried out occasional experiments on red and orange opaques, using both specimens of ancient glasses and experimental melts. These experiments have included X-ray diffraction, scanning electron microscopy, gradient furnace heating, reflectance spectra measurements, and individual crucible remelts. They do not at all constitute a comprehensive study of the subject, but we are reporting some of the findings here because they might serve as a starting point for other investigators wishing to pursue the subject more systematically.

From numerous microscopic examinations of both ancient examples and experimental melts, there can be little doubt but that the opacifying phases in the orange glasses are usually much finer-grained than those in the red glasses. Barely resolvable at 100X, and not easily seen at 500X, the shapes of the individual yellowish orange crystallites are not discernible by light microscopy. Even by scanning electron microscopy, the shapes of the particles of the major phase are not well defined, but they are clearly of submicron dimensions.

These micrographs also showed a minor phase of fine particles which we took to be metallic copper. In the red glasses, the crystallites are markedly larger. Moreover, there is a difference—at least a superficial difference—in morphology. The smallest particles in the red glasses are about 5–10 microns across. They are bright red, and one can almost see cubic or octahedral forms in this phase. Some aggregate into rods and long, straight filaments. The rods develop perpendicular branches and generate dendritic forms. In other dense red glasses, the major phase consists of stubby fern-like crystal growths radiating from nuclei. (Our crystallographer friends have described these as spherulitic dendrites or radiated stellate clusters.) These seem to be orange along the "spines" of the growths, but noticeably redder in the spreading "leaves." As the fern-like clusters grow, they take on a stronger red color.

Microscopic examinations give one the distinct impression that the transition from a bulk orangy yellow color to orange to red is accompanied by a progressive growth of crystallites and the onset of increasingly better-defined dendritic structures. This impression is borne out by gradient furnace experiments. Strips of an experimental glass, hav-

20. This may not, however, be true of copper rubies, where tin apparently can play a crucial role.

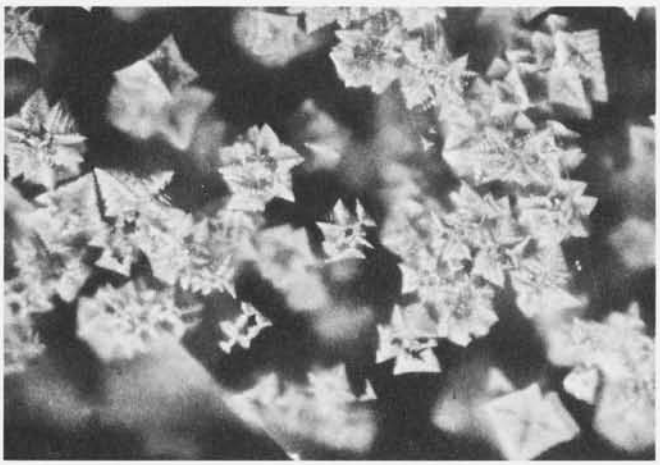

FIG. 1. *Photomicrograph of cuprite crystals grown in synthetic glass with composition resembling Nimrud red opaque (No. 200). Soaked at 1050°C for six hours. Largest cluster is about 1.0 mm across.*

ing a composition approximating that of the Nimrud red opaque cullet (No. 200), were remelted in platinum boats and placed in a furnace with a temperature gradient of 500° to 1150°C running along the boat. They were left in the furnace to soak for 16 hours in a reducing atmosphere. Other experiments using different times and gradients were also run. The resulting glasses were removed from the boats, and ground and polished.

In general, for high-copper, high-lead glasses, the colorant-opacifier phases precipitated out over a temperature range of about 550° to 750°C. At the lower temperature end, the colorant phase showed a yellowish orange bulk color, and at the higher temperature end, a red opaque. The yellowish glass contained a fine-grained phase, while the red glass contained dendritic formations. The largest dendritic clusters were about 0.6 mm across, but some linear aggregates of bright red crystallites with short perpendicular branches were some 2.5 mm long. The most dense bulk red color occurred at about 650°C. (See Fig. 1.)

Separate crucible melts of a glass with the same composition produced a dense (fine-grained) orange color when heated under reducing conditions for 16 hours at 550°C. The same experiment carried out at 700°C produced a dense (dendritic) red color. When strips of glass already colored orange, but not remelted, were heated in the gradient boat, they developed a dense red color as the fine-grained orange phase was transformed into a dendritic red phase. The largest red dendrites occurred at about 1020°C. In several instances where prolonged heat treatments were used, larger dendritic crystals, surrounded by zones of transparent glass, were found among fields of fine-grained orange particles. The dendrites had clearly grown at the expense of the smaller crystallites, which had gone into solution as a consequence of the heat treatment.

In several of our experimental glasses, the red color of some patches of the dendritic growths was enhanced by small surrounding zones of a transparent copper ruby glass, although that does not seem to be true in all examples examined.

X-ray diffraction patterns of several samples from ancient glasses and from experimental melts did reveal a somewhat unexpected result. Whereas all the glasses showed identical major patterns of $Cu_2O$, most of the orange glasses also contained metallic copper.

### *Chemical Analysis of the Sardis Red Opaque*

With all of the above information in mind, we had anticipated that two types of experiments would be useful in studying the Sardis red opaque: a quantitative chemical analysis and a lead-isotope determination. The latter can be useful for identifying the sources of lead used for making ancient objects.[21] As will be seen below, however, the Sardis glass was found to contain very little lead, and therefore it was impossible to do a lead-isotope determination. This is regrettable because lead-isotope data could have been very helpful in learning whether the glass was made at Sardis or whether it was brought there from somewhere else.

21. Most of our lead-isotope data on ancient glasses are as yet unpublished. However, some data are published in the following sources: Brill [note 6]; Robert H. Brill, "Lead Isotopes in Ancient Glass," *Annales du 4e Congrès International des "Journées Internationales du Verre"*, Ravenne-Venise, 1967, Liège, Association Internationale pour l'Histoire du Verre, 1969, pp. 255–261; Robert H. Brill, "Lead and Oxygen Isotopes in Ancient Objects," *The Impact of the Natural Sciences on Archaeology*, London: The British Academy, 1970, pp. 143–164; Brill, Barnes, and Adams [note 11]; Brill [note 16]; Brill [note 12], Part II, pp. 23–39; I. Lynus Barnes, Robert H. Brill, and Emile C. Deal,

The lack of lead in the Sardis glass shows up in its rather low density of 2.232 g/cc. By comparison, the density of the red glass in a Hellenistic bowl which contains 25.1% PbO (No. 5040 in Table 1) is 3.292 g/cc.

Quantitative chemical analyses of the major and minor components of the Sardis glass (No. 3222) were carried out by atomic absorption.[22] In addition, semiquantitative emission spectrographic analyses were used to estimate the levels of trace elements. Silica was not determined separately, but was estimated by difference from 100%. The sample contained only unweathered red opaque glass; none of the greenish weathering products were included. Two complete chemical analyses were run on samples removed from different parts of the glass submitted. The results, which were in excellent agreement with one another, are presented as a mean composition in Table 1. The cuprite colorant is present at a level of 13.4%, and antimony oxide, which is often found in red opaques, at 3.78%. There are two puzzling aspects of this composition: the low level of soda and the absence of lead.

As was remarked above, red opaques were generally prepared by adding the copper- and lead-introducing ingredients to what amounted to an ordinary soda-lime composition. The Sardis glass, however, is very low in soda, the two separate determinations showing only 0.40 and 0.31% $Na_2O$. The copper-introducing ingredient would have served, in effect, as the network-modifier of the glass, replacing the soda. It must have been present in the original batch because without it the other ingredients could not have been melted to a glass at temperatures then available to glassmakers. The composition is unusual, but it certainly produced a well-melted, homogeneous, and very nice red opaque glass. Also, because no tin was found in the glass, the glassmakers apparently used scrap copper, instead of bronze, for producing their red color in this particular glass; alternatively, a copper-containing mineral could have been used.

The fact that the Sardis sample does not contain lead is somewhat surprising. As noted above, substantial percentages of lead have been found in all the other red opaque glasses of this period which we have analyzed. (It should be kept in mind, however, that the number of these analyses is rather small.) One explanation might be that the glassmakers simply deviated from their regular practices that day. The vagaries of day-to-day procedures in a glass factory (or any other ancient technological operation, for that matter) are rarely taken into account by analysts, but they might go a long way toward explaining the puzzling little inconsistencies we sometimes uncover by chemical analyses. On the other hand, realizing how tricky the preparation of a red opaque is, it is reasonable to believe that the glassmakers would not have started out to make a red glass unless they really had everything in good working order. In light of that, it would be plausible to conclude that this unusual composition illustrates the fact that glassmakers in different regions adhered to their own traditions and had their own ways of doing things. Possibly these glassmakers had just not yet learned from others that the presence of lead helps in forming a red glass. Still another possibility, namely that the glass is much older than a Lydian date, can be all but ruled out by the archeological context.

It is hoped that continuing excavations may someday tell us more about the nature of the workshop and about the uses for which the glass was intended. One wonders, for example, if the glass represents evidence of a local glass factory, or if the glass had been brought to Sardis to be used for ornamentation of some sort, or to be resoftened for manufacturing jewelry.

*Sample Descriptions*

In the descriptions which follow, the term *bright red opaque* is used to describe the brightest blood-red color seen among early glasses. *Red opaque* indicates

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"Lead Isotope Studies of Early Chinese Glasses," *Research in Ancient Chinese Glasses; Proceedings of the International Symposium on Glass, Beijing, 1984*, ed. Gan Fuxi, Chinese Building Industry Publications, 1986, pp. 36–46.

22. Previously we had analyzed 34 samples of glass from Sardis. These have not yet been published. Because the analyses were carried out many years ago, a few will be rerun to be certain that they are in calibration with current analyses. The samples included tesserae from the Synagogue and vessels from the Byzantine shops. All were low-$K_2O$, low-MgO soda-limes.

a strong, basically red color but one which can have a slight brownish cast. *Dendritic* describes cuprite phases which can clearly be seen to be dendritic at a magnification of 40X, whereas *fine-grained* describes glasses in which dendritic formations cannot be discerned at magnifications of 100–200X.

3222

Sardis, two samples of an irregular chunk of red opaque glass; mid-6th c. B.C. Red opaque glass with thick layer of green weathering products. (Fine-grained red in patches; finer-grained orange veins.) Trench MMS–IA, 9. viii. 1982. Lot XLI: coordinates E148.3–150.2/S53.2–57.3, elevation ca. *99.60. Fieldbook MMS–1A 1982, 1, p. 61. Context is the backfill of the glass workshop belonging to 6th-c. B.C. Lydian houses, destroyed ca. 547–542 B.C. and ransacked probably soon thereafter. One piece shows flat, bubbly surface with mud brick fired onto exterior; rest of shape is rounded. Some pieces have charcoal on exterior. d = 2.232 g/cc; PbO = 0.002%.

198

Persepolis, chunk of red opaque glass, probably 5th c. B.C. Bright red opaque glass with green weathering products. (Fine-grained red.) No. PT7 380 in Frederick R. Matson, "Analyses of Various Substances," in *Persepolis*, by E. F. Schmidt, University of Chicago Press, 1957, v. 2, pp. 127–132. Sample lent by F. R. Matson. (Same as Pb-463.)

199

Persepolis, flat slab of red opaque glass with drilled hole; probably 5th c. B.C. Bright red opaque glass, moderately weathered. (Fine-grained orangy red.) No. PT7 379 in Matson [No. 198]. Sample lent by F. R. Matson. (Same as Pb-464.)

200

Nimrud, chunk of red opaque glass, thought to be 6th c. B.C., but some possibility of post-220 B.C. date. Bright red opaque glass with green weathering products. (Dendritic red.) Preserves matching curvature of shallow crucible and upper coating of charcoal or similar charred material. From Burnt Palace. See Plenderleith's and Bimson's analysis, published by W. E. S. Turner, "Studies of Ancient Glasses and Glass-Making Processes. Part II," *Journal of the Society of Glass Technology*, v. 38, October 1954, no. 184, pp. 445T–456T. Sample given to R. H. Brill by W. E. S. Turner. (Same as Pb-90.)

706

Hasanlu, fused mosaic glass beaker, ca. 850 B.C. Bright red opaque glass, heavily weathered. (Fine-grained red.) Has 64.129. Axel von Saldern, "Mosaic Glass from Hasanlu, Marlik, and Tell al-Rimah," *Journal of Glass Studies*, v. 8, 1966, pp. 9–25. Sample submitted by Robert Dyson, The University Museum, University of Pennsylvania. (Same as Pb-411).

970 and 3060 series

Kenchreai, *opus sectile* panels, ca. A.D. 360. Nine red opaque glasses (some slightly brownish), heavily weathered. (Fine-grained red.) R. H. Brill, "Scientific Studies of the Panel Materials," in *Kenchreai, Eastern Port of Corinth*, by L. Ibrahim, R. Scranton, and R. Brill, Leiden, the Netherlands: E. J. Brill, 1976, pp. 225–255.

1063

Orissa (India), "Indian red" bead, ca. A.D. 200. Orange opaque glass, heavily weathered. (Fine-grained, orange.) R. H. Brill, "Chemical Analyses of Some Early Indian Glasses," *Archaeometry of Glass, Archaeometry Session of the XIVth International Congress on Glass, New Delhi, 1986*, Calcutta: Indian Ceramic Society, 1987, Section I, pp. 1–25. Sample submitted by the late W. G. N. van der Sleen.

2373

St. Demetrius, Thessalonike, glass tessera, 9th c. Red opaque glass, some weathering. (Fine-grained red.) Sample submitted by Wanda Gaddoni of the Istituto di Antichità Ravennati e Bizantine, Ravenna.

2745

San Clemente, Rome, glass tessera, ca. 1130. Red opaque glass, lightly weathered. (Fine-grained red.) From the semi-dome of the apse. Sample submitted by Oystein Hjort, University of Oslo.

3223

Egypt, cast inlay glass head, probably mid-7th–5th c. B.C. Bright red opaque glass, with white opaque and blue opaque details, and traces of Egyptian blue in eye; heavily weathered. (Fine-grained red.) CMG 55.1.63. Sidney M. Goldstein, *Pre-Roman and Early Roman Glass in The Corning Museum of Glass*, Corning, N.Y.: the Museum, 1979, pp. 88–89, no. 161 and plate 10. (Same as Pb-1316.)

Note: This object poses some questions in that its date could be earlier. The red glass contains only a trace of lead, but lead-isotope analysis shows that it differs greatly from known 18th-Dynasty leads in glasses and kohls, resembling instead leads in Mesopotamian and Iranian glasses and other materials, and also those in later Egyptian glasses.

3224

Tara Hill, Ireland, large chunk of red opaque cullet, date uncertain. Bright red opaque glass, apparently heavily weathered. (Dendritic red.) British Museum no. 92-5-25 1. V. Ball, *Transactions of the Royal Irish Academy*, v. 30, 1893, pp. 277–281. Sample submitted by Anthony Werner. (Same as Pb-174.)

3230 series

Nimrud, group of three small glass inlays of various shapes and one piece of cullet, 7th c. B.C. Bright red opaque glasses, very heavily weathered. (Incipient dendritic red; some devitrification.) ND 6410, 10246, 5***. Jeffery J. Orchard and Robert H. Brill, "Some Miniature Glass Plaques from Fort Shalmaneser, Nimrud. Part I: Description and a Restoration; Part II: Laboratory Studies," *Iraq*, v. 40, Spring 1978, pp. 23–29. Samples submitted by Jeffery J. Orchard. (Same as Pb-400 series.)

3255

Egypt, *wedjet*-eye plaque ("miniature mosaic inlay"), probably Ptolemaic, 3rd–1st c. B.C. Very well made in six colors. Red opaque glass, moderately weathered, but with polished surfaces. CMG 59.1.96. No. 663 and plate 32 in Goldstein [No. 3223]. R. H. Brill and S. Moll, "The Electron-Beam Probe Microanalysis of Ancient Glasses," *Recent Advances in Conservation*, London: Butterworth, 1963, pp. 145–151; R. H. Brill and S. Moll, "The Electron-Beam Probe Microanalysis of Ancient Glasses," *Advances in Glass Technology: Part 2*, New York: Plenum Press, 1963, pp. 293–302; R. H. Brill, "Lead Isotopes in Ancient Glass," *Annales du 4e Congrès International des "Journées Internationales du Verre"*, Ravenne-Venise, 1967, Liège, Association Internationale pour l'Histoire du Verre, 1969, pp. 255–261. (Same as Pb-171.) This sample is of some historical interest because it was among the first group of glasses of *any* sort analyzed by an electron microprobe. The analyses were performed in 1960 and were subject to certain errors, such as matrix effects and volatilization, which have since been corrected. The data reported here (averages of seven analyses) are more accurate and more precise than the earlier analyses. This analysis was carried out by Dr. Stephen S. C. Tong of Corning Glass Works.

3355

Tell el Amarna, cane of red opaque glass, 18th Dynasty. Red (slightly brownish) opaque glass, unweathered. (Fine-grained red, but thin, not dense.) Sample submitted by Barbara Adams, Department of Egyptology, University College, London.

5040

Bowl fragment, Eastern Mediterranean, possibly 3rd–2nd century B.C. Bright red opaque glass, moderately weathered. (Fine-grained red.) CMG 59.1.86. Goldstein [No. 3223], p. 135, no. 278 and plate 37. d = 3.292 g/cc.

5420

Hasanlu, small chunk of irregularly shaped red opaque glass, possibly an artifact, 1000–800 B.C. Bright red opaque glass with green weathering crust and frothy surface. (Fine-grained red.) From Has C 31 4, a group of glass beads. Sample submitted by Maude de Schauensee, The University Museum, University of Pennsylvania. (Same as Pb-2138.)