# Every Cloud has a Silver Lining: Using Silver Concentration to Identify the Number of Sources of Lead used in Shang Dynasty Bronzes



LIU Ruiliang<sup>1</sup>, A. Mark POLLARD<sup>1,\*</sup>, LIU Cheng<sup>2</sup> and Jessica RAWSON<sup>1</sup>

<sup>1</sup> School of Archaeology, University of Oxford, Oxford, United Kingdoms (OX1 3TG)

<sup>2</sup> School of Cultural Heritage, Northwest University, Xi'an 710069, China

**Abstract:** The use of lead, some of which is characterized by a highly radiogenic signature, sharply distinguishes Bronze Age China from the rest of Eurasia. Scholars have long hypothesized that silver can offer an independent proxy to characterize lead minerals. The summary of silver distribution associated with Shang and Western Zhou bronzes in this paper reveals an important difference between the south (Sanxingdui, Hanzhong, Jinsha, Panlongcheng, Xin'gan) and the Central Plains. Correlating silver with lead content as well as with the isotopic signature indicates that south China and the Central Plains had different lead sources during the late Shang period, and also that the highly radiogenic and common lead used at Anyang come from geochemical environments which cannot be distinguished by the level of silver.

Key words: lead Isotopes, highly radiogenic, silver, Shang and Western Zhou, Bronze Age China

Citation: Liu et al., 2020. Every Cloud has a Silver Lining: Using Silver Concentration to Identify the Number of Sources of Lead used in Shang Dynasty Bronzes. Acta Geologica Sinica (English Edition), 94(3): 585–593. DOI: 10.1111/1755-6724.14530

# **1** Introduction

The Bronze Age of dynastic Central China is completely unlike that encountered elsewhere in Eurasia. The first bronze objects perhaps arrive in the Hexi Corridor (the present Gansu province) in the far west of modern China around the first half of the second millennium BCE (Mei et al., 2015; Chen, 2017). They consist of the single bladed knives or personal ornaments in the steppe style and are made of an alloy very similar to that seen elsewhere in southern Siberia - pure copper, tin bronze or copper arsenic alloys (Chernykh, 1992). What happens next is remarkable. The transformation begins at Erlitou, where we see cast bronze objects in its Phase II (e.g. the bell) and Phase III (bronze ritual vessels). The shapes are changed from the 'Steppe style' to ritual vessel forms based on those of Neolithic ceramics from the east coast of China (Zhang et al., 2019). All the objects are cast in ceramic piece moulds, which are the forerunners of the complex moulds found at Anyang in the Late Shang period (ca. 1300-1046 BCE). The metal used is also changed from the Steppe metal to a ternary copper-tin-lead alloy (leaded bronze), which dominates all future Chinese bronze metallurgy (Liu et al., 2015; Pollard et al., 2017).

Some of these very earliest Chinese bronze vessels cast at Erlitou (c. 1750–1500 BCE) can contain over 30% lead (IA CASS, 2014: 1515–1518). The Erlitou bronzes are highly variable in lead and tin content, but in the subsequent Erligang period the range of variation in lead becomes much narrower, suggesting that the addition of lead had become highly organized and controlled. Leaded tin-bronze was subsequently used to cast the overwhelming majority of ritual vessels in the Central Plains during the Erligang (c. 1500-1300 BCE) and Anyang (c. 1300–1046 BCE) periods of the Shang, and also into the Western Zhou period (c. 1046-771 BCE). These bronze vessels were normally used for ritual purposes, especially in the ceremonies of worshipping ancestors. Each of them may contain from 2-10 kg of metal and there are hundreds of thousands of examples surviving. The heaviest one known weighs ~836 kg. The tomb of Fu Hao at Anyang, the highest ranking royal tomb discovered intact, contained nearly three hundred bronze ritual vessels with an overall weight of ~1600 kg. The sources of this lead are, therefore, of great importance to an understanding of the nature of the Shang and Zhou bronze industries. In this paper, we present a systematic summary of the relationship between silver, lead concentration and lead isotopes in Chinese bronzes, which contributes to the debate about metallurgical resource exploitation and trade in early Bronze Age China.

### 2 Lead Isotopes in Chinese Bronzes

Lead isotope analysis is the primary method that has been applied to the question of lead sources in ancient China (e.g., Cui and Wu, 2008; Jin Z, 1987, 1990, 2008; Chen, 2014; IA CASS, 2014; Mei et al., 2015; Liu et al., 2015, 2018; Jin et al., 2017). In previous publications a new visual tool has been employed for exploratory data analysis to the existing body of Chinese lead isotope data from the Erlitou to the Eastern Zhou periods (c. 1750–256 BCE), clearly showing a number of changes in the lead

© 2020 Geological Society of China

<sup>\*</sup> Corresponding author. E-mail: mark.pollard@arch.ox.ac.uk

isotope signal over this time (Jin et al., 2017; Liu et al., 2018). In most of the Shang and Zhou ritual bronze vessels the lead levels are sufficiently high (~2-20%) that the measured lead isotope ratio in a particular object must reflect that in the added lead, rather than the traces introduced by the copper or tin. However, despite several decades of applying lead isotopic analysis to sourcing the lead used in the Shang period, it has not been possible to definitively quantify the number of sources of lead used at a particular time, or their geographical location. This paper approaches the question from a different direction, by looking at the silver levels in the objects, which, for explained below, potentially reflect the reasons geochemical nature of the lead sources used. The levels of silver have rarely been considered in the chemical study of Chinese bronzes, apart from the work on the Hanzhong metal assemblage (Chen et al., 2009). Here we return to an important but neglected point about silver made by Barnard and Satō (1975: 22, 70), discussed in more detail below.

One of the most significant observations made over recent years is the now well-known fact that Shang Dynasty bronzes often contain lead which is usually described as 'highly radiogenic' (which we define as having  $^{206}Pb$   $/^{204}Pb \geq 19;$   $^{207}Pb/^{204}Pb \geq 15.7;$   $^{208}Pb/^{204}Pb \geq$ 40). On this basis, Jin Zhengyao and his colleagues have argued that the lead contained in the ritual bronze vessels of Anyang might have originated in southwest China, specifically northeast Yunnan, which is around 1200 kilometres in linear distance from the Shang capital at Anyang (Fig. 1; Jin, 1987; Jin et al., 1995, 2004, 2006, 2017). It was argued at the time that northeast Yunnan appeared to be the only region in China capable of vielding highly radiogenic lead similar to (but not exactly as same as) that found in the Anyang bronzes. Moreover, the same research showed that their successors, the Western Zhou, usually used lead with a lower ratio of 206Pb/204Pb (< 19), often referred to as 'common lead'. More generally, lead isotope analysis has also shown the predominance of objects containing radiogenic lead at the site of Sanxingdui in the south-west, approximately contemporary with Shang Anyang, with its remarkable deposits of human-like heads and masks (Jin et al., 1995). Subsequently, several other sites have been shown to have a preponderance of objects containing highly radiogenic lead. These include Sanxingdui's successor site at Jinsha (Jin et al., 2004), and also Hanzhong, with both locally made and imported bronzes (Jin et al., 2006; Chen et al. 2019) in the southwest. Further south, Panlongcheng (Peng et al., 2001; Sun et al., 2001), closely related to the Erligang capital at Zhengzhou (Bagley, 1977; Tian, 2013; Liu et al. 2017), and Xin'gan, the site of a large deposit of bronze vessels and weapons related to but distinct from those at Zhengzhou and Panlongcheng have also been shown to contain objects with highly radiogenic lead (Jin et al. 1994). This dominance of highly radiogenic lead in bronzes from the south and south-west has been seen to reinforce the idea of a single lead supply coming from somewhere to the south of the Yangzi river towards the Central Plains. In the Central Plains, changes in the lead isotope ratios from highly radiogenic to common between



Fig. 1. Locations of sites in the text (distribution of highly radiogenic lead).

Anyang and Western Zhou bronzes have been taken to imply a change of lead source from the Shang to the Western Zhou, although the sources remain unknown (Jin et al., 2017).

Recent work has revealed even more stimulating results. New analytical studies of copper ores as well as objects from the sites of Mogou, Baishantang in the Hexi corridor, Tianshanbelu in eastern Xinjiang and those in the highlands of Shaanxi and Shanxi have shown the use of highly radiogenic lead (Cao, 2014; Wang, 2018; Liu et al., 2020; Chen et al., 2020). A similar situation has also been found in the Wanliu site of the lower Xiajiadian in northeast China (Wang, 2012). These discoveries have significantly extended the distribution of different types of highly radiogenic lead beyond what was previously thought, but have also deepened the mystery of the source or sources of the lead.

The debate about the possible source(s) of the highly radiogenic lead during the Shang dynasty still continues, with even Africa recently cited as a potential source (Sun et al., 2017) - a suggestion which has been firmly rebutted on both archaeological and geological grounds (Liu et al., 2018). There are therefore several major questions still to answer - how many sources of lead were exploited during the Chinese Bronze Age, and where were they? Does the ubiquity of highly radiogenic lead during the Shang Dynasty across large parts of China reflect the use of a single source of lead, which would imply an extremely highly organized distribution system? If not, why did so many places use highly radiogenic lead at the same time? New fieldwork in China is gradually providing much better information about the locations and nature of Shang and Zhou dynasty mining sites (Chen, 2014; Li, 2014), and new revelations are continuously being made, but such work is inevitably slow.

This paper returns to a point discussed in Needham's Science and Civilisation in China (Golas, 1999: 107), which in turn derives from an earlier observation made by Barnard and Satō (1975: 22, 70). The original observation was that Shang and Zhou bronzes are relatively low in silver, which the authors suggested might arise from the use of cerussite (PbCO<sub>3</sub>) rather than galena (PbS) as the source of added lead. They further argued that, if this was the case, then it is possible that cerussite and cassiterite

 $(SnO_2$ , the most likely source of tin) could have been confused by the smelters, explaining why lead was introduced into Shang dynasty bronzes.

Both of these arguments are extremely interesting, and are certainly worth pursuing, although we show below that actually some Shang and Zhou bronzes are higher in silver relative to others. The principal mode of formation of cerrusite is from the weathering of primary galena deposits, and it is to be expected that the secondary cerrusite will be depleted in silver compared to the primary galena as a result of recrystallization (Eissler, 1891). Clearly, however, the actual levels of silver in cerrusite will be primarily controlled by the amount of silver in the primary sulfide deposit. Thus, although Patterson (1971: 304) shows massive cerussite to contain < 0.01% Ag, Conophagos (1980) reports that cerussite at Laurion contains 0.05 - 0.5% Ag. These levels are quite clearly comparable to the silver levels reported in galenas, and could therefore, if smelted, provide argentiferous lead.

At the purely mineralogical level, the confusion of cerussite and cassiterite appears highly unlikely, since cerussite is usually transparent or white (it is known as 'white lead ore'), whereas cassiterite is most often black. However, we should not make the mistake of projecting modern chemical mineralogical knowledge into the past. We note that Needham points out that the ancient Chinese called tin 'white tin (白锡)' and lead 'black tin (黑 锡)' (Golas, 1999: 106). These terms, therefore, do not necessarily completely coincide with our modern understanding of tin and lead. Most mineralogical sources of tin are likely to be steel-grey or blackish minerals (e.g., cassiterite, stannite ( $Cu_2FeSnS_4$ )), so it is entirely possible that, in the search for 'white tin', the smelting of silvergrey/black minerals such as galena could have inadvertently produced 'black tin'.

Inspired by the work of Needham, we have carried out a large survey in ancient Chinese documents and discovered two pieces of records which are precisely associated with lead and silver. The document of Guanzi Dishu (管子•地 数, written in the Warring States to the Han period, 475 BCE - 220 CE) notes that there must exist silver in the lower part of a mountain if one can find lead in its upper part (上有铅者, 其下有银). Similar description can also be found in the later document Houhanshu (后汉书, written in around 5th Century CE about the Eastern Han history 25-220 CE) where lead and silver can be extracted from the same place (the Paoding Mountain has silver and lead... the Yang Mountain has silver and lead抛町山出 银、铅...羊山出银、铅). While these later documents should not be directly superimposed on the Shang dynasty, it indicates that silver might be a useful index to characterize lead.

Whatever the interpretation of these ideas, the original observation has brought our attention to differences in the silver levels in Chinese bronzes, which might vary according to the source of lead used. In combination with the abundance and isotopic ratio of the lead, this may reveal further information on the number of lead sources exploited in Ancient China. Here we address two specific questions:

i) Did the different regions of China use the same

sources of lead? Differences in silver levels can indicate the addition of lead from different geochemical provinces - i.e., more than one 'source' on a large scale.

ii) Did the common and highly radiogenic lead added to bronzes in a particular region come from the same or different geochemical provinces? If the common and highly radiogenic leads are associated with different levels of silver, then we might infer that these two isotopically distinguished types of lead came from different geochemical provinces.

#### 3 Mineralogical Sources of Silver: A Geological Review

Silver can occur in three forms – native (elemental) silver, minerals containing silver as the main metallic element, and as traces of silver within ores of other metals such as galena or chalcopyrite.

A native metal is one which occurs naturally in metallic form, either as pure metal or in combination with others. Native silver occurs either as an alloy with gold (in which the percentage of silver can range from 10 to 20%) or as pure silver, typically with a purity of 98-99% (other elements can include Hg, Sb, Au and Cu). It is formed in primary hydrothermal deposits, and also by secondary processes, especially in the oxidized zones of mineral deposits, and is therefore quite common in mineralized deposits. In fact, native silver can be found in most localities which contain silver, but mostly in small quantities. Exceptionally, large masses can be found, such as at Kongsberg in Norway, where lumps weighing between 50 and 600 lbs were found (23-270 kg: Eissler, 1889: 14). The most common silver-rich minerals are argentite and acanthite  $(Ag_2S)$ , which by formula contains 86% silver. Argentite is the richest and most abundant source of silver, and has been mined in Saxony, Bohemia and Hungary, as well as in Mexico. In a salt water environment, Ag<sub>2</sub>S converts to chlorargyrite (AgCl, horn silver).

In the past, much of the world's silver has been obtained from silver-containing minerals such as the sulfides of copper, copper-nickel, lead and lead-zinc. The silver is either substituted into the lattice of the primary mineral (and is therefore limited by the degree of solid substitution structurally allowed), or exists as finely-divided silver minerals dispersed throughout the host species (in which the silver content can therefore exceed the solid solubility). Whilst it is true to say that the ultimate source of silver is attributed to the hot brines (~100–300°C) that circulate on the lithospheric-hydrospheric boundary, various factors govern the distribution of silver, including its solubility in different precipitating basic sulfides at different temperature, the rate of the temperature fall, the activity of antimony and bismuth, changing pressuretemperature conditions, diffusion rates and deformation. A simplified picture regarding the controls over the silver associated with galena and chalcopyrite would be as follows. The drop in temperature, probably due to the influence of sea water, causes selective precipitation from the brine. The precipitation of chalcopyrite starts around  $300^{\circ}$ C, whereas galena will precipitate around ~ $250^{\circ}$ C. The existence of silver in galena can also be in the form of compounds, such as PbS-Ag<sub>2</sub>S-Sb<sub>2</sub>S<sub>3</sub> or PbS-Ag<sub>2</sub>S-Bi<sub>2</sub>S<sub>3</sub>, whilst it exists only in the directly incorporated form in chalcopyrite (Hoda and Chang, 1975). The level of silver in galena is therefore partly a function of the ratio Ag/ (Sb+Bi) in the ore (Amcoff, 1984). Normally, silver is chemically only a very minor component (< 1–2%) of the mineral, although it can be economically the most significant.

Historically the major source of silver has been galena (PbS), which is the principal ore of lead. The proportion of silver in galena is highly variable, but some argentiferous deposits can contain 1-2%, either as included silver sulfide mineral phases, or as limited solid solution within the galena structure (or both). The silver is extracted from such argentiferous galenas by a process known as cupellation (Kassianidou, 2003). The galena is smelted to produce lead which might contain up to 1% silver. To recover the silver, the lead is then re- melted in an oxidizing atmosphere (cupellation), which removes the lead in the form of lead oxide (PbO, litharge), until only the silver remains, which inevitably contains a trace of the lead. The lead can be recovered from the litharge by resmelting, but such de-silvered lead is likely to contain less than a few tenths of a percent of silver. Copper ores can also contain silver, but usually at levels lower than those found in galena. Prior to the period of electrolytic refining, raw copper typically contained < 0.3% silver.

## **4 Silver in Chinese Bronzes**

There are five basic ways silver can enter a bronze object, but of course a combination of these routes is always possible:

i) by deliberate addition of metallic silver, or by contamination from surface silvering and inlaying,

ii) by the accidental inclusion of silver minerals in the smelt,

iii) as a trace component with any lead, especially if the object is deliberately leaded,

iv) as a trace component with the copper,

v) as a contaminant in any recycled metal.

In the context of Shang dynasty bronzes, i) and v) are unlikely, because silver objects are extremely rare in Shang dynasty contexts, and the use of silver surface decoration on Chinese metal is also unknown until the Warring States. The most likely source of the silver is as a trace contaminant in the added lead, especially since the lack of value of silver during the Shang means that any argentiferous galena is unlikely to have been de-silvered.

Figure 2 shows a plot of %Ag vs %Pb for Shang and Western Zhou Bronzes from the Sackler collection (Bagley, 1987; Rawson, 1990). It shows a general linear positive relationship between silver and lead (expanded in Figure 3), but two values are above 0.5% Ag (Western Zhou Sackler 231V Ag = 3.18%, Pb = 14.2%; Shang Sackler 155V, Ag = 0.55%, Pb = 2.58%). The Ag/Pb ratios of these two objects (0.224 and 0.213, respectively) are far too high to represent any likely argentiferous galena, and may reflect the accidental incorporation of a silver mineral during the smelting of the lead. The correlations between Ag and Cu for the same Shang and Western Zhou data (with Ag > 0.5% removed) are shown in Figure 4, and are in both cases negative, which strongly suggests that the major source of the silver in the bronzes is associated with the addition of lead, and not related to the base copper. It can easily be shown that there is no correlation in a plot of %Ag vs. %Sn, confirming that the silver is not associated with the tin.

Figure 3 shows the %Ag vs %Pb for both the Shang and the Western Zhou bronzes in the Sackler collection, with the two points above 0.5% Ag removed. The Shang data (Fig. 3a) show a weak but positive correlation between silver and lead ( $R^2 = 0.32$ , r = 0.563). Although one might argue that the value of  $R^2$  is relatively low, it is still significant compared to that of the Western Zhou data ( $R^2$ = 0.0874, r = 0.296). Meanwhile, the dispersive data distribution could suggest input of leads containing different Ag/Pb ratios from more than one source, or at least veins around the same geographical area but formed



Fig. 2. Plot of %Ag vs % Pb for Shang and Western Zhou Bronzes from the Sackler collection (Bagley, 1987; Rawson, 1990).



Fig. 3. Plot of %Ag vs % Pb for (a) Shang and (b) Western Zhou Bronzes from the Sackler collection (Bagley, 1987; Rawson, 1990), with Ag >0.5% removed.

in different geological periods/environments. Moreover, the correlation between silver and copper in objects of both Shang and Western Zhou is negative (Fig. 4), which reinforces the possibility that silver is more likely associated with lead in many Shang bronzes (see below).

If we consider the absolute levels of silver in a wider range of Chinese bronzes over time, we see some significant changes. Figure 5, using the data assembled from the literature (online supplementary materials), shows box-and-whisker plots representing the total variation in silver concentration across assemblages derived from the sites listed along the horizontal axis. The sites are in approximately chronological sequence, starting with Erlitou. Here, Hanzhong has been divided between the objects assigned to the Early Shang and those to the Late Shang (Cao, 2006; Zhao, 2006; Mei et al., 2009; Chen, 2009, 2019; Rawson, 2011). The columns labelled 'Sackler Shang' and 'Sackler Western Zhou' refer to the objects analysed from the Sackler collection (Bagley, 1987; Rawson, 1990), which are largely without provenance or precise date. The columns labelled 'Anyang I' to 'Anyang IV' are derived from material excavated at Anyang, and are allocated to the four chronological phases recognised at Anyang (Yinxu I-IV: Zhao, 2004). There is clearly a wide range of variation in the silver contents between all of these assemblages, most notably seen in the higher interquartile range of the objects from Erlitou, Hanzhong (Early Shang), and Anyang I. (very few objects attributed to the earliest phase of Anyang (n = 8), and its status is somewhat uncertain). In order to compare the variation between the other sites more closely, Figure 5b shows an enlarged version of Fig. 5a, with the silver axis



Fig. 4. Plot of %Ag vs % Cu for (a) Shang and (b) Western Zhou Bronzes from the Sackler collection (Bagley, 1987; Rawson, 1990), with Ag > 0.5% removed

truncated at 0.3%.

Figure 5b shows that bronzes from a wide range of sites, namely Panlongcheng, Hanzhong (Late Shang), Xin'gan and Sanxingdui in general have a much lower median value of silver than Qianzhangda and bronzes of the Shang and Western Zhou. Geographically, this is highly significant, because the first set of sites are in the south and southwest, whereas the second group all relate to the Central Plains (Fig. 1). This suggests that there are two broad categories of lead being used in the Chinese Bronze Age, one that is relatively argentiferous, supplying Qianzhangda, the Shang and Western Zhou, and one silver -poor, used in Panlongcheng, Hanzhong, Xin'gan and Sanxingdui. This does not of course mean that there are only two sources of lead used in China, one argentiferous and one silver-poor. Since the ratio of lead to silver is likely to reflect the geochemistry of the original orebearing fluid, which may be broadly similar over quite large geographical areas, what it is more likely to mean is that the lead came from two different metalliferous regions. In this case, these might be related to the six major geochemical provinces identified in China (southern China, Yangzi, northern China, northern Xinjiang, Jiamusi (northeast China) and Tibet: Zhu, 1995; Hsu and Sabatini, 2019). Jinsha, close to Sanxingdui in the south-west, and chronologically slightly later, appears to be an exception to this simple division, which requires further investigation.

In addition to this general observation, there are a number of more specific points to be made from Fig. 5. Erlitou, the earliest major bronze using society in central China, is shown to be different from the succeeding cultures of Zhengzhou (the Erligang period of the Shang) and Anyang, having higher silver. The bronzes from Zhengzhou are intermediate between Erlitou and the later Shang and Western Zhou sites. This suggests that the later Shang period bronzes are accessing lead from a different source to that used in Erlitou. The marked difference in silver levels between the earlier and later bronzes from Hanzhong is also interesting, although previous scholars



Fig. 5. Variation of silver in different metal assemblages from the Shang and Western Zhou dynasties. a) shows all data, inset b) restricted to Ag < 0.3% (ELT-Erlitou, ZZ-Zhengzhou, PLC-Panlongcheng, HZ ES-Hanzhong Early Shang, XG-Xin'gan, SXD-Sanxingdui, QZD-Qianzhangda, SS-Shang Sackler, AY\_I-Anyang Phase I, AY\_II-Anyang Phase II, AY\_III-Anyang Phase II, AY\_U-Anyang Phase V,SWZ-Sackler Western Zhou, JS-Jinsha ).

have already commented on the silver levels in this material (Chen et al., 2009).

### 5 Silver in Relation to the Isotopic Ratios of Lead

The silver levels discussed above reveal a broad distinction between the sources of lead used in the Central Plains and the south and south-west. As noted above, lead isotope ratios have shown a clear distinction between the highly radiogenic lead ores used in the Shang bronzes compared to the common lead isotope ratios in the succeeding Western Zhou Dynasty, which has been taken to imply a switch in lead source from the Shang to the Zhou. Does adding a consideration of the silver levels in these bronzes confirm this picture?

Figure 6 shows the variation in one of the lead isotope ratios (<sup>206</sup>Pb/<sup>204</sup>Pb) over the same time period as shown in Figure 5 (from Erlitou to Western Zhou: Jin et al., 2017). Erlitou does not use highly radiogenic lead, but there is a significant use of such lead from the Erligang (Zhengzhou) period to the later phases of the Anyang period (Yinxu III/IV), and an almost exclusive use of such lead during the Yinxu II period. By Yinxu IV and the subsequent Western Zhou period, the use of highly radiogenic lead is once more almost non-existent. It is also known that Sanxingdui, Hanzhong, Jinsha and Xin'gan almost exclusively used highly radiogenic lead (Fig. 7). This is highly significant because, if the evidence



Fig. 6. Changes in lead isotopic data in Shang and Western Zhou bronzes (from Jin et al., 2017).



Fig. 7. Lead isotopes in objects from the south and southwest (Jin et al., 1995, 2004, 2006).

presented above based on silver levels is correct, it suggests a crucial correlation between dominance of highly radiogenic lead and absence of silver in south (-west) China. This information is not easily obtainable from the lead isotope data alone, if at all. Incidentally, Fig. 7 also shows a component of common lead at Jinsha  $(^{206}\text{Pb}/^{204}\text{Pb} < 19)$  which is largely absent at the neighbouring but slightly earlier site of Sanxingdui, which, as with the silver levels noted above, suggests a difference in lead supply between these two sites.

Figures 5 and 7 allow us to compare the evidence from lead isotopes with that from the silver concentrations in the objects. The silver concentration in the bronzes of the Shang and Western Zhou dynasties (Figure 3) shows some small change, perhaps interpretable as Western Zhou accessing a wider range of sources than the Shang, but broadly within the same range of Ag/Pb ratios. In contrast, the lead isotopes show a marked change from the late Shang into Western Zhou. What does this mean? The general continuity of silver levels suggests no great change in the source (at least when thinking at the metalliferous region level), whereas in contrast the shift from highly radiogenic to common lead is quite distinct. This is highlighted by Fig. 8, which shows a plot of %Ag vs %Pb in Anyang bronzes from the Sackler collection (Bagley, 1987), where the points are classified as either highly radiogenic ( $^{206}Pb/^{204}Pb > 19$ ) or common lead. Although there is a slight indication that the highly radiogenic samples contain slightly lower silver, there is no obvious highly systematic difference in the relationship between common or highly radiogenic lead and the percentage of silver, as might be anticipated if they came from completely different geological environments (such as seen between the Central Plains and the south-west, discussed above). Further division is shown in Fig. 9, using all of the Anyang bronzes with secure archaeological context and chronological markers (Anyang I-IV phase). Again, it appears that there is no significant difference in terms of the amounts of silver, lead and associated isotopic values between them, even with this finer chronological resolution. In the absence of further analytical data, this suggests that both the highly radiogenic and common lead samples found in the bronzes from Anyang come from some geochemical environment which cannot be distinguished by silver. A more focused study on the site



Fig. 8. A plot of %Ag vs %Pb in the Anyang-style bronzes from Shang Dynasty in the Sackler collection (Bagley, 1987), classified as either highly radiogenic or common lead using cut-off of <sup>206</sup>Pb/<sup>204</sup>Pb=19.

Panlongcheng in the south also supports this argument (Fig. 10). Panlongcheng has played a critically important role in the discussion of metal supply to the Central Plains because (i) it has long been regarded by archaeologists as the military outpost set up by the early Shang court at Zhengzhou to secure the movement of metal from the Yangzi River to the Central Plains (Bagley, 1977; Liu et al., 2019), and (ii) both Zhengzhou and Panlongcheng were among the earliest sites which, almost simultaneously, utilized highly radiogenic lead. As Fig. 10 shows, although objects from Panlongcheng have much lower silver levels than are seen at Anyang (suggesting that the lead is coming from a different geological region), there is again no systematic patterning between %Ag vs % Pb when classified as either common or highly radiogenic lead using values of  $^{206}$ Pb/ $^{204}$ Pb, again supporting the idea that the highly radiogenic and common leads are coming from the same geological environment that cannot be differed by silver.



Fig. 9. Comparing silver and lead of Anyang bronzes, separated into four chronological phases (CL: common lead; HRL: highly radiogenic lead).



Fig. 10. A plot of %Ag vs %Pb in the bronzes from Panlongcheng (Chen et al., 2001; Sun et al., 2001; Peng et al., 2001), classified as either highly radiogenic or common lead using cut-off of <sup>206</sup>Pb/<sup>204</sup>Pb=19.

#### **6** Conclusions

The use of lead is one of the major characteristics of Bronze Age Central China, which is in significant contrast to its borderlands with steppe people. Therefore, the distribution network of lead, for instance, highly radiogenic lead, can effectively signify the exchange of either raw materials or finished objects among various groups of people and add extra dimension to the communication between Central China and beyond. This paper has presented the first systematic summary of the relationship between silver, lead and lead isotopes in Chinese bronzes. Whilst there are several ways silver can be incorporated into leaded bronzes, by comparing silver with the lead content, it becomes clear that the most likely source of the silver in the bronze of the Central Plains is associated with argentiferous lead added to create a leaded bronze alloy. More intriguingly, the variation of silver is subjected to a wider geographical patterning. We have shown that the median silver levels differ between the sites of the Central Plains (using both highly radiogenic lead and common lead) and those to the south and southwest (dominated by highly radiogenic lead). Therefore, it is possible to draw the conclusion that the differing levels of silver are indicative of two different source regions for the lead, one richer in silver (supplying the Central Plains) and one less rich, used in the south and south-west (also the Central Plains). This does not necessarily mean that only two mines were used to supply all of Bronze Age China, merely that two geochemically-distinct regions were used.

The variation of silver can also be plotted against chronology, particularly for the Central Plains, which has the most abundant data and a finer chronological basis. There appears a remarkable change in the proportion of silver between Erlitou and Zhengzhou, which clearly echoes the change in the lead isotopes from common to highly radiogenic lead. This strongly suggests a dramatic change in the lead supply to these two major sites in early Bronze Age China. At Panlongcheng or Anyang, there appears little or no systematic correlation between the amount of silver and lead isotopic signature.

### Acknowledgements

This work has been partially supported by European Research Council Horizon 2020 Advanced Project FLAME (ERC AdG 670010, Flow of Metal Across Eurasia).

> Manuscript received Feb. 21, 2020 accepted Apr. 2, 2020 associate EIC: CHEN Fahu edited by FEI Hongcai

#### References

- Amcoff, Ö., 1984. Distribution of silver in massive sulfide ores. Mineralium Deposita, 19: 63–69.
- Bagley, R.W., 1977. P'an-lung-ch'eng: A Shang city in Hupei. Artibus Asiae, 39(3/4): 165–219.
- Bagley, R.W., 1987. Shang Ritual Bronzes in the Arthur M. Sackler Collections. Washington, D.C: Arthur M. Sackler Foundation, 1–598.
- Barnard, N., and Satō, T., 1975. Metallurgical Remains of Ancient China. Tokyo: Nichiōsha, 1–343.
- Cao, D., 2014. The Loess Highland in a Trading Network (1300-1050 BC) (Ph.D thesis). Princeton: Princeton University, 1– 380.
- Cao, W., 2006. Shang Bronzes at Hanzhong. In: Cao, W. (ed.), Shang bronzes at Hanzhong. Chengdu: Bashu Press, 1–44 (in

Chinese).

- Chen, G., 2017. A preliminary study on the early single-blade knife in Gansu. Nanfang Wenwu, 02: 77–85 (in Chinese with English abstract).
- Chen, G., Cui, Y., Liu, R., Wang, H., Pollard, A.M., and Li, Y., accepted (online available). Lead isotopic analyses of copper ores in the early Bronze Age Central Hexi Corridor, northwest China. Archaeometry.
- Chen, J., Sun, S., Han, R., Chen, T., Zhai, T., Ban, B., and Tian, K., 2001. Report on trace element analysis of the Panlongcheng metal assemblage. In: Hubei Institute of Archaeology (eds.). Excavation of Panlongcheng 1963–1994. Beijing: Wenwu Press, 559–573 (in Chinese).
- Chen, J., 2014. New Exploration of the Civilisation of Smelting and Casting in Ancient China. Beijing: Science Press, 1–481 (in Chinese).
- Chen, K., 2009. Scientific Study on the Shang Dynasty Bronzes Unearthed from Hanzhong, Shaanxi Province: Materials and Manufacturing Techniques (Ph.D thesis). Beijing: University of Science and Technology Beijing, 1–181 (in Chinese with English abstract).
- Chen, K., Rehren, T., Mei, J., and Zhao, C., 2009. Special alloys from remote frontiers of the Shang Kingdom: scientific study of the Hanzhong bronzes from southwest Shaanxi, China. Journal of Archaeological Science, 36: 2108–2118.
- Chen, K., Mei, J., Rehren, T., Liu, S., Yang, W., Martinón-Torres, M., Zhao, C., Hirao, Y., Chen, J., and Liu, Y., 2019. Hanzhong bronzes and highly radiogenic lead in Shang period China. Journal of Archaeological Science, 101: 131–139.
- Chernykh, E.N., 1992. Ancient metallurgy in the USSR: the early metal age. Cambridge: Cambridge University Press, 1–359.
- Conophagos, C.E., 1980. Le Laurium antique et la technique grecque de la production de l'argent. Athènes: Ekdotike Hellados, 1–458.
- Cui, J., and Wu, X., 2008. The Study of Lead Isotopic Archaeology—Provenance Study of Bronze Artifacts Unearthed from Yunnnan Province, China and Vietnam. Beijing: Wenwu Press, 1–174 (in Chinese).
- Eissler, M., 1889. The Metallurgy of Silver. London: Crosby Lockwood, 1–336.
- Eissler, M., 1891. The Metallurgy of Argentiferous Lead. London: Crosby Lockwood, 1–396.
- Golas, P.J., 1999. Joseph Needham's Science and Civilisation in China. Volume 5, Part 13 Mining. Cambridge: Cambridge University Press, 1–352.
- Hoda, S.N., Chang, L.L.Y., 1975. Phase relations in the system PbS-Ag<sub>2</sub>S-Sb<sub>2</sub>S<sub>3</sub> and PbS-Ag<sub>2</sub>S-Bi<sub>2</sub>S<sub>3</sub>. American Mineralogist: Journal of Earth and Planetary Materials, 60: 621–633.
- Hsu, Y.K., and Sabatini, B.J., 2019. A geochemical characterization of lead ores in China: An isotope database for provenancing archaeological materials. PloS One, 14(4), p.e0215973.
- IA CASS (Institute of Archaeology Chinese Academy of Social Science), 2014. Erlitou: 1999–2006. Beijing: Wenwu Press, 1500–1543 (in Chinese).
- Jin, Z., 1987. Sources of metals for the bronze production in the Central Plain during the late Shang period. In: Jin, Z. (ed.), Lead Isotope Archaeology in China. Hefei: Press of University of Science and Technology, 292–302.
- Jin, Z., 1990. The source of bronze during the late Shang period. Paper presented at the third international conference of Chinese scientific history, Beijing.
- Jin, Z., 2008. Lead Isotopic Archaeology in China. Hefei: Press of University of Science and Technology, 1–233 (in Chinese).
- Jin, Z., Chase, T., Hirao, Y., Peng, S., Mabuchi, H., Miwa, K., and Zhan, K., 1994. Lead isotopic study of bronzes from Xin'gan Dayangzhou Cemetery. Kaogu, 8: 744–747 (in Chinese).
- Jin, Z., Liu, R., Rawson, J., and Pollard, A.M., 2017. Revisiting Lead Isotope Data in Shang and Western Zhou Bronzes. Antiquity, 91: 1574–1587.
- Jin, Z., Chase, T., Hirao, S., Peng, H., Mabuchi, K.M., and Zhan, K., 1994, The study of lead isotope in the bronzes of

Dayangzhou, Xin'gan, Jiangxi, Kaogu, 8(8): 744–747 (in Chinese).

- Jin, Z., Mabuchi, H., Chase, T., Chen, D., Miwa, K., and Hirao, Y., 1995. Lead Isotopic Study of Sanxingdui bronzes. Wenwu, 2: 80–85 (in Chinese).
- Jin, Z., Zhu, B., Chang, X., Xu, Z., Zhang, Q., and Tang, F., 2004. The study of Jinsha bronzes at Chengdu. Wenwu, 7: 76 -88 (in Chinese).
- Jin, Z., Zhu, B., Chang, X., Zhang, Q., and Tang, F., 2006. Lead isotopic study of bronzes from Baoshan and Chenggu/ Yangxian and associated issues. In: Zhao, C. (ed.), Chengyang Bronzes. Beijing: Science Press, 250–259 (in Chinese).
- Kassianidou, V., 2003. Early extraction of silver from complex polymetallic ores. In: Craddock, P.T., and Lang, J. (eds.), Mining and Metal Production Through the Ages. London: British Museum Press, 198–206.
- Li, Y., 2014. Preliminary study of the bronze industry in the early Central Plains and North. Weekly Newspaper of Chinese Archaeology (in Chinese).
- Liu, C., Liu, R., Pollard, A.M., Yang, C., Hommel, P., Ma, J., Cui, J., Bray, P., Tong, J., Rawson, J., 2020 accepted. Metallurgy at the Crossroads: New analyses of copper-based objects at Tianshanbeilu, eastern Xinjiang, China. Acta Geologica Sinica (English Edition) (in press).
- Liu, R., Bray P., Pollard, A.M., and Hommel, P., 2015. Chemical analysis of ancient Chinese copper-based objects: Past, present and future. Archaeological Research in Asia, 3: 1–8. Liu, R., Pollard, A.M., Rawson, J., Tang, X., and Zhang, C.,
- Liu, R., Pollard, A.M., Rawson, J., Tang, X., and Zhang, C., 2017. Revisiting the movement of metal between Zhengzhou and Panlongcheng in early Bronze Age China. Jianghan Kaogu, 3: 119–129 (in Chinese with English abstract).
- Liu, R., Pollard, A.M., and Rawson, J., 2018. Beyond ritual bronzes: identifying multiple sources of highly radiogenic lead across Chinese history. Scientific Reports, 8: 11770.
- Liu, R., Pollard, A.M., Rawson, J., Tang, X., and Zhang, C., 2019. Panlongcheng, Zhengzhou and the movement of metal in Early Bronze Age China. Journal of World Prehistory, 32: 393–428.
- Liu, S., Chen, K.L., Rehren, T., Mei, J., Chen, J.L., Liu, Y., and Killick, D., 2018. Did China import metals from Africa in the Bronze Age? Archaeometry, 60: 105–117.
- Mei, J., Chen, K., and Cao, W., 2009. Scientific examination of Shang-dynasty bronzes from Hanzhong, Shaanxi Province, China. Journal of Archaeological Science, 36: 1881–1891.
- Mei, J., Wang, P., Chen, K., Wang, L., Wang, Y., and Liu, Y., 2015. Archaeometallurgical studies in China: some recent developments and challenging issues. Journal of Archaeological Science, 56: 221–232.
- Patterson, C. C., 1971. Native copper, silver, and gold accessible to early metallurgists. American Antiquity, 36: 286–321. Peng, Z., Wang, Z., Sun, W., Liu, S., and Chen, X., 2001. Lead
- Peng, Z., Wang, Z., Sun, W., Liu, S., and Chen, X., 2001. Lead isotopic study of Panlongcheng bronzes. In: Hubei Institute of Archaeology, (ed.), Excavation of Panlongcheng 1963-1994. Beijing: Wenwu Press, 552–558.
- Beijing: Wenwu Press, 552–558. Pollard, A.M., Bray, P., Hommel, P., Hsu, Y.-K., Liu, R., and Rawson, J., 2017. Bronze Age metal circulation in China. Antiquity, 91: 674–687.
- Rawson, J., 1990. Western Zhou Ritual Bronzes from the Arthur M. Sackler Collections. Washington, D.C.: Sackler Foundation, 1–776.
  Rawson, J., 2011. Ornaments and territories—the case of
- Rawson, J., 2011. Ornaments and territories—the case of Hanzhong bronzes. In: Rawson, J. (ed.), Ancestors and Eternity. Beijing: Sanlian Press, 3–47.
- Shi, Z., 1927. Shiya. Geological Institute of Republic of China, 310–328.
- Sun, S., Han, R., Chen, T., Zhai, T., Ban, B., and Tian, K., 2001. Report of the lead isotopic measurements of Panlongcheng bronzes. In: Hubei Institute of Archaeology (ed.), Excavation of Panlongcheng 1963–1994. Beijing: Wenwu Press, 545– 551.
- Sun, W.-D., Zhang, L.-P., Guo, J., Li, C.-Y., Jiang, Y.-H., Zartman, R.E., and Zhang, Z.-F., 2016. Origin of the mysterious Yin-Shang bronzes in China indicated by lead isotopes. Scientific Reports, 6: 23304.
- Tian, J., 2013. The Study of Zhengzhou Erligang Bronzes (Ph.D

thesis). Hefei: University of Science and Technology China, 1 - 145 (in Chinese with English abstract).

- Wang, Y., 2012, Scientific Study on Copper and Bronze Artefacts of the Lower Xiajiadian Culture (Master thesis). Hefei: University of Science and Technology Beijing, 18–42 (in Chinese with English abstract).
- Wang, L., submitted. Scientific Analysis of Early Copper Objects at Gansu and Qinggai—Using Lintan Mogou as the Central Site (Ph.D thesis). Beijing: University of Science and Technology Beijing, 81–104 (in Chinese with English abstract).
- Zhang, C., Pollard, A. M., Rawson, J., Huan, Li., Liu, R., and Tang, X., 2019. China's major Late Neolithic centres and the rise of Erlitou, Antiquity, 93: 588–603.
- Zhao, C., 2004. The compositional analysis of Yinxu bronzes. Kaoguxue jikan, 15: 243–268 (in Chinese).
- Zhao, Č., 2006. Chengyang Bronzes. Beijing: Science Press, 218 -280.
- Zhu, B., 1995. The mapping of geochemical provinces in China based on Pb isotopes. Journal of Geochemical Exploration, 55: 171–181.

#### About the first author



LIU Ruiliang, male, born in 1988 in Ji'nan City, Shandong Province; Ph.D; graduated from the University of Oxford; Junior Research Fellow in the School of Archaeology, University of Oxford. He is interested in archaeometallurgy, radiocarbon dating and east-east communication in antiquity. Email: ruiliang.liu@arch.ox.ac.uk, phone: +44 01865 285219.

# About the corresponding author



A. Mark POLLARD, male, born in 1954 in New Zealand; Ph.D; graduated from York University, the United Kingdom; Edward Hall Professor in Archeological Science in the School of Archaeology, University of Oxford. He is now interested archaeological science. Email: mark. Pollard@arch.ox.ac.uk; phone: +44 01865 285228.