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Nondestructive Analysis of Dragonfly Eye Beads from the Warring States Period, Excavated from a Chu Tomb at the Shenmingpu Site, Henan Province, China

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Abstract: Dragonfly eye beads are considered to be the earliest types of glass objects in China, and in the past have been considered as evidence of culture interaction or trade between West and East Asia. In this article, synchrotron radiation microcomputed tomography and μ-probe energy dispersive X-ray fluorescence were used to determine the chemical composition, microstructure, and manufacturing technology of four dragonfly eye beads, excavated from a Chu tomb at the Shenmingpu site, Henan Province, China, dated stylistically to the Middle and Late Warring State Period (475 BC–221 BC). First, a nondestructive method was used to differentiate the material types including faience (glazed quartz), frit, glazed pottery (clay ceramic), and glass. Three beads were identified as faience and one bead as glazed pottery. The glaze recipe includes quartz, saltpeter, plant ash, and various copper, and is classified as belonging to the K_2O-CaO-SiO_2 glass system, which indicates that these beads were not imported from the West. Based on computed tomography slices, the manufacturing technology of the faience eye beads appears to include the use of an inner core, molding technology, and the direct application glazing method. These manufacturing features are consistent with the techniques used in China during this same time period for bronze mold-casting, proto-porcelain, and glass.

Key words: dragonfly eye beads, faience, ancient Chinese glass, EDXRF, SR-μCT

Introduction

Compound, stratified, or inlaid mosaic eye beads made from glass have been reported from Anatolia beginning as early as the 2nd millennium BCE and various techniques of eye bead production spread to other regions, including the Mediterranean, Central Asia, and China (Kerr & Wood, 2004). In China, glass eye beads are often referred to as dragonfly eye beads and are considered to be the earliest example of ancient Chinese glass (Gan et al., 2006), which first appeared around 500 BC and are assumed to have been imported from abroad (Gan et al., 2009). These initial imported glass beads are thought to have stimulated the production of indigenous glass beads and the manufacture of other types of glass objects in China. This current research on early Chinese dragonfly eye beads will help further refine our understanding of the origin and development of Chinese glass and also of cultural interactions between West and East Asia.

There are two basic forms of dragonfly eye beads in China that relate to the technique of applying the eye motif on the monochrome surface of the bead. One type of beads is made by the application of multiple layers of colored glass trails on a base bead to create approximately concentric circles. The other type is made with conical projections or horns protruding from a base bead that was decorated with concentric circles. The patterns of concentric circles or protruding horns resemble dragonfly eyes, giving the beads their name. In their initial appearance in China, these beads were usually deposited in high status burials such as in the tomb of the wife of Fuchai, King of Wu kingdom (buried in 504 BC) (Zhang et al., 1983). During the middle and late Warring States Period (475 BC–221 BC), when these types of beads began to be produced locally, the dragonfly eye beads became more popular and were buried not only in big tombs but also more frequently in medium and small tombs with modest funerary furnishings. Most of the locally produced dragonfly eye beads are composed of lead-barium glass that is characteristic of China and found in the middle Yangzi River region. This has led scholars to suggest strong links between eye bead production and the Chu kingdom existing in this region from about 1046 BC to 223 BC (Brill & Shirahata, 2009; Cui et al., 2011). The tradition of burying dragonfly eye beads in tombs declined rapidly at the end of the 3rd century BC, when China was unified under the Qin Dynasty (221 BC–207 BC) and then the Western Han Dynasty (202 BC–AD 8). It is thought that the production of eye beads ended with the collapse of the Chu kingdom (Hou, 1995; Braghin, 2002).

The earliest known dragonfly eye beads in China were excavated from an ancient tomb (M10) dating to around 500 BC at the Xujialing Cemetery, Xichuan County, Henan

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Table 1. The Chronology and Bead Developments.

Period	Date	Event
Shang Dynasty	1600 BC–1046 BC	The proto-porcelain appeared.
Western Zhou Dynasty	1046 BC–771 BC	The faience bead appeared in China.
Spring and Autumn Period	770 BC–476 BC	Eye beads were imported to China at the end of this period.
Warring and States Period	475 BC–222 BC	The indigenous large-scale production of dragonfly eye beads and other glass objects
Qin Dynasty	221 BC–207 BC	China was unified and the use and production of dragonfly eye beads declined.
Western Han Dynasty	202 BC–AD 8	

Province. The individual buried in this tomb is thought to have been a senior official of the Chu kingdom due to the burial of precious artifacts including bronze wares and jades (HICRA, 2004). The beads from M10 all have similar shapes and colors, with a sky-blue base bead, dark-blue pupils, and trails with concentric circles on inlaid eyeballs. The chemical analysis of some beads showed that these objects belong to soda-lime-silicate glass system (Na_2O-CaO-SiO_2) with cobalt as the deep-blue color-generating element and that they were most probably imported from the West (Gan et al., 2009).

The Shenmingpu Site excavated between 2007 and 2009 is also located in Xichuan County, and its linear distance from the Xujialing Cemetery is around 35 km. During the 2008 excavation season, two intact and two fragmentary dragonfly eye beads were discovered in a small-sized tomb numbered M65. According to the burial style including tomb size and other buried objects (just a few pottery containers, no bronze and jade), the individual buried in M65 was thought to be an average citizen of the Chu kingdom in the Middle and Late Warring State Period (475 BC–221 BC).

Both tombs, M10 at the Xujialing Cemetery and M65 at the Shenmingpu Site, belong to the people of the Chu kingdom and their chronological period is relatively similar. However, the beads from the nobleman's tomb (M10) at the early site appear to have been imported from the West, while the beads from the other tomb (M65) are thought to have been produced locally; thus, the archaeometrical analysis for the dragonfly eye beads from the Shenmingpu Site would help better understand the indigenous manufacturing technology of dragonfly eye beads in the Chu kingdom and the development of early glass in China.

Dragonfly eye beads in China with a glassy surface are possibly made of faience (refers to glazed quartz in this article), frit, glazed pottery, or glass. For fragmentary beads, it is relatively easier to differentiate these four material types by directly observing the inner part; but for intact beads, it is hard to observe the inner part, so it is more difficult to differentiate material types from just looking at the glassy surface. In fact, there is no nondestructive method to distinguish these different materials. By contrast, the computed tomography (CT) scanning method is able to provide a solution, because it can provide detailed information about the internal structure of objects in a nondestructive manner. This technique has been used in ancient glass analysis (Roemich et al., 2005) and was the inspiration for applying this method for the study of eye beads.

In this study, synchrotron radiation microcomputed tomography (SR-μCT) and energy dispersive X-ray fluorescence (EDXRF) were used to identify material types—faience, frit, glazed pottery, or glass for the beads from the Shenmingpu Site and infer the detailed manufacturing procedure. In addition, based on the analysis of the chemical composition data, an attempt has been made to determine the recipe for making these beads. In the following sections, we will summarize the chemical composition types of dragonfly eye beads in China based on both our results and the data previously published by other scholars.

Materials and Methods

Samples

Dragonfly eye beads from the tomb M65 at the Shenmingpu Site are coded as QTY1-QTY4; QTY2 has two fragments coded as QTY2a and QTY2b. These beads were first observed under an optical stereomicroscope (see Figs. 1–5). These beads have an exterior glassy surface, on which protruding green conical horns were used to mimic eyeballs and a white circle trail was delineated at the bottom of each horn. Many semiopaque quartz particles are visible interspersed on the bead surface and the horned eyes of these four beads, as well as the interior body of QTY1. However, the body of QTY2 looks like pottery (clay ceramic) rather than quartz ceramic or frit. Thus, the fragmentary QTY1 and QTY2 are not totally made of glass and should be called glazed objects. In the perforation of QTY2b, there remains a tube to support the perforation when shaping and firing (see Fig. 3). These four beads have a similar decoration style, implying that these beads were produced locally and buried quickly after manufacture. For the intact QTY3 and QTY4, it is difficult to differentiate only using an optical microscopy whether they are glazed objects or relatively homogenous glass beads. Before analysis, the beads were cleaned in a supersonic water bath to remove attached soils. The general chronology of the major periods and developments in bead technology discussed in this article is listed in Table 1.

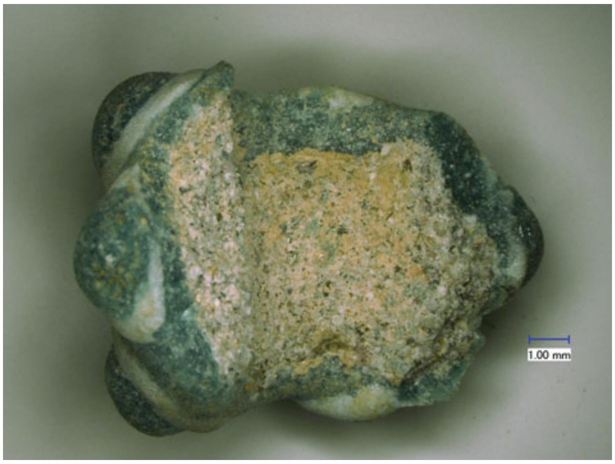

Figure 1. View of QTY1 from the quartz body.

Figure 2. View of QTY2a from the glaze surface.

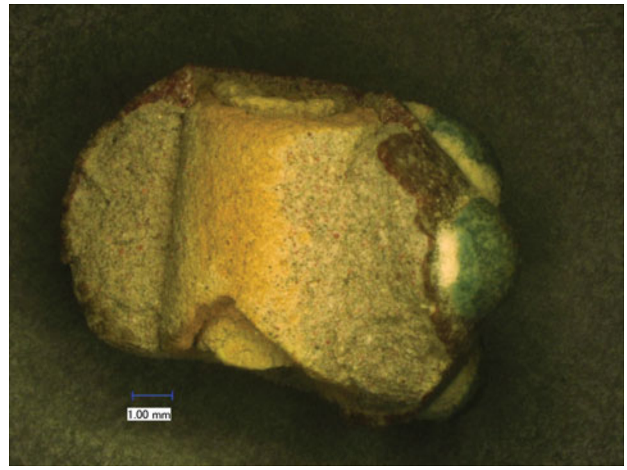

Figure 3. View of QTY2b from the pottery body.

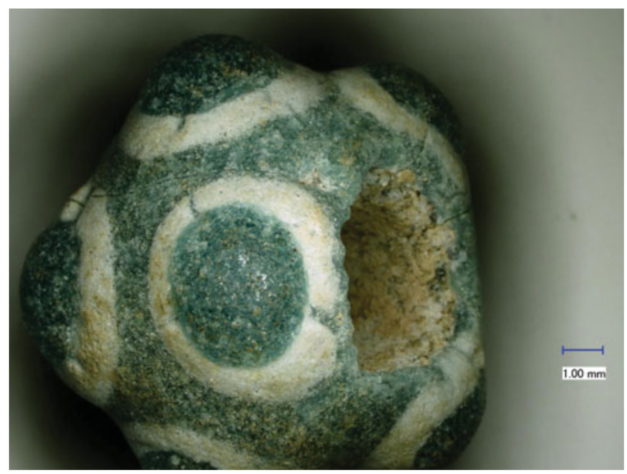

Figure 4. View of QTY3 from the glaze surface.

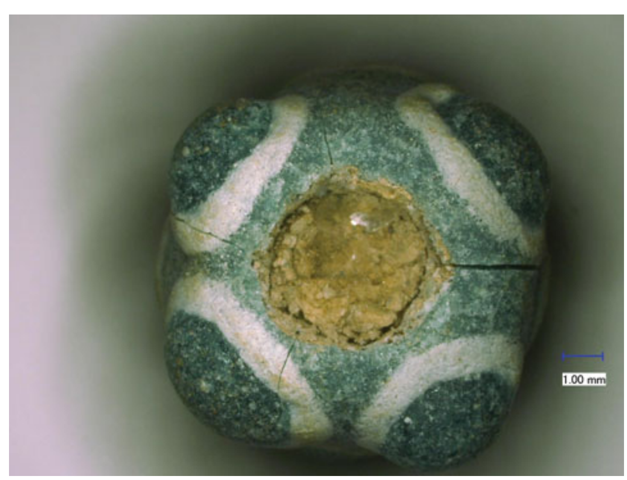

Figure 5. View of QTY4 from the perforation.

Methods

Synchrotron Radiation Micro-CT (SR-μCT) Scanning and Three-Dimensional Reconstruction

Dragonfly eye beads were scanned by SR-μCT at the Shanghai Synchrotron Radiation Facility, Shanghai city, China. The scanned object was put on an open sample platform. The parallel SR X-ray with the height of 4 mm and the width of 2 cm was directed at the object with the source energy setting of 30 keV. The charge-coupled device detector has a space resolution of 13 μm. In each scan, 339 slices were obtained. The scan time was about 10 min. Scan data were imaged and analyzed using Mimics 12 (Materialise, Leuven, Belgium). According to CT imaging principles, heavy elements have more absorption for X-rays than light elements; accordingly, when a region on a CT slice contains more heavy elements, this region looks brighter; therefore, the variation of brightness on a slice reflects the variation of density and chemical composition (Baruchel et al., 2006).

EDXRF

An Eagle III μ-Probe EDXRF spectrometer (EDAX, Mahwah, NJ, USA) with a Mo tube and a 125 μm Be window was calibrated using appropriate primary standards and used to perform nondestructive analysis for QTY1, QTY2a, and QTY4. This spectrometer has an incident beam angle of 65° and an emergence angle of 60°. The detector is a liquid-nitrogen-cooled Si (Li) crystal with a resolution of about 160.3 eV at Mn K. In this experiment, the diameter of the X-ray beam spot was set as 0.1 mm, then the voltage and current of the X-ray tube were operated at 50 kV and 800 μA, respectively. All of the obtained spectra were analyzed with VISION32 software, which has all of the basic EDX functions. Concentrations of the analyzed major and some minor elements were beyond the detection limit of 20 ppm. Relative errors are 1–3% for elements present at the 1 wt% or more level, and up to 10% for elements present at the 0.1 wt% or less level. Results for QTY1, QTY2, and QTY4 are listed in Table 2 with some previously published data from the literature.

Results and Discussion

Identification of Faience and Glazed Pottery

In terms of microstructures disclosed by CT slices (see Figs. 6–10), these four beads could be divided into two groups: one group includes QTY1, QTY3, and QTY4, whose bodies are loose with many irregular pores; the other is QTY2, whose body is much more dense. From the chemical composition data in Table 2, the body of QTY1 has a higher content of SiO_2 (more than 88 wt%) and is composed of quartz particles bound by glassy phases, but the body of QTY2 is sintered clay. Therefore, QTY1 is a kind of non-clay–based ceramic composed of crushed quartz or sand with glaze on its outer surface, namely faience (glazed quartz); and QTY2 should belong to glazed pottery (clay ceramic). Moreover, the CT slice of QTY2a in Figure 7 shows that some minerals intersperse in the pottery body because these minerals have distinct chemical composition in comparison with the pottery matrix. This is a common phenomenon in low-temperature fired pottery,

On the CT slice of QTY1 (see Fig. 6), the color of the glaze is lighter gray, the color of the quartz body is darker gray, and the color of pores is black. This color variation is consistent with the chemical composition variation and indicates that the glaze contains higher amounts of heavy elements, such as K, Ca, Fe, Cu, and that the body is mainly composed of quartz particles. Furthermore, the internal microstructure of QTY1 in Figure 6 is similar to that of Egyptian faience examined by scanning electron microscopy (SEM) for polished thin cross sections (Tite et al., 2007), showing that many irregular pores are scattered in a quartz body. Since QTY3 and QTY4 have similar microstructures with QTY1, then QTY3 and QTY4 are also identified as faience. On CT slices, horned eyes and white circles of these beads have similar microstructures as the glaze, being dense with scattered round air pores; thus, the horned eyes and white circles are also made of glassy phases.

From the above case study and previous research about ancient glass (Roemich et al., 2005; Mees et al., 2009), a nondestructive method was established to differentiate faience, frit, glazed pottery, or glass through CT. For glass objects, CT slices of the outer and inner parts should be similar with air pores scattered in the continuous glassy phase. For frit objects, as an unglazed material, CT slices of

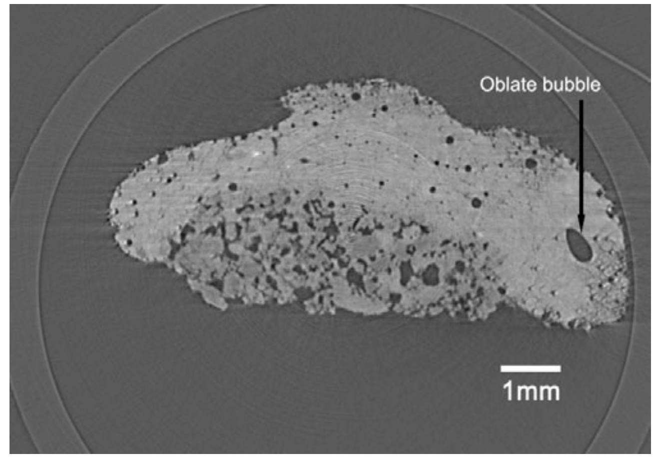

Figure 6. One CT slice of QTY1.

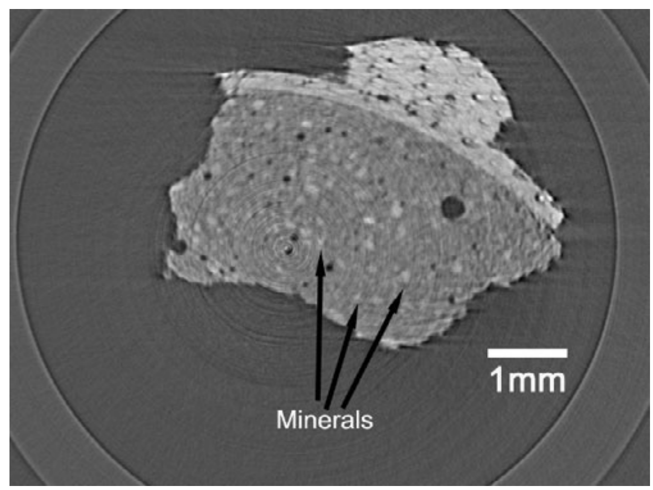

Figure 7. One CT slice of QTY2a.

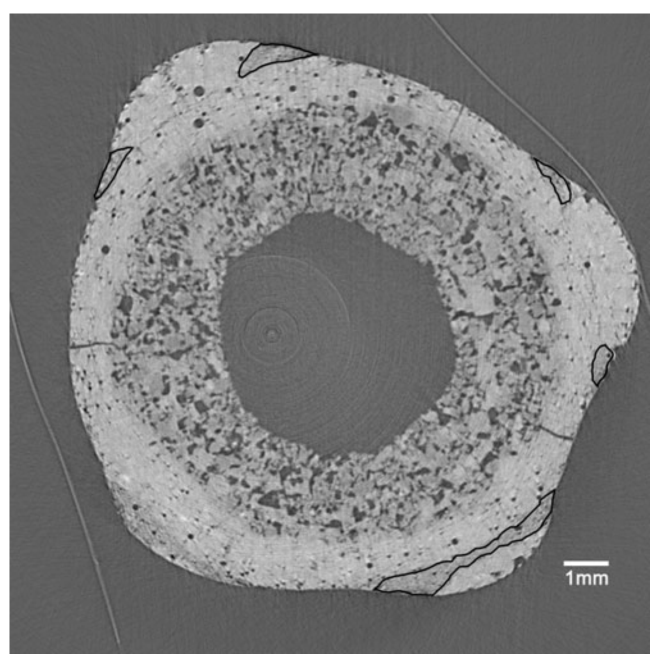

Figure 8. One transverse section of QTY3 with outlined white layers.

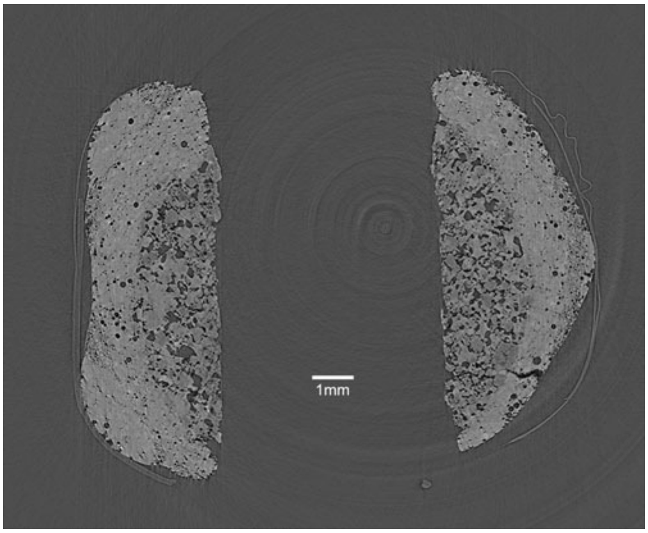

Figure 9. One longitudinal section of QTY3.

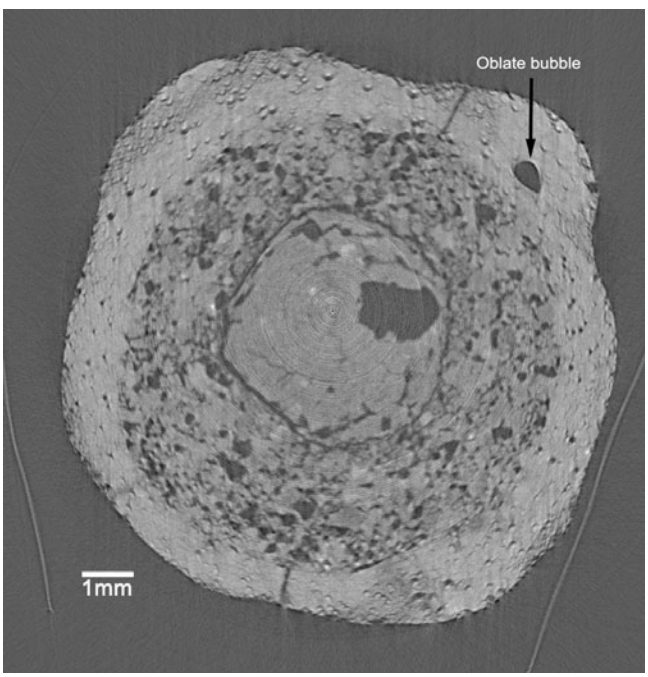

Figure 10. One transverse section of QTY4.

the inner and outer parts should be similar, but it is easy to see unmelted quartz particles on the surface under an optical microscope. For faience and glazed pottery, a distinct boundary exists between the glaze and the body as Figures 6 and 7 show, but some minerals can be clearly seen on the CT slice of a pottery body.

There have been relatively few studies of the microstructure of dragonfly eye beads in China. The beads with a glassy surface in China are generally thought of as being glass objects, but the beads from the Shenmingpu Site do not support this opinion. When it is possible to undertake destructive analysis, a polished thin cross section of the object is studied using SEM (Tite et al., 2007; Hatton et al., 2008). This destroys samples and cannot be used to obtain different cross sections from different angles for the same sample. If destructive methods are not allowed to analyze beads, then micro-CT is the only method that can be used to determine the microstructure and judge the artifact type—faience, frit, glazed pottery, or glass objects.

The Manufacturing Procedure

The longitudinal section of QTY3 in Figure 9 shows that profile lines of the perforation approximately form a straight line, and the CT slice of QTY3 in Figure 8 shows that the transverse section of the perforation is like a circle; so the shape of the perforation in QTY3 is basically a cylinder. Thus, there should be some kind of inner core to support the perforation when shaping and firing. Furthermore, this inner core in the perforation should be made of organic materials; otherwise, it would be very difficult to strip the core because clay or metal core would be sintered together with glaze or quartz particles in firing, just as QTY2b shows (Fig. 3). Additionally, in the longitudinal section (Fig. 9) and transverse section (Fig. 8) of QTY3, the quartz body looks round. So the shaping procedure of the quartz body could be described as follows: quartz particles were piled on a cylindrical core and shaped as a spherical body, which would be later glazed.

There are three glazing technologies for faience, namely direct application, efflorescence, and cementation methods, and it is very difficult to judge with certainty which method was used in glazing (Nicholson, 1993; Vandiver, 1998; Tite et al., 2007; Hatton et al., 2008). The beads analyzed in this study have a similar shape and consist of a similar glaze recipe, a potassic glass phase (K_2O-CaO-SiO_2), so it is deduced that the same manufacture including glazing, inlay, and firing method was used. Since QTY2 is a glazed clay ceramic for which the efflorescence process is not possible, therefore it was probably glazed using application or cementation. If the other beads were made with the same technique as the clay ceramic bead, then they may have also been glazed using cementation or direct application techniques. If a cementation method was used, redundant glaze materials should be wiped off after firing. However, there is no grinding mark in the glaze of these beads under an optical microscope. Consequently, it is most likely that the direct application method was used for glazing.

In the CT slice of QTY3 (see Fig. 8), bold black lines were used to outline the white trails, whose color is darker than that of the glaze and brighter than that of the quartz body. It is evident that the glaze and horned eyes are completely or partly separated by the white trails in Figure 8, so each white circle should be like a ring, covered by a horned eye. This situation is also observed on the CT slices of other beads.

Air bubbles in glass phases are spherical, and Figure 11 is the three-dimensional (3D) reconstruction of such a typical spherical bubble. Sometimes there exists an oblate bubble between a horned eye and glaze surface, and Figure 12 is the 3D reconstruction of such a typical oblate bubble. The shape of oblate bubbles is very distinct to that

Table 2. Chemical Composition of Dragonfly-Eyed Beads from Different Sites (wt%).

Sample[a]	SiO_2	Al_2O_3	P_2O_5	K_2O	CaO	Fe_2O_3	CuO	PbO	BaO	TiO_2	ZnO	MnO	Na_2O	MgO	CoO	Sb_2O_3	SnO_2
QTY1-glaze-green	67.54	3.47	0.20	18.46	5.23	1.61	1.22	0.01	n.d.	0.35	0.03	0.24	1.30	0.34	n.d.	n.d.	n.d.
QTY1-inlaid-white	65.60	10.18	0.58	11.93	6.87	2.33	0.54	0.01	n.d.	0.44	0.03	0.15	0.82	0.54	n.d.	n.d.	n.d.
QTY1-body	87.34	3.57	0.24	4.34	1.75	0.86	0.14	0.01	n.d.	0.20	0.01	0.05	1.07	0.41	n.d.	n.d.	n.d.
QTY2-inlaid-green	72.47	4.39	0.19	12.98	4.92	1.68	0.63	0.01	n.d.	0.38	0.04	0.17	1.58	0.56	n.d.	n.d.	n.d.
QTY2-glaze-red	65.90	5.73	0.25	15.64	6.04	2.00	1.93	0.01	n.d.	0.63	0.08	0.24	1.00	0.55	n.d.	n.d.	n.d.
QTY2-inlaid-white	68.28	4.73	0.16	3.27	5.50	2.66	0.10	0.01	4.16	8.09	0.03	0.40	1.94	0.50	n.d.	n.d.	n.d.
QTY2-body	72.83	13.14	0.34	2.35	2.92	5.17	0.02	0.01	n.d.	0.96	n.d.	0.10	0.84	1.31	n.d.	n.d.	n.d.
QTY4-glaze-green	70.20	5.08	0.24	14.50	4.57	1.74	1.06	0.01	n.d.	0.36	0.07	0.19	1.36	0.62	n.d.	n.d.	n.d.
QTY4-inlaid-white1	67.35	4.71	1.12	14.19	8.84	1.81	0.61	0.01	n.d.	0.35	0.03	0.18	0.51	0.30	n.d.	n.d.	n.d.
QTY4-inlaid-white2	68.84	4.95	0.72	14.18	6.77	1.75	0.47	0.01	n.d.	0.40	0.02	0.20	1.14	0.54	n.d.	n.d.	n.d.
HNZZ03-body-blue[b]	76.70	3.00	0.69	1.06	6.73	0.48	0.70	n.d.	n.d.	0.05	n.d.	n.d.	8.89	0.35	n.d.	n.d.	n.d.
HNZZ03-pupil-blue	71.30	5.70	0.33	1.16	8.21	3.27	0.70	n.d.	n.d.	0.24	0.09	0.05	6.65	0.77	0.14	n.d.	n.d.
HNZZ03-ochre circle	57.5	3.30	0.25	2.23	26.6	3.88	0.40	n.d.	n.d.	1.27	n.d.	0.42	0.73	n.d.	0.55	n.d.	n.d.
HNZZ03-inlaid-white	67.00	5.10	0.54	1.05	12.70	1.29	0.20	n.d.	n.d.	0.28	n.d.	0.09	6.17	0.33	0.08	n.d.	n.d.
CHD–G–13–inlaid-red[b]	30.66	3.54	0.13	1.11	1.85	31.54	n.d.	13.28	9.80	0.35	0.01	n.d.	0.85	0.54	n.d.	0.20	6.02
CHD–G–13–body-blue	58.00	5.18	0.04	2.58	1.46	2.27	5.30	10.48	7.90	0.37	0.03	n.d.	4.37	1.11	n.d.	0.40	0.41
lgd1-body-blue[b]	75.06	2.14	n.d.	0.97	11.34	0.81	0.90	0.52	n.d.	n.d.	0.09	1.04	4.29	0.33	n.d.	2.60	n.d.
lgd1-inlaid-brown	73.96	2.18	n.d.	0.92	11.49	1.00	0.50	0.70	n.d.	n.d.	0.35	0.91	4.62	0.32	n.d.	3.30	n.d.
lgd4(blue glass tube)	72.73	1.07	0.35	15.63	1.66	0.40	1.50	0.52	n.d.	n.d.	n.d.	n.d.	0.09	n.d.	n.d.	n.d.	n.d.

[a]QTY1-glaze-green indicates the green glaze of QTY1, QTY1-inlaid-white indicates the white circle on QTY1, QTY1-body indicates the body of QTY1, and QTY2-inlaid-green indicates the inlaid green horn eye on QTY2.

[b]The archaeological information is listed in Table 3.

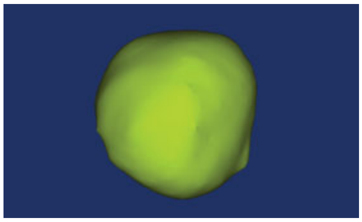

Figure 11. The 3D reconstruction of a spherical air bubble distributed in the glass phase of QTY4.

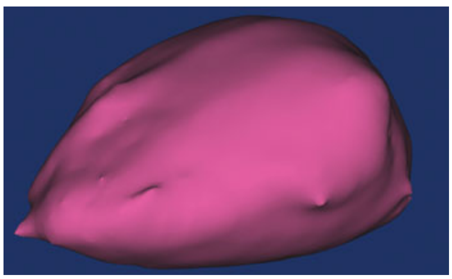

Figure 12. The 3D reconstruction of an oblate air bubble in QTY4 located at the boundary of a horned eye and glaze.

of spherical bubbles. Given their position and shape, oblate bubbles should be the result of the inlay of horned eyes on the glaze. For QTY2, the red glaze and horned green eyes have similar chemical composition (see Table 2) but present different colors, so it is unlikely that they were fired at the same time, further indicating that horned eyes were inlaid after the firing of the initial glaze. Therefore, the inlay procedure is described as follows: a white ring trail is inlaid first on a bead surface, and subsequently a horned eye is inlaid on the area drawn by the white ring.

As mentioned above, horned green eyes are made of a glassy phase interspersed with small quartz particles and inlaid after glaze firing, so they should be produced alone with each horned eye coming from a stick consisting of glass interspersed with small quartz particles, namely frit. Therefore, the inlay procedure can be described as follows: a green frit stick was made first, and then the end of the stick was heated, softened, and poured into a hemispherical mold to form the hemispherical surface of a horned eye, which was then attached to the area outlined by a white circle trail on a bead surface. This inlay procedure is therefore closely associated with mold casting technology. Except for beads and tubes, other early Chinese glass objects in the Warring States Period (475 BC–221 BC) are solid objects, including Bi disc, sword ornaments, and stamp seals, which were also produced through mold casting (Li et al., 2009). Thus, the production of eye beads has a close relationship with technologies used in the production of early solid glass objects during the same period.

The Recipe of Glaze and White Trails

From the chemical composition data of the glaze and green eyes (frit) listed in Table 2, these glazes and frits consisted of a similar recipe, a potassic glass phase (K_2O-CaO-SiO_2) with iron and copper as color-generating elements. The silicon should come from quartz. The calcium may come from plant ash due to the detection of Mg and P elements. The potassium has two possible sources—plant ash or saltpeter (mainly KNO_3). From the typical chemical composition of plant ash in China (Li, 2005), whether the content of CaO is higher than that of K_2O or not, all ratios of K_2O/MnO are less than 20; but the analyzed glaze of QTY1, QTY2, and QTY4 contained higher potassium and much lower manganese (the chemical ratio of K_2O/MnO is at least more than 70). Moreover, the P_2O_5 content in the glaze is not too high (less than 1 wt%). Thus, it is inferred that most of the potassium did not come from plant ash, but more likely from saltpeter. The copper content is much higher than that of lead, and there is no detection of Sn or As element, so copper could not come from bronze. Thus, the raw material of glaze may include quartz, plant ash, saltpeter, and some mineral of copper, such as malachite or azurite.

Different methods have been used to obtain the chemical compositions of glass eye beads, such as PIXE (Gan et al., 2009), LA-ICP-AES (Cui et al., 2009), WDXRF (Qin et al., 2009), and EDXRF in this study. Archaeological information of previously published data is listed in Table 3, and major elements can be used to undertake some broad qualitative comparisons. From the Shang Dynasty (1600 BC–1046 BC) to the West Zhou Dynasty (1046 BC–771 BC), vitreous proto-porcelains were produced and found in many sites in China. Most proto-porcelain glazes contain more CaO than K_2O (Li, 1998). Proto-porcelain glazes with high

Table 3. The Archaeological Information of Previously Published Data in Table 2.

Sample	Site	Date	Reference
QTY	Shenmingpu Site, Xichuan County, Henan Province	Middle and Late Warring State Period (475 BC–221 BC)	This article
HNZZ03	Xujialing Cemetery, Xichuan County, Henan Province	Around 500 BC	Gan et al. (2009)
CHD-G-13	Some Chu cemeteries in the drainage area of the Yuanshui River in Hunan Province	Warring State Period (475 BC–221 BC)	Cui et al. (2009)
Lgd	Leigudun site, Suizhou County, Hubei Province	Early Warring State Period (475 BC–221 BC)	Qin et al. (2009)

Table 4. Some Glaze Compositions of Proto-Porcelains with High K_2O Contents*

Sample Number	Period	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	MnO	P_2O_5
No. 8	Shang Dynasty	61.69	17.97	5.00	0.96	4.49	1.72	7.43	0.47	0.05	0.22
No. 12	Shang Dynasty	72.67	8.57	4.24	0.34	3.65	0.68	8.99	1.27	0.00	0.00
No. 21	Western Zhou Dynasty	76.41	6.69	4.22	0.66	1.08	0.68	8.77	0.69	0.58	0.00

*Cited from Li (1998).

K_2O contents (listed in Table 4) have a relatively higher ratio of Al_2O_3/K_2O, implying that the glaze recipes include potassium feldspar and plant ash. From the West Zhou Dynasty (1046 BC–771 BC) to the end of the Spring and Autumn Period (770 BC–476 BC), the early faience beads in China generally contain more than 80% SiO_2, less than 3% K_2O, and less than 1% PbO (Li et al., 2009). The imported eye beads excavated at Xujialing Cemetery in Xichuan County belong to Na_2O-CaO-SiO_2 glass (the typical data coded as HNZZ03 in Table 2). But the glaze/frit recipe of eye beads from the Shenmingpu Site belongs to K_2O-CaO-SiO_2 glass. Therefore, although ancient people of the Chu kingdom in Xichuan County had been influenced by imported eye beads, they created their characteristic glaze/frit recipe, distinct from other vitreous materials, including proto-porcelain glazes, earlier faience beads, imported eye beads, and contemporary PbO-BaO-SiO_2 glass. Furthermore, the glaze/frit recipe analyzed in this study and ancient K_2O-SiO_2 glass in China (the typical data coded as lgd4 in Table 2) are in some sense similar, implying that both should have some links. To date, four kinds of glaze/glass recipes of eye beads could be summarized, including Na_2O-CaO-SiO_2 (the typical data coded as HNZZ03 in Table 2), PbO-BaO-SiO_2 (the typical data coded as CHD in Table 2), CaO-MgO (PbO)-SiO_2 (the typical data coded as lgd1 in Table 2), and K_2O-CaO-SiO_2 systems.

Chemical composition of white rings on QTY1, QTY2, and QTY4 (coded as QTY*-inlaid-white) is listed in Table 2, showing a common trait of lower copper content than the glaze, but no distinct difference of iron content with the glaze; so iron has a lower influence on color than copper, and copper plays a more important role on the color of the glassy phases in these beads.

Moreover, the three white rings present different recipes. Chemical composition of the white ring on QTY4 is similar to that of glaze except for the lower copper content. The white ring on QTY1 contains more aluminum than the white ring on QTY4, implying that the source of quartz may be different. The white ring on QTY2, compared to other white rings, contains additional barium and titanium, and thus its recipe should include some barium-related mineral. Given that barium-related minerals were widely used in the production of PbO-BaO-SiO_2 glass during the same period (Cui et al., 2011), the use of barium in faience beads further reflects the technical interrelationship with glass production. Thus, ancient bead makers appear to have mastered some different glass/frit recipes, and this demonstrates their deep understanding about the raw materials.

Conclusions

In general, eye beads are precious culture relics, and destructive analysis is not allowed in most cases. For scientific analysis of dragonfly eye beads, nondestructive methods are mainly X-ray diffraction and chemical composition analysis. When microstructural analysis by examining polished thin cross sections is not possible, the nondestructive CT is the optimal method to observe the internal microstructure of eye beads. In this article, SR-μCT was first used to differentiate faience, frit, and glazed pottery in combination with EDXRF. Also, CT slices provide different cross sections from different angles for the same sample and 3D models, which is useful to disclose the relationship among horned eye, circle, and bead surface. Therefore, SR-μCT has great potential in eye bead research.

For the excavated dragonfly eye beads from the Shenmingpu Site, Henan Province in central China, three of four beads were identified as faience and the other bead as glazed pottery (clay ceramic). For faience beads, the manufacture is described as follows: based on a cylinder core, quartz particles were piled and shaped as a spherical body, which would be later glazed by the application method; after firing, white ring trails were first drawn on the glaze surface, and then horned eyes cast in hemispherical molds were inlaid on white rings to mimic eyes. In China before the Qin Dynasty (221 BC–207 BC), shaping technology on the basis of inner cores and molds was widely applied in bronze casting (Tan et al., 1999) and the glazing technology through the direct application method was widely used in proto-porcelain production (Wu et al., 2011); therefore, manufacture of these faience eye beads appears to have been influenced by contemporary bronze casting and proto-porcelain production. Furthermore, the glaze recipe is closely related to glass recipes of the same period. Thus, the manufacture of these beads was influenced by contemporary glass technology.

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