Computational analysis of lead isotope ratios in artefacts and ores from China: tracing connections, quantifying ambiguity, and rethinking provenance

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A Methodological Case Study of Lead Resource Movements during the Warring States Period and Western Han Dynasty: Applying Kernel Density Estimation to Four Lead–Barium Glass *Bi* Artifacts

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Abstract

This methodological case study applies lead isotope analysis and Kernel Density Estimation (KDE) to explore the provenance of four lead-barium silicate glass artifacts from the Harvard Art Museums. Through a detailed methodological framework, this study demonstrates how KDE can be used to analyze lead resource distribution and movements. The lead from one artifact, attributed to the Warring States Period, is traced to southern Chinese regions such as Yunnan, Guizhou, Guangdong, or Guangxi. Two artifacts display distinctive lead isotope signatures potentially linked to materials used in the Shang Dynasty, highlighting unique methodological challenges. Another artifact exhibits anomalous lead isotopic and stylistic features, raising the possibility of it stemming from a different cultural context, possibly with lead sourced from Central China. By employing KDE in combination with lead isotope analysis, this case study not only demonstrates the effectiveness of this combination in archaeological provenance research but also offers insights into the use of lead in ancient Chinese glass production. The results reveal multiple lead sources for the glass-making industry during the Warring States Period and the Western Han Dynasty, and further suggest that certain artifacts contain highly radiogenic lead, likely sourced from South China. These findings underscore the utility of KDE as a powerful tool in both provenance studies and the authentication of museum objects.

Keywords

Methodological Case Study, Chinese ancient glass, glass disk, provenance study, typological analysis, Kernel Density Estimation (KDE)

2.1 Introduction

2.1.1 Background of Chinese ancient glass

Glass is an amorphous solid material that has been made by people for over four millennia (Glover and Henderson 1994). Silica, such as quartz, serves as the fundamental raw material for glass production. Flux agents were necessary for lowering the melting point during the glass-making process, as the melting point of silica is 1710°C (Gan 2016), but the temperature of ancient furnaces is believed to have been around 1400°C. Lead, natron, plant ash, and saltpeter were common fluxing agents utilized in the ancient world (Henderson, Evans, Sloane, Leng, and Doherty 2005; Gan 2009). In addition, colorants such as copper (Cu), cobalt (Co), and manganese (Mn) were often essential components in glass-making recipes.

Ancient Chinese glass is renowned for its distinctive chemical composition. Lead barium silicate glass is one of the most common types. This glass typically contains 10–60 wt% lead(II) oxide (PbO), 5–15 wt% Barium oxide (BaO), less than 15 wt% total alkali oxides ($Na_2O + K_2O$), and 30–60 wt% silicon dioxide (SiO_2) (Gan 2009; Li, Li, and Gu 2016; Shi, He, and Zhou 1986). The high concentration of lead (Pb) is believed to have been intentionally added as a flux. Barium (Ba) is thought to have been used as an opacifier to imitate the opaque appearance of jade, which was highly valued in ancient China. There are various theories on how barium may have worked as an opacifier, including crystallization of barium silicate ($BaSiO_3$) (Han, Wang, Ma, and Ma 2017) or barium disilicate ($BaSi_2O_5$) (Ma, Braekmans, Shortland, and Pollard 2021), or the creation of unmelted barium sulfate ($BaSO_4$) with substantial bubbles (Lin, Zhou, Freestone, and Rehren 2018), resulting in semi-transparent or opaque glass. Lead-barium glass is considered to be the earliest indigenous Chinese glass and was used from the Warring States Period (476 BCE-221 BCE) to the Eastern Han Dynasty (25 CE-220 CE) (Gan 2009; Henderson, Guo, and Martinón-Torres 2018).

From the Eastern Han Dynasty (25 CE-220 CE) to the Qing Dynasty (1636 CE-1912 CE), barium gradually lost its significance in the glass-making process and ultimately disappeared, with lead silicate glass, potassium lead silicate glass, and potassium calcium silicate glass emerging and becoming prevalent (Henderson, Guo, and Martinón-Torres 2018).

The study of ancient Chinese glass has revealed that its use was primarily restricted to ritual objects and adornments, rather than being used for utilitarian vessels. This might be attributed to its high content of poisonous lead if the toxicity was known, or its traditional association with the imitation of jade (Gan 2009).

Chemical research on ancient Chinese glass has been ongoing for several decades and remains a topic of great interest. In the 21st century, studies on Chinese glass have intensified due to advances in instrumentation for chemical composition analysis, including spectral analysis, trace element analysis, and isotope ratio analysis. Furthermore, studies have focused on classifying glasses according to their chemical compositions, areas, and styles, as well as on the technologies of glass-making and glass-working, the types of raw materials, the provenance of raw materials, the social groups using them, resource control, trade, and the cultures behind these (Fu and Gan 2006; Cui, Wu, and Huang 2011; Xia, Liu, Wang, Liu, Li, and Gu 2013; Fu, Kuang, Lü, Mo, Li, and Gan 2013; Han, Wang, Ma, and Ma 2017; Lin, Zhou, Freestone, and Rehren 2018; Liu, Lü, Li, and Xiong 2019; Zhao 2020; Li 2022). In addition, experimental replications have been conducted to simulate ancient glass production (Qin, Wang, Chen, Li, Xu, and Li 2016; Ma, Braekmans, Shortland, and Pollard 2021; Ma, Wen, Yu, et al. 2022; Wang, Xu, and Zhou 2022), yielding unexpected conclusions about the raw materials used in glass-making.

2.1.2 Raw materials for glass making

Currently, there is a lack of identified and excavated ancient Pb-Ba glass-making sites in China, which limits our knowledge about the specific sources of raw materials used in glass production, leaving much room for speculation (Wang, Xu, and Zhou 2022). For glass from later periods, studies have analyzed the production of $K_2O-CaO-SiO_2$ glass from the 12th to 14th centuries in Shandong (Zhou, Gao, Rehren, Wei, Wei, and Cui 2024), along with a review of glassmaking practices during the Qing Dynasty (Ma, Henderson, Cui, and Chen 2020).

Before conducting LI (lead isotope) analysis on glass in this study, it is important to understand how lead (Pb) becomes a part of the glass and what type of ore is reflected in the LI data. In lead barium silicate glass ($PbO-BaO-SiO_2$), the amount of PbO ranges from 10 wt% to 60 wt%, which is too high to be considered an impurity. Furthermore, when examining the PbO and BaO content in ancient glass using cluster analysis, these two components do not appear to be related. This suggests that lead and barium were added separately as independent components (Zhang 2004; Lin, Zhou, Freestone, and Rehren 2018). Additionally, the amount of lead in the glass was found to be related to the shape of the glass artifacts. For example, glass disks generally had higher lead content, ranging from 30 wt% to 70 wt%, compared to glass beads (Cui, Wu, and Huang 2011).

Although there is no direct proof from archaeological findings about the use of lead ingots or specific types of ores to provide the lead for the lead barium silicate glass, it is widely accepted that lead was intentionally included in the glass-making process. Lead ores, in particular galena, are the most likely raw material for this lead, due to their high lead content and their capacity to meet the substantial demand for lead. As a result, LI ratios in lead barium silicate glass can potentially provide information about the lead ores used directly or the lead ores used in the lead ingots used.

2.2 Research aim

While previous studies have focused on the chemical composition and production techniques of ancient Chinese glass, this paper aims to explore the methodological approaches in studying lead isotope (LI) characteristics of glass. By employing lead isotope analysis and the Kernel Density Estimates (KDE) method, this study provides new insights into how these techniques can help determine the provenance and circulation of raw materials used in lead-barium glass disks. The novelty of introducing the KDE method in lead isotope analysis of Chinese glass marks an important advancement in the field. Additionally, this study is also uniquely dedicated to the lead isotope characteristics of glass disks from museum collections, which facilitating their interpretation within museums and aiding in identification.

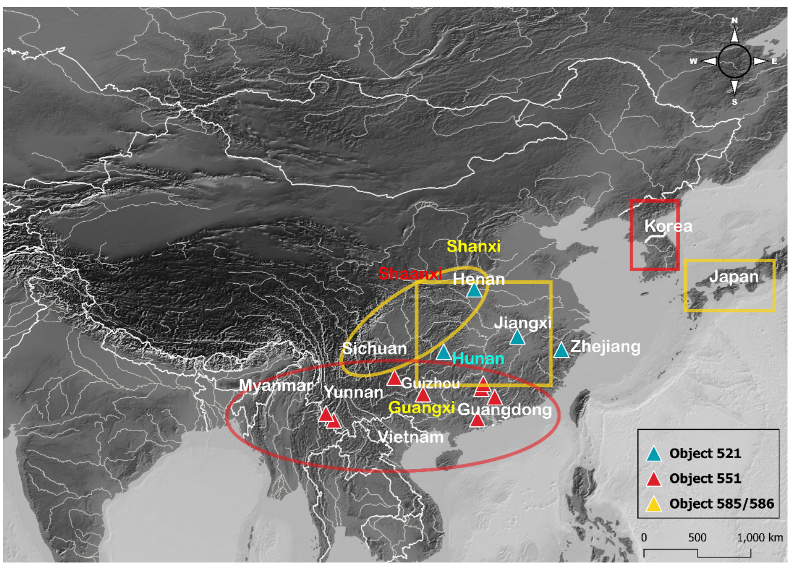

Figure 2.1: the map of the corresponding 'lead mining districts' and 'lead usage districts' of our objects. Red represents the matched regions for the disk 551, blue represents the matched regions for the disk/ring 521, yellow represents the matched regions for the discs 585 and 586. The triangular points represent the possible sources (lead deposits), while the areas within the ovals represent the distributed areas of bronze with matching lead isotopes. The geographic name in red shows where typologically similar objects to disk 551 have been found. Geographic names in yellow show where typologically similar objects to disks 585 and 586 have been found.

2.3 Case description

The disk (*bi* 璧) held significant cultural and religious importance in ancient China, as it was conjectured to act as a pass or guide for souls to enter heaven (Wu 2011). In this study, there are four glass disks (or rings) presented, sampled and analyzed. Disks were made from various materials, including jade, glass, wood, bone, and metal. Glass disks emerged during the middle of the Warring States Period (476 BCE-221 BCE) and their numbers began to increase significantly, reaching a maximum during the later Warring States period. During the Han Dynasty (202 BCE-220 CE), glass disks disappeared gradually (Fu and Xu 2010). In the Chu State, glass disks constituted up to 13.2% of all disks (Chen 2019).

Figure 2.2: Glass disk, Western Han dynasty, Harvard Art Museums, 1943.50.521, Harvard Art Museums/Arthur M. Sackler Museum, Bequest of Grenville L. Winthrop. Photo: © President and Fellows of Harvard College; **Comparative examples**: a stone ring (Photo: Fig. 101 in Museum et al. (2000)) and three glass rings from the Hunan Provincial Museum (Photo: the official website of Hunan Provincial Museum).

Object 1943.50.521 is a narrow, sharp-edged, plain disk (or ring) of pale green glass, the surfaces of which are polished smooth (Fig. 2.2). There are green stains of bronze oxide, soft calcareous areas, and what have been termed textile markings on it. Object 521 is more likely to be a ring (Appendix. A.1. shows more information about the identification of object 521 and similar artefacts unearthed). (The appendix of this article is available in the published version.[1]) Object 1943.50.551 is a subtly greenish,

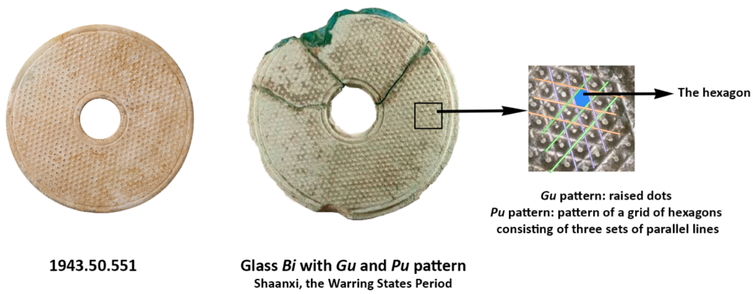

Figure 2.3: Glass disk, Western Han dynasty, Harvard Art Museums, 1943.50.551, from Harvard Art Museums/Arthur M. Sackler Museum, Bequest of Grenville L. Winthrop. Photo Credit: Photo © President and Fellows of Harvard College; **Comparative examples**: glass disk (*bi*) with gu and pu pattern. Photo adapted from Fig. 43 in Fu and Xu (2010).

nearly colorless glass with a surface adorned by an uneven creamy white and slightly iridescent corrosion (Fig. 2.3). On both sides of the glass, a pattern of raised dots is arranged in a grid of hexagons. It has wide, flat margins and includes a cylindrical hole (Appendix. A.2. shows more information about the patterns on object 551 and similar artefacts).

Object 1943.50.585 is a milky white glass with powdery weathering (Fig. 2.4). One side is decorated with beveled, four-sided elevations forming a square grid pattern (The red lines/rectangles in the figure explain why it is called a square grid pattern, as the rows and columns are perpendicular to each other), while the reverse side is plain. The hole is conical. Save for an apparently colorless core, the glass paste has turned into a chalky white substance with a buff surface. Object 1943.50.586 is a light green glass, with a brittle and creamy brown surface layer (Fig. 2.4). One side is decorated with raised dots forming a square grid pattern. The margins are slightly sunken. The reverse side is plain. (Appendix. A.3. shows more information about the patterns on objects 585/586 and similar artefacts unearthed).

The four glass disks with high lead content, dating from the Warring States to the Han Dynasty period, provide a unique opportunity to apply lead isotope analysis, which is a valuable tool for understanding the historical use of lead in glass-making industry in China. The KDE method allows for the more precise identification of potential sources of lead used in these glass disks. The method allows the addition of further information to sources that are unclear, thus clarifying their backstories and contexts. These glass disks are therefore ideal candidates for testing the KDE method's ability to trace the provenance and circulation of their raw materials.

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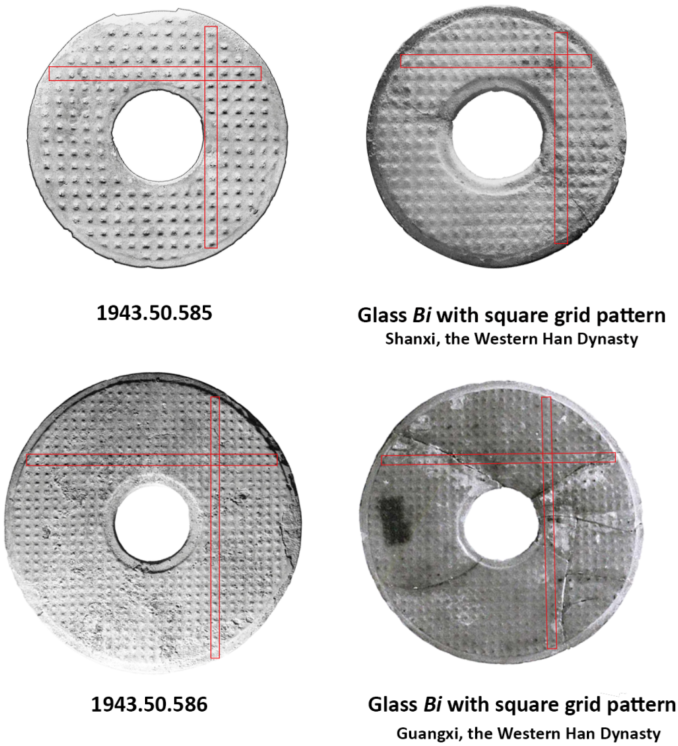

Figure 2.4: Disk, Western Han dynasty, 1943.50.585, Harvard Art Museums/Arthur M. Sackler Museum, Bequest of Grenville L. Winthrop. Photo: © President and Fellows of Harvard College; large glass disk, Warring States period to Western Han dynasty, 1943.50.586, Harvard Art Museums/Arthur M. Sackler Museum, Bequest of Grenville L. Winthrop. Photo: © President and Fellows of Harvard College; **Comparative examples**: two glass disks (*bi*) with the square grid pattern. Photo: Fig. 48 in Yang (2004) and Fig. 18 in Huang (2014)

2.4 Methodological framework and application

2.4.1 X-ray fluorescence (XRF) analysis

The four glass disks (1943.50.521, 1943.50.551, 1943.50.585, and 1943.50.586) were previously analyzed using in-situ X-ray fluorescence (XRF) at the Harvard Art Museums to identify their glass composition. The analysis was entirely non-destructive, and while the results provided qualitative data on the glass type, they were not quantified against calibrated standards. This approach allows for the identification of general compositional trends but may limit the precision of the quantitative results. The XRF system employed is a Bruker Artax XRF spectrometer with a Silicon Drift Detector (SDD) and a rhodium anode X-ray tube. The primary X-ray beam is collimated to give a spot size of 0.65 mm . Spectra were acquired for 100 seconds live time at 50 kV and 600 μA. A Helium flux was used to increase the detection efficiency for light elements (atomic number of potassium and lower).

2.4.2 Lead isotope composition

Lead isotope (LI) analysis is a widely used technique for tracing the origin of lead in archaeological materials, offering insights into trade and resource control. In this study, surface samples of glass corrosion for lead isotopic (LI) analysis of all four objects were analyzed according to the methodology adapted from Rademakers, Verly, Somaglino, and Degryse (2020), dissolving the powdered samples in strong acids and concentrating only the Pb fraction through ion exchange chromatography for multi collector–inductively coupled plasma-mass spectrometry (MC-ICP-MS) isotopic analysis.

2.4.3 Kernel density estimates (KDE) method

Kernel Density Estimation (KDE) is a statistical method used to estimate the probability density function of a continuous random variable. It is commonly used to visualize data distributions and identify trends, particularly in complex datasets. The combination of LI and KDE in this study allows for a comprehensive analysis of lead sources in ancient Chinese glass artifacts, marking a novel methodological approach in this field. In this study, the lead isotope composition of four glass disks was identified using a kernel density estimate approach (KDE) (De Ceuster and Degryse 2020). While kernel density estimates have been previously applied in archaeological Chinese bronze (Hsu, Rawson, Pollard, Ma, Luo, Yao, and Shen 2018), this study represents the first application to the LI analysis of ancient Chinese glass.

A LI database was constructed for natural "lead mining districts", which characterizes the LI compositions of lead mines in different regions. Another lead isotopic database was compiled for artificial spatio-temporal "lead usage districts", comprising previously published lead-containing ancient artefacts (bronze and glass) from various locations and periods that exhibit the LI characteristics of the lead resources used during those times and in those regions. The classification of these lead usage districts was based solely on the excavated locations and dates assigned.

The relative probability that a sample is composed of lead ore from a specific source is determined by calculating the definite integral under the kernel density estimates plot of the lead isotope composition of lead ores from different "lead mining districts". The relative probability that a sample is made of lead from the same source as other artefacts is determined by calculating the definite integral under the kernel density estimate plot of the lead isotope composition of artefacts from different "lead usage districts". The interval for all the calculations of the integration of density function is 10 times the standard deviation. The choice of bandwidth is based on the bandwidth estimator introduced by Sheather and Jones (1991), which has consistently performed well when dealing with smooth density distributions in simulated settings. This estimator's effectiveness has been confirmed through practical testing, especially in the study of lead isotopic origin, as demonstrated in the research conducted by De Ceuster, Machaira, and Degryse (2023).

All comparisons were performed using R© software and legacy data for the mines and the artefacts. A match of three LI ratios with the reference dataset may indicate that the sample originated from the same source or used the same lead resources as the reference material, while a lack of match may indicate an unknown origin (i.e. not present in the database of mineral resources or not the same as other artefacts), or the composite or recycled nature of the sample.

2.5 Results

2.5.1 Chemical elemental composition

Although the glass disks differ slightly in color, this is not reflected in the XRF spectra which are extremely similar. The areas of unweathered glass or less weathered glass in all four disks contain high levels of lead, barium and silicon, with traces of calcium, iron and strontium. Weathered areas of all four disks, including the corrosion crust and powdery white areas, contain lower levels of silicon, barium and strontium, with higher levels of lead, calcium and iron. The higher calcium and iron are attributed to the effects of burial, whilst the higher lead and lower silicon, barium and strontium reflect the presence of high proportions of lead corrosion products, likely lead carbonates, in the weathering layer.

2.5.2 Lead isotope composition

Table 2.1 displays the lead isotope ratios of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$, for the samples examined. As shown in Fig. 2.5, the LI signatures of these four samples

Table 2.1: The lead isotope ratios of samples from the four glass disks

Sample	$^{206}Pb/^{204}Pb$	$\pm 2\sigma^{+}$	$^{207}Pb/^{204}Pb$	$\pm 2\sigma^{+}$	$^{208}Pb/^{204}Pb$	$\pm 2\sigma^{+}$
1943.50.521	17.973	0.008	15.535	0.009	39.189	0.028
1943.50.551	18.636	0.011	15.737	0.011	39.029	0.033
1943.50.585	22.561	0.047	16.099	0.038	42.968	0.132
1943.50.586	22.381	0.024	16.109	0.018	42.987	0.052

are dissimilar, with the exception of samples from disks 585 and 586, which display similar LI signatures. The data suggests that three distinct lead sources may have been utilized in the creation of these disks. Samples from glass disks 585 and 586 exhibit pronounced highly radiogenic lead, similar to those commonly observed in bronzes produced during the Shang Dynasty (1600 BCE-1046 BCE), but no longer prevalent by the end of the Western Zhou Dynasty (1046 BCE-771 BCE).

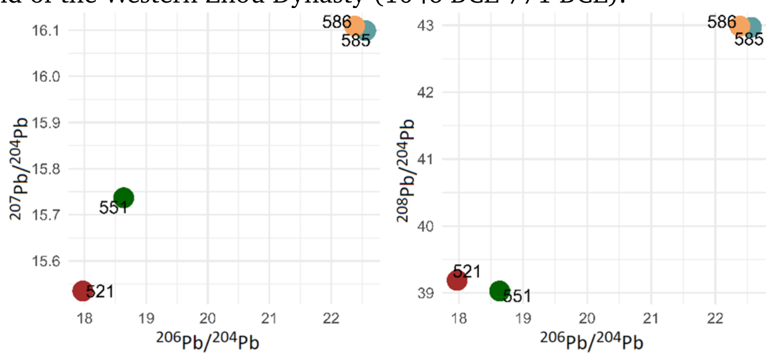

Figure 2.5: The lead isotope compositions of four samples

2.5.3 Kernel density estimates (KDE) method

2.5.3.1 Origin of raw materials

As previously mentioned, the four glass objects are all lead barium silicate glass, hence their lead isotope composition can reveal the source of the lead ores used. The "natural lead mining districts" database was established based on the geochemical lead ore database of Hsu and Sabatini (2019). They divided all Chinese modern lead resources into 16 regions (termed ore provinces) based on geological setting and ore formation processes, which is more suitable for archaeological provenance study than modern administrative divisions. The LI signatures of the glass samples are compared to each ore province to determine the most likely source(s). However, since ore provinces are very large, they only provide a rough indication of the source. Therefore, our samples will be compared to the individual lead deposits within the provinces to determine a most probable origin.

According to the data presented in supplementary figure 1 (SFig. 1), it can be inferred that the LI signature of glass ring 521 corresponds with the LI signatures of ores from the Upper Yangtze ore province in China. Subsequently, individual lead deposits were compared with ring 521. To ensure a precise LI characterization for KDE application, a minimum count of 10 ore samples, analyzed each comprising the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$ ratios of one ore, was established, as recommended by Baron, Day, and Garvey (2014). The Wushan deposit (in Jiangxi Province) and Heigou deposit (in Henan Province) are identified as the most probable sources of the lead ore used in glass ring 521. Zhilingtou in Zhejiang Province and Yutang in Hunan Province are other possible sources but with lower probability, as shown in SFig. 2. (The Supplementary Materials of this article is available in the published version. [2])

The Baoshan deposit in Hunan Province and the Tiantang deposit in Guangdong Province are identified as the most likely sources of lead ores for glass disk 551 (see SFig. 4) by comparing with specific lead deposits. The deposits Dachang (Guangxi Province), Dabaoshan (Guangdong Province), Cangyuan (Yunnan Province), Laochang (Yunnan Province), Xianghualing (Hunan Province), Shanshulin (Guizhou Province) are also possible sources but with lower probabilities. However, the best matched ore province is Tibet (see SFig. 3). All ore provinces contain numerous deposits, which might be the reason for this inconsistency. This underscores the importance of comparing results with individual deposits.

In contrast, glass disks 585 and 586 do not match any known lead source in the current database, as indicated in SFig. 5. This could be due to the use of an unknown ore or to the use of mixed or recycled lead resources.

2.5.3.2 Comparison with Chinese bronze

In ancient China, the bronze of the Shang Dynasty (1600 BCE-1046 BCE) and Zhou Dynasty (1046 BCE -256 BCE) is renowned for its high lead (Pb) content, which is a unique technological feature (Lu, Han, and Ke 2007; Su, Hua, Li, and Lu 1995). The lead concentration in these bronzes was typically more than 5 wt% (Liu, Bray, Pollard, and Hommel 2015). Lead ores or lead ingots were added during the alloying process to improve fluidity and facilitate the casting of intricately decorated vessels. The study of lead provenance in bronze has continued for decades, generating an extensive 'bronze lead usage districts' database of lead isotope datasets (see the supplementary tables). By matching our glass objects with the bronze lead usage districts, we can determine whether there are bronzes that use similar lead sources as the glass objects. Although a definitive connection between these bronzes and the glass disks in this

[2] https://doi.org/10.1016/j.culher.2024.11.007

study has not been established, the extensive lead isotope data from the bronzes can function as "lead resource usage indicators", offering insights into potential patterns of lead utilization. Specifically, this data may help identify other contexts, in which the lead used in the glass disks might have been employed.

Within SFig. 6, ring 521 shows no match in LI to bronze objects. In contrast, disk 551 has similar LI characteristics a to bronze from Southeast Asia (SFig. 7 and STab.2), including a bronze drum of Vietnam and bronze artifacts from Myanmar. To be more specific, a comparison was made between disk 551 and subareas in Bronze Age Southeast Asia, as well as the surrounding lead usage districts of Guangxi, Guangdong, Yunnan, Sichuan, and Guizhou (SFig. 8). The best match occurs for Myanmar, with Yunnan, Vietnam, and Guangdong also providing matches. Notably, the bronze culture and metallurgical industry system in South China and Southeast Asia share a close relationship. For example, the famous bronze drum of Đông Sn (600 BCE-200 CE) has been widely discovered in Vietnam, Yunnan, and other areas of Southeast Asia and Southern China Le Meur, Cadet, Van Doan, Trien, Cloquet, Dillmann, Thote, and Pryce (2021). Therefore, it is reasonable to suggest that lead ores or bronze products from these areas have been exchanged, resulting in closely aligned lead isotopic characteristics among the bronzes from these regions. The lead in disk 551 might also source from the areas of this cultural background.

Disks 585 and 586 have LIs which only match with those of bronze from the Shang Dynasty (SFig. 9 and STab.3). Specifically, the Shang bronze is divided into 14 lead usage districts according to their excavated locations. The best match for disks 585 and 586 is with bronze from Sanxingdui in Sichuan Province and Runlou in Henan Province (SFig. 10).

2.6 Discussion

2.6.1 The dominant region for glass-making: South China

Our results have been visualized in Fig. 2.1, which maps out the geographical relationships among these various archaeological landmarks.

We used scatterplots supplemented with density curves to visually illustrate the connections among our objects, the bronze from the Shang Dynasty, and the glass from Japan and Korea, as shown in Fig. 2.6. This figure provides several valuable insights: 1) Disks 551, 585, and 586 demonstrate a significant similarity to the previously documented Pb-Ba glass from China; 2) The lead isotopic characteristics of disks 585 and 586 closely resemble those of the Shang Dynasty bronze; 3) Ring 521 maintains its distinctiveness in the scatterplots and does not overlap with any elements in the plot; 4) The peaks of the density curves for glass from China and glass from Japan almost perfectly align, which indicates that they were likely to share consistent sources of lead, or even had been made together; 5) The density curves for glass and bronze exhibit distinct peaks.

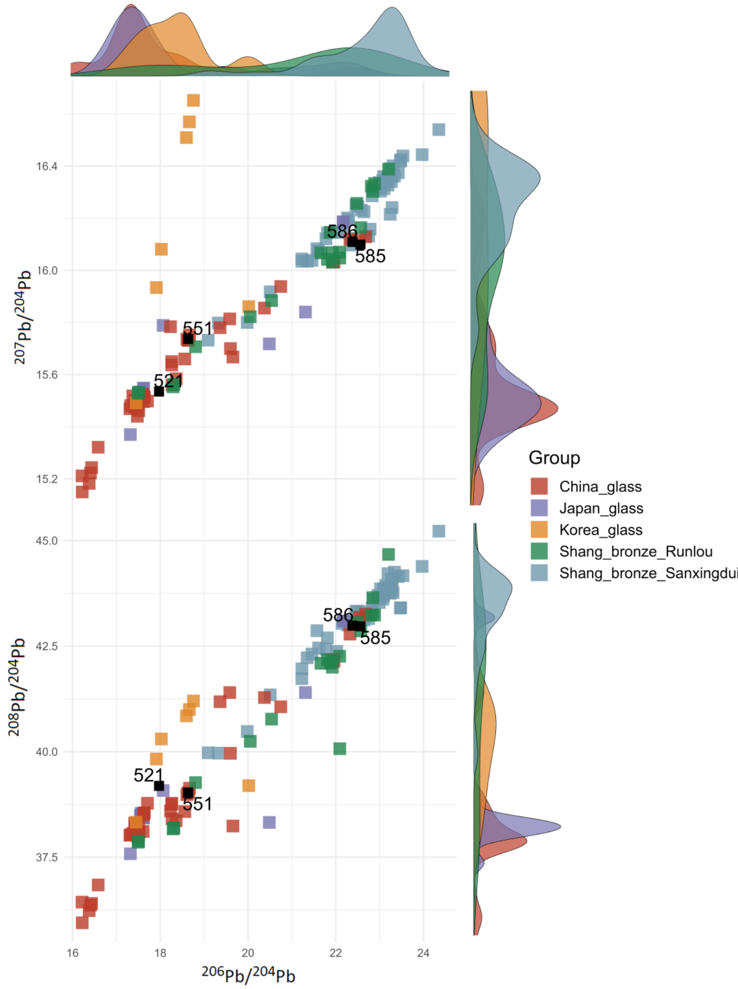

Figure 2.6: This figure presents scatter plots depicting the relationship between the glass objects, and various lead usage districts corresponding with them, including the glass from China (Pb-Ba glass from the Changde, Hunan province, in the Warring States Period, the ancient Chinese Pb-Ba glass from the collection of Kwan, the Pb-Ba glass chimes from Jiangsu, the Western Han Dynasty), the lead-containing glass from Japan and Korea, and the bronze from the Sanxingdui site (Sichuan province, the Shang Dynasty) and Runlou site (Henan Province, the Shang Dynasty), accompanied by density curves.

Disks 585 and 586 contain a distinct type of lead known as highly radiogenic lead, which was notably prevalent during the Shang Dynasty (1600 BCE-1046 BCE), a period that significantly predates the initiation of glass production in China. Despite the temporal disparity, a conjecture arises that the same lead deposits might have been engaged during the Warring States Period (476 BCE-221 BCE). It is, however, crucial to highlight that the Shang bronze and the glass artifacts show distinct LI density curve peaks. This suggests that it is unlikely they employed precisely the same lead resource system, but overlaps might happen between the lead sources of Shang bronze and ancient glass.

Moreover, disks 585 and 586 display varying degrees of similarity among different groupings of Shang bronze, as illustrated in SFig. 10. While disks 585 and 586 closely match the Sanxingdui and Runlou bronze in LI, they less resemblance to Shang Dynasty bronzes from other regions. Additionally, it's worth noting that the Sanxingdui and Runlou areas have historical connections to glass production centers like the Chu State during the Warring States Period in China (as documented by Cui, Wu, and Huang 2011, Zhao 1991, Hou 1995). The Runlou area was part of the Chu State during that period, while the Sanxingdui area belonged to the Ba State, which was adjacent to the Chu State. These regions had close cultural and economic ties with each other (Chen 2010). This cultural kinship suggests the possibility that the lead sources for disks 585 and 586 were situated in close proximity to the Chu State. This source of lead might have been exploited and circulated in the surrounding areas, such as Sanxingdui and Runlou, during the Shang Dynasty.

All potential sources of origin for the objects fall within the broader region defined as South China, encompassing the territory south of the Qinling Mountains and the Huai River Boundary. This is consistent with earlier provenance studies, which have suggested the potential role of the Chu State as a hub for the glass-making industry (Cui, Wu, and Huang 2011).

From a geographical perspective (Fig. 2.1), it is possible to speculate that the glass-making industry relied on multiple sources for lead. These lead sources could extend beyond the Hunan region. For disk 551, the LI composition suggests that there might be a close relationship between Southeast Asia and the Yunnan, Guizhou, Guangdong, and Guangxi regions. Similarly, the LI composition of disks 585 and 586 correspond to lead usage districts in Henan and Sichuan. This suggests the presence of highly radiogenic lead deposits in these areas.

Ultimately, the South China region appears to have played a more significant role in glass production, especially concerning the supply of raw materials, as compared to North China. The South China region's favorable natural environment and its manufacture industries with long history fostered the emergence of a thriving manufacturing sector during the Warring States Period and the Western Han Dynasty.

2.6.2 Strengths and limitations of using KDE method

KDE is a non-parametric method, meaning it does not assume any underlying distribution (such as normal distribution) for the data. This is beneficial in archaeological contexts, where lead isotope data may not follow typical statistical distributions.

In comparison to the utilization of a conventional bi-plots for the visualization of potential overlap among the LI characteristics of disparate items, the KDE methodology offers a more exact and statistically sound approach for the identification of potential consistency in the LI characteristics in question. Furthermore, it is not always straightforward to distinguish between datasets or items using traditional scatter plots, particularly when the datasets are large and the samples are numerous. The naked eye cannot calculate the exact distances between the LI values of studied samples and the comparing groups, nor can it discern patterns when thousands of points are superimposed on one another. The KDE method effectively and efficiently addresses this issue.

In archaeology, LI analysis with KDE processing has thus developed into a statistically robust and mathematically founded big data analysis, offering greater reliability and possibly acceptance across a broader range of disciplines.

A limitation of the KDE method is that it only displays probabilities, there are as such always multiple potential sources for a given object. Although the most probable source is identified, this does not render the sources of lower probabilities impossible. It is possible that low probabilities may in fact represent a true source. This also presents a challenge in interpreting KDE results. Furthermore, these results are significantly influenced by the selection of the bandwidth, which determines the degree of smoothing. An inappropriate bandwidth can result in either over-smoothing or under-smoothing, which in turn affects the interpretation of provenance and lead sources.

2.7 Conclusions

This study highlights the effectiveness of a KDE-based method combined with lead isotope analysis in examining the origins and circulation of lead in ancient glass artifacts. Four glass artifacts from the Harvard Arts Museums were typologically compared to archaeological glass from Asia and analyzed for their LI compositions based on KDE method.

Using a KDE based assessment of lead isotopic data, glass disk 551 has a high probability of representing a prototypical lead barium silicate glass that was manufactured during the Warring States Period in China. The primary source of its lead can be traced back to Yunnan, Guizhou, Guangdong or Guangxi area. Glass disks 585 and 586 exhibit lead isotope characteristics that are highly radiogenic, and the lead found in these disks corresponds closely to lead in the bronze materials from Henan and

Sichuan in the Shang Dynasty. This connection may be attributed to the geographical relevance of the Sanxingdui and Runlou sites to the Chu State, a region known for its thriving glass-making industry. Finally, ring 521 deviates from the characteristics of Chinese glass or bronze artifacts. Its lead may originate from the deposits in Central China.

Our research has also suggested multiple sources for the glass-making industry during the Warring States Period. Furthermore, Yunnan, Guizhou, Guangdong, and Guangxi regions likely shared a common reservoir of lead resources with the manufacturing industries in Southeast Asia during that historical era.

Methodologically, these findings underscore the significance of the KDE method as a valuable LI analysis tool, starting with its role in discerning the origins of cultural artifacts and extending further to aid museums in identifying and interpreting artifacts with unclear provenance. By facilitating direct comparisons with lead deposits and groups of artifacts, these methodologies can effectively contribute to illustrating potential correspondences among varied spatial-temporal contexts.

Despite the constraints imposed by limited data availability, the process of comparative approach can potentially explore deeper interconnections among ancient resources and manufacturing practices from various geographic regions and historical periods, thereby enhancing our comprehension of the socio-economic systems during antiquity.

In the future, the bandwidth selection in KDE should be refined, influencing the interpretations made in terms of provenance. These improvements will further reinforce the KDE method's position as a robust tool for archaeological research.

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