Scientific Analysis of Two Compound Eye Beads Unearthed in Hejia Village, Zhouling

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Research Article

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Abstract

Glass compound eye beads is the exquisite embodiment of the glass making technology of ancient craftsmen, and is an example of the cultural exchange between China and the West in the Warring States Period. In the existing scientific research of compound eye beads, only the chemical element composition and fabrication process are discussed, and the weathering mechanism of this kind of objects are rarely discussed. In this study, two dots & mesh beads with seriously weathered surfaces were unearthed in Hejia village, Zhouling. Micromorphology, X-ray fluorescence spectroscopy (XRF) and microscopic laser Raman spectroscopy were used for non-destructive testing to analyze them. The results show that the two compound eye beads belong to the lead-barium silicate system. The substrate of the beads is glassy, the yellow weathered layer in is cerussite, the white weathered layer is barium sulfate and the blue weathered layer is walstromite. It is the first time that the walstromite has been found in the weathered layer of ancient glass. This study focused on the analysis of weathered layers of two compound eye beads, and inferred about their weathering mechanism. In order to provide data support for the subsequent protection of glass compound eye beads, it has certain scientific value.

Introduction

Glass compound eye beads, that is, a type of bead decorated with eye pattern. Because it is similar to the shape of dragonfly's eye, it is often called dragonfly's eye bead in China. In Western countries, it is called “compound glass eye bead” [1]. Glass compound eye beads first appeared in ancient Egypt in the 18th dynasty (around BC 1400), as a decoration was set on coffins, mummies and other artifacts. Because its appearance is related to “evil eye” consciousness, glass compound eye beads are also called “evil-eye bead” by anthropologists. The earliest appearance of glass compound eye beads in China can be traced back to the time which between end of Spring and Autumn and the beginning of the Warring States period (around BC 475) [2]. The glass compound eye beads appeared at this time should be imported from Central Asia, which is a physical example of ancient Chinese and foreign cultural exchanges. After the Warring States period, glass compound eye beads produced in China appeared. Different from the imported with the higher content of sodium and calcium, the beads produced in China had the higher content of lead and barium [3], and were extremely popular in Chu. Glass compound eye beads were found in the civilian tombs of Hunan and Hubei in the late Warring States period [4], and were used as decoration in the following ways: Coffin Decorations [5]; Baldric (Head, chest [6], waist [7]; wear alone or in combination; regardless of gender [8]; implements inlay (be inlaid with bronze mirrors, jade, lacquer, bone or bamboo pins [9].

Research aim

There are two glass compound eye beads in this study, which were excavated from the late Warring States cemetery in Hejia village, Zhouling. The cemetery is located in the former site of Hejia Village, Zouling Town, Weicheng District, Xianyang, Shaanxi Province, on the second-level platform on the north bank of the Weihe River. 10.4 kilometers to the east from the site of Xianyang City of Qin, 1.7 kilometers to the northwest is Mausoleum of King Wu of Zhou. Since August 2020, in order to cooperate with the infrastructure construction of Qinhan New City in Xixian New Area, Shaanxi Provincial Institute of Archaeology has carried out continuous excavation of Hejia cemetery, clearing a large number of tombs, trenches, roads and other relic units. At present, a total of more than 1400 tombs have been excavated, and the large number of unearthed tombs and the rich funerary objects are rare in the sites of the same period. These tombs should belong to the civilian tombs of Xianyang City of Qin. According to the structure of tombs and the combination of unearthed artifacts, except for a small number of Wei, Jin and Ming tombs, most of these are Warring States and Qin tombs. The excavation unearthed a total of more than 2,800 pieces (groups) of funerary issues including daily necessities, weapons. Among them, pottery is the bulk. Copper ware mainly see copper belt hooks. And there are a small
number of copper mirrors and arrowheads. A large number of lead barium silicate artifacts are excavated from there, including glass beads.

**Materials and methods**

**Materials**

The two compound eye beads in this study are obviously different from other glass beads of the same type because of their unique decoration and large size. And the two glass beads are seriously weathered on the surface and have obviously different weathering performance, so they are considered to have unique research value.

**Sample 1:** Archaeological number M709:3–1. The color of the beads is yellow. The beads are almost flat at both ends. Beaded, height 18.3mm, maximum diameter 21.3mm, aperture 7.5mm. The surface is three rows of concentric eye ornaments. The surface decoration is divided into three types of concentric eye decoration and point-like straight line, and the small eye decoration is connected by a small circular concave arranged in a straight line. The surface of the beads is seriously weathered, and the weathered is soil induration doped with a large area of yellow weathered layer. The dark blue substrate is faintly visible.

**Sample 2:** Archaeological number M961:7. The color of the beads is blue. The beads are almost flat at both ends. Beaded, height 18.7mm, maximum diameter 21.3mm, aperture 8.5mm. The surface decoration is also divided into three types of concentric eye decoration and point-like straight line, and the small eye decoration is connected by a small circular concave arranged in a straight line. The surface of the beads is seriously weathered, and the weathered is soil induration doped with a large area of blue weathered layer. The dark blue substrate is faintly visible.

As can be seen from Fig. 1 and sample information, the two samples have the same size and similar decoration. Their patterns are: The dotted mesh pattern fills in the gaps between the eye pieces and makes the eye pattern more symmetrical. The mesh separates the eyes on the surface of the beads to form several independent small units. Archaeological typologically, these two compound eye beads belong to the dots & mesh bead [8], or the H-shaped geometric line spacing eye bead [10].

This type of bead first appeared in the M14 tomb of Qiancheng, Huaihua, Hunan Province in the early Warring States period [11]. It was also found in Chenxi, Hunan Province and Wangshan, Hubei Province during this period. The object diagram of dots & mesh bead which are similar in shape to small reticulated dragonfly eye glass beads unearthed in Hejia village, Zhouling is summarized in Fig. 2 [8][11][24–27]. In the early Warring States period, this type of compound eye beads was extremely popular in Hunan and Hubei. In the mid and late Warring States period, it began to appear in Sichuan, Shaanxi and Hebei, and was still popular in Guangdong in the Qin and Han dynasties. In addition, this kind of compound eye beads were mostly unearthed in Hunan, Hubei, Sichuan and other areas deeply influenced by Ba & Chu culture. Therefore, this kind of dots & mesh bead has a very close relationship with Ba & Chu culture. At present, this kind of beads is only found in China, popular in the Warring States period, is considered to be unique to China.

**OM analysis**

The microscopic morphology of beads was observed using a super depth of field 3D microscope (HIROXKH-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 100x and 400x, and the most suitable representative area was later selected for subsequent analysis.

**X-ray Fluorescence Spectrometry**
Bruker ARTAX400 mobile micro area X-ray fluorescence spectrometer. The test conditions were voltage 30kv, current 900µA, atmosphere Helium and test time 300s.

**Raman spectroscopy**

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 633 nm ion laser at the laboratory of the College of Chemistry and Materials Science, Northwest University in Xian, China.

**Results**

**Micromorphology**

A small part of the weathered layer is scraped off the surface of the samples, and small area of the sample substrate is obtained. The surface of the samples are observed by ultra depth of field microscopy at 100-fold field and 400-fold field respectively. The surface observation results of the two beads are shown in the Fig. 3.

It can be seen from the figure that the surface of the two samples is seriously weathered and the substrate is dark blue. Large areas of the weathered layer coated on the surface are coarse and yellow. The weathered layer near the substrate in the sample are all shiny white substances, or the accumulation of milky yellow shiny substances. However, due to the presence of blue weathered layer in the weathering products on the surface of Sample 2, such weathering products are mixed with yellow crusts, making the surface of the sample appear a large area of light blue when viewed by the naked eye. Therefore, X-ray fluorescence spectrum analysis us performed on the substrate and the weathered layer of the samples. The substrate, white weathered layer, yellow weathered layer and blue weathered layer are analyzed by Raman spectroscopy.

**Elemental composition**

In order to ensure the scientific data, X-ray fluorescence X-ray fluorescence spectrometer was carried out at three random points in the substrate and regolith of the two samples. The quantitative analysis results of Elemental composition by X-ray fluorescence spectra of compound eye beads unearthed in Hejia village of Zhouling are shown in the Table 1.

The BaO and PbO contents in the substrate were 7.7%-11.8% and 1.6%-6.7%, respectively. So the two glass beads were probably lead-barium glass. In addition, the PbO content of sample 2 is higher than that of sample 1, and the BaO content is lower than that of sample 1, which also causes the substrate of sample 2 to be more transparent than that of sample 1. This is also evident in the photograph of substrate (Fig. 3) at 400x the field of view observed by the micromorphology.

The content of BaO in the weathered layer of samples ranged from 1.9–21.7%. However, the BaO content in the regolith points 2 and 3 of sample 1 was significantly higher than that in the substrate, and the BaO content in the regolith points 1 and 2 of Sample 2 was significantly lower than that in the substrate. That is, the distribution of barium on the weathered layer of samples is not uniform, and a few barium-rich regions were formed. In the study on the corrosion characteristics of lead-barium glass in the Qin dynasty, it was also found that the distribution of barium element was not uniform in the weathered layer of the sample MB-10, and a few barium-rich regions were formed, and this barium-rich region was detected by Raman spectroscopy as a mixed state of lead carbonate and barium sulfate [12]. Therefore, it is believed that the uneven distribution of barium element on the surface was caused by the good water solubility of barium salt. That is, the barium in the regolith has been lost to the burial environment with water during the burial process, resulting in the uneven distribution of barium on the weathered layer.
The content of PbO in the weathered layer is higher than that in the substrate, and the content range is 11.8%-31.4%. According to the result of lead content on the surface of the substrate, these two glass beads are both low-lead glass at this time. The precipitation of lead is closely related to the temperature, humidity and pH of the buried environment. In the acidic environment of high temperature and high humidity, glass are easily eroded in the burial environment. The Pb content of the weathered layer of the samples is up to about 20% higher than that of the substrate, which also means that the surface structure of the substrate of the samples has been destroyed under long-term erosion in the buried environment [13][14]. Therefore, more attention should also be paid to the control of precipitation of lead in the conservation of silicate cultural relics.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
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<tbody>
<tr>
<td>Region</td>
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<td>Regolith</td>
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<tr>
<td>Content</td>
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<tr>
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<tr>
<td>MgO</td>
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<tr>
<td>BaO</td>
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</table>

**Physical phase structure**

The results of Raman spectrum analysis on the substrate of the two beads are summarized in Fig. 4. The Raman spectra of the two beads’ matrices showed envelope around 500cm⁻¹ and 1000cm⁻¹ respectively, which corresponds to the
bending and stretching vibration of Si-O bond in the glass, and there were no obvious characteristic peaks in other regions of the two beads. It indicates that the substrate of the two beads is glassy.

The Raman spectral analysis results of yellow, white and blue weathered layer of samples 1 and 2 are shown in Fig. 5, Fig. 6 and Fig. 7.

It can be seen from the results of Raman spectra that the yellow weathered layer in samples 1 and 2 are cerussite. The white weathered layer shows a mixture of barium sulfate and cerussite. This may be related to the choice of points, because white particles are surrounded by a large number of yellow weathered layer, so it is believed that the main component of white weathering products is barium sulfate. The large area of blue weathered layer covered by sample 2 is walstromite [BaCa\(_2\)Si\(_3\)O\(_9\)].

### Discussion

#### Fabrication process of glass

Micromorphology shows that large bubbles are unevenly distributed on the surface of the substrate of the two glass beads, and many small bubbles can be observed in the substrate. It means that the melting temperature of the two glass beads is low, so that the gas is difficult to escape and is retained in the substrate to form small bubbles, which proves that the production process of the glass beads is not fine. The weathered will also increase the glass transition degree of the substrate.

In addition, the substrate of both samples showed dark blue. The content of CuO in the substrate of samples 1 and 2 ranges from 0.4–0.8%, and the content of Fe2O3 ranges from 0.4–1.8%. In the non-destructive analysis of compound eye beads unearthed in Zhengzhou, it was found that the content of Fe and Cu in Zg01 diamond shaped area of lead-barium glass eye bead was high, which suggested that CuFeS2 may have been used as raw materials [15]. However, the color of the analyzed areas in this analysis is darker blue, which is different from the gold in Sample Zg01, and it is also different from the common coloration of Cu — green or blue. The color of two samples are believed to be composed of Fe and Cu. The appearance of the “dark” blue is due to the intervalence charge transfer (IVCT) between the Fe(II) and Fe(III) ions located in the octahedral position [16].

#### Weathering mechanism

The yellow weathered layer in samples 1 and 2 are cerussite, and the white weathered layer is barium sulfate. The large area of blue weathered layer covered by sample 2 is walstromite [BaCa\(_2\)Si\(_3\)O\(_9\)].

The color of cerussite itself is warm white. And in the case of impurity, it will gradually yellowed in the oxidation process, and then become light yellow. The large area of yellow weathered layer on the surface of samples should be formed by the accumulation of yellowed cerussite. In the fabrication process of glass beads, white lead, red lead, yellow lead may become the choice of raw materials for its firing, and the existence of cerussite can not be ruled out the possibility of residual raw materials for glass [17]. Since the yellow weathered layer does not belong to the same part as the glass. It is in the upper layer of the substrate, and the shape is extremely irregular, so PbCO\(_3\) is judged to be the weathering product on the surface of the sample. The formation process of cerussite is discussed in lead rust of bronzes [18][12]: First, the Pb on the surface of the glass beads are slowly oxidized to lead oxide in the buried environment. It is then transformed into a white, amorphous colloidal precipitate or solid — PbO·xH\(_2\)O. When carbonates, organic acids and air conditions in moist burial environment are satisfied, dissolved oxygen, water and carbonates gradually react with PbO·xH\(_2\)O on the surface of glass beads and slowly transform into more stable pale yellow PbCO\(_3\).
Barium sulfate [BaSO$_4$] is called barite in mineralogy. Qin [19] used mineral raw materials including barite to simulate the fabrication of lead-barium glass, believing that barite or its calcined products could not be used as raw materials for the fabrication of lead-barium glass, and it was almost impossible for ancient craftsmen to obtain BaO from barite. Based on the fact that the weathered layer in the test area are irregular in shape and obviously not in the same layer with the glass substrate, barium sulfate is considered to be the weathered. The formation of this weathered layer should be: due to better water solubility, Ba in the lead-barium glass substrate collected on the surface of the glass, with the loss of water molecules [12]. However, the water solubility of SO$_4^{2-}$ in the soil is worse than that of Ba, and the barium element that has not been lost is captured by SO$_4^{2-}$ in the soil on the glass surface and reacts to form barium sulfate.

The blue weathered layer is walstromite [BaCa$_2$Si$_3$O$_9$]. This mineral is found only in metamorphic rocks in North America, the northern USA and Yukon Territory, Canada [20][21]. The mineral is formed by the long-term contact with quartz and the low-temperature alteration of high-temperature rocks, so volcanic eruption is one of the causes of the mineral[22][23]. The mineral has been detected for the first time in weathering products from ancient glass samples. The Ca in this weathered layer should be provided by calcite [CaCO$_3$] in cadaver bones and soil. Sample 2 was buried close to the cadaver, so the harsh alteration conditions of the mineral is likely to have been provided by microbes that are abundant near the cadaver. The sample was in contact with soil for a long time in the burial environment, and the suitable low temperature alteration conditions were provided by water and microorganisms. The sample 2 reacted with Ca$^{2+}$ provided by the cadaver and soil, and Ba$^{2+}$ collected on the surface of glass, together with the white mineral barium sulfate that had been generated by weathering, resulting in the formation of walstromite in the low temperature burial environment.

In addition, although the two samples are similar in size and shape, the surface weathered layer on the surface are different due to different burial environments. From the weathering products, it can be seen that the burial environment of sample 1 is stable, but the moisture in the environment leads to a large loss of Ba in its substrate, resulting in the reaction of lead element with poor water solubility on the surface with carbonate, resulting in the accumulation of a large area of PbCO$_3$ on the surface. Because the burial location of sample 2 is close to the cadaver, there are more Ca and microorganisms around it, so that the rare blue weathering product walstromite is produced under the right environment.

**Conclusions**

1. The substrate of the two compound eye beads analyzed in the study are amorphous glass, and they both belong to the lead-barium silicate glass system. Combined with the type of dot & mesh, these two glass compound eye beads should be produced in China. And the darker blue of the substrate surface is caused by the IVCT between Fe(II) and Fe(III) ions.
2. The yellow weathered layer in samples 1 and 2 are cerussite, and the white weathered layer is barium sulfate. The large area of blue weathered layer covered by sample 2 is walstromite [BaCa$_2$Si$_3$O$_9$]. The weathering mechanism of PbCO$_3$ and BaSO$_4$ was explored. Walstromite was detected in glass weathering products for the first time. It is speculated that the harsh alteration conditions of walstromite are probably provided by the microorganisms near the cadaver, which should be generated by the reaction of barium on the surface of the glass with calcium in the bones and soil of the cadaver.
3. With the objects unearthed in the same cemetery, there are a large number of eight-edges pole of copper barium silicate, cerussite beads, lead-barium glazed pottery beads, lead-barium glass beads. They are all artifacts of the lead-barium silicate system. Therefore, the raw material source, fabrication process and origin of these artifacts of the lead-barium silicate system are likely to be the same, and may even be different products generated by the same batch of firing. Therefore, in the follow-up study, the relevant production source of this batch of lead-barium silicate system samples should also be studied.
Declarations

Acknowledgments

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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 JL, FS, and WH. FS provided the samples. The first draft of the manuscript was written by JL, 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 to participate

Not applicable.

Consent for publication

Not applicable.

Conflict of interests

The authors declare no competing interests.

References


Figures

Figure 1

Compound eye beads unearthed in Hejia Village, Zhouling.
The Warring State

<table>
<thead>
<tr>
<th>Early</th>
<th>Mid &amp; Late</th>
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<tr>
<td>GUANGDONG</td>
<td></td>
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</tbody>
</table>

Figure 2

Dots & mesh beads unearthed by China.

Figure 3
Microscopic observation of samples. Sample 1 (above), Sample 2 (below). A is the observation results of the bare surface of the beads at 100x, b is the observation results of the selected areas in the red box in Fig a at 400x, and c is the observation result of the weathered products on the surface of the beads at 100x.

Figure 4

Raman spectrum of body of Samples.
Figure 5

Raman spectrum of yellow weathered layer of Sample 1 and 2.
Figure 6

Raman spectrum of white weathered layer of Sample 1 and 2.
Figure 7
Raman spectrum of blue weathered layer of Sample 1 and 2.

Supplementary Files
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