Chapter 2. Scientific Study and Conservation Treatment of Artifacts Excavated from Krang Kor

Tomomi Tamura
Center for Archaeological Operations,Nara National Research Institute for Cultural Properties

1. Glass Beads

An excavation survey conducted at the Krang Kor Ruins located in Kampong Chhnang Province in the suburb of Phnom Penh, Cambodia yielded numerous glass beads. Based on the understanding that acquiring information on bead-making technique and chemical compositions is indispensable to studying the production areas and distribution routes of glass artifacts, we launched an examination of the bead-making technique, glass system, and colorant of the excavated glass beads using analytical methods.

(1) Materials and method

The examination was conducted on 10 glass beads from among 118 that were excavated during the third excavation survey at the Krang Kor site. The 10 beads included 8 opaque light blue beads with relatively good preservation conditions (Nos. 13, 17, 21, 26, 37, 38, 40, 52); 1 pale yellowish-white bead that is heavily weathered (No. 5); and 1 bead showing an alternating pattern of opaque light blue stripes and white weathered stripes (No. 12).

The bead-making technique was estimated by observation through a stereo microscope. Then, the density of a number of the more well-preserved beads was measured using Archimedes' principle, and their glass system and coloring factor were estimated by nondestructive surface analysis based on X-ray fluorescence analysis. The nondestructive measuring method is not effective for identifying the original chemical composition of materials that are weathered or have distinct shapes, but it can estimate glass system and coloring factor. The measurement results were standardized according to a fundamental parameter (FP) method using standard glass samples and displayed in terms of oxide weight percentages. The measurement was conducted in a vacuum using an energy dispersive X-ray fluorescence analyzer (EAGLEIII manufactured by EDAX) under the following specifications: X-ray target. Mo, voltage. 20/50 kV, current. 100 µA, time. 300 seconds.

(2) Results

Bead making technique

Judging by the etch streaks running in perpendicular direction to the hole and the small projection at the end that looks to be the beginning or end of a spiral coil, we believe the beads were made by winding a heat softened string-like glass two, three times around a rod (Fig 1). Bead No. 5 is entirely pale yellowish-white in color due to severe weathering, but we assume it was made according to the same coiling method, as it displays faint traces of etch streaks running perpendicular to the hole.

Glass system

According to X-ray fluorescence analysis, the beads, excluding Nos. 5 and 12 which were severely weathered, are chemically composed of 29.1 – 36.6% PbO, 7.04 – 10.8% K_2O, and 49.3 – 51.6% SiO_2. This means that the beads are made of potassium lead glass.

The severely weathered No. 12 bead contains 30.1% PbO and 5.6% K_2O, so we assume it is also made of potassium lead glass as the above beads that were found in relatively good condition. The slightly lower K_2O content is probably due to weathering, as potassium lead glass is known to have reduced levels of K_2O in surface layers as an effect of weathering (Koezuka 1997).

Bead No. 5 is the most severely weathered among all other beads. It contains 20.3% PbO but an extremely small amount of K_2O, probably for the same reason as mentioned above. The possibility of its being a lead glass not including K_2O was considered, but in the case of a two-component lead glass, the weathered surface should normally have a significantly high PbO level and a largely reduced SiO_2 level. However, since the bead in question has only a small amount of PbO and a large amount of SiO_2 compared to the other beads, it seems more likely that it is made of potassium lead glass that originally contained a certain amount of K_2O.

Coloring factor

All of the beads are an opaque, light blue color, excluding Bead No. 5 whose original color cannot be confirmed. The color apparently comes from their color-related content of 0.14 – 0.29% Fe_2O_3 and 0.43 – 0.81% CuO. However, it is difficult to know whether Fe_2O_3 was intentionally added as a coloring agent, because Fe_2O_3 is also found in quartz sand, the raw material of basic glass. The beads also characteristically contain around 0.1% of ZnO, which is seen as an impurity associated with the copper material that was added as a coloring agent.

The source of the opaqueness was difficult to identify. However, where transparent potassium lead glass typically contains less than 1% Na_2O and CaO, the beads in question had from 2 to 4%, so these components may have some bearing on producing the opaqueness.

Bead No. 5 contained a rather larger amount of Fe_2O_3 and a rather smaller amount of CuO compared to the other beads. In regard to Fe_2O_3, it has been noted that large amounts of iron adsorb to substances that are derived by weathering in cases where the artifact has been buried in an iron-rich environment. Taking this into consideration, Bead No. 5 may have exhibited a higher level of Fe_2O_3 content than usual because soil in Cambodia is mainly composed of eluvium such as iron and aluminum. CuO, on the other hand, is known to largely remain constant, although it may increase slightly on weathered surfaces, so Bead No. 5 probably contained only a small amount of CuO to begin with. Similarly, CaO content, which is also said to remain relatively constant even with the effect of weathering, is low. When taking all of the above into consideration, it is possible that the color of Bead No. 5 originally differed from the other glass beads.

(3) Discussion

All conditions indicate that the glass beads excavated from the Krang Kor site are potassium lead glass made by coiling method, and potassium lead glass is known to have existed in China at least from the Song Period (An 1984).

In the Southeast Asian region, including Cambodia, glass beads called Indo-Pacific Beads, which were made by drawing method, were widely traded between the 3rd century BC and the 17th century AD. Most of these beads were made of alkali silicate glass. Meanwhile, glass beads that were made by coiling method are called Chinese Coil Beads, and are said to have been introduced from China around the 12th century (Francis 2002). Therefore, the recent discovery of potassium lead glass beads at the Krang Kor site provides important insight into relationships that existed during this period.

Chinese potassium lead glass was also introduced to Japan, but the lead isotope ratios for potassium lead glass in Japan around the 12th century revealed in most case a similar composition with that of lead ore of the Taishu mine in Japan. Similarly, the original production region of the glass beads excavated at the Krang Kor site also needs to be ascertained in future. Since there are few data on the analysis of glass beads that circulated throughout Southeast Asia during the Middle Ages, we feel we have been able to provide valuable information in this regard.

Reference

An Jia Yao 安家瑶 . 1984, *Chugoku Souki Hari Kibei*. 中国早期玻璃器皿 Goukogakuhou. 考古学報

Francis, P. 2002 *Asia's Maritime Bead Trade*. University of Hawaii Press

Koezuka, T. 1997 *Nihon de shutudoshita Kodai Garas no Rekishiteki Hensen ni Kansuru Kagakuteki Kenkyu*. Ph.D. Dissertation. In Japanese

<Supplementary Discussion>

In our study, we also examined glass beads that were collected from around the Krang Kor site, as discussed below.

The beads that were examined included 4 opaque yellow beads (Nos. 1 – 4), 2 opaque light blue beads (Nos. 5 – 6), and 1 transparent, reddish-brown bead (No. 7).

All seem to be made by the coiling method. However, while all beads except for Bead No. 1 seem to be made by coiling a softened string-like glass one to two times around a central rod and have an unpolished surface, Bead No. 1 seems to be made by coiling the glass a larger number of times around a central rod and has a polished surface (Fig. 2).

The basic glass type appears to be potassium lead glass for all of the beads. Compared to typical potassium lead glass, however, these beads have smaller amounts of K_2O despite the fact that they are in good condition. They can therefore be said to have a slightly unique composition.

The opaque yellow color of Beads Nos. 1 to 4 seem to come from artificial yellow pigment $PbSnO_3$, since prominent traces of Sn were detected from these beads, and also because a spectrum indicating the characteristics of $PbSnO_3$ was obtained in a Raman spectroscopic analysis of Bead No. 2. This coloring technique was used to make Indo-Pacific Beads since before 1 BC. However, no examples of this coloring technique have been found in potassium lead glass in China and Japan. The original production region of these beads should be investigated in future.

The opaque light blue color of Beads Nos. 5 and 6 seems to come from copper ion. However, unlike the earlier-mentioned beads excavated from the Krang Kor site, no Zn content was detected, so a different copper material may have been used as the coloring agent. Additionally, the beads contain around 2% Na_2O and CaO, so it is possible that these components have some bearing on their opaqueness.

The transparent reddish-brown Bead No. 7 hardly contains any components related to coloring, but it has a 0.35% content of CuO. It is possible that the color comes from metal copper colloid.

These glass beads are made by the same bead-making technique using the same type of glass as those excavated from the Krang Kor site, but they differ in size, shape, and coloring. These differences may perhaps be attributable to the time or place of their production, or to both.

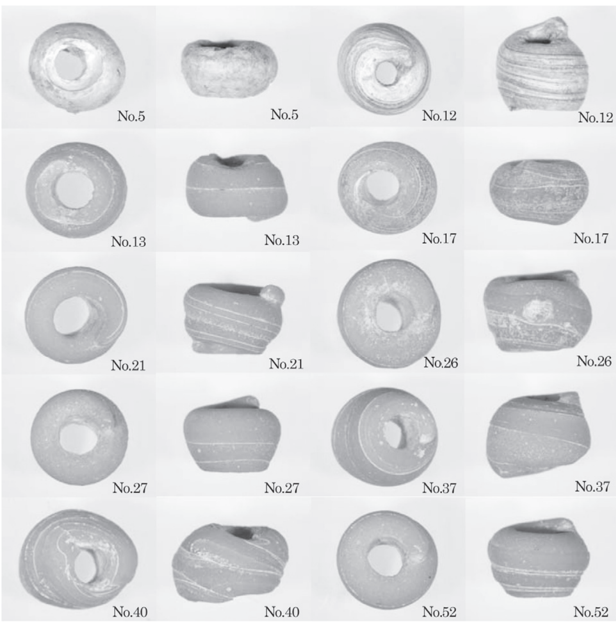

Fig.1 Glass beads excavated from Burial No.1

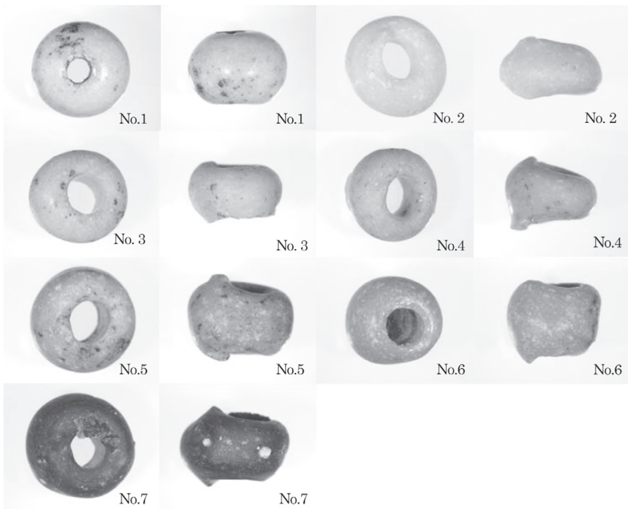

Fig.2 Glass beads from surface collection

Sample No.	Color	Density	Chemical composition (wt%)																	Notes
			Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CuO	ZnO	PbO	Rb_2O	SrO	ZrO_2	SnO_2	
5	White opaque		0.39	0.38	4.52	71.2	1.42	0.07	0.63	0.1	-	0.59	0.19	0.03	20.3	-	0.03	0.09	tr	Heavily weathered
12	Light blue opaque / white opaque marble		0.89	0.34	1.16	58.6	0.28	5.6	2.38	0.02	-	0.14	0.43	0.08	30.1	-	0.05	-	tr	Weathered
13	Light blue opaque	3.4	2.31	0.27	0.92	51.6	-	10.3	3.88	0.02	-	0.27	0.79	0.14	29.2	-	0.12	0.15	tr	
17	Light blue opaque		2.64	0.35	0.57	49.3	-	7.04	2.64	0.02	-	0.14	0.48	0.09	36.6	-	0.09	0.04	tr	
21	Light blue opaque	3.4	2.22	0.22	0.75	50.5	-	10.5	3.92	0.01	-	0.28	0.8	0.13	30.4	-	0.05	0.19	tr	
26	Light blue opaque	3.3	2.13	0.14	0.66	50.9	-	10.6	3.94	0.03	-	0.29	0.79	0.11	30	-	0.05	0.37	tr	
37	Light blue opaque	3.3	1.96	-	0.54	51.3	-	10.8	4.22	0.03	-	0.28	0.8	0.09	29.9	-	0.04	0.12	tr	
38	Light blue opaque	3.4	1.81	-	0.52	50.4	-	10.6	3.96	0.03	-	0.26	0.81	0.13	31.2	-	0.04	0.23	tr	
40	Light blue opaque		2.17	-	0.58	51	-	10.6	4.03	0.02	-	0.27	0.79	0.12	30.2	0.01	0.04	0.2	tr	
52	Light blue opaque		3.14	0.27	0.73	50.6	-	10.6	4.09	0.03	-	0.26	0.8	0.12	29.1	-	0.08	0.16	tr	

Table 1 Chemical composition (wt%) of the glass beads excavated from Krang Kor analyzed by XRF

Sample No.	Color	Density	Chemical composition (wt%)																	Notes
			Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CuO	ZnO	PbO	Rb_2O	SrO	ZrO_2	SnO_2	
1	Yellow opaque	3.9	0.34	0.13	0.51	43.3	-	2.36	1.72	0.02	-	0.33	0.09	-	50.7	0.02	0.14	0.3	0.12	White translucent area
			0.64	0.24	1.36	60.7	-	2.3	1.16	0.02	-	0.58	0.06	-	32.2	-	0.07	0.39	0.34	Yellow particle
2	Yellow opaque	3.8	0.62	0.31	0.76	44.2	-	3.84	0.68	0.01	-	0.28	0.04	-	39.6	-	0.11	0.33	9.26	
3	Yellow opaque	3.8	0.54	0.11	0.71	40	-	3.82	0.1	0.01	-	0.37	0.17	-	51.5	-	0.18	0.46	2.07	
4	Yellow opaque	3.9	0.16	0.15	1.04	41.7	-	3.73	0.09	0.01	-	0.38	0.19	-	50.7	-	0.07	0.16	1.67	
5	Light blue opaque	3.4	2.27	0.15	0.63	45.2	-	6.4	2.77	0.01	0.17	1.2	1.59	-	39.4	-	0.06	0.22	tr	
6	Light blue opaque		1.31	-	0.64	47.6	-	5.87	2.65	0.01	-	0.3	1.38	-	39.9	-	0.17	0.26	tr	
7	Reddish brown transparent	3.7	0.26	-	0.56	46.3	-	5.6	0.31	0.01	-	0.24	0.35	-	46	-	0.17	0.21	tr	

Table 2 Chemical composition (wt%) of the glass beads excavated from Krang Kor analyzed by XRF

2. Metal Items

The excavation survey at the Krang Kor site yielded a total of 4 metal items. They included 2 iron knives and 2 earrings that appear to be made of bronze. Metal items found in the earth frequently show rapid corrosion after being excavated, due to the sudden change in environment. For this reason, excavated metal items must be placed in temporary storage in a dry state without exposing them to oxygen, and proper conservation treatment must be applied in accordance with their materials and conditions to prevent further corrosion. Based on this understanding, conservation treatment was applied to the metal items excavated from the Krang Kor site, as reported below.

(1) Survey Preceding Conservation Treatment

Before applying proper conservation treatment to excavated artifacts, it is necessary to examine the materials and structures of the artifacts and to gain an accurate grasp of their existing condition. Therefore, prior to applying conservation treatment to the metal items excavated from the Krang Kor site, we performed a microscopic observation, an examination of the inner structure by X-ray imaging, and a nondestructive materials examination by X-ray fluorescence analysis. The X-ray fluorescence analysis was based on a nondestructive method, so we were able to obtain information only about the weathered surface of the items, and could not use the measurement results to estimate the original content of each component contained in the items.

As a result of microscopic observation and X-ray imaging, there were no "bad" corrosion product on the knives or earrings indicating continuous corrosion. However, there were portions at the tip of the blade of the knives and the surface of the earrings that had little X-ray absorption (Fig. 3). This result suggested weakening of the items, so we judged that reinforcement treatment is necessary. The earrings appear to be made by coiling a cord-like metal around a cylindrical rod.

X-ray fluorescence analysis detected iron (Fe) as the main component of the two knives, as well as silicon (Si) and titanium (Ti), but the latter two are probably components from the soil that adhered to the surface of the items (Fig. 4). A similar result was obtained from the cylindrical metal fitting.

The main component of the earrings was copper (Cu). Hardly any traces of tin (Sn) were found, but zinc (Zn) was detected instead. Additionally, there were slight differences between the components detected from the inner core and the surface. The surface had trace amounts of lead (Pb) and bismuth (Bi), which were not found from the inner core (Fig. 5).

(2) Conservation Treatment

1) Knives

As a result of observations, the knives were found to be covered with a stable corrosion product, which indicated that there was little possibility of the advancement of new corrosion. Therefore, we cleaned the knives to the minimum extent necessary, taking care not to destroy the layer of stable corrosion components. Using brushes, bamboo picks, scalpels, and grinder, we removed soil particles from the surface. Then, after cleaning the knives, we reinforced them by conducting vacuum impregnation three times using a 20% concentration of Paraloid NAD-10 acrylic resin.

2) Earrings

As with the knives, the earrings were also covered with a stable corrosion product, indicating little possibility of the advancement of new corrosion, so we cleaned the earrings to the minimum extent necessary, taking care not to destroy the layer of stable corrosion components. We refrained from using a grinder, however, because copper and copper alloy are softer and more susceptible to scratches compared to iron.

New corrosion of copper and copper alloy can be effectively prevented by applying stabilization treatment using BTA (bensotriazol). The method prevents further advancement of corrosion by causing a reaction between uncorroded metal remaining on the inside and BTA and creating a stable layer. Therefore in this study, we attempted to stabilize the materials by conducting vacuum impregnation in a BTA 2% ethyl alcohol solution for 24 hours after cleaning.

Then, as the last step, we applied reinforcement treatment by conducting vacuum impregnation two times using a 5% concentration of Paraloid B72 acrylic resin.

(3) Storage

Metal items should preferably be stored in a low-humidity environment that allows no exposure to oxygen. In this case, we adopted a system that maintains a relative humidity below 10% and an oxygen concentration of less than 0.1% by placing an RP agent inside a bag specially made of impermeable film.

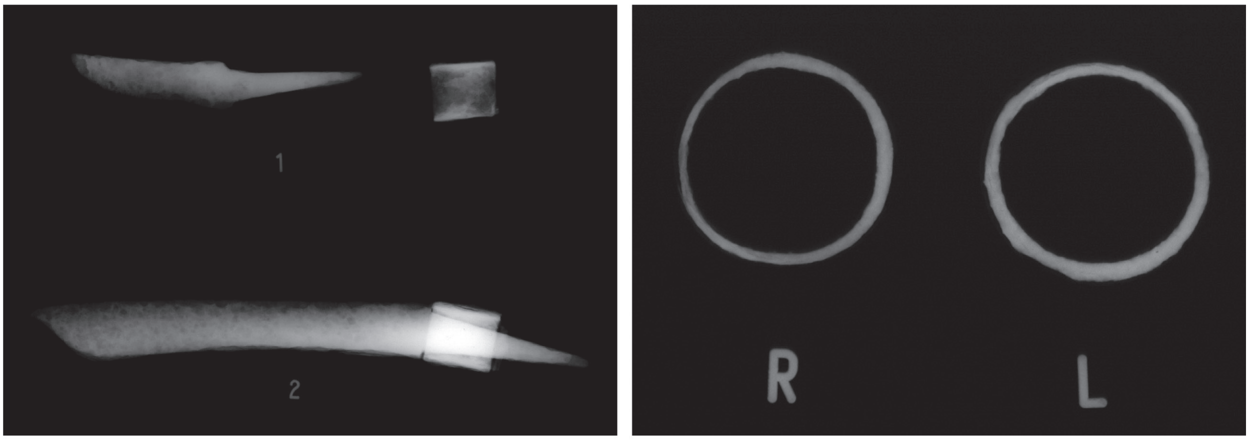

Fig.3 X-ray images of metalic objects excavated from Burial No.1(left:knife, right:bracelet)

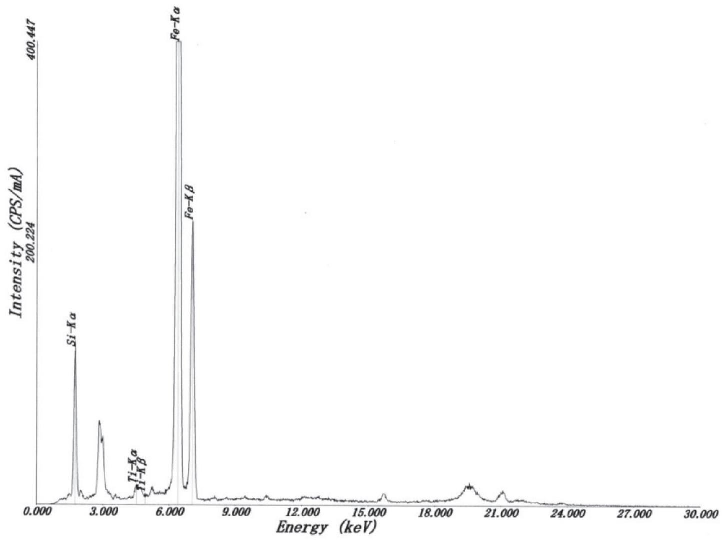

Fig.4 XRF spectrum of Knife No.1

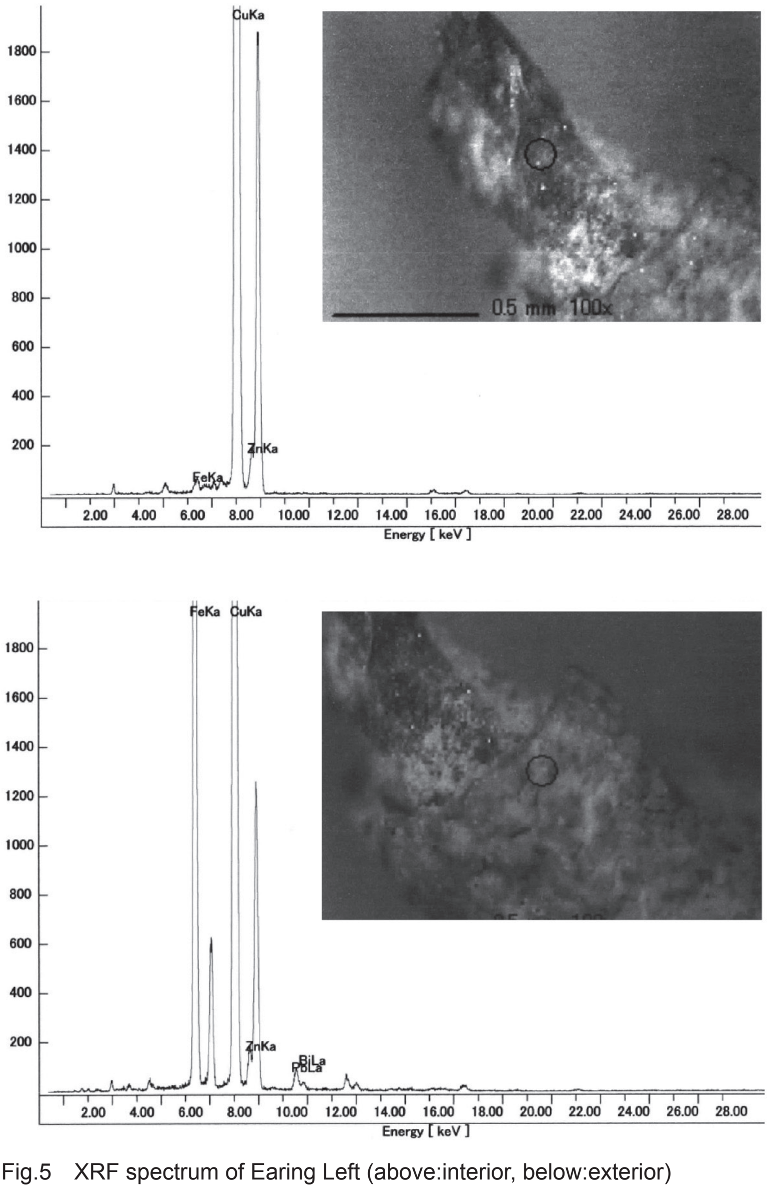

Fig.5 XRF spectrum of Earing Left (above:interior, below:exterior)