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

Wang, C.

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1

Introduction

1.1 Background of the study

1.1.1 The history and use of metallic lead (Pb)

Lead (Pb) has been used by humans for over 8000 years, valued for its malleability, low melting point, and resistance to corrosion (Yahalom-Mack, Langgut, Dvir, Tirosh, Eliyahu-Behar, Erel, Langford, Frumkin, Ullman, and Davidovich 2015). Metallic lead beads dating back to 7000–6500 BCE have been found in Asia Minor and may represent the first example of metal smelting (Rich 1994; Hansen, Montero-Ruiz, Rovira, Steiniger, and Toderaş 2019).

Lead was used in China before the rise of the Qin Dynasty. The *Shangshu Yugong* (尚书 禹贡), a geographical and administrative treatise, said to date back to the early Zhou or even pre-Zhou periods, includes records about lead and lead deposits (Liu and Pollard 2022a). A Cu-Sn alloy containing Pb and Zn was unearthed from the Jiangzhan site in Lintong (临潼姜寨遗址), dating back approximately 5000 to 6000 years (Fan, Harbottle, Gao, Zhou, Gong, Wang, Yu, and Wang 2012). In the Longshan culture (龙山文化) (approximately 3000 BC), situated within the Yellow River Basin in China, a number of leaded bronzes have been unearthed (Mao, Li, and Wang 2024). It can be stated that the use of lead was evidenced between 2000 BCE and 1500 BCE. This is evidenced by the discovery of a pure lead ingot in the late Erlitou period (approximately 1500 BCE) (Li 1984; Li, Wei, Gao, Wang, Liu, and Wu 2023; Pollard, Bray, Hommel, Hsu, Liu, and Rawson 2017; Liu and Pollard 2022b). Please refer to Table 1.1. for the chronological framework of ancient China. Fig. 1.1 summarises the locations of archaeological sites mentioned in this study where early lead use has been documented.

During the Shang (1250-1046 BCE) and Western Zhou (1046-776 BCE) dynasties, metal alloys used in China typically contained copper, tin, and lead, with tin concentration showing two popular patterns: primarily around 15% and a secondary lower range (below 7%) (Li 1984). Lead was not merely an additive but often served as a substitute for copper in alloys, particularly in lower-quality vessels. Higher-quality bronze artifacts often contained less lead, which may suggest that elite groups had access to better resources. In contrast, artifacts linked to lower social classes tended to contain more lead. This distinction reflects a hierarchical access to resources in ancient China, with lead being an economical substitute used by lower strata or during periods of resource shortage (Zhang and Cui 2022; Chen, Mei, Rehren, et al. 2019).

Lead smelting techniques likely developed alongside the production of lead-based pigments. By-products of lead extraction, such as litharge (PbO) and minium (Pb_3O_4), were initially produced while smelting lead from minerals like galena (PbS). These compounds were used as early pigments, primarily found in the Shang (c.1600-1046 BCE) and Zhou (c.1046-256 BCE) dynasties. Litharge provided a yellowish pigment, while minium, commonly known as red lead, was favored for its bright red hue (Schafer 1956; Han, Zhang, Chong, et al. 2022).

The earliest evidence of synthetic lead white in China was discovered at the Liangdaicun (梁带村) site in northern China, dating back to the 8th century BCE (Han, Zhang, Chong, et al. 2022). At the Liangdaicun site, lead white was found in tombs of the aristocracy, including the king of the Rui state (芮国) and his family members. These cosmetics were used by both aristocratic women and men, marking one of China's earliest trends of male facial cosmetics. This fashion became even more prevalent during the Warring States period (475-221 BCE) (Han, Zhang, Chong, et al. 2022).

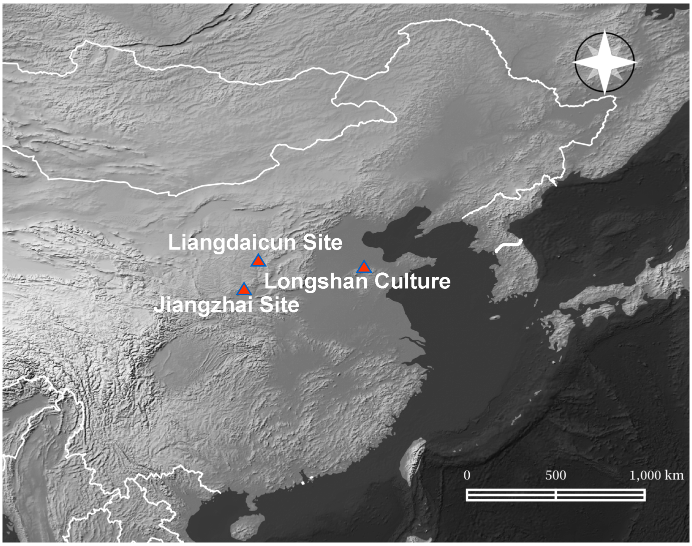

Figure 1.1: Map showing archaeological sites in China where early lead use has been mentioned above.

Archaeological evidence indicates that lead was among the earliest metals exploited in the Near East, with smelted lead artefacts documented from the late fifth millennium BCE in the southern Levant (Yahalom-Mack, Langgut, Dvir, Tirosh, Eliyahu-Behar, Erel, Langford, Frumkin, Ullman, and Davidovich 2015). In ancient Egypt and Mesopotamia, lead compounds such as galena were widely used in eye cosmetics (kohl), and these materials are frequently recovered from burial contexts (Riesmeier, Keute, Veall, et al. 2022). In the Aegean region, lead artefacts have been identified in Early Bronze Age and Minoan contexts, including funerary assemblages, and lead was occasionally used architecturally, for example in clamps and lining elements (Gale and Stos-Gale 1981). Cuneiform texts from Mesopotamia attest to the circulation and valuation of metals, including lead, within economic systems of the early second millennium BCE (Moorey 1994). Archaeological evidence from Sumerian burial contexts further demonstrates

Table 1.1: Outline of Chinese Historical Chronology

Period / Dynasty	Date Range	Notes
Paleolithic Age	c. 2.5 million–10,000 BCE	Early human activity in China;
Neolithic Age	c. 10,000–2070 BCE	e.g., Yangshao, Longshan cultures;
Xia Dynasty	c. 2070–1600 BCE	Traditionally regarded as first dynasty;
Shang Dynasty	c. 1600–1046 BCE	
Zhou Dynasty	1046–256 BCE	Western Zhou; Eastern Zhou (Spring–Autumn, Warring States period)
Qin Dynasty	221–206 BCE	
Han Dynasty	206 BCE–220 CE	
Three Kingdoms	220–280 CE	Wei, Shu, Wu states
Jin Dynasty	266–420 CE	
Northern and Southern Dynasties	420–589 CE	Political fragmentation
Sui Dynasty	581–618 CE	
Tang Dynasty	618–907 CE	
Song Dynasty	960–1279 CE	
Yuan Dynasty	1271–1368 CE	
Ming Dynasty	1368–1644 CE	
Qing Dynasty	1644–1912 CE	Last imperial dynasty

the presence of lead artefacts in funerary assemblages (Moorey 1994).

In Classical Greece, lead was primarily associated with silver extraction from argentiferous ores, particularly in mining regions such as Laurion, where the exploitation of metal resources played an important role in the Athenian economy. The state exercised ownership over these mines and derived substantial revenue from their operation, while silver ingots produced from these ores were further processed into coinage, vessels, and other valuable objects (Treister 1996, p. 271). Archaeometallurgical evidence also indicates that some lead artefacts and ingots circulating in the Greek world may have originated from Laurion ores, as suggested by isotopic analyses of archaeological finds (Treister 1996, p. 302).

Lead was extensively used in Roman society in a wide range of applications, including water distribution systems, domestic utensils, cosmetics, food and wine processing, and various metallurgical products, reflecting both its abundance and technological accessibility (Nriagu 1983; Waldron 1973). Estimates based on historical and environmental evidence suggest that annual Roman lead production may have reached on the order of 80,000 tonnes at its peak, indicating an unprecedented scale of metal exploitation in antiquity (Hong, Candelone, Patterson, and Boutron 1994; Nriagu 1983). Bioarchaeological studies further show that individuals living during the Roman period often exhibit elevated skeletal lead concentrations compared with earlier or later populations, suggesting increased environmental exposure associated with intensified mining, metallurgy, and urban life (Waldron 1973). Some scholars have proposed that chronic lead exposure among Roman elites, who had greater access to luxury goods and processed food products, may have contributed to reproductive and health problems, although such interpretations remain debated and should be regarded cautiously (Nriagu 1983; Waldron 1973).

1.1.2 Lead isotopes as windows into past societies

Lead isotope analysis provides a powerful means of connecting artefacts, people, and environments across time because the isotopic composition of lead reflects the geological history of ore deposits and generally remains unchanged during metallurgical processing (Pernicka 2014). This relative isotopic stability allows archaeologists to use lead isotopes as geochemical tracers linking artefacts to specific mining regions, thereby reconstructing patterns of resource procurement, technological choices, and long-distance trade networks (Tomczyk, Costa, Giosa, Brun, and Petit 2021; Stos-Gale and Gale 2009).

Such provenance studies contribute to the reconstruction of object biographies by revealing where raw materials were extracted, how they circulated, and how objects moved between production, use, reuse, deposition, and modern collection contexts. These approaches also provide insight into human decision-making in the past, including economic organisation, technological traditions, and cultural preferences in material selection (Pernicka 2014). Lead isotope data derived from human skeletal tissues further extend these perspectives beyond artefacts to lived human experience. Analyses of bones and teeth can record exposure to environmental pollution, metallurgical activity, diet, and mobility, offering evidence for differences in exposure among populations and social groups (Erel, Pinhasi, Coppa, Ticher, Tirosh, and Carmel 2021; López-Costas, Kylander, Mattielli, Fernández, Pérez-Rodríguez, Mighall, Bindler, and Martínez Cortizas 2020). Such bioarchaeological applications demonstrate how metal use affected human health and everyday life in past societies (Erel, Pinhasi, Coppa, Ticher, Tirosh, and Carmel 2021).

Environmental archives such as ice cores, lake sediments, and peat deposits also preserve signals of ancient lead pollution, showing that large-scale mining and smelting activities during antiquity had measurable atmospheric impacts (Hong, Candelone, Patterson, and Boutron 1994; Silva-Sánchez and Armada 2023). These records allow the reconstruction of long-term interactions between human industry and the environment, situating archaeological metallurgy within broader histories of anthropogenic environmental change (Silva-Sánchez and Armada 2023).

Taken together, lead isotopic studies provide not merely technical provenance information but a means of integrating archaeological materials, human biology, and environmental records. They therefore offer a uniquely multi-scalar perspective on past societies, from technological practice and trade to health, mobility, and environmental impact.

1.1.3 Lead isotope research in China today

Lead isotopic analysis has become an essential part of Chinese archaeology, helping to determine the provenance of artefacts and the dynamics of ancient trade and resource distribution. By studying the isotopic signatures of lead in artefacts, researchers can trace the origins of raw materials and understand the technological and economic interactions of past societies. Research objects usually include bronze, glass and glazes. While lead isotope analysis provides valuable insights, it also faces challenges. The interpretation of isotopic data requires careful consideration of geological factors, possible mixing of ores and the complexity of ancient trade networks.

Hsu and Sabatini (2019) created a comprehensive isotope database for Chinese lead ores. This was an important step forward. However, challenges remain when trying to match a specific object to a lead deposit. The main problem is that lead ores from different regions often have overlapping isotope ratios. Another problem is that the isotope ratios seen in ancient artifacts do not always match those of modern lead mines.

As illustrated in Fig. 1.2, there are notable discrepancies between the currently documented artefacts and ores in terms of their isotopic distributions. Lead isotope data compiled from published sources (Chen, Yang, Wang, Wang, and Luo 2021; Li, Zhou, Liu, Wang, Wang, Wang, Tian, and Cui 2020; Li, Zuo, Cui, Tian, Yang, Yi, Zhou, and Fan 2020; Li, Zuo, Cui, et al. 2020; Dai, Zhang, Liu, et al. 2021; Wang 2019; Wen, Ling, Zhao, Zhang, Yao, Zong, Yuan, and Wu 2013; Chen, Qiao, and Luo 2021; Zhang, Fan, Lin, Liu, Shuai, and Chen 2021; Luo, Song, Hu, and Chen 2020; Liu 2017; Sun, Han, Chen, Saito, Sakamoto, and Taguchi 2001; Zhang, Wang, Jia, and Chen 2019; Song and Nan 2012; Bai, Xu, Chen, and Zhang 2021; Li, Jin, Chen, Tian, Wan, and Li 2018; Jin 1993; Liu, Li, and Wang 2019; Jin, Mabuchi, Chase, Chen, Miwa, Hirao, and Zhao 1995; Cui, Han, Jin, and Wu 2009; Nan, Jia, Gao, and Luo 2021; Jin 2008; Cui and Wu 2008; Yang 2005a; Ma, Jin, Fan, Xiang, and Chen 2016; Wang,

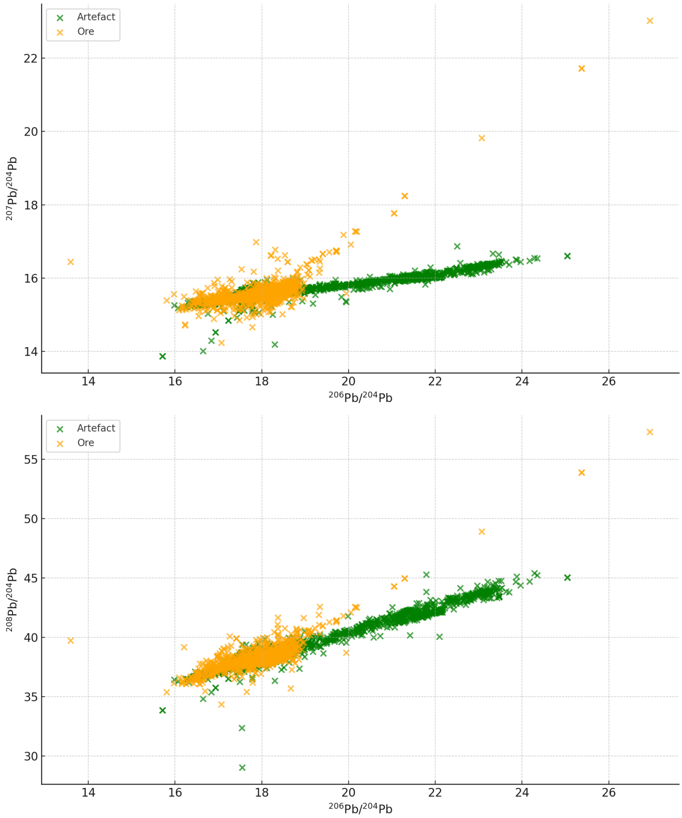

Figure 1.2: Lead isotope ratios for Chinese lead-containing artefacts and galena ores. The upper plot shows ^{207}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb, and the lower plot shows ^{208}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb. Artefact data (green crosses) represent all currently published isotopic measurements of lead-containing archaeological objects from China. Ore data (orange crosses) are derived from the galena isotope database compiled by Hsu and Sabatini (2019). As illustrated, artefacts exhibit a narrower isotopic range, forming a relatively tight cluster compared to the broader, more scattered distribution of ore samples. This contrast suggests selective sourcing or possible refining practices in antiquity, and highlights the need for expanded modern ore sampling and the investigation of ancient mining sites to improve the precision of provenance studies.

Guo, Chen, Liu, Fang, Li, and Fang 2021; Tian, Jin, Li, Yan, and Cui 2010; Liu 2015a; Jin, Liu, Rawson, and Pollard 2017; Chen, Mei, Rehren, et al. 2019; Zhangsun, Liu, Jin, Pollard, Lu, Bray, Fan, and Huang 2017; Liu, Xiao, Mei, Chen, Zhang, and Chen 2016; Xiao, Chu, Yu, Sun, Mei, Chen, and Chen 2016; Han 2017; Jin 1999; Ren 2017; Li 2010; Cui, Wu, Bai, Huang, and Gu 2009; Jin 1993; Hao, Zhang, Du, Huang, and Chen 2021; Zhang, Sun, Hao, et al. 2020; Yang 2014; Li, Li, and Dong 2015; Wang, Zhang, Lei, and Chen 2019; Wei, Wang, Li, Chen, Zhang, and Li 2019; Gao, Dong, Wu, Wang, Huang, and Wang 2024; Liu 2015b; Zhang, Bai, Liang, et al. 2022; Mu, Luo, Huang, et al. 2018; Yu 2015; Li, Chen, Cui, Wu, Yang, Huang, and Xu 2020; Uchida, Xiang, and Hirao 2009; Wang, Wei, Li, et al. 2021; Li, Zuo, Cui, Tian, Yang, Yi, Zhou, and Fan 2020; Mu, Song, Cui, Wang, Wang, and Luo 2014; Liu et al. 2020; Chen, Yang, Du, et al. 2020; Wang, Luo, Yang, Chen, Du, and Tang 2020; Gao, Jin, Wang, Chang, Wang, Lv, Fan, and Yeung 2021; Chen, Yang, Jiang, Yang, Tang, and Luo 2021; Chen, Han, Wang, Chen, Cai, and Liu 2021; Zhangsun, Liu, Jin, Pollard, Lu, Bray, Fan, and Huang 2017; Huang, Wu, Chen, et al. 2021; Zhang, Cui, and Chen 2020; Jia, Yao, Zhao, Ling, Liu, and Yuan 2015; Ma, Wang, Li, Wang, Yang, Yang, and Luo 2024; Ma, Wang, Li, Yang, Yang, Wang, and Luo 2024; Wang, Yang, Wang, and Luo 2024; Wei, Zhang, Shi, and Wang 2024; Wang, Liu, Gao, Pollard, Fan, Huang, Li, Zhang, Hua, and Jin 2024; Yang, Wu, Liu, Wang, Shi, Qu, Tian, Hua, and Zhang 2023; Sun, Zhang, Wei, et al. 2024; Chen, Luo, Zeng, and Cui 2018).

Firstly, the isotopic values for the artefact (green points) tend to cluster within a distinct range, resembling a narrower band, while the ore (orange points) displays a broader and more scattered distribution. Secondly, artefacts exhibit less variability compared to ores, which may indicate the potential for refinement or selective sourcing in the production of artefacts. The isotopic distinction suggests that ancient Chinese metallurgists may have relied on a subset of the lead sources currently available, potentially due to accessibility, quality, or technological constraints. This contrast also highlights the importance of constructing a robust lead isotope database for modern ores to facilitate more precise provenance studies for ancient artefacts. Furthermore, the investigation of ancient lead mines would be beneficial in this regard.

1.1.3.1 Regional frameworks in lead isotope studies of China

In Fig. 1.3, we could see that the ore data shows high-density clusters primarily in the very central area of China (Henan area), the Yangtze River Basin, Southwest China, and parts of North China. These areas correspond to major metallogenic belts, such as the Middle-Lower Yangtze Metallogenic Belt and the Qinling-Dabie Metallogenic Belt. In contrary, Western China and certain parts of Central China display sparse or no data points, indicating either a lack of mineralization or insufficient exploration efforts. This visual representation explicitly captures the spatial unevenness in ore

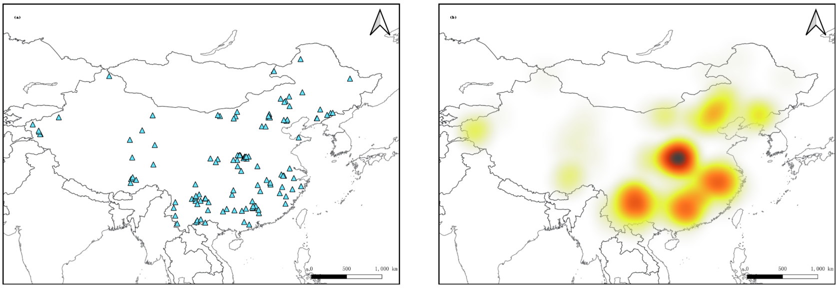

Figure 1.3: the distribution of modern lead deposits in China, from the database of Hsu and Sabatini (2019). On the left, individual deposit's locations are represented as blue triangular markers. On the right, a heatmap further illustrates the density distribution of ore locations. High-density clusters are represented with dark red and yellow gradients, corresponding to the same regions identified in the left panel.

data distribution.

Several factors contribute to this uneven distribution. First, geological conditions play a key role, as the clustering of ore data aligns with areas of favorable tectonic and magmatic activities essential for mineralization. Conversely, regions with sparse data often lack these conditions. Second, the disparity in exploration efforts significantly influences data distribution. Historically, economically significant and easily accessible regions, such as Eastern and Central China, have received more attention, while remote areas like Tibet and Xinjiang remain underexplored due to logistical challenges and harsh environmental conditions. A third issue is that historical and economic factors shaped mining activities. Regions rich in resources were often prioritized because of their economic value. Areas with sparse data may have been overlooked due to limited industrial or economic incentives. Lastly, gaps in the dataset may also arise from incomplete reporting, inconsistent methodologies, or a lack of regional studies.

The density and spatial distribution map (Fig. 1.4) shows the number of lead isotope datasets for lead-containing artifacts in each province of China. Regions with higher densities reflect a greater number of LI datasets, whereas regions with lower densities indicate fewer datasets.

From this map, it is evident that Shanxi province contains the highest number of LI datasets. Other provinces, such as Henan, Shaanxi, Shandong, and Sichuan, also display darker shades on the map, reflecting a relatively higher density of lead isotope data. In contrast, peripheral regions, particularly in the northeast, northwest, and southern coastal provinces, exhibit significantly lower densities or even complete gaps in data coverage.

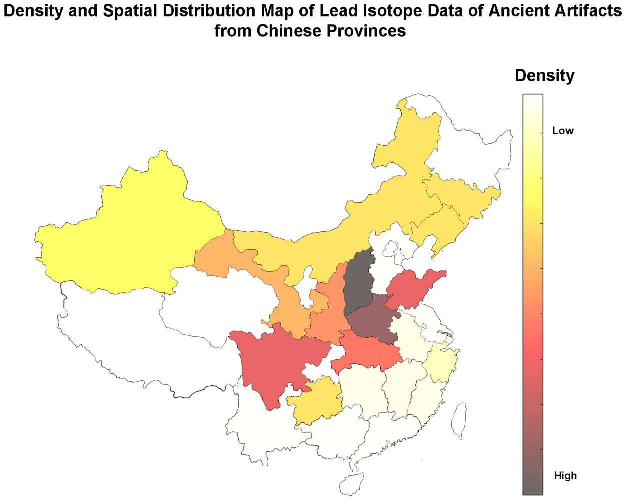

Figure 1.4: Density and spatial distribution of lead isotope data from ancient artifacts across Chinese provinces (The data sources are the same as those used in the published data shown in Fig. 1.2.). This choropleth map visualizes the number of published lead isotope measurements associated with archaeological artifacts within each province. A gradient colour scheme, ranging from light yellow (low density) to dark red (high density), is used to represent relative data concentration, as shown in the legend on the right. The darker regions, including Henan, Hubei, and Shaanxi, correspond to areas with more intensive sampling or reporting in the current literature, potentially reflecting both archaeological research focus and historical centres of metallurgical activity. In contrast, provinces in lighter shades indicate lower data availability, highlighting regional disparities in isotopic documentation.

The uneven distribution of lead isotope data from ancient Chinese artifacts, as shown in the figure, can be attributed to several potential factors: 1) Regions with lower data density may simply have had fewer ancient artifacts. This might reflect historical underdevelopment, with smaller populations or less metallurgical and cultural activity. 2) The size of ancient populations directly influenced the production and use of artifacts. Regions with smaller populations, such as remote areas in the northwest or northeast, likely produced fewer artifacts. This in turn left fewer opportunities for isotope analysis today. 3) Academic research often focuses on regions of well-known historical importance, such as the Yellow River and Yangtze River basins, where ancient Chinese civilization developed. Peripheral areas, or regions seen as less significant for archaeology, have received less attention. In addition, limited funding and logistical challenges make exploration and data collection in remote regions more difficult. 4) Modern excavation and conservation practices are often linked to local infrastructure and political interest. Remote regions with limited resources or infrastructure may face greater challenges in conducting systematic archaeological surveys.

1.1.3.2 Spatial frameworks in lead isotope studies of China

Figure 1.5 presents a pie chart of lead isotope data by dynasty. The chart shows clear variation in the amount of data available for each period. Eastern Zhou period (770–256 BCE) accounts for the largest proportion of lead isotope data, about 38% of the total. This dominance suggests that the Eastern Zhou was a very active era for lead use. It also reflects the strong archaeological focus on this period, with both extensive use of lead resources and good preservation of artifacts. Ranking second, Shang dynasty (1600–1046 BCE) contributes nearly a quarter of the total data. This indicates significant exploitation and recording of lead resources during this time. The Western Zhou period (1046 BCE–771 BCE) accounts for a substantial share of the data (18.7%), suggesting a continuity or evolution in lead resource use from the Shang to the Zhou periods. The Pre-Shang period, despite its early date, provides a notable portion of the dataset. This suggests initial experimentation with lead, though less extensive than in subsequent dynasties. The Western Han (202 BCE–9 CE) data constitute a smaller portion, indicating either reduced reliance on lead or limited archaeological records from this period. Together, the Eastern Han and Tang account for less than 1% of the total. Such low representation may reflect historical, technological, or preservation factors. It suggests either limited lead use or less research focus on these periods.

This distribution provides valuable insights into the relationship between LI data and the focus of bronze artifact research, as well as potential directions for future studies:

1. The high concentration of LI data in the Eastern Zhou, Shang, and Western Zhou matches their role as major eras of bronze production. Most current lead isotope research focuses on bronzes, so it is not surprising that these periods provide abundant data. The widespread use of bronze in these dynasties left a large archaeological record that has been studied in detail. This also means that the scarcity of LI data in other periods does not necessarily show a lack of lead use, but rather reflects a research bias toward bronzes.

2. Lead isotope data from the Han dynasty and later periods are minimal. This highlights the need for broader research on non-bronze lead artifacts. Ceramics with lead glaze, glass, and pigments were widely used in these eras and deserve more attention. Expanding research to these materials could give a fuller picture

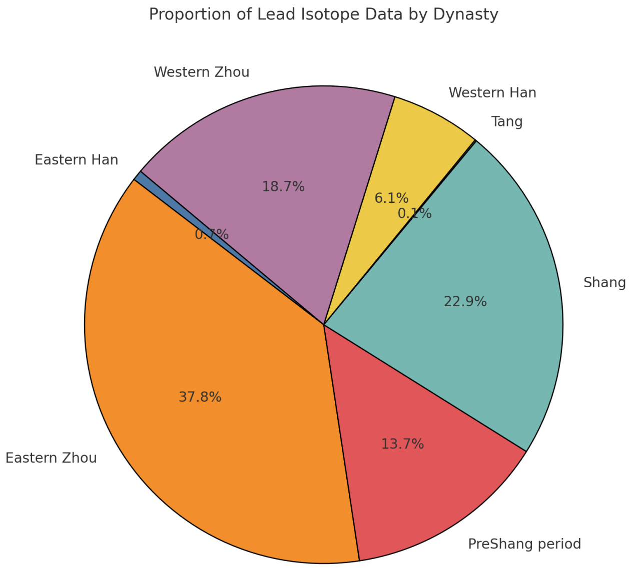

Figure 1.5: Proportion of lead isotope data from ancient Chinese artifacts by dynastic period (The data sources are the same as those used in the published data shown in Fig. 1.2.). The pie chart illustrates uneven representation across periods, with the Eastern Zhou accounting for the largest share (38%), followed by the Shang (23%) and Western Zhou (19%) periods. The Pre-Shang period also contributes a notable portion (14%). In contrast, later periods such as the Western Han, Eastern Han, and Tang exhibit minimal data, possibly reflecting reduced lead usage, limited archaeological recovery, or lower research focus.

of lead use and its technological development. For example, lead-glazed ceramics in the Han or pigments in Tang paintings may offer new insights into technology and trade networks of these periods.

1.1.3.3 Methods for the interpretation of lead isotope data

Traditional bivariate plots are mainly used to analyze data by visually comparing the lead isotope signatures of artifacts and ore deposits (De Ceuster and Degryse 2020). By plotting two isotopic ratios against each other, commonly $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, researchers can discern patterns, identify groupings, and infer the provenance of archaeological artifacts or geological samples. These plots also help detect mixing lines, indicating the combination of materials from different sources. In geology, bivariate plots assist in understanding ore formation processes and the evolution of lead isotopic compositions over time.

However, bivariate plots have several limitations that can hinder the interpretation of complex datasets. For example, when samples result from the mixing of materials from multiple sources, their isotope ratios often align along a straight line in the plot. While this indicates mixing, it does not quantify the contributions from each source. They also struggle to disentangle the contributions when more than two sources are involved, making it challenging to accurately interpret mixing processes. In regions where lead isotope ratios from different ore deposits are similar, data points often cluster together on the plot, making it difficult to distinguish between sources. This is particularly problematic in geologically homogeneous regions, where isotopic overlaps are common. When data points overlap, small but significant trends may be obscured, making the analysis harder to interpret. Bivariate plots often depend on visual matching when comparing samples and ore deposits. While useful, this method is partly subjective and offers limited statistical robustness.

While traditional bivariate plots are intuitive and useful for initial data exploration, their limitations make them unsuitable for addressing the complexities of modern LI analysis. Advanced techniques, such as multivariate statistical methods (e.g., PCA), mixing models, isochron analysis, and density estimation, are necessary to overcome these challenges. These approaches can better account for data complexity, uncertainty, and multidimensionality, providing more robust insights into provenance and mixing processes. For example, Longman, Veres, Ersek, Phillips, Chauvel, and Tamas (2018) applied a Bayesian isotope mixing model to study dust sources in pre-industrial samples, to trace changes in ore exploitation during the Roman era, and to identify the origin of a Roman mining artifact. The study shows that this approach can effectively detect shifts in lead sources. It works for both natural Pb cycling in pre-anthropogenic periods and for Roman times, when human activity created significant pollution. This makes the method a reliable tool for tracing Pb sources in different environmental contexts.

Pollard and Bray (2015) also presented a new methodology for interpretation of lead isotope data from cooper alloy artefacts. Their method adapted from isotope mixing models, which are more commonly utilized for presenting strontium isotope data. The method involves plotting LI ratios against lead concentrations, allowing hyperbolic or linear mixing lines to emerge, which indicate contributions from different isotopic sources. This presentation aids in identifying mixing events, pinpointing sources with consistent isotopic values, and discerning recycling or alloying processes.

No new methodology has gained widespread acceptance, as most scholars continue to rely on traditional scatter plots for analysing lead isotope data. This phenomenon can be attributed to several factors: 1) Traditional scatter plot analyses have been used for decades and are deeply entrenched within the academic community. Scholars often prefer familiar methodologies rather than investing time and resources to learn and validate new approaches. 2) The adoption of new methodologies typically requires time. Academic recognition often depends on the accumulation of high–quality case studies and peer-reviewed validations, which take significant effort and time to establish. 3) Traditional methods are widely supported by existing analytical software and tools, whereas new methodologies may necessitate the development of novel computational tools or technical support, potentially limiting their dissemination. 4) New approaches might require data of different formats or qualities, rendering traditional datasets incompatible. This creates additional barriers for reanalysing existing research. Also, bi–plots are still effective when addressing simple research questions.

Currently, the field of LI analysis in archaeology is increasingly experimenting with novel methodologies. In the future, it is likely that a coexistence of multiple approaches will emerge, each tailored to specific research questions, data contexts, and analytical needs. This diverse environment could enrich the discipline by providing complementary insights and fostering methodological innovation.

1.2 Research problem

1.2.1 Provenance and circulation of lead in ancient Chinese glass and glaze: evidence from eight samples of the Warring States and Han periods

The provenance and circulation of lead in ancient Chinese glass and glaze remain underexplored topics in archaeological science. While lead is a key component in both materials, its specific sources and the mechanisms of its distribution across different regions and periods are not yet fully understood. Four lead-barium glass disks and four lead glazed potteries from the Warring States Period (475–221 BCE) and the Han dynasty (202 BCE–220 CE) China are analysed in this study. The lead glazed potteries from Han China are analysed by lead isotopic characteristics for the first time. These studies sheds light on the technological and economic exchanges in these periods China.

1.2.2 Overlap, indistinctiveness and grouping of lead resources in China

Lead resources in China show extensive isotopic overlap. This makes source attribution difficult. Traditional frameworks group deposits using geographic or geological categories together with isotope data. Such priors may not match the structure of the isotope space. This study asks whether deposits can be grouped directly from their lead-isotope signatures, without geographic assumptions. It also asks how such isotope-based groupings relate to the grouping of lead-containing artifacts through time and space. To address the overlap, the study develops a measure of indistinctiveness that quantifies how similar deposit signatures are.

1.3 Research objectives and aims

This study investigates the provenance and circulation of lead in ancient Chinese glass and glaze artifacts with the aim of improving our understanding of the technological and economic activities associated with these materials. Specifically, it seeks to identify the sources of lead used in ancient glass and glaze through isotopic analysis of four lead-barium glass disks and four lead-glazed pottery samples. The research also conducts lead isotopic analysis of Han-period lead-glazed pottery to explore patterns of lead resource utilization and circulation. Although the number of samples is limited, the study aims to provide preliminary insights into ancient resource supply networks and the movement of raw materials or finished products through an examination of lead use in these materials.

In addition, this research addresses the issue of overlap, indistinctiveness, and grouping of lead resources in China. It aims to develop a methodological framework that tackles the challenge of isotopic overlap in Chinese lead resources by moving beyond traditional geography–or geology–based grouping approaches. Instead, the study evaluates isotope-driven classifications and introduces a new measure of indistinctiveness designed to capture isotopic overlap and ambiguity. This involves critically assessing the statistical validity and archaeological applicability of existing lead resource zoning definitions that have been used for many years. The study further explores whether previously defined Pb resource zones can actually be distinguished using lead isotopic analysis and, if not, considers possible alternative zoning approaches.

A key component of this work is the introduction and formalization of the concept of indistinctiveness through the development of an Indistinctiveness Index, intended as a quantitative measure of isotopic overlap and ambiguity among lead deposits. The research also examines whether lead found in artifacts from different temporal and spatial contexts can be reliably classified using isotopic data, and whether isotopically grouped artifacts can correspond to proposed lead resource zones, thereby shedding light on the complexity of lead resource movement, mixing, and distribution in ancient China.

1.4 Scope of the study

This study primarily focuses on lead–containing objects from ancient China, with particular emphasis on understanding their provenance and circulation. While the core dataset consists of Chinese artifacts, comparative perspectives from neighboring regions, including Japan, the Korean Peninsula, and Southeast Asia are also considered where relevant. The research encompasses three main categories of artifacts: lead–barium glass objects, which are examined to understand material composition, production technology, and possible resource origins; lead-glazed pottery, which is analyzed to identify isotopic characteristics and reconstruct patterns of lead use in ceramic technologies; and bronze artifacts, which are included as a comparative dataset to evaluate potential overlaps in lead sources and broader patterns of resource utilization.

It should be noted that this study does not extend to the investigation of lead ore deposits located outside China. Instead, the analysis focuses on lead sources within China and their implications for resource exploitation, technological practices, and cultural interactions during the ancient periods under consideration.

1.5 Significance of the study

1.5.1 Contribution to ancient Chinese glass and glaze research

Lead isotopic research on ancient Chinese glass and glaze remains a relatively underexplored area, particularly in relation to Han Dynasty lead–glazed pottery. By examining the isotopic characteristics of these materials, this study seeks to contribute to a better understanding of ancient Chinese glass and glaze, offering preliminary perspectives on the technological practices and material exchanges of this period.

1.5.2 Revisiting lead resource overlap and zoning

Large-scale studies on the overlap and distribution of lead resources in China are still limited. This study evaluates the statistical reliability and practical use of existing lead resource zoning frameworks. It also explores possible refinements or alternative groupings through isotopic and statistical analysis. These steps are important for improving the accuracy of archaeological lead provenance studies.

1.5.3 Quantifying indistinctiveness to understand lead isotopic ambiguity

The significance of this study lies in the introduction of indistinctiveness as a new way to address the long–standing challenge of isotopic overlap in lead provenance research. Previous frameworks often relied on grouping deposits within geographic or geological boundaries, which imposed rigid categories and obscured the true extent of isotopic similarity. By contrast, the Indistinctiveness Index quantifies ambiguity directly, making overlaps between deposits visible rather than forcing them into predefined groups. This shift provides archaeologists with a more transparent and flexible tool for evaluating provenance questions.

1.5.4 Integrating geochemical and computational approaches

By combining geochemical methodologies with computational techniques within an archaeological framework, this study uses interdisciplinary approaches (kernel density estimates and k–means) to investigating ancient resource use. This integration offers a more robust means of analyzing lead isotopes, enabling deeper insights into ancient societies, their resource networks, and their cultural interactions.

1.6 Methodological framework

1.6.1 Experimental tools and methods

1.6.1.1 Artifact sampling:

Fragments were lifted from the glaze/glass with stainless steel tools (spatula, pick) cleaned with lab wipes and ultra–pure (milliQ) water (>18 Mohm/cm3). Preparation includes grinding to powder for isotopic and microscopic analysis.

1.6.1.2 X–ray fluorescence (XRF) analysis and scanning electron microscopy with energy dispersive microanalysis (SEM–EDX):

This study applied a combination of non–destructive and micro-destructive analytical techniques, specifically X–ray fluorescence (XRF) and scanning electron microscopy with energy dispersive X–ray microanalysis (SEM–EDX), to investigate the elemental composition of glass and ceramic glaze samples.

For the glass samples, including four glass disks (1943.50.521, 1943.50.551, 1943.50.585, and 1943.50.586), in situ XRF analysis was conducted at the Harvard Art Museums. The instrument used was a Bruker Artax spectrometer equipped with a Silicon Drift Detector (SDD) and a rhodium anode X-ray tube. The X–ray beam was collimated to a spot size of 0.65 mm. Operating conditions were set at 50 kV and 600 μA, with a live acquisition time of 100 seconds per spectrum. A helium flush was applied to enhance sensitivity to low atomic number elements such as sodium and potassium. This method was entirely non-destructive and provided qualitative data on glass composition, enabling the identification of general compositional trends. However, as no calibration against reference standards was performed, the results are not quantitative.

For the ceramic vessels, portable XRF was first employed to identify elemental components and confirm the lead-rich nature of the glaze. To obtain more accurate quantitative data, small fragments of glaze were subsequently sampled from pre–existing damaged areas. These samples were mounted and polished in preparation for analysis using SEM–EDX. This method enabled high-resolution, quantitative characterization of the glaze's elemental composition, providing insights into technological choices, raw material selection, and production techniques.

1.6.1.3 Lead isotope analysis (LIA):

Lead isotope analysis was performed on both glass and glaze samples. The analytical procedures were adapted from Rademakers, Verly, Somaglino, and Degryse (2020), with consistent instrumentation and data correction protocols applied across all sample types.

While abbreviated methodological descriptions were provided in previously published papers, a more detailed analytical overview is presented here to improve reproducibility and methodological transparency.

Sample preparation and digestion. For the glass samples, surface corrosion products and small detached particles were carefully collected and manually powdered. For the glaze samples, unmounted fragments not used for SEM analysis were ground to a fine powder using an agate mortar. Approximately 10–30 mg of powdered material was weighed into 7 ml Savillex PFA screw-top beakers and subjected to a multi-stage acid digestion procedure.

Samples were first digested in a mixture of concentrated HF and HNO_3 on a hotplate at approximately 110 °C overnight. After evaporation to near dryness, residues were treated with aqua regia (HCl–HNO_3 mixture) under similar heating conditions to ensure complete dissolution. The final residues were taken up in dilute HNO_3 prior to chromatographic lead separation.

Lead separation chemistry. Lead purification was achieved using ion-exchange chromatography with Pb–SPEC resin (Eichrom Technologies). Chemical separation procedures were carried out in a Class 10 clean laboratory environment at Ghent University (Belgium), following established isotope geochemistry protocols designed to minimise contamination. Procedural blank Pb concentrations were negligible relative to sample Pb concentrations.

Instrumental analysis. Lead concentrations of purified solutions were determined using a Thermo Scientific Element XR sector-field ICP-MS to calculate appropriate dilutions for isotopic measurements. Samples were diluted in 3% HNO_3 to approximately 200 $\mu g L^{-1}$ Pb to match the NIST SRM 981 common lead standard used for sample–standard bracketing.

Lead isotope ratios were measured using a Thermo Scientific Neptune multi–collector inductively coupled plasma mass spectrometer (MC–ICP–MS). A seven-collector configuration simultaneously monitored $^{202}Hg^+$, $^{203}Tl^+$, $^{204}Pb^+/^{204}Hg^+$, $^{205}Tl^+$, $^{206}Pb^+$, $^{207}Pb^+$, and $^{208}Pb^+$ signals. Thallium (NIST SRM 997) was added as an internal standard for mass bias correction, and isobaric interference of ^{204}Hg on ^{204}Pb was evaluated by monitoring ^{202}Hg.

Quality control and data correction. Blank corrections were applied to all measurements. Raw isotope ratios were corrected for instrumental mass discrimination using Tl normalisation following Russell's law, calibrated against repeated measurements of the NIST SRM 981 standard. Measurement uncertainties were calculated following standard isotope data reduction approaches, with analytical precision typically better than 0.03% for ratios involving ^{204}Pb and better than 0.008% for ratios normalised to ^{206}Pb. Between each sample and standard measurement, a 3% HNO_3 blank was analysed and the sample introduction system rinsed to minimise memory effects.

Consideration of corrosion sampling and potential diagenesis. Because some glass samples were derived from surface corrosion products, potential diagenetic effects cannot be entirely excluded. However, lead glasses and lead-rich glazes generally contain Pb at weight-percent levels, meaning that environmental Pb contributions from burial contexts are typically minor relative to the intrinsic Pb content of the artefacts. Corrosion processes may even result in Pb enrichment within alteration layers. Where quantitative Pb concentration data are unavailable, this uncertainty is acknowledged as a limitation when interpreting isotopic signatures.

Lead isotope analyses followed established analytical procedures including acid digestion, ion-exchange chromatographic Pb purification, MC-ICP-MS isotope ratio measurement, and standard data correction protocols (Rademakers, Nikis, De Putter, and Degryse 2018; Smet, De Muynck, Vanhaecke, and Elburg 2010; Walder, Platzner, and Freedman 1993; Ketterer, Peters, and Tisdale 1991; Galer and Abouchami 1998). Measurement uncertainties were calculated following the approach of Ludwig (Ludwig 1980).

1.6.2 Analytical and statistical methods

Statistical methods, such as Kernel Density Estimates (KDE) and K–means clustering, were applied to evaluate lead isotopic compositions and visualize patterns in the dataset. Software such as R© and PyCharm© was used extensively for data analysis and modelling.

1.6.2.1 Kernel density estimates (KDE):

Kernel density estimates (KDE) was used in this study to assess the potential provenance of lead used in both glass and glaze samples. KDE is a non–parametric statistical method for estimating the probability density function of a continuous variable and has been increasingly adopted in archaeological lead isotope (LI) research to visualize complex isotopic distributions and assess source attribution. While KDE has previously been applied to Chinese bronze artifacts Hsu, Rawson, Pollard, Ma, Luo, Yao, and Shen (2018), this study represents the first application of the method to ancient Chinese glass and glaze materials.

For each sample, its isotopic ratios were compared to two reference datasets: one comprising geological lead mining districts, and the other composed of archaeological lead usage districts. The mining district dataset consists of published lead isotope compositions of galena from different ore sources. The usage district dataset aggregates isotopic data from ancient artefacts (e.g., bronze, glass) that share spatial and chronological contexts, reflecting historical patterns of lead exploitation and consumption.

The relative probability that a sample originates from a specific mining or usage district was determined by integrating the area under the KDE curve corresponding to the sample's lead isotope ratios ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$). The integration interval for these calculations was set at ten times the standard deviation of the KDE distribution. Bandwidth selection followed the method proposed by Sheather and Jones (1991), which has demonstrated consistent performance in geochemical provenance studies (De Ceuster, Machaira, and Degryse 2023).

All KDE calculations and graphical comparisons were performed using R© software, utilizing both newly generated and legacy datasets. A match in all three isotope ratios with a given reference distribution may indicate shared provenance or common lead sourcing, whereas a lack of match could reflect the use of lead not represented in the reference datasets, or suggest a composite or recycled origin of the material.

In addition, KDE was also applied to calculate the degree of overlap among Chinese ore deposits. This provided the foundation for Chapter 4, which develops a risk-aware framework for assessing lead isotope indistinctiveness, introduces the Indistinctiveness Index, evaluates regional trends and risk distributions, and discusses robustness and limitations, with exploratory grouping analyses included in the appendix.

1.6.2.2 K–means clustering:

This unsupervised machine learning algorithm partitions data points into clusters. The elbow method is applied to determine the optimal number of clusters based on the within–cluster sum of squares (WCSS). This approach ensures the effective grouping of isotopic data.

1.6.2.3 Legacy data integration:

The study compiled extensive databases of lead isotopic signatures from natural ore deposits and previously published archaeological artifacts. These datasets provided a comparative framework for determining the provenance of the studied artifacts and identifying new or unexpected patterns of lead circulation.

1.6.2.4 Visualization of overlap and probabilistic matching:

A novel approach was used to visualize overlaps in lead isotopic data using KDE–generated plots and overlap matrices (De Ceuster and Degryse 2020). Probabilistic matching was performed by integrating the isotopic characteristics of the studied samples with reference datasets, enabling hypotheses about their geological origins or their relationship to other artifacts.

1.6.3 Approaches to provenance and circulation studies

The methodologies described in this study are integrated to create a comprehensive framework for investigating the provenance and circulation of raw materials in ancient artifacts. This integrative approach highlights the complementary roles of experimental tools and statistical analyses, ensuring robust and reproducible results. Key aspects of this integration include:

1.6.3.1 Combining experimental and statistical techniques

Experimental methods such as XRF, SEM–EDX, and LIA provide foundational data on elemental composition and isotopic ratios. Statistical tools, including KDE and K–means clustering, enhance the interpretive power of these datasets by identifying patterns, overlaps, and distinctions in material provenance.

1.6.3.2 Visualization and data interpretation

KDE and clustering analyses are used to show the distribution and relationships of lead isotopic data. Color–coded matrices, dendrograms, and heatmaps provide intuitive views of complex datasets. Conventional tools such as scatter plots, density curves, and bar charts are also applied in this dissertation to illustrate isotopic patterns in simple ways. The framework further includes approaches that make isotopic ambiguity explicit. This allows uncertainties to be assessed in a systematic and transparent manner.

1.6.3.3 Innovative application to historical materials

The KDE method has been applied in a few studies of archaeological materials. In this dissertation, it is applied to lead isotopic analysis of ancient glass and ceramics. This combination offers new insights into the circulation of lead resources in historical contexts. Machine learning methods, such as K-means and hierarchical clustering, are also integrated.

1.6.3.4 Significance in historical interpretation

This study integrates multiple methods. It identifies potential sources of raw materials. It also reconstructs the circulation networks of lead during specific historical periods. In doing so, it connects scientific data with archaeological narratives. These combined approaches offer deeper insights into ancient technological practices and economic systems.

1.7 Thesis outline

Chapter 1 (Introduction) reviews the historical use of metallic lead and lead isotope research in China, and sets out the research problem, objectives, aims, scope, and significance of the study. It also introduces the methodological framework adopted and outlines the overall structure of the thesis.

Chapter 2 presents a methodological case study of lead resource movements during the Warring States period (475–221 BCE) and the Western Han dynasty (202 BCE–8 CE), focusing on four lead–barium glass disks. This chapter applies kernel density estimates (KDE) to isotopic analyses, and compares the results with both raw materials and other archaeological artifacts.

Chapter 3 examines circulation dynamics in the Han dynasty (202 BCE–220 CE) through isotopic analysis of lead-glazed pottery. It describes the materials, methods, and analytical results, and discusses the origin of the raw materials, their relation to other artifacts, and the broader implications for Han expansion and exchange networks.

Chapter 4 develops a risk–aware framework for assessing lead isotope indistinctiveness in Chinese ore deposits. It introduces and constructs the Indistinctiveness Index, evaluates regional trends and risk distributions, and discusses robustness and limitations. An appendix provides additional analyses of grouping attempts and their implications.

Chapter 5 (Discussion) situates the findings within broader archaeological debates. It argues that lead isotopes function more like mitochondrial DNA than fingerprints in provenance studies, and discusses artifacts as carriers of isotopic “lineages”. It also evaluates the justification of proximity-based procurement, explores grouping strategies for artifacts, and reflects on what comparing cultural and natural lead can reveal about ancient societies.

Chapter 6 (Conclusion and Future work) summarizes the main contributions of the study and suggests directions for future research in both methodological development and archaeological application.