# Archaeometrical investigation of natron glass excavated in Japan ☆

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## ARTICLE INFO

## ABSTRACT

This study examines the chemical compositions, colorants, and bead-making techniques of natron glass beads excavated in Japan. The authors classified the natron glass discussed in this study into seven main types, as well as other minor types, based on their chemical compositions. We also compared these specimens with natron glass excavated in the Mediterranean world. Type B2, which was distributed in the first half of the 5th century CE, corresponds to Levantine I type; Type A1, which was distributed mainly in the 2nd century CE, is likely to correspond to specimens containing antimony only as decolorant. However, others do not obviously match any existing groups. The results of the measurement of lead isotope ratios revealed relatively similar values between the natron glass analyzed in this study and the ore containing lead found in Iran. This showed the origin of cobalt added as colorants.

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## 1. Introduction

This study reports the results of archaeometrical research on natron glass artifacts unearthed in Japan. Chemical examination by X-ray fluorescence spectrometry (XRF) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) revealed that there were more than 500 natron glass artifacts in Japan. Natron glass, which is soda glass with very little $K_2O$ and $MgO$, is unique to the Mediterranean world. Natron glass is also found in ancient Japan, distributed mainly in the 2nd century CE (the second half of the late Yayoi period and the end of the Yayoi period) and in the first half of 5th century CE (the first half of the middle Kofun period).

Recognition of natron glass began with the studies of Sayre and Smith [41] and Sayre [40]. They analyzed glass artifacts dating between the 15th century BCE and the 12th century CE unearthed in Europe and West Asia and confirmed that most were soda glass and that the chemical compositions were divided by high or low concentrations of $MgO$ and $K_2O$ in two groups. Soda glass containing a low content of $MgO$ and $K_2O$ was named natron glass [42] as it was shown that natron was used as a raw material of soda. On the other hand, as plant ash is used as a raw material for soda, soda glass containing high $MgO$ and $K_2O$ is called plant-ash glass.

The distinction between natron glass and plant-ash glass is generally conducted using the 1.5% content of $MgO$ and $K_2O$ as an index.

Furthermore, in previous studies, basic understanding has been that natron glass appeared in the Mediterranean world from the 7th century BCE to the 9th century CE, and most Roman glass corresponds to this type of soda glass, with the application of the decoloring technique using antimony and manganese (cf. [40]).

Subdivision of natron glass has been attempted based on its compositional diversity. Various types, such as Levantine I, Levantine II, HIMT, Egypt I, and Egypt II, have been established due to the explosion of material data, in particular after the turn of the century (cf. [3,9,12,20,32,47,48]). Each type is also considered to come from a different production area from analysis of the trace elements and isotope ratios occurring in them (cf. [4,7,13]).

It is only recently that the existence of natron glass in Japan has been recognized. In 2008, the authors recognized the existence of soda glass containing low contents of $MgO$ and $K_2O$ during the compositional investigation of glass unearthed from Kazefukiyama, an ancient mound tomb. The authors also recognized the possibility and necessity of distinguishing between natron glass and plant-ash glass among the soda glass found in Japan [25].

During the investigation of glass beads from Kazefukiyama, we recognized that natron glass appeared only in cobalt blue beads made by the restricted methods of folding, winding, segmenting, and attaching. Using this relation between the material and the technique as a clue, artifacts presumed to have been made from natron glass are now able to be determined correctly from observation. In this study, therefore, we intensively investigated glass artifacts unearthed in Japan that were considered with high probability to have been made from natron glass.

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## 1.1. Identification of natron glass from bead assemblages excavated in Japan

Glass artifacts uncovered at sites dating back to ancient Japan between 3rd century BCE and the 7th century CE were made of soda, potash, and lead glass, with each glass group classified into subcategories. Among them, lead glass is considered to be originated in ancient China (cf. [5,31,43,44,46]). Potash glass is also unique in Asia, especially from S-SE Asia to East Asia (cf. [6,29,30]). Soda glass is most common in all over the Eurasian Continent and the coastal areas, and most complicate in chemical composition. The authors classified soda glass into Groups SI to SV, with natron glass being classified into Group SI [33].

The glass artifacts that we analyzed as belonging to Group SI were all glass beads. The majority were small cobalt-colored monochrome beads (Fig. 1b–f), including a few specimens of multi-layered glass beads (these are so-called gold sandwich beads) (Fig. 1a) and tubular beads. Among them, we classified the cobalt-colored beads into five types by bead-making technique (the details are described later). The categories were segmenting, folding, winding, attaching, and either folding or segmenting (these were difficult to identify). Most importantly, Indo-Pacific beads [10,11], that is, glass beads made by a drawing technique, do not include natron glass.

There are other groups whose MgO and $K_2O$ content would cause them to be classified as natron glass, but these are excluded from the natron glass group (Group SI). The reasons for their exclusion are given below.

Group SIV is soda glass that contains a lower amount of MgO and $K_2O$. The majority of the artifacts classified into Group SIV contain less than 1.5% MgO and $K_2O$. However, Group SIV includes products containing between 1.5% and 2.0% $K_2O$. There are certain important differences between the Group SIV glass and the typical natron glass classified as Group SI. The majority of Group SI glass contains MgO in amounts greater than or equal to $K_2O$ while Group SIV shows a clear tendency for amounts of MgO less than the $K_2O$ content. The second important difference is that Group SI glass contains greater than 5.5% CaO while the majority of glass classified into Group SIV contains between 3.0% and 6.0% CaO. The third important difference is that glass artifacts classified into Group SI are glass beads produced by the segmenting, folding, winding, and attaching methods, including multi-layered glass beads, while all Group SIV glass beads were made by the drawing method. Based on these facts, the authors distinguished Group SIV beads from typical natron glass. It is possible that Group SIV glass beads correspond to what are called mNC [29] or m–Na–Ca–Al [30]; however, further investigation is needed to clarify this.

Group SV beads are soda glass containing relatively large amounts of MgO and $K_2O$. The majority of the beads classified into Group SV contain greater than 2.0% MgO and $K_2O$. However, the difference in chemical composition is significant, with some beads containing less than 1.5% MgO and $K_2O$. The content of CaO is low, with the majority of the beads in Group SV containing less than 5.0%. The majority of Group SV glass beads were typical Indo-Pacific beads made by the drawing method. Therefore, we did not include Group SV beads with natron glass.

## 1.2. Aims

Few of the beads unearthed at the excavation sites are Group SI (approximately 1,000 artifacts). The authors divided Group SI into Groups SIA and SIB based on the presence or absence of antimony [33]. Group SIB beads, which contain no antimony, were also classified into Group SIBa, SIBb, and SIBc based on MnO content and other differences. However, we identified some specimens during surveys on related samples that did not correspond to any of the categories.

In this study, we reconsider the classification of Group SI and compare each subgroup to the natron glass in the Mediterranean world, including northwestern Europe, in order to determine the origins of natron glass found in Japan.

## 2. Materials

This study focuses on more than 485 glass beads found in 12 archeological sites (Table 3). These 12 sites are all burial sites, such as mound tombs, and all glass beads in our sample were unearthed from burial facilities. In Japan, an overwhelmingly large number of glass beads were found in tombs as glass beads were used as grave goods. It is relatively easy to estimate the date of the glass beads found in tombs because of the existence of abundant accompanying relics, such as pottery. Although some glass beads were also found in places other than tombs, such as dwelling sites or cultural layers, we excluded such relics from examination to avoid the risk of contamination during the deposition process.

In Japan, natron glass beads were mainly distributed in the 2nd to early 3rd century CE and in the 5th century CE. Natron glass beads from the 2nd to early 3rd century CE were unearthed from a different tomb in Nishitani than the five burial facilities in the five sites that we are dealing with in this study, but there are a few other examples. In the 5th century CE, a relatively large number of examples existed besides the three sites mentioned in this study. However, most natron glass beads from the 5th century were found in Kazefukiyama, in one excavation. Other examples aside from the two sites dealt with in this study, Namitsuki and Mengahira, are nearly nonexistent, next to these two peaks in the distribution curve.

The number of glass beads unearthed at each site varies. In some cases, because of the existence of several damaged beads, the total number of natron glass beads is uncertain, and there is a possibility that the number is more than that shown. In many cases, other compositional groups of glass beads were found together with natron glass beads. Almost all of the accompanying glass beads are monochrome drawn beads called Indo-Pacific beads. As the compositional types of such Indo-Pacific beads in Japan differ depending on the period, the
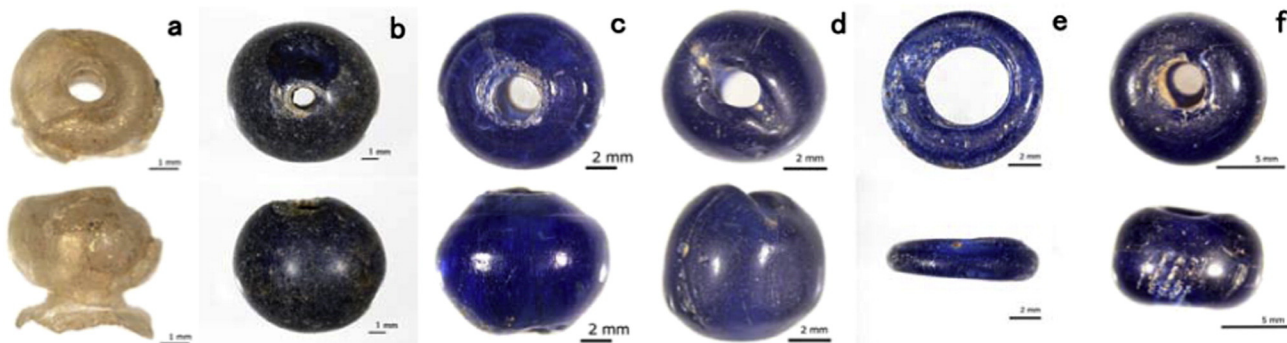


Fig. 1. Typical glass artifacts of natron glass excavated in Japan.

compositional types of glass beads accompanying natron glass beads also varies depending on the site.

Regarding examples between the 2nd century and the early 3rd century, natron glass beads from the sites of Ochayadori, Osandai, and Odappe are accompanied by potash glass beads that contain moderate $Al_2O_3$ (Group PI in [33]). At the Nishitani site, natron glass beads were unearthed accompanied by bangles made of lead glass probably made in China. From Mengahira, dated to the 4th century CE, potash glass beads containing high $Al_2O_3$ (Group PII in [33]) were found together with natron glass. Only natron glass beads were unearthed from the site of Yadani, dating to the 2nd century, and Namitsuki, from the 4th century. From three sites in the early 5th century, potash glass (Group PI) and two types of soda glass (Group SII and Group SIV) were also found. Group SII is characterized by the high concentration of $Al_2O_3$ (>4%) [33] and corresponds to mNA [29] or m-Na-Al [49]. After the late 5th century, the plant-ash type of soda glass beads (Group SIII) was distributed, and the main accompanying glass beads had changed to groups SII and SIII.

## 3. Analytical methods

### 3.1. Stereoscopic microscope

The bead-making technique was determined by observation with a stereoscopic microscope. Clues that show the bead-making technique, such as the shapes of bubbles contained in the beads, the surface conditions of the beads, and the holes in them were observed with the stereoscopic microscope (Leica MZ16 with digital camera Nikon DXM1200F).

### 3.2. X-ray fluorescence spectrometry

Quantitative analyses of the glass were performed using a micro-focused energy-dispersive X-ray fluorescence spectrometer (EDAX, EAGLE III). XRF has commonly used for compositional analysis of ancient glass artifacts in Japan and also in the Mediterranean world, and many articles has been published (cf. [2,21,26]). The target of the X-ray tube is molybdenum (Mo) and the X-ray tube voltage is set to 20 kV for quantitative analysis by the FP method and to 50 kV for some objects to obtain spectra above 20 keV for qualitative analysis. The X-ray tube current is set to 100 μA, the X-ray irradiation diameter is set to 112 μm, and a measurement time (live time) of 300 s is used. The measurements are conducted in a vacuum. The measurement results are normalized by the fundamental parameter (FP) method in a way that the total amount of the oxides of elements detected will be 100%. The FP method was calibrated using glass standard samples (CG-A, SG5, SG7, SGT5, NIST620). We confirmed the accuracy of quantification of the FP method in this study as follows. Eleven randomly chosen locations were measured on the standard glass EC 1.1 (a float glass available from the British Glass Industry Association). The measured values calculated in this manner and the reference values of the standard samples [8] were then compared, and the dispersion of the measured values and the accuracy were evaluated. The results are shown in Table 1. As a result, the values of $Na_2O$ by XRF in this study shows nearly 0.7% lower than reference values. And, on the other hand, the values of MgO show slightly higher: approximately 0.4%, and values of $K_2O$ also show nearly 0.3% higher levels.

### 3.3. Laser ablation inductively coupled plasma mass spectrometry

Four samples were also analyzed by LA-ICP-MS using 7500cx (Agilent Technologies) and UP213 (New Wave Research; ESI) conducted by the JFE Techno-Research Corporation. The elements measured were Na, Mg, Al, P, Si, K, Ca, Ti, Mn, Fe, Cu, Zn, Pb, Sn, and Sb, output as weight % oxides. Trace elements measured were Co, Ni, Rb, Sr, Zr, Cs, Ba, Th, and U. The calculation of sensitivity correction coefficients was achieved using NIST610. Comparison of the results of XRF and LA-ICP-

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

| EC1.1 | Measured composition (XRF) | Known composition |
|---|---|---|
| | Mean (wt%, $n = 11$) ± SD (1σ) (RSD%) | Reference values (wt%) ± SD (1σ)** |
| $Na_2O$ | 12.7 ± 0.2 (1%) | 13.41 ± 0.11 |
| MgO | 4.2 ± 0.1 (2%) | 3.78 ± 0.10 |
| $Al_2O_3$ | 1.4 ± 0.1 (3%) | 1.08 ± 0.06 |
| $SiO_2$ | 72.2 ± 0.2 (0%) | 71.97 ± 0.14 |
| $K_2O$ | 0.6 ± 0.1 (2%) | 0.59 ± 0.05 |
| CaO | 8.7 ± 0.1 (1%) | 8.63 ± 0.09 |
| $TiO_2$ | 0.04 ± 0.01 (13%) | 0.040 ± 0.002 |
| $Fe_2O_3$ | 0.09 ± 0.00 (5%) | 0.103 ± 0.004 |

\* Standard glass available from the British Glass Industry Association.
\*\* [8].

MS in the same sample is shown in Table 2. While the difference in the values of PbO and $Sb_2O_3$, in particular, between LA-ICP-MS and XRF is a little large, similar values were obtained for other elements except for MgO and $K_2O$ mentioned above.

### 3.4. Lead isotope analysis

Lead isotope ratios were also measured, and these data have been cross-checked with the lead isotope ratios of bronze objects or lead ores from Japan, China, Korea, Thailand, and Iran known to have been worked from previous studies. Lead isotope ratios were measured with a Finningan-MAR262 mass spectrometer by NIPPON STEEL & SUMIKIN TECHNOLOGY Co., Ltd. The measurement procedure is as follows. After dissolving a sample in nitric acid and hydrofluoric acid, the sample is electrolyzed with a two-volt direct current. Lead dioxide separated out on the platinum electrode plate is dissolved by nitric acid and hydrogen peroxide water. The solution to which a phosphoric acid and silica gel have been added is applied to a rhenium filament and introduced into a mass spectrometer. Heating temperature was 1200 °C, and ascending heat time was 20 min. Results were standardized using lead isotopic standard NBS-SRM-981.

## 4. Results

### 4.1. Bead-making techniques

It is possible to determine the bead-making technique by observing the overall shape, shape of the hole, and roughness of the wall of the hole. Glass beads made by the segmenting technique are onion-shaped and have a trace of fracture at both ends (Fig. 1c). Bubbles are often prolonged into a lens and are prolonged spirally, and not parallel with the hole. The hole is sometimes swelled at the central part. Here, we call such beads *segmented beads*.

Glass beads made by the folding technique have a round form, but the shape is different at each end (Fig. 1d). Here, for convenience, we call the side with a bigger hole the "upper side," and there are often several wrinkles radiating from the opening of the hole at the upper side. We name these beads *folded beads*.

*Ring-shaped beads* are considered to have been made by the winding method (Fig. 1e). The hole is large, and they are thought to have been made by winding glass string two or three times around a large core.

Glass beads made by the attaching technique have a round, cylindrical shape (Fig. 1f). There is a boundary where two pieces of glass were attached at the center of the side. They contain few bubbles, and bubbles do not indicate regular arrangement. We call such beads *attached beads*. These were made by attaching two glass pieces together by partially melting the pieces; we analyzed 110 sections of 55 such specimens. Some glass beads showed differences in chemical composition between their two pieces. In particular, seven sections on seven specimens were

**Table 2**
Comparison of quantitative values of some natron glass analyzed by LA-ICP-MS and XRF.

| Site | composition type (bead type) | analytical method | $Na_2O$ | $MgO$ | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $K_2O$ | $CaO$ | $TiO_2$ | $MnO$ | $Fe_2O_3$ | $CuO$ | $ZnO$ | $PbO$ | $SnO_2$ | $Sb_2O_3$ | $Co$ | $Ni$ | $Rb$ | $Sr$ | $Zr$ | $Cs$ | $Ba$ | $Th$ | $U$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Namitsuki No.1 kofun | Type A1 (Rd) | LA-ICP-MS | 19 | 0.5 | 2.0 | 69 | <0.001 | 0.7 | 5.8 | 0.1 | 0.02 | 1.3 | 0.2 | 0.01 | 0.2 | 0.005 | 0.9 | 0.05 | 0.002 | <0.001 | 0.04 | 0.006 | <0.001 | 0.01 | <0.001 | <0.001 |
| | | XRF | 19.1 | 0.8 | 2.3 | 67.7 | | 0.7 | 5.9 | 0.10 | 0.03 | 1.09 | 0.20 | | 0.08 | | 1.76 | 0.07 (CoO) | | 0.02 ($Rb_2O$) | 0.03 (SrO) | 0.04 ($ZrO_2$) | | | | |
| Kazefukiyama kofun | Type B1 (Se) | LA-ICP-MS | 18 | 0.6 | 1.8 | 70 | <0.001 | 0.4 | 6.6 | 0.1 | 0.08 | 1.3 | 0.3 | 0.01 | 0.4 | 0.006 | <0.001 | 0.05 | 0.007 | <0.001 | 0.05 | 0.005 | <0.001 | 0.01 | <0.001 | <0.001 |
| | | XRF | 18.4 | 0.8 | 2.3 | 69.6 | | 0.4 | 6.5 | 0.10 | 0.10 | 1.10 | 0.21 | 0.01 | 0.18 | | | 0.10 (CoO) | | 0.01 ($Rb_2O$) | 0.03 (SrO) | 0.07 ($ZrO_2$) | | | | |
| Kazefukiyama kofun | Type B1 (Fo) | LA-ICP-MS | 18 | 0.7 | 2.0 | 69 | <0.001 | 0.9 | 6.8 | 0.1 | 0.04 | 1.2 | 0.2 | 0.01 | 0.5 | 0.005 | 0.001 | 0.05 | 0.009 | <0.001 | 0.05 | 0.006 | <0.001 | 0.01 | <0.001 | <0.001 |
| | | XRF | 19.6 | 0.9 | 2.3 | 68.2 | | 0.4 | 6.8 | 0.11 | 0.05 | 1.00 | 0.22 | 0.00 | 0.19 | | | 0.06 (CoO) | | 0.004 ($Rb_2O$) | 0.03 (SrO) | 0.06 ($ZrO_2$) | | | | |
| Kazefukiyama kofun | Type B3a (Ring) | LA-ICP-MS | 19 | 0.9 | 2.2 | 66 | <0.001 | 0.5 | 6.7 | 0.2 | 0.6 | 1.7 | 0.4 | 0.02 | 0.8 | 0.02 | 0.01 | 0.06 | 0.01 | <0.001 | 0.05 | 0.008 | <0.001 | 0.02 | <0.001 | <0.001 |
| | | XRF | 19.7 | 1.2 | 2.4 | 66.2 | | 0.5 | 6.6 | 0.20 | 0.57 | 1.51 | 0.31 | 0.01 | 0.35 | | | 0.08 (CoO) | | 0.03 ($Rb_2O$) | 0.06 (SrO) | 0.06 ($ZrO_2$) | | | | |

the plant-ash type of soda glass containing 4% or greater levels of MgO and $K_2O$.

There are other small glass beads that are difficult to identify as having been produced either by folding or segmenting. The overall shape is similar to folded beads, but the feature of the hole is shared with segmented beads. While it is difficult to identify the bead-making technique, the similarity of shape, condition of the hole wall, and the shape and layout of bubbles or seeds show the uniformity of the bead-making technique (Fig. 1b). Here, these are called *round beads* for convenience.

*Multi-layered beads* are manufactured using a double tube of colorless glass (Fig. 1a). The bead-making technique is the segmenting method, and the features of overall shape and layout of bubbles are common with segmented beads. To improve the decorative effect, a gap is often left between the outer and the inner glass tubes (Fig. 2). Therefore, the outer layer of unearthed objects is often lost. Moreover, metallic foil is often inserted between the glass tubes. In this study, we detected gold (Au) from the foil left on the inner layer as described later.

*Tubular beads* were also found, but they were heavily weathered; the bead-making technique cannot be identified. This type of glass bead was found at one site only. All such beads are of an opaque, light blue appearance.

### 4.2. Subdivision of natron glass based on chemical composition

The diversity of chemical composition in the 500 beads in Group SI is shown in Table 3. An asterisk (*) shows the minimum number of natron glass beads unearthed at each site where a lot of fragments of beads probably made of natron glass were discovered but were not analyzed because they were not complete specimens.

As a result of reconsideration of the variations of chemical compositions, here we will call natron glasses with antimony *Type A* and those without antimony *Type B*. We divided Type A into four compositional subtypes, namely types A1–A4. Types A1–A3 consist of cobalt blue glass beads manufactured by various techniques. Type A4 is composed of multi-layered beads. Type B is divided into three compositional subtypes: Types B1 to B3. All these consist of cobalt-colored small beads.

#### 4.2.1. Type A

*4.2.1.1. Type A1: high $Sb_2O_3$ and low MnO.* The concentration of $Sb_2O_3$ is high in type A1 (>1–2%); this type is strongly colored dark blue by cobalt, which makes the purpose of adding antimony unclear, although antimony is considered to be added for decolorization (cf. [40]). This possibly shows that coloring was done sometime after glass production. Small amounts of copper (CuO: 0.15–0.30%) and lead (PbO: 0.04–0.17%) considered to be associated with cobalt material were also detected. The
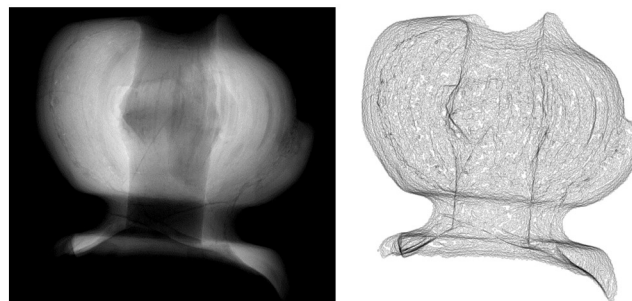


**Fig. 2.** left: X-ray computed radiography image of a multi-layered glass bead (Type A4) from Utsukushi No.1 kofun (by Micro-focus X-ray Magnification Imaging. right: black/white reversed and outline-emphasized image by Adobe Photoshop CS4. System: FUJIFILM, µFX-1000, Imaging Analyser: FUJIFILM, BAS-5000, and Imaging Plate: BAS-SR2025). The photographing conditions are as follows. The voltage is 40 kV, the current is 40 µA, and the exposure time is 60 s. We can see the gap between glass layers.

**Table 3**
A summary of analyzed artifacts in this study.

| Site | Age | Number | Type A 1 (Rd) | 2 (Fo) | 3 (Fo) | 4 (Ml) | Others (Tb) | Type B 1 (Fo) | 1 (Se) | 1 (At) | 2a (Fo) | 2b (Fo) | 3a (Ring) | 3a (At) | 3b (At) | Others (Se) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ochayadori site No.1 tomb | early 2c | 3 | 3 | | | | | | | | | | | | | |
| Osandai site No.5 tomb | early 2c | 4 | 4 | | | | | | | | | | | | | |
| Nishitani site No.2 tomb | early 2c | 1 * | | | | | 1 | | | | | | | | | |
| Yadani D site No.2 tomb | 2c | 3 | 3 | | | | | | | | | | | | | |
| Odappe kofun | early 3c | 9 * | 9 | | | | | | | | | | | | | |
| Mengahira kofun | early 4c | 8 * | 8 | | | | | | | | | | | | | |
| Namitsuki No.1 kofun | latter 4c | 60 | 60 | | | | | | | | | | | | | |
| Kazafukiyama kofun | early 5c | 381 * | | 3 | 4 | | | 92 | 87 | (74) | 30 | 8 | 97 | (10) | (19) | 2 |
| Utsukushi No.1 kofun | early 5c | 6 | | | | 3 | | | | | | | 3 | | | |
| Kuninari kofun | early 5c | 8 | | | | | | 8 | | | | | | | | |
| Meikegaya No.25 kofun | latter 5c | 1 | | | | | | 1 | | | | | | | | |
| Taku-Urigasaka | 6c | 1 | | | | 1 | | | | | | | | | | |

Rd: round beads; Fo: folded beads; Ml: multi-layered beads; Tb: tubular beads; Se: segmented beads; At: attached beads; Ring: ring-shaped beads.

cobalt colorant is discussed further later in this paper. The manganese content is very low (MnO: <0.3%). All specimens of Type A1 are cobalt blue round beads made by an uncertain method. They are found in 6 sites from the early 2nd century to the late 4th century CE. Type A1 accounts for the majority of Type A.

*4.2.1.2. Type A2: high $Sb_2O_3$ and moderate MnO.* Type A2 contains moderate MnO (0.3–0.6%) as well as high $Sb_2O_3$ (>2%). However, the concentrations of MgO and $K_2O$ of this type of glass bead varied (Fig. 5). Only three specimens can be recognized from one site in the early 5th century, and all samples are relatively weathered. The variance in the concentrations of MgO and $K_2O$ is possibly due to weathering. The bead-making technique is the folding method, clearly different from Type A1.

*4.2.1.3. Type A3: low $Sb_2O_3$ and moderate MnO.* We recognized only four samples from one site dating to the early 5th century. All are cobalt blue beads made by the folding technique. This type contains low $Sb_2O_3$ (0.1–0.3%) and moderate MnO (0.3–0.4%). Although the quantitative values of $Sb_2O_3$ content are not accurate, as was mentioned above,
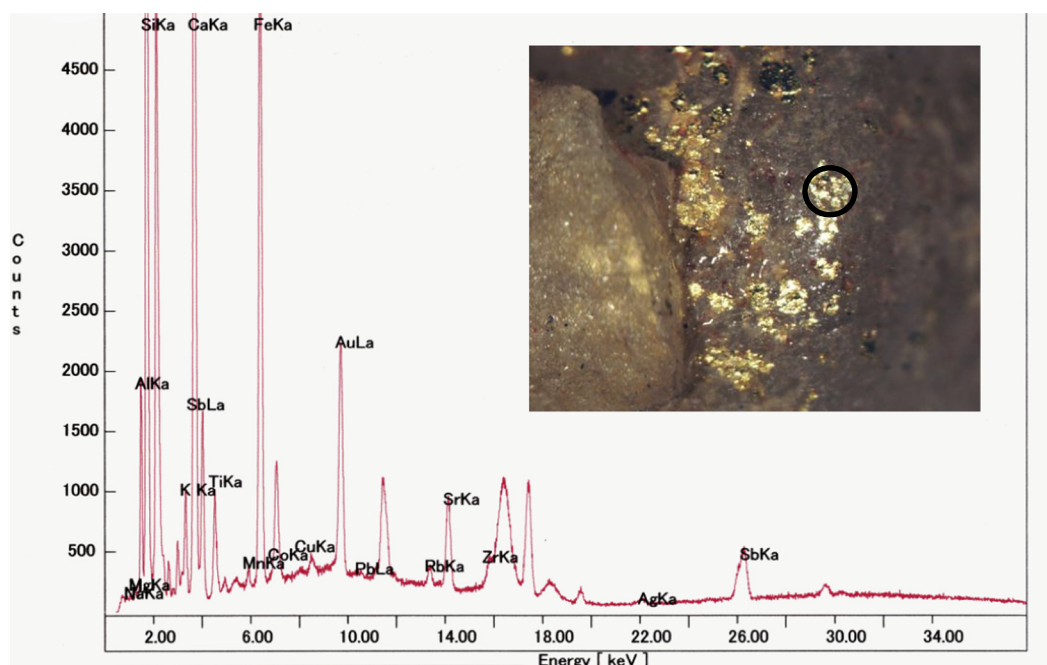


Fig. 3. XRF spectrum of metallic foil between glass layers. Significant level of gold (Au) is detected from the foil.

concentrations of $Sb_2O_3$ of Type A3 are clearly lower than those of Types A1 and A2. Furthermore, these glass beads contain relatively higher levels of MgO and $K_2O$ (Fig. 5). Paynter [35] pointed out that these ingredients (in particular, $K_2O$) increase in the context of recycling of glass due to the incorporation of the potash-rich vapor from fuel.

*4.2.1.4. Type A4: multi-layered beads with moderate $Sb_2O_3$ as decolorant.* Only four specimens were uncovered at two sites, and all were of almost the same chemical composition. That is, the concentrations of $K_2O$ varies, but a tendency for high CaO (>8.0%) is common (Fig. 5). A range of 0.5–0.6% of $Fe_2O_3$ as impurities of silica sand was identified. The concentration of $Sb_2O_3$ was moderate (0.17–0.65%), and this caused a discharge of colors to create a colorless translucent appearance. Gold was detected on the surface of the inner layer (Fig. 3), which is a distinctive commonality of natron glass because multi-layered glass beads other than natron glass in Japan contained either silver foil or no metallic foil between layers.

*4.2.1.5. Type A others: tubular beads.* There are also tubular beads classified as Type A. This type of glass bead was found at one site only. Chemical analysis was conducted on one specimen only; therefore, it is impossible to examine the compositional variations. This sample has a light blue opaque appearance. Colorants detected from this specimen were copper, and calcium antimonate ($CaSb_2O_6$), considered to be an opacifier, was detected by XRD (Fig. 4).

### 4.2.2. Type B

*4.2.2.1. Type B1: low MnO, $TiO_2$, and $Fe_2O_3$.* The most significant feature of Type B1 is that the concentrations of MnO are very low. Type B1 (Fo) is made by the folding method, Type B1 (Se) is made by the segmenting method, and Type B1 (At) is made by the attaching method. Type B1 (Fo) and Type B1 (Se) were of almost identical chemical compositions. Type B1 (At), however, shows a slightly higher level of $TiO_2$ (Fig. 6), and its contents of MgO and $K_2O$ vary (Fig. 5). It is, however, difficult to regard only Type B1 (At) as an independent group; Type B1 (Fo), Type B1 (Se), and Type B1 (At) are now considered to be the same compositional type. Type B1 (Fo) was found in three sites, and Type B1 (Se) and Type B1 (At) were unearthed from one site in the 5th century.
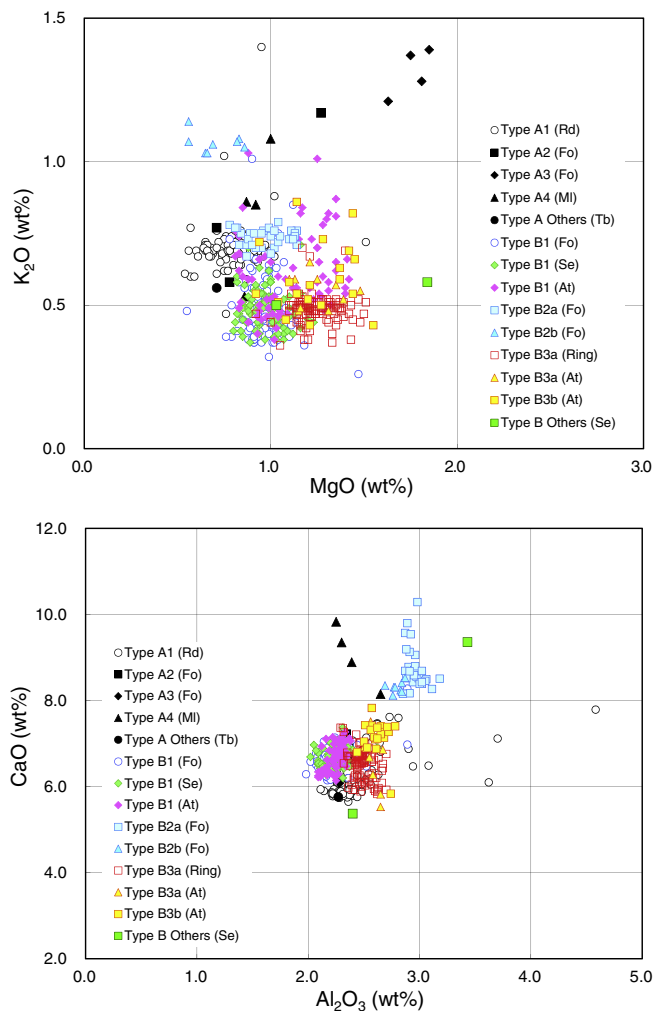


Fig. 5. Comparison of the chemical compositions among natron glasses. Upper: $K_2O$ vs. MgO; lower: CaO vs. $Al_2O_3$.
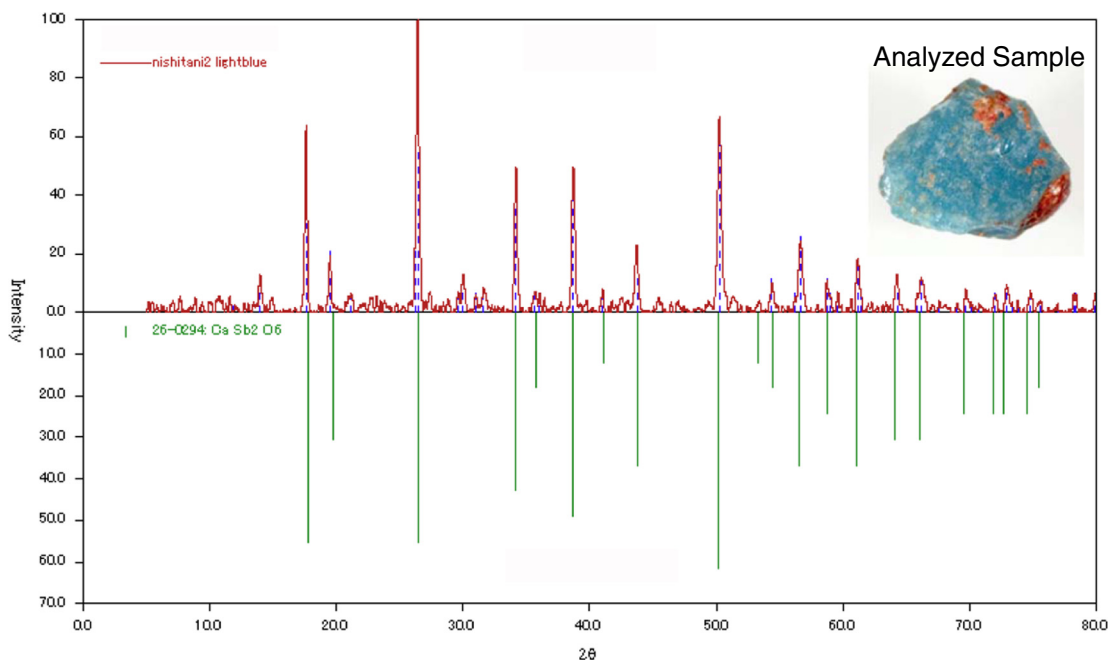


Fig. 4. XRD spectrum of a tubular bead (Type A Others) from Nishitani site.

*4.2.2.2. Type B2: high MnO, low TiO$_2$, and low Fe$_2$O$_3$.* Type B2 contains glass beads with high MnO (1.3–1.9%). All are manufactured by the folding method. They were unearthed from one site. Furthermore, they can be classified into two groups; one in which the MgO content is greater than K$_2$O (Type B2a) and one in which the MgO content is less than K$_2$O (Type B2b) (Fig. 5). A comparison between Types B2a and B2b shows that MnO content is greater in Type B2b, and Fe$_2$O$_3$ content is greater in Type B2a.

*4.2.2.3. Type B3: various levels of MnO, high TiO$_2$, and high Fe$_2$O$_3$.* Compared with other natron glass beads, Type B3 contained significantly higher levels of Fe$_2$O$_3$ and TiO$_2$ (Fig. 6), and relatively greater levels of MgO than other types (Fig. 5). They also contain MnO; however, their contents vary. Type B3 consists mainly of ring-shaped beads, and all ring-shaped beads found belong to this type. Further, 10 analytical points of the attached beads have similar chemical compositions to the compositions of ring-shaped beads, and the other 19 points of the attached beads also matched the characteristics of ring-shaped beads, apart from the MnO content. MnO contents in ring-shaped beads showed no correlation with Fe$_2$O$_3$ and TiO$_2$, and the range of the diversity was significantly large (Fig. 6). This suggested that MnO was added separately, and that the basic glass materials of the 19 points of attached beads containing relatively lower MnO are the same. We call Type B3 with higher MnO Type B3a (Ring) or Type B3a (At) and call Type B3 with lower MnO Type B3b (At).
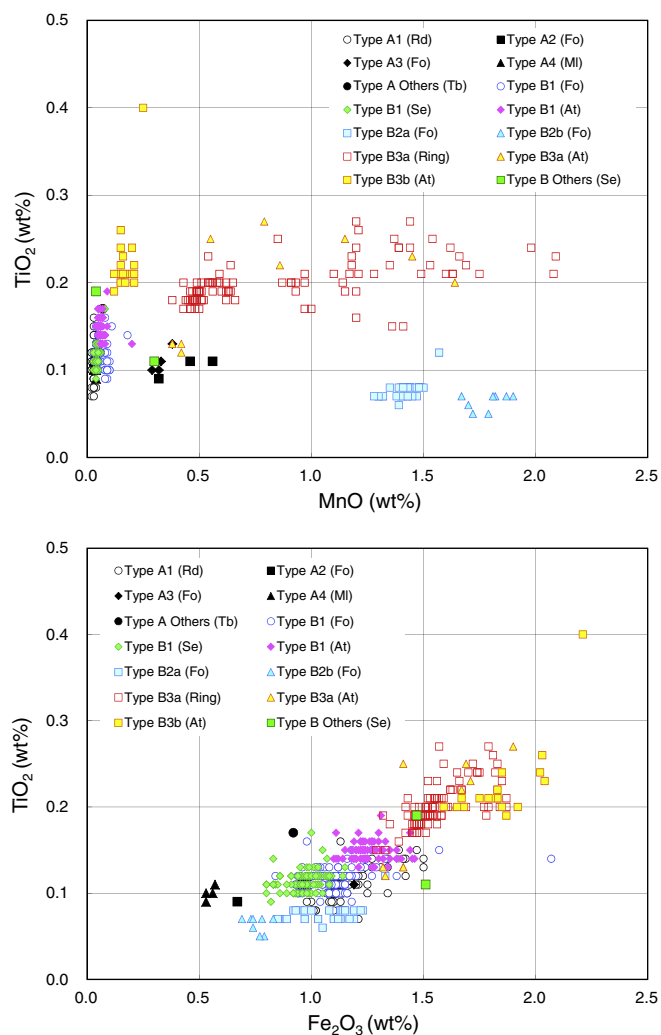
*4.2.2.4. Type B Others: two segmented beads.* One segmented bead contains moderate MnO (0.30%), and another segmented bead contains significantly higher levels of CaO and Al$_2$O$_3$ than those found in others (CaO: 9.4%, Al$_2$O$_3$: 3.4%) (Fig. 5). These two specimens are isolated in chemical compositions from any other natron glass, so we exclude these from classification.

## 5. Discussion

### 5.1. Comparison with previous studies on chemical compositions of natron glass

Studies on the compositional classification of natron glass have made rapid progress and have identified the archeological assemblages termed Roman blue-green and HIMT, as well as the types Levantine I, Levantine II, Egypt I, and Egypt II (cf. [3,9,12,20,32,47,48]). While in the Mediterranean world, specimens not intentionally colored have been analyzed, the majority of the specimens that the authors examined were colored dark blue by cobalt, which suggests the possibility that systematic diversity had been created in the chemical composition. In addition, the chemical compositions varied to a great degree among the total number of specimens in this study, and this made it difficult for us to observe simple correlations between natron glasses in Japan and those in the Mediterranean world.
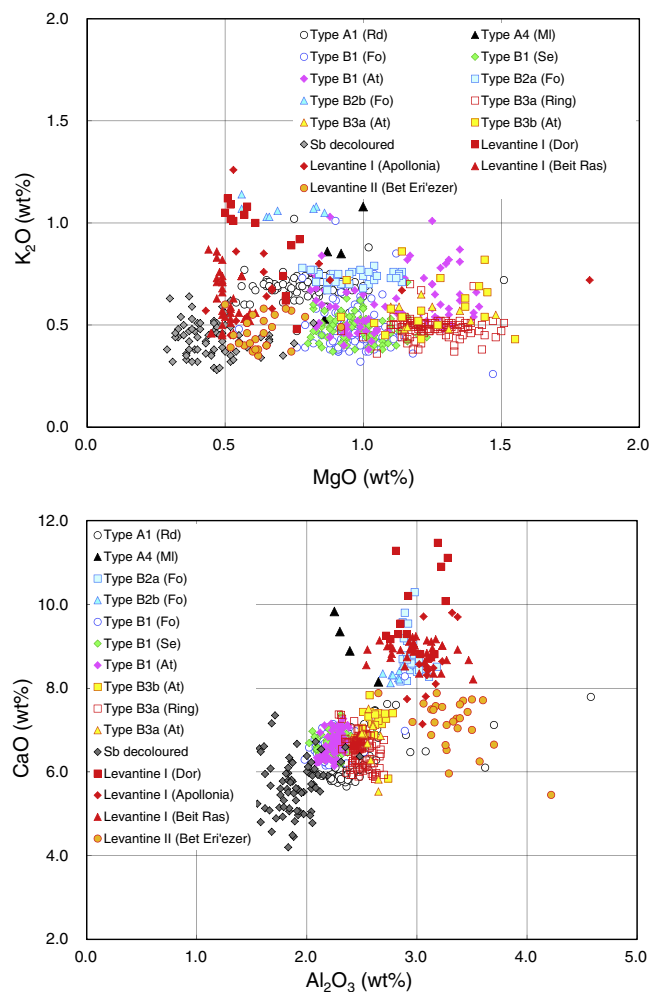


Fig. 6. Relation between the concentrations of TiO$_2$ and MnO (upper), and between the concentrations of TiO$_2$ and Fe$_2$O$_3$ (lower).



Fig. 7. Comparison of the chemical compositions between natron glasses found in Japan and those in the Mediterranean World. (upper): K$_2$O vs. MgO, (lower): CaO vs. Al$_2$O$_3$. Reference data of Sb decolored is from [20,47]. Levantine I: Dor is from [12], Levantine I: Apollonia is from [14], Levantine I: Beit Ras is from [1] and Levantine II: Bet Eli'ezer is from [12].

Natron glass containing antimony in the Western world, such as "Group 1a [20]," "Colorless1 [47]," "antimony-decolored" [38], and "antimony-only" [34] natron glass, contained relatively small amounts of MgO, $K_2O$, CaO, and $Al_2O_3$ (Fig. 7). This is similar to Type A1. In this study, however, Type A1 shows relatively higher levels of MgO and $Al_2O_3$. The values of these ingredients by XRF in this study show slightly higher (about 0.4 and 0.3% higher, respectively) levels (Table 4). Considering the above, it is likely to that Type A1 corresponds to such antimony containing glass. However, further investigation is also necessary to determine if these differences are also caused by the addition of cobalt material as colorant. Rehen [36] pointed out that cobalt material could increase $Al_2O_3$ to some extent.

Type B2 is similar to the Levantine I type (Fig. 7). Type B2 contains a large amount of CaO (greater than 8.0%), and $Al_2O_3$ contents are largely between 2.5% and 3.5%. These characteristics are similar to the Levantine I type. Types B2a and B2b were separated according to MgO and $K_2O$ contents, and there are also two different types of Levantine I. These include glass found at Dor that contains a relatively large amount of $K_2O$ as well as glass found at Apollonia and Beit Ras that contains a relatively small amount of $K_2O$ [1,12,47]. There is also another Levantine I type found at Jalame that contains MnO [4].

Type B3a contains relatively high concentrations of MgO and $Al_2O_3$ as well as extremely high $Fe_2O_3$, $TiO_2$, and MnO. These characteristics are similar to the HIMT type. However, in the HIMT type, the contents of $Fe_2O_3$, $TiO_2$, and MnO showed a positive correlation, while Type B3a yielded no correlation between the contents of MnO and the contents of $Fe_2O_3$ and $TiO_2$ (Fig. 8). This suggests that Type B3a is different from HIMT. In regard to its MnO content, Type B3b, which is similar to Type B3a, is also different from HIMT. In recent studies, the presence of HIMT glass without manganese (called HIT glass in [37]) is pointed out. Rehen and Cholakova [37] also suggest that the manganese in HIMT glass were added intentionally in order to change the appearance
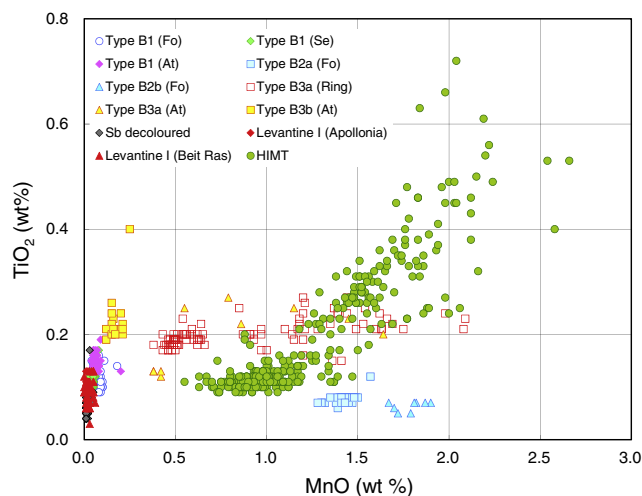


**Fig. 8.** Comparison of the concentrations of $TiO_2$ and MnO between natron glasses found in Japan and those in the Mediterranean World. Reference data of Sb decolored is from [20,47], Levantine I: Apollonia is from [14], Levantine I: Beit Ras is from [1] and HIMT is from [9].

of glass. This idea, however, does not explain that the contents of $Fe_2O_3$, $TiO_2$, and MnO showed a positive correlation in the most part of HIMT.

### 5.2. Cobalt colorants

Cobalt is a most dominant colorant in the natron glass artifacts excavated in Japan. The properties of cobalt ingredient have been discussed with relation to glass production areas previously [2,17,29]. It is possible that the source of cobalt of Type A1 and Type B1 is the same. It does not

**Table 4**
Results of XRF analysis of natron glass artifacts in Japan.

| Site | Mean/SD | Na$_2$O | MgO | Al$_2$O$_3$ | SiO$_2$ | K$_2$O | CaO | TiO$_2$ | MnO | Fe$_2$O$_3$ | CoO | CuO | PbO | Rb$_2$O | SrO | ZrO$_2$ | Sb$_2$O$_5$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Type A1 | Mean(wt%) | 17.4 | 0.8 | 2.4 | 69.3 | 0.7 | 6.0 | 0.10 | 0.03 | 1.13 | 0.07 | 0.20 | 0.09 | 0.01 | 0.04 | 0.08 | 1.73 |
| n = 79* | SD(1σ) | 1.8 | 0.1 | 0.2 | 1.5 | 0.1 | 0.3 | 0.01 | 0.01 | 0.07 | 0.01 | 0.02 | 0.03 | 0.01 | 0.01 | 0.04 | 0.32 |
| Type A2 (Fo) | Mean(wt%) | 16.2 | 0.9 | 2.3 | 67.9 | 0.8 | 6.8 | 0.10 | 0.45 | 0.87 | 0.05 | 0.22 | 0.16 | 0.01 | 0.03 | 0.11 | 2.69 |
| n = 3 | SD(1σ) | 0.6 | 0.3 | 0.1 | 1.1 | 0.3 | 0.4 | 0.01 | 0.12 | 0.17 | 0.01 | 0.11 | 0.05 | 0.00 | 0.02 | 0.03 | 0.14 |
| Type A3 (Fo) | Mean(wt%) | 16.3 | 1.8 | 2.3 | 69.2 | 1.3 | 6.5 | 0.11 | 0.33 | 1.16 | 0.12 | 0.20 | 0.12 | 0.01 | 0.04 | 0.08 | 0.22 |
| n = 4 | SD(1σ) | 1.3 | 0.1 | 0.1 | 0.8 | 0.1 | 0.4 | 0.01 | 0.04 | 0.07 | 0.01 | 0.02 | 0.02 | 0.01 | 0.01 | 0.04 | 0.07 |
| Type A4 (Ml) | Mean(wt%) | 18.5 | 0.9 | 2.4 | 67.0 | 0.8 | 9.1 | 0.10 | 0.04 | 0.55 | 0.01 | 0.01 | 0.02 | 0.01 | 0.06 | 0.05 | 0.38 |
| n = 4 | SD(1σ) | 1.5 | 0.1 | 0.2 | 1.9 | 0.2 | 0.7 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.05 | 0.20 |
| Type A Others | *** | 16.7 | 0.7 | 2.3 | 67.1 | 0.6 | 5.8 | 0.17 | 0.07 | 0.92 | 0.04 | 1.59 | 0.44 | 0.00 | 0.04 | 0.09 | 3.42 |
| n = 1 | | | | | | | | | | | | | | | | | |
| Type B1 (Fo) | Mean(wt%) | 17.3 | 1.0 | 2.2 | 70.4 | 0.5 | 6.6 | 0.12 | 0.06 | 1.09 | 0.06 | 0.23 | 0.19 | 0.01 | 0.04 | 0.07 | n.d. |
| n = 98** | SD(1σ) | 1.0 | 0.1 | 0.1 | 1.0 | 0.1 | 0.2 | 0.01 | 0.02 | 0.11 | 0.01 | 0.04 | 0.04 | 0.01 | 0.01 | 0.04 | n.d. |
| Type B1 (Se) | Mean(wt%) | 17.3 | 1.0 | 2.2 | 70.5 | 0.5 | 6.7 | 0.11 | 0.04 | 0.97 | 0.06 | 0.21 | 0.18 | 0.01 | 0.04 | 0.07 | n.d. |
| n = 87 | SD(1σ) | 0.6 | 0.1 | 0.1 | 0.7 | 0.1 | 0.2 | 0.01 | 0.01 | 0.09 | 0.01 | 0.03 | 0.03 | 0.01 | 0.01 | 0.04 | n.d. |
| Type B1 (At) | Mean(wt%) | 17.8 | 1.1 | 2.3 | 69.2 | 0.6 | 6.7 | 0.15 | 0.06 | 1.26 | 0.08 | 0.26 | 0.25 | 0.01 | 0.04 | 0.07 | n.d. |
| n = 74 | SD(1σ) | 0.8 | 0.2 | 0.1 | 1.1 | 0.1 | 0.3 | 0.01 | 0.02 | 0.08 | 0.01 | 0.02 | 0.04 | 0.01 | 0.01 | 0.04 | n.d. |
| Type B2a (Fo) | Mean(wt%) | 16.0 | 1.0 | 3.0 | 67.4 | 0.7 | 8.8 | 0.08 | 1.42 | 1.06 | 0.07 | 0.11 | 0.06 | 0.01 | 0.04 | 0.07 | n.d. |
| n = 30 | SD(1σ) | 0.4 | 0.1 | 0.1 | 0.6 | 0.0 | 0.5 | 0.01 | 0.07 | 0.13 | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 | 0.04 | n.d. |
| Type B2b (Fo) | Mean(wt%) | 15.5 | 0.7 | 2.8 | 68.5 | 1.1 | 8.3 | 0.06 | 1.79 | 0.76 | 0.06 | 0.09 | 0.06 | 0.01 | 0.04 | 0.04 | n.d. |
| n = 8 | SD(1σ) | 0.3 | 0.1 | 0.1 | 0.5 | 0.0 | 0.1 | 0.01 | 0.08 | 0.04 | 0.01 | 0.01 | 0.01 | 0.00 | 0.01 | 0.04 | n.d. |
| Type B3a (Ring) | Mean(wt%) | 19.1 | 1.2 | 2.5 | 66.6 | 0.5 | 6.5 | 0.20 | 0.87 | 1.56 | 0.09 | 0.30 | 0.30 | 0.01 | 0.04 | 0.08 | n.d. |
| n = 100 | SD(1σ) | 0.9 | 0.1 | 0.1 | 0.9 | 0.1 | 0.3 | 0.02 | 0.45 | 0.13 | 0.01 | 0.17 | 0.05 | 0.01 | 0.01 | 0.04 | n.d. |
| Type B3a (At) | Mean(wt%) | 18.5 | 1.3 | 2.6 | 66.9 | 0.6 | 6.7 | 0.19 | 0.80 | 1.55 | 0.09 | 0.29 | 0.25 | 0.01 | 0.04 | 0.10 | n.d. |
| n = 10 | SD(1σ) | 0.5 | 0.1 | 0.1 | 1.0 | 0.1 | 0.6 | 0.06 | 0.47 | 0.20 | 0.02 | 0.04 | 0.06 | 0.01 | 0.01 | 0.03 | n.d. |
| Type B3b (At) | Mean(wt%) | 18.5 | 1.2 | 2.6 | 66.6 | 0.6 | 7.2 | 0.22 | 0.17 | 1.84 | 0.12 | 0.35 | 0.22 | 0.01 | 0.04 | 0.07 | n.d. |
| n = 19 | SD(1σ) | 1.4 | 0.2 | 0.1 | 1.3 | 0.1 | 0.4 | 0.05 | 0.03 | 0.15 | 0.02 | 0.07 | 0.04 | 0.01 | 0.01 | 0.05 | n.d. |
| Type B Others | *** | 18.3 | 1.0 | 2.4 | 69.7 | 0.5 | 5.4 | 0.11 | 0.30 | 1.51 | 0.14 | 0.26 | 0.15 | 0.03 | 0.04 | 0.00 | n.d. |
| n = 1 | | | | | | | | | | | | | | | | | |
| Type B Others | *** | 16.5 | 1.8 | 3.4 | 65.7 | 0.6 | 9.4 | 0.19 | 0.04 | 1.47 | 0.08 | 0.25 | 0.20 | 0.01 | 0.03 | 0.11 | n.d. |
| n = 1 | | | | | | | | | | | | | | | | | |

* Eight specimens heavily weathered are excluded.
** Three specimens heavily weathered are excluded.
*** These specimens were analyzed one time.

contain any significant amount of MnO, but small amounts of PbO and CuO are contained (Fig. 9). On the other hand, significant levels of MnO are contained in Type B2 and Type B3. However, there is no positive correlation between CuO or PbO and MnO. In addition, there is no positive correlation between MnO and $Fe_2O_3$ in these groups (Fig. 9). In the case of Type B2 and Type B3, the relatively high level of MnO is probably not due to cobalt colorant. It is likely that the cobalt colorant

of Type A1, B1, B2, and B3 are similar when only considering PbO and CuO contents. In addition, the common characteristic of the cobalt colorant of Type A1, B1, B2, and B3 is the lack of nickel and zinc. This cobalt colorant has similarity with the cobalt colorant used after Late Period of ancient Egypt, and this type of cobalt colorant is subdivided into two groups based on the MnO contents [2]. The cobalt colorant of natron glass of Type A1 and B1 correspond to the low MnO type in the previous studies, and the colorant of Type B2 and B3 is probably the same as Type A1 and B1.
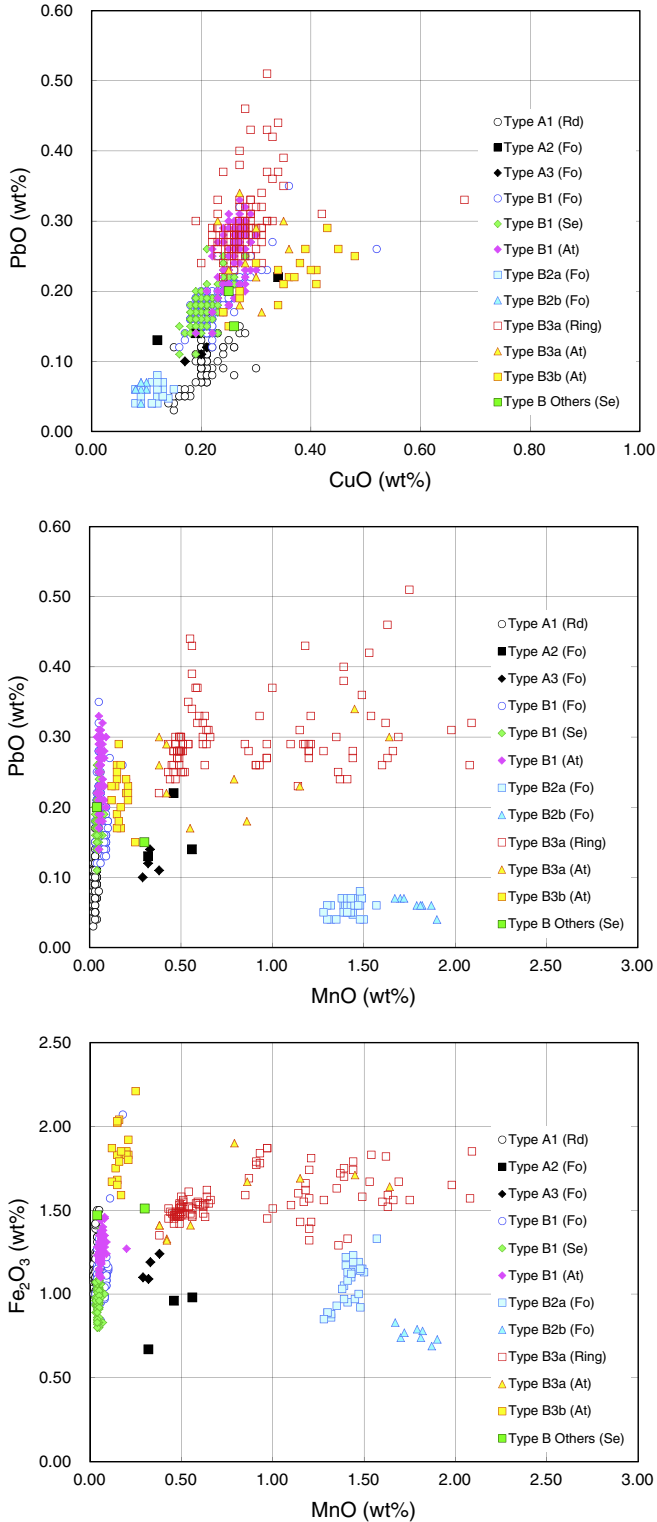
### 5.3. Lead isotope ratios of natron glass

We analyzed the lead isotope ratios to identify the origin of raw materials of the natron glass. Fig. 10 (upper) shows [208]Pb/[206]Pb versus [207]Pb/[206]Pb, and Fig. 10 (lower) shows [207]Pb/[204]Pb versus [206]Pb/[204]Pb. Fig. 10 also shows glass artifacts of different compositional groups distributed throughout ancient Japan. However, it is necessary to note that the lead contained in each different compositional group was derived from different raw materials. Group LI, Group LIIA, and Group LIIB glass contain lead as a main ingredient; therefore, the results show the production area of the main ingredient of the glass. Group SIIB and Group SVA glass contain lead as a colorant, namely, lead stannate; therefore, the results show the production area of the lead material of the colorant. Others contain only a small amount of lead, which is considered to be an impurity of the copper or cobalt material used as colorants; therefore, the results show the production area of the colorant.



Fig. 9. Characterization of cobalt raw materials: upper: PbO vs. CuO; middle: PbO vs. MnO; bottom: $Fe_2O_3$ vs. MnO.
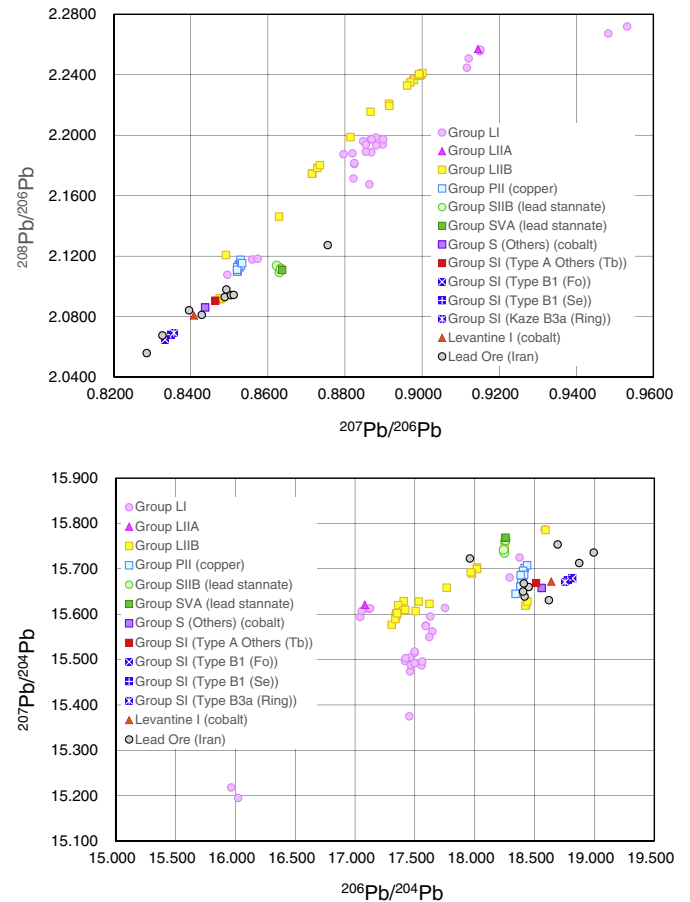


Fig. 10. Lead isotope ratios of glass and some lead ore. Lead isotope ratios of Group LI, LIIA, LIIB, PII, SIIB, SVA, and S include the data of following articles: [5,15,16,18,23,24, 27,28,31,46]. Reference data of Levantine I is from [4] and Lead Ore (Iran) is from [45].

The lead isotope ratios have relations to the compositional group of glass. Groups LI and LIIA are thought to have been produced in China [5], and lead isotope ratios divide them into four groups. Group LIIB is divided into two groups: a group of glass that lines up on a straight line and whose ends are approximately 2.2400 for $^{208}Pb/^{206}Pb$ and 0.9000 for $^{207}Pb/^{206}Pb$ and a group of glass that falls within a range of 2.0880 and 2.0930 for $^{208}Pb/^{206}Pb$ and within a range of 0.8470 and 0.8480 for $^{207}Pb/^{206}Pb$. The former artifacts were produced in Baekje, which is located in the southwestern part of the Korean peninsula [22], and the latter are formed from lead from a mine in Japan [23,39]. Groups SIIB and SVA fall within a range of 2.1090 and 2.1110 for $^{208}Pb/^{206}Pb$, and within a range of 0.8630 and 0.8640 for $^{207}Pb/^{206}Pb$, which confirms that the lead was from the Song Toh mine in Thailand [19].

Group PII falls within a range of 2.1090 and 2.1160 for $^{208}Pb/^{206}Pb$, and within a range of 0.8520 and 0.8540 for $^{207}Pb/^{206}Pb$. This group shows similar lead isotope ratios to a group of Group LI, which is the same value as bronze mirrors confirmed to have been produced in China. This prompted the conclusion that the origin of the copper material, probably bronze, used as colorant in items of Group PII, was China.

The lead isotope ratios of natron glass revealed values that differed from those mentioned above. Type B1 (Fo), Type B1 (Se), and Type B3 (Ring) colored with cobalt showed extremely similar lead isotope ratios. Type B1 (Fo) and Type B1 (Se) have the same chemical composition and colorant characteristics; however, Type B3 (Ring) is completely different from these two types. Therefore, similar lead isotope ratios in these three types should be noted. Type A Others (tubular beads), which contains copper as a colorant, yielded different lead isotope ratios. Although the plot of $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ of Type A others (tubular beads) shows lead isotope ratios similar to lead produced in Japan, the plot of $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ is completely different. Lead isotope ratios indicate a high probability that the glass beads unearthed at the Hirabaru site in Fukuoka (those labeled as Others within Group S in Fig. 10) are of the same group as the Type A Others (tubular beads). These glass beads were manufactured by the segmenting method and colored with cobalt. They are soda glass; however, it is necessary to examine them further in order to classify the material.

Lead isotope ratios in natron glass are characterized by lower $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios as well as higher $^{206}Pb/^{204}Pb$ ratios. With the exception of the special glass beads from the Hirabaru site, natron glass was different from other materials. We found no similarities in many bronze artifacts used in the same era. This indicates that the natron glass was not produced in East Asia. Although limited data is available, there is an Iranian ore containing lead that has lead isotope ratios similar to the natron glass (Fig. 10) [45]. This raises the possibility of identifying a mine in the relevant area yielding the same lead isotope ratios.

## 6. Conclusion

Previous studies have also confirmed the existence of natron glass in ancient Japan [33]. Although the number of natron glass artifacts excavated in Japan is not large, the majority are glass beads colored with cobalt, which differ from the artifacts excavated from areas within the Mediterranean world. This study examined the chemical compositions, colorants, and bead-making techniques of natron glass beads excavated in Japan. The authors reclassified the natron glass in this study into two main types and seven subtypes based on their chemical compositions. We also compared these specimens with natron glass excavated in the Mediterranean world. Type B2 corresponds to the Levantine I type, and Type A1 is likely to correspond to specimens containing antimony, especially "antimony-only" containing glass; however, others do not obviously match any existing groups. The results of the lead isotope ratios measurement revealed relatively similar values between the natron glass analyzed in this study and ore containing lead from Iran. This indicates the source of cobalt added as colorants. The results of our study

show that Japan, which is located very far from glass production areas of Roman glass, had close relation with other areas in the world and was affected quickly by various changes in the Mediterranean world.

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