Journal of Conservation Science
Vol.34, No.4, pp305-311(2018)
DOI https://doi.org/10.12654/JCS.2018.34.4.06
Printed in the Republic of Korea

pISSN: 1225-5459
eISSN: 2287-9781

A Study on the Provenance of an Opacifying Agent($PbSnO_3$) in Yellow and Green Glass Beads Excavated from the Korean Peninsula

Heisun Yu[1] | Jihyun Ro
Conservation Science Division, National Museum of Korea, Seoul, 04383, Korea

[1]Corresponding Author: consrv2@korea.kr, +82-2-2077-9420

ABSTRACT The yellow crystalline material present in yellow and green glass beads excavated from sites in the Baekje region of Korea was previously analyzed through scanning electron microscopy with energy dispersive spectroscopy and X-ray diffraction, revealing that the yellow crystalline material was $PbSnO_3$. This material is a pigment that is rarely seen in the Korean peninsula. Furthermore, some studies have been published on the provenance of lead in this material, which revealed no relationship to Korea, China, or Japan. In this study, we collected all accessible results of analyses on the lead isotope ratio of yellow and green glass beads excavated from the Korean peninsula, specifically from 7 sites in the Baekje region(located in the vicinity of Seoul, Wanju, Hwaseong, Osan, Gongju, Buyeo, and Iksan) and 2 sites in the Silla region(located in the vicinity of Gyeongju and Changnyeong). We subsequently investigated the lead provenance of the opacifying agents in the glass beads through comparison with the current extent of the galena data accumulated for the East Asian region, including Korea, China, and Japan, and for Thailand(Kanchanaburi Province), Southeast Asia. Our analysis determined that the lead provenance of the glass beads excavated from the Korean peninsula was Thailand(Kanchanaburi Province). Beyond our results, further studies should seek to determine the production sites of the glass beads. Obtaining and comparing the scientific analyses of glass beads from India and Southeast Asia would enable research on the glass beads trade through the maritime silk road.

Key Words: Yellow and green glass beads, Opacifying agent($PbSnO_3$), Provenance estimation, Baekje, Southeast Asia

1. INTRODUCTION

The yellow crystalline material present in yellow and green glass beads excavated from Pungnap Fortress in Seoul, King Muryeong's Tomb in Gongju, and Nung-san ri in Buyeo was analyzed through scanning electron microscopy with energy dispersive spectroscopy(SEM-EDS) and X-ray diffraction, revealing that the yellow crystalline material was $PbSnO_3$(Yu and Kang, 2003; Gongju National Museum, 2007). This material is a pigment that is rarely seen on the Korean peninsula. Furthermore, lead isotope ratio analysis of these glass beads found that the provenance of lead contained in this material was not Korea, China or Japan. In other words, this yellow material is an opacifying agent (i.e., coloring agent) for creating yellow and green glass beads, which is considered to come from a third region rather being a raw material from East Asia. In fact, researchers studying glass believe that the glass excavated from King Muryeong's Tomb was brought to the Baekje region through trade.

The studies by Lee In-suk on the ancient trade route of glass beads have consistently argued that the glass beads in King Muryeong's Tomb have a close relationship with glass beads from India, Indonesia, and Thailand(Lee, 1993). Kim Gyu-ho has further proposed that the glassware with various unique colors and shapes in King Muryeong's Tomb differs from glassware in other parts of Korea, suggesting that it may have a different production site and origin of the raw material(Gongju National Museum, 2007).

In Japan, analyses conducted on lead isotope ratio data

Received July 07, 2018 / Revised July 31, 2018 / Accepted August 16, 2018

for galena in the Southeast Asia region reported that the yellow opacifying agent in 4 pieces of yellow-green glass excavated from Odara(小田良) Kofun in Kumamoto prefecture (態本県) was $PbSnO_3$, and the provenance of the raw lead material was Southeast Asia(Ro *et al.*, 2009; Shirataki *et al.*, 2010). Furthermore, another study suggested that raw lead material from Thailand may have been used as an opacifying agent for yellow and green glass beads excavated from King Muryeong's Tomb(Ro, 2010).

Additionally, studies on the raw lead material from Thailand were conducted in Japan. A lead isotope ratio analysis was conducted on 5 samples from 3 mines: The Song Toh mine(2 samples), Mue Nan mine(2 samples), and Bo Yai mine(1 sample), all of which are located in Kanchanaburi Province of Thailand(KAKENHI, 2012; Hirao *et al.*, 2014). The results of these studies showed that the 3 mines had the same lead isotope ratios. Although traces of previous smelting have been identified in the mines in Kanchanaburi Province, no related literature was found. Nevertheless, the result of the carbon dating of the smelting furnace and slag at the mines revealed that Song Toh mine and Bo Yai mine were active in 300 to 1500 AD and 1300 to 1600 AD, respectively(Peter and Hartmut, 1981; Waiyapot, 2009).

Particularly, Song Toh mine in Thailand is the largest lead mine in Southeast Asia with a long history of operation, and it is estimated that the lead from the mine has been in use since the early 1st millennium AD (Waiyapot, 2009). In this regard, the analysis result for a piece of yellow glass excavated from Phum Snay (before 5th century AD) in Cambodia is remarkable. The result of lead isotope ratio analysis on the yellow glass excavated from Phum Snay identified that the raw lead material was from Thailand (Kanchanaburi Province)(NICHIBUNKEN, 2008), suggesting that raw materials or products from Thailand (Kanchanaburi Province) had been distributed to neighboring regions since an early period.

There has been a continued interest in the provenance of $PbSnO_3$, which was used as an opacifying agent for yellow and green glass beads. An opacifying agent, which is one of the constituents of glass, is separated during the cooling process of glass, forming small crystals inside the substrate with cloudy and hazy opalescence.

Ancient glassmakers seem to have added small crystals to create opaque opalescent glass. Tin oxide(SnO_2) and antimony oxide(Sb_2O_5) are the compounds which were conventionally used to produce opaque glass. Lead(Pb)-antimony(Sb) compounds(lead antimonate) were used to produce yellow opaque glass from the 1st to the 2nd centuries AD, and tin oxide was used as an opacifying agent in addition to antimony oxide from the 2nd to the 4th centuries AD(Goffer, 1980). Some argue that tin oxide had begun to be used as an opacifying agent from the 2nd century BC, and that opaque yellow was produced with lead stannate, resulting in a paler color than that of lead-antimony compound(National Museum of Korea, 2018). Additionally, $Pb_2Sb_2O_7$ was mainly used as a yellow opacifying agent during a relatively early period(BC), while $PbSnO_3$ containing tin was found in artifacts excavated from Greek, Turkish, and Israeli sites dating from the 2nd to the 5th centuries AD(Brill, 1968).

Among the glass beads excavated from the Oc Eo site in Vietnam, which was an outer port of Funan, an ancient port state in Southeast Asia, a high content of lead oxide(PbO) was detected in green glass beads, which is related to the yellow crystalline material $PbSnO_3$, which was used as an opacifying agent(Kim *et al.*, 2016). Although the study result did not include the lead isotope analysis results for this glass bead, its shape, color, and chemical composition is similar to those excavated in the Baekje region of Korea, indicating that these samples are highly relevant.

In comparison with other regions, a relatively larger amount of yellow and green glass beads containing the $PbSnO_3$ pigment were excavated in the Beakje region from sites dating to the Three Kingdoms period of Korea. Because this yellow pigment contains lead, the provenance of the raw material can be determined by analyzing the lead isotope ratio. Although the results of the lead isotope ratio analysis on these glass beads have already been published, there were some errors in the analysis results, which were based only on the data on galena in the East Asian region, including Korea, China, and Japan(Yu and Kang, 2003). Therefore, in

Table 1. Results of the lead isotope ratio analysis of yellow and green glass beads excavated from Baekje area (G: green, Y: yellow)

No	Site	Color	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
1	Pungnap Fortress in Seoul	G	18.207	15.698	38.307	0.8622	2.1039
2	Sangwoon-ri in Wanju	G	18.266	15.731	38.479	0.8613	2.1067
3		G	18.258	15.739	38.488	0.8620	2.1080
4		G	18.240	15.740	38.469	0.8629	2.1091
5	Mahari in Hwaseong	Y	18.247	15.756	38.499	0.8635	2.1099
6	Sucheong-dong in Osan	Y	18.256	15.757	38.521	0.8631	2.1100
7		G	18.256	15.764	38.541	0.8635	2.1112
8		G	18.257	15.756	38.527	0.8630	2.1103
9	King Muryeong's Tomb in Gongju	Y	18.213	15.729	38.415	0.8636	2.1092
10		Y	18.254	15.745	38.506	0.8626	2.1094
11		Y	18.248	15.736	38.479	0.8624	2.1087
12		Y	18.248	15.737	38.478	0.8624	2.1086
13		Y	18.256	15.748	38.513	0.8626	2.1096
14		Y	18.273	15.769	38.583	0.8630	2.1115
15		Y	18.218	15.699	38.332	0.8617	2.1041
16		G	18.251	15.732	38.461	0.8620	2.1074
17		G	18.250	15.729	38.454	0.8618	2.1070
18		G	18.249	15.726	38.446	0.8618	2.1068
19		G	18.254	15.733	38.467	0.8619	2.1074
20		G	18.264	15.747	38.514	0.8622	2.1087
21		G	18.254	15.732	38.465	0.8619	2.1072
22		G	18.213	15.676	38.262	0.8607	2.1008
23	Nung-san ri in Buyeo	Y	18.254	15.731	38.404	0.8618	2.1039
24	Mireuk temple site in Iksan	Y	18.230	15.720	38.463	0.8624	2.1079

this study, we have collected all accessible results of analyses on the lead isotope ratios of yellow and green glass beads excavated from the Korean peninsula. We subsequently investigated the lead provenance of the opacifying agents in glass beads through comparison with the current extent of the galena data that has been accumulated for the East Asian region, including Korea, China, Japan, and for Thailand(Kanchanaburi Province).

Specifically, the artifacts used in this study are the yellow and green glass beads excavated from sites in the Baekje region, including Pungnap Fortress in Seoul, Sangwoon-ri in Wanju, Mahari in Hwaseong, Sucheong-dong in Osan, Nung-san ri in Buyeo, and Mireuk Temple Site in Iksan (Kim, 2001; Gongju National Museum, 2001; Yu and Kang, 2003; Gongju National Museum, 2007; Chonbuk National University Museum, 2010; Gyeonggi Cultural Foundation, 2012; National Research Institution of Cultural Heritage, 2014). This study further investigated the results of the lead isotope ratio analysis of the opacifying agent in the yellow glass beads excavated from the site in the Silla region, including the Great Tomb of Hwangnam in Gyeongju and Kyeseong Tomb in Changnyeong(Kim, 2001).

2. REVIEW OF RESULTS

The present study divided the results of the lead isotope ratio analysis of the opacifying agent of yellow and green glass beads excavated from the Korean peninsula into the two regions of Baekje and Silla. Subsequently, this study compared the results to the current extent of the galena data

that has been accumulated for East Asia including Korea, China, Japan, as well as Southeast Asia(Thailand) to investigate the lead provenance of the glass opacifying agent.

2.1. Review of lead isotope ratio analysis of yellow and green glass beads excavated from the Baekje region

The yellow and green glass beads excavated from the Baekje region, which had previously been analyzed, were a total of 24 pieces, including 1 piece from Pungnap Fortress in Seoul(2nd to 4th centuries), 3 pieces from Sangwoon-ri in Wanju(post-2nd century), 1 piece from Mahari in Hwaseong(4th century), 3 pieces from Sucheong-dong in Osan(post-4th century), 14 pieces from King Muryeong's Tomb in Gongju(6th century), 1 piece from Nung-san ri in Buyeo(6th century), and 1 piece from Mireuk Temple Site in Iksan(6th to early 7th century). Table 1 summarizes the current extent of the published lead isotope ratio data for the glass opacifying agent. Figures 1 and 2 show the differences between $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$, which have been plotted onto lead isotope ratio distribution maps. As displayed in the figures, the lead provenance of the yellow opacifying agent($PbSnO_3$) in all of the yellow and green glass beads from the Baekje region was Kanchanaburi Province, Thailand.

The provenance of the yellow opacifying agent $PbSnO_3$ in the glass beads excavated from the Pungnap Fortress in Seoul, Nung-san ri in Buyeo, Mahari in Hwaseong, Sangwoon-ri in Wanju, and the Mireuk Temple Site in Iksan in the Baekje region were previously unknown because it did not originate from anywhere in Korea, Japan, or China. Therefore, this study has revealed that the lead provenance is Thailand(Kanchanaburi Province).

2.2. Review of lead isotope ratio of yellow and green glass beads excavated from the Silla region

In comparison with the Baekje region, fewer yellow and green glass beads have been excavated in the Silla region, and analysis of the lead isotope ratio has rarely been conducted. We confirmed only two cases where the lead isotope ratio had been analyzed, including 1 yellow glass bead that was excavated from the Great Tomb of Hwangnam in Gyeongju(5th century), and 1 yellow glass bead that was excavated from the Kyeseong Tomb in Changnyeong(6th century). $PbSnO_3$ was detected as an opacifying agent in the bead excavated from the Great Tomb of Hwangnam in Gyeongju, and the provenance of the raw material was estimated to be southern China through lead isotope ratio analysis(Jo *et al.*, 1999). Furthermore, Pb and Sn were identified in the yellow glass bead excavated from the Kyeseong Tomb in Changnyeong, and the lead isotope ratio analysis demonstrated a high correlation to raw materials in China(Kim, 2001). Table 2 displays the lead isotope ratio data for the opacifying agent in the two yellow glass beads from the Silla region.

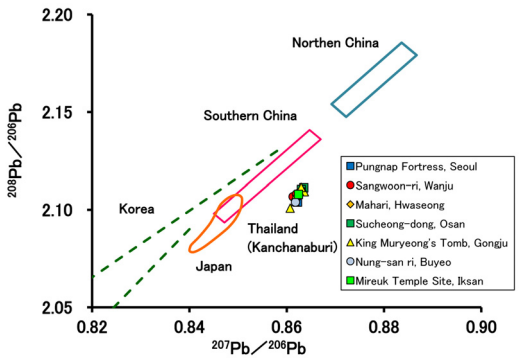

Figure 1. Lead isotope ratio distribution map for yellow and green glass beads excavated from Baekje area ($^{207}Pb/^{206}Pb$ vs $^{208}Pb/^{206}Pb$).

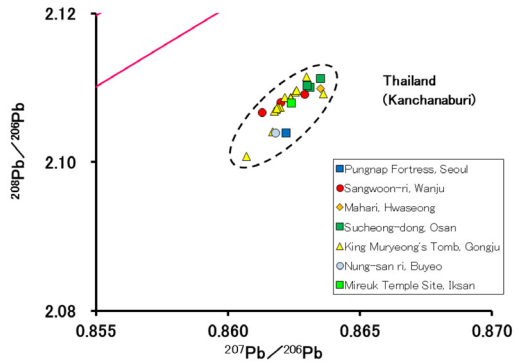

Figure 2. Detail of Figure 1, showing the precise lead isotope distribution for yellow and green glass beads excavated from the Baekje area($^{207}Pb/^{206}Pb$ vs $^{208}Pb/^{206}Pb$).

Table 2. Results of the lead isotope ratio analysis for yellow glass beads excavated from the Silla region (Y: yellow)

No	Site	Color	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
1	Great Tomb of Hwangnam(north mound) in Gyeongju	Y	18.294	15.771	38.595	0.8621	2.1097
2	Kyeseong Tomb in Changnyeong	Y	18.227	15.750	38.461	0.8641	2.1101

Figures 3 and 4 show the differences between $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ plotted onto lead isotope ratio distribution maps. As described above, the lead provenance of the yellow opacifying agent($PbSnO_3$) in the yellow glass beads excavated from the Silla region belonged to the Kanchanaburi Province of Thailand, in contrast with previous estimates of the provenance as being southern China.

Furthermore, PbO and SnO were detected in some of the yellow glass beads found in the Sarira deposits that were excavated from the foundation of a wooden pagoda in Wanghung-sa, Buyeo, suggesting that $PbSnO_3$ was likely used as an opacifying agent. One study reported that these glass beads are similar to those of King Muryeong's Tomb, Gongju(Buyeo National Research Institute of Cultural Heritage, 2009). However, the study did not include an analysis of the lead isotope ratio or provide accurate information on lead provenance. Future investigation could conduct a provenance analysis of the yellow glass beads excavated from Wanghung-sa, Buyeo.

2.3. Implications in terms of the production sites of the yellow and green glass beads

We determined that the provenance of the lead containing $PbSnO_3$, an opacifying agent that was found in yellow and green glass beads excavated from the Baekje and Silla regions on the Korean peninsula, was the Kanchanaburi Province in Thailand. However, it cannot be concluded that the beads originated from Thailand simply because the main component of the opacifying material was originated in Thailand. In other words, it is highly likely that lead was imported from Thailand and subsequently used to create the glass beads. For example, there are many production sites for Indo-Pacific glass beads in South Asia and Southeast Asia, and it is possible that each producer group made glass with raw materials(i.e., quartz sand or soda raw material), and that the opacifying material was the only component from a different region that was used.

For instance, in a Japanese study, Tamura(2012) compared the chemical composition of glass beads that were excavated

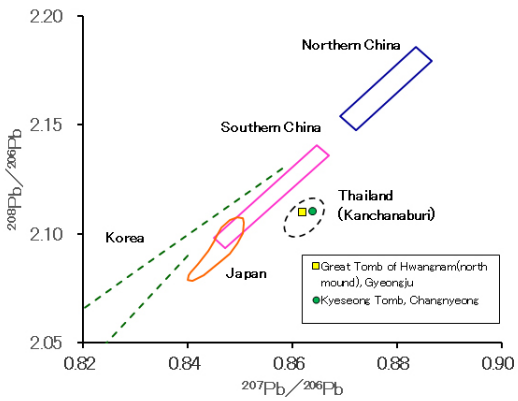

Figure 3. Lead isotope ratio distribution map of yellow glass beads excavated from the Silla area($^{207}Pb/^{206}Pb$ vs $^{208}Pb/^{206}Pb$).

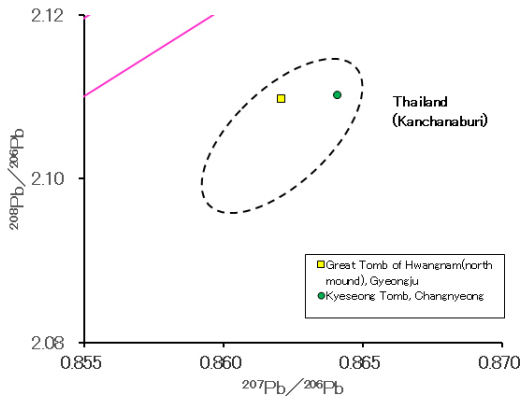

Figure 4. Detail of Figure 3, showing the precise lead isotope distribution for yellow and green glass beads excavated from the Baekje area($^{207}Pb/^{206}Pb$ vs $^{208}Pb/^{206}Pb$).

from King Muryeong's Tomb with glass beads that were excavated from numerous sites in Japan from the same period. The results showed that the orange and yellow beads had similar compositions, however the yellow-green beads deviated somewhat in their provenance(Tamura, 2012). In the context of this study, although it is highly probable that the opacifying agents found in the yellow and green glass beads from the Three Kingdoms period could have been produced using the same raw material, the production sites of the glass beads could have been different.

Furthermore, a study conducted by Kim *et al.*(2016), which considered glass beads excavated from the Oc Eo site in Vietnam(an outer port of Funan and an ancient port state in Southeast Asia), detected a high content of lead oxide(PbO) in the green glass beads that had been excavated there. PbO is related to the yellow crystalline material $PbSnO_3$. Although the study did not include a lead isotope analysis, it is considered highly likely that the green glass beads are related to those excavated in the Baekje region of Korea. Furthermore, it is plausible that both direct and indirect trade took place between Baekje and Funan. The Kinmei-Records(欽明記) in Nihonshoki(日本書紀-the second oldest book from classical Japanese history-), note that King Seong of Baekje had sent commodities from Funan as well as two slaves to Japan, which could have included glass beads(Kim *et al.*, 2016). Further studies could reveal the exact lead provenance through a lead isotope ratio analysis of $PbSnO_3$ from the Oc Eo site.

Furthermore, the results of the lead isotope ratio analysis for the yellow glass bead excavated from Phum Snay (before 5th century, AD), Cambodia, identified the raw lead material as being from Thailand, suggesting that the raw materials or products from Thailand were distributed to neighboring regions from at least this time period.

3. CONCLUSION

The present study reviewed data from the lead isotope ratio analysis of the opacifying agent($PbSnO_3$) from the yellow and green glass beads excavated from the Baekje and Silla regions on the Korean peninsula. These data were compared with lead isotope ratio data on the galena of Southeast Asia(Thailand), leading to the following conclusions:

The yellow pigment material used as opacifying agent in the 24 yellow and green glass beads excavated from the sites on the Korean peninsula—Pungnap Fortress in Seoul, Sangwoon-ri in Wanju, Mahari in Hwaseong, Sucheong-dong in Osan, King Muryeong's Tomb in Gongju, Nung-san ri in Buyeo, and Mireuk Temple Site in Iksan—was determined to be $PbSnO_3$, and the lead isotope ratio analysis revealed that the raw lead materials came from the mine located in the Kanchanaburi Province of Thailand.

The yellow pigment used as an opacifying agent in the yellow glass beads excavated from Great Tomb of Hwangnam, Gyeongju and Kyeseong Tomb, Changnyeong in the Silla region, was identified as $PbSnO_3$—the same as in the Baekje region. Furthermore, the lead isotope ratio analysis revealed that the lead raw material was from Kanchanaburi Province of Thailand, which was the same as in the Baekje region.

As described so far, the opacifying agents in the yellow and green glass beads excavated from the historical sites of the Three Kingdoms period on the Korean peninsula were all determined to be $PbSnO_3$, a yellow pigment synthesized using lead from Thailand. Moreover, the raw materials used as opacifying agents for the yellow glass beads excavated from Phum Snay in Cambodia were identified as being from Thailand. However, further studies should seek to determine the location of the production sites of glass beads. Obtaining and comparing the scientific analyses of glass beads from India and Southeast Asia(i.e., Thailand, Cambodia, Indonesia, Vietnam, etc.) would enable research on the glass beads trade through the maritime silk road.

REFERENCES

Brill, R.H., 1968, The scientific investigation of ancient glasses. Proceedings 8th International Congress on Glass, London, July1-6, 47-68.

Buyeo National Research Institute of Cultural Heritage, 2009, Wangheung Temple site(III). 182-243. (in Korean)

Chonbuk National University Museum, 2010, The research

report of the Sangwoon-ri Site(II). 495-531. (in Korean)

Goffer, Z., 1980, Archeological chemistry. John Wiley&Sons, New York.

Gongju National Museum, 2001, King Sama of Baekje-excavation of King Muryeong's Tomb for 30 years achievements. 209-214. (in Korean)

Gongju National Museum, 2007, The research of artifacts from King Muryeong's Tomb(III). 104-131. (in Korean)

Gyeonggi Cultural Foundation, 2012, The research of Osan Sucheong-dong burial ground(V). 55-178. (in Korean)

Hirao, Y., Iinuma, K. and Murai, S., 2014, Japan and metal trading in the era of great voyage. Sibunkaku, Kyoto, 76-79. (in Japanese)

International Research Center for Japanese Studies (NICHIBUNKEN), 2008, Phum Snay: Preliminary report of the excavation at 2007. 69-86. (in Japanese)

Jo, K.M., Yu, H.S. and Kang, H.T., 1999, Scientific analysis of the glass from Hwangnam-daech'ong Tomb No.98. Conservation Science in Museum, 1, 61-74. (in Korean with English abstract)

Kim, G.H., 2001, A study of archaeological chemistry on ancient glasses found in Korea. Doctor's thesis, Chung-ang University, Seoul. (in Korean with English abstract)

Kim, G.H., Yun, J.H., Kwon, O.Y., Park, J.Y. and Nguyen, T.H., 2016, A study on the materials and characteristics of glass beads from Oc Eo Site, Vietnam. MUNHWAJAE, 49, 158-171. (in Korean with English abstract)

Lee, I.S., 1993, Ancient glass in Korea. Chang-moon, Seoul. (in Korean)

National Museum of Korea, 2018, Opacifier. https://en.wikipedia.org/wiki/Main_Page (July 2, 2018)

National Research Institution of Cultural Heritage, 2014, Sarira reliquary of stone pagoda of Mireuksa Temple Site in Iksan. 238-247. (in Korean)

Peter, D. and Hartmut, K., 1981, Geology, mineralogy, and geochemistry of some carbonate-hosted lead-zinc deposits in Kanchanaburi Province, Western Thailand. Economic Geology, 76, 2128-2146.

Report of the Grant-in-Aid for Scientific Research(KAKENHI) by Ministry of Education, Culture, Sports, Science and Technology(MEXT), 2012, Historical study of metal transportation in East Asia using lead isotope method. 187-210. (in Japanese)

Ro, J.H., Hirao, Y.H., Simomura, S. and Ikeda, T., 2009, Provenance study of materials excavated from Odara burial, Kumamoto prefecture. Proceeding of the 26th Symposium on Conservation Science for Cultural Heritage, Nagoya, July 11-12, 272-273. (in Japanese)

Ro, J.H., 2010, Exchange on history period between Japan, Korea and Southeast Asia through copper, lead, glass products using by lead isotope ratio analysis. Doctor's thesis, Beppu University, Oita. (in Japanese)

Shirataki, J., Abe, Y., Tantrakarn, K., Nakai, I., Ikeda, T., Sakaguchi, K. and Goto, K., 2010, An archaeological study of glass beads excavated from Kumamoto prefectural tombs, Proceeding of the 27th Symposium on Conservation Science for Cultural Heritage, Osaka, June 26-27, 254-255. (in Japanese)

Tamura, T., 2012, Ancient trade route seen through glass-focusing on the comparison between glasses excavated from King Muryeong's Tomb and Japan-. The Journal of Baekjae Culture, 46, 123-144. (in Korean and Japanese)

Waiyapot, V., 2009, The standard and characteristic of lead deposits of Thailand. Report of bureau of mineral resources, departmet of Mineral Resources, Bangkok. (in Thai)

Yu, H.S. and Kang, H.T., 2003, Compositions and particles embedded in Korean ancient glass beads. Scientific Research in Field of Asian Art: Proceeding of the First Forbes Symposium at the Freer Gallery of Art, Washington, D.C., September 18-20, 178-182.