

Scientific Analysis on the glass and stone artifacts in Ulaanbaatar State University

Daisuke NAKAMURA*, Tomomi TAMURA*, Tetsuo WARASHINA*, Diimaajav
ERDENEBAATAR*

X-ray fluorescence analysis of glass and stone artifacts in Bronze Age and Xiongnu period was conducted at the Ulaanbaatar State University. As same as many Xiongnu sites, the glass material was mainly natron glass. One of the natron glass was found to have lead-barium glass attaching to it. Regarding the stone beads and a vessel, the products excavated from the Xiongnu tombs were presumed to be made of nephrite; the blue cylindrical bead in Bronze Age was not lapis lazuli but a type of phosphate mineral.

As a result, it was found that ornament plaques on harness sent from the Han dynasty were made with inlaying natron glass. This fact indicates Han dynasty also obtain artifacts from the Mediterranean world to some extent.

Keywords: glass beads, nephrite, Xiongnu, Mongolia

1. Introduction

From 20th to 21st of March 2019, we conducted non-destructive analysis for glass and stone artifacts in Ulaanbaatar University. The artifacts analyzed were excavated from the Xiongnu burials at Gol Mod II site in Arkhangai province, the Xiongnu burial at Khökh Üzüüriin Dugui II site in Khovd province at the eastern foot of the Altai Mountains, and a late Bronze Age burials at Baruun Gyalat site in Bayankhongor Province.

* Associate Professor, Graduate School of Humanities and Social Sciences, Saitama University. Archaeology.

* Senior Researcher, Nara National Research Institute for Cultural Prosperities.

* Director, Institute for artifacts and materials.

* Professor, Ulaanbaatar State University, Faculty of Humanities, Archaeology.

Gol Mod II site is one of the largest Xiongnu cemeteries, as well as Noyon Uul. Tomb No. 1 is the largest platform tomb in the Gol Mod II cemetery and contains many exotic goods such as gold gilded iron harness plaques (Fig. 1) and silver harness plaques, and a high-quality jade Bi-disk. 14C dating of tomb No. 1 is 2070±35 yrs. bp (Erdenebaatar et al. 2015: 217), 176BC to 22AD (IntCal 20). This is nearly the same period as the platform tombs in other cemeteries. Burial No. 30 is a circler burial, 19.5m in diameter, located between tomb No. 1 and its satellite burial group. Han lacquer plates, animal-band mirror (Han mirror), and Roman glass bowls with marble pattern were found here. The Roman glass is assumed to be the 1st century BC (Erdenebaatar et al. 2015: 218), while the Han mirror is estimated to be the late Western Han dynasty period: the latter half of 1st century BC (Otani 2014: 68). Tomb 189 and its satellite burials have not yet been reported.

Khökh Üzüürin Dugui II site consists of 5 circler burials. Burial No. 1 was well preserved and many artifacts such as bronze harness ornaments and bronze vessels. Many of them were brought from the Han dynasty (Kovalev et al 2011). An iron sword was also found at this burial and was made in the Han dynasty (Sakagawa et al. 2020). It has been dated to the late Han dynasty and is thought to have been a burial of the high class before the appearance of platform tombs (Kovalev et al 2011: 301-302). In Burial No. 2, some glass and stone beads were found but most of the funeral goods were already robbed.

Baruun Gyalat site is a Late Bronze Age site famous for its hourglass burials. Several necklaces were excavated and were composed of blue, red and white stone beads. The blue stone bead has cylindrical shape. It was reported as being made of lazurite (Kovalev and Erdenebaatar 2009: 165). If it is made of lazurite (lapis lazuli), it would be the oldest



Fig.1 Gold gilded iron harness plaques from Gol Mod II tomb No. 1 (Erdenebaatar 2016)

example in North and East Asia, hence we have analyzed it.

2. Methods and samples

We deduced bead-making technique based on positions and shapes of air bubbles in the glass beads and the characteristic shapes of the stringing holes with stereo microscope (Nikon Fabre Photo EX). The chemical composition of the glasses was analyzed by a non-destructive method using a portable energy dispersive X-ray fluorescence (XRF) analyzer (OURSTEX 100FA). XRF has commonly used for compositional analysis of ancient glass artifacts (cf. Kato et al., 2009, Abe et al., 2012). The target of the X-ray tube is palladium (Pd) and the tube voltage is set to 40 kV, the tube current is automatically adjusted to optimize the detector's dead time, and a measuring time (live time) is 100 seconds. The measurements were carried out in a vacuum. The measurement results were normalized by the fundamental parameter (FP) method calibrated using a standard glass sample (Corning Glass A) in a way that the total amount of the oxides of elements detected will be 100 wt.%.

The accuracy of quantification of the FP method was confirmed in this study as follows. Five randomly chosen locations were measured on the standard glass EC 1.1 (a float glass available from the British Glass Industry Association (Table 1). The measured values calculated in this manner and the reference values of the standard samples were then compared, and the dispersion of the measured values and the accuracy were evaluated. The results are shown in Table 1. The result shows that the accuracy is enough to determine the type of glass such as natron glass and plant-ash glass.

However, it must be noted that we conducted a completely non-destructive method to analyze the weathered surface of the glass artifacts. Therefore, the

Table 1 Known composition of EC1.1 against normalized XRF results for EC1.1.

EC1.1	Measured composition	Known composition
	Mean (wt.%, n=5) ± SD (1σ)	Reference values (wt.%) ± SD (1σ) *
Na ₂ O	13.47 ± 0.20	13.41 ± 0.11
MgO	4.03 ± 0.11	3.78 ± 0.10
Al ₂ O ₃	0.96 ± 0.20	1.08 ± 0.06
SiO ₂	72.03 ± 0.60	71.97 ± 0.14
K ₂ O	0.61 ± 0.05	0.59 ± 0.05
CaO	8.47 ± 0.55	8.63 ± 0.09
TiO ₂	<0.01	0.040 ± 0.002
Fe ₂ O ₃	0.13 ± 0.02	0.103 ± 0.004

* Fletcher 1976

results of analysis do not directly indicate the chemical composition of the glass in its original or non-weathered state, but nevertheless, they are thought to provide certain hints to identify the compositional types and colorants of the glasses.

In the following, the results of the analysis will be described for each site in the order of glass and stone beads. Fig. 2 shows analyzed glass vessels and beads, and Fig. 3 shows analyzed stone artifacts and beads.

3. Analysis results of glass

The results of the X-ray fluorescence analysis are summarized in Table 2. Besides, the characterization of the chemical composition of glass artifacts is shown in Fig. 4a and Fig. 4b.

a) Gol Mod II tomb No.1

Five fragments of glass vessel (GMII-1 BWV1, BWV2; GMII-1 PV1, PV2, PV3; Fig. 2a-e) and three glass artifacts (GMII-1 I1, I2, I3; Fig. 2f) inlaid on a gold gilded iron harness plaques (cf. Fig. 1) were analyzed. Regarding the color of the five glass vessels, GMII-1 BWV1 and BWV2 have marble pattern of translucent dark blue and opaque white, and GMII-1 PV1, PV2, PV3 are translucent deep purple. GMII-1 BWV2 had another white opaque glass attached to the marble glass body. Inlaid glass artifacts (GMII-1 I1, I2, I3) have hemispherical shape without hole and have brown color. We did not obtain good results on two (GMII-1 PV3 and GMII-1 I2) of the eight glass specimens due to weathering and surface irregularities.

As a result of XRF analysis, four glass vessels and two hemispherical brown samples were natron type of soda glass (natron glass). Natron glass was a kind of glass produced in the Mediterranean world; the representative one is Roman glass. The deep purple translucent glass (GMII-1 PV1, PV2) tends to have a slightly higher concentration of magnesium (MgO) or MgO and potassium (K₂O) than that of the dark blue and white marbled glass (GMII-1 BWV1, BWV2), which is slightly higher than the standard concentration for natron glass (MgO and K₂O < 1.5-2%). However, considering the effects of weathering and other factors, it is highly likely that the glass is natron glass from an overall perspective.



a. Marble glass vessel 1, b. Marble glass vessel 2, c. purple glass vessel 1, d. purple glass vessel 2, e. purple vessel 3, f. 3 brown glass beads inlaid on a horse ornament (a-f: Gol Mod II burial No.1), g. 15 cobalt blue glass beads (Gol Mod II burial No.30), h. burrel-shaped brown glass beads (Gol Mod II burial No. 189-S9), i. 7 purple glass beads, j. stone beads and segmented glass beads (i-j: Khökh Üzüürin Dugui II burial No.2) *a-e, g: S=1/1; f, h, i, j: S=2/1

Fig.2 Analyzed glass and stone artifacts in Ulaanbaatar University Museum



Fig.3 Analyzed stone artifacts in Ulaanbaatar University Museum (S=2/3)

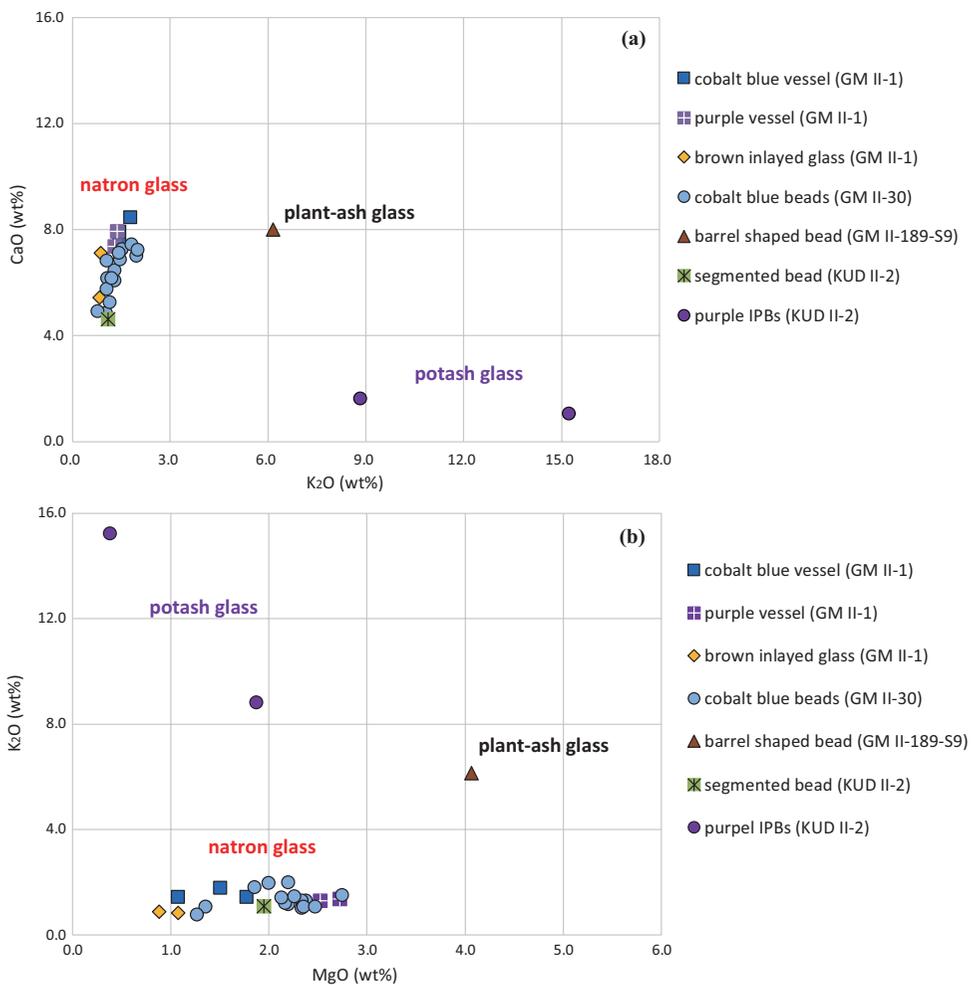


Fig.4 Characterization of glass artifacts based on the chemical composition

Table 2 Characteristics and chemical composition of analyzed glass samples

sample No.	site and burial	style/shape	bead-making technique	glass type	compositional type	group*	color	colorant	transparency	note	size (mm)
GMII-1 BAWV1-1	Gol Mod II tomb I	vessel		Soda	Natron	Group S1	dark blue/white	cobalt	translucent(tl)	deep blue part	
GMII-1 BAWV1-2	Gol Mod II tomb I	vessel		Soda	Natron	Group S1	dark blue/white	Mn, Sb, decolorant	translucent(tl)	deep blue part	
GMII-1 BAWV2-1	Gol Mod II tomb I	vessel		Soda	Natron	Group S1	dark blue/white	cobalt	translucent(tl)	attached opaque white	
GMII-1 BAWV2-2	Gol Mod II tomb I	vessel		Lead	Lead-barium	Group L1	dark blue/white	Sb decolorant	op	purple	
GMII-1 PV1	Gol Mod II tomb I	vessel		Soda	Natron	Group S1	purple	manganese	tl	inlaid beads	7.97
GMII-1 PV2	Gol Mod II tomb I	vessel		Soda	Natron?	Group S1	purple	manganese	tl	inlaid beads	8.26
GMII-1 I1	Gol Mod II burial No. 30	hemisphere	segmented (big)	Soda	Natron?	Group S1	brown		tp	inlaid beads	5.13
GMII-1 I3	Gol Mod II burial No. 30	hemisphere	segmented (big)	Soda	Natron?	Group S1	brown		tp	inlaid beads	4.79
GMII-30 B1	Gol Mod II burial No. 30	bead	segmented (big)	Soda	Natron	Group S1	dark blue	cobalt	tl	Mn, Sb	6.59
GMII-30 B2	Gol Mod II burial No. 30	bead	segmented (big)	Soda	Natron	Group S1	dark blue	cobalt	tl	Mn, Sb	5.19
GMII-30 B3	Gol Mod II burial No. 30	bead	segmented (big)	Soda	Natron	Group S1	dark blue	cobalt	tl	Mn, Sb	9.56
GMII-30 B4	Gol Mod II burial No. 30	bead	segmented (big)	Soda	Natron	Group S1	dark blue	cobalt	tl	Mn, Sb	7.40
GMII-30 B5	Gol Mod II burial No. 30	bead	segmented (big)	Soda	Natron	Group S1	dark blue	cobalt	tl	Mn, Sb	4.93
GMII-30 B6	Gol Mod II burial No. 30	bead	segmented (big)	Soda	Natron	Group S1	dark blue	cobalt	tl	Mn, Sb	5.61
GMII-30 B7	Gol Mod II burial No. 30	bead	segmented (big)	Soda	Natron	Group S1	dark blue	cobalt	tl	Mn, Sb	6.69
GMII-30 B8	Gol Mod II burial No. 30	bead	segmented (big)	Soda	Natron	Group S1	dark blue	cobalt	tl	Mn, Sb	5.65
GMII-30 B9	Gol Mod II burial No. 30	bead	segmented (big)	Soda	Natron	Group S1	dark blue	cobalt	tl	Mn, Sb	6.01
GMII-30 B10	Gol Mod II burial No. 30	bead	segmented (big)	Soda	Natron	Group S1	dark blue	cobalt	tl	Mn, Sb	6.83
GMII-30 B11	Gol Mod II burial No. 30	bead	segmented (big)	Soda	Natron	Group S1	dark blue	cobalt	tl	Mn, Sb	6.82
GMII-30 B12	Gol Mod II burial No. 30	bead	segmented (big)	Soda	Natron	Group S1	dark blue	cobalt	tl	Mn, Sb	5.84
GMII-30 B13	Gol Mod II burial No. 30	bead	segmented (big)	Soda	Natron	Group S1	dark blue	cobalt	tl	Mn, Sb	6.7
GMII-30 B14	Gol Mod II burial No. 30	bead	segmented (big)	Soda	Natron	Group S1	dark blue	cobalt	tl	Mn, Sb	4.96
GMII-30 B15	Gol Mod II burial No. 30	bead	segmented (big)	Soda	Natron	Group S1	dark blue	cobalt	tl	Mn, Sb	5.69
GMII-189S9 B1	Gol Mod II burial No. 189-S9	bead	segmented (big)	Soda	Natron	Group S1	dark blue	cobalt	tl	Mn, Sb	3.87
KUDII-2 IPB1	Khokh Uzunim Dugui II burial No. 2	bead	segmented	Soda	Potash	Group P	light brown	Cu, Sb?	tp	three-segmented bead	1.13
KUDII-2 IPB2	Khokh Uzunim Dugui II burial No. 2	bead	drawing	Potash	Potash	Group P	heavily weathered purple	manganese	tp	microbeads	4.15
KUDII-2 IPB2	Khokh Uzunim Dugui II burial No. 2	bead	drawing	Potash	Potash	Group P	purple	manganese	tp	microbeads	3.62
KUDII-2 IPB2	Khokh Uzunim Dugui II burial No. 2	bead	drawing	Potash	Potash	Group P	purple	manganese	tp	microbeads	2.12
KUDII-2 IPB2	Khokh Uzunim Dugui II burial No. 2	bead	drawing	Potash	Potash	Group P	purple	manganese	tp	microbeads	2.12

*Oga and Tamura 2013

On the other hand, it was found that attached white glass on GMII-1 BWV2 is lead-barium glass, and completely different from the body material (Fig. 2b). As lead-barium glass was originated from China, after the glass vessel was imported from the Mediterranean world, the lead-barium glass might have been added to it in the Han Dynasty or been modified by Han craftsmen in the Xiongnu.

Regarding the coloring of glass, the dark blue part of the marble pattern was colored by cobalt that contains manganese (MnO) and antimony (Sb_2O_5). The content of Sb_2O_5 of the white part is clearly higher than that of the dark blue part, while the content of MnO is almost the same between the white and dark blue. Considering that the content of calcium (CaO) is also slightly higher in the white part, calcium antimonate is assumed to have been used as an opacifier.

The white lead-barium attached glass of GMII-1 BWV2 also contains much Sb_2O_5 , but less CaO. It may contain cassiterite as an opacifier because of its high content of tin (SnO_2) instead. However, lead barium glass with a high content of Sb_2O_5 and SnO_2 is not common and needs further investigation in light of the specific situation of its adhesion to natron glass.

Fragments of deep purple glass vessels (GMII-1 PV1, PV2) contain MnO apparently higher than that of the marble-pattern glass vessel. In addition, since the content of coloring components is very low except for MnO, it is assumed that deep purple is colored by manganese. Hemispherical brown glass artifacts (GMII-1 I1, I3) scarcely contain the colored component except for iron (Fe_2O_3). It indicates that these glasses were colored by iron.

b) Gol Mod II burial No.30

The dark blue, translucent glass beads (GMII-30 B1-B15; Fig. 2g) were produced by the segmented method and were made of natron glass of Mediterranean origin. These beads are colored by cobalt (CoO: 0.12-0.31%). The presence of MnO (1.73-2.57%) and Sb_2O_5 (0.10-1.01%) is a common feature with the dark blue parts of the glass vessel fragments with the marbled pattern described above. However, the MnO content in these glass beads is significantly higher than in the vessel fragments.

c) Gol Mod II burial No.189-S9

Transparent yellow brown glass beads (GMII-189S9 B1; Fig. 2h) were made by folding method. As a result of XRF analysis, it was found that plant-ash type of soda glass (plant-ash glass) because of high contents of MgO and K₂O. Plant-ash glass is considered to have been made in West Asia and its neighboring area such as Central Asia. GMII-189S9 B1 has relatively high content of Al₂O₃ and the content of MgO is lesser than K₂O. This feature indicates that it was not made in West Asia but in Central Asia or India/Pakistan.

Regarding coloring materials, this sample has high content of Fe₂O₃ (5.93%) and scarcely contain other colored components. It showed that it is colored by iron.

(d) Khökh Üzüüriin Dugui II

Compositional analysis was conducted on three small glass beads. One of the beads (KUDII-2 S1; Fig. 2j) is a segmented bead and the other two (KUDII-2 IPB1, IPB2; Fig. 2i) are typical Indo-Pacific beads (IPB) made by the drawing method. The original color of KUDII-2 S1 is uncertain due to weathering. The KUDII-2 IPB1 and IPB2 are dark purple and transparent.

The results of the analysis suggest that KUDII-2 S1 is natron glass and that the dark purple IPBs (KUDII-2 IPB1, IPB2) are potash glass. Potash glass is thought to have been produced in India and Southeast Asia.

As regards the color, the segmented bead is likely to have a bluish color, as CuO has been detected. The dark purple potash glass has a particularly high MnO content of 4-5% and is colored with manganese. A large number of glass beads with similar characteristics in terms of bead-making technique, compositional type and coloring agent have been found at the Zamiin Utug burial No. 3-1 in Uvs Province (Tamura et al. 2019). Dark purple IPBs have also been found at the Alag Tolgoi in Dundgovi Province and other sites. Currently, it is the most widespread IPBs in the Mongolian plateau.

4. Analysis results of stone beads

This time, X-ray fluorescence analysis was conducted on the artifacts unearthed from Gol Mod II tomb No. 1 (GMII-1), Khökh Üzüüriin Dugui II burial No. 2 (KUDII-2) and Baruun

Table 3 Chemical Composition of analyzed stone beads

	GMI-1 J1 W1	KUDII-2 J1	KUDII-2 WS1	KUDII-2 GS1	BG-2 BS1-1	BG-2 BS1-2	BG-2 WS1
	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Na ₂ O	8.84	3.14	3.58	0.58	1.63	0.95	3.37
MgO	32.85	2.30	26.02	0.68	10.43	5.01	29.03
Al ₂ O ₃	0.00	0.00	2.64	34.50	27.29	22.82	2.87
SiO ₂	37.61	90.36	62.73	4.74	2.71	26.41	59.43
P ₂ O ₅	0.15	2.18	0.45	43.50	45.74	33.64	0.00
SO ₃	0.35	0.47	1.16	3.01	2.43	1.42	2.69
K ₂ O	0.14	0.81	0.69	0.20	0.34	0.72	0.42
CaO	19.36	0.30	1.45	0.56	3.22	6.71	0.93
TiO ₂	0.00	0.00	0.08	0.03	0.03	0.01	0.08
Cr ₂ O ₃	0.02	0.01	0.01	0.01	0.00	0.01	0.01
MnO	0.00	0.00	0.00	0.00	0.28	0.00	0.04
Fe ₂ O ₃	0.63	0.10	0.74	1.68	2.88	1.86	1.01
CoO	0.02	0.00	0.02	0.03	0.00	0.00	0.01
NiO	0.00	0.00	0.00	0.00	0.01	0.00	0.00
CuO	0.02	0.01	0.04	9.04	0.02	0.01	0.01
ZnO	0.01	0.00	0.00	1.39	0.00	0.00	0.01
Rb ₂ O	0.00	0.00	0.00	0.00	0.01	0.00	0.00
SrO	0.00	0.00	0.00	0.04	1.18	0.34	0.00
ZrO ₂	0.01	0.00	0.03	0.00	0.00	0.09	0.00
SnO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sb ₂ O ₅	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BaO	0.00	0.32	0.35	0.00	1.80	0.00	0.10
PbO	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Gyalat burial No.2 (BG-2). We determined the chemical composition (Table 3) such as a fragment of jade vessel (GMI-1 J1, Fig.3a), stone tusk-shaped ornament (KUDII-2 S1), a white cylindrical bead (KUDII-2 WS1, Fig.2j), a green cylindrical bead (KUDII-2 GS1, Fig.2j), a blue cylindrical bead (BG-2 BS1-1 & 2, Fig.2b.) and a white cylindrical bead (BG-2 WS1, Fig. 2b).

As a petrographic analysis was not conducted in this study, no precise mineral identification was possible. However, based on observation and chemical composition, materials of these artifacts are estimated to be as follows. The fragment of jade vessel (GMI-1 J1) is considered to be made of nephrite, which is commonly used in China. The white cylindrical beads (KUDII-2 WS1, BG-2 WS1) are likely to be talc, and the green cylindrical bead (KUDII-2 GS1) corresponds to turquoise. The blue cylindrical bead (BG-2 BS1-2) was reported to be lapis lazuli, but it is a phosphate mineral, not a silicate mineral. Therefore, this bead is not a lapis lazuli (lazurite). The exact mineral name cannot be determined, but it has a possibility of a lazulite. However, even if it was made of a lazulite, the distribution and the source are not yet known at present.

5. Conclusion

As for the stone beads and artifacts, we could only estimate the material, but for the glass, we gained some interesting insights. Roman artifacts are often found in the Xiongnu burials, and it is considered that the Xiongnu had their own trade network with the west.

In the Han Dynasty, glass beads and vessels were concentrated in southern China and less in the central region. In this context, however, a green Roman glass long-necked jar with a white marbled pattern was excavated in Luoyang, and a dark blue Roman glass fragment with a white marbled pattern approximating Gol Modo II-1 was excavated from Nanjing (Otani 2017). Considering the amount of excavated artifacts imported from the Mediterranean world and Central Asia, the Xiongnu were more active in trade with the west than the Han. However, the results of our analysis indicate that the Han also obtained natron glass from the Mediterranean world, inlaid it into decorative panels, and sent them to the Xiongnu. There is also a possibility that the Roman glass vessel analyzed at this time was also processed by the Han dynasty and sent to the Xiongnu.

Although it has not yet been confirmed by archaeological excavation and research, the Han Shu depicts the exoticism of Emperor Wu, and he possessed many exotic goods from outside of Han dynasty including those from western countries (Nagasawa 2017: 132-133). It has also been noted that such exoticism was widespread among the aristocracy of Changan. Sanfu huangtu also contains a description of Emperor Wu making curtains of purple glass (Nagasawa 2017: 134). If the purple glass is the same as dark purple beads found from the Xiongnu burials such as Khökh Üzüürin Dugui II burial No.2, Alag Tolgoi, Zamiin Utug burial No. 3-1, the Han dynasty also had access to IPBs via the Silk Road.

After the dispatches of Zhangqian (139-126 BC, 115-114 BC) and expeditions Li Guangli (104 BC, 102 BC), goods from the west surely have been brought to the Han dynasty more than before. While the Han and the Xiongnu competed to acquire western trade goods, the Han dynasty seems to have been generous in giving such goods to important diplomatic targets. Regarding the export of these western items, it is not clear whether the Han dynasty used them as export goods for reasons that did not fit their traditions, or whether they were the result of highly strategic diplomacy; this will be an issue for the future.

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