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

Wang, C.

Citation

Wang, C. (2026, May 13). *Computational analysis of lead isotope ratios in artefacts and ores from China: tracing connections, quantifying ambiguity, and rethinking provenance*. Retrieved from https://hdl.handle.net/1887/4303477

3

Exploring Circulation Dynamics in Han Dynasty China: Insights from Isotopic Analysis of Lead Glazed Pottery

This chapter was adapted from:

Wang, C., De Ceuster, S., Eremin, K., Laursen, S., Degryse, P., 2024. Exploring circulation dynamics in Han Dynasty China: Insights from isotopic analysis of lead–glazed pottery. *Archaeological and Anthropological Sciences*, 16, 189. `https://doi.org/10.1007/s12520-024-02096-0`

Abstract

This study investigates lead provenance and circulation patterns in Han Dynasty (202 BCE–220 CE) China through the analysis of lead glazed pottery. Four objects were studied using a combination of typological study, elemental chemistry and lead isotope ratio analysis. The results for each object were compared with databases of "lead mining districts" (lead ore provinces and deposits) and "lead usage districts" (lead–containing artifacts unearthed in different spatial and temporal ranges) to assess the lead sources used for each sample and offers a spatial–temporal range of the use of these lead resources. Three distinct groups of lead and their possible circulating spatial–temporal scales are identified across six samples in this study. A possible change in lead supply networks between the Western Han Dynasty (202 BCE–9 CE) and the Eastern Han Dynasty (25 CE-220 CE) is proposed. This study also highlights the probable changes in the movement of lead resources from the Western Han Dynasty to the Tang Dynasty (618 CE–690 CE), suggesting improvements in long–distance transport capabilities, and the development of economic divisions and exchange connections in ancient Chinese society. Our findings contribute to a deeper understanding of the economic and political dynamics during the Han Dynasty and emphasize the significance of lead isotope analysis of glazed pottery in exploring resource movement.

Keywords

Han Dynasty, lead glazed pottery, lead provenance and circulation, typological analysis, kernel density estimation.

3.1 Introduction

A glaze is a vitreous layer that forms a continuous coating on the surface of ceramic bodies. Low–temperature glazes in China predominantly refer to lead glaze. Lead (Pb) functions as a flux in the firing process, with melting temperatures ranging from 800°C to 1000°C, although certain scholars define this range as 700°C to 900°C (Zhao and Wei 2020; Luo and Zheng 2022).

In Chinese ceramic history, low–temperature lead glazed pottery gained prominence with the production of green lead glazed pottery in the Han Dynasty (202 BCE–220 CE) and tri–colored pottery in the Tang Dynasty (618–907 CE) and Liao Dynasty (907–1125 CE). The earliest evidence of lead glazed pottery in China was unearthed at the capital site of the Qi State during the Warring States Period (475–221 BCE) (Lang and Cui 2017). The popularity of lead glazed pottery reached its zenith in the Western Han Dynasty (202 BCE–8 CE) and experienced a subsequent surge in production that culminated in its first peak during the Eastern Han Dynasty (25–220 CE) before gradually declining and eventually disappearing. After several centuries, a resurgence of lead glazed pottery occurred during the Tang Dynasty (618–907 CE) with the emergence and development of tri-colored pottery (Luo and Zheng 2022; Wang 2013).

Lead glazed pottery artifacts from the Han Dynasty in China exhibit three distinct characteristics: their relative scarcity compared to unglazed clay gray pottery (泥质灰陶), their non–functional nature for daily life purposes, and their lack of exclusive shapes. Firstly, the quantity of lead glazed pottery artifacts is notably smaller than that of clay gray pottery during the same period. For instance, in the Shaogou Han burials (烧沟汉墓), lead glazed potteries represent only 4.4% of the total pottery discovered. Clay gray pottery remains the predominant type used for burial purposes (Wang and Tian 2010). Even during the most prosperous period, the number of lead glazed pottery artifacts found in burials remains lower than that of clay gray pottery. In the Dongyuan Burials (董院墓地), the burials with lead glazed pottery in them account for 94% of the early Eastern Han Dynasty burials, yet lead glazed pottery's proportion in all pottery of these burial is only 34% (Xu 2019). The distribution of lead glazed pottery within the Han Dynasty is also uneven, with higher concentrations found in Henan and Shaanxi provinces compared to other regions (Wang 2013). Secondly, lead glazed pottery artifacts serve no functional purpose in daily life (though they are grave goods with a proper function in that context). These artifacts exhibit visible marks of how they were manufactured such as trimming marks (which are the visible marks or lines left on the surface of a ceramic piece because of the trimming process), seams, brush marks, and the presence of flowing glaze after the glazing process. Additionally, the glaze layers are sometimes uneven and prone to peeling (Wang and Tian 2010).

Thirdly, lead glazed pottery, particularly vessels, lacks distinctive shapes and styles. Apart from the glaze, they closely resemble gray clay pottery in terms of their basic characteristics (Wang and Tian 2010; Chen 2005). The use of lead glazed pottery in ancient China might have been limited due to the potential hazards associated with the easily peeled glaze layer and the poisonous lead content. Consequently, lead glazed pottery has primarily been found in burial contexts rather than residential sites (Wang and Tian 2010; Xiong 2014; Wang 2013). Due to their non–exclusive shapes and rough craftsmanship, lead glazed pottery has been considered a cost-effective substitute for bronze (or bronze with patina) and lacquerware (Wood 1999).

The initial investigation of excavated lead glazed pottery from the Han Dynasty in China was carried out in the 1940s under the coordination of Bingqi Su (Su 1948). Subsequently, during the 1980s, research on Han Dynasty lead glazed pottery expanded significantly (Wang, Xu, and Zhou 2022; Dong, Li, and Liu 2020; Wang 2013). Studies on lead glaze primarily focus on various aspects, including origins, developments, evolutions, production techniques, decorative styles, distribution patterns, typological classifications, burial contexts, regional studies, and its relationship with glass and faience (Luo 1990; Chen 2005; Yang 2005b; Yu and Teng 2008; Xie 2010; Wang and Tian 2010; Tang 2011; Du 2011). Chemical composition analyses of lead glaze and its corrosive properties have also been conducted by researchers such as Zhang and Zhang (1982), Zhu, Wang, Mao, Li, and Huang (2010), Wang, Zhou, Yang, and Cui (2019).

On a global scale, lead isotope analysis has been applied to the provenance of ceramics and glazes. For example, Wolf, Stos, Mason, and Tite (2003) conducted lead isotope analyses on Islamic lead–glazed pottery from Fustat, Egypt, dating from the 8th to the 14th centuries AD. Their results indicated that the lead used in these glazes came from distant regions, including Iran, Tunisia, Sardinia, Spain, and the Taurus Mountains. Huntley, Spielmann, Habicht-Mauche, Herhahn, and Flegal (2007) examine pottery production in the Rio Grande region of New Mexico, highlighting the use of mixed ores from a variety of sources. Renson, Jacobs, Coenaerts, Mattielli, Nys, and Claeys (2013) and Renson, BenShlomo, Coenaerts, CharbitNataf, Samaes, Mattielli, Nys, and Claeys (2014) use lead isotopes to distinguish between local and imported pottery, and show that certain fabric types correspond to different lead isotope compositions in Cyprus. Medeghini, Fayek, Mignardi, Coletti, Contino, and De Vito (2020) analyse ceramic deposits in Britannia, with a particular focus on their role in Roman architectural ceramics, highlighting the contribution of the British Isles to the Roman Empire's pottery industry. Paghi, Manca, Casalini, Chiarantini, Bragagni, Tommasini, and Benvenuti (2024) carry out a study of Italian maiolica, a type of tin-glazed pottery, using lead isotope analysis to identify different production centres and their material sources.

Other isotopes have also been used in ceramic studies. Ma, Henderson, and Evans (2014) analyzed ash glazes and limestone glazes from different artefacts in Yue Kiln and Jingdezhen, China, revealing distinct isotopic signatures indicating different limestone sources and production technologies. Renson, Neff, Martínez-Cortizas, Blomster, Cheetham, and Glascock (2021) extended the use of isotopic analysis to Early Formative pottery from ancient Mexico. The use of lead and strontium isotopes successfully distinguished different production centers, identified imports, and provided new insights into production strategies during this period. Frigolé et al. (2024) introduce a multi-isotope approach combining strontium, neodymium, and lead isotopes to better understand ceramic provenance in South America.

However, the modern scientific and technological analyses of Chinese glaze have primarily focused on tri–colored glazed pottery from the Tang Dynasty and subsequent dynasties, as well as a set of low–fired glazed pottery from the Warring States Period, rather than on lead glaze from the Han Dynasty. Lead isotopic analysis is recognized as the most effective method for studying the provenance of lead in glazes (Henderson, Ma, Cui, Ma, and Xiao 2020), and it has been applied to ancient Chinese glaze (Shen, Ma, Henderson, Evans, Chenery, Wang, and Wen 2019; Henderson, Ma, Cui, Ma, and Xiao 2020; Shen, Henderson, Evans, Chenery, and Zhao 2018; Tatsumi, Furihata, and Cheng 2011; Chang 2019; Chang, Ma, Cui, Zhang, Shi, Gong, and Lei 2021; Cui, Lei, Jin, Huang, and Wu 2010). The predominant focus of lead isotopic studies concerning Chinese glaze has concentrated on the tri–colored glaze of the Tang Dynasty, the Liao Dynasty, and the Bohai State (698 CE–926 CE, also known as Baohaiguo or Balhae). Research into the lead isotopic signatures of lead–glazed pottery from the Han Dynasty remains notably scarce.

This study, marking a significant advancement, undertakes the first examination of the lead isotopic characteristics of four lead-glazed vessels from the Han Dynasty. By addressing this gap in knowledge, our research contributes invaluable insights into this important historical epoch, encompassing the exploration of trade networks, technological progressions, artistic evolution, and enriching the broader context of Chinese ceramic history.

3.2 Materials

The materials (Fig. 3.1) used for this study were obtained from the collection of the Harvard Art Museums. The materials used for this study were obtained from the collection of the Harvard Art Museums.

Bowl with landscape décor 2006.170.191, hereafter referred to as bowl 191, is a straight–sided bowl adorned with a decorative motif of flying ducks amidst scrolling clouds within a stylized landscape. The bowl is made of red earthenware with a lead–fluxed emerald–green glaze that covers the molded decoration and extends across the entire vessel, including the base. The outward rim of bowl 191 resembles the lid of a pottery box discovered in the Xibeiyiliao Cemetery M1 (burial number) burial site in Xi'an city in 1988 by the Xi'an Institute of Conservation and Archaeology (Cheng, Han, and Zhang 2004). This particular type of glazed pottery box is known as a Ba type box, characterized by a child and mother type mouth (outward rim for the cover and inward rim for the box), an arc-shaped belly, and a cover that can be inverted and used as a separate vessel resembling a bowl, with a low circular foot (Tang 2011). The Ba type glazed pottery box emerged during the period from the fifth year of the Yuanhou reign (元狩五年) to the reign of Han Emperor Yuan (118–33 BCE) and gained popularity in the late Western Han Dynasty (33 BCE–7 CE). During this time, green and dark green glazes became prevalent colors, while molded impressions of running animal patterns emerged as common decorative motifs. The earthenware used for these glazed pottery items was predominantly red clay (Tang 2011). Typologically, bowl 191, representing the Ba type pottery boxes, exhibits a distribution primarily concentrated in the Xi'an area during the middle and late Western Han Dynasty.

Cylindrical tripod vessel (*lian*) with conical lid 2006.170.197.A–B, hereafter referred to as tripod vessel 197, is a cylindrical tripod vessel featuring bear–shaped legs and a conical lid resembling a mountain with multiple peaks. The vessel is decorated with depictions of hunters pursuing animals on its sides and amid the mountain peaks. Made of red earthenware, it is adorned with a lead–fluxed emerald–green glaze that covers the molded decoration. Some glaze overflow can be observed on the underside of the vessel and the lid. Typologically, tripod vessel 197 closely resembles the CII type pottery *lian* (奁) found in the Tongxindalou M28 and Xibeiyiliao M1 burial sites in Xi'an, as excavated by the Xi'an Institute of Conservation and Archaeology (Cheng, Han, and Zhang 2004). This type of *lian* typically features bear–shaped feet, and molded impressions of mountains, running animals, and hunters are often found on the belly. Additionally, two symmetrical decorative collar ornaments known as *pushou* (辅首) can be present on the belly, similar to tripod vessel 197 and the *lian* from Xibeiyiliao M1. The CII type pottery *lian* emerged during the late Western Han Dynasty (33 BC–7 CE) and gained popularity from the Xinmang period (新莽时期) (9–23 CE) to the early Eastern Han Dynasty. During this period, the *boshanlu* lid (博山炉盖), a conical lid resembling a multi–peaked mountain, became prevalent, similar to the lid of tripod vessel 197. Typologically, tripod vessels like 197, representing the CII type pottery *lian*, was prevalent during the late Western Han Dynasty and early Eastern Han Dynasty, but disappeared during the middle Eastern Han Dynasty.

Lamp with base in the form of a bear 2006.170.200, referred to as lamp 200, represents a lamp characterized by a wide, shallow, straight–sided dish receptacle designed for holding oil. It is elevated on a faceted stem with a base in the form of a fierce bear, featuring a plump body and a humped back, seated on a high domed pedestal base. Made of yellow earthenware, the lamp showcases a lead–fluxed emerald green glaze that covers the molded decoration. The glaze exhibits a silvery iridescence on the surface, while the underside of the base remains unglazed. Lamp 200 corresponds to a bear–based Dou–form pottery lamp (熊座豆形陶灯). Although the number of lamps of this kind is not substantial, with only a few dozen found in the Gansu, Shaanxi, and Henan regions, their shapes are not uniform, as nearly all bear–based lamps differ from one another. Determining the prevalent period of this lamp type is challenging due to the limited number of unearthed bear–based pottery lamps, hindering a comprehensive analysis of their developmental trajectory (Ma 2012). However, considering the overall development of lead glazed pottery, it is noteworthy that molded decorations emerged during the middle of the Western Han Dynasty and gradually declined by the middle Eastern Han Dynasty (Tang 2011). Therefore, it can be inferred that the molded bear–based lamp falls within the period spanning from the middle Western Han Dynasty to the middle Eastern Han Dynasty.

Mountain–form censer with tortoise–form base 2006.170.202.A–B, referred to as incense burner 202, represents a *boshanlu* (博山炉), an incense burner characterized by a conical lid in the form of a forested mountain, with a height of 25.3 cm and a diameter of 12 cm. It features a hemispherical bowl raised on a short stem and a base shaped like a tortoise with its head turned back towards the stem. The lid is adorned with small circular openings and molded decorations of human figures and mythical animals, including the legendary hare with a mortar and pestle. The stem is decorated with molded images of foreigners. Made of red earthenware, incense burner 202 showcases a lead–fluxed, emerald–green glaze on the lid and a lead–fluxed, caramel–brown glaze on the receptacle and base. The underside and interior of the receptacle remain unglazed. Incense burner 202 closely resembles the pottery *boshanlu* unearthed in Henan province. According to the typological analysis in Tang (2011), it belongs to the D type incense burner category, prevalent in the late Western Han Dynasty (33 BCE–7 CE) in the Luoyang–Jiyuan area of Henan province. There are records of glazed pottery *boshanlu* with different colors on the cover and base separately in Shaanxi during the Han Dynasty (Wang, Wang, and Li 2010). Hence, it is believed that the cover and base of incense burner 202 are an original set. The *boshanlu* is a unique artifact due to its impressive shape and exquisite appearance. Its emergence is attributed to the prevalence of incense culture, the pursuit of immortality, and the personal preferences of Wu Emperor of Han. *boshanlu* became popular during the middle Western Han Dynasty and underwent simplification during the Eastern Han Dynasty. During the Wei, Jin, Southern, and Northern Dynasties period (220–589 CE), with the spread and prosperity of Buddhism, *boshanlu* gradually transformed into a Buddhist offering and acquired some Buddhist characteristics such as lotus decorations. Some researchers believe that pottery *boshanlu* were primarily used as burial objects, while bronze *boshanlu* served daily applications in bathrooms and ritual activities (Yang 2004). More *boshanlu* artifacts have been unearthed in South China compared to North China, with Chongqing and Guangzhou areas having the highest number of *boshanlu* findings in China (Wang 2013). Nevertheless, incense burner 202 likely dates from the late Western Han Dynasty to the Eastern Han Dynasty.

3.3 Methodogy

3.3.1 Chemical composition analysis

All four vessels underwent non–destructive portable X–ray fluorescence analysis to identify the elements present and validate the lead–rich composition of all the glazes. Subsequently, tiny sections of glaze were extracted from areas of damage and/or loss. These samples were prepared, mounted, and meticulously polished to facilitate analysis using scanning electron microscopy with energy dispersive microanalysis (SEM–EDX), enabling the acquisition of quantitative data.

3.3.2 Lead isotopic analysis

Four samples not used in SEM analysis, left unmounted, were used for lead isotopic analysis according to the methodology adapted from Rademakers, Verly, Somaglino, and Degryse (2020). The samples were manually ground to a fine powder using an agate mortar. These powdered samples were brought into solution following a high temperature acid digestion procedure (using concentrated HF, HCl and HNO_3) and subsequently subjected to a lead isolation procedure using Pb–SPEC resin (Eichrom Technologies). Raw LI ratios were measured on a Thermo Scientific Neptune Multi-Collector–Inductively Coupled Plasma–Mass Spectrometer (MC–ICP–MS) and corrected for Tl–based mass discrimination following Russel's law, based on replicate measurements of the NIST SRM 981 (commonly accepted ratio values from Galer and Abouchami (1998). Error values were better than 0.05% for the corrected ratios to ^{204}Pb.

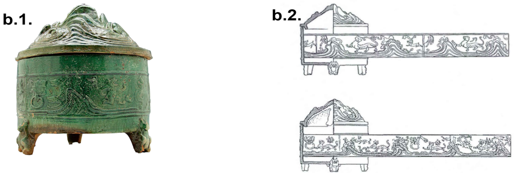
3.3.3 Kernel density estimates method

In this study, the lead isotope composition of four lead glazes was evaluated using a kernel density estimates approach (KDE) (De Ceuster and Degryse 2020). While KDE has been previously applied in archaeological Chinese bronze (Hsu, Rawson, Pollard, Ma, Luo, Yao, and Shen 2018), this study represents the first application to ancient Chinese glaze.

In using KDE, 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 estimate plot of the lead isotopic composition of ores from different "lead

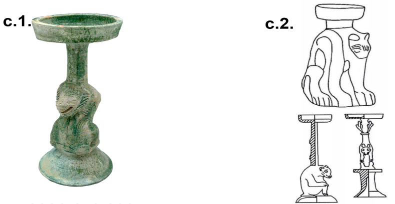
2006.170.191

pottery box from Xi'an



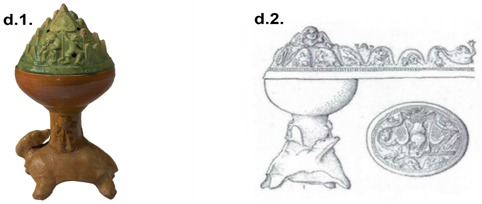
2006.170.197

pottery *Lian* from Xi'an



2006.170.200

bear-based pottery lamps from the Han Dynasty



2006.170.202

pottery incense burner unearthed from Henan

Figure 3.1: Han dynasty green lead–glazed vessels.

a.1. Bowl with landscape décor. Han dynasty, 1st century BCE–2nd century CE. Earthenware with green lead glaze. Harvard Art Museums/Arthur M. Sackler Museum, Partial gift of the Walter C. Sedgwick Foundation and partial purchase through the Ernest B. and Helen Pratt Dane Fund for Asian Art, 2006.170.191. Photo: © President and Fellows of Harvard College; **a.2.** the pottery box (陶盒) from Xi'an. Their covers are typologically like bowl 191 (Fig. 2.9 in Tang 2011); **b.1.** Cylindrical tripod vessel (*lian*) with conical lid. Han dynasty, 1st century BCE–1st century CE. Earthenware with green lead glaze. Harvard Art Museums/Arthur M. Sackler Museum, Partial gift of the Walter C. Sedgwick Foundation and partial purchase through the Alpheus Hyatt Purchasing Fund, 2006.170.197.A–B. Photo: © President and Fellows of Harvard College; **b.2.** the CII type pottery *lian* (陶奁) from Xi'an. They are typologically like tripod vessel 197 (Fig. 2.8 in Tang 2011); **c.1.** Lamp with base in the form of a bear. Eastern Han dynasty, 1st–3rd century CE. Earthenware with green lead glaze. Harvard Art Museums/Arthur M. Sackler Museum, Partial gift of the Walter C. Sedgwick Foundation and partial purchase through the Ernest B. and Helen Pratt Dane Fund for Asian Art, 2006.170.200. Photo: © President and Fellows of Harvard College; **c.2.** other bear–based pottery lamps from the Han Dynasty (Fig. 2.7 in Ma 2012); **d.1.** Mountain–form censer (*boshanlu*) with tortoise–form base. Western Han dynasty, 1st century BCE. Earthenware with green and brown lead glazes. Harvard Art Museums/Arthur M. Sackler Museum, Partial gift of the Walter C. Sedgwick Foundation and partial purchase through the Alvan Clark Eastman Bequest Fund, 2006.170.202.A–B. Photo: © President and Fellows of Harvard College; **d.2.** pottery incense burner (*boshanlu* 博山炉) unearthed from Jiyuan, Henan (Fig. 10 in Henan Provincial Museum 1973(2)) 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 selection of bandwidth is predicated upon the bandwidth estimator introduced by Sheather and Jones (1991). This estimator’s efficacy has been substantiated through empirical evaluation, in the investigation of lead provenance conducted by De Ceuster and Degryse (2020). All comparisons were performed using R© software. A match of all three LI ratios with the reference datasets may indicate that the sample originated from the same source or used the same lead as the reference materials, while a lack of match may indicate an unknown origin (i.e., not present in the datasets), or the composite or recycled nature of the sample.

3.4 Results

3.4.1 X–ray fluorescence

Analysis of the green glaze of ceramics 2006.170.191, 2006.170.197.A–B (from the body and lid of the burner respectively) and 2006.170.200 showed that the glaze had high levels of lead and silicon with some copper, tin and iron, as well as traces of calcium and strontium. Analysis showed that both the green and yellow glaze on 2006.170.202.A–B had high levels of lead, similar to those in the green glaze of the other ceramics. However, the yellow glaze (.A) lacked detectable copper or tin, whilst the green glaze (.B) contains some copper and barium and likely trace tin. The presence of tin with copper suggest use of bronze as the colorant.

3.4.2 Scanning electron microscopy with energy dispersive microanalysis

Analysis of glaze samples by scanning electron microscopy with energy dispersive microanalysis (SEM–EDX) confirmed that all samples had high levels of lead, from around 52 to 68% PbO. As found by XRF, barium was present only in the green glaze from 2006.170.202.B. The glaze samples from 2006.170.191 and 2006.170.197 were the most homogenous, whilst the glaze from 2006.170.200 and 200.170.202 contain abundant crystals. Analysis of the crystals in the glaze from 2006.170.202.A shows these have high levels of aluminum, silicon and potassium. An interaction layer with a concentration of crystalline phases occurs in all the samples at the ceramic to glaze boundary. Most samples contain a red ceramic body, but the sample from 2006.170.200 has a buff colored ceramic. Deterioration and/or cracking of the glaze is visible in several samples and there is a thick burial crust on sample 2006.171.191 (see Supplementary Table 1, STable 1). (The Supplementary Materials of this article is available in the published version. [1])

For Sample 191, the glaze thickness measures at least 1.2 mm, with the analyzed areas ranging from 200 to 550 microns in length and 280 to 550 microns in width. In Sample 197A, the glaze thickness is between 35 and 40 microns, with areas ranging from 10 to 50 microns in length and 10 to 40 microns in width. The glaze is homogeneous, and inclusions are observed only near the boundary with the ceramic, although these inclusions were not analyzed. Sample 197B exhibits a glaze thickness of 75 to 125 microns, with area dimensions ranging from 150 to 200 microns in length and 40 to 50 microns in width. This glaze is also homogeneous, with inclusions limited to the boundary with the ceramic, which were not analyzed. In Sample 200, the glaze thickness is 15 to 35 microns, with areas measuring between 5 and 15 microns in both length and width. Inclusions are again only observed near the boundary with the ceramic and were not analyzed. Sample 202A presents a glaze thickness ranging from 35 to 100 microns, with area dimensions of 5 to 90 microns in length and 5 to 70 microns in width. Numerous inclusions are present in the glaze, some of which were included in the area analyses, and the inclusions consist of aluminum, silicon, and potassium (Al–Si–K). Sample 202B has a glaze thickness of 200 to 300 microns, with areas measuring 20 to 100 microns in length and 20 to 85 microns in width. This sample also contains a significant number of inclusions, some of which were included in the area analyses, with the inclusions consisting of Al–Si–K. The analysis was conducted with a count time of 60 seconds.

Regarding the colorants, although the precise colorant for the yellow glaze is uncertain, it is assumed to be iron. For the green glaze, it is likely a combination of lead (Pb) and copper (Cu), with a possible contribution from iron (Fe). Furthermore, it is assumed that tin is dissolved within the glaze, as no tin particles were observed in the samples.

3.4.3 Lead isotopic analysis

The lead isotope (LI) ratios of ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{208}Pb/^{204}Pb for the four glazed objects have been presented in STable 2. The lead isotopic profiles for samples from incense burner 202 exhibit a linear distribution (see SFig.1), suggesting the possibility that the lead used in both the base and cover of incense burner 202 may originate from the same source (Pollard and Heron 2008), although this is refuted by comparison with the lead deposits in the discussion section of this paper. This finding implies that the lead raw materials employed in the production of incense burner 202 were consistent. Conversely, samples from the objects 191, 197, and 200 exhibit distinct LI signatures compared to incense burner 202, indicating potential variations in their geographical origins or manufacturing periods. Although these glaze samples

---

[1] https://doi.org/10.1007/s12520-024-02096-0

exhibit proximity to each other on the LI diagram, further comparative analysis will be necessary to discern their respective sources. (The Supplementary Materials of this article is available in the published version.)

3.5 Discussion

3.5.1 The origin of lead raw materials

Given that all four glazes analyzed in this study exhibit high lead contents ranging from 50% to nearly 70% by weight, their lead isotopic (LI) compositions indicate the potential sources of the lead used. To ascertain the likely origins, the 'natural lead mining districts' database was utilized, which was derived from the geochemical lead ore database compiled by Hsu and Sabatini (2019). In order to identify the specific deposits associated with the glaze samples, comparisons are made with all the deposits in China. Each lead deposit included in the analysis must comprise a minimum of 10 ore samples (galena) to ensure the highest level of accuracy in the comparison results (Baron, Day, and Garvey 2014). In comparing samples with deposits, a match is defined as a result where all three relative probability values exceed 0.1, in which context, the deposit with the lowest value exceeding the lowest value of any other deposits is considered the closest match. A table with the data of the natural lead mining districts (those most relevant) could be seen in Supplementary ore data. (The Supplementary Materials of this article is available in the published version. [2])

A comparison was made between the LI signatures of glaze sample 191 and the deposits in China. SFig.2 (Supplementary Figure 2) highlights the Qixiashan deposit in Jiangsu Province as the most closely aligned with the lead resources utilized in glaze sample 191. Zhenzigou (Liaoning Province), Yutang (Hunan Province), Xiquegou (Liaoning Province), Shuiji (Fujian Province), Qingchengzi (Liaoning Province), Linglong (Shandong Province), Haopingou (Henan Province), Dongtongyu (Shaanxi Province) deposits are also the possible sources.

As shown in SFig.3, the lead ores used for glaze sample 197 exhibits the closest resemblance to the Linglong deposit located in Shandong Province. Wenyu (Henan Province), Yutang (Hunan Province), Shuiji (Fujian Province), Qixiashan (Jiangsu Province), Xiquegou (Liaoning Province), Dongtongyu (Shaanxi Province) deposits are also possible sources.

As shown in SFig.4, the Linglong deposit located in Shandong Province, is the most likely deposit associated with the lead source for glaze sample 200. Shuiji (Fujian Province), Qixiashan (Jiangsu Province), Dongtongyu (Shaanxi Province) deposits are also possible sources.

---

[2] `https://doi.org/10.1007/s12520-024-02096-0`

The Jinding and Gejiu deposits in Yunnan Province is the most likely source of the lead used in glaze sample 202A (SFig.5). Tianbaoshan (Sichuan Province), Fankou (Guangdong Province), Dalingkou (Zhejiang Province), Tianqiao (Guizhou Province), Qibaoshan (Hunan Province), Niuchang (Yunnan Province), Hetaoping (Yunnan Province), Dingjiashan (Fujian Province), Dajing (Inner Mongolia) deposits are also possible sources.

The Zhilingtou deposit in Zhejiang and Fujian Provinces emerges as the most probable source of the lead in glaze sample 202B1 (SFig.6). Yindongzi (Shaanxi Province), Qingchengzi (Liaoning Province), Heigou (Henan Province), Beishan (Guangxi Province), Bafangshan (Shaanxi Province), Kalayasikake (Xinjiang Uyghur Autonomous Region), Kalangu (Xinjiang Uyghur Autonomous Region), Tamu (Xinjiang Uyghur Autonomous Region) deposits are also possible sources.

The Bafangshan deposit in Shaanxi Province demonstrates the highest match with the lead resources used in glaze sample 202B3 (SFig.7). Heigou (Henan Province), Yindongzi (Shaanxi Province), and Kalayasikake (Xinjiang Uyghur Autonomous Region) deposits are also possible sources.

Moreover, it is noteworthy that the potential sources of glaze sample 202B1 may encompass all of the potential origins of glaze sample 202B3. These origins include the Bafangshan, Heigou, Yindongzi, and Kalayasikake deposits. Conversely, the potential sources of glaze sample 202A exhibit no overlap with any of the potential sources of either glaze sample 202B1 or 202B3.

This observation might indicate that the lead present in the glaze of the lid and body of object 202 originated from diverse deposits located in different geographical regions. Furthermore, the chemical compositions of the lid glaze and body glaze exhibit notable disparities, as illustrated in STable 1, where the lid glaze exhibits a barium content that is absent in the body glaze. These disparities further substantiate the proposition that the lid and body might have been manufactured independently of each other (either in the same workshop using different recipes and raw materials or in different workshops).

3.5.2 Comparison with archaeological objects

3.5.2.1 Glaze

Due to the scarcity of research on the LI signatures of Han lead glazed pottery, our data were compared to Tang Dynasty (618–907 CE) lead glazes from Henan province (Tatsumi et al. 2011; Chang 2019; Cui et al. 2010) and Shaanxi province (Chen 2019; Cui, Lei, Jin, Huang, and Wu 2010), and from the Tang capitals of Xi'an (Chang, Ma, Cui, Zhang, Shi, Gong, and Lei 2021; Chang 2019) and Luoyang city (Chang 2019). Furthermore, a comparison was made to lead glazes from Balhae (the Bohai state) (698–926 CE) in Northeast China, the Korean Peninsula, and the Russian Far East from

698 CE to 926 CE (Chang 2019), as well as glazes from 9th-century Japan (Sasaki, Shirahata, and Yamasaki 1994) and tri-color glazes found in Japan (Tatsumi, Furihata, and Cheng 2011; Chang 2019), and glazes from the Silla period (57 BCE–676 CE) in Korea (Cho, Huh, Kim, and Kang 2007). Additionally, two sets of data are available from western and central Eurasia, comprising Roman lead glazes from the 1st to 4th centuries (Walton and Tite 2010) and lead glazes from Kazakhstan dating from the 9th to 12th centuries (Klesner, Renson, Akymbek, and Killick 2021). 2021). See the data in Supplementary glaze data.

Based on SFig.8, it can be deduced that glaze sample 191 exhibits a similar LI signature to the glaze from Xi'an during the Tang Dynasty. Likewise, glaze sample 202B#3 displays a comparable LI signature to the glaze from Balhae (as Bohaiguo in the SFig. 8). Glaze sample 202B#1 shows a resemblance to the LI signature of the Tangsancai glaze from the Huangye kiln in Henan Province and the Liquanfang Kiln in Shaanxi Province. Glaze samples 197 and 200 exhibit resemblances to the glazes found in Xi'an during the Tang Dynasty. In contrast, glaze sample 202A does not manifest any discernible affinities with any of these aforementioned glazes. Samples 197 and 200 have similar LI ratios as the Kazakhstan glazes, for which raw material origin is attributed to the Central Asian Orogenic Belt and Xinjiang in China (Klesner, Renson, Akymbek, and Killick 2021), these deposits/regions are not plausible raw material sources for samples 197 and 200, as ore deposits formed during the same geological period in different locations can exhibit very similar ranges of LI abundance ratios (Pernicka 2014).

3.5.2.2 Bronze

The LI signatures found in Han Dynasty bronze artifacts provide valuable information regarding the origin of the lead ores employed. A comparative assessment is made between our glazed pottery artefacts and Han Dynasty bronzes. The LI signature database of Han bronze artifacts encompasses bronzes from Guizhou (Huang, Wu, Chen, Tao, Wu, Shi, Li, Ritchey, Huang, and Jin 2021), Shaanxi (Zhangsun, Liu, Jin, Pollard, Lu, Bray, Fan, and Huang 2017), Chengdu city (Li, Zuo, Cui, Tian, Yang, Yi, Zhou, and Fan 2020), Shandong (Wei and Dong 2007; Cui and Wu 2007), Sichuan (Ma, Wang, Li, Yang, Yang, Wang, and Luo 2024; Wei, Zhang, Shi, and Wang 2024), Hubei (Li, Wei, Gao, Wang, Liu, and Wu 2023), Fujian, Anhui, Zhejiang and Jiangsu (Yang, Wu, Liu, Wang, Shi, Qu, Tian, Hua, and Zhang 2023; Wang, Liu, Gao, Pollard, Fan, Huang, Li, Zhang, Hua, and Jin 2024), as well as from Henan (Chen, Luo, Zeng, and Cui 2018). These diverse bronze artifacts represent distinct "lead usage districts" within the Han Dynasty. The Han bronze artefacts used for comparison (mostly) contain lead added to alloy (with lead contents above 2%), therefore LI ratios of bronze artefacts indicate the source of lead. See the data in Supplementary bronze data.

In SFig.9, it can be inferred that glaze samples 191 and 197 potentially share the same lead resources as the bronze artifacts from Eastern Han Jiangsu, Western Han Henan, Western Han Shandong, and Western Han Guizhou. The LI signature of glaze sample 200 exhibits similarity to these Han Dynasty bronzes, same as samples 191 and 197, but the relative possibilities of glaze sample 200 are low (less than 10%). Glaze sample 202A's LI signature corresponds to the bronze artifacts from Eastern Han Jiangsu, while 202B#1's LI signature aligns with those from Eastern Han Fujian. Glaze sample 202B#3's LI signature corresponds to the bronze artifacts from Western Han Anhui.

3.5.3 Different products, different lead sources?

Our glaze samples establish intriguing connections among the glaze from the Tang Dynasty, glaze from the Han Dynasty, and bronze from the Han Dynasty. Notably, each glaze sample exhibits unique patterns of overlap with these materials. This prompts an inquiry: do glaze and bronze, both of which contain lead, share common sources of lead, or do they rely on independent supplies? Do these supply dynamics undergo alterations over time?

In Fig. 3.2, we can observe the differences in the LI signatures of the lead used in the Western Han Dynasty Bronze (WHan bronze, see data reference in Bronze section), Eastern Han Dynasty Bronze (EHan bronze, see data reference in Bronze section), Han Dynasty glass (Li, Li, and Gu 2016), and Tang Dynasty glaze (see data reference in Glaze section). The LI compositions of the Tang glaze exhibit distinct concentrated zones as evident from the density curves, as well as the LI ratios for the Tang glaze differ from those of the Han bronzes, indicating a different lead supply sources/source between Tang glaze and Han bronze. Nevertheless, the lead isotope compositions of Han bronze, Han glass and three of our samples exhibit a correlation, which suggests that they may have derived from corresponded sources of lead.

We could draw a hypothesis to explain this phenomenon, suggesting that during the Eastern Han Dynasty, the production of lead glaze became more independent from the bronze industry. Subsequently, during the Tang Dynasty, the glazed pottery industry further developed its independent lead supplies and sources. As the bronze industry declined in the Eastern Han Dynasty and subsequent dynasties, it probably gradually lost its dominance over lead resources, while glaze pottery emerged as a significant consumer of lead. However, to confirm this inference, additional LI data on bronze, leaded glass, and leaded glaze, accompanied by clear archaeological information, is required. Further investigations involving these materials are necessary.

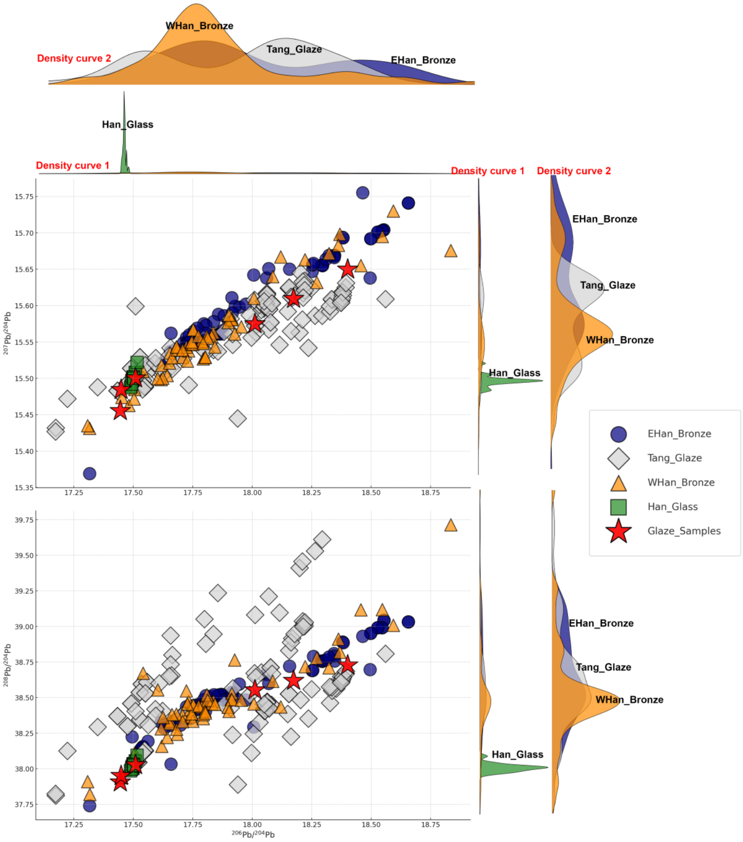


Figure 3.2: Scatter plots depicting the relationship between samples and various lead usage districts, accompanied by density curves. The lead usage districts represented in the figure include the bronze artifacts from the Western Han Dynasty (WHan_Bronze), the bronze artifacts from the Eastern Han Dynasty (EHan_Bronze), the glass artifacts from the Han Dynasty (Han_Glass), and the glaze artifacts from the Tang Dynasty (Tang_Glaze). The fill colors of the density curves and the points are coordinated and coherent with the legend. Because the distribution of Han_Glass in the scatter plots is too narrow, its density curves dominate. Hence, we need to exclude the curves of the Han_Glass to see other variations more explicitly. Density curve 2 is obtained by excluding the samples in this study (green curves) and the Han glass from density curve 1, providing a clearer representation of the density variations in the LI signatures between the Han Dynasty bronzes and the Tang Dynasty glazes

3.5.4 The expansion of the Han Dynasty

When we plot all potential lead mining and usage locations on maps in chronological order (Fig. 3.3), we discern the presence of at least three distinct lead types, which are the lead identified in glaze samples 191, 197, and 200; the lead within glaze sample 202A; and the lead in glaze samples 202B#1 and 202B#3.

Firstly, the lead in glaze samples 191, 197, and 200 shares a common origin, potentially linked to deposits in the regions of Shaanxi, Jiangsu, Fujian, or Shandong. This type of lead might have been employed in Henan and Guizhou during the Western Han Dynasty, in Jiangsu during the Eastern Han Dynasty, and in Shaanxi during the Tang Dynasty.

Secondly, considering that glaze samples 202B#1 and 202B#3 are derived from the same segment of object 202, it is highly probable that the lead in them originates from the same source. In this case, the plausible sources are the deposits in Henan or Shaanxi, which probably have been utilized in Shandong during the Western Han Dynasty, in Jiangsu and Fujian during the Eastern Han Dynasty, and in Shaanxi, Henan, and Balhae during the Tang Dynasty.

Conversely, the lead in glaze sample 202A exhibits distinctive characteristics when juxtaposed with any other lead types in this study. It is strongly indicative of a South China origin. It was also used in Jiangsu during the Eastern Han Dynasty, while in Korea during the Tang Dynasty.

Based on Fig. 3.3, discernible transformations are shown in the utilization patterns of these three distinct types of lead from the Western Han Dynasty to the Tang Dynasty. In the case of the lead type in glaze samples 191, 197, and 200, there is strong evidence to suggest that it was actively exploited and employed over the span of numerous centuries, indicative of its abundant yield. Notably, its utilization spectrum appears to have contracted over time. Conversely, the lead variety utilized in glaze samples 202B#1 and 202B#3 displayed an expansion in usage domains, particularly from the Eastern Han to the Tang Dynasty. A similar trend is observable in the case of the lead in glaze sample 202A.

In the *Han Shu* (汉书), the number of lead deposits during the Eastern Han Dynasty surpasses that of the Western Han Dynasty (Chen 2008). Moreover, the Han Dynasty is renowned for its significant achievements in trade and unprecedented territorial expansion (Yu 1967). In the Han Dynasty, the Chinese government employed trade as a political instrument to maintain control over the frontier “barbarians”. Commodities, including products containing lead, were among the items included in this exchange network, resulting in the long–distance transportation of lead resources. Additionally, there were also significant transformations between the Eastern Han Dynasty and the Tang Dynasty. The development of long–distance exchange could relate to the Grand Canal in China, first built during the Sui Dynasty (581–618 CE), which greatly

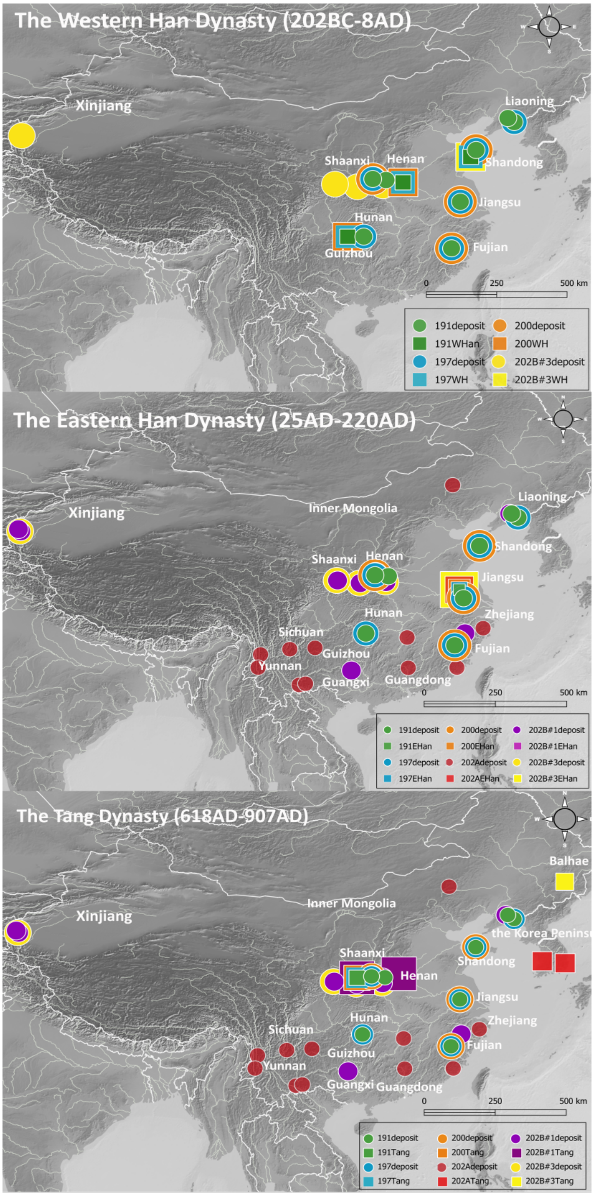


Figure 3.3: Maps of lead resources provenances and circulations in different periods. The circles indicate the lead deposits which are possible sources. The squares indicate the location where lead products are unearthed. The circles and squares of the same color mean that the LI signatures of their lead ores or lead products correspond. (the red squares in Tang period Korea represent the glass corresponding with sample 202A, details could be seen in SFig.10)

contributed to the transportation capacity between the South and the North (Quan 2011).

Nonetheless, the discernible trends in transformations spanning the Western Han Dynasty, the Eastern Han Dynasty, and the Tang Dynasty underscore a number of potential advancements: 1) an increase in the number of lead sources; 2) an expansion of the geographical scope of lead circulation and a territorial expansion towards southwest and southeast China.

3.6 Conclusion

This study focuses on the analysis of four lead glazed objects from the Han Dynasty in China. Utilizing kernel density estimate method, it is concluded that there are at least three types of lead in these samples. The lead used in glaze samples from 2006.170.191, 2006.170.197, and 2006.170.200 likely originated from the Jiangsu, Shaanxi, Fujian or Shandong areas. On the other hand, the lead in glaze samples from 2006.170.202 is consistent with the lead from Shaanxi and Henan, or South China.

By further comparison, it is inferred that bowl 2006.170.191, tripod vessel `2006.170.197`, and lamp 2006.170.200 were likely produced in the Western Han Dynasty, while incense burner 2006.170.202 corresponds to the Eastern Han Dynasty.

Moreover, a hypothesis is developed to explain the possible change in the lead supply network between the Western Han Dynasty and the Eastern Han Dynasty. In the Western Han Dynasty, lead glaze and lead bronze might share the same lead resources supply network, while in the Eastern Han Dynasty, the lead supply for glaze might gradually become independent from the bronze. The changing patterns of lead resource movement in different periods is also considered. It is speculated that the movement ranges expanded from the Western Han Dynasty to the Tang Dynasty, indicating an improvement in long–distance transportation capabilities.

Lead isotope data help us to learn more about the production and circulation of ancient glazes, shedding light on manufacturing industries in Han Dynasty China. The KDE method used in this study facilitates the quantification of relative probabilities in numerical form, allowing us to identify variations in probability associated with different deposits or groups. This study highlights the contribution that archaeometric results can make to the reconstruction of historical knowledge and the ability of archaeometric evidence to resolve historical and archaeological questions.

Acknowledgments

Chen Wang greatly benefits from the financial support from the China Scholarship Council (CSC NO. 202108060012). We appreciate the help of Angela Chang with sampling.