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Scientific and technical analysis of lead-barium glaze dragonfly eye beads from the Late Warring States period in China

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Abstract

This paper analyzed five dragonfly eye beads excavated from M176 of the Hejia Cemetery in the Late Warring States period (around 3rd c. BC) by using a super depth of field 3D microscope system (OM), scanning electron microscope-energy dispersive spectrum (SEM–EDS) and Raman spectroscopy. The analytical results confirmed that all the beads were glazed pottery and the glaze material belongs to the lead-barium-silicate (PbO-BaO-SiO_2) system. The color component of the glaze is Chinese Blue ($BaCuSi_4O_{10}$). Three beads, M176-2, M176-3, and M176-4, were formed with an inner core support and were made in the same batch. Additionally, two weathering products, $CuPb_4(SO_4)_2(OH)_6$ and $PbCO_3$, were detected on the glaze layer surface. The results of scientific and technological analysis show that these beads have differences in the composition of the body and glaze, and the color composition in the glaze layer is relatively rare in previous studies. The discovery of lead-barium glazed pottery beads from the Late Warring States period in northern China provides new evidence for further exploration into the origins and evolution of early glazed pottery. The identification of weathering products formed on the beads' surface within an alkaline burial environment holds valuable implications for the study of weathering and deterioration in silicate artifacts.

Keywords Dragonfly eye beads, Glazed pottery, Late Warring States period, Lead-barium glaze

Introduction

Dragonfly eye beads are a type of bead imitating the structure of a dragonfly's compound eye by inlaying different colored-glass onto the base [1, 2]. It first appeared in ancient Egypt during the 18th dynasty (1550–1307 BC) [3], then became widely popular on the Mediterranean coast and the Iranian plateau [4, 5], and came into China through trade at a later time. However, the exact route of transmission has not been found clearly. Many different shapes of dragonfly eye beads have been excavated from various sites in China. Currently, the earliest dragonfly eye glass bead found in China can date back to the mid-Western Zhou to the mid-Spring and Autumn period (around the 9th to sixth century BC), excavated at the IM27 of Luntai Qunbak Cemetery in Xinjiang [6]. According to the different raw materials, dragonfly eye beads can be categorized into different types such as glass, faience [7], frit [8], glazed pottery [9], pottery and so on. Among them, dragonfly eye glass beads made of different silicate systems have been found in Shaanxi, Hebei, Hubei, and Sichuan and other provinces. Based on the research contents and methods, the studies related to Chinese dragonfly eye beads can be concluded into three main categories. The first category focus on classifying dragonfly eye beads from the similarities and differences in the production process and their characteristics across different periods. The second category involves identifying the origin and transmission routes by combining their

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spatial and temporal distribution in both China and the Western regions. The third category involves employing various modern scientific and technological methods to conduct archaeological research on dragonfly eye beads.

The excavation of dragonfly eye glass beads in China has facilitated and broadened existing research. With the help of scientific and technological analysis, the findings are diverse and comprehensive. Therefore, archaeologists have attained a clearer comprehension of the types and applications of dragonfly eye glass beads across different periods in ancient China. They also achieved further investigations in the study of the production process and origin. However, due to the small number and less representative of dragonfly eye beads in other materials, there is a gap between the native derivatives and original dragonfly eye beads in China.

Research aim

The Hejia Cemetery, located at the former site of Hejia village in Xianyang, Shaanxi Province, contains a large number of tombs. Most of the tombs can date back to the Warring States (475 BC-221 BC) and Qin Dynasty (221 BC-206 BC), with a small number belonging to other dynasties. A certain number of purple octagonal prismatic wares and a few dragonfly eye beads were excavated. To further investigate the origin and evolution of dragonfly eye beads as well as their chemical composition system, color components, and chemical changes within the burial environment, this study employed non-invasive testing and analysis on dragonfly eye beads excavated from the Hejia Cemetery dating back to the Late Warring States period (around 3rd c. BC) in northern China. The results will provide references for subsequent research.

Materials and methods

Dragonfly eye beads

The study samples consisted of 5 beads excavated from M176 of the Hejia Cemetery (Fig. 1). These beads were found on the east side of the humerus of the tomb owner and used as ornaments. Beads M176-1 and M176-5 were poorly preserved, the glaze layer of M176-1 had almost completely flaked off, revealing its red pottery body, while the surface of M176-5 was weathered seriously and contaminated in some areas. Beads M176-2, M176-3, and M176-4 were better preserved, with no obvious weathering traces on the surface, partially broken.

The detailed information of the samples is shown in Table 1.

OM analysis

The microscopic morphology of beads was observed using a super depth of field 3D microscope (HIROX KH-7700 model from Japan). The observation aimed to study the preservation condition, color, and detailed information of these beads. The sample surface was observed at magnifications of 50×, 100×, and 200×, and the most suitable representative area was later selected for subsequent analysis.

SEM–EDS analysis

The microstructure and chemical composition of each bead were analyzed using scanning electron microscopy with energy-dispersive spectroscopy (SEM–EDS). It was

Fig. 1 Dragonfly eye beads analyzed in this paper

Table 1 The detailed information of dragonfly eye beads in this paper

Sample	Shape	Glaze color	Inner diameter (mm)	Outer diameter (mm)	Height (mm)
M176-1	Orb-shaped	Blue	3.5	14.1	11.9
M176-2	Flattened round	Blue	4.8	13.2	8.5
M176-3	Flattened round	Blue	4.8	12.3	7.9
M176-4	Flattened round	Blue	4.8	12.3	8.7
M176-5	Orb-shaped	Blue	4.5	16.4	15.1

carried out with a TESCAN VEGA 3XM scanning electron microscope equipped with an Oxford X-ACT type X-ray energy spectrometer detector and AZtec software for data analysis at the Ministry of Education Key Laboratory of Cultural Heritage Study and Conservation, Northwest University in Xi'an, China. To ensure non-invasive analysis, the samples were placed directly in the sample compartment using conductive adhesive tape. The test conditions were: acceleration voltage of 20 kV, magnification of 800 ~ 1000×, and working distance (WD) of 14.1 mm.

Raman analysis
The physical phase structure of samples was studied using Raman Spectroscopy. It was carried out with a Thermo Fisher DXR 2 Raman Spectroscopy equipped with a 532 nm ion laser at the laboratory of the College of Chemistry and Materials Science, Northwest University in Xi'an, China. The test was performed by placing the samples on slides and observing them with a microscope at low magnification, followed by switching to high magnification to determine the measurement points. The spectra obtained from the experiments were processed with OMNIC software. The test conditions were: magnification of 500×, a grating slit of 50 µm, and laser output power of 2.5 mW.

Results

Archaeological typology classification
Based on the appearance of the samples, the five beads analyzed belong to the same type—"concentric circular pattern eye beads" (M176-1 surface weathering is too serious to be distinguished from the shape, ignored). These beads have a convex surface decoration slightly protruding from the surface, two layers. The bottom layer is white oval, while the surface layer is light blue round. Beads M176-2, M176-3, and M176-4 have 4 groups of concentric circular patterns on the surface, with one at the top and one at the bottom in a regular arrangement. Bead M176-5 has 8 groups of concentric circular patterns on the surface, with no obvious order of arrangement.

According to the size information of the beads, the inside diameter, outside diameter, and height of beads M176-2, M176-3, and M176-4 are nearly the same, with a similar shape, which is highly likely that they were produced in the same batch.

Micromorphology
Figure 2 shows some of the sample micrographs. All samples are glazed pottery material, with a red pottery body and blue glaze layer. The glaze layer consists of blue, white, yellow, and brown granular materials of different shades, among which blue particles are the main color-revealing material. Figure 2c shows a micrograph of the perforation of M176-3, with smooth internal hole walls and traces of spiral drilling. The shape, size, and dimension of the perforations of beads M176-2, M176-3, and M176-4 are very similar, combined with the appearance and morphology, they should have been produced in the same batch and made by sintering after using a hard inner core to form a uniform size.

Elemental composition
The results of the elemental analysis of the glaze layer of the samples are shown in Table 2. The glaze layer was Pb-Ba silicate system and all samples had more

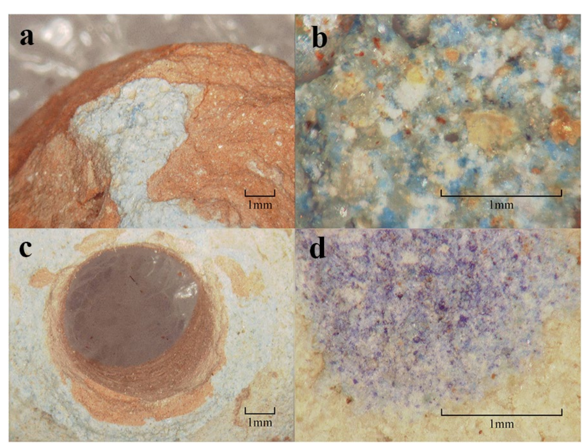

Fig. 2 Micrograph of dragonfly eye beads (**a** M176-1-50×; **b** M176-1-200×; **c** M176-3-50×; **d** M176-2-200×)

Table 2 Elemental analysis results of the glaze layer of dragonfly eye beads (wt%)

Sample	Measured point	C	O	Mg	Al	Si	Cu	Ba	Pb	K	Ca	Fe	P
M176-1	Blue-1	17.30	40.91	0.22	1.06	17.61	3.03	7.82	12.06	\	\	\	\
	Blue-2	21.96	42.03	0.22	1.17	15.90	2.82	7.24	8.10	\	0.57	\	\
M176-2	Blue-1	6.78	37.34	0.23	0.96	13.48	2.32	7.91	28.97	\	1.16	\	0.85
	Blue-2	10.48	36.17	0.35	1.60	11.72	2.38	8.90	27.05	0.35	\	0.94	0.87
M176-3	Blue-1	11.85	44.62	0.42	1.57	19.25	2.57	7.14	9.70	\	1.09	0.83	0.95
	Blue-2	16.60	41.89	0.40	1.46	16.00	3.36	9.89	7.47	\	1.00	0.80	0.69
M176-4	Blue-1	\	41.79	0.38	1.58	14.86	1.32	6.35	29.66	0.16	1.62	0.64	1.64
	Blue-2	\	42.19	0.46	1.74	12.67	1.45	6.17	29.83	0.29	1.91	0.93	2.36
M176-5	Blue-1	8.76	41.71	0.22	1.02	16.89	3.22	7.61	17.56	\	1.34	0.54	1.14
	Blue-2	2.99	47.73	0.27	1.33	23.83	2.76	6.27	11.86	\	1.33	0.37	1.26

concentrated Ba content values, ranging from 6.17 to 9.89%, with an average value of 7.53%; while the Pb content values varied widely, ranging from 7.47 to 29.83%, with an average value of 18.23%. Among the results, the Pb/Ba value of M176-1 and M176-3 were lower than the other three groups, and the Pb content was significantly lower. According to the research from Wood N [10], the elemental loss is often present in lead-barium silicate products and bronze artifacts, and Pb is more easily lost compared to Ba. Therefore, the Pb/Ba value in the results of the elemental analysis can be used as an indicator to identify the weathering degree of the samples to evaluate the preservation condition.

The results of the elemental analysis of the samples' body are shown in Table 3, expressed in oxide contents. Compared to the glaze layer, the type and content of elements in the body were relatively different, containing elements such as Al, Ca, K, and higher Fe, which are commonly found in clay, without Cu and Ba.

Physical phase structure

The common colorants in ancient silicate products are Co^{+}, Cu^{2+}, and Fe^{3+}/Fe^{2+} [11–15]. All samples analyzed in this study contained Cu in the blue glaze layer, with elemental content ranging from 1.32 to 3.36% and an average value of 2.52%, which may be typical of Cu^{2+} chromogenic. However, bead M176-2 (Fig. 2d) had mostly purple surface circular areas with a few blue particles at the edges, and microscopic observation also revealed a very small amount of purple particle masses in the blue glaze layer. Therefore, further analysis was performed to investigate the chromogenic composition of the samples.

Beads M176-2 and M176-4, which were in relatively good condition, were selected for Raman Spectroscopy analysis, and some of the results obtained are shown in Fig. 3. In both M176-2 and M176-4, the physical phase structures of Chinese Blue ($BaCuSi_4O_{10}$) and Chinese Purple ($BaCuSi_2O_6$) were detected, and the Raman signals of the samples were strong. Through the microscope window of the Raman spectrometer, the copper barium silicate crystals were full-colored, with white crystal particles interspersed around. In addition to copper barium silicate crystals, other physical phase structures, $CuPb_4(SO_4)_2(OH)_6$, $PbCO_3$, SiO_2, and TiO_2, were detected in the glaze layer of the samples (Fig. 4). Among them, $CuPb_4(SO_4)_2(OH)_6$ and $PbCO_3$ are considered as the weathering products in this paper, while SiO_2 and TiO_2 are common raw material components.

Discussion

Lead-barium glazed pottery

Lead-barium glaze is a kind of low-temperature glaze [16, 17], fired under a relatively low-temperature condition.

Table 3 Elemental analysis results of the body of dragonfly eye beads (wt%)

Sample	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	FeO	PbO	P_2O_5
M176-1	2.76	3.39	15.53	45.50	5.05	5.27	9.73	12.62	\
M176-2	2.09	3.20	15.03	47.31	4.66	9.25	11.97	6.14	\
M176-3	1.45	2.44	12.73	38.35	4.43	3.55	10.38	23.56	2.17
M176-4	2.88	3.10	15.11	45.66	4.54	4.54	10.95	12.25	\
M176-5	1.74	3.16	14.25	48.39	5.94	3.68	15.72	6.89	\

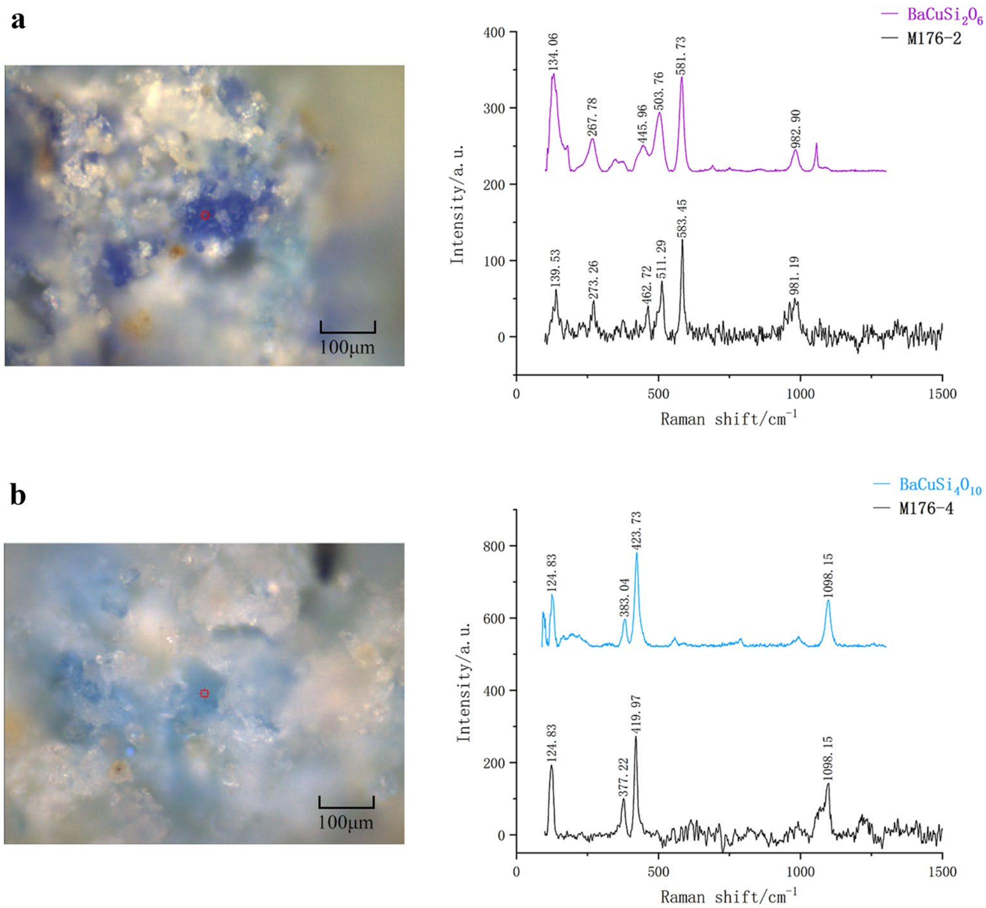

Fig. 3 Raman spectral results of the blue glaze layer of dragonfly eye beads (**a** $BaCuSi_2O_6$ found in the surface of M176-2, **b** $BaCuSi_4O_{10}$ found in the surface of M176-4)

Its origin has been a controversial point in academia. Early views presumed that the technology of lead-barium glaze originated from lead-barium glass. While another view gradually emerged with the emergence of more archaeological evidence, suggesting that lead-barium glaze and lead-barium glass did not inherit from each other but coexist [18, 19].

The painted glazed pottery excavated from Jiangsu Hongshan Cemetery shows that artisans had mastered the production technology of lead-barium glazed pottery as early as the early Warring States period [19]. However, the early lead-barium glazed pottery archaeological excavations are few, partly collected in foreign countries, and the related scientific analysis and research are relatively less. Available data from scientific and technical analysis studies are primarily concentrated in Hubei and Jiangsu Provinces in China [9, 20].

Dong Junqing found that the content of PbO in the glaze layer of glazed pottery beads excavated from Hongshan Yue Cemetery in Jiangsu Province dating back to the early Warring States period ranged from 0.14 to 16.63% [9]. The content of BaO in the glaze layer ranged from 11.21 to 26.60%, with copper and iron ions as coloring elements. In the meantime, they also found the content of PbO in the glaze layer of glazed pottery pieces and beads excavated from the Jiangling Chu Cemetery in Hubei Province dating back to the Warring States period ranged from 0.33 to 12.25%, while the content of BaO in glaze layer ranged from 0.00 to 13.48%. The Pb and Ba content of these glazed pottery objects was lower than that of the early lead-barium glass in China (Warring States period and Han Dynasty).

Dong Junqing analyzed some glazed pottery tubes and beads excavated from the Jiangling Chu Cemetery in Hubei Province dating back to the Warring States and found that the content of PbO in the glaze layer ranged from 7.77 to 38.66%, while the content of BaO in glaze layer ranged from 4.72 to 17.29% [20]. Compared with Pb and Ba element contents of early glazed pottery (Fig. 5), the distribution range of Pb and Ba content of glazed pottery beads excavated from the Hejia Cemetery is more similar to that of Hubei

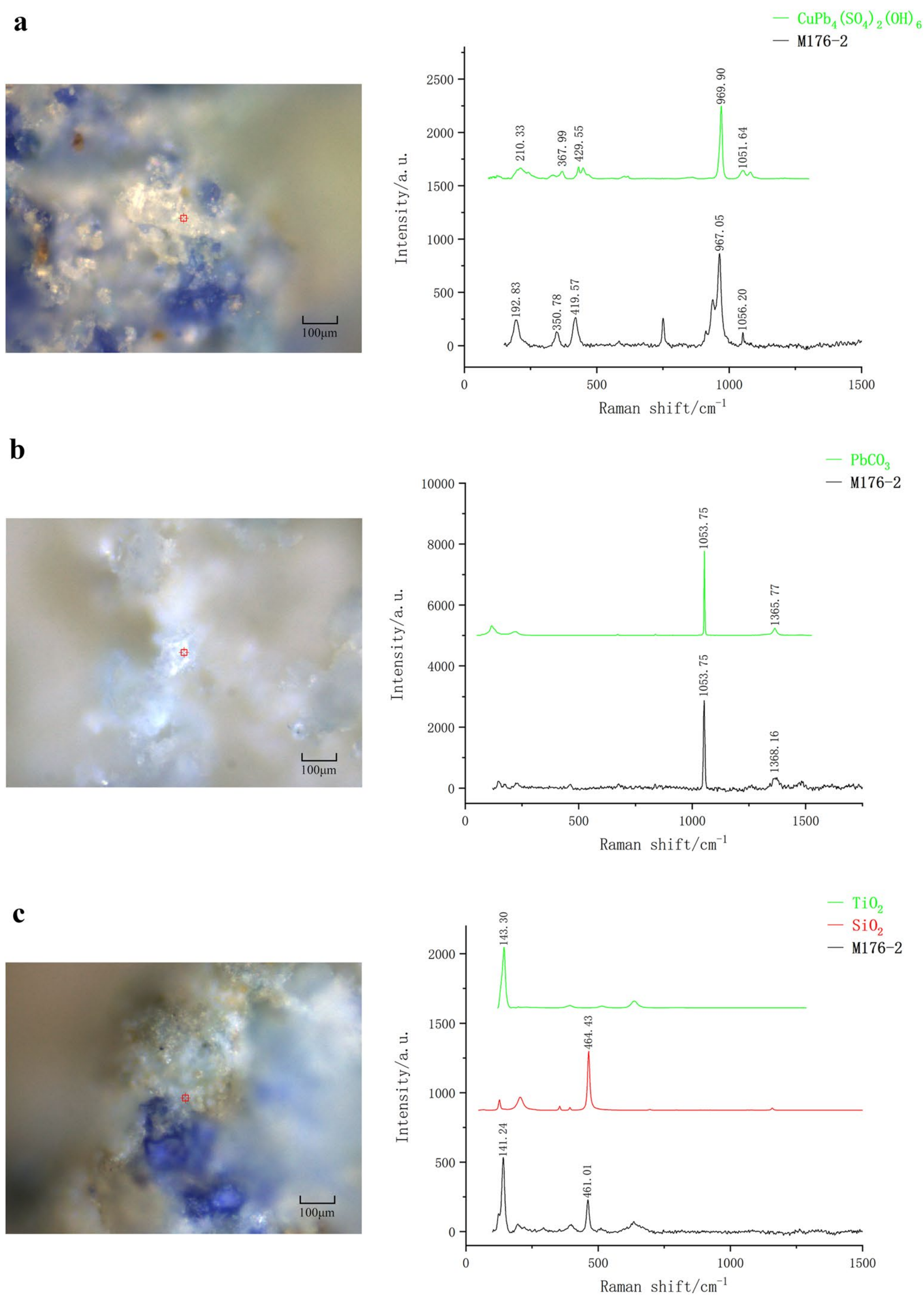

Fig. 4 Raman spectral results of other physical phase structures in the glaze layer of bead M176-2 (**a** $CuPb_4(SO_4)_2(OH)_6$, **b** $PbCO_3$, **c** TiO_2 and SiO_2)

Province, with the content of Pb spanning a wide range and generally higher than the content of Ba, though the content of Pb and Ba is more concentrated in the former. In contrast, the content of Pb and Ba in glazed pottery excavated from Jiangsu Province is close to each other, with the content of Pb slightly lower than Ba. In addition, the content of Cu in glazed pottery beads excavated from the Hejia Cemetery is slightly higher than that of the Hubei and Jiangsu Provinces.

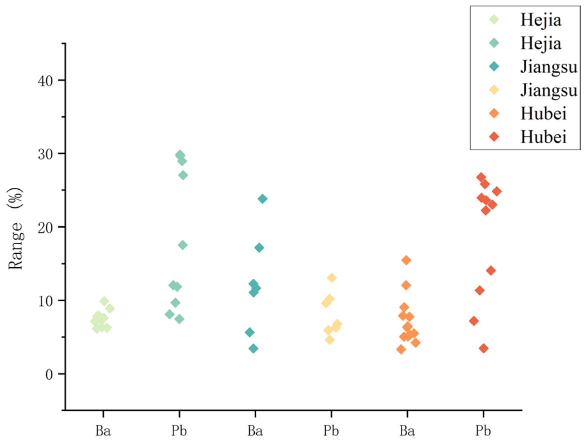

Fig. 5 Pb and Ba content of glazed pottery artifacts from different regions in China

Lead-barium silicate artifacts

Except for lead-barium glazed pottery, there are also other lead-barium silicate artifacts such as lead-barium faience, lead-barium glass, and copper barium silicate.

Faience artifacts are often recognized as the former of glass and consists of a large amount of quartz sand interspersed with a small amount of glass phase. From the Western Zhou (1046BC-771BC) to Spring and Autumn period (770BC-476BC) in China, faience artifacts unearthed from archaeological excavations contained rich potassium fluxes, which were mostly blue or green glaze (Cu^{2+}) [9, 21–23]. During the Warring States period, there was still a relatively high Cu content. But lead fluxes replaced potassium fluxes and the original composition of the glaze has been changed due to the addition of Ba, which facilitated the formation of faience with copper barium silicate as a colorant [21].

Lead-barium glass was a unique glass system in ancient China that only existed from the Warring States to the Eastern Han period (206BC-220AD). There were plenty of lead-barium glass products during this time and the earliest lead-barium glass was excavated from Chaijiagou Cemetery in Bozhou, Anhui Province, dating back to Late Spring and Autumn and early Warring States [24]. According to the available archaeological excavations, early lead-barium glass was mainly concentrated in the Chu region centered on Hubei and Hunan Provinces, and later spread to other regions. Compared to lead-barium glazed pottery, there are higher content of Pb and Ba in lead-barium glass and more types of colorants (Co^{+}, Cu^{2+}, Fe^{3+}/Fe^{2+}), with Co^{+} coloration being more common [24, 26, 27].

As the earliest artificial synthetic pigment in China, the earliest trace of copper barium silicate was found on a spindle-shaped bead excavated from the Dabuzishan site in Li County, Gansu Province, dating back to the early Spring and Autumn period. It was recognized as a product of unintentional generation. Early traces of the use of copper barium silicate were found in silicate products such as beads, faience, and octagonal pillars from the Spring and Autumn to the Warring States period. A larger number of objects were excavated from the Warring States in particular, while the emergence of Chinese purple as a pigment was not seen until the Qin Dynasty.

Lead-barium glass, lead-barium glazed pottery, and copper barium silicate flourished from the end of the Spring and Autumn period to the Han Dynasty. Among these artifacts, lead-barium glass and lead-barium glazed pottery constantly changed the type and ratio of raw material and derived more kinds based on the development of the prototype. While copper barium silicate was only produced and used during the historical period from the Spring and Autumn period to the Eastern Han Dynasty and then disappeared. Early lead-barium glazed pottery excavations were not very common and concentrated in Hubei and Jiangsu Provinces. There is a large overlap with the territory of lead-barium glass excavation, which suggests a deeper connection between the two. Copper barium silicate products were mostly found in the Yellow River basin of Gansu, Shaanxi, and Henan Provinces in the early days and later expanded to Jiangsu and Shandong, and other provinces.

The excavation of many copper barium silicate products in the early days indicates that artisans at that time had already skilled in processing and production by controlling kiln temperature, raw material ratios, fluxes, and other conditions. However, the appearance of copper barium silicate on the surface of these samples was intentional or unintentional? Combined with the results of elemental analysis and previous research, the appearance of copper barium silicate on these beads is considered to be accidental in this paper. From the viewpoint of material synthesis conditions, the glazed pottery contains elements like Ba, Cu, Si, and Pb in the glaze layer. It is available to synthesize copper barium silicate under the condition of raw materials and synthesis temperature [28, 29]. There are a series of simulation synthesis studies carried out by several scholars in China and abroad [30, 31]. From the results of the physical phase structure analysis, except for Chinese Blue, a very small amount of Chinese Purple was also detected. The mixture of multiple products implies that the appearance of Chinese Blue was not the main production purpose. In addition, purple copper barium silicate octagonal prisms, which are relatively rare in archaeological excavations, were found in large quantities in the Hejia Cemetery. This suggests that ancestors had mastered the production of copper barium silicate octagonal prisms and formed a certain scale in the Late

Warring States period. Therefore, the appearance of copper barium silicate on the surface of glazed pottery beads may have been influenced by their processing technology.

Weathering products

The occurrence of the two weathering products and the results of elemental analysis are mutually verified. $CuPb_4(SO_4)_2(OH)_6$ is a type of lead-copper secondary ore (Chenite), discovered in Scotland in 1986 [32]. In a Raman analysis of corrosion products of bronze, Bouchard M detected three rarely seen alkaline copper sulfate minerals on the surface: $CuPb_4(SO_4)_2(OH)_6$, $CuPb_4(SO_4)(OH)_8$, and $Cu_2Pb_5(SO_4)_3(OH)_6$, in addition to some common rusts such as alkaline copper carbonate and blue copper ore [33]. Bronze is usually a Cu-Sn-Pb ternary alloy that can easily generate various corrosion products in contact with H_2O, CO_2, SO_2 and other compounds. To lower the melting point in the process of firing copper barium silicate, ancient artisans would add lead compounds as fluxes. The appearance of lead compounds is an important fingerprint for the identification of the artificial synthetic copper barium silicate. In this study, $CuPb_4(SO_4)_2(OH)_6$ crystals appeared on the surface of the sample intermingled with copper barium silicate crystals, which can be seen in Figs. 3, 4. Since these beads were excavated in northern China with an alkaline soil environment [34], it is tentatively assumed that $CuPb_4(SO_4)_2(OH)_6$ is a weathering product generated by the reaction of Cu and Pb in the glaze layer with sulfur oxides in an alkaline environment. This has not been detected in the previous similar artifacts, providing new evidence for the study of weathering of silicate artifacts.

$PbCO_3$ is a common weathering product of silicate artifacts such as lead-containing glass [35, 36]. In addition, it is also detected in Pb-containing bronzes [37]. In burial environment, the deterioration of Pb will generate new weathering products deposited on the surface of the object, completely changing the original composition and structure. Glazed pottery beads with high content of Pb in the glaze layer are prone to generate $PbCO_3$ in an alkaline burial environment.

Conclusions

In the present paper, five dragonfly eye beads excavated from the Hejia Cemetery in Shannxi Province were analyzed using technological methods from multiple perspectives. All five dragonfly eye beads were made of glazed pottery material and had a significant difference between body and glaze. The body was made of red pottery and the glaze layer was lead-barium glaze with Chinese Blue ($BaCuSi_4O_{10}$) as the main colorant. Based on the previous studies, the occurrence of Chinese Blue in the glaze layer is considered to be fortuitous. Combing the microscopic observation results with the morphological characteristics of the sample appearance, it is presumed that the three glazed pottery beads, M176-2, M176-3, and M176-4, were produced in the same batch and were made by sintering after using a hard inner core to form a uniform size. The detection of alkaline Pb compounds, $CuPb_4(SO_4)_2(OH)_6$ and $PbCO_3$, indicates that the loss of Pb in the glaze layer combined with other substances to generate new compounds under an alkaline burial environment, which provides a reference for the study of weathering of silicate artifacts.

The occurrence of dragonfly eye glazed pottery beads in the Yellow River basin of northern China and their origin is another focus of our attention. In comparison with other studies, although the glazed pottery beads excavated from the Hejia Cemetery have some similarities with early glazed pottery objects from Hubei Province in terms of Pb and Ba elemental content, there is no clear correlation in the principal component analysis. Therefore, it still needs further studies with more archaeological background and scientific analysis, whether these glazed pottery beads are commodities of inter-regional technology exchange and dissemination, trade exchange, or local products imitating dragonfly eye glass beads.

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Author contributions

All authors contributed to the conception and design of the study. Material preparation, data collection, and analysis were performed by HY, FS, and YZ. YZ provided the samples. The first draft of the manuscript was written by HY, and all authors read and revised the previous versions of the manuscript. All authors reviewed and approved the final manuscript.

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Availability of data and materials

All data generated or analyzed during this study are included in this published article.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare no competing interests.

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