

DOI: 10.1007/s11431-006-2036-8

Origin of Chinese ancient glasses—— study on the earliest Chinese ancient glasses

GAN Fuxi^{1,2}, CHENG Huansheng¹ & LI Qinghui²

1. Fudan University, 220 Handan Road, Shanghai 200433, China;

2. Shanghai Institute of Optics and Fine Mechanics, CAS, P.O. Box 800-211, Shanghai 201800, China

Correspondence should be addressed to Gan Fuxi (email: fxgan@mail.shcnc.ac.cn)

Received April 20, 2005; accepted August 18, 2006

Abstract The earliest Chinese ancient glasses before the West Han Dynasty (200 BC) from different regions are studied. The glass samples were unearthed from Hunan, Hubei, Yunnan, Sichuan, Guizhou, Guangdong and Xinjiang of China. The chemical composition of these glasses samples is analyzed by proton induced X-ray emission (PIXE) technique, energy dispersive X-ray fluorescence (EDXRF) method and inductively coupled plasma atomic emission spectrometry (ICP-AES). It is shown that the glass chemical compositions belong to barium-lead silicate BaO-PbO-SiO_2 , potash soda lime silicate $\text{K}_2\text{O}(\text{Na}_2\text{O})\text{-CaO-SiO}_2$ ($\text{K}_2\text{O}/\text{Na}_2\text{O}>1$), soda potash lime silicate $\text{Na}_2\text{O}(\text{K}_2\text{O})\text{-CaO-SiO}_2$ ($\text{K}_2\text{O}/\text{Na}_2\text{O}<1$) and potash silicate $\text{K}_2\text{O-SiO}_2$ glass systems, respectively. The origins of the earliest Chinese ancient glasses are discussed from the archaeological and historical points of view. These four types of Chinese ancient glasses were all made in Chinese territory using local raw materials. The glass preparation technology was related to the Chinese ancient bronze metallurgy and proto-porcelain glaze technology. The glass technology relationship between the East and the West is analyzed at the same time.

Keyword: ancient glass, glass origin, chemical composition analysis.

The scientific archaeological study on ancient Chinese glass was started from 1930s. The pioneer work was carried out by Beck, Seligman and Ritchie. After chemical analysis of dozens of ancient Chinese glass samples dated to the pre-Han and Tang Dynasties, Western researchers realized that these glasses were made in China from the Han Dynasty (about 200 BC) and noted that early Chinese ancient glasses were characterized by high lead and barium contents, but the glass making technology was introduced into China from the West ^[1,2]. In 1970s we put forward the “Self-invention” hypothesis ^[3], namely that the Chinese ancient glass making was originated from China. This touched off a dispute among researchers in this field. In recent half century, the glass artifacts

have been discovered frequently in the excavated ancient tombs in China. Since 1980s with continued cooperation between archaeologists and glass scientists, a new prospect for ancient Chinese glass studies was opened up, and quite a lot of glass analysis data were accumulated, but most unearthed glass artifacts belong to the Han Dynasty and after Han Dynasty (later than 200 BC). The ancient Chinese glass belonged to pre-Han Dynasty was less studied before. For approaching the origins of ancient Chinese glasses, one must pay attention to the study of unearthed ancient Chinese glasses dated to pre-Han Dynasty. In this paper, the experimental results of the earliest ancient Chinese glass are presented and their origins are discussed.

1 Condition of ancient glass samples

The glass samples in the present study were unearthed from Baicheng and Tacheng as well as Hami and Hetian of Xinjiang Uygur Autonomous Region (provided by Xinjiang Institute of Cultural Relics and Archaeology), Jiangling and Suixian counties of Hubei Province (provided by Hubei Institute of Archaeology), Qingchuan of Sichuan Province (provided by Sichuan Institute of Cultural Relics and Archaeology), Haozhang of Guizhou Province (provided by Guizhou Institute of Cultural Relics and Archaeology), Zhaoqing of Guangdong Province (provided by Guangdong Institute of Cultural Relics and Archaeology), Jiangchuan of Yunnan Province (provided by Yunnan Museum), and Holabeil of Inner Mongolia Autonomous Region (provided by Inner Mongolia Institute of Cultural Relics and Archaeology). Most of these glass artifacts are single color beads. The descriptions of the glass samples are shown in Table 1-3. The date of all these glass samples belongs to pre-Han Dynasties (before 200 BC). For understanding the distribution of Chinese ancient glasses, several glass samples in remote area of China after 200 BC have also been analyzed. The condition of those samples is listed in Table 1-4

During the preparation of proto-porcelain, when the furnace temperature was high enough, the glaze would be melted and flowed down, and then formed the glaze droplet (popularly called glaze bead). The glaze droplet was transparent glassy material; maybe it was the earliest Chinese ancient glass. The glaze droplet samples, studied in this paper, were unearthed from Boluo of Guangdong Province (provided by Guangdong Institute of Cultural Relics and Archaeology). The condition of glaze droplets is shown in Table 1-5.

2 Experimental

Chemical composition analysis of most of glass samples was carried out at the Institute of Modern Physics, Fudan University, by proton induced X-ray emission (PIXE). External-beam PIXE was adopted for all samples, performed on the NEC 9SDH-2-beam line of the 3.0 MeV tandem accelerators. Samples were placed outside the beam exit window (7.5 μm Katon). After passing through the Katon film and air, 2.8 MeV protons hit the sample with a small spot. The induced X-rays were detected by an ORTEC Si(Li) detector with an energy resolution of 165 eV (FWHM) at 5.9 keV. The obtained PIXE spectra were recorded and analyzed with conventional electronics, followed by a multi-channel analyzer. The chemical composition ($Z > 11$) of the sample was measured

from the PIXE spectrum by using the deconvolution program GUPIXE-96. For sodium content measurement, some samples were put in the ambient of flowing helium gas to prevent the atmosphere absorption. The detailed measurement can be found in ref. [4].

Table 1 Condition of unearthed glass sample

Name	Number of sample	Number of cemetery	Unearthed site	Description of sample	Date
1-1 Kiziltur village, Baicheng county and E'min village, Tacheng county, Xiji-ang Province	XJ-1A	90BKKM36: 6	Kiziltur cemetery	M26 glaucous glass bead	West Zhou to Spring and Autumn Period (1100–800 BC)
	XJ-2A	90BKKM36: 6		M26 buff glass bead	
	XJ-2B	90BKKM36: 6		M26 buff glass bead	
	XJ-3A	90BKKM4: 7		M4 corroded glass bead	
	XJ-4A	90BKKM11		MII fragment of corroded glass bead	
	XJ-30	91BKKM3: 9	E'min village cemetery, Tacheng	M3 fragment of corroded glass bead	Spring and Autumn Period (700–500 BC)
1-2 Xichuan, Henan Province, Jiangling and Suixian, Hubei Province	XJ-44			M1 fragment of corroded glass bead	
	HB-1	Xujialing Chu tomb No. 1	Xichuan, Henan	White eye in blue bead body (frit)	Early Warring States (500–400 BC)
	HB-3	Jiudian tomb M533	Jiangling, Hubei	Broken blue color bead piece	Warring States (400–300 BC)
	HB-6	Zenghou Yi tomb	Suixian, Hubei	Small blue glass piece	Late Spring and Autumn to early Warring State (500–400 BC)
	GD01	Songshan tomb	Zhaoqing, Guangdong	Eye bead with white eye and blue glass body	Warring States (400–300 BC)
	GZH-2	Kele tomb M-91	Haozhang, Guizhou	Green glass bead	Late Warring States (300–250 BC)
1-3 Southern China	M13-15	Haojiaping	Qingchuan, Sichuan	Eye bead with three color eyes	Warring States (400–300 BC)
	SX-14	Yujiaba, Sanxia reservior	Kaixian, Chongqing	Deep blue eye-bead with blue and white inlayed	Warring States (400–300 BC)
	GZH-17	Zhongshan Li-yuan M-42	Weining, Guizhou	Blue glass bead	West Han–Warring States (250–200 BC)
	44-18-35A	—	Lixian, Sichuan	Yellow glass bead	West Han–Warring States (250–200 BC)
	XJ-5A	Bao-Zi-Dong M-41	Wensu, Xinjiang	Blue and green bead fragment	Qin–Warring States (250–300 BC)
	XJ-37A	Han tomb	Weiwu, Gansu	Green ear-pendant	
1-4 Remote area in China	NM02-2	Zhalainuer tomb	Holabial, Inner Mongolia	Green bead	Han Dynasty (200–100 BC)
	XJ-46	No. 14	Hami, Xinjiang	Blue squach shaped bead fragment	
	XJ-42	Ancient Akesipili castle	Hetian, Xinjiang	Eye-bead with black body and green inlayed	Jin–Han Dynasties
	Boluo 1			Pale yellow droplet along the straight wall	
1-5 Glaze droplet (Glaze beads)	Boluo 2	Wanling-Shan	Boluo, Guangdong	Glaze droplet along the straight wall	Late West Zhou (1000–800 BC)
	Boluo 3			Yellow calcined glaze droplet along the curved wall	Early Spring and Autumn Period (800–700 BC)
	Boluo 4			Transparent pale green glaze droplet along the curved wall	

The chemical composition of a few samples was measured by energy dispersive X-ray fluorescence (EDXRF) method using EDAX Eagle equipment at Shanghai Institute of Ceramics, CAS. The inductively coupled plasma atomic emission spectrometry

(ICP-AES) was applied for determining the chemical composition of glass fragment samples at Shanghai Institute of Optical and Fine Mechanics, CAS. The optical glasses, such as ZF-1 (high lead silicate glass) and BaF-1 (Lead-barium silicate glass), as well as window sheet glass (soda-lime silicate glass), whose chemical compositions are known, were used as standard specimens. The experimental results were compared with those of PIXE and EDXRF.

3 Results and discussion

The chemical composition analysis results of the studied ancient glass samples are listed in Table 2. The chemical composition of early ancient Chinese glasses before Han Dynasty can be divided into three groups: (i) Alkali lime silicate glass (R_2O -CaO- SiO_2). R_2O represents K_2O and Na_2O . Due to the different Na_2O and K_2O contents, it can be divided into two sub-groups: (a) $K_2O/Na_2O < 1$ and (b) $K_2O/Na_2O > 1$. (ii) lead-barium silicate glass (BaO-PbO- SiO_2). (iii) potash silicate glass (K_2O - SiO_2).

Form Table 2 it can be seen that the chemical composition of most glass samples unearthed from Xinjiang is quite different from that of unearthed from Central and South-Western China, which just belongs to sub-group i(a) ($K_2O/Na_2O < 1$). The ancient glass samples with the chemical composition of three groups mentioned above were all found in Central and South-Western China.

According to the experimental results mentioned above, the chemical compositions of early ancient Chinese glasses unearthed from Central China (Yellow River and Yangtze River valleys) and from North-Western China (Xi Yu in ancient name) are different. It can be estimated that the origins of Chinese ancient glasses from different regions should be different too.

3.1 The origin and evolution of chemical composition of early ancient Chinese glasses in Central China

The Chinese ancient bronze and lead metallurgy was originated in the Shang Dynasty (11–16th centuries BC), and the proto-porcelain appeared also at that time. The furnace temperature could be up to 1000–1200°C, and the plant ash was applied as flux agent. Therefore, due to different sources of plants, the compositions of plant ashes were also not the same. The proto-porcelain glazes were divided into high-calcium glaze and low-calcium glaze. Table 3-1 lists the chemical composition of low-calcium proto-porcelain glaze from Jiangxi, and Table 3-2 shows the chemical composition of high-calcium glaze from Boluo, Guangdong [5]. It can be seen that the chemical composition of Chinese proto-porcelain glazes was characterized by its higher K_2O content than that of Na_2O , either low-calcium glaze or high-calcium glaze. It shows the speciality of plant ash application.

From the West Zhou to early Spring and Autumn Period, the furnace temperature could be even higher. The glaze droplets could be formed by over heating, and these transparent glaze droplets has belonged to glassy materials. According to the chemical composition of glaze droplets unearthed from Boluo, Guangdong (Table 3), the K_2O

Table 2 Chemical composition of unearthed glass sample

Name	Number of sam- ple	Chemical composition of glass (mass percentage)																Measurement method
		SiO ₂	Na ₂ O	CaO	MgO	K ₂ O	Al ₂ O ₃	PbO	BaO	CuO	Fe ₂ O ₃	TiO ₂	MnO	Sb ₂ O ₅	Cr ₂ O ₃	P ₂ O ₅	SO ₃	
2-1 Baicheng and Tacheng, Xijiang; ancient glass in Western Asia	XJ-1A	63.10	18.27	5.88	5.20	2.57	1.12	0.09	0.02	0.79	0.57	0.07	0.04					ICP-AES, PIXE
	XJ-2A	65.38	11.54	8.88	5.02	1.59	1.99	1.93	0.01	0.01	1.03	0.02	0.04	0.72				
	XJ-2B	64.31	12.05	4.80	2.67	2.42	1.36	9.01	0.008	0.001	1.10	0.07	0.02	1.60				
	XJ-3A	65.19	15.27	6.65	3.66	2.93	1.44	0.02	0.02	0.76	0.86	0.13	0.03					
	XJ-4A	66.11	14.29	6.61	4.58	2.19	1.89	0.62	0.01	0.90	1.07	0.17	0.03	1.44				
	XJ-30	75.44	9.08	7.74	3.35	1.51	1.43	0.02	0.005	0.56	0.34	0.11	0.02	0.03				
	XJ-44	68.88	15.93	6.11	4.03	2.20	0.87	0.02	0.005	1.10	0.56	0.04	0.08	0.01				
	Ancient glass in Western Asia	65.5	16.0	7.0	4.5	2.0	2.0											
2-2 Henan and Hubei	HB-1	76.9	6.03	8.18	0.48	0.69	3.26		0.11	1.28	0.46					0.73	1.12	PIXE
		71.3	1.81	2.37	1.75	10.70	6.83	1.0	0.14	2.64	1.19	0.16	0.11			0.51	0.32	
	HB-3	78.45		2.36	0.57	9.6	5.68	0.1		1.76	0.83		0.06					EDXRF
	HB-6	79.67	7.97	6.03	0.53	0.6	3.07	0.02		0.2	1.3		0.01					
2-3 Southern China	GD01 (blue body)	49.95		2.87		1.81	9.01	18.58	15.82	0.06	1.43	0			0.03	0.45		
	GZH2	58.10		1.14		0.6	6.10	19.71	9.14	0.58	1.88	0	0.05		0	1.22	0.05	
	M 13:15	54.72		1.27		0.47	3.05	25.16	11.82	2.54	0.44	0			0.04			
	SX-14	58.53		0.57		0.51	2.65	28.78	6.97	0.64	0.27					1.07		PIXE
	GZH-17	77.38		0.48		10.83	6.8		0.18	0.20	1.41	0.27	1.09		0.03	0.25	1.09	
	44-18-35A	73.87		7.04		9.75	3.44	0.36	0.03	0.01	1.07	0.17			0.19			
	XJ-5	75.13		1.74		18.40	2.47			1.09	0.74	0.09	0.04				0.04	
Name	Number of sample	Chemical composition of glass (mass percentage)																Measurement method
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	PbO	BaO	K ₂ O	Na ₂ O	CuO	MnO	TiO ₂	P ₂ O ₅	Li ₂ O	ZnO		
2-4 Remote area in China	XJ-37A	56.45	1.53	0.66	3.80		24.10	10.34	0.57		0.09	0.34						PIXE
	NM02-2	49.91	3.22	0.37	2.91		35.04	0.08	0.49		0.26							
	XJ-46	20.18	1.00	12.03	1.90	0.28	47.14	14.62	0.36	2.2	0.06	0.01					ICP	
	XJ-42b	43.52	3.65	9.96	1.50		31.28	1.43	0.76		5.28	0.03						
	Body black																	PIXE
	Green glass	49.35	3.19	0.82	2.52		34.24	7.87	0.34		0.64	0.01						
	White calcined	68.46	2.07	0.65	0.78		25.38	1.10	0.68		0.33	0.01						
2-5 Glaze droplet of proto-porcelain, Boluo, Guang- dong	Boluo-1		9.93	2.02	19.16	2.50		0.13	1.13	0.22		0.70	0.77	0.05	0.04	0.01		ICP
	Boluo-2		15.76	2.24	11.34	1.91		0.10	2.81	0.36		0.50	0.92	0.03	0.05	0.01		
	Boluo-3		12.15	2.31	27.85	2.95		0.22	1.74	0.28		0.50	0.65	0.06	0.09	0.01		
	Boluo-4		11.30	1.34	19.01	2.80		0.25	3.60	0.42		0.70	0.57	0.06	0.10	0.01		

content is higher than that of Na_2O too. The glaze droplets should be the earliest ancient glass in China, which were used as very precious ornaments at that time, such as glass inlaid in pommel of swords.

The earliest ancient true glass artifacts were unearthed from famous tombs in late Spring and Autumn Period to early Warring States. There were only three cases: eye-beads unearthed from No. 1 tomb of Gushigou, Henan (tomb of the wife of King Wu-Fuchai, 504 BC)^[6], blue glass inlaid in pommel of Wu King's sword unearthed from Huixian, Henan^[7], blue glass inlaid in pommel of Yue King's (Goujian) sword from Jinglin, Hubei (496–464 BC)^[8]. For beads unearthed from Zenhou Yi, Suixian, Hubei (about 400 BC), it was not complete glassy material, and belonged to frit^[9]. The study on these ancient Chinese glasses was not complete at that time. The analytic results of chemical composition of these glasses were diverse (see Table 4), but they belonged to alkali lime silicate glass system ($\text{R}_2\text{O}-\text{CaO}-\text{SiO}_2$) with different $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio.

Recently further investigation on the early ancient Chinese glasses mentioned above has been carried out. The glass pieces inlaid in pommel of Yue King's sword were roughly studied by PIXE technique at the beginning of 1980s. Its chemical composition belonged to potash silicate glass. The PIXE spectrum was found recently as shown in Fig. 1(a)^[12]. We determined the chemical composition of a piece of glass bead fragment (HB-3) unearthed at the same place (Wangshan, Jiangjin, Hubei) by PIXE and EDXRF (see Table 2-2). It belonged to the high K_2O containing alkali lime silicate glass. Fig. 1(b) shows the PIXE spectrum of this glass piece. Date of this glass bead (450–400 BC) was a little bit later than that of Yue King's sword (496–464 BC). In comparison of Fig. 1(a) with (b), the PIXE spectra are very similar. It can be concluded that both glass samples are in the same glass system, and their chemical composition is unusual and has not been found in ancient Egyptian and Babylonia glasses. It is worthy to point out that the chemical composition of glass sample HB-3 (see Table 2-2) from Hubei Province is similar to that of proto-porcelain glaze sample from Jiangxi Province (see Table 3-1). Both the unearthed sites are located in the Yangtze River valleys. This fact demonstrates that the early ancient Chinese glass technology in Central China was evolved from preparation technique of proto-porcelain glaze. The proto-porcelain glaze is prepared by dipping the glaze emulsion on pottery surface and then densified at high temperature. In preparation of glasses, raw materials should be melted in a ceramic crucible, which was also used in bronze and lead metallurgy originated in the Shang Dynasty (11–16th centuries BC). Accordingly, there were available technical bases to supply the ceramic crucible for glass making.

In order to improve the glass transparency and decrease the glass melting temperature, ancient Chinese people developed new flux agents. Plumbum salt (lead oxide) and salt-peter (potassium nitrate) were used, and these two materials were familiarized in the Spring and Autumn Period (3–5th centuries BC) and utilized as medical drugs. Therefore, in the Warring States Period both the potash-silicate and lead-barium silicate glasses were developed firstly in the Yangtze River valleys.

The applications of lead materials were originated from bronze metallurgy. Because

Table 3 Chemical composition of ancient Chinese proto-porcelain glaze

Name	Number of sample	Date	Unearthed site	Chemical composition of glass (mass percentage)									
				SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	MnO	TiO ₂	P ₂ O ₅
3-1 Proto-porcelain glaze, Ji-angxi	Proto-porcelain glaze	Shang to West Zhou	Fanchengdui, Qingjiang, Jiangxi	72.67	8.57	4.24	3.65	0.68	8.99	1.27	0	0.34	0
		Late Shang Dynasty	Jiaoshan, Yingtan, Jiangxi	61.69	17.97	5.00	4.49	1.72	7.43	0.47	0.05	0.96	0.22
3-2 Proto-porcelain glaze Boluo Guangdong	Proto-porcelain glaze h21-g	Early Qin	Henglingshan, Boluo, Guangdong	63.94	15.41	1.73	11.23	3.18	2.28	0.53		0.48	
	Proto-porcelain glaze m21-g		Meihuadun, Boluo, Guangdong	61.33	14.22	1.84	14.19	3.98	2.42	0.7		0.32	

Table 4 Chemical compositions of early ancient glasses

Name	Number of sample	Date	Unearthed site	Measurement method	Chemical composition of glass (mass percentage)										Reference
					SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	BaO	PbO	K ₂ O	Na ₂ O	CuO	
4-1 Earliest ancient glass in China	Eye-bead	500 BC	Tomb of Gushihou, Henan				0.65	9.42	0.35			0.52	10.94		10
	Glass inlayed in sword pommel of King of State Wu (Fuchai) sword	495–473 BC	Tomb of early Warring states, Huixian, Henan		xxx			xx							7
	Glass inlayed in sword pommel of King of State Yue's (Goujian) sword	496–464 BC	Tomb of Wangshan Jianglin, Hubei	PIXE	xxx		x	xx				xx		x	8
	Eye-bead	About 400 BC	Tomb of Zenhou Yi Suixian, Hubei	C.A XRF	56.1 xxx	1.37	1.02	4.07 xx	2.24	0.05	2.8	2.60 xx	6.99	0.37	9 11
4-2 Ancient glasses unearthed in Spring and Autumn to Warring States	White Bi (ritual disk)	Warring States	Chu tomb Changsha		36.57	0.46	0.15	2.1	0.21	10.1	44.71	0.1	3.72	0.02	13
	Semi-transparent grey eye-bead	Late Spring and Autumn to early Warring States	Boxian, Anhui		47.15	9.5	0.86	1.61	0.29	12.12	22.46	1.74	2.99	0.82	14
	Hexahedral green glass bead	Late Warring States	Jiangchuan, Yunnan		81.36	2.7		1.8				14.27			15
4-3 Ancient potash silicate glasses unearthed in South-Eastern Asia	Glass bead	300–600 BC	Hastinapur, India		80	<1	2.6	3.9	<1		—	10.7	<1	—	21
	Glass bead	68 BC	Dingcun, Vietnam		Mostly	1.3	0.75	2.8	0.5			18	0.22–1	1.3 MnO ₂ 0.5	22
	Glass fragment	300–400 BC	Thailand		75–80	1–2		3–6	<1			12–15	1–3		23

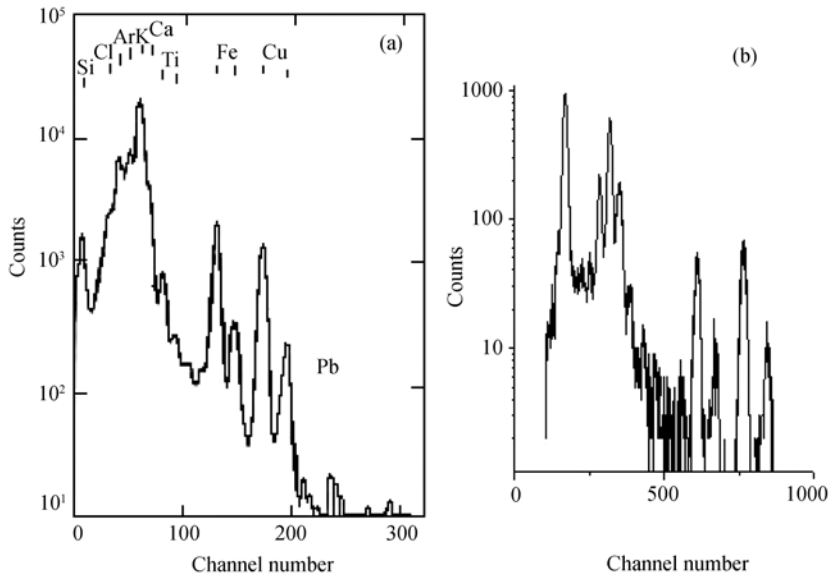


Fig. 1. PIXE spectral diagram of ancient glasses. (a) Glass inlaid in sword pommel of King of Yue State (Goujian), Wangshan, Jiangling, Hubei; (b) glass bead fragment of Chu State, Wangshan, Jiangling, Hubei (HB-3).

lead could decrease the melting temperature and increase the melt flow-ability, the bronze was a alloy of copper, tin and lead at early stage. There were a quite lot of experiences of application of lead materials in the Shang and Zhou Dynasties. In the Yangtze River valleys, such as Hubei, Anhui and Jiangxi, there were lead and barium rich-containing minerals, such as galena (PbS) and barite (BaSO_4), which could be applied as the flux agents in glass preparation. The unearthed sites of ancient Chinese barium-lead silicate glasses are coincided with the ancient lead minerals (galena, PbS) deposition sites, which are mainly located in the Yangtze River valleys. The earliest bead-barium silicate glass semi-transparent beads had been found in Bozhou, Anhui in the late Spring and Autumn Period and the early Warring States. As many as 200 pieces of glass Bi (ritual disks), beads tubes and stamps were unearthed from more than 100 tombs in Changsha, Hunan, dated to the East Zhou Period [16]. As shown in Table 2-3, the lead-barium silicate glasses had also been found in South and South-West of China, dated to the middle and late Warring State.

The mould-pressing technique applied for preparation of glass artifacts was also copied from bronze manufacture technology. To the Han Dynasty the flat glass plate with large sizes up to $9.5 \text{ cm} \times 4.5 \text{ cm} \times 3.5 \text{ cm}$ from the tomb of South Yue King [17], the big glass Bi (ritual disk) with 23.4 cm in diameter, 1.8 cm in thickness and 1.9 kg in weight [18] and the thick glass plate with the size of $32.5 \text{ cm} \times 14.8 \text{ cm} \times 35 \text{ cm}$ and 5.25 kg in weight [19] had been unearthed in Mo King's tomb, Shanxi and Jimo, Shandong respectively. It is demonstrated that the technology for preparing lead barium silicate glass wares was advanced from the Warring States to Han Dynasty and the glass artifacts had been distributed from Central China to Southern China (Guangdong, Guangxi), South-Western China (Sichuan, Guizhou), as well as to North-Western China (Gansu,

Chenghai) and North-Eastern China (Liaoning) (Fig. 2).

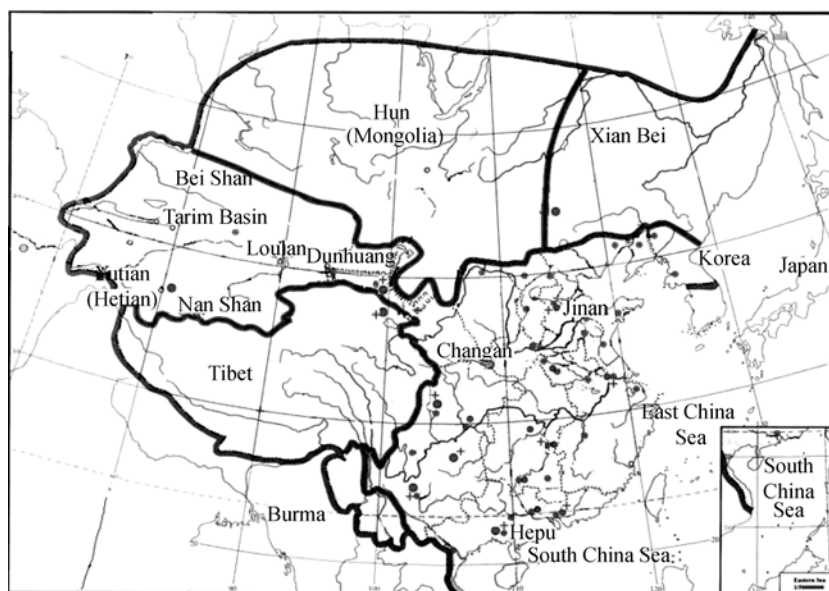


Fig. 2. Unearthed sites of lead-barium silicate and potash silicate glasses in the period of Warring States to Han Dynasty (● lead-barium silicate glass; + potash silicate glass).

Another approach to improve the glass flux was that ancient Chinese people tried to increase the K_2O content in alkali lime silicate glasses using saltpeter (KNO_3) instead of plant ashes. They used saltpeter as natural drug in very early time and knew the low melting point ($330^\circ C$) of saltpeter applied in ancient lead metallurgy.^[20]

In 1980s a new group of ancient Chinese glasses with low content of Al_2O_3 , CaO and Na_2O (<3%) and high content of K_2O (>10%) belonged to potash silicate was unearthed from the tombs dated to Han Dynasty in Guangxi^[15]. Up to now the earliest ancient potash silicate glasses dated to the Warring States have been found in Jianglin, Hubei and Changsha, Hunan, together with the lead-barium silicate glass artifacts, as shown in Tables 2-2 and 4-2. It can be understood that the early potash silicate and lead barium silicate glasses were developed in the Yangtze River valleys firstly. The saltpeter is easily formed on the soil surface in warm weather places, especially after rainy seasons. Reasonably Southern China (Guangdong and Guangxi) became main production area of potash silicate glasses.

Potash silicate glasses were also found in ancient India and South-Eastern Asia, as shown in Table 4-3, but the unearthed glass samples were not much. As mention above, we had found the earliest ancient Chinese glasses with high K_2O content, which was earlier than that of found in India. The earliest ancient Chinese potash silicate glasses were made in the Warring States and massively produced in West Han Dynasty. the date was close to that of ancient India, but the quantity of the unearthed potash silicate glass artifacts, including pressed glass vessels, was much more than that of ancient India. The

Hepu and Guixian, Guangxi were the port cities in ancient Maritime Silk Road, where the cultural and technical exchange between the East and the West must exist at ancient time. It was possible that the glass making technique came from outside and the glasswares were manufactured at local places. As mentioned before the lead-barium silicate glasses had been unearthed in Guangdong and Guangxi from the Warring States to West Han Dynasty (see Table 1-3) and some glass artifacts were made very preciously, such as the lead-barium silicate glass plate unearthed from South Yue King's tomb in Guangzhou. Therefore, it is quite possible that the glass making technology was moved from Central China to the south of China and local rich saltpeter sources were utilized to make potash silicate glasswares.

3.2 *The origin and characteristics of chemical composition of Chinese ancient glasses in the North-Western China (Xi Yue)*

The Xinjiang region (Xi Yue was the old name) is located in the Middle Asia, and it was an important place in ancient trade and cultural routes. The ancient glasses unearthed from Xinjiang possessed the distinctive characteristics resulted from cultural and technical exchange between the East and West. As shown above, the earliest glass beads unearthed from Baicheng and Tacheng, Xinjiang, were single color beads without inlaid. The single color glass beads had existed in the West dated to the 16th to 13th centuries BC. In the 13th century BC the multi-color glass beads appeared in ancient Egypt and Babylonia, and then eye-beads were flourished in 10–6th century BC. The date of the single color beads unearthed in Kiziltur and Baicheng, Xinjiang was around 11–8th century BC, but there were very few eye-beads found. The chemical composition of the glass samples from Kiziltur, Xinjiang, as shown in Table 2-1, is similar to that of Mesopotamia glasses, but the glass quality was poor with many small bubbles. The technical level was lower than that in Mesopotamia. It is shown that the glass preparation technique was imported from the West, and the glass beads were made locally using local raw materials, such as talc, serpentine, diopside, plant ashes, etc. It can be also seen from other analytical results of early glass beads unearthed from Kiziltur cemetery by scanning electron microscope (SEM-EDM), which is shown in Table 5 ^[24]. Different from chemical composition of Mesopotamia glasses, the K_2O/Na_2O ratio of Kiziltur's glass approached to 1, and some Kiziltur's glasses were characterized by high PbO and Sb_2O_3 contents, as shown in samples XJ-2A and 2B of Table 2-1 and in 91BKMM-2 and 26 of Table 5. It is quite unique in comparison with Mesopotamia glasses that these glass beads demonstrated again that they were made locally related with local raw materials and local bronze metallurgy ^[25].

As mentioned above the date of Kiziltur's glass beads was in the time of the West Zhou to Spring and Autumn Period in China (1100–500 BC), the same time of late Second Assyria Kingdom in Western Asia (1100–700 BC) and early Persia Empire in Middle Asia (550–529 BC). In the late Neolithic (4000 BC), the Indo-Europeans barbarian tribes moved to the East and South-East, such as Aryans moved to the Middle East in 3000 BC and to Iran and India in 2000 BC ^[26]. The language of ancient people in Tarim Basin, Xinjiang belonged to Indo-Europeans. Some people think that they maybe were

Aryans.

Table 5 Chemical compositions of several ancient glasses in Xinjiang

Name	Number of cemetery	Chemical composition of glass (mass percentage)												Reference
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	BaO	PbO	K ₂ O	CuO	Na ₂ O	MgO	ZrO ₂	Sb ₂ O ₃	
Kiziltur ancient cemetery in Xinjiang	91BKMM21	73.80	0.39	1.23	7.51	0.34		5.21	0.11	4.33	6.89		0.19	24
	91BKMM21	72.19	0.47	1.18	7.98	0.49	0.23	3.03	2.11	5.86	5.67	0.01	0.77	
	91BKMM2	69.3	0.06	0.73	7.95	0.01	6.37	3.29	0.26	3.76	6.56	0.02	1.70	
	91BKMM26	70.14		1.43	7.71	0.30		3.20	1.40	4.08	6.97		4.77	
	91BKMM37	82.30		1.14	5.02	0.41	0.87	0.36	2.2		5.96	1.15	0.56	

We can understand more details from the spreading of glass making techniques from Western Asia. During Indo-Europeans moved to the Middle East and Western Asia, one of Aryans, called Hurrian, knew the bronze, iron and glass making techniques. After collapse of Mitanni Dynasty in 7th century BC, they moved to Urartu of Northern Iran. After Assyrian invasion in 7th century BC, the Hurrian moved to Armenia, and one of them, called Scythian came to Xinjiang^[27]. The Scythian with great influence of Persia was called Saka. The name always appeared in ancient Persian and Indian historical writings and another name Sere was called in Hellenic and Roman literatures. They lived in Xinjiang, Altai, and Mongolian steppe and played an explorer role in the cultural dissemination between the East and the West.

From the analysis mentioned above, the soda potash lime silicate glass beads unearthed from Xinjiang in 10—6th centuries BC were made locally by ancient Saka people. The glass making technique was from Western Asia. Therefore, generally speaking, the exporting Chinese silk was the representative of the cultural exchange between the East and the West in ancient time, and the importing glass making technology maybe was the evidence of the technical exchange between the East and the West.

As mentioned above, the date of Chinese ancient glass making in Central China was later than that in Xinjiang region about 400—500 years. From the West Zhou to Warring States there were some possibilities for transporting the ancient glass beads from Xinjiang region to Central China through Steppe Silk Road, just as along the same route, the jades from Hetian, Xinjiang were transported to Central China. Due to the transportation difficulty the imported glass artifacts (mainly beads) were quite few. The chemical composition of eye-bead from tomb of Gushihou, Henan, as show in Table 4-1 and bead from tomb of Zanghou Yi, Hubei (HB-6) (see Table 2-2) is similar with that of glass beads from Kiziltur, Xinjiang.

The glass culture and technology exchange between the East and the West was mainly started from Zhangqian exploration to West in 1st to 5th centuries AD. At that time there were four strong empires: East Han in East, Rome in Western Europe and Western Asia, Persia in Middle Asia and Kushan in Southern Asia. The Silk Road connected these four empires and greatly promoted the exchange between them. Great Yen Chin, one of Indo-Scythians, brought glasswares and utensils, as well as glass making technology from Shi-Yue (Xinjiang region). The single color beads and multi-color eye-beads of lead barium silicate glasses made in the Han and Jin Dynasties were also transferred to Hetian and Hami, Xinjiang region from Central China. Their chemical composition is shown in

Table 2-4. The glass eye-bead unearthed from Akesipili, Hetian, Xinjiang was a black glass body with white calcined eye inlaid with green glass. It was a very precise artifact showing the progress of glass making at that time.

4 Conclusion

From the chemical composition analysis results of the earliest ancient Chinese glasses, we can see that the development of Chinese ancient glass technology possesses its own characteristics. The early ancient glass making technology in Central China was evolved from proto-porcelain technique using plant ashes as flux, and started from the Spring and Autumn Period to early Warring States. The glass chemical composition belonged to alkali lime silicate system and its main characteristics were the content K_2O higher than that of Na_2O , which is different from ancient Babylonian and Egyptian glass compositions. With the improvement of flux application in glass preparation, lead oxide was introduced in the middle and late Warring States. Lead salts had already been adopted in bronze and lead metallurgies before. Thus, the lead-barium silicate glasses with the Chinese speciality were invented. In another site by adopting saltpeter as the flux agent for glass melting, the potash silicate glasses were developed. These two-glass sorts were extended to the Han Dynasty and distributed to South and North of China, as well as exported to Korea Peninsula, Japan, South-Eastern Asia and Middle Asia.

The earliest ancient glass artifacts were unearthed in Kiziltur's cemetery, Baicheng, Xinjiang. The main chemical composition of these glasses was similar to that of Western Asia, but characterized by its application of local minerals with special glass components such as PbO , Sb_2O_3 , etc. The glass quality and art design were not as good as that of ancient Babylonian and Egyptian levels. It was possible that the glass making technique was introduced from the West by Eurasian steppe nomad tribes, such as Hurrian and Scythian, and then Saka people made the glass beads locally. A few glass beads were transferred into Central China along the ancient Steppe Silk Road. The main glass cultural and technical exchange was developed after Zhangqian exploration to the West (Shi Yue) in the Han Dynasty.

Acknowledgments The authors are grateful to Dr. Wu Juan in Shanghai Institute of Ceramics, Dr. Zhang Bin in Fudan University and Prof. Gu Donghong in Shanghai Institute of Optics and Fine Mechanics for their help in the relative experiments. This work was supported by the National Natural Science Foundation of China (Grant No. 50672106) and the Intellectual Innovation Project of the Chinese Academy of Sciences.

References

- 1 Beck H C, Seligman C G. Barium in ancient glass. *Nature*, 1934, 133(6): 982
- 2 Seligman C G, Ritchie P D, Beck H C. Early Chinese glass from pre-Han to Tang's times. *Nature*, 1936, 138: 721
- 3 Gan F X, Huang Z F, Xiao B Y. The origin of ancient Chinese glass. *J Chin Ceram Soc* (in Chinese), 1978, 6: 99–104
- 4 Li Q H, Zhang B, Cheng H S, et al. Application of proton induced X-ray emission technique in chemical composition analysis of Chinese ancient glasses. *J Chin Ceram Soc* (in Chinese), 2003, 31: 39–43

- 5 Luo H J, Li J Z, Gao L M. Study on chemical composition and microstructure of proto-porcelain. *J Chin Ceram Soc* (in Chinese), 1996, 24: 114–118
- 6 Henan Institute of Cultural Relics and Archaeology. *Ancient Tombs of the Spring and Autumn Period in Xichuan*. Beijing: Cultural Relics Press (in Chinese), 1991
- 7 Cui M C. Study on sword of Wu's King (Fuchai) (in Chinese). Special Issue of Cultural Relics in Central China, 1981
- 8 Chen Z Y. Date and person of No. 1 ancient tomb in Wangshan. *Proceedings of the First Annual Meeting of the Chinese Archaeology Society*. Beijing: Culture Relics Press (in Chinese), 1978
- 9 The Museum of Hubei Province. *Tomb of Zengyihou*. Beijing: Culture Relics Press (in Chinese), 1989. 658
- 10 Zhang F K, Chen Z H, Zhang Z G. Study on Chinese ancient Luli. *J Chin Ceram Soc* (in Chinese), 1983, 11: 67–76
- 11 Hou D J. Several problems concerning Chinese ancient glasses. In: Gan F X, ed. *Proceedings of the Archaeology of Ancient Glasses Session of International Symposium on Glass*, Beijing, 1984. Beijing: China Architecture Press (in Chinese), 1986. 60
- 12 Chen J X, Li H K, Ren C G, et al. PIXE research with an external beam. *Nuclear Instrum Method*, 1980, 168: 437–440 [\[DOI\]](#)
- 13 Shi M G, He O L, Zhou F Z. Study on several Chinese ancient glasses. In: Gan F X, ed. *Proceeding of the Archaeology of Ancient Glass Session of International Symposium on Glass*, Beijing, 1984. Beijing: China Architecture Press (in Chinese), 1986. 5–9
- 14 Shi M G, He O L, Zhou F Z. Chemical composition of ancient glasses unearthed in China. In: *Proceedings of 15th International Congress on Glass, Session Archaeology*, Leningrad, 1989. 7–12
- 15 Shi M G, He O L, Zhou F Z. Study on several potash-silicate glasses from Han tomb. *J Chin Ceram Soc* (in Chinese), 1986, 14(3): 307–313
- 16 Zhou S R. Importance and characteristics of glasswares unearthed from Han tombs. *Archaeology* (in Chinese), 1988, (6): 547–555
- 17 Guangzhou Committee of Culture Relics Management. *Guangzhou Tomb of Han Dynasty*. Beijing: Cultural Relics (in Chinese), 1982
- 18 Wang Z J, Zhu J Y. Important relics discovered in Mao tomb and related cemetery of Han Dynasty. *Cultural Relics* (in Chinese), 1976, 7: 55
- 19 Shi M G, Zhou F Z. Investigation on ancient flat glass unearthed from China. In: *Proceedings of 16th International Congress on Glass*. Madrid: Bol Soc Esp Cerm-Vid, 1992, 7: 161–166
- 20 Meng N C. Expedition on the name of saltpeter in Han and Tang Dynasties. *Res Natural Sci History* (in Chinese), 1983, 2(2): 97–111
- 21 Lal B B. Examination of some ancient Indian glass specimens. *Ancient India*, 1952, 8: 17–27
- 22 Nyen Troung KY (Ruan C Q). *Ko Thuy Tinh co D Viet Nam (Vietnam Ancient Glass)*. Hanoi, 1998
- 23 Brill R H, Fang D M, Lange D E. Chemical analysis of some Asian glass. In: *Proceedings of 17th International Congress on Glass*. Beijing: Chinese Ceramic Society, 1995, 6: 463–468
- 24 Qian W, Zhang P, Li Q M. Study on early glass beads unearthed from graveyard in Kiziltur, Xijiang Province. In: Wan F B, Bamo Er, eds. *Proceedings of the 5th International Conference of Chinese Minorities Science and Technology History*. Nanning: Guangxi Nationality Press (in Chinese), 2001. 138–145
- 25 Gan F X, Li Q H, Gu D H, et al. Study on early glass beads unearthed form Baicheng and Tacheng of Xinjiang. *J Chin Ceram Soc* (in Chinese), 2003, 31(7): 663–668
- 26 Stavrianos L S. *A Global History*. 4th Ed. New Jersey: Prentice Hall, Englewood Cliffs, 1988. 58–66
- 27 Engle A. Glass making in China. *Reading in Glass History*, 1976, 7-6: 1–54