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

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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 Na₂O is provided by including soda-lime glass in the mixture. This particular formulation provides a potential explanation for the source of the sodium in lead-barium glass.

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), [1] 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 K₂O is higher than Na₂O [2]. Wood ash glass did not appear in Europe until around 800 CE [3]. Abd-Allah [1] noted that there is no published data from contemporary Egyptian and Mediterranean plant ash glasses in which the K₂O value is higher than the Na₂O 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 the Eurasian Steppe can be dated to the 10th century BCE, which was the Late Shang and the Early Zhou Dynasty (1046 - 256 BCE: [4]). Merchants brought marine products such as shells from the eastern coastal region of China to Taklamakan in the Shang Dynasty (1600 - 1046 BCE: [5]). silk was exported from China to Europe in the 4th century BC [6]. 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 the robbery of trade caravans almost suspended the commodity circulation between China and Europe [7]. When the Qin Empire (221 - 207 BCE) united 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, commanded officer Zhang Qian 张骞 to investigate the old 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

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been imported from the Han Empire [7]. Lead-barium glass was invented in China during the Warring States period, probably due to technology exchange with the western world. It has, however, 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 5th century BCE) and suddenly disappeared after the Han Dynasty (around the 2nd century CE - [8]). Chinese glassmakers produced glass to simulate other materials, such as hardstones, or as a vehicle for pictorial presentation [9]. 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 Daoists 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 As₄S₄), Bai Fan 白矾 (alum KAl(SO₄)₂·12H₂O), Zeng Qing 曾青 (copper sulfate CuSO₄) and Ci Shi 慈石 (magnetite Fe₃O₄), 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 (CaCO₃) is ground into powder and sealed in a bamboo pipe with saltpetre (KNO₃); then the bamboo pipe is soaked in vinegar (acetic acid: CH₃COOH) 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 (KNO₃) and 100 g borax (Na₂B₄O₇·10H₂O). Lead oxide, saltpetre and borax could all function as fluxes, so this could be the formula for the PbO-Na₂O-K₂O 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 (KNO₃), 100 g alum (KAl(SO₄)₂·12H₂O), 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, Cui et al., [10] 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 Cui et al., [10] 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% [11]. In contrast, PbO/BaO ratios for glass unearthed in Dayunshan Site (Zhejiang) are close to 2 [12], whereas the average PbO/BaO ratio for lead-barium glass unearthed in Xi'an is also around 6 [13]. Gan [14] collected 534 lead isotopic measurements from ores and compared them with over 250 lead isotopic measurements from glass. The results show that some lead-barium glass with radiogenic lead signature could have been 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 [11]. 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): SiO₂ = 51.39%, PbO = 27.25%, BaO = 9.02%, Na₂O = 2.27%, Al₂O₃ = 3.00%, SO₃ = 2.20%, CaO = 1.50%, Cl = 1.22%. From the BaO-PbO-SiO₂ phase diagram [35], the lowest melting point in the system is approximately 700° C, but for glass of typical Chinese composition the melting point is likely to be in excess of 1000° 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 Na₂O = 2.27%, K₂O = 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 Na₂O, 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 Na₂O% 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., [24,43]). Only 258 of the 401 analyses assembled contain definite values for Na₂O. However, according to wet chemistry and LA-ICP-AES analyses, some lead-barium glass samples can show over 6% Na₂O (e.g., [6,11]). Fig. 1 shows the distribution of Na₂O in the dataset, indicating that a small proportion of samples do indeed have values greater than 6%. Henderson [18] believes that the contents of K₂O and Na₂O are generally negligible in most lead-barium glass, but he classifies those with Na₂O ranging between 5.29-9.3% as soda-lead-barium glass.

There is no doubt that PbO functioned as the main flux in lead-barium glass, but there is evidence that other fluxes, especially Na₂O, also played a role, as discussed above. Hou [19] suggested that the Na₂O was from a sodium/lime bearing material. Gan [12] believed that

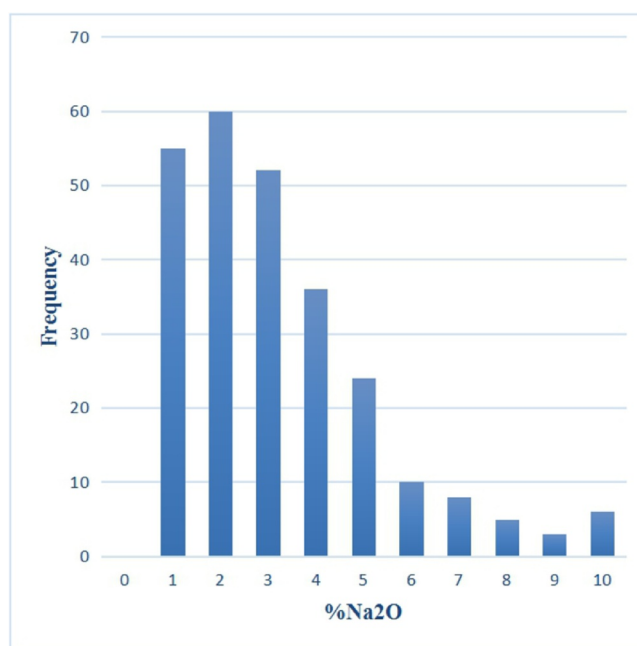


Fig. 1. Distribution of %Na₂O in published analyses of Pb-Ba glass

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

Weight%	SiO ₂	BaCO ₃	BaSO ₄	PbO	PbS	CaCO ₃	Na ₂ CO ₃	Na ₂ O·Al ₂ O ₃ ·6SiO ₂	Na ₂ B ₄ O ₇ ·10H ₂ O	Cu ₂ (OH) ₂ CO ₃	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	-	-	-	-	-
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	-	-	15	-
Crucible 22	43	-	15	25	-	2	15	-	-	-	-
Crucible 23	48	20	-	30	-	2	-	-	-	-	-
Crucible 24	30	10	-	20	-	1	-	-	39	-	-

the Na₂O in lead-barium glass was sourced from mirabilite (Glauber's salt: Na₂SO₄·10H₂O), which is an evaporite mineral sometimes associated with gypsum (CaSO₄·2H₂O), perhaps also explaining the CaO content in lead-barium glass. Saltpeter (KNO₃) was a commonly used flux for potash glass from the 5th century BCE to the 4th century CE in India, Thailand, Vietnam, China, Korea and Japan [20,21,22]. Gan [12] suggested that during the Warring States and the Han dynasty the Chinese could not differentiate between mirabilite and saltpetre, but this seems unlikely. Both Li et al., [23] and Gan [14] have successfully replicated lead-barium glass by mixing and firing SiO₂, PbO, BaCO₃ and sodium feldspar (albite - Na₂O·Al₂O₃·6SiO₂). 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 [15]. 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 SiO₂ 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 (BaCuSi₄O₁₀) and Chinese Purple (BaCuSi₂O₆), regarded as the Chinese analogues of Egyptian Blue [14,16]. These are synthetic pigments invented during the Qin (221-207 BCE) and Han dynasties [17]. Both pigments were used as the blue and purple decoration on the surface of the Terracotta Warriors [14,11]. The main difference between lead-barium glass and lead-barium faience is that the glass has higher Na₂O and PbO, and lower Al₂O₃, K₂O, and CaO, resulting in the lead-barium faience being less vitrified. According to Gan [14] replication experiment, 1) by mixing and burning BaO/BaCO₃, CuO and SiO₂ without PbO as a catalyst, Chinese purple were first generated when the temperature reached over 800°C; by increasing the temperature with sufficient SiO₂, Chinese purple turned into Chinese blue. 2) By mixing BaO/BaCO₃, CuO and SiO₂ 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 SiO₂. Gan et al., [16] replication experiment shows that by mixing CuO and SiO₂ with lead sources as catalyst, BaCO₃ is a better source compared with BaSO₄ to produce Chinese blue and purple. Chinese blue can be produced when the temperature reached to 700°C by using BaCO₃, while temperature needs to reach 1000°C to produce Chinese blue by using BaSO₄. PbO,

PbS and PbCO₃ all can be used as catalyst for producing Chinese blue and purple, but PbCO₃ 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 Na₂O, or do not report Na₂O, 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 BaSO₄, witherite BaCO₃, galena PbS, lead oxide PbO, silica quartz SiO₂, lime CaCO₃, natron Na₂CO₃·10H₂O, sodium feldspar (albite) Na₂O·Al₂O₃·6SiO₂, borax Na₂B₄O₇·10H₂O, and copper carbonate Cu₂(OH)₂CO₃, 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°C during six hours was 5°C/min, except in the range 90–110°C when a slower heating rate of 1°C/min was used in order to eliminate humidity. The cooling rate was 2.5°C/min down to 700°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 BaSO₄ vs BaCO₃ and PbO vs PbS were tested. Crucible 5 additionally contains CuCO₃ 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 BaSO₄ vs BaCO₃ and PbO vs PbS in the crucible charges were again tested. Crucible 7 additionally contains CuCO₃ 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 [18,19]. The main difference between the three compositions is the percentage of sodium (1.35%, 2.83% and 9.31% Na₂O). 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 Na₂O, again to test the importance of sodium in the charge. The chemical composition of replicated Roman glass is shown in Table 3.

After firing and cooling, the crucibles were sectioned by electric saw for cross-sectional observation using SEM-EDS. After carbon coating the sections were analyzed using a JSM 5910 scanning electron microscope (SEM) equipped with an Oxford Instrument INCA 300 energy dispersive analyzer (EDA). Observations were made primarily in secondary electron mode and EDS analysis was performed using a 20 kV accelerating voltage and a live count time of 100 seconds. Primary standards were used to quantify the data. Detail information about primary standards can be found in Supplementary.2, and Table 2 shows the data accuracy and precision by testing Corning standards.

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 Na₂O concentration [24], probably because a large proportion of the crucible charge was lost due to outgassing of BaCO₃ and Cu₂(OH)₂CO₃. 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 Na₂O, which is discussed in more detail below. All of

Table 2

Precisions and accuracies for major and minor elements based on Corning A, B, and D standards [6].

Standard	Elements	Certified	Measured (n = 20)	%Error	S.D.	%R.S.D.
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
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
	Mg	3.9	3.6	10.5	0.1	1.5
	Al	5.3	4.5	17.8	0.1	1.4
	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

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 BaSO₄). Those glasses made using Roman glass with BaCO₃ tended to be yellowish in colour, whereas those with Roman glass and BaSO₄ were greenish. Crucibles charged with SiO₂, PbO, CaCO₃, Na₂CO₃ and either BaCO₃ (17, 21) or BaSO₄ (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 Na₂CO₃. It does have a high proportion of PbO (and some Cu₂(OH)₂CO₃) which presumably provided sufficient flux to produce a glass. Crucible 20 used 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 Na₂B₄O₇·10H₂O 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.

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, SiO₂). 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 PbO₃²⁻ trigonal pyramids linked to SiO₄²⁻ tetrahedra [25]. As shown in Fig. 1, the

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

Crucible	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	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
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	[10]
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	[10]
Glass Earring	9.3	2.2	1.7	45.9	-	-	0.3	0.8	-	-	12.9	27.3	[31]

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

Crucible	Charge	Result	%Na ₂ O in Charge	%Na ₂ O in Product
Transparent glass				
6	10 BaCO ₃ /40 PbO/50 RG	Yellowish transparent glass with cracks	8.0	6.8
7	10 BaCO ₃ /40 PbO/45 RG/5 Cu ₂ (OH) ₂ CO ₃	Blue transparent glass with cracks	7.2	6.2
8	10 BaSO ₄ /40 PbS/50 RG	Black transparent glass with a layer of white dendritic crystalline material	8.0	6.5
9	10 BaSO ₄ /40 PbO/50 RG	Greenish transparent glass with a layer of white flocculent material	8.0	7.1
10	20 BaCO ₃ /30 PbO/50 RG	Yellowish transparent glass with cracks and partial layer of white opaque crystals	8.0	7.8
11	10 BaSO ₄ /30 PbO/60 RG	Greenish transparent glass with white opaque layer on top	9.6	6.9
17	33 SiO ₂ /10 BaCO ₃ /45 PbO/3 CaCO ₃ /5 Na ₂ CO ₃	Emerald green translucent glass	2.9	2.5
18	33 SiO ₂ /10 BaCO ₃ /50 PbO/3 CaCO ₃ /4 Cu ₂ (OH) ₂ CO ₃	Emerald green translucent glass	0.0	0.0
19	30 SiO ₂ /15 BaSO ₄ /45 PbO/2.5 CaCO ₃ /4 Na ₂ CO ₃ /3.5 Cu ₂ (OH) ₂ CO ₃	Green transparent glass with a layer of green and white opaque crystalline material	2.3	1.9
20	30 SiO ₂ /10 BaCO ₃ /50 PbS/2.5 CaCO ₃ /4 Na ₂ CO ₃ /3.5 Cu ₂ (OH) ₂ CO ₃	Yellow transparent glass with a layer of green and white opaque crystalline material	2.3	1.5
21	43 SiO ₂ /15 BaCO ₃ /25 PbO/2 CaCO ₃ /15 Na ₂ CO ₃	Greenish transparent glass with cracks	8.8	7.5
22	43 SiO ₂ /15 BaSO ₄ /25 PbO/2 CaCO ₃ /15 Na ₂ CO ₃	Greenish transparent glass with white opaque crystalline material on the top surface	8.8	5.8
24	30 SiO ₂ /10 BaCO ₃ /20 PbO/1 CaCO ₃ /39 Na ₂ B ₄ O ₇ ·12H ₂ O	Greenish-yellow transparent glass	6.3	8.5
Opaque partially vitrified				
12	10 BaCO ₃ /40 PbO/50 albite	Ivory opaque partially vitrified material with air bubbles on the top layer	5.9	3.9
13	55 SiO ₂ /15 BaCO ₃ /25 PbO/2.5 CaCO ₃ /2.5 Na ₂ CO ₃	White opaque partially vitrified material with big air holes	1.5	1.0
14	57 SiO ₂ /15 BaCO ₃ /25 PbO/3 CaCO ₃	White opaque partially vitrified material with big air holes	0.0	0.0
15	55 SiO ₂ /15 BaSO ₄ /25 PbO/2.5 CaCO ₃ /2.5 Na ₂ CO ₃	White opaque partially vitrified material	1.5	1.1
Opaque granular				
2	40 SiO ₂ /15 BaCO ₃ /45 PbO	Pale green opaque granular material	0.0	0.0
3	40 SiO ₂ /15 BaSO ₄ /45 PbS	White opaque granular material	0.0	0.0
4	60 SiO ₂ /10 BaCO ₃ /30 PbO	White opaque granular material, partially vitrified	0.0	0.0
5	35 SiO ₂ /15 BaCO ₃ /45 PbO/5 Cu ₂ (OH) ₂ CO ₃	Dark blue opaque granular material	0.0	0.0
16	55 SiO ₂ /15 BaCO ₃ /25 PbS/2.5 CaCO ₃ /2.5 Na ₂ CO ₃	Pale blue opaque granular material with large bubbles	1.5	1.1
23	48 SiO ₂ /20 BaCO ₃ /30 PbO/2 CaCO ₃	White granular opaque material with big air holes	0.0	0.0

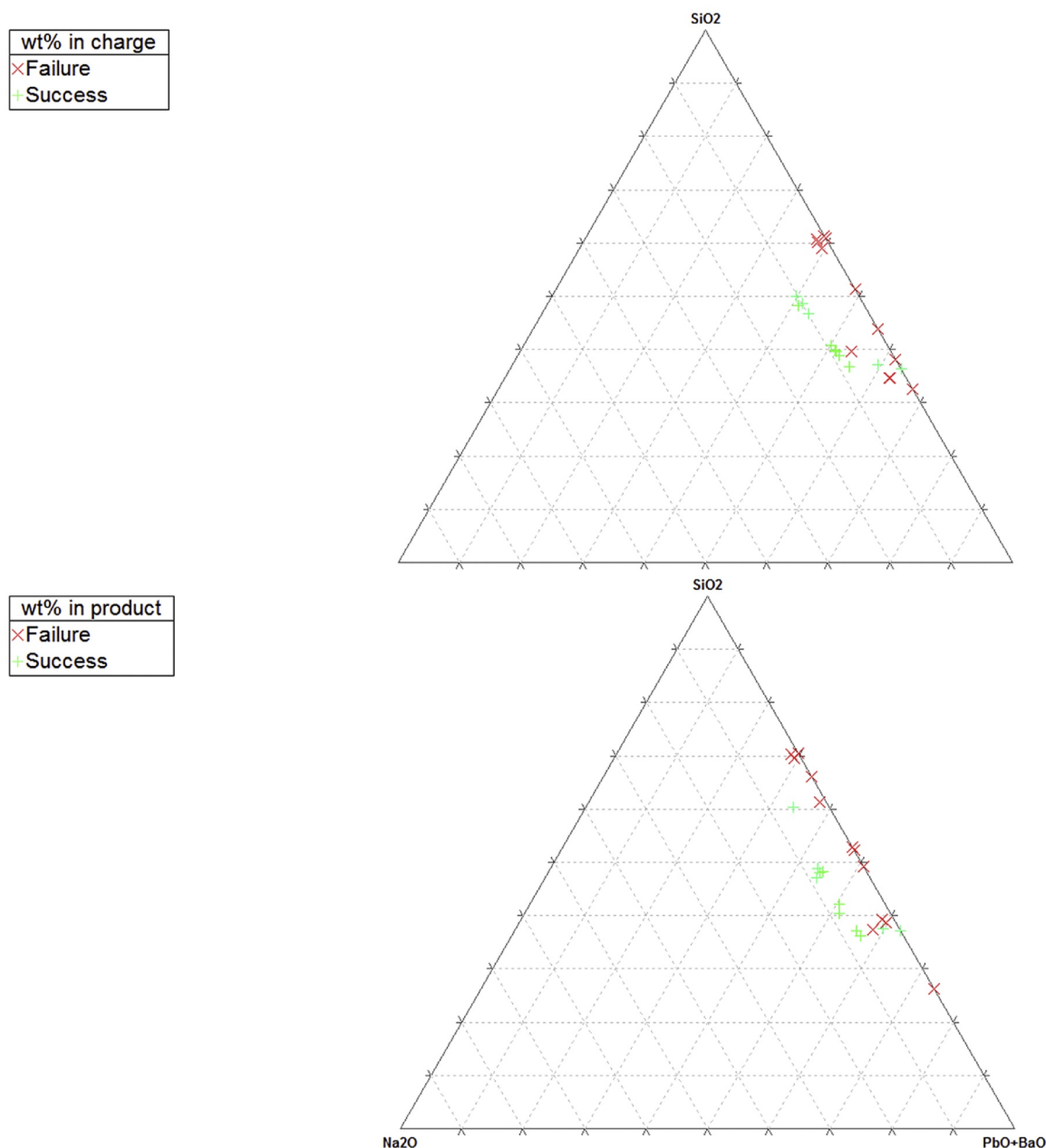


Fig. 2. $\text{SiO}_2\text{-Na}_2\text{O-PbO} + \text{BaO}$ phase diagrams of components in charge and in product

previously analyzed examples of Chinese Pb-Ba glass tend to contain amounts of Na_2O up to 10%. The question to be addressed here is why, with so much PbO available to act as a network modifier, does Na_2O 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%. Fig. 2 shows the $\text{SiO}_2\text{-Na}_2\text{O-PbO} + \text{BaO}$ phase diagrams of components in charge and in product. As shown, a certain amount of Na_2O 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_2O – apart from crucible 17 and 18 (with low or no Na_2O), all charges contained greater than 7% being more typical. Conversely, the crucibles which did not vitrify contained <1.5% Na_2O , with the exception of crucible 12,

which contained 5.92% Na_2O in the form of albite ($\text{NaAlSi}_3\text{O}_8$). It is therefore clear that under the conditions of this experiment sodium can facilitate glass formation in the lead-barium-silica system.

The data in Table 4 and Fig. 2 show that the measured $\text{Na}_2\text{O}\%$ are lower than the calculated $\text{Na}_2\text{O}\%$, which could be detecting error or a flux loss during the melting process. Still, it is noticeable that the crucibles using BaSO_4 , such as 11 and 22, show a higher loss of Na_2O (about 3%). According to the EDS chemical data and the mapping results (Supplementary 3), the white material in crucibles 11 and 22 contain a certain amount of Na_2SO_4 , which would explain the lower values of Na_2O in the glass. Nevertheless, it is immediately apparent that all the samples which produced transparent glass generally contain more than 7% Na_2O , whereas comparison with Fig. 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 $\text{Na}_2\text{O}\%$ might be underestimated in the literature: i), XRF and PIXE analysis can underestimate $\text{Na}_2\text{O}\%$, and ii) weathering effects can result in the loss

of Na₂O.

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 mould coloured glass [26–31]. 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 [28,29,33]. 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 [32]. 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 [34,35,36]. 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 [37], where typical values would be both greater than 1.5% respectively [38]. 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 [14,39,40] 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., K₂O, CaO, MgO, Al₂O₃, TiO₂, Fe₂O₃) 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 [41], 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 BaSO₄ and BaSi₂O₅ 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 BaSO₄ and PbO with natron glass rather than by using BaCO₃ as the barium source. It is possible, therefore, that both BaSO₄ and BaCO₃ were used selectively in the past to control for the degree of opacity. In our work, the crucibles with BaSO₄ generated both BaSi₂O₅ and unmelted BaSO₄ which can function as opacifiers, although in our replications BaSO₄ 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 [42], we suggest that the products of the primary melting might have needed to be re-melted to mix the opacifier into the glass.

According to Table 4, the loss of Na₂O is lower than 3%, then all other concentrations indeed go up when the data are normalized to 100%. It particularly affects SiO₂, BaO and PbO (as the major constituents), but they only go up about 1% (absolute) for each one. Thus, such small overestimates of SiO₂, 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 PbCO₃ (secondary formed) and BaSO₄ (probably by leaching) will formed on the lead-barium glass surface [43].

In this replication experiment, we did not observe any PbO leaching effect. As for crucibles used BaSO₄ and formed glass, a layer of white opacifier remains on the surface glass identified as BaSO₄ and BaSi₂O₅. 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 Na₂O 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 BaCO₃ or BaSO₄. 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.

Authors' contributions

Qian Ma wrote the main manuscript, and the replication experiment and SEM-EDS analysis was done by Qian Ma.

Mark Pollard supervised Qian Ma for this project and revised the manuscript when Qian Ma finished the draft.

Dennis Braekmans supervised Qian Ma for the replication experiment.

Andrew Shortland helped get permission to conduct this experiment in Cranfield University.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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