Journal of Archaeological Science 38 (2011) 1671–1679

Contents lists available at ScienceDirect

Journal of Archaeological Science

journal homepage: http://www.elsevier.com/locate/jas

Chemical and lead isotope analysis of some lead-barium glass wares from the Warring States Period, unearthed from Chu tombs in Changde City, Hunan Province, China

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ARTICLE INFO

Article history:
Received 17 September 2010
Received in revised form
19 February 2011
Accepted 26 February 2011

Keywords:
Lead-barium glass
Chu Kingdom
Chemical analysis
Lead isotope analysis

ABSTRACT

In the context of the present study, we have conducted chemical and lead isotope analyses on twelve ancient glass samples unearthed from Chu tombs in Changde City, Hunan Province. The results of the chemical analysis of these samples show that all samples are PbO–BaO–SiO_2 glasses, thus indicating that they are all traditional ancient Chinese glasses. The chemical results also suggest that all Bi wares may either share a common source or were produced according to similar recipes. In turn, the eye beads are different from the Bi wares for their distinct chemical composition. The chemical results indicate that silica, lead-bearing material, barium-bearing material, and sodium/lime-bearing material are the main independent components of the raw materials employed in the production of these glass wares.

However, the lead isotope data pertaining to the Changde lead-barium glass wares show a wide variety of lead isotope ratios corresponding to lead-barium glasses, ranging from the highest to the lowest groups of ancient lead-barium glasses identified in the existing literature. Furthermore, the lead isotope analysis (LIA) results are not consistent with the results of the chemical analysis, for the latter suggest that the different chemical compositions of the Bi wares and the eye beads were not caused by distinct ore sources, but by different technologies. The LIA results also indicate that the early Chinese lead-barium glasses with the lowest and highest $^{207}Pb/^{206}Pb$ values were mainly made in the southern region of the ancient Chu Kingdom during the Warring States Period.

1. Introduction

Since the 1930s, early Chinese glasses have been renowned for their unique chemical compositions (Beck and Seligman, 1934). The results of chemical analyses indicate that PbO was used as the major flux in the production of these unusual glasses. Their high BaO contents render this type of glasses very peculiar among ancient glass varieties all over the world, and their composition is completely different from that of the Western traditional soda-lime glasses. Hitherto, this type of glass has never been found outside of ancient East Asia. The use of BaO–PbO–SiO_2 glass emerged as a much later development in the Western glass industry, as BaO has started to be added into glass only since the late 19th century (Brill et al., 1986).

In 1966, Brill and Wampler applied the lead isotope method in the context of a provenance study of ancient glasses. They found that the lead isotope field of ancient Chinese glasses can be considered distinct from all the other signatures identified anywhere else. Their study also showed that the lead in some early Chinese glasses fell into two main isotopic groups, and these groups contained the highest and lowest lead isotope ratios in their database (Brill and Wampler, 1967). As a result, most scholars considered that the early BaO–PbO–SiO_2 glasses were invented by ancient Chinese craftsmen, and that this type of glass was of Chinese origin.

Many chemical analyses of ancient lead-barium glass wares have been undertaken since the 1980s (e.g., Brill et al., 1986; Yamasaki and Murozumi, 1986; Shi et al., 1989, 1991; Shi and Zhou, 1992; Brill, 2001, 2005; Gan et al., 2006; Brill and Shirahata, 2009). The origin and development of the ancient lead-barium glasses have been summarised by Brill (1999) and Gan (2005). The results suggest that this type of glasses was mainly used in China from the late Spring and Autumn period (770–476 BC) to the Eastern Han Dynasty (25–220 AD) (Gan, 2005). However, concerning the lead isotopic study of the glasses, no significant research has been conducted after Brill's study (see Brill et al.,

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doi:10.1016/j.jas.2011.02.034

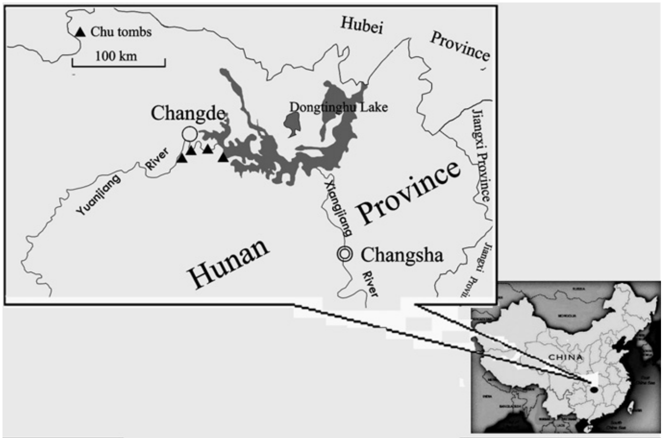

Fig. 1. The location of the Changde Chu tombs.

1991). Recently, Brill and Shirahata (2009) reported the lead isotopic data of 22 other ancient Pb-Ba glasses. These results also matched the conclusions reached earlier by Brill and Wampler (1967). However, Brill's samples were all part of museum collections, and their find places were unspecified. Although hundreds of glass wares have been unearthed since the 1980s, only a small number of them were analysed by the lead isotopic method. Therefore, the existing lead isotopic data pertaining to archaeologically excavated samples is not sufficient to verify Brill's results.

As a result, the place of manufacture for those glasses with uncommon lead isotope ratios still remains a mystery. In addition, it is worth noting that one of the major early glass types identified to date is the so-called 'Bi ware', a disk-shaped glass which was produced as an imitation of the same-shaped ware made of jade. This type of jade vessel served as ritual wares for worshipping gods. Some scholars considered $PbO-BaO-SiO_2$ glasses to have been mainly produced as alternatives to jade wares, because of their opaque appearances, due to the $BaO-SiO_2$ crystallisation (Gan, 2005). However, a significant number of translucent $PbO-BaO-SiO_2$ glasses have also been found; therefore, imitating similar jade vessels might have been only one of their purposes.

In China, early $PbO-BaO-SiO_2$ glasses were mostly found in the Hunan and Hubei Provinces, where the ancient Chu Kingdom was located during the Warring States Period (475 BC ~ 221 BC). Some archaeologists believed that the Chu Kingdom was the cradle for the production of $PbO-BaO-SiO_2$ glasses (Hou, 1995). The major types of Chu glass identified to date include Bi wares (disk-shaped wares), eye beads, sword decorations, and so on.

Changde City is located in north-western Hunan, in the Yuanjiang River drainage area, which used to be part of the Chu Kingdom. Since 1949, Chinese archaeologists have excavated hundreds of Chu tombs in this area, along the Yuanjiang River (see Fig. 1). Thousands of artefacts originating from these tombs were unearthed, among which there were a number of Chu glass wares, including Bi wares and eye beads.

The purpose of this paper is to present the chemical compositional and lead isotopic results of some glass fragments found in this area. Furthermore, we also provide a comparison between our results and the data previously published by other scholars.

2. Samples

The samples studied here were provided by the Changde Administration Bureau of Cultural Relics. They were all archaeologically excavated from Chu tombs in the Changde area. All

Fig. 2. Some Changde lead-barium glass wares used as samples in this study; top: Bi wares (disk-shaped wares), bottom: eye beads (M1532).

samples are dated to the late Warring States Period. Fig. 2 shows a photograph of some of these samples. A total number of 12 samples, of which 10 Bi wares and 2 eye beads, was analysed in the context of the present study. Table 1 provides a catalogue of all these samples.

3. Methodology

3.1. Chemical analysis

The chemical compositions of Changde glass wares were determined using Laser Ablation Inductively Coupled Plasma Atomic Emission Spectrometry (LA-ICP-AES). In this study, a LEEMAN-Prodigy ICP-AES with a NEW-WAVE laser ablation system was used to carry out this task. Operation conditions for the LA-ICP-AES system are as follows: 1) RF generator: 40.82 MHz; 2) RF Power: 1.1 kw; 3) Argon flow rate: Plasma: 1.4 l/min; 4)Auxiliary pressure: 0 psig; Nebuliser pressure: 30 psig; 5)Laser: Nd-YAG; 6)Laser mode: Q-switched; 7) Laser Wavelength: 266 nm; 8) Output energy: 15 ± 1 mJ; 9) Facular aperture: 610 μm; 10) Helium flow rate: 1050 ml/min.

When analysing silicate material (glass, ceramics, jades) using an LA-ICP system, analysts often employ silica as an internal standard, as this can generate very good results for the minor and trace elements (Ducreux-Zappa and Mermet, 1996A, 1996B; Russo et al., 1998). However, for major elements (especially for those elements whose concentrations are higher than 5%), the method does not work very well, because of the different silica content in the samples and standards; as a result, we cannot obtain the real silica content of the samples. Thus, if no data calibration is carried out, the analytical precision can be strongly influenced by some uncontrolled factors, produced by the laser ablating process itself. According to our own experience, data calibration is an indispensable step for quantitative analysis using LA-ICP-AES. Our calibration process consists of the following procedure: first, one external standard is used to acquire relative values of each element, then all results are summed up, and finally the total is divided by each value in order to obtain the exact composition of each specimen. After calibration, for homogenous material such as glass, most relative standard deviations of major elements are typically less than 1%, and those of minor and trace elements less than 5%. Moreover the data recoveries for major elements can commonly

Table 1
Catalogue of samples.

Sample ID	Tomb No.	Description	Date	Archaeological Context	Location
M680	WK97HAM3	Bi ware	LWS	White opaque ritual disk to imitate jade	Deshan Township
M655	WK94DSM21	Bi ware	LWS	White opaque ritual disk to imitate jade	Deshan Township
M699	WL84FJLM13	Bi ware	LWS	White opaque ritual disk to imitate jade	Lianhuachi Township
M653	WK94DSM17	Bi ware	WS	White opaque ritual disk to imitate jade	Deshan Township
M633	WK94LJSM1	Bi ware	LWS	White opaque ritual disk to imitate jade	Deshan Township
M939	DH01M67	Bi ware	LWS	White opaque ritual disk to imitate jade	Dinghuang Township
M621	WL86JZM1	Bi ware	LWS	White opaque ritual disk to imitate jade	Laomatou Township
M641	WK92LHWM1	Bi ware	WS	Green opaque ritual disk to imitate jade	Deshan Township
M704	WLDQCM1	Bi ware	LWS	White opaque ritual disk to imitate jade	Lianhuachi Township
M1575	HD98M3	Bi ware	LWS	White opaque ritual disk to imitate jade	Niejiaqiao Township
M1522	HZ87M14	Eye bead	LWS	Multicoloured bead (blue, red and white) from a necklace	Zhumushan Township
M85	WM85M24	Eye bead	LWS	Multicoloured bead (blue, red and white) from a necklace	Maowan Township

WS: Warring States Period (475 BC ~ 221 BC) LWS: Late Warring States Period (306 BC ~ 221 BC).

reach 100 ± 5%, and for minor and trace elements 100 ± 20% (see Table 2). Thus, this calibrating method is a simple but effective strategy for the chemical analysis of glass samples using LA-ICP-AES.

Eighteen elements were determined in the bodies, including Si, Al, Fe, Mg, Ca, Na, K, Ti, Mn, Pb, Ba, P, Cu, Sn, Sr, Co, Sb, Zr. The Corning C glass standard was used as standard reference material because the Changde samples are all lead-barium glasses. The Corning D glass standard was employed as a quantitatively controlling material. Table 2 shows the results pertaining to some major and minor elements for three repeat analyses of the Corning D glass standard. According to the analytical results for the major and minor elements, most relative standard deviations are less than 1% for major elements, and less than 5% for trace elements. Usually, the data recoveries for major elements are 100 ± 5%, and for minor and trace elements 100 ± 20%.

3.2. Lead isotope analysis

Lead isotope ratios were measured using a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) of the type VG Elemental at the School of Earth and Space, Peking University. The sample preparation procedure is described in detail elsewhere (Cui et al., 2010). The full sequence of the process is the following: 1) Small glass fragments of approximately 10 mg are chipped off using a sharp scalpel; 2) Then, the fragments are dissolved in pure nitric acid in a 50 ml glass beaker; 3) Subsequently, the clear solution is leached and diluted in a 100 ml flask using deionised water; 4) The solutions are then measured to detect the lead contents using ICP-AES; 5) According to the results representing the lead contents, the solutions are then diluted down to the tolerance limit of the instrument, which is 1 ug/l; 6) The thallium (Tl) standard SRM997 are then added in the solutions; 7) The lead isotope ratios of the samples can be measured on the MC-ICP-MS.

Based on repeated analysis of SRM981, it was determined that the overall analytical 2σ error for all lead isotope ratios was less than 0.04% (see Table 3). The standard deviation of mean values for the 20 measurements of each 5 ratios carried out during the analysis of one sample was less than 0.04%.

4. Results

4.1. Chemical analysis

The chemical compositional data are shown in Table 4. Each eye bead is measured so as to acquire 4–5 different sets of data since each bead has three colours, namely white, blue and red. The results suggest that all samples are $PbO-BaO-SiO_2$ glasses, thus indicating that they are all traditional ancient Chinese glasses.

We processed the compositional data with Principal Components Analysis using the SPSS software (version 15.0). All the analysed elements are included into the PCA analysis. Fig. 3 shows the plot of the first three PCA components. And Table 5 is the component loading matrix derived from the PCA. It can be concluded from this chart that all Bi wares might either have a single source or be made according to the same pattern of manual craft. The two beads are separated from the group including all the Bi wares, and the data of the different colours of the same bead are grouped together although their data are more scattered than those corresponding to the Bi wares because of their multicoloured aspect.

Fig. 4 shows bivariate plots of the concentrations of PbO vs. SiO_2 (4a), PbO vs. BaO (4b), and Na_2O vs. CaO (4c).

4.2. Lead isotope analysis

We carried out lead isotope analyses on all the samples, except for samples M633 and M85, as only non-destructive analyses were permitted for these two samples. Table 6 shows the lead isotope ratios of all glass wares. The data are also shown on the plots of $^{207}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ vs. $^{206}Pb/^{204}Pb$ in Fig. 6.

The chemical results show that the compositions of the Bi wares are quite homologous. However, the LIA results show wide variations of all the lead isotopic ratios of these lead-barium glasses, including the highest and the lowest groups mentioned by Brill. Thus, the LIA data indicate that there might be diverse ore sources

Table 2
The results of three runs for the Corning D glass standard and published values from Brill (1999) (in wt%).

Run Number	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Fe_2O_3	PbO	BaO
1	1.379	3.990	5.801	54.083	3.937	12.186	15.390	0.431	0.563	0.470	0.499
2	1.400	3.952	5.649	53.810	4.163	12.665	15.076	0.405	0.544	0.496	0.483
3	1.357	4.014	5.722	54.054	4.043	12.364	15.238	0.406	0.544	0.483	0.485
average	1.38	3.99	5.73	53.98	4.05	12.41	15.24	0.41	0.55	0.48	0.49
published value	1.2	3.94	5.3	55.24	3.93	11.3	14.8	0.38	0.52	0.48	0.51

Table 3
The results of six runs for the SRM981 determination and the average analytical error.

Run number	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
1	0.9147	2.1676	16.943	15.498	36.726
2	0.9147	2.1675	16.940	15.496	36.718
3	0.9147	2.1675	16.946	15.500	36.730
4	0.9146	2.1675	16.940	15.494	36.718
5	0.9147	2.1672	16.935	15.490	36.700
6	0.9148	2.1675	16.946	15.502	36.731
Analytical error (%)	0.006	0.007	0.03	0.03	0.03

for these glasses. Brill et al. (1991) already noted this situation, as they pointed out that "in some instances the isotope data group together samples having similar chemical compositions, but – somewhat surprisingly – there does not seem to be a strong overall correlation between the ratios and chemical composition. Perhaps we have not yet found the best way of interpreting the chemical analyses" (Brill et al., 1991).

5. Discussion

5.1. Major and minor components

The compositions of the Bi wares are pointedly different from those of the eye beads. There is a negative correlation between SiO_2 and PbO, and their sum often reached up to 80%. All the Bi wares have more than 35% PbO, while the concentration of lead oxide in the eye beads is less than 20%. In reverse, the SiO_2 contents of Bi wares are all less than 40%, and those of the eye beads are more than 50%. This suggests that these two oxides are the most important independent ingredients of the glasses, and the level of their contents was carefully controlled. However, the level of BaO contents for all samples varies randomly, spanning the entire range from 2.8% to 18.1%, while a large number of them cluster on a level of about 10%. This indicates that BaO might be the other individual primary ingredient of the glasses, yet one whose content was out of the control of the craftsman. Thus, one could conclude that these three oxides are the most significant independent components of the glasses.

It is worth noting that the Na_2O contents in all Bi wares are higher than 3 wt% and CaO contents are higher than 1%. However, the K_2O and MgO contents are all very low, especially in the Bi wares. If we subtract the PbO and BaO from these glasses and normalise the results (see Table 7), it can be observed that the compositions of all glasses are similar to soda-lime glass to a certain extent, a composition which is a prominent feature of the traditional western glass system. This situation has been observed by Brill when he carried out research on Kwan's glass collection (Brill, 2001). All early lead-barium glasses in Kwan's collection contain high soda, some even higher than 6%. Among these samples, some also contain high lime, such as samples 6700, 6748 and 6746. Thus, our results indicate that the Na_2O and CaO may have originated from some other independent material. In addition, this aspect also suggests that the Pb-Ba glasses may have some common features with the soda-lime glasses.

From the abovementioned data, it can be concluded that all Bi wares may either share a single source in terms of the raw materials employed, or that they were made using the same recipes. The eye beads are completely different from the Bi wares due to their distinct chemical compositions. However, are the differences between the Bi wares and the eye beads caused by the ore sources or the distinct crafts employed in their making? This is a puzzle that should be explored further.

The chemical results also suggest that the glasses were mainly made from four independent components, including silica, lead-bearing material, barium-bearing material, and sodium/lime-bearing material.

Following the analyses, we compared our results with the published data on ancient lead-barium-silica glass samples (Li, 2005). Forty samples were selected for comparison, including Bi wares and beads, all dating from the Warring States Period. Fig. 5 presents a three-dimensional PbO–BaO–SiO_2 plot of some published data on ancient Chinese lead-barium glass. The plot indicates once again that Bi wares all have PbO contents higher than 35%. However, most beads have PbO contents of less than 30%. Thus, we can conclude that the production techniques involved in the making of Bi wares might have been standardised during the Warring States Period. Therefore, a production centre for Bi wares might have possibly existed, or, alternatively, Bi wares might have had their own particular recipes.

Based on the archaeological background, Gao (1986) and Hou (1995) considered that the southern Chu Kingdom was once the production centre for lead-barium glasses during the Warring States Period. So far, most of the archaeological Bi wares were unearthed in Changsha City and its surrounding area, a region corresponding to the southern territory of the Chu Kingdom. Thus,

Table 4
Chemical results of the Changde glasses (in wt%).

Sample ID	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CuO	SrO	SnO_2	BaO	PbO
M680	3.54	0.31	1.47	38.00	0.04	0.18	1.07	0.04	0.05	0.19	0.01	0.06	0.05	5.11	49.83
M655	2.74	0.34	1.34	38.79	0.02	0.22	1.23	0.04	0.03	0.23	0.06	0.06	0.05	9.19	45.64
M699	2.92	0.48	1.93	39.64	0.05	0.24	1.26	0.07	0.06	0.31	0.03	0.13	0.07	8.66	44.03
M653	3.17	0.49	1.42	40.14	0.05	0.16	1.13	0.07	0.05	0.45	0.01	0.08	0.11	6.35	46.31
M633	3.44	0.38	2.53	36.08	0.03	0.45	1.50	0.11	0.04	0.60	0.03	0.19	0.12	12.25	42.21
M939	3.96	0.58	1.71	38.00	0.07	0.31	2.45	0.06	0.04	0.39	0.06	0.20	0.15	10.67	41.21
M621	4.09	0.33	1.16	34.90	0.02	0.08	1.05	0.04	0.04	0.13	0.02	0.05	0.06	4.61	53.36
M641	2.83	0.28	1.15	34.75	0.10	0.29	1.71	0.03	0.10	0.20	1.48	0.08	0.04	8.54	48.46
M704	2.92	0.42	0.71	35.91	0.02	0.12	2.00	0.02	0.06	0.17	0.06	0.06	0.03	10.58	46.94
M1575	3.26	0.31	1.16	39.70	0.04	0.17	1.43	0.04	0.04	0.23	0.02	0.15	0.05	8.64	44.73
M1522-RED1	0.93	0.29	1.75	57.33	0.46	1.55	2.42	0.14	0.15	1.86	0.43	0.28	0.34	9.08	23.01
M1522-RED2	1.35	0.20	1.10	55.57	0.14	1.05	1.26	0.08	0.09	1.75	0.42	0.30	0.36	11.62	24.64
M1522-BLUE	1.17	0.22	1.31	60.70	0.13	1.00	1.33	0.09	0.10	1.21	1.93	0.25	0.25	10.62	19.61
M1522-WHITE	0.99	0.37	1.84	54.52	0.61	1.92	3.01	0.11	0.19	0.76	0.23	0.30	0.17	11.12	23.90
CHD-M85-RED1	0.83	0.57	4.68	34.98	0.11	1.34	1.56	0.41	0.04	29.20	0.03	0.17	5.63	7.94	12.44
CHD-M85-RED2	0.85	0.54	3.54	30.66	0.13	1.11	1.85	0.35	0.05	31.54	0.03	0.21	6.02	9.80	13.28
CHD-M85-BLUE1	4.37	1.11	5.18	58.00	0.04	2.58	1.46	0.37	0.09	2.27	5.25	0.40	0.41	7.90	10.48
CHD-M85-BLUE2	3.96	0.91	4.03	53.73	0.00	2.03	1.22	0.26	0.06	1.05	5.07	0.38	0.20	18.08	8.88
CHD-M85-WHITE	2.91	0.63	6.24	60.09	0.02	2.13	0.71	0.25	0.09	1.92	0.09	0.09	0.30	0.42	11.70	12.51

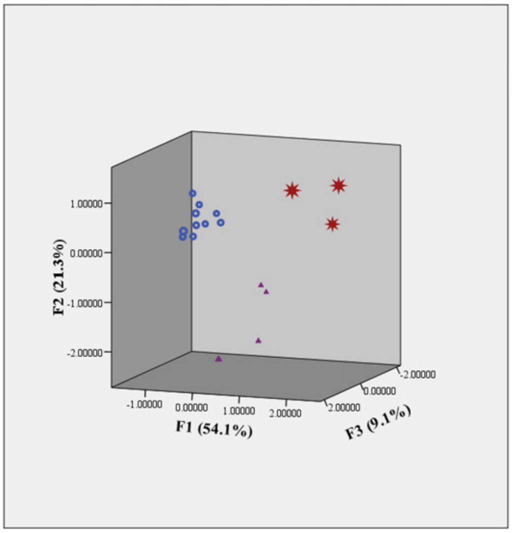

Fig. 3. The plot of the first three components derived from the principal component analysis (PCA) of the chemical compositions of the analysed glass samples (the two data pertaining to M85 RED are discarded due to their unique compositions).

it can be concluded that this area might indeed have been the production centre for Bi wares.

5.2. Colourants

All Bi wares are opaque. As in the case of jades, the dominant colours of these wares are white and green. As pointed out by Gan (2005), the opaque appearances of these wares are due to the $BaO-SiO_2$ crystallisation. This opaque appearance makes the Bi wares look like jade, which is the most important material used for the making of ritual objects in ancient China. Therefore, Chu craftsmen might have been familiar with the function of BaO in glass. They intentionally added ores bearing barium into the raw materials used for glass-making in order to achieve the effects of jade.

M641 is the only green Bi ware among the samples analysed in this study. Its composition is similar to other Bi wares, except for its higher CuO concentration, which is about 1.5%. Thus, copper is the colourant element for this ware.

The main colours of two eye beads are white, blue and red (see Fig. 2). According to the chemical compositions, the blue parts of the two eye beads also contain higher amounts of CuO. Thus, the colourants employed for the making of the blue parts are also copper-based. According to the ligand field theory, the colour of the transition metal ion will change if its oxygen coordination changes from four to six, i.e. if the structure of a crystal changes from tetrahedral to octahedral co-ordination (Pollard and Heron, 1996: 163–173). For a glass system in which the colourant is Cu^{2+}, if the copper ions replace the silicon, they become the network formers, and then the resulting glass will be blue. If the copper ions replace the lead ions in the network, they become the network modifiers, and then the colour will be yellow or brown. Thus, as the lead content increases, the colour will change from blue to yellow. Also, when a certain critical value is exceeded, the colour will change to green, whose wavelength is between blue and yellow. It is possible that Chu glass craftsmen were very familiar with this phenomenon, just as Pollard and Heron (1996; 170) thought about the medieval glassmakers that they "were adept co-ordination chemists".

The results show that the red parts of two eye beads are a result of different causes. The red parts of M85 have Fe_2O_3 contents higher than 30%, which suggest that the colourants of the red parts are Fe^{3+}. This can also be seen in the ancient glass collections of Kwan (2001, No.38 and No. 41 collections). Therefore, the red part of M85 may be a result of adding hematite or other iron bearing ores. However, the Fe_2O_3 contents in M1522 are not very high. In this case, the level of iron ions in the red part is the same as in the other parts. The only elemental differences between the white part and the red one is that the CuO contents of the red part are slightly higher than in the white one. Therefore, we can conclude that the red part of the M1522 is caused by its reduced content of univalent copper ions.

5.3. Provenance

According to the chemical analysis, the Changde glasses can be distinguished by ware type for their different chemical compositions, i.e., the Bi wares all have higher PbO contents than the eye beads (Cui et al., 2009). However, with regard to this aspect, the lead isotopic results are not in agreement with the chemical results. One of the Bi wares (M939) has almost the same lead isotope ratios as the only analysed eye bead (M1532), an aspect which indicates that these two glasses share the same lead source. The verification of the same lead isotopic ratios also means that these two wares might have been made from the same batch of lead materials. Thus, these two glass wares may have been made in one workshop. This in turn indicates that the same workshop could have produced different glass varieties with different recipes. The LIA results also reveal that the different chemical compositions of the Bi wares and the eye beads were not caused by the distinct ore source, but by different craft.

On the plot of $^{207}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$, the data almost overlay all data areas corresponding to the published LIA data on ancient lead-barium glass. According to the LIA database of ancient glasses published by Brill et al. (1991), early Chinese lead-barium glasses cover a particular lead isotope field, which can be categorised into five groups. The Chinese database contains the lowest and the highest lead isotope ratios of the entire database. The group of LIA data with the lowest lead isotope ratios in Brill's database corresponds to a $^{207}Pb/^{206}Pb$ value of less than 0.80, and the highest ones to a value of more than 0.87. Brill's database also includes the middle group, with a $^{207}Pb/^{206}Pb$ value between 0.80 and 0.87. Thus, the lead isotope data of Changde glasses occupy all the ranges in Brill's database, especially the lowest and highest ones.

Since Brill's samples were all from a museum, the location of the places where they were made and found was still unknown. This still represents a crucial problem in the study of Chinese glass history. Thus, the Changde glasses are much more important, due to their clearly identifiable unearthing places. Hitherto, lead-barium

Table 5
Component loading matrix derived from the PCA.

	F1	F2	F3
Na_2O	−0.017	0.953	0.094
MgO	0.715	0.589	0.218
Al_2O_3	0.821	0.316	−0.194
SiO_2	0.843	−0.436	−0.181
P_2O_5	0.160	−0.859	0.330
K_2O	0.957	−0.190	0.012
CaO	−0.018	−0.575	0.724
TiO_2	0.950	0.212	−0.059
Fe_2O_3	0.870	−0.278	−0.299
BaO	0.541	−0.072	0.309
PbO	−0.961	0.213	0.030
CuO	0.752	0.350	0.170
SrO	0.946	−0.200	0.142
SnO_2	0.852	−0.283	−0.296
Eigenvalue variance (%)	54.1	21.3	9.1

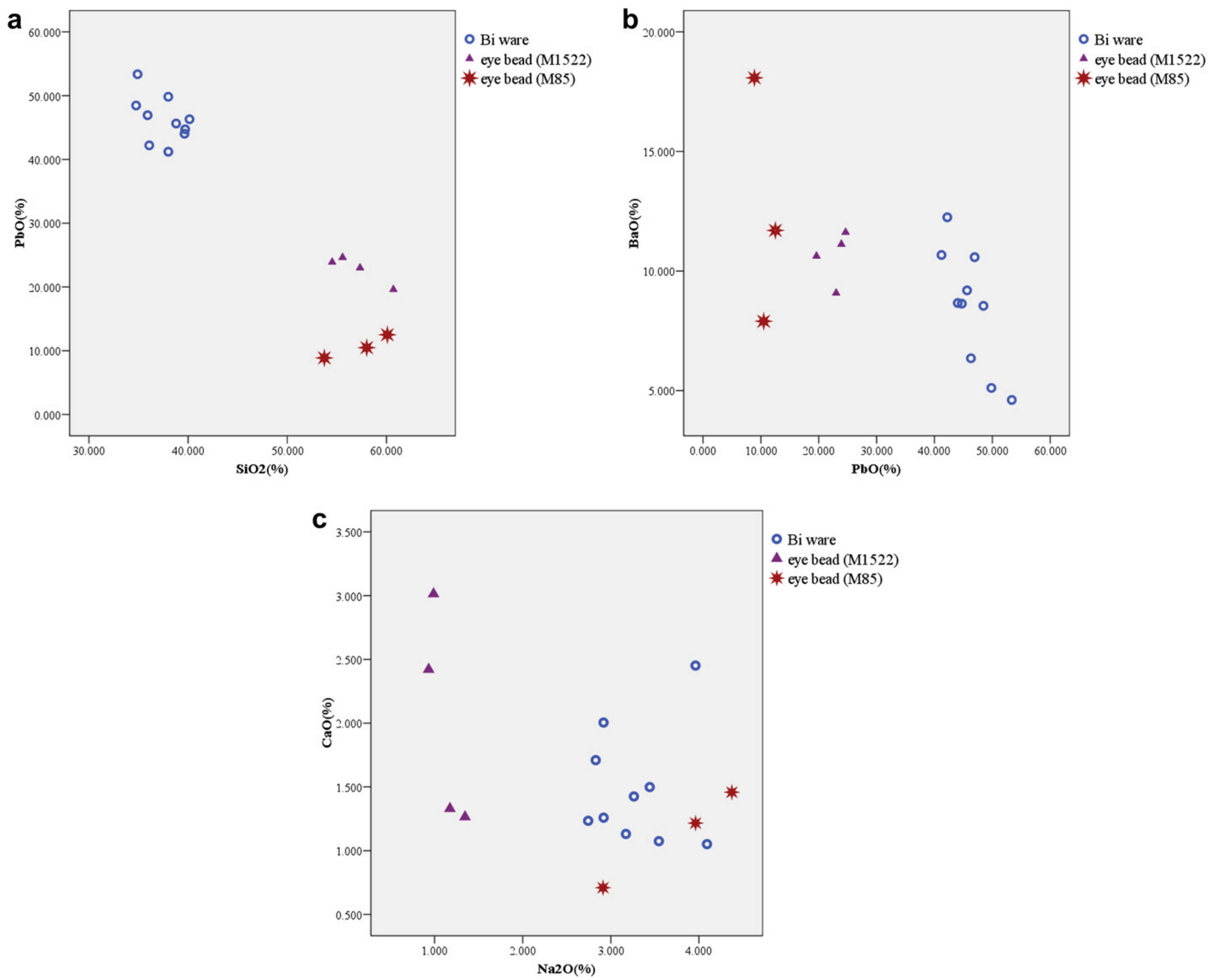

Fig. 4. Bivariate plots corresponding to the concentrations of some elements as oxides (values expressed in wt%).

glass Bi wares have mainly been found in the area corresponding to the ancient Chu Kingdom, especially in its southern part, including the present-day Changde City. As a result, some archaeologists concluded that southern Chu was the lead-barium glass-making centre of the Chu Kingdom during the Warring States Period. The Chu glass craftsmen used these unique glass materials to imitate jade (Gao, 1986). Some scholars even thought that southern Chu was the cradle of lead-barium glass (Zhao, 1991; Hou, 1995: 270–275). The LIA data of ancient Changde glasses provide a proof for these assumptions. Hitherto, all the glass Bi wares were found in tombs belonging to southern Chu people; this aspect indicates that this type of ware was an important and common form of buried goods for these people. However, according to the archaeological

Table 6
Lead isotope ratios for the lead-barium glasses from Changde Chu tombs.

Sample ID	Type	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
M 1575	Bi ware	0.7682	1.9792	20.747	15.938	41.063
M 653	Bi ware	0.8149	2.1268	19.364	15.780	41.183
M 641	Bi ware	0.8443	2.0942	18.632	15.731	39.019
M 655	Bi ware	0.8437	2.0933	18.646	15.732	39.031
M 939	Bi ware	0.8934	2.1949	17.327	15.481	38.031
M 680A	Bi ware	0.7300	1.9190	21.962	16.032	42.144
M 621	Bi ware	0.7310	1.9235	21.931	16.032	42.184
M 699	Bi ware	0.8568	2.1231	18.263	15.650	38.777
M 704	Bi ware	0.8438	2.0963	18.668	15.752	39.133
M 699	Bi ware	0.8563	2.1219	18.262	15.637	38.751
M 1532	Eye bead	0.8935	2.1961	17.310	15.469	38.018

Table 7
The normalized results for the major elements of Bi wares after subtracting the PbO and BaO (in wt%).

Sample ID	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3
M680	7.91	0.70	3.28	84.79	0.41	2.40	0.09	0.43
M655	6.10	0.76	2.98	86.32	0.48	2.75	0.10	0.51
M1575	7.05	0.66	2.50	85.77	0.36	3.08	0.09	0.50
M699	6.23	1.03	4.12	84.60	0.52	2.69	0.15	0.66
M653	6.74	1.05	3.03	85.32	0.34	2.40	0.16	0.96
M633	7.63	0.84	5.62	80.01	1.00	3.32	0.25	1.33
M939	8.34	1.23	3.61	80.06	0.65	5.16	0.13	0.81
M621	9.79	0.79	2.79	83.52	0.20	2.52	0.09	0.32
M641	6.86	0.69	2.79	84.26	0.71	4.15	0.07	0.48
M704	6.90	0.99	1.67	84.96	0.29	4.74	0.05	0.39

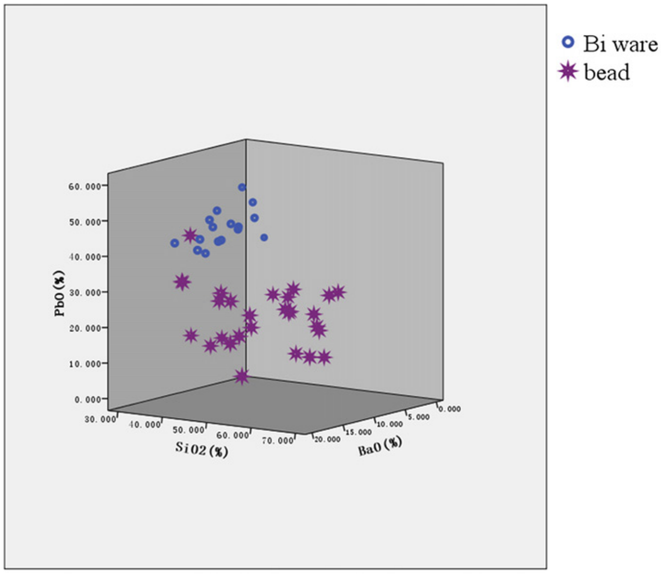

Fig. 5. Three-dimensional PbO–BaO–SiO_2 plot of some published data on ancient Chinese lead-barium glass.

finds unearthed to date, this was not the common case in other vassal kingdoms during the Warring States Period (Gao, 1986). The lead isotopic data of these lead-barium glasses indicate that the early Chinese lead-barium glasses with the lowest and highest $^{207}Pb/^{206}Pb$ values might have been made in the southern area of the ancient Chu kingdom during the Warring States Period. Thus, the Bi wares could have all been made locally in the area of ‘southern Chu’.

The ‘low lead isotope ratios’ mentioned by Brill et al. (1991) are indicative of a type of so-called ‘high radiogenic lead’. This type of lead contains higher radiogenic isotopes (i.e. ^{208}Pb, ^{207}Pb and ^{206}Pb) than the common mined lead. In fact, this type of lead is commonly found in Shang Dynasty bronzes. However, the origin of these leads remains a conundrum among Chinese scholars (Jin, 2003). It is remarkable that in most circumstances where the low lead ratios were identified, the ‘high lead ratios’ also appeared; this aspect indicates that these two types of lead could originate from the same source.

According to the lead isotopic geochemical theory, if the lead ore deposits are carbonate-hosted, the lead isotope ratios of the ores could be much more complicated than the massive sulphides because of their more complex origins. The carbonate-hosted deposits are thought to have diverse sources. Such types of lead deposits are isotopically heterogeneous. However, the variation is not random; on the plots of $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$, the data will exhibit overall linear trends with high correlation (Gulson, 1986). This line is called isochrone. The most famous lead deposits with this character are the Mississippi Valley lead-zinc deposits (MVT deposits), where the ores contain more radiogenic lead isotopes than lead-rich massive sulphide mines. The leads in the ancient Changde glasses with $^{206}Pb/^{204}Pb$ values of more than 20.0 are very similar to the MVT lead ores. Thus, the issue of their source could be much more complicated. Before the 1990s, MVT lead deposits had been mostly found in Southwest China, including the Yunnan, Sichuan and Guizhou Provinces (Chen et al., 1980). Recently, more and more MVT ores have been found in central China (Zhang et al., 2009). Zhong and Mao (2008) reported that a large MVT lead-zinc metallogenic belt has been found in the northwest Hunan Province, which is very close to Changde City. However, the authors did not report any lead isotope data. As a result of this, it is difficult to assess whether the lead-barium glasses found in Changde City are in any way related to this MVT deposit.

We have carried out linear regressions for these data, and the results are shown in Fig. 7. The data presented in this figure also include the results published by Brill et al. (1991) and Brill and Shirahata (2009). From the figure, we can conclude that all these lead-barium glasses might have two lead sources. However, the ‘low ratios’ and the ‘high ratios’ always appeared together. Furthermore, from Fig. 7, we can see that these two lines intersect at a point of the middle ratio where the value of $^{207}Pb/^{204}Pb$ is about 15.75 and that of $^{206}Pb/^{204}Pb$ is about 18.50. These data are similar to the two stage evolution model proposed by Stacey and Kramers (1975). Thus, all these glasses may have a single lead ore source.

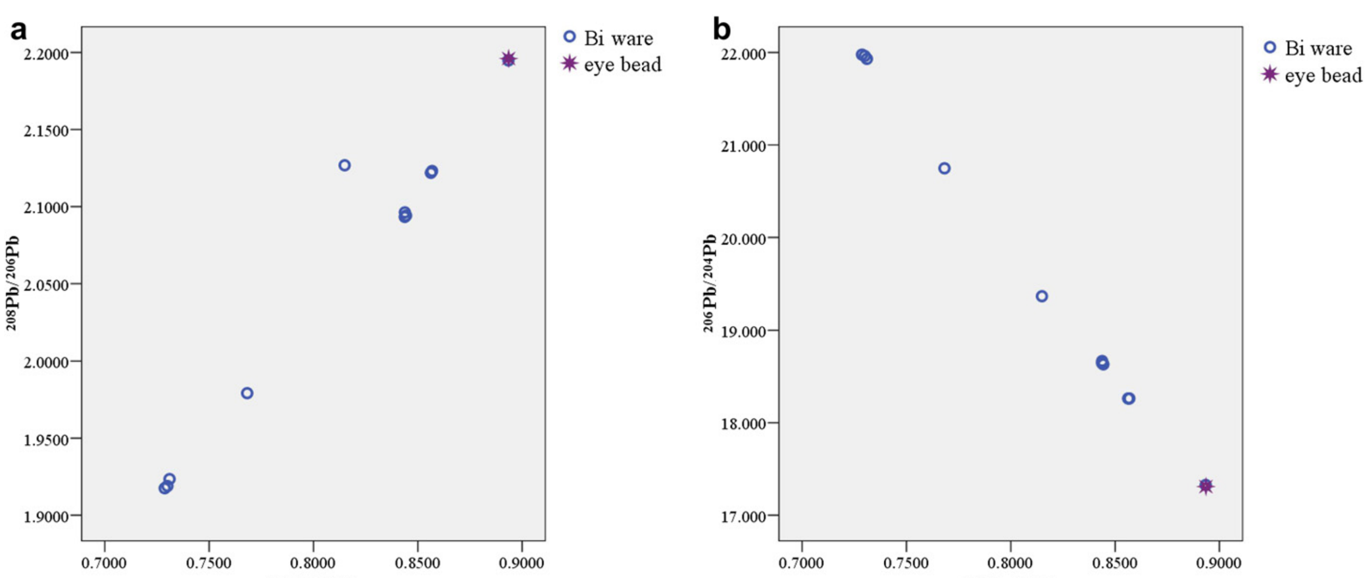

Fig. 6. Lead isotope ratios for the lead-barium glasses from the Changde Chu tombs.

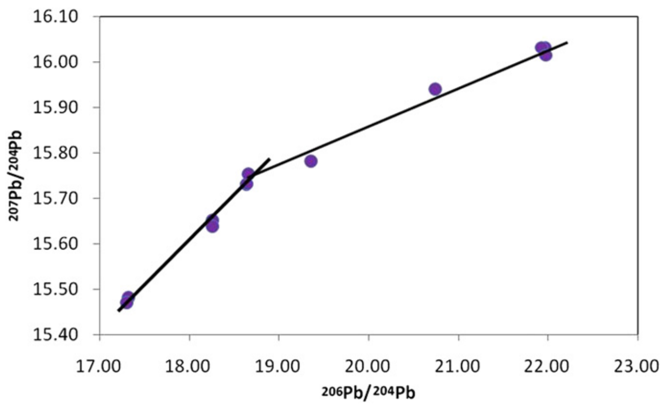

Fig. 7. The linear regression for the values of $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$.

6. Conclusion

The chemical analysis results show that all Bi wares might either have a single source for their raw materials or that their production was based on the same recipes. The eye beads are completely different from the Bi wares due to their distinct chemical compositions. The chemical results also suggest that silica, lead-bearing material, barium-bearing material, and sodium/lime-bearing material are the main independent components of the raw materials used for making the glass. Comparing these results with the published data on ancient lead-barium-silica glass disks indicates that the southern region of Hunan Province could have been a major production centre for this type of glass during the Warring States Period.

The colourants that give the green and blue colours of these glasses are all bivalent copper ions. The coluorant of the red part of one eye bead (M85) consists of trivalent iron ions, while the red colour of another eye bead (M1522) might be caused by univalent copper ions.

The lead isotope data of the Changde lead-barium glass wares show wide variations of all lead isotope ratios, including the highest and lowest groups identified in the published data on ancient lead-barium glasses. The LIA results also indicate that the lead isotope ratios of Bi wares are considerably scattered despite their similar chemical compositions; this situation is very similar to the one suggested by Brill et al. (1991). One of the Bi wares (M939) has almost the same lead isotope ratios as the only analysed eye bead (M1532), which suggests that they were produced by the same workshop during the same period. This result is also discordant with the chemical analysis. Consequently, the different chemical compositions between the Bi wares and the eye beads were not caused by the distinct ore source, but by different craft.

Since all these glass wares have specified unearthing locations, their lead isotope ratios can be regarded as references for the published data. The lead isotopic data of these lead-barium glasses overlay the LIA field of ancient Chinese lead-barium glasses published by other authors. This indicates that the early Chinese lead-barium glasses with the lowest and highest $^{207}Pb/^{206}Pb$ values may have been produced in the southern area of the ancient Chu Kingdom during the Warring States Period. This result is consistent with the archaeological discoveries of the recent years.

Acknowledgements

This work is financially supported by the National Social Science Foundation of China (Project No: 10CKG003). The authors would like to thank Director Y.B. Wang and Professor Y.H. Tan of the Changde Administration Bureau of Cultural Relics for providing the glass samples. We are indebted to Dr. C.W. Chen for his kind help with improving the English language of this study. Professor Th. Rehren is gratefully acknowledged for his comments on the early manuscript and his help with improving the English of our study. We are also very grateful to Mr. Raul Carstocea for his help with the English language corrections of the final manuscript. Comments by three anonymous reviewers have greatly improved the manuscript and are gratefully appreciated.

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