Brill, R. H. "Scientific Research in Early Asian Glass." Proceedings of XVII International Congress on Glass, v. 1, Invited Lectures. Beijing: Chinese Ceramic Society, 1995, pp. 270-279.

SCIENTIFIC RESEARCH IN EARLY ASIAN GLASS

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Introduction

Except for the pioneering work of a few archaeological chemists like Prof. Kazuo Yamasaki, serious scientific research on the ancient glass of Asia began only about fifteen years ago. At the 1984 International Symposium on Glass in Beijing, several sessions were devoted to scientific investigations of ancient Chinese glass [1], and since then, in addition to work on Chinese and Japanese glass, research on Asian glass in general has flourished. Analyses of Korean glasses have been published [2] and analyses of glasses excavated in Southeast Asia, India, and Central Asia were reported at subsequent TC-17 symposia in New Delhi (1986) and St. Petersburg (1989) [3, 4]. In this paper, some recent findings are reported along with illustrations of the usefulness of chemical analysis and lead isotope analysis. A few specific examples have been selected of objects in collections that participants in this Congress might see if they visit museums during their stay in China. Wherever mentioned here, the museums are set in boldface type.

In the Introduction to the publication of the 1984 Symposium [1] a number of questions regarding early Chinese glass were raised. Interested readers might like to refer to that list to check progress that has been made in this field since then. One question, centering around beads excavated in Baoji and Fufeng Country, has now been settled. (The beads are presently housed in the **Baoji City Museum** and the **Zhouyan Museum**.) It was once thought that these beads, dating from the 11th–10th c. B.C., were the earliest glass found in China. However, it turned out that they are actually made of faience, not glass. Nevertheless, the beads are extremely important archaeologically, because faience is but rarely found in China and they therefore are evidence of very early trade contacts with civilizations in the Near East or Central Asia [5, 6, 7].

Perhaps the most important archaeological finds of glass in China since the 1984 Symposium are the objects discovered in the crypt beneath the **Famensi**, a rebuilt pagoda about three hours drive west of Xian. Sealed in the crypt in 874 with magnificent metals, porcelains, silks, and relics, were

several scratch-decorated dishes, a luster bowl, and assorted other vessels [8, 9]. The glasses are probably imports, most likely from near Nishapur.

Chemical Compositions of Asian Glasses

The heavily-leaded Chinese glasses of the Warring States Period (475–221 B.C.) and Han Dynasties (206 B.C.–220 A.D.) are well-known [1]. Many, but not all, also contain substantial levels of barium. That they were made in China has been verified by lead-isotope analysis [1]. Some such glasses excavated in Japan and Korea were made in China, but other pieces of early Japanese and Korean glasses were made locally [2, 10]. There are several examples of $PbO:BaO:SiO_2$ glasses in the **Chinese History Museum** in Beijing. In fact, most of the eyebeads, "ear spools", and *bi* disks displayed in museums in China have high-lead compositions.

However, other compositional families have also emerged among Asian glasses. These have been discussed elsewhere at this Congress [11]. A few examples are shown here in Table 1, and Fig. 1 summarizes the geographical distributions as they are presently known. The new families are useful for classifying Asian glasses according to when and where they were made, and thus should help us someday to understand better the evolution of glassmaking throughout Asia. Undoubtedly, many hypotheses about these families will be stated in the future and proven and restated—only to be replaced by newer ones before we have a complete picture. But that is part of the excitement of this field: almost every group of analyses someone does teaches us something new about Asian glass.

(1) Potash:Silica Glasses ($K_2O:SiO_2$)

Shi Meiguang and his colleagues were among the first to have recognized the importance of potash:silica glasses to the study of Chinese glass[12]. The glasses are interesting not just because they seem to have been made only in Asia and India, and only for a relatively short period of time (ca. 2nd c. B.C.–4th c.), but also because they pose questions related to their physical properties and possible batch materials.

The mean composition in Table 1 might appear to be a glass of rather poor durability. With about 16% potash (10.8 mole percent) and about 1.5% lime (1.6 mole percent), only the alumina (1.5 mole percent) would seem to offer any protection against weathering. Therefore, it is somewhat suprising that the archaeological specimens recovered are in rather good condition. But realizing that looks can sometimes be deceiving, nine ancient $K_2O:SiO_2$ beads and fragments were heated at 125° for two hours. None were noticeably weathered at the outset, but after being heated, three of the glasses became severely crizzled, two were moderately crizzled, and only

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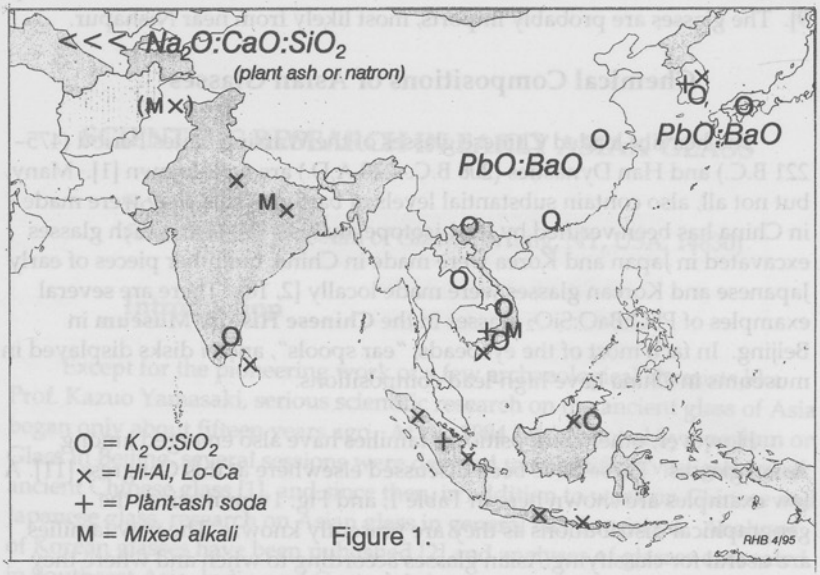

Figure 1.

Table 1. COMPOSITIONS OF SOME ASIAN GLASSES **

	$K_2O:SiO_2$†	High-alumina† low-lime	Arikamedu 6300–21		Han Dyn. beads†† 6382–91		Cup††† 5770
SiO_2*	78.2	67.0	78.0	71.6	77.5	79.5	76.8
Na_2O*	0.66	17.2	0.51	13.7	0.55	0.73	0.68
CaO*	1.41	2.78	1.94	3.96	1.10	1.12	0.94
K_2O*	15.6	2.19	15.6	3.46	16.2	15.4	14.9
MgO*	0.36	0.85	0.41	1.72	0.36	0.33	0.37
Al_2O_3*	2.36	8.18	2.08	4.03	2.86	2.20	3.41
Fe_2O_3*	1.33	1.85	1.52	1.51	1.40	0.77	0.92
TiO_2	0.14	0.53	0.15	0.25	0.16	0.13	0.27
MnO	1.31	0.088	1.60	0.13 [5]	1.44	1.43	0.15
CuO	0.043	–	0.02	1.81 [4]	0.097	0.038	0.01
CoO	0.063 [21]	0.01 [5]	0.10 [4]	nd	0.050	0.045	nd
PbO	0.036 [25]	0.15 [23]	0.03 [4]	0.03	0.66	0.04	0.09
P_2O_5	0.18	0.11	0.27	0.64	0.18	0.16	0.12
(n)	(32)	(34)	(6)	(6)	(5)	(5)	

** In wt. %.

* For first seven oxides original data were normalized to 100% before calculating means. (Exception: 5770 are raw data.)

† Means calculated from archaeological specimens. See Refs. 11 and 16.

†† Based on quantitative analyses, the mean MnO/CoO ratio is 30.2.

††† Cup belonging to W. H. Shorenstein. Electron microprobe analysis by D. Lange; XRF by J. Carlson. Also contains: 0.11% Sb_2O_5; 0.09% SnO_2.

(n) Number of samples used for calculating means. [ ] Partial calculations excluding intentional additives or including intentional CoO only. For 90% C.L. see Ref. 11.

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four showed little or no change in surface appearance. Clearly then, many of these glasses suffer from incipient crizzling [13]; they have taken up moisture without showing visible signs of alteration, but become crizzled upon dehydration. Their hydration rims are about 0.2 mm thick.

Strings of both purple and dark blue Han Dynasty potash:silica beads are on exhibition in the **Municipal Museum in Guangzhou**, where they have been studied by Mai Yinghao. The beads are very similar to those mentioned above and to some referred to later on in this paper.

With a softening point of about 645° C, most of these $K_2O:SiO_2$ glasses are somewhat softer than typical Roman and Islamic soda-lime glasses which generally have softening points between about 690° and 735°. Elizabeth Brill, a flameworker who makes beads, reported that a synthetic glass approximating the composition in Table 1 is a bit more difficult to work than commercial canes commonly used today. The synthetic glass behaves more like borosilicate laboratory tubing. Elton Harris, of Corning, Inc., melted the glass. He reported that even at 1500°C, a batch containing alkali in the form of carbonates reacted sluggishly. Glassmakers in ancient times probably would have had difficulty making these glasses if they used plant ashes as their source of alkali. From the analyses it is clear that the alkali must have been rather pure—by ancient standards. If it was a plant ash, as opposed to a natural mineral or evaporite, it must have been purified. There is, in fact, evidence that early unleaded Chinese glasses were made from leached potash or saltpeter. In connection with the potash:silica glasses, TC-17 members might undertake analyses of ashes of rice plants grown under different conditions.

The densities and refractive indices of the $K_2O:SiO_2$ glasses are somewhat lower than those of most ancient soda-limes. Thus, it might be possible to identify objects or fragments made of such glasses by non-sampling techniques or by sacrificing only minute chips of the glass.

The mean index of ten ancient $K_2O:SiO_2$ glasses analyzed recently is 1.492, with a range of 1.478 to 1.506. The upper limit lies just below the lower limit of indices of most ancient soda-limes. They range from about 1.516 to 1.524. Thus, if an index can be measured for an unknown object or fragment of historical interest, one might, with a bit of luck, be able to distinguish between a potash:silica glass and ordinary ancient soda-limes.

The densities of most ancient soda-limes average about 2.52 g/cc, with expected ranges of perhaps 2.47 to 2.58. Our experience has been that potash:silica glasses are lower, averaging perhaps 2.37 g/cc and usually not exceeding about 2.42. Thus, by weighing an object in air and water (where

the circumstances and condition of the object will safely permit that) one has a good chance of distinguishing between potash:silica and soda:lime compositions. However, this will not work if the glass is hollow or particularly bubbly, or if its shape precludes getting useable measurements.

The method was applied to an unusual Han Dynasty glass spearhead at the **Hunan Province Museum** in Changsha. The object was published by Xiong Zhuanxin [1, Chap. 17]. Its specific gravity is 2.36, indicating that it is probably a potash:silica glass—an indication that makes good sense to this author, judging from the object's appearance and "feel". The museum contains other interesting glasses as well.

(2) High-Alumina Low-Lime Glasses

Another chemical family consists of soda glasses that are high in alumina ($Al_2O_3 \geq 4\%$), relatively low in lime ($CaO \leq 4\%$), and higher than most ancient glasses in titania ($TiO_2 \geq 0.4\%$) [11, 14]. Such glasses were made in India from perhaps the 2nd c. B.C. to the 9th c., but not elsewhere, as far is known at present. Examples have been found not only throughout India but also throughout Southeast Asia. They have been found as far eastward as Korea, where tiny seed beads with this composition were excavated in the tomb of King Muryung dated to the first half of the 6th c. [2]. These particular beads are among the smallest we have ever seen, some measuring not greater than 1.0 mm in diameter. Towards the west, one of eight glasses analyzed from the site of Jenné-jeno in Mali has this same high-alumina low-lime composition [15]. It is a cylindrical drawn bead dated by the excavators, R. J. and S. K. McIntosh, to 900–1500. Apparently, it traveled more than 5000 mi over maritime and caravan routes—or simply through fortuitous meandering—ending up in the Inland Niger Delta in West Africa. Even more astonishingly, one of the other Jenné-jeno glasses, a medium-sized dark blue bead, turned out to be a potash:silica glass. It seems to have made a similar journey over 2000 years ago.

Among the newest analyses from Southeast Asia are those of 53 glasses (mostly beads) collected by Dezsö Benedek. The glasses came from several sites covering a wide range of dates. As expected, the compositions varied considerably [11]. It is difficult enough to define, much less obtain, a "representative sampling" from sites where thousands of beads are uncovered. Nevertheless, findings for small groups of beads can still be enlightening. Thirteen of the beads from Oc Eo have the typical "Indian" high-alumina low-lime composition. These beads, though not well-dated, are thought to be of the late 1st millennium B.C. Three seed beads from another site, Thi Xi, proved to be potash:silica glasses. These had been recovered by the excavator, N. T. Ky, from a bronze drum that had rolled out of a sandy embankment on the River Ha. From the other contents of the

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drum, the beads are estimated to date from the 1st c. Thus, examples of two families of glasses—potash:silica and high-alumina low-lime—had been found. Lead isotope analyses of seven of the same glasses (the lead having been introduced with colorant additives) showed that all contained the same isotopic type of lead [16], indicating that the lead in the colorants almost certainly had a common origin, and that the glasses themselves, in all probability, had been made nearby one another. As will be seen below, the lead-isotope trail, as well as the chemical trail, seems to be backtracking towards India as the place where these particular beads were made.

(3) Arikamedu

Arikamedu, near the southern tip of India, was probably not the only place in India where glass was made in ancient times (or at least formed into objects), but it is the best known. It has a long-standing reputation as a bead making center. At the TC-17 meeting in New Delhi, E. M. Stern gave the author a selection of small pieces of cullet and glassmaking waste for chemical analysis [17, 18]. We have completed chemical analyses of 22 samples of various colors and several lead-isotope analyses. Table 1 gives mean chemical compositions for this small sampling of Arikamedu glasses.

Of the samples analyzed, nine were found to be potash:silica glasses, three high-alumina low-lime glasses, six high-alumina, but moderate-lime glasses, and four were strays. Of all the samples, only one—a piece of a light blue opaque plate [18, Fig. 6.8]—is definitely a western import. It is a natron type soda-lime containing 7.7% Sb_2O_5. (Two other glasses are borderline possibilities.) All the rest were well-defined chemical types known from India, but unknown in the West. It should be noted, too, that B. B. Lal reported analyses of Arikamedu glasses that have potash:silica compositions [19]. Although his CaO, Na_2O, and MgO values are higher than those in Table 1, there can be but little doubt that he was dealing with the same kind of glass.

These few samples cannot necessarily be assumed to be representative of the numerous glass finds on the site, but they do serve to reenforce the view that locally-made (or regionally-made) glass was being worked nearby. Moreover, these analyses suggest rather strongly that Arikamedu was one of those easterly glassmaking centers—roughly contemporaneous with the soda-based Hellenistic, Roman, and Sasanian centers—where potash:silica glasses were made. If that turns out to be true, the question would still remain as to whether or not all the potash:silica glasses of the time were made in India. We are inclined to believe that at least in later times, such glasses were made in more than one place from India eastward.

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Although much attention has been paid to Arikamedu as a bead making center, not much has been said about the prospects that glass vessels might also have been made there. This is understandable, because relevant archaeological evidence is scarce—except for one intriguing fragment. This is a fragment of a small cup excavated by Sir Mortimer Wheeler[20]. Having been found with what appears to be a part of a typical Roman ribbed bowl, this piece has also been presumed to have had a western origin. A careful look at Wheeler's drawing, however, suggests that that may not be the case

Potash:Silica Glasses Found in China

In **The Chinese History Museum** in Beijing is a small aqua cup found in a Han Dynasty tomb in Guangxi Province [21] (Fig. 2). Because it does not have a traditional Chinese shape, and because it is not a lead glass, the object has generally been considered to be an import. However, it differs from its supposed Hellenistic and Roman parallels in several subtle ways. It was made by turning a blown blank on a lathe-like tool, has a ground and polished rim, and has a raised horizontal ridge around its waist. Cut grooves on the ridge create a notched appearance in profile. Two other glass vessels excavated in China have similar notched ridges [22].

Recently Walter Shorenstein acquired a small, bluish-aqua cup (Fig. 3) that has all the same features as the piece described above. In addition, the quality of the glass and its imperfections are also the same. Having examined both objects very carefully, this author is convinced that neither is "Western", and that they are so closely related, that they could well have been made in the same workshop.

A quantitative electron microprobe analysis of Mr. Shorenstein's cup by David Lange of Harvard University, showed that it is a potash:silica glass (no. 5770 in Table 1). The glass also contains small amounts of lead, antimony, and tin. On its base is a greenish encrustation of foreign matter that proved to be $Cu_2(CO_3)(OH)_2$, a known corrosion product of bronze. A lead-isotope analysis of the encrustation showed that it contains lead with isotope ratios matching those in Han Dynasty glasses [1]. If that foreign matter is ancient, perhaps the cup had rested for centuries on a bronze artifact (possibly even a stand made for the cup itself). The isotopic match would then verify its Chinese association.

As was the case with the beads in Guangzhou, none of this tells us where the potash:silica glass vessels were made. They could have been made in China; or they could have been imported—if so, most likely through some port in southern China. Until new archaeological evidence is forthcoming, there is still plenty of room for all sorts of theories.

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Fig. 2. Cup excavated in Guangxi.

Fig. 3. W. H. Shorenstein's cup (CMG 5770).

Having no where else to turn, our attention is drawn back to Arikamedu. Wheeler's published drawing and photograph of the fragment described above lead us to believe that the Guangxi cup, Mr. Shorenstein's cup, and the Wheeler cup are all the same breed of cats. All are roughly contemporaneous. They share physical features that are distinctly different from Western glasses, and perhaps they share a chemical composition unique to Asia. Mr. Shorenstein's cup is definitely a potash:silica glass; the Guangxi cup probably is; and the Arikamedu fragment was found in a place where potash:silica glasses are believed to have been worked and might have been made. We would love to analyze that Arikamedu fragment to see if it, too, is a potash:silica glass, but unfortunately, according to Marianne Stern, it has mysteriously dropped out of sight [23].

Lead-Isotope Analyses of Some Potash:Silica Glasses

Having at our disposal suitable samples of potash:silica glasses that contain various levels of lead, it seemed worthwhile to run lead-isotope analyses to see if that would yield any clues as to where the glasses had been made. Therefore, a selection of samples is being analyzed by Robert D. Vocke, Jr. at the National Institute of Standards and Technology. Some of the glasses came from Arikamedu while the others were dark blue Han Dynasty beads from Jiangsu Province. Five of the Arikamedu samples contained lead in the form of $PbSnO_3$, a yellow colorant-opacifier; seven contained trace levels of lead (~ 0.05% PbO). All but one were either potash:silica or high-alumina low-lime glasses of chemical types associated with India. The remaining sample was the natron type blue plate from Arikamedu, containing $Ca_2Sb_2O_7$ and 7.7% PbO. The ten Chinese beads were potash:silica glasses. Seven had only traces of lead (~ 0.05% PbO) believed to have come in with the cobalt and the other three had about 1.0% PbO thought to be associated with copper colorants derived from bronzes.

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The analyses are still underway as this paper is being written, but some early data are plotted in Fig. 4. They cover a very wide isotopic range. The leads in the opacifiers of the Arikamedu yellow opaques have much higher ratios than the two trace leads accompanying the cobalt colorant. A single uncolored glass containing only traces of lead lies in the extreme lower left corner. Sample no. 5770 is mentioned above in the text.

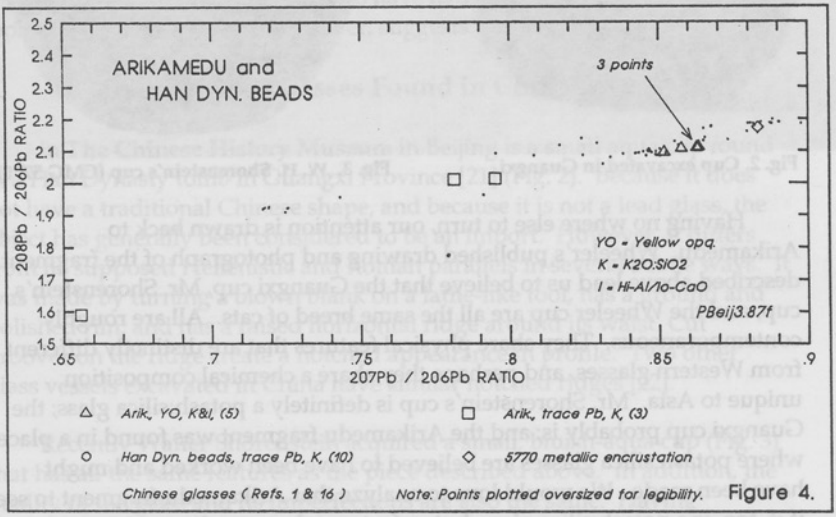
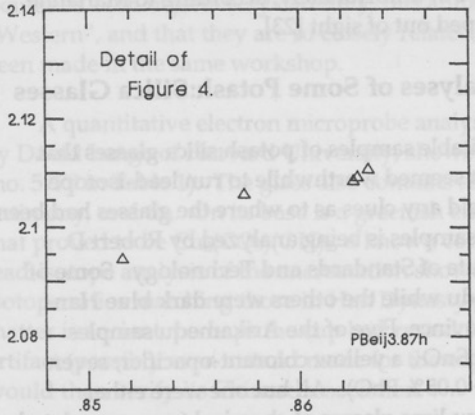


Figure 4.



The rest of the findings will be reported at the Congress. They will include several more Arikamedu leads and the Han Dynasty beads. We hope this will shed some light on the question of whether or not the potash:silica beads and vessels that were found in China were actually made there.

Acknowledgements

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