

## The Production and Composition of Chinese Lead-Barium Glass through Experimental Laboratory Replication

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### Highlights:

- Sodium is essential for lead-barium glass forming.
- Previous chemical analysis of ancient lead-barium glass underestimates the sodium content.
- Opaque lead-barium glass cannot be produced during the primary production.
- Lead-barium glass can be produced by mixing natron glass with lead and barium minerals.

### Abstract

Lead-barium glass appeared during the late Warring States period in China (457- 221 BCE) and was considered as a Chinese invention due to the unique presence of high barium. There is no indication as to how it was made. A set of twenty-four different combinations of possible raw materials were melted to test and systematically evaluate the possible recipes for lead-barium glass. Specifically, the function and source of sodium in lead-barium glass were explored. The results show that sodium source is crucial for lead-barium glass forming in this particular system. This paper explores an alternative formulation since sodium flux is not reported in historical Chinese sources, in which the Na<sub>2</sub>O is provided by including soda-lime glass in the mixture. This particular formulation provides a potential explanation for the source of the sodium.

*Keywords:* Lead-barium glass; Crucibles; Sodium; Opacifier; Chinese glass

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## 1. Introduction

The origins of glass bead-making in China have been attributed to an accidental by-product of ceramic glaze manufacture. The Chinese term 'proto-porcelain' (which in the West is referred to as 'stoneware') refers to the low-fired glazed ceramics which appeared from the Shang (1700 - 1027 BCE) to the Zhou (1027 - 221 BCE) dynasties. During the production process, it appears that drops of glaze can flow down from the stoneware during the firing process and subsequently produce a glass drop. According to the analysis of glass drops found in the Henglingshan Tomb Site in Boluo, Guangzhou, dating the Early Spring and Autumn period (~800 - 700 BCE), Gan *et al.* (2007) argued that these drops of glaze were the prototype of Chinese glass beads. Given their rarity and value, they could have been used as jewels or ornaments in the swords of nobles. A decorative glass drop on a sword was, for example, excavated from No. 1 Chu Mausoleum (496 - 464 BCE), Hubei Province. PIXE analysis of this particular decorative glass showed that it is a wood ash glass, and the proportion of  $K_2O$  is higher than  $Na_2O$  (Hou, 1989). Wood ash glass did not appear in Europe until around 800 CE (Wedepohl and Simon, 2010). Gan *et al.* (2007) noted that there is no published data from contemporary Egyptian and Mediterranean plant ash glasses in which the  $K_2O$  value is higher than the  $Na_2O$  value, which in their view suggested that this decorative glass was produced in China. Therefore, it was concluded that Chinese glass evolved from stoneware glazes made using wood ash.

According to scientific research and historical records, the trade between Mediterranean and China through Eurasia Steppe can be dated to the 10<sup>th</sup> century BC, which was the Late Shang and the Early Zhou Dynasty (1046 - 256 BCE: He and Wan, 1998). Merchants brought marine products from the eastern coastal region of China to Taklimakan in the Shang Dynasty (1600 - 1046 BCE: Bao, 2015). silk was exported from China to Europe in the 4th century BC (Gan, 2006). Nomadic people conquered some of the areas of Middle Asia through which the Steppe Route passed in the 1st century BC, and the wars that these nomadic people started with

neighbouring countries and robbery of trade caravans almost suspended the commodity circulation between China and Europe (Liu, 2012). When the Qin Empire (221 – 207 BCE) united the China after the Warring States period (475 – 221 BCE), it was soon replaced by the Han Empire (202 BCE – 220 CE) fifteen years later. The social economy and currency economy soon recovered with the implementation of low-taxation policy during the early Han Period and the Han Empire became one of the most powerful countries. Later, Emperor Han Wudi (156 - 87 BCE), the 7th emperor of the Han Dynasty (202 BCE - 220 CE), commanded officer Zhang Qian 张骞 to investigate the past trade route between China, the Middle East and Europe. Zhang Qian started his first journey from the city of Chang'an (modern Xi'an) in 139 BCE. Merchants joined with Zhang Qian for his second investigation in 119 BCE, and they gained huge profits during this trip by exchanging their products with foreigners. The prosperous age of commodity circulation along the Northwest (Desert) Silk Road began then, as Egyptians and Romans began purchasing silk products from the Parthians, which had been imported from the Han Empire (Liu, 2012). Lead-barium was invented in China during the Warring States period due to the technology exchange with the western world. Still, this type of glass has commonly been considered to be a uniquely Chinese-made glass due to its high proportion of barium. This type of glass arose during the Late Warring States period (around the 5<sup>th</sup> century BCE) and suddenly disappeared after the Han Dynasty ((around the 2<sup>nd</sup> century CE - Li, 1996). Chinese glassmakers produced glass to simulate other materials, such as hardstones, or as a vehicle for pictorial presentation(Tait, 2011). A few contemporary documents mention glass, but none of them clearly refer to lead-barium glass. For example, 'Lun Heng Shuai Xing Pian' 论衡 率性篇, written by Wang Chong 王充 in 87 CE, first documents the formulation of glass. He mentioned that Taoists used 'Wu Shi' 五石(five different components) to produce imitation jade, and that this glass could also be used as the sun flint (magnifying glass) after polishing. 'Wu Shi' included Dan Sha 丹砂 (mercuric sulfide HgS), Xiong Huang 雄黄 (realgar As<sub>4</sub>S<sub>4</sub>), Bai Fan 白矾 (alum KAl(SO<sub>4</sub>)<sub>2</sub>•12H<sub>2</sub>O), Zeng Qing 曾青 (copper sulfate CuSO<sub>4</sub>) and Ci Shi 慈石 (magnetite Fe<sub>3</sub>O<sub>4</sub>), as the main ingredients for the elixir. Chinese Emperors all sought longevity, and Daoists were required to provide the appropriate elixir. Clearly, these five

components cannot produce glass, but the context suggests that there may be some connection between Daoist alchemy and glass production.

The documentation in 'Formula of Tai Qing Elixir' 太清丹经要诀 written by Sun Simiao 孙思邈 in the Late Sui and the Early Tang Dynasty (618-907 CE) reinforces this hypothesis. He mentioned that the white 'Tai Qing' elixir was made by mixing and firing 100 g Shui Jing 水精 (silica crystal) powder with 1000 g lead oxide (PbO), and this could actually be the formula for high lead glass. This book also documents the formula for making 'Jade': '500 g shell (CaCO<sub>3</sub>) is ground into powder and sealed in a bamboo pipe with saltpetre (KNO<sub>3</sub>); then the bamboo pipe is soaked in vinegar (acetic acid: CH<sub>3</sub>COOH) for twenty days; 500 g silica quartz powder is poured into the bamboo pipe after twenty days and directly fired with coal. The shell functioned as the stabilizer and saltpetre was the flux. It is clear that the 'jade' in this case was actually a potash glass.

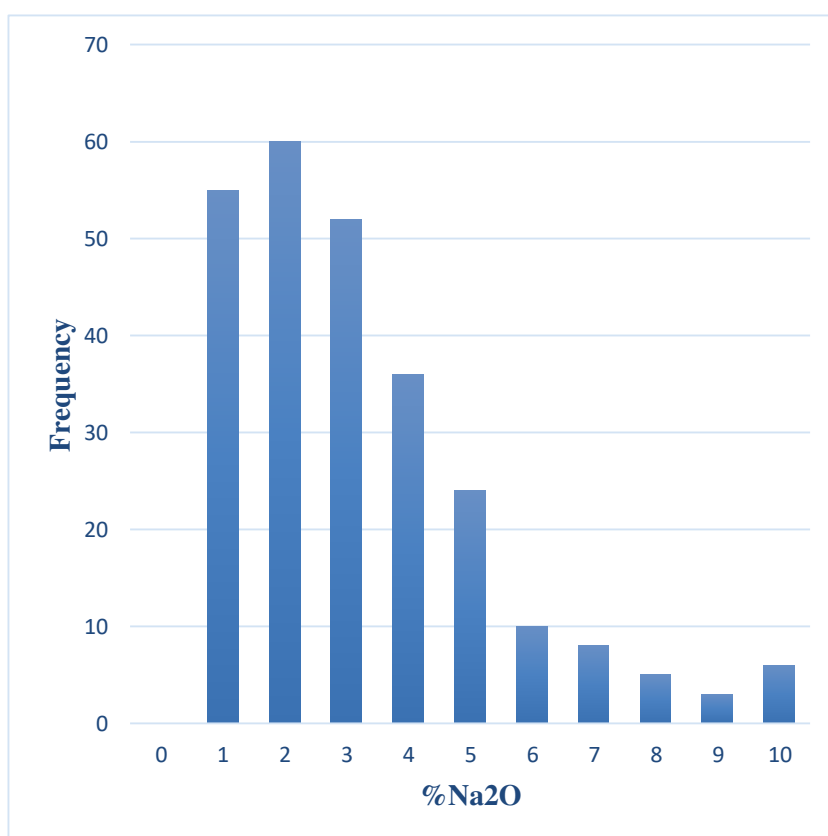
The formula for 'Liu Li' 琉璃 is documented in 'Jin Hua Yu Ye Elixir' 金华玉液大丹 (anonymous) during the Tang Dynasty, which was a mixture of 250 g lead oxide (PbO), 100 g saltpetre (KNO<sub>3</sub>) and 100 g borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O). Lead oxide, saltpetre and borax could all function as fluxes, so this could be the formula for the PbO-Na<sub>2</sub>O-K<sub>2</sub>O glass during the Tang Dynasty. 'Duo Neng Bi Shi' 多能鄙事 written by Liu Ji 刘基 in the Early Ming Dynasty (1368-1644 CE) documents another formula for a type of 'Liu Li': 200 g metallic lead, 150 g saltpetre (KNO<sub>3</sub>), 100 g alum (KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O), and 100 g silica quartz are ground and mixed, then fired with coal. Saltpetre and alum could both be the fluxes, so the 'Liu Li' in this case was a potash lead glass.

In one of the first modern discussions of the chemistry of such glass, Brill and Wosinski (1984) summarized five types of Chinese lead-barium glasses. The main difference between these five groups was the total concentrations of PbO and BaO, although the PbO/BaO ratios appear to have been fixed at either 3/1 or 3/2. During the last few decades of research on lead-barium

glass, it seems that its chemical composition is more complicated than this, meaning that it can no longer be simply summarized as five types. Although the original classification of Brill and Wosinski (1984) has subsequently been shown to be too simplistic, patterns can still be seen in the PbO/BaO ratio for the glass excavated from different regions in China. For example, the average PbO% and BaO% for lead-barium glass excavated from the Shirenzigou Site (Xinjiang) are 49.63% and 7.64% (Wen *et al.*, 2016). In contrast, PbO/BaO ratios for glass unearthed in Dayunshan Site (Zhejiang) are close to 2 (Gan, 2005), whereas the average PbO/BaO ratio for lead-barium glass unearthed in Xi'an is also around 6 (Zhao *et al.*, 2015). Li (1996) collected 534 lead isotopic ore data and compared with over 250 lead isotopic glass data. The results show that some lead-barium glass with radiogenic lead signature could be manufactured in Yunnan Province. PCA analysis for lead-barium glass unearthed from different provinces also indicates that there could be multiple workshops producing lead-barium glass in the past (Wen *et al.*, 2016). These examples not only indicate that there was probably more than one workshop producing lead-barium glass, but also that, given the range of variation measured in the PbO/BaO ratio, the lead-barium minerals were probably separately added to the glass batch.

From the literature, we have assembled a representative database of the composition of Chinese Pb-Ba glass containing in excess of 400 samples (Supplementary 1), although not all samples report all elements. Taking the median of each major element oxide, we can suggest that a 'typical' example of Pb-Ba glass has the following composition (by weight): SiO<sub>2</sub> = 51.39%, PbO = 27.25%, BaO = 9.02%, Na<sub>2</sub>O = 2.27%, Al<sub>2</sub>O<sub>3</sub> = 3.00%, SO<sub>3</sub> = 2.20%, CaO = 1.50%, Cl = 1.22%. From the BaO-PbO-SiO<sub>2</sub> phase diagram (Toropov *et al.*, 1974), the lowest melting point in the system is approximately 700<sup>o</sup> C, but for glass of typical Chinese composition the melting point is likely to be in excess of 1000<sup>o</sup> C – by no means unachievable in ancient furnaces, and illustrating the fluxing power of the PbO. Nevertheless, from the analyses, it is clear that Pb-Ba glass contains low but significant levels of alkalis (median Na<sub>2</sub>O = 2.27%, K<sub>2</sub>O = 0.57%) and alkaline earths (CaO = 1.24%, MgO = 0.53%). It must be acknowledged that there are limitations in the dataset assembled, particularly in terms of measurements of Na<sub>2</sub>O, and also

because it is not always certain that the reported samples are glass rather than faience. Many of the analyses were achieved by either XRF or PIXE, and hence the  $\text{Na}_2\text{O}\%$  was either unreported, or may have been underestimated due to the high detection limits of X-ray analytical techniques with respect to light elements (e.g., Li *et al.*, 2005; Zhao *et al.*, 2015). Only 258 of the 401 analyses assembled contain definite values for  $\text{Na}_2\text{O}$ . However, according to wet chemistry and LA-ICP-AES analyses, some lead-barium glass samples can show over 6%  $\text{Na}_2\text{O}$  (e.g., Brill and Rising, 1999; Wen *et al.*, 2016). Figure 1 shows the distribution of  $\text{Na}_2\text{O}$  in the dataset, indicating that a small proportion of samples do indeed have values greater than 6%. Henderson (2013) believes that the contents of  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  are generally negligible in most lead-barium glass, but he classifies those with  $\text{Na}_2\text{O}$  ranging between 5.29-9.3% as soda-lead-barium glass.



**Figure 1. Distribution of  $\text{Na}_2\text{O}$  in published analyses of Pb-Ba glass**

There is no doubt that  $\text{PbO}$  functioned as the main flux in lead-barium glass, but there is evidence that other fluxes, especially  $\text{Na}_2\text{O}$ , also played a role, as discussed above. Cui *et al.*

(2011) suggested that the Na<sub>2</sub>O was from a sodium/lime bearing material. Gan (2016) believed that the Na<sub>2</sub>O in lead-barium glass was sourced from mirabilite (Glauber's salt: Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O), which is an evaporite mineral sometimes associated with gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), perhaps also explaining the CaO content in lead-barium glass. Saltpeter (KNO<sub>3</sub>) was a commonly used flux for potash glass from the 5<sup>th</sup> century BCE to the 4<sup>th</sup> century CE in India, Thailand, Vietnam, China, Korea and Japan (Lankton *et al.*, 2006; Lankton and Dussubieux, 2006; Siqin *et al.*, 2014). Gan (2016) suggested that during the Warring States and the Han dynasty the Chinese could not differentiate between mirabilite and saltpetre, but this seems unlikely. Both Qin *et al.* (2016) and Chen (2014) have successfully replicated lead-barium glass by mixing and firing SiO<sub>2</sub>, PbO, BaCO<sub>3</sub> and sodium feldspar (albite - Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·6SiO<sub>2</sub>). They gave no justification for using albite as the source of alkali, but were probably influenced by the use of albite in the bodies of later porcelains (Pollard and Wood, 1986). This paper investigates an alternative suggestion, in which the alkali is provided by the use of re-cycled soda-lime-silica glass. The average concentration of SiO<sub>2</sub> is significantly lower in lead-barium glass than in soda-lime glass, so our working hypothesis is that lead-barium glass was made from a mixture of soda-lime glass with lead and barium minerals.

Other synthetic barium-containing materials also have a Chinese origin, such as lead-barium faience in the form of Chinese Blue (BaCuSi<sub>4</sub>O<sub>10</sub>) and Chinese Purple (BaCuSi<sub>2</sub>O<sub>6</sub>), regarded as the Chinese analogues of Egyptian Blue (Chen, 2014; Li, 2014). These are synthetic pigments invented during the Qin (221-207 BCE) and Han dynasties (Xia *et al.*, 2014). Both pigments were used as the blue and purple decoration on the surface of the Terracotta Warriors (Chen, 2014; Fitzhugh and Zycherman, 1992). The main difference between lead-barium glass and lead-barium faience is that the glass has higher Na<sub>2</sub>O and PbO, and lower Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, and CaO, resulting in the lead-barium faience being less vitrified. According to Chen's (2014) replication experiment, 1) by mixing and burning BaO/BaCO<sub>3</sub>, CuO and SiO<sub>2</sub> without PbO as a catalyst, Chinese purple were first generated when the temperature reached over 800°C; by increasing the temperature with sufficient SiO<sub>2</sub>, Chinese purple turned into Chinese blue. 2) By

mixing BaO/BaCO<sub>3</sub>, CuO and SiO<sub>2</sub> with PbO as a catalyst, Chinese blue were first generated (over 800°C), but then turned into Chinese purple when the temperature kept increasing without sufficient SiO<sub>2</sub>. Li's (2014) replication experiment shows that by mixing CuO and SiO<sub>2</sub> with lead sources as catalyst, BaCO<sub>3</sub> is a better source compared with BaSO<sub>4</sub> to produce Chinese blue and purple. Chinese blue can be produced when the temperature reached to 700°C by using BaCO<sub>3</sub>, while temperature needs to reach 1000°C to produce Chinese blue by using BaSO<sub>4</sub>. PbO, PbS and PbCO<sub>3</sub> all can be used as catalyst for producing Chinese blue and purple, but PbCO<sub>3</sub> shows better catalytic effect compared with the other two.

The aim of this replication experiment is therefore to explore the different possibilities of how lead-barium glass could have been produced by testing a series of probable recipes with varying proportions of each raw material. This paper emphasizes and explores the significance of sodium in the technological process of lead-barium glass production. This is important because although it has been suggested elsewhere that sodium is necessary to produce Pb-Ba glass, it is noteworthy that many analyses either record low values for Na<sub>2</sub>O, or do not report Na<sub>2</sub>O, meaning that the role of sodium in the process is not clear. Two hypotheses are tested: (1) whether lead-barium glass can be directly produced by mixing lead, barium and silica sources with controlled ratios, and (2) if it can be produced by mixing natron glass with lead-barium minerals. Moreover, it is also important to understand how different lead and barium minerals could influence the process of glass forming.

## **2. Materials and Methods**

The aim of this series of experimental firings was to answer a series of questions:

- i) to confirm that melts without a source of sodium did not produce glass at temperatures consistent with ancient glass furnace technologies;
- ii) to estimate the minimum amount of sodium required to produce glass;
- iii) to test the effects of varying the mineralogy of the various sources of lead and barium.



The raw materials used were barite  $\text{BaSO}_4$ , witherite  $\text{BaCO}_3$ , galena  $\text{PbS}$ , lead oxide  $\text{PbO}$ , silica quartz  $\text{SiO}_2$ , lime  $\text{CaCO}_3$ , natron  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , sodium feldspar (albite)  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ , borax  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , and copper carbonate  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ , all purchased as laboratory reagents from either Thermo Fisher Scientific or Potclays (<https://www.potclays.co.uk/>). All materials are of greater than 99% purity. In addition, replicated Roman natron glass was provided by Professor Andrew Shortland from Cranfield University.

In total, 24 different combinations were fired in high-alumina ceramic crucibles, as listed in Table 1. The weight of each batch was approximately 30g in total. For the glass replications a Monometer EF laboratory electric muffle furnace was used and the firing was conducted in air. The heating rate up to the maximum temperature of  $1050^\circ\text{C}$  during six hours was  $5^\circ\text{C}/\text{min}$ , except in the range  $90 - 110^\circ\text{C}$  when a slower heating rate of  $1^\circ\text{C}/\text{min}$  was used in order to eliminate humidity. The cooling rate was  $2.5^\circ\text{C}/\text{min}$  down to  $700^\circ\text{C}$  after which the furnace cooled naturally. The furnace was opened after twelve hours. All experimental mixtures were heated in ceramic crucibles, and the outer layer in contact with the crucible was subsequently removed in order to minimize contamination for subsequent analysis. The first five crucibles (1-5 in Table 1) were to test whether lead-barium glass can be produced directly by mixing a silica source with different combinations of lead and barium minerals. This helps to confirm that sodium is a necessary component for making lead-barium glass. As for lead and barium sources, differences between  $\text{BaSO}_4$  vs  $\text{BaCO}_3$  and  $\text{PbO}$  vs  $\text{PbS}$  were tested. Crucible 5 additionally contains  $\text{CuCO}_3$  to produce a green colour. Crucibles 6-11 were designed to test if lead-barium glass can be directly produced by controlled ratios of soda-lime glass with different lead and barium minerals. Differences between the use of  $\text{BaSO}_4$  vs  $\text{BaCO}_3$  and  $\text{PbO}$  vs  $\text{PbS}$  in the crucible charges were again tested. Crucible 7 additionally contains  $\text{CuCO}_3$  to produce a green colour. Crucible 12 was designed to test if lead-barium glass can be replicated by mixing sodium feldspar (albite) with lead and barium minerals. Crucibles 13-24 can be divided into three groups of four, with each group aimed at replicating one of three published chemical

compositions for ancient lead-barium glass, as shown in Table 3 (Cui *et al.*, 2009; Shi and Zhou, 1990). The main difference between the three compositions is the percentage of sodium (1.35%, 2.83% and 9.31% Na<sub>2</sub>O). Each group contains four crucibles, which were designed to test different lead and barium minerals for glass forming. One of the four crucibles in each set was without Na<sub>2</sub>O, again to test the importance of sodium in the charge. The chemical composition of replicated Roman glass was shown in Table 3.

**Table 1. The weight% of the raw materials for 24 crucibles**

Weight%	SiO <sub>2</sub>	BaCO <sub>3</sub>	BaSO <sub>4</sub>	PbO	PbS	CaCO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·6SiO <sub>2</sub>	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	Cu <sub>2</sub> (OH) <sub>2</sub> CO <sub>3</sub>	soda-lime glass
Crucible 1	40	15	-	45	-	-	-	-	-	-	-
Crucible 2	40	-	15	-	45	-	-	-	-	-	-
Crucible 3	30	-	20	50	-	-	-	-	-	-	-
Crucible 4	60	10	-	30	-	-	-	-	-	-	-
Crucible 5	35	15	-	45	-	-	-	-	-	5	-
Crucible 6	-	10	-	40	-	-	-	-	-	-	50
Crucible 7	-	10	-	40	-	-	-	-	-	5	45
Crucible 8	-	-	10	-	40	-	-	-	-	-	50
Crucible 9	-	-	10	40	-	-	-	-	-	-	50
Crucible 10	-	20	-	30	-	-	-	-	-	-	50
Crucible 11	-	-	10	30	-	-	-	-	-	-	60
Crucible 12	-	10	-	40	-	-	-	50	-	-	-
Crucible 13	55	15	-	25	-	2.5	2.5	-	-	-	-
Crucible 14	57	15	-	25	-	3	-	-	-	-	-

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Crucible 15	55	-	15	25	-	2.5	2.5	-	-	-	-
Crucible 16	55	15	-	-	25	2.5	2.5	-	-	-	-
Crucible 17	33	10	-	45	-	3	5	-	-	4	-
Crucible 18	33	10	-	50	-	3	-	-	-	4	-
Crucible 19	30	-	15	45	-	2.5	4	-	-	3.5	-
Crucible 20	30	10	-	-	50	2.5	4	-	-	3.5	-
Crucible 21	43	15	-	25	-	2	15	-	-	-	-
Crucible 22	43	-	15	25	-	2	15	-	-	-	-
Crucible 23	48	20	-	30	-	2	-	-	-	-	-
Crucible 24	30	10	-	20	-	1	-	-	39	-	-

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electric saw for cross-sectional

<b>Standard</b>	<b>Elements</b>	<b>Certified</b>	<b>Measured (n=20)</b>	<b>%Error</b>	<b>S.D.</b>	<b>%R.S.D.</b>
Corning A	Na	14.3	12.4	15.4	0.1	1.0
	Mg	2.7	2.4	9.8	0.1	2.6
	Al	1.0	0.8	25.2	0.1	6.0
	Si	67.1	69.3	-3.2	0.3	0.5
	K	2.9	3.1	-8.1	0.1	1.7
	Ca	5.0	5.2	-2.9	0.1	1.5
	Ti	0.8	0.9	-6.6	0.0	5.0
	Cu	1.2	1.2	-4.3	0.1	6.0
	Ba	0.6	0.6	1.4	0.1	10.3
	Pb	0.1	0.0	/	0.0	/
Corning B	Na	17.0	14.7	-13.4	0.2	1.3
	Mg	1.0	0.9	-8.4	0.0	3.7
	Al	4.4	3.8	-13.6	0.1	1.4
	Si	62.3	64.7	3.9	0.3	0.5
	K	1.0	1.2	17.5	0.0	2.3
	Ca	8.6	9.0	5.1	0.0	0.5
	Ti	0.1	0.0	/	0.0	/
	Cu	2.7	2.9	8.7	0.1	3.4
	Ba	0.1	0.0	/	0.0	/
	Pb	0.6	0.9	39.7	0.1	10.0
Corning D	Na	1.2	1.1	8.3	0.1	5.0
	Mg	3.9	3.6	10.5	0.1	1.5
	Al	5.3	4.5	17.8	0.1	1.4

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Si	55.5	55.1	0.7	0.3	0.6
K	11.3	11.7	-3.4	0.1	1.1
Ca	14.8	14.4	2.9	0.2	1.1
Ti	0.4	0.4	-10.4	0.1	17.2
Cu	0.4	0.4	0.9	0.1	14.1
Ba	0.5	0.4	16.4	0.0	5.0
Pb	0.5	0.4	9.4	0.0	10.3

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### 3. Results

A detailed description, including photographs, SEM secondary electron images of cross sections and chemical analyses (where available), is given for each sample in Supplementary 3. Table 3 shows the chemical results (by energy dispersive spectrometry) for 23 crucibles, with the omission of crucible 1, which only retained a limited amount of material after firing.

The results of the experiment can be divided into three broad categories – those which produced transparent glass (6, 7, 8, 9, 10, 11, 17, 18, 19, 20, 21, 22, 24) those which produced opaque partially vitrified material (12, 13, 14, 15), and those which gave opaque granular material (2, 3, 4, 5, 16, 23). Crucibles 17 and 18 produced only a thin layer of glass, and their chemical compositions are more close to lead-barium glaze with low Na<sub>2</sub>O concentration (Wood, 1999), probably because a large proportion of the crucible charge was lost due to outgassing of BaCO<sub>3</sub> and Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>. Although crucibles 19 and 20 formed glass, they were considered to be failures since they were high lead glass instead of lead-barium glass according to the EDS analysis (Table 3). The transparent glass is generally produced by those crucible charges with the highest input of Na<sub>2</sub>O, which is discussed in more detail below. All of the samples made with the synthetic Roman glass (crucibles 6-11) produced transparent glass, apart from the sample made with PbS (8, which produced black glass and a thick layer of white BaSO<sub>4</sub>). Those glasses made using Roman glass with BaCO<sub>3</sub> tended to be yellowish in colour, whereas those with Roman glass and BaSO<sub>4</sub> were greenish. Crucibles charged with SiO<sub>2</sub>, PbO, CaCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and either BaCO<sub>3</sub> (17, 21) or BaSO<sub>4</sub> (19, 22) all produced translucent glass. Crucible 18 is somewhat exceptional, in that it is the only one to produce transparent glass which

contained no  $\text{Na}_2\text{CO}_3$ . It does have a high proportion of  $\text{PbO}$  (and some  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ) which presumably provided sufficient flux to produce a glass. Crucible 20 used  $\text{PbS}$  as the lead source, and gave a multilayered product which included a yellow transparent glass as well as a black and green layer. Crucible 24, in which the sodium source was borax  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  also produced a greenish-yellow transparent glass. Our analyses for crucibles 19 and 20 shows that they are high lead glasses with only 1% barium oxide.

The group which produced white or ivory coloured partially vitrified opaque material (12-15) in general had a lower sodium and higher silica content than those in the above group. The least vitrified material (2-5, 16, 23) retained a granular appearance, and had either no or very low sodium.

295 **Table 3. EDS semi-quantitative results (wt.%) for 23 crucibles**

Crucible	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>2</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	CuO	BaO	PbO	Description
2	-	-	-	51.5	-	1.0	-	-	1.7	-	5.8	40.1	Pale green opaque granular material
3	-	-	0.2	23.7	-	8.0	-	-	1.5	-	18.6	48.0	White opaque granular material
4	-	-	-	70.4	-	-	-	-	-	-	4.9	24.7	White opaque granular material, partially vitrified
5	-	-	-	47.2	-	-	-	-	0.3	3.9	11.1	37.5	Dark blue opaque granular material
6	6.8	0.8	1.6	34.8	-	-	0.6	3.2	-	-	8.9	43.3	Yellowish transparent glass with cracks
7	6.2	0.8	1.4	32.8	-	-	0.6	3.1	-	3.7	8.5	42.9	Blue transparent glass with cracks
8	6.5	1.1	1.6	44.6	-	-	0.7	4.3	-	-	8.6	32.7	Black transparent glass with a layer of white dendritic crystalline material
9	7.1	0.9	1.7	44.3	-	-	0.9	4.5	-	-	5.6	35.0	Greenish transparent glass with a layer of white flocculent material
10	7.8	0.8	1.4	37.9	-	-	0.6	3.5	-	-	17.1	31.0	Yellowish transparent glass with cracks and partial layer of white opaque crystals
11	6.9	0.9	1.8	39.3	-	-	0.6	3.8	-	-	5.9	41.0	Greenish transparent glass with white opaque layer on top
12	3.9	-	9.7	33.4	-	-	0.4	0.7	-	-	10.6	41.4	Ivory opaque partially vitrified material with air bubbles on the top layer
13	1.0	-	-	60.7	-	-	-	1.1	-	-	11.0	26.3	White opaque partially vitrified material with big air holes
14	-	-	-	64.9	-	-	-	1.7	-	-	11.4	22.1	White opaque partially vitrified material with big air holes
15	1.1	-	-	69.0	0.5	-	-	1.5	-	-	2.5	25.5	White opaque partially vitrified material
16	1.1	-	-	67.4	-	1.4	-	1.2	0.6	-	4.9	23.5	Pale blue opaque granular material with large bubbles
17	2.5	-	0.2	35.4	-	-	0.4	2.0	-	3.2	9.0	47.3	Emerald green translucent glass
18	-	-	-	35.3	-	-	-	1.8	-	3.5	8.0	51.5	Emerald green translucent glass
19	1.9	-	-	37.3	-	-	0.1	1.9	-	3.0	1.7	54.1	Green transparent glass with a layer of green and white opaque crystalline material
20	1.5	-	-	37.6	-	-	-	1.8	-	1.3	1.1	56.8	Yellow transparent glass with a layer of green and white opaque crystalline material
21	7.5	-	-	48.1	-	-	0.3	1.4	-	-	14.2	28.6	Greenish transparent glass with cracks
22	5.8	-	-	59.6	-	-	-	1.2	-	-	6.0	27.4	Greenish transparent glass with white opaque crystalline material on the top surface
23	-	-	-	51.1	-	-	-	1.1	1.1	-	20.2	26.6	White granular opaque material with big air holes



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24	8.5	-	0.7	46.0	-	-	0.6	1.0	-	-	12.1	31.1	Greenish-yellow transparent glass
Natron glass	15.9	1.6	2.9	70.9	-	-	0.8	7.9	-	-	-	-	Transparent
White glass Bead	1.4	0.2	1.1	55.6	0.1	-	1.1	1.3	0.1	0.4	11.6	26.6	(Cui <i>et al.</i> , 2009)
Green glass Bi disk	2.8	0.3	1.2	34.8	0.1	-	0.3	1.7	0.0	1.5	8.5	48.5	(Cui <i>et al.</i> , 2009)
Glass Earring	9.3	2.2	1.7	45.9	-	-	0.3	0.8	-	-	12.9	27.3	(Shi and Zhou, 1990)

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## 4. Discussion

### 4.1 The prerequisite of a sodium source

PbO is classified as an intermediate in terms of glass structure, meaning that it cannot itself form a glass, but that it can enter the network of other glass-forming oxides (in this case, SiO<sub>2</sub>). When the PbO concentration is above c. 50 mol%, the co-ordination number of Pb is about 3, and PbO switches from being a network modifier to a network former, in which the network consists of PbO<sub>3</sub><sup>2-</sup> trigonal pyramids linked to SiO<sub>4</sub><sup>2-</sup> tetrahedra (Takaishi *et al.*, 2000). As shown in Figure 1, the previously analyzed examples of Chinese Pb-Ba glass tend to contain amounts of Na<sub>2</sub>O up to 10%. The question to be addressed here is why, with so much PbO available to act as a network modifier, does Na<sub>2</sub>O appear to be necessary to form lead-barium glass? Table 4 compares calculated sodium compositions according to the recipes presented in Table 1 with the measured chemical compositions for each crucible (from Table 3). The calculated value was obtained by mathematically converting each component in the charge into an oxide formulation, and then normalizing the sum of these oxides to 100%. Figure 2 shows the SiO<sub>2</sub>-Na<sub>2</sub>O-PbO+BaO phase diagrams of components in charge and in product. As shown, a certain amount of Na<sub>2</sub>O plays an essential role for lead-barium glass forming compared with failures. Transparent glass (or crucibles containing a component of transparent glass) was formed most easily when the charge contained high levels of Na<sub>2</sub>O – apart from crucible 17 and 18 (with low or no Na<sub>2</sub>O), all charges contained greater than 7% being more typical. Conversely, the crucibles which did not vitrify contained <1.5% Na<sub>2</sub>O, with the exception of crucible 12, which contained 5.92% Na<sub>2</sub>O in the form of albite (NaAlSi<sub>3</sub>O<sub>8</sub>). It is therefore clear that under the conditions of this experiment sodium can facilitate glass formation in the lead-barium-silica system.

**Table 4 The comparison of calculated and measured chemical compositions for crucibles formed glass**

Crucible	Charge	Result	%Na <sub>2</sub> O in Charge	%Na <sub>2</sub> O
Transparent glass				
6	10 BaCO <sub>3</sub> /40 PbO/50 RG	Yellowish transparent glass with cracks	8.0	6.8
7	10 BaCO <sub>3</sub> /40 PbO/45 RG/5 Cu <sub>2</sub> (OH) <sub>2</sub> CO <sub>3</sub>	Blue transparent glass with cracks	7.2	6.2
8	10 BaSO <sub>4</sub> /40 PbS/50 RG	Black transparent glass with a layer of white dendritic crystalline material	8.0	6.5
9	10 BaSO <sub>4</sub> /40 PbO/50 RG	Greenish transparent glass with a layer of white flocculent material	8.0	7.1
10	20 BaCO <sub>3</sub> /30 PbO/50 RG	Yellowish transparent glass with cracks and partial layer of white opaque crystals	8.0	7.8
11	10 BaSO <sub>4</sub> /30 PbO/60 RG	Greenish transparent glass with white opaque layer on top	9.6	6.9
17	33 SiO <sub>2</sub> /10 BaCO <sub>3</sub> /45 PbO/3 CaCO <sub>3</sub> /5 Na <sub>2</sub> CO <sub>3</sub>	Emerald green translucent glass	2.9	2.5
18	33 SiO <sub>2</sub> /10 BaCO <sub>3</sub> /50 PbO/3 CaCO <sub>3</sub> /4 Cu <sub>2</sub> (OH) <sub>2</sub> CO <sub>3</sub>	Emerald green translucent glass	0.0	0.0
19	30 SiO <sub>2</sub> /15 BaSO <sub>4</sub> /45 PbO/2.5 CaCO <sub>3</sub> /4 Na <sub>2</sub> CO <sub>3</sub> /3.5 Cu <sub>2</sub> (OH) <sub>2</sub> CO <sub>3</sub>	Green transparent glass with a layer of green and white opaque crystalline material	2.3	1.9
20	30 SiO <sub>2</sub> /10 BaCO <sub>3</sub> /50 PbS/2.5 CaCO <sub>3</sub> /4 Na <sub>2</sub> CO <sub>3</sub> /3.5 Cu <sub>2</sub> (OH) <sub>2</sub> CO <sub>3</sub>	Yellow transparent glass with a layer of green and white opaque crystalline material	2.3	1.5
21	43 SiO <sub>2</sub> /15 BaCO <sub>3</sub> /25 PbO/2 CaCO <sub>3</sub> /15 Na <sub>2</sub> CO <sub>3</sub>	Greenish transparent glass with cracks	8.8	7.5
22	43 SiO <sub>2</sub> /15 BaSO <sub>4</sub> /25 PbO/2 CaCO <sub>3</sub> /15 Na <sub>2</sub> CO <sub>3</sub>	Greenish transparent glass with white opaque crystalline material on the top surface	8.8	5.8
24	30 SiO <sub>2</sub> /10 BaCO <sub>3</sub> /20 PbO/1 CaCO <sub>3</sub> /39 Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·12H <sub>2</sub> O	Greenish-yellow transparent glass	6.3	8.5
Opaque partially vitrified				
12	10 BaCO <sub>3</sub> /40 PbO/50 albite	Ivory opaque partially vitrified material with air bubbles on the top layer	5.9	3.9

13	55 SiO <sub>2</sub> /15 BaCO <sub>3</sub> /25 PbO/2.5 CaCO <sub>3</sub> /2.5 Na <sub>2</sub> CO <sub>3</sub>	White opaque partially vitrified material with big air holes	1.5	1.0
14	57 SiO <sub>2</sub> /15 BaCO <sub>3</sub> /25 PbO/3 CaCO <sub>3</sub>	White opaque partially vitrified material with big air holes	0.0	0.0
15	55 SiO <sub>2</sub> /15 BaSO <sub>4</sub> /25 PbO/2.5 CaCO <sub>3</sub> /2.5 Na <sub>2</sub> CO <sub>3</sub>	White opaque partially vitrified material	1.5	1.1
Opaque granular				
2	40 SiO <sub>2</sub> /15 BaCO <sub>3</sub> /45 PbO	Pale green opaque granular material	0.0	0.0
3	40 SiO <sub>2</sub> /15 BaSO <sub>4</sub> /45 PbS	White opaque granular material	0.0	0.0
4	60 SiO <sub>2</sub> /10 BaCO <sub>3</sub> /30 PbO	White opaque granular material, partially vitrified	0.0	0.0
5	35 SiO <sub>2</sub> /15 BaCO <sub>3</sub> /45 PbO/5 Cu <sub>2</sub> (OH) <sub>2</sub> CO <sub>3</sub>	Dark blue opaque granular material	0.0	0.0
16	55 SiO <sub>2</sub> /15 BaCO <sub>3</sub> /25 PbS/2.5 CaCO <sub>3</sub> /2.5 Na <sub>2</sub> CO <sub>3</sub>	Pale blue opaque granular material with large bubbles	1.5	1.1
23	48 SiO <sub>2</sub> /20 BaCO <sub>3</sub> /30 PbO/2 CaCO <sub>3</sub>	White granular opaque material with big air holes	0.0	0.0

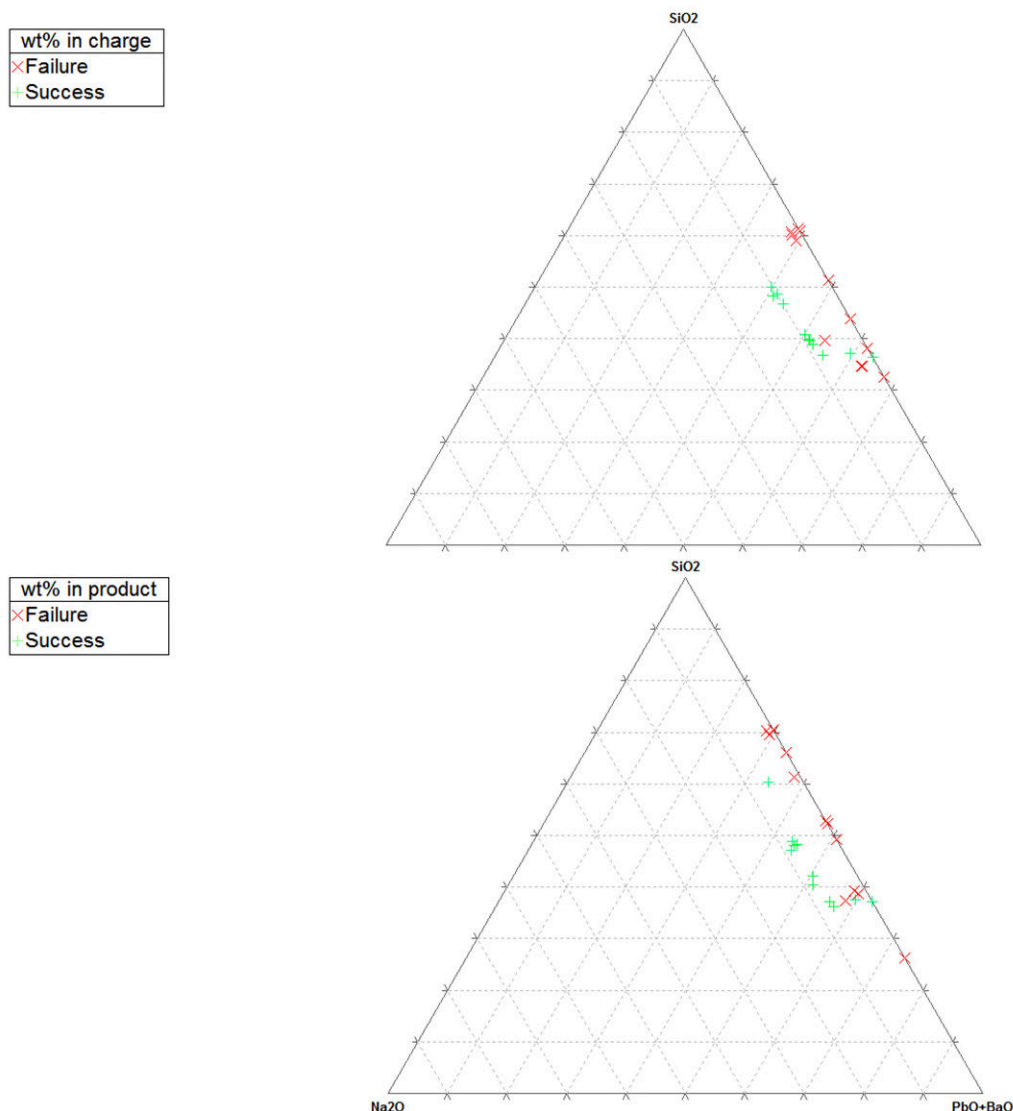


Figure 2 SiO<sub>2</sub>-Na<sub>2</sub>O-PbO+BaO phase diagrams of components in charge and in product

The data in Table 4 and Figure 2 show that the measured Na<sub>2</sub>O% are lower than the calculated Na<sub>2</sub>O%, which could be detecting error or a flux loss during the melting process. Still, it is noticeable that the crucibles using BaSO<sub>4</sub>, such as 11 and 22, show a higher loss of Na<sub>2</sub>O (about 3%). According to the EDS chemical data and the mapping results (Supplementary 3 C), the white material in crucibles 11 and 22 contain a certain amount of Na<sub>2</sub>SO<sub>4</sub>, which would explain the lower values of Na<sub>2</sub>O in the glass. Nevertheless, it is immediately apparent that all the samples which produced transparent glass generally contain more than 7% Na<sub>2</sub>O, whereas comparison with Figure 1 shows that most of the lead-barium glass analyzed to date appears to have values around 2%. As noted above, there are two other possible reasons why Na<sub>2</sub>O% might be underestimated in the literature: i), XRF and PIXE analysis can underestimate Na<sub>2</sub>O%, and ii) weathering effects can result in the loss of Na<sub>2</sub>O.

There are three possibilities for the deliberate addition of sodium to these Pb-Ba glasses:

- i) direct addition of a mineral which contains sodium (e.g., natron, albite, mirabilite),
- ii) direct addition of a soda-rich plant ash,
- iii) indirect addition, via the re-use of glass which already contains sodium.

There is no archaeological evidence to suggest that Chinese glass makers could produce soda-lime glass during the Warring States period and the Han Dynasty, and nor are there any literary sources which suggest that other contemporaneous Chinese vitreous materials used a mineral or plant-based sodium source as the flux during this period. According to Chinese chronicle *Beishi* 北史 (History of the Northern Dynasties), during the Wei Taiwu period (408–452 CE), the inhabitants of Middle Asia who were in trade with China taught the Chinese to melt and to mold coloured glass (An, 1998; Bezborodov and Zadneprovskii, 1967). This is the earliest documentation about glass making in China. Thus, although there are numerous soda-lime silica glass beads found in early China, they are all assumed to be imported from Western Asia (An, 1998; Gan *et al.*, 2009; Li *et al.*, 2013). Commonly used flux for the silicate materials during the Warring States and the Han period were lead and wood ash, such as lime glaze and wood ash glaze. As for Chinese lime based ceramic glazes, the source of lime initially was from wood ash, and subsequently replaced by limestone (Wood, 1999). The low-temperature lead-glazed ceramics (and lead-barium glazed) appeared no later than the Han Dynasty, and were only used for burial and architectural objects (Wang *et al.*, 2019; Wood, 1999; Yin *et al.*, 2020). According to the published data for lead-barium glass, the potassium and magnesium concentrations (medians 0.57% and 0.53% respectively from the published literature) are too low to represent a plant ash flux (Wen *et al.*, 2016), where typical values would be both greater than 1.5% respectively (Rehren and Freestone, 2015). This effectively rules out the direct production of Pb-Ba glass using soda-rich plant ash, as was common in Western Asia. The known mineral soda-rich sources used in ancient western Eurasian glass could either be a natron (evaporate) source, such as that from Egypt, or a reh (saline soil) source from the Indo-pacific region, both of which have analogous occurrences in China.

A mineral source of sodium cannot therefore be ruled out in the production of Pb-Ba glass, and both the experiments reported here (crucibles 17-22, 24) and those of previous researchers (Chen, 2014; Li, 2010; Qin *et al.*, 2016) have shown that this is plausible. There is, however, little evidence that the Chinese knew the function of mineral forms of sodium in the production of vitreous artefacts during this period. Also, the minor element composition of Pb-Ba glass (i.e., K<sub>2</sub>O, CaO, MgO, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>) could also be explained by the use of imported soda-lime glass as the sodium source. The Levantine coast appears to have been the location of large-scale glass making in antiquity (Ali and Abd-Allah, 2015), which could be source of soda-lime glass.

#### **4.2 Opaque Glass**

Chinese Pb-Ba glass can be either transparent or opaque. Many of the products listed in Table 3 show that a clear glass is produced but with an opaque crystalline material on the surface (crucibles 8-11, 19, 20, 22). In most cases this white material is identified as BaSO<sub>4</sub> and BaSi<sub>2</sub>O<sub>5</sub> from the stoichiometry of the chemical analysis (Supplementary 3: crucible 11). According to this replication experiment, it is apparent that more white opaque material can be generated by mixing BaSO<sub>4</sub> and PbO with natron glass rather than by using BaCO<sub>3</sub> as the barium source. It is possible, therefore, that both BaSO<sub>4</sub> and BaCO<sub>3</sub> were used selectively in the past to control for the degree of opacity. In our work, the crucibles with BaSO<sub>4</sub> generated both BaSi<sub>2</sub>O<sub>5</sub> and unmelted BaSO<sub>4</sub> which can function as opacifiers, although in our replications BaSO<sub>4</sub> forms on the top of the glass rather than being uniformly dispersed within the glass. It might not be possible to produce white opaque lead-barium glass during primary glass production due to potential separation of the opaque materials during the slow cooling down process. As colouring, clarifying or opacifying agents could be added to the glass batch during the secondary production (Abd-Allah, 2010), we suggest that the products of the primary melting might have needed to be re-melted to mix the opacifier into the glass.

As mentioned, a small Na<sub>2</sub>O loss is noticed. Then BaO and PbO are indeed overestimated, but such a small loss of Na<sub>2</sub>O cannot statistically enrich BaO and PbO to higher concentrations than they used to be. Thus, such small shifts of BaO and PbO could not make much difference for the formation of lead-barium glass. Still, in some extreme cases, when lead-barium glass is badly weathered, a layer of PbCO<sub>3</sub> (secondary formed) and BaSO<sub>4</sub> (probably by leaching) will formed on the lead-barium glass surface (Wang *et al.*, 2014).

In this replication experiment, we did not observe any PbO leaching effect. As for crucibles used BaSO<sub>4</sub> and formed glass, a layer of white opacifier remains on the surface glass identified as BaSO<sub>4</sub> and BaSi<sub>2</sub>O<sub>5</sub>. Thus, there is a small loss of BaO in glass phase.

## 5. Conclusions

The direct mixing and firing of lead and barium minerals with silica cannot easily produce lead-barium glass, and the chemical analysis of a large number of Chinese Pb-Ba glasses show that the Na<sub>2</sub>O concentration is typically between 2 and 10%, suggesting that a source of sodium was deliberately included in the melt as an additional flux. The use of a source of sodium to successfully achieve lead-barium glasses is connected with the fact that it could also lower the melting point of this kind of glasses. Although mineral sources of soda could have been used, no Chinese historical records during the Warring States period to the Han Dynasty mention the use of a sodium source as flux. The experiments reported here have shown that lead-barium glass can easily be achieved by mixing imported soda-lime glass with mineral sources of PbO and either BaCO<sub>3</sub> or BaSO<sub>4</sub>. The direct use of PbS was less successful, but in practice prior roasting would have converted this to the oxide form. If we accept that soda-lime silica glass was imported into China from the west during the Warring States period (which it must have been if we believe that China did not make soda-lime silica glass), then it is easy to see how some of this material could have been used as a raw material to locally make Pb-Ba glass. The impetus for this would probably have been the desire to produce synthetic jade. The disappearance of this type of glass could then subsequently be explained by the disruption of trade at the end of the Han Dynasty, in which no more primary glass was imported across the Silk Roads. The frequent change of dynasties after the Han Dynasty might have played a crucial role in these developments.

## Bibliography

- Abd-Allah, R., 2010. Chemical characterisation and manufacturing technology of late Roman to early Byzantine glass from Beit Ras/Capitolias, Northern Jordan. *J. Archaeol. Sci.* 37, 1866–1874. <https://doi.org/10.1016/j.jas.2010.02.004>
- Ali, N., Abd-Allah, R., 2015. The Authentication and Characterization of Glass Objects Excavated from Telles-Sukhnah, Jordan. *Mediterr. Archaeol. Archaeom.* 15.



- An, J., 1998. Historical Narrative of Glass Ware. Encyclopedia of China Publishing House, Beijing.
- Bao, Z., 2015. A General Discussion on the Historical Function of the Ancient Silk Road. *Stud. Cult. & Art* 8, 20–30.
- Bezboradov, M.A., Zadneprovskii, YU.A., 1967. Ancient and Medieval glass of Central Asia, in: Levey, M. (Ed.), . Presented at the Archaeological Chemistry: a symposium [3rd: 1962: Atlantic City, NJ], University of Pennsylvania Press, Philadelphia, pp. 29–57.
- Brill, R.H., Rising, B.A., 1999. Chemical analyses of early glasses. Corning Museum of Glass, Corning, N.Y.
- Brill, R.H., Wosinski, J.F., 1984. Physical Properties of Early Chinese Glasses, in: *Scientific Research in Early Chinese Glass*. Corning glass Museum, New York, pp. 109–117.
- Chen, Q., 2014. A Primary Study on Simulated Sintering Experiment of Manmade Barium Silicate Products in Ancient China (Masters Dissertation). University of Science and Technology of China, Hefei.
- Cui, J., Wu, X., Huang, B., 2011. 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. *J. Archaeol. Sci.* 38, 1671–1679.
- Cui, J., Wu, X., Tan, Y., Wang, Y., 2009. Chemical Analysis of Ancient Wares Unearthed from Chu Cemeteries of the Warring State Period in the Drainage Area of the Yuanshui River, Hunan Province. *J. Chin. Ceram. Soc.* 37, 1909–1913.
- Fitzhugh, E.W., Zycherman, L.A., 1992. A purple barium copper silicate pigment from early China. *Stud. Conserv.* 37, 145–154. <https://doi.org/10.1179/sic.1992.37.3.145>
- Gan, F., 2016. *The History of Technology Development of Ancient Chinese glass*. Shanghai Scientific & Technical Publishers, Shanghai.
- Gan, F., 2006. The Silk Road and Ancient Chinese Glasses, *Chinese Journal of Nature*. *J. Nat.* 28, 253–260.
- Gan, F., 2005. *Development of Chinese Ancient Glass*. Shanghai Scientific & Technical Publishers, Shanghai.
- Gan, F., Cheng, H., Hu, Y., Ma, B., Gu, D., 2009. Analysis of the Chinese Earliest Eye Beads unearthed from Xujialing, Xichuan, Henan Province. *Science China Press* 39, 787–792.
- Gan, F., Cheng, H., Li, Q., 2007. The Origin of Chinese Ancient Glass- Analysis of the Earliest Chinese glass. *Science China Press* 37, 382–391.
- He, F., Wan, M., 1998. *The Culture Exchange Between Ancient China and the West*. The Commercial Press, Beijing.
- Henderson, J., 2013. *Ancient glass: an interdisciplinary exploration*. Cambridge University Press.
- Hou, D., 1989. The Investigation of the Chu Glass Production. *Cult. Relics Cent. China* 24–29.
- Lankton, J.W., Dussubieux, L., 2006. Early glass in Asian maritime trade: a review and an interpretation of compositional analyses. *J. Glass Stud.* 121–144.
- Lankton, J.W., Dussubieux, L., Gratuze, B., 2006. Glass from Khao Sam Kaeo: transferred technology for an early Southeast Asian exchange network. *Bull. L'École Fr. Extrême-orient* 317–351.

- Li, M., 2014. Simulated Experiment of Faience and Analysis of Lead Barium Glass During the Warring State and the Han Dynasty (Masters Dissertation). Beijing University of Chemical Technology, Beijing.
- Li, Q., Dong, J., Su, B., Chen, G., Liu, S., Gu, D., 2013. Non-destructive Analysis of the Warring States Glass Beads Unearthed from Jingzhou, Hubei by pXRF and Discussions on Relative Issues [J]. *Dunhuang Res.* 1, 92–97.
- Li, Q., Zhou, H., Huang, J., Gan, F., Zhang, B., 2005. Chemical Composition Analytic Results of Ancient Chinese Compound Eye-beads. *Hanjiang Archaeol.* 79–83.
- Li, X., 2010. Analysis and Simulated Experiment of Ancient Glass Unearthed from Suzao Sites, Hubei Province (Masters Dissertation). University of Science and Technology of China, Hefei.
- Li, X., 1996. About the Origin of Chinese Lead-Barium glass. *Stud. Hist. Nat. Sci.* 15, 144–150.
- Liu, J., 2012. The Commodity Circulation of the Ancient Silk Road. *Lantai World* 21–22.
- Pollard, A.M., Wood, N.D., 1986. Development of Chinese porcelain technology at Jingdezhen, in: Olin, J.S., Blackman, M.J. (Eds.), *Proceedings of the 24th International Archaeometry Symposium*. Washington DC, pp. 105–114.
- Qin, Y., Wang, Y., Chen, X., Li, H., Xu, Y., Li, X., 2016. The research of burning ancient Chinese lead-barium glass by using mineral raw materials. *J. Cult. Herit.* 21, 796–801.  
<https://doi.org/10.1016/j.culher.2016.04.003>
- Rehren, Th., Freestone, I.C., 2015. Ancient glass: from kaleidoscope to crystal ball. *J. Archaeol. Sci.* 56, 233–241. <https://doi.org/10.1016/j.jas.2015.02.021>
- Shi, M., Zhou, F., 1990. Investigation on Glasses of the Han Dynasty Unearthed from Datong, Qinghai Province. *Sci. Conserv. Archaeol.* 2, 22–26.
- Siqin, B., Li, Q., Gan, F., 2014. Investigation of ancient chinese potash glass by laser ablation inductively coupled plasma atomic emission spectroscopy. *Spectrosc. Lett.* 47, 427–438.
- Tait, H., 2011. 5000 years of glass. British Museum Press, London.
- Takaishi, T., Jin, J., Uchino, T., Yoko, T., 2000. Structural Study of PbO–B<sub>2</sub>O<sub>3</sub> Glasses by X-ray Diffraction and <sup>11</sup>B MAS NMR Techniques. *J. Am. Ceram. Soc.* 83, 2543–2548.
- Toropov, N.A., Barzakovskii, V.P., Lapin, V.V., Kurtseva, N.N., Boikova, A.I., 1974. Phase Diagrams of Silicate Systems: Handbook; Third Issue; Ternary Systems. Army Foreign Science and Technology Center Charlottesville Va.
- Wang, Jie, Li, M., Ma, Q., Zhang, Z., Zhang, M., Wang, Julin, 2014. Weathering of an Octagonal PbO-BaO-SiO<sub>2</sub> Glass Stick from the Warring States Period. *Glass Enamel* 42, 6–13.
- Wang, Y., Zhou, Y., Yang, Z., Cui, J., 2019. A technological combination of lead-glaze and calcium-glaze recently found in China: Scientific comparative analysis of glazed ceramics from Shangyu, Zhejiang Province. *PLoS One* 14, e0219608.
- Wedepohl, K.H., Simon, K., 2010. The chemical composition of medieval wood ash glass from Central Europe. *Chem. Erde - Geochem.* 70, 89–97. <https://doi.org/10.1016/j.chemer.2009.12.006>
- Wen, R., Zhao, Z., Ma, J., Wang, J., 2016. Chemical Analysis of Ancient Glass Beads from Shirenzigou Sites in Balikun County, Xinjiang. *Spectrosc. Spectr. Anal.* 36, 2961–2965.

Wood, N., 1999. *Chinese Glazes: their origins, chemistry, and recreation*. University of Pennsylvania Press.

Xia, Y., Ma, Q., Zhang, Z., Liu, Z., Feng, J., Shao, A., Wang, W., Fu, Q., 2014. Development of Chinese barium copper silicate pigments during the Qin Empire based on Raman and polarized light microscopy studies. *J. Archaeol. Sci.* 49, 500–509.

Yin, X., Huang, T.J., Gong, H., 2020. Chemical evolution of lead in ancient artifacts -A case study of early Chinese lead-silicate glaze. *J. Eur. Ceram. Soc.* 40, 2222–2228.

<https://doi.org/10.1016/j.jeurceramsoc.2020.01.002>

Zhao, F., Chen, B., Chai, Y., Dong, J., Li, Q., 2015. pXRF Analysis of Sereval Glass Objects Unearthed from Xi' An and Discussion of relative issues. *Archaeol. Cult. Relics* 111–119.