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A Multivariate Approach to Investigate Metallurgical Technology: The Case of the Chinese Ritual Bronzes

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Abstract
Research into ancient Chinese metallurgy has flourished over recent years with the accumulation of analytical data reflecting the needs of so many archaeological finds. However, the relationship between technology and society is unlikely to be revealed simply by analysing more artefacts. This is particularly evident in the debates over the sources of metals used to manufacture the Chinese ritual bronzes of the Shang (c. 1500-1046 BCE), Western Zhou (c. 1046–771 BCE) and Eastern Zhou (c. 771–256 BCE) dynasties. This article recognises that approaches to analytical data often fail to provide robust platforms from which to investigate metallurgical technology within its wider social and cultural contexts. To address this issue, a recently developed multivariate approach is applied to over 300 Chinese ritual bronzes from legacy data sets and nearly 100 unearthed copper-based objects from Anyang and Hanzhong. Unlike previous investigations that have relied predominantly on interpreting lead isotope signatures, the compositional analyses presented here indicate that copper and lead used to manufacture the bronzes are derived from mining progressively deeper ores in the same deposits rather than seeking out new sources. It is proposed that interpretations of social, cultural and technological change predicated on the acquisition of metals from disparate regions during the Chinese Bronze Age may need to be revised.

Keywords Shang · Zhou · Bronze · Multivariate · Lead isotopes · Composition

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Introduction

Increasing emphasis on the social and cultural dimensions of metallurgical technologies in ancient China (Jin et al., 2017; Liu et al., 2020a; Mei, 2009; Mei et al., 2015) is often predicated on the acquisition of key resources such as copper, lead and tin in disparate regions. Shang dynasty (c. 1500–1046 BCE) bronze objects recovered at Anyang (Henan), for example, and the presence of Anyang-type vessels at distant sites (Liu & Chen, 2003, 2012) have been used to suggest a highly organised system capable of obtaining metals from regions over 500 km away (Bagley, 1977; Liu et al., 2019), far beyond the Shang heartland. In turn, this system has been used to advocate the spread of technological capital, such as the techniques associated with mould-making, casting bronze and metallurgy in general (Pollard et al., 2017). Furthermore, proposed shifts in the bronze-producing system during the Western Zhou dynasty (c. 1046–771 BCE) have been interpreted as reflecting a transition from centralised to regional power structures (Hsu et al., 2021).

Relationships between social, cultural and ritual values and modes of production, circulation and consumption of metals in the Chinese Bronze Age, however, require relating contexts to metal objects in the archaeological record, by revealing any 'hierarchical structure' (Liu et al., 2020a) in the metallurgical practices carried out to produce the artefacts. In effect, to investigate metallurgical technology within its wider social and cultural contexts, robust analytical platforms are required to investigate alloying and impurity patterns in metal objects.

There are two main analytical approaches in archaeology that have been applied to investigate metal objects: compositional analyses and lead isotope analyses (LIA). Because of the data generated from these approaches, it is now recognised that there was wide use of highly radiogenic lead (i.e. lead formed in the presence of excess uranium and/or thorium) and predominance of leaded bronze recipes (i.e. Cu–Sn–Pb) to make objects during the Shang dynasty and Zhou dynasties (R Liu et al., 2018). However, the pattern of metal circulation revealed by the existence of highly radiogenic lead remains controversial. All major sites from the Central Plains to the Yangtze River have metal artefacts with highly radiogenic lead signatures from the time period associated with the Shang Dynasty (Jin et al., 2017; R Liu et al., 2018; Shelach-Lavi, 2015). This could suggest that a single lead source, presumably in areas controlled by the Shang, supplied metals to regional metallurgical centres, or that many centres had local metallurgical operations. Although an African provenance (Sun et al., 2016) for the Anyang ritual bronzes has been thoroughly refuted (S Liu et al., 2018a, b; Sun et al., 2018), research remains focussed on using these radiogenic signatures to locate the ore deposits that supplied the metals during the Shang and Zhou dynasties. The presence of radiogenic lead in copper-based objects of south-west China, for example, has led some researchers (Jin et al., 2003, 2017) to suggest that Yunnan and Sichuan were major suppliers of metal during the Shang dynasty rather than the mineral resources closer to smelting sites (e.g. Laoniupo and Huaizhenfang near Xi'an in Shaanxi province—Mei et al., 2015) in the Central

Plains, such as metalliferous regions in the Zhongtiao and Taihang mountains in Shanxi and the Qinling mountains in Shaanxi (Shi, 1955; Saito et al., 2002) (Fig. 1). This scenario would require that highly radiogenic lead sources are rare in China and that lead ingots travelled from Yunnan to Sichuan and beyond, perhaps along with copper. As a source of radiogenic lead in Yunnan, or anywhere else, that matches unequivocally bronze objects has yet to be located, the argument rests on the view that it was more economical to acquire copper from native copper deposits in Yunnan than mine for copper closer to the Shang heartland (Campbell, 2014:165). Nonetheless, because radiogenic lead and common lead are impossible to differentiate without modern instruments, neither position can provide a mechanism (social nor metallurgical) as to why either one or many metallurgical centres of the Shang dynasty would start and then suddenly stop using highly radiogenic lead after about three hundred years.

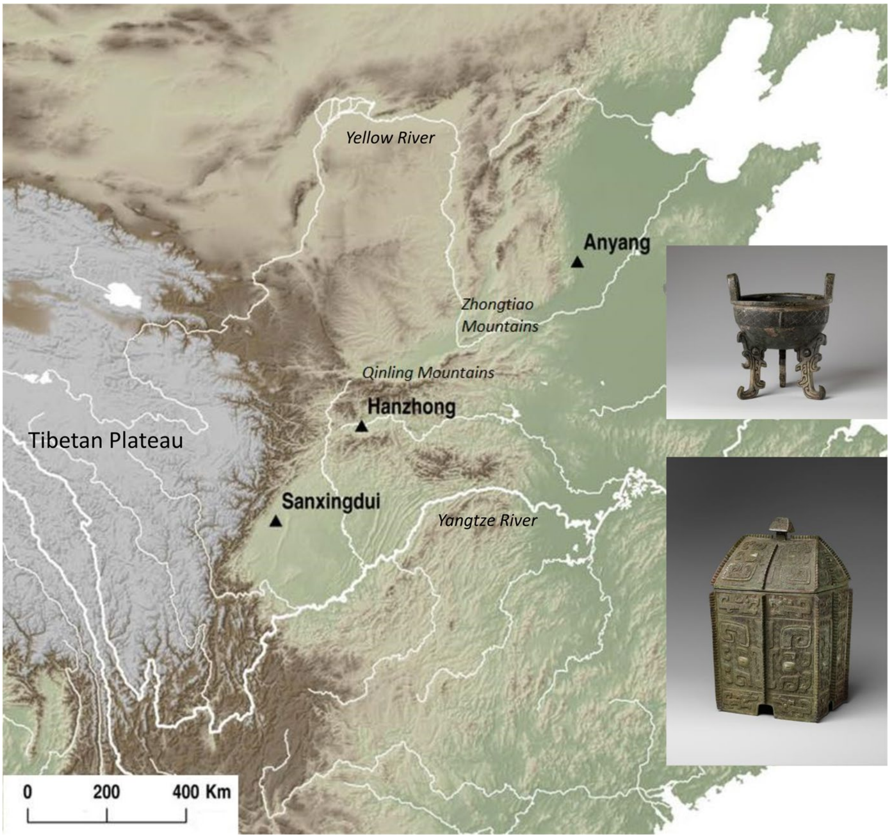


Fig. 1 Map showing main sites mentioned in text. Insets are two Shang bronzes from The Metropolitan Museum of Art (top—Ding: eleventh-century BCE (catalogue no. 81); bottom—Fanyi: twelfth-century BCE (catalogue no. 78) The Met CC.0))

Studies that have focussed mainly on the composition of bronze artefacts have also proven to be problematic. For example, three classes of bronzes, namely, Cu–Sn–Pb, Cu–Sn and Cu–Sn–As, were found (Xiao et al., 2004) at the Shang–Western Zhou site of Jinsha in Sichuan (eleventh–tenth- century BCE) before an additional two more classes were identified (Cu–Pb and Cu) (Jin et al., 2004). At Sanxingdui, also in Sichuan, ritual vessels and local objects have been attributed to Cu–Sn–Pb and to Cu–Sn–Pb and Cu–Sn, respectively (Ma et al., 2012). Other researchers have identified compositional recipes of only the first type in both ritual and local objects (Cui & Wu, 2013). Furthermore, in addition to Cu–Sn–Pb and Cu–Sn alloys, unusual alloys, such as Cu–As, Cu–Sb and Cu–As–Ni, have been recovered at Hanzhong, a site contemporary with the Shang dynasty, in south-west Shaanxi (Chen et al., 2009; Mei et al., 2009, 2015). Although these compositions may reflect either deliberate (by mixing ores) or accidental alloying at the sites, it must also be considered that instruments with different levels of precision, accuracy and detection limits, as well as misidentification of analytical peaks in spectrometry, can introduce inconsistencies into interpretations based on compositional measurements.

The treatment of compositional and isotopic data can also affect archaeological interpretations. For instance, although approaches which classify continuous compositional data with a discontinuous method (i.e. a yes/no presence or absence of certain elements) have been advocated by researchers applying the Oxford (FLAME) system for interpreting chemical and isotopic data in Chinese Bronzes (Pollard et al., 2017, 2018), it needs to be recognised that such methods are unlikely to be able to deal with variation in complex datasets, especially if the aim is to ascertain provenance of the sources of metals. Moreover, as noted by Pernicka et al. (2016), empirical limits used to delineate the presence or absence of elements are generally not informed by the geology or metallurgy of the system under investigation. Furthermore, it needs to be recognised that compositional data are fundamentally multivariate in nature and their components necessarily interdependent. That is, even if one part of a composition is reported, it is implicitly related to the other components and that the use of absolute values can result in 'spurious correlations' (Chayes, 1949). For example, the copper and bronze objects excavated at the late Shang (thirteenth–eleventh-century BCE) site of Yinxu in Anyang have been presented as having concentrations of tin that decreased and concentrations of lead that increased between Yinxu Phase I and Phase IV (Mei et al., 2015; Zhao, 2004). For compositional analyses that add up to 100%, however, a decrease in the proportion of one component, necessarily, requires increases in the proportions of other components. Interpretations that fail to consider this constant sum constraint (which compel the data to lie between 0 and 100%) could potentially result in erroneous archaeological interpretations.

The current article recognises that the emphasis often placed on acquiring new data can overshadow how the data are analysed. The aim here is to make the most of the remarkable compositional and lead isotopic datasets of Chinese ritual bronzes from the Shang (Bagley, 1987), Western Zhou (Rawson, 1990) and Eastern Zhou (So, 1995) dynasties that are already in the archaeological literature to identify indicators that can inform on the Chinese Bronze Age. These indicators are subsequently applied to unearthed copper-based objects from the Bronze Age sites of Anyang in Henan and Hanzhong in south-west Shaanxi.

Chinese Ritual Bronzes

As China emerged from the Neolithic period and entered the Bronze Age, it began making bronze vessels in its northern regions from around 1700 BCE (e.g. Erlitou period c. 1750–1500 BC). These ritual objects have been found in the ancient Chinese tombs of royal and noble families from the Shang (c. 1500–1046 BCE) and Zhou (1046–256 BCE) dynasties (Rawson, 1980). The technology to make these bronze objects included the ability to locate and extract deposits of copper, tin and lead as well as to develop foundries capable of heating to high enough temperatures to smelt ores and to mix and cast metal (Watson, 1971:70–80).

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, the Western Zhou period (c. 1046–771 BCE) and Eastern Zhou (c. 770–256 BCE) dynasties were cast using leaded bronze (Chase & Ziebold, 1978; Liu et al., 2015; Pollard et al., 2017). These bronze vessels were normally used for ritual purposes, especially for the worship of ancestors (Chang, 1980: 205–207). Lead was added to improve castability by lowering the melting range of the alloy (although amounts are often in excess of the few per cent required for this purpose) and tin contributed to lowering the melting range and hardening the bronze (Linduff, 1977; Craddock & Giumlia-Mair, 1988: 317–327). In addition to these technological deterministic interpretations of compositional recipes, the early metallurgy in other regions also suggests that the use of leaded bronze, or any type of copper alloy, may have been associated with other properties of the material, such as its colour, touch, taste and sound (Fang & McDonnell, 2011; Hosler, 1994; Jones, 2004; Mödlinger et al., 2017; Radivojević et al., 2018).

Bronze contains copper from ores that contain greater or lesser amounts of other metals such as arsenic, antimony and silver (Craddock & Giumlia-Mair, 1988: 317–327; Pernicka et al., 2016). In most ore deposits, there are three distinct horizons, the primary un-weathered deposit, normally consisting of sulphide, above that the weathered horizon which has been exposed to the action of air and rain and the contact zone between them. For copper deposits, the weathered zone consists of brightly coloured copper minerals such as malachite ($Cu_2CO_3(OH)_2$), azurite ($Cu_3(CO_3)_2(OH)_2$), cuprite (Cu_2O) and even native copper. Because of leaching and percolation of metallic salts to the water table and contact zone, the oxidised copper ores will be deficient in other metals. Conversely, the ores of the contact zone (e.g. fahlore $Cu_{12}Sb_4S_{13}$) will tend to be relatively rich in the associated metals. Lead deposits can have similar distinct horizons of oxidised ores (e.g. cerussite $PbCO_3$) and sulphidic (e.g. galena PbS) ores, with minerals of lead and zinc (e.g. sphalerite ZnS) often associated in the primary sulphide ore body (Gale & Stos-Gale, 1981).

Oxidised copper ores have been found at Shang dynasty production sites (Watson, 1971, 72). Slag and a quantity of malachite ($Cu_2CO_3(OH)_2$) have been found on a foundry floor dated to c. thirteenth–eleventh-century BC at Xiaotun in Anyang

(Liu & Chen, 2003, 2012). Recently, however, sites at Xiwubi and Qianjinba in the Zhongtiao Mountains (about 200 km west of Erlitou) in modern Shanxi Province, that is, in the heartland of the Xia (c. 2070–1600 BCE) and Shang dynasties, have produced abundant remains of mining and smelting activities (Huan, 2021: 165). At Xiwubi (Erlitou Phase III, c. 1650–1600 BC), scanning electron microscopy–electron dispersive spectroscopy (SEM–EDS) analyses indicate that the ores were oxidised and sulphur-rich, while slag samples suggest that the smelting products were relatively pure copper (Institute of Archaeology of the National Museum of China et al., 2021). At the earlier site of Xichengyi (in the middle part of the Hexi corridor) dated to c. 2000 BCE (placing it ahead of most of the middle Yellow river metal-production communities, such as Erlitou, by a few hundred years), two types of ores were found: relatively pure copper oxide ores and polymetallic ores (Huan, 2021: 271). Furthermore, although most slags are attributed to the smelting of copper oxide ores, inclusions in the remaining slags have suggested that copper is derived from ores that included arsenic and antimony (Li et al., 2015). In effect, different types of ore appear to have been used for copper production from the earliest times.

Approaches to the Data Sets

Chinese ritual bronzes in the Arthur M. Sackler collections can be found in the Metropolitan Museum of Art in New York (Fig. 1 inset); the Art Museum, Princeton University; the Sackler Collections, New York; and the Sackler Gallery, Smithsonian Institution, Washington, D.C. A three-volume catalogue meticulously describes and illustrates bronze vessels from the Shang (Bagley, 1987), Western Zhou (Rawson, 1990) and Eastern Zhou (So, 1995) dynasties. The objects are discussed and organised according to vessel types following conventional Chinese labels inherited from Song dynasty cataloguers (e.g. ding, jue, yu, etc.) and are listed alongside each vessel's proposed chronology based on their typologies.

Of particular interest here are the compositional and lead isotopic analyses (LIA) of the artefacts that are included at the end of each volume of the catalogue. Although these objects and the data from the catalogues have been analysed previously (e.g. Bagley, 1987; Linduff, 1977; Liu et al., 2020a, b; Rawson, 1990; So, 1995), the current approach incorporates the chronologies of the bronzes determined from typological assessments, lead isotope analyses, and applies a multivariate approach to the elemental data. Although 'standard' techniques using the original compositional values are often considered sufficient in archaeology (Baxter & Freestone, 2006), the approach advocated involves logarithmically transformed ratios, or logratios (Aitchison, 1986, 2005; Aitchison & Greenacre, 2002; Baxter, 1989; Buxeda i Garrigós, 1999, 2008; Pawlowsky-Glahn & Buccianti, 2011; Greenacre, 2018, 2021), as it is considered that this approach is more mathematically rigorous than traditional ones. Furthermore, it is considered that the analyses conducted here, which incorporate the expert knowledge of the archaeological scientist during, rather than after, the statistical investigation, can improve transparency of the stages in the analyses (Wood & Greenacre, 2020).

All data used for the plots in this article and the associated R-code for each stage of the analysis are presented in Supplementary Materials.

The main reason to investigate these particular objects is that the scientific analyses were performed using the same techniques and often by the same people (P. Meyers, L.L. Holmes and E.V. Sayre (compositional) at Brookhaven National Laboratory, USA, and by I.L. Barnes, W.T. Chase, E.C. Deal and E.C. Joel (LIA) at the National Bureau of Standards (Washington, USA) and the National Institute of Standards and Technology (Gaithersburg, USA)). Overall, 319 ritual bronzes are catalogued—Shang: 104; Western Zhou: 129; and Eastern Zhou: 86—with nearly all having undergone scientific analyses.

Essentially, although an obvious advantage of working on newly excavated objects is a better understanding of the archaeological background of the objects, while those in museums and private collections often have questionable dating, provenance and even authenticity, it is considered that the data from the bronzes in these collections have more to reveal about the origins of the metals used to manufacture these vessels from the Chinese Bronze Age and the actions of the people who acquired them.

Grouping the Bronzes

The hypothesis behind the current article is that the ritual bronze vessels in the collections investigated here, which were made over a period of about 1200 years, will exhibit variation in their elemental and lead isotopic signatures related to the ore sources from which the metals derived, and this will be reflected in the chronologies of their manufacture.

The catalogues group the bronzes by dynasty: Shang (Bagley, 1987), Western Zhou (Rawson, 1990) and Eastern Zhou (So, 1995). Each vessel is provided with an approximate date of manufacture based on its typology.

Dating bronzes is clearly a difficult task (Childs-Johnson, 1989; Rawson, 1980: 61–79). For example, the approach used for the Shang bronzes by Bagley, (1987) is based on the Loehr Styles (Loehr, 1953:42–53), which code the stylistic development of Shang bronze imagery. Style I, for instance, represents the earliest style and refers to vessels with thread-relief designs. Style II images abandon the thread for a broader band relief. During the next evolutionary phase, Style III, designs fill bands decorating the greater part of the vessel body and are often composed of thin filament-like extensions or quills. In Style IV, there is a separation of a background (cloud scrolls) and a central ground (the animal mask). In Style V, the vessel is decorated with high relief and a new variety of supplementary motifs. Bagley, (1987) generally assigns Style I vessels (represented by only one example, No. 1) to the fifteenth-century BCE; Style II vessels (Nos. 2–4 and 80) to the fifteenth–fourteenth-century BCE; standard Style III vessels to the late fourteenth-century BCE; standard Style IV vessels to the thirteenth-century BCE; and standard Style V vessels to the twelfth- and eleventh-century BCE. These dates are presumably based on the dating methods proposed by Watson, (1977: 29), who assigns the Erligang Period (Styles II and III) to the fifteenth- and fourteenth-century BCE and the Anyang Period to the thirteenth–eleventh-century BCE with 273 years (according to conventional dates of the Bamboo Annals), covering the years of reign at Anyang, the last Shang capital.

The current article accepts the dates of the vessels presented in the catalogues and those in the cited articles but appreciates that these dates may change and affect interpretations. Nonetheless, the main aim here is to identify patterns in the elemental and lead isotope data which allow these interpretations to be made.

Figure 2 presents histograms of the midpoints of the ranges of chronologies assigned to each object; that is, if the chronology was recorded as the twelfth-century BCE (i.e. between 1200 and 1101 BCE), it was plotted as -1150 (i.e. 1150 BCE), and so forth. All catalogued objects were plotted, apart from the few items that were suspected to be modern copies. These histograms in Fig. 2 may seem perfunctory. However, bronzes from the Shang period are not always easy to separate

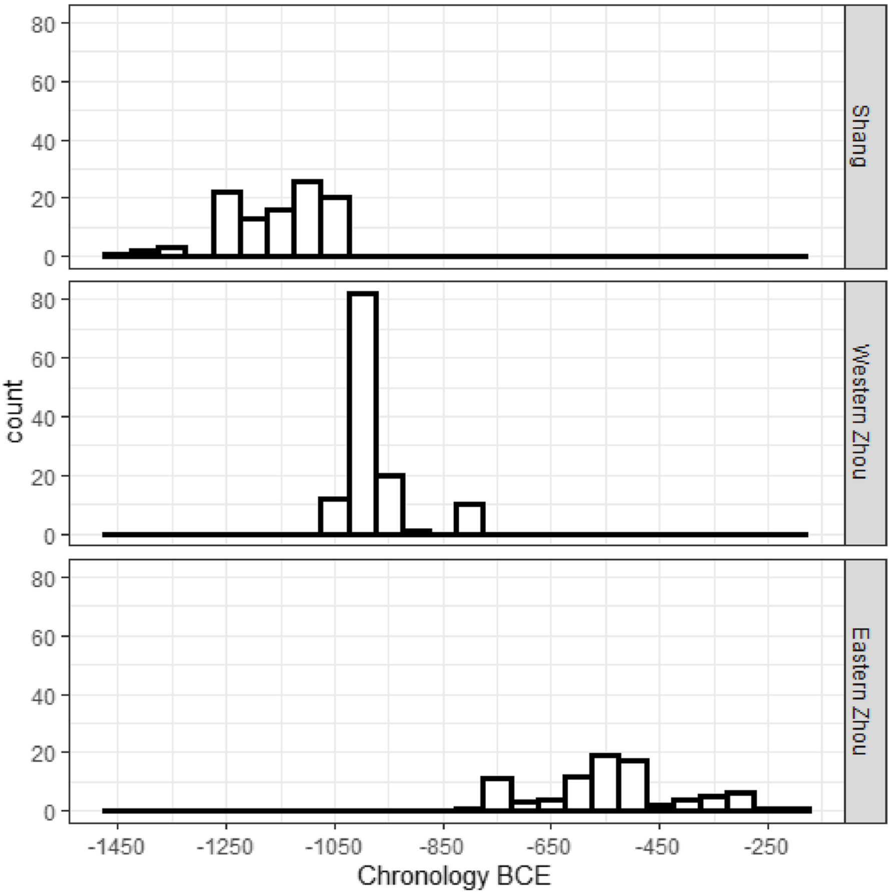


Fig. 2 Histograms of the ages of manufacture of each bronze vessel determined from their typologies (Shang—Bagley, 1987, Western Zhou—Rawson, 1990, Eastern Zhou—So, 1995), delineated by dynasty. All vessels were included apart from those few suspected of being copies (103/104 Shang vessels, 125/129 Western Zhou vessels and 86/86 Eastern Zhou vessels)

from those of the Zhou; that is, the term bronzes 'of the Three Dynasties' can refer to three chronological periods (associated with the Xia, Shang and Zhou dynasties) and three overlapping political entities (Chang, 1980: 21). Nonetheless, and unsurprisingly, despite some overlap, Fig. 2 shows that the bronze vessels classified as being from the Shang dynasty are older than those of the Western Zhou dynasty and, in turn, the Western Zhou bronzes are older than those from the Eastern Zhou dynasty.

In addition to the chronological groups based on typological assessments, the approach adopted here is to group the bronzes using the lead isotope data that had been measured for almost all these vessels. The lead isotope ratios of the Earth's crust are close to 206Pb/204Pb ≈ 18.5, 207Pb/204Pb ≈ 13.3 and 208Pb/204Pb ≈ 38.3. Lead minerals with these values are known as *common* lead and can generally be described by isotope evolutionary models to determine the geological age, usually measured in millions of years (Ma), of the deposits in which they are found. Conversely, the ages of *radiogenic* deposits cannot be calculated from measurements of the lead isotope ratios using simple evolutionary models—they can give predicted ages which are in the future. As all terrestrial lead deposits contain varying proportions of radiogenic lead, this is problematic. Nonetheless, the ability to differentiate between the occurrence of common and radiogenic lead in archaeological artefacts is clearly a potential aid to provenance.

Several arbitrary but useful empirical limits have been suggested by the Oxford group (e.g. Pollard et al., (2017); R. Liu et al., (2018); Liu et al., 2020b) between common and what is sometimes called 'highly' radiogenic lead. Figure 3 presents a traditional LIA plot for the Shang, Western Zhou and Eastern Zhou bronzes showing how the vessels can be delineated using one of their empirical limits (radiogenic: 206Pb/204Pb > 19.5; common: 206Pb/204Pb < 19.5). Traditional LIA plots have been used to indicate that radiogenic lead in Chinese ritual bronzes was used from the Erligang (Zhengzhou) period until the Yinxu II Period of Anyang (c. 1200–1046 BCE), and also outside the Central Plains of China—that is, Sanxingdui in Sichuan, and Panlongcheng and Xin'gan on the Middle Yangtze River, have shown almost concurrent use of radiogenic lead in their cast bronzes (R. Liu et al., 2018). This has been used to support the premise that areas outside the Central Plains manufactured bronzes used locally derived metals (Liu et al., 2019). Radiogenic lead decreases markedly in the later Anyang bronzes and is almost completely absent in the subsequent Zhou dynasty bronzes (Jin et al., 2017). The degrees of overlap (Fig. 3) could support the view that similar (and perhaps the same) common lead sources were used in the manufacture of these bronzes during the three chronological periods.

Figure 4 plots histograms of the calculated Pb crustal ages (also known as model ages) from the LIA values for the bronzes of the Shang and Zhou dynasties using the model and parameters presented in Desaulty et al., (2011). Despite the emergence of negative ages (which suggest anomalous lead deposits comprising radiogenic lead), these histograms complement the traditional LIA plots by visualising the numbers of objects which derive from radiogenic or common lead.

Although it has been suggested that Chinese lead isotopic ratios measured from the bronzes of the Shang dynasty (c. 1500–1046 BC) present much larger isotopic

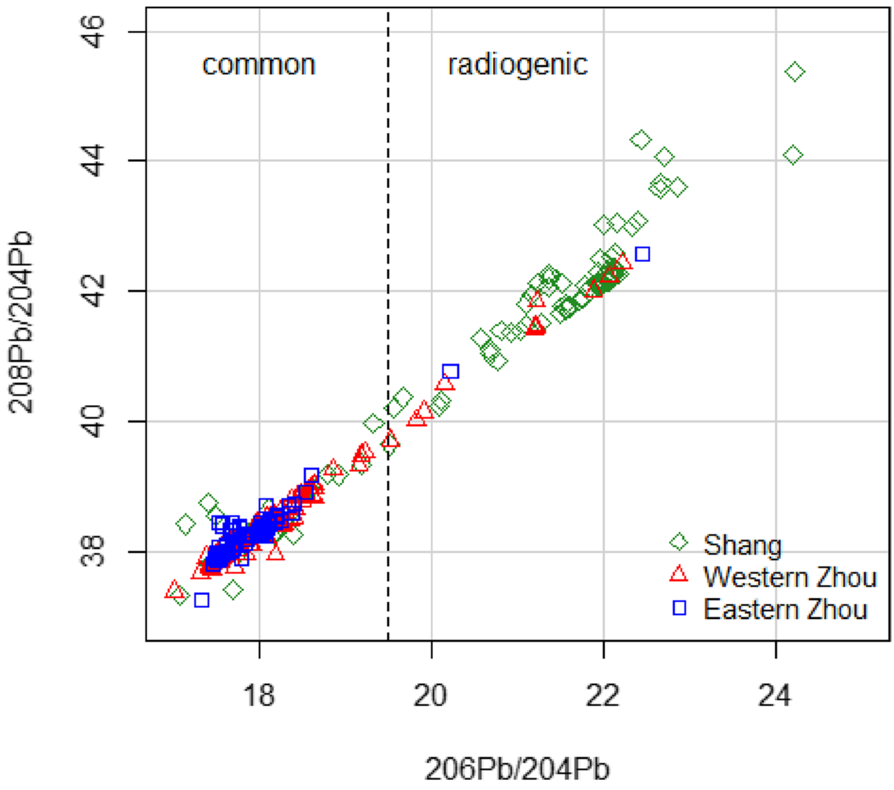


Fig. 3 Traditional LIA plot showing the bronze vessels from the collections delineated by the dynastic period. The dashed line is an empirical limit between radiogenic and common lead sources. Note that R. Liu et al. (2018) use the term 'highly radiogenic' for values of $^{206}Pb/^{204}Pb > 19.5$)

variation than those found in many other parts of the world, such as Europe (R. Liu et al., 2018), it needs to be recognised that these plots (Fig. 4) show that there are two main groups of vessels rather than one population. This bimodal signature is useful. Because Bronze Age metallurgical workers had no means of distinguishing between radiogenic and common lead in their objects, three groups (A, B and C) have been created based on the peaks in the frequency histograms in Fig. 4.

Table 1 presents the numbers of objects and analyses in each group (i.e. A, B or C), as well as the approximate corresponding ranges of lead isotope values and the calculated Pb crustal ages associated with the objects. The frequency peaks (Fig. 4) suggest that about two-thirds of the Shang dynasty bronze objects were made using lead that is derived from highly radiogenic or radiogenic lead sources (negative ages) and about one-third from common lead sources (positive ages). Conversely, lead found in the objects from the Western and Eastern Zhou dynasties appears to have derived primarily from common lead sources (positive ages).

Figure 5 is a histogram of the chronologies of Shang dynasty bronzes determined from their typologies, delineated by the three groups based on lead isotopes

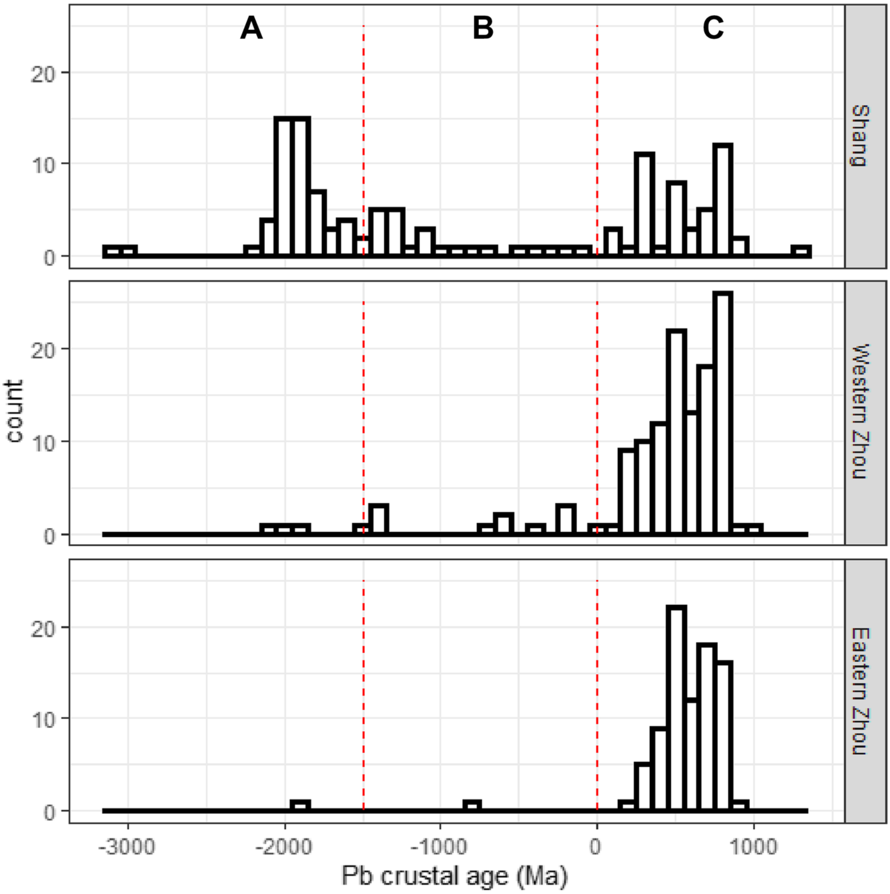


Fig. 4 Histograms of the Pb crustal age (also known as model age) measured in millions of years (Ma) for the bronze vessels determined from lead isotopic analyses (LIA) using a two-stage evolution model and the parameters of Desaulty et al., 2011. The vertical dashed lines delineate the three groups (A, B and C) based on the frequency of vessels of the Shang (top) Western Zhou (middle) and Eastern Zhou (bottom) dynasties. Negative values represent radiogenic lead; positive values represent common lead

(Table 1). Based on typologies, Group C appears to be made up of vessels that were considered to be made predominantly in the late Shang period (i.e. c. eleventh-century BCE) when the capital was at Anyang. In effect, unlike the majority of the earlier Shang bronzes (fifteenth–twelfth-century BCE), the late Shang bronzes were made using lead derived predominantly from common lead sources (Fig. 4).

There are a number of bronze vessels in Fig. 4 that lie between the main peaks (i.e. Group B), particularly for the Shang bronzes (Shang Group B). The Shang isotopic signatures could have emerged because:

i) Several lead sources were exploited (Shang Group B) to make these few bronze vessels around the same time a major source was exploited (Shang Group A).

Table 1 Numbers of vessels and lead isotope analyses used in Figs. 3, 4 and 5 delineated by groups (A, B and C). The terminology used here for these groups is: Group A (highly radiogenic), Group B (radiogenic) and Group C (common)

Lead isotope analyses (LIA)

GROUP	**Pb crustal ages (Ma)**	**Terminology**	$^{206}Pb/^{204}Pb$
A	below -1500 Ma	highly radiogenic	≈ 21.5–24.5
B	between -1500 Ma and 0 Ma	radiogenic	≈19.0–21.5
C	above 0 Ma	common	≈17.0–19.0

	Shang dynasty bronzes		**Western Zhou dynasty bronzes**		**Eastern Zhou dynasty bronzes**	
GROUP	no. of analyses (Total = 123)	no. of objects with LIA (97* out of 104**)	no. of analyses (Total = 128*)	no. of objects with LIA (121 out of 129**)	no. of analyses (Total = 86)	no. of objects with LIA (75 out of 86*)
A	51	42	3	3	1	1
B	25	24	12	10	1	1
C	47	33	113	108	84	73

Shang dynasty bronzes: No. of objects with LIA = 97 (i.e., 104 catalogued objects minus 7 objects not sampled for LIA). Total number of lead isotope analyses = 123 (97+26 duplicates)
* Note: Two objects have duplicate analyses in different groups to the first measurement.
** One object considered modern.

Western Zhou dynasty bronzes: *Total number of analyses =132–4 (probable copies) = 128.
**No. of objects with LIA = 129 catalogued objects - 4 (objects not sampled for LIA) – 4 (probable copies) = 121.

Eastern Zhou dynasty bronzes: No. of objects with LIA = 75 (i.e., 86 catalogued objects minus 11 objects not sampled for LIA)
*Only catalogued objects included.

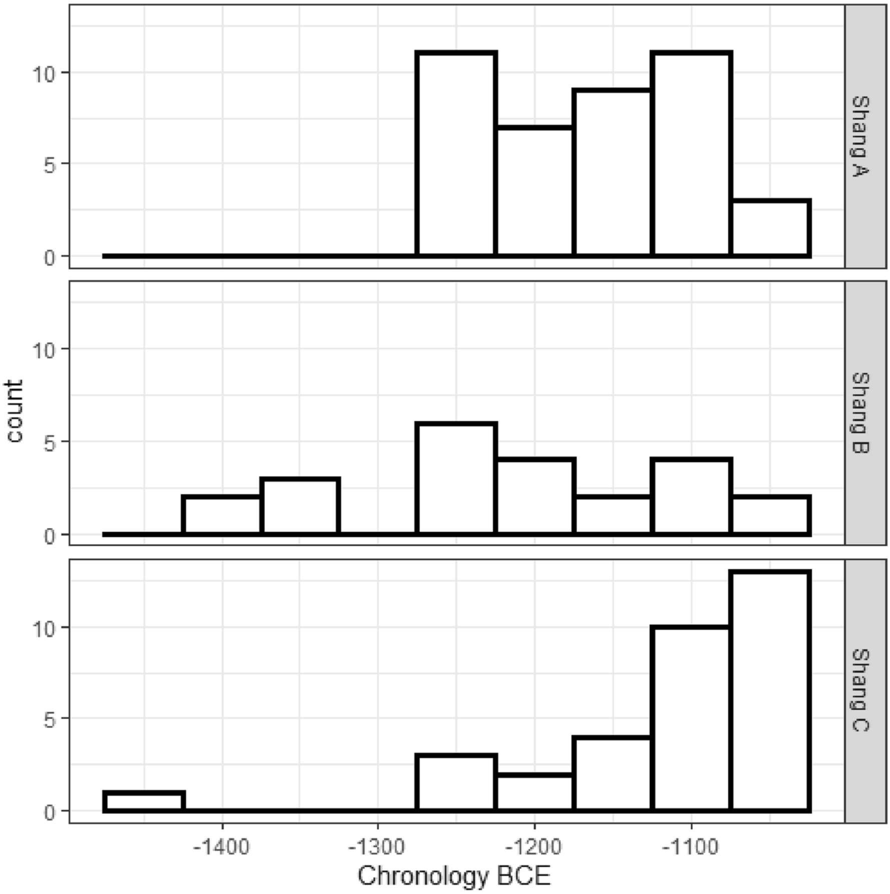


Fig. 5 Histograms of the chronologies of the Shang vessels delineated by the groups based on lead isotope values. The mean values are Shang A = 1165 BCE; Shang B = 1212 BCE; and Shang C = 1117 BCE. Note that Shang Group B includes vessels attributed to the Erligang period, that is, Styles II and III

ii) The ritual vessels in Shang Group B were made from recycled bronze; that is, bronze that used lead derived from a common lead deposit had been mixed with bronze that used lead from a radiogenic lead deposit to make these vessels.
iii) Similarly, lead used for these vessels may have derived from lead that was a mixture of lead from radiogenic and common lead deposits; that is, lead ingots were cast from both types of lead.
iv) The lead ores used to smelt the lead for these bronzes were from deposits that exhibit variation in radiogenic and common lead; that is, ores had intermediate signatures or both types of ore found in the *same* deposit had been smelted together.

The first scenario is possible, although this would suggest that these discrete lead sources were exploited for only the few bronze vessels found in Shang Group B. The second scenario seems unlikely because, according to typological assessments, the majority of vessels from Shang Group C were made after Shang Groups A and B; that is, both types of bronze would have needed to be available to make a mixture for the vessels in Shang Group B. Similarly, the third scenario would suggest that both common and radiogenic sources were available at the same time to make the mixed lead ingots, which again is not indicated by the chronologies of the bronzes. The fourth scenario is interesting as it suggests that lead deposits *cannot* be defined as being either radiogenic or common. It is well known that deposits with radiogenic lead can be very heterogeneous. Cannon et al., (1963) attributed variation in common lead deposits to the mixing of lead with an increasingly radiogenic signature in the ore-forming fluid during ore genesis. In effect, there might be systematic zoning within a deposit, with anomalous, radiogenic lead ores being very localised within deposits showing otherwise common lead isotopic signatures. This will be examined in the discussion. The few bronzes with radiogenic signatures from the Western Zhou and Eastern Zhou dynasties may reflect recycling of Shang bronzes to make new objects, or the exploitation of localised pockets of radiogenic lead in common lead sources.

Compositional Analyses

This section investigates whether there are any compositional differences among the three groups (A, B and C) of bronzes in Fig. 4.

Methods

The approach followed here treats the system as a series of subcompositional components, or parts, realising that the elements being analysed are a subset of a potentially larger set, which affects their percentage values. The main idea is to analyse element ratios, which are unchanged whether observed in subcompositions or extended compositions, and to logarithmically transform the ratios to put them on an additive (interval) scale, resulting in logratios. This method was first proposed by Aitchison, (1986), who defined a relative geometry where only the pairwise logratios of the different components were considered—see Aitchison, (2005). The motivation for an archaeologist to use a method based on ratios of components is that this makes compositional data, and thus, the results of the statistical analysis, invariant to the particular choice of components. In this study, there were 12 components in the form of elements measured in the Shang and Western Zhou datasets, but 10 in the Eastern Zhou dataset. The major elements (Cu, Sn and Pb) were measured using atomic absorption spectroscopy (AAS) and the trace elements using neutron activation analysis (NAA). Details of the experimental protocol are provided in each volume of the catalogue (Bagley, 1987; Rawson, 1990; So, 1995).

As will be described below, certain elements were removed from the analyses. However, the method employed here means that although extending or reducing the number of components would change the compositional data when closed to 1 (or 100%), the ratios between components remain unchanged.

Apart from the simple pairwise logratios of parts, other logratio transformations are possible, the most useful being the centred logratios (CLR), the logarithm of each component (element) x_j relative to the geometric mean of all the parts:

$$log\left(x_j/\left(\Pi_k x_k\right)^{1/D}\right) = log\left(x_j\right) - \left(\Sigma_k log\left(x_k\right)\right)/D \; j = 1, \cdots, D \quad (1)$$

It has been shown that the principal component analysis (PCA) of the D CLRs is equivalent to the PCA of all ½$D(D-1)$ pairwise logratios (Aitchison & Greenacre, 2002). This method of dimension reduction is called logratio analysis (LRA), and its interpretation differs from that of regular PCA in that it is not the parts themselves that are interpreted in the solution but rather the directions linking pairs of parts, which represent the logratios (for a practical introduction, see Greenacre, 2018).

Basing the analysis of compositions on logratios is subcompositionally coherent as it removes the effects of the constant sum constraint (which compels the data to lie between 0 and 100%). In essence, the logratio approach considers from the outset that the interest lies in the relative magnitudes and variations of components, instead of in their absolute values, and that the data are unconstrained (thereby retaining the proper covariance structure of any compositional data). The transformation to logratios then allows the full range of standard statistical methods, both exploratory and inferential, to be available for identifying and confirming groups or patterns in the data.

A further development of the logratio approach was introduced by Greenacre, (2018), who showed that a careful stepwise selection of a small set of simple pairwise logratios could explain essentially all the variance in the total set of logratios and that this selection could be enhanced by expert knowledge of the data context (Wood and Greenacre, 2021). This is the approach adopted here: namely, identify a small set of pairwise logratios, which have both a substantive interpretation and as high as possible statistical explanation of the total logratio variance.

The procedure adopted here also makes use of bootstrapping methods in order to determine univariate or multivariate confidence limits. Bootstrapping involves taking a large number (in this application, 1000) of samples of the original sample, with replacement, computing the group means on each one, giving an approximate empirical distribution of the mean. In multivariate space, bootstrapping allows the computation of a region enclosing a multivariate mean with prescribed confidence, usually 95%. In reduced-dimension plots such as Figs. 6, 7 and 8, as well as regular bivariate plots such as Fig. 13, these regions are represented by confidence ellipses (Greenacre, 2016). Similarly, Greenacre, (2016) defines a univariate confidence plot (Fig. 9), where the bootstrapping method is used to construct the confidence interval, with 'whiskers' extending from the mean (shown as a dot) to the upper 97.5th and lower 2.5th percentiles, thus giving an estimated 95% confidence interval for the mean. To enhance the interval in a style similar to the boxplot, a box has been added to show the boundaries of the 75th and 25th percentiles, thus enclosing 50% of the mean's distribution. Thus, there is a 50:50 chance that the box covers the true mean, and a 95% chance that the range of the extended interval includes the true mean. In

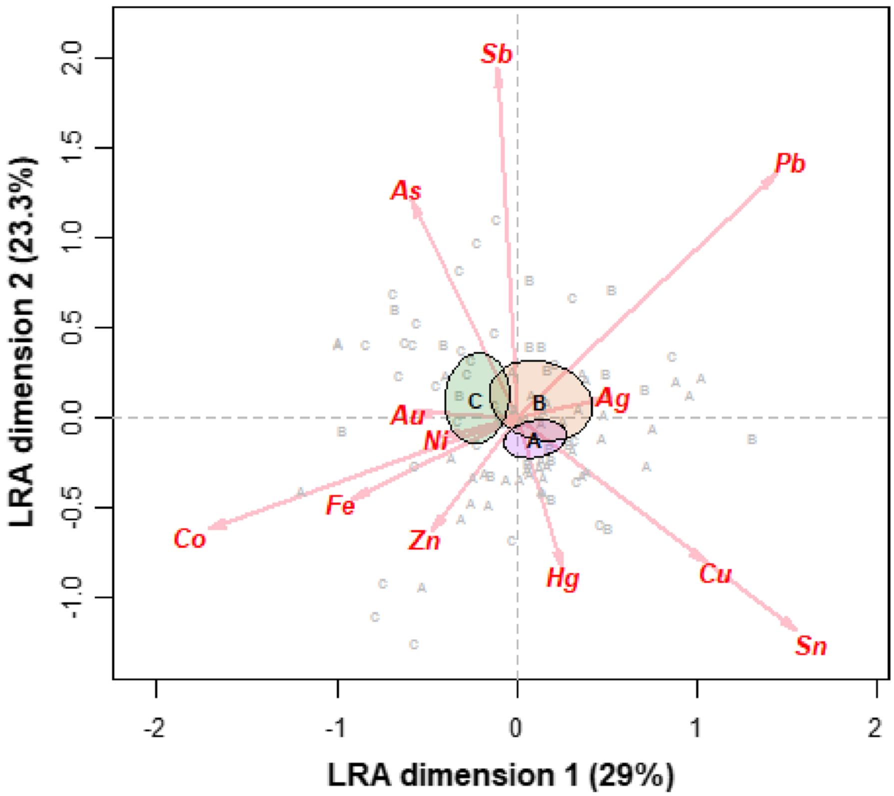


Fig. 6 Logratio analysis (LRA) of the Shang dynasty compositional data. Note that 95% confidence ellipses around the group means (large symbols: A, B and C) of the three groups clearly demonstrate that A (Shang Group A) is separate from C (Shang Group C), with B (Shang Group B) overlapping with both A and C. 52.3% of the variance is explained by the two principal dimensions

effect, these confidence plots show the variability in the mean rather than the variability in individual values.

First Analysis: Shang Bronzes

The first part of the compositional analysis focuses solely on the Shang dynasty bronzes (Table 2) (Bagley, 1987).

The compositional data of the Shang dynasty bronzes include 12 elements: Cu, Sn, Pb, Fe, Zn, Au, Ag, Hg, As, Sb, Co and Ni (Table 2). Some compositional measurements had elements which had not been analysed, that is, those denoted as '*na*' in the catalogue data tables. Furthermore, some analyses were recorded as being below the detection limit. In these cases, a value had been recorded as being less than an assigned value.

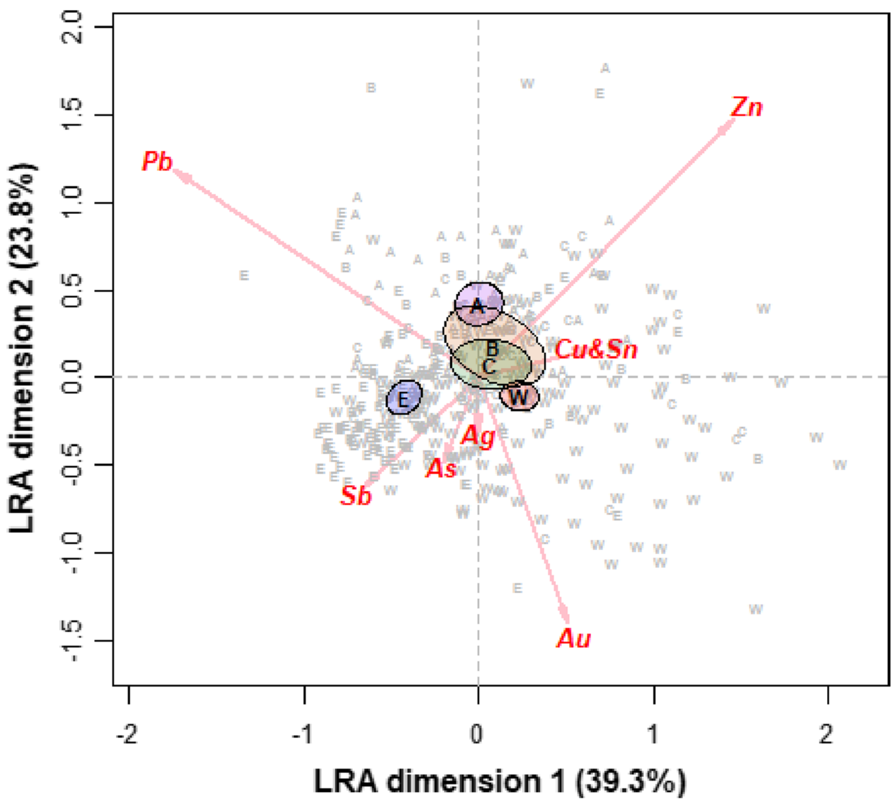


Fig. 7 Logratio analysis (LRA) of the Shang (A, B and C), Western Zhou (W) and Eastern Zhou (E) compositional data after iron, cobalt, nickel and mercury were removed. Copper and tin have been amalgamated. 63.1% of the variance is explained by the two principal dimensions

It should be noted that two of the 113 measurements from the Shang bronzes were removed at the outset, leaving 111 measurements for the analyses conducted here: one measurement was from an object which had been classified as 'modern' (Shang catalogue: No. 11) and the other was a measurement which had only the three main elements recorded (Cu, Pb and Sn) for the object. It is also necessary to highlight that although there are ways to deal with zeroes in multivariate analyses (see Greenacre, 2018), the approach applied here was to remove measurements with *na* values; that is, a whole compositional measurement was removed from the analysis if one element had not been measured. For the first analyses, this reduced the number of compositional measurements to 94. Those elements with values below detection limits were accorded the value of the limit recorded; for example, Fe% < 0.048 was given the value 0.048%.

This first analysis comprised 94 compositional measurements, each containing 12 elements, from 86 objects. Figure 6 represents the LRA of all pairwise logratios (numbering 66 combinations) for this first analysis of the Shang bronzes.

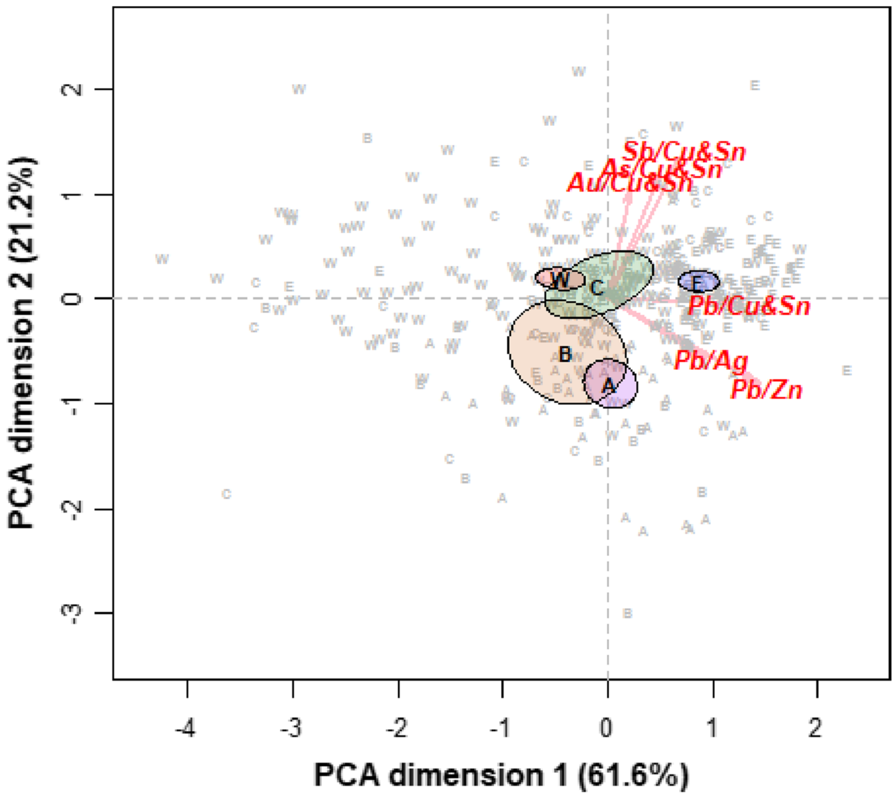


Fig. 8 PCA of the six logratios selected, which account for 92.1% of the total logratio variance. Since $21.2+61.6=82.8\%$ of the variance is explained by these two dimensions, this means that $0.828\times92.1=76.26\%$ of the total logratio variance is explained by this two-dimensional solution

Figure 6 presents the three groups based on the lead isotopes (Shang Groups A, B and C). The shaded regions show 95% confidence ellipses around the means of the three groups, clearly demonstrating that the *highly radiogenic* group (A) is separate from the *common* lead group (C), with group B (referred to here as the *radiogenic group*, for convenience) overlapping with both groups A and C. The compositional logratio variances for the Shang Groups A, B and C are 0.6453, 0.7922 and 0.7910, respectively. The confidence ellipses of the mean values for each group reflect these variances and the number of samples in each group. As a rule of thumb, if two confidence intervals do not overlap, then there will be significant difference between the respective groups (Krzywinski & Altman, 2013). Multivariate permutation tests for group differences using the vegan package in R (Oksanen et al. 2015) confirm that Groups A and C are significantly different in their compositions ($p=0.001$). Furthermore, B is significantly different to A ($p=0.031$) and to C ($p=0.035$).

Compositional differences among these groups are perhaps not so surprising because the groups have different lead isotope profiles (Fig. 4), which could

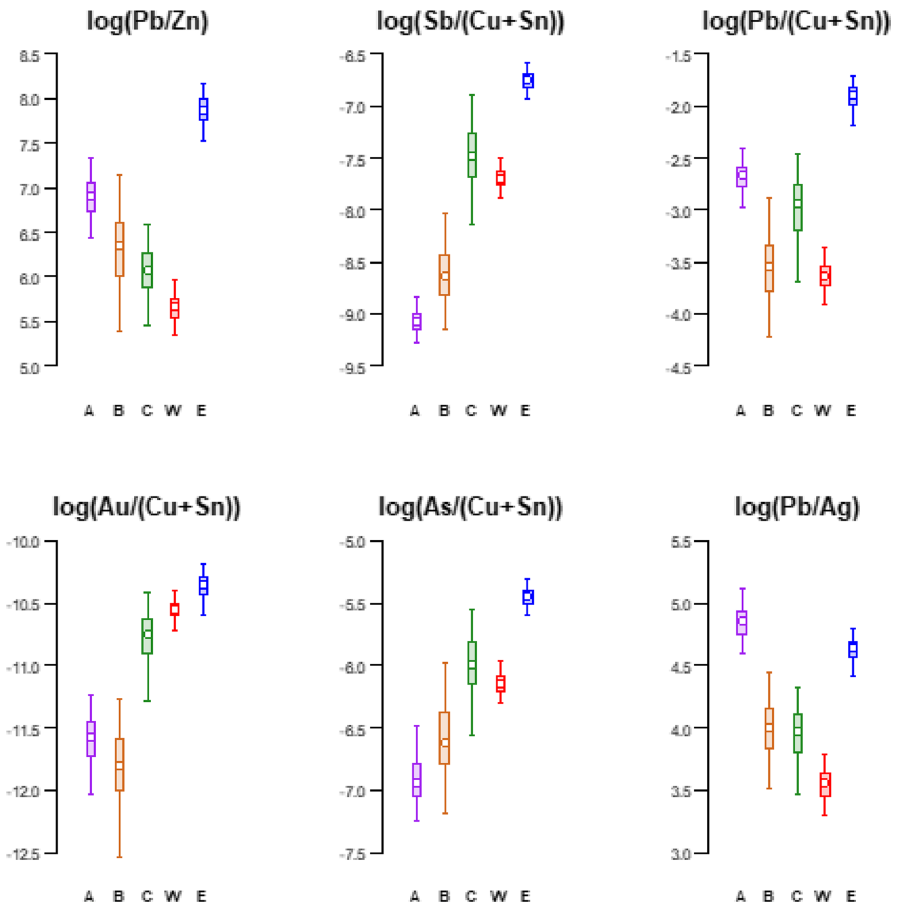


Fig. 9 Confidence interval plots for mean logratios, based on 1000 bootstrap samples. The mean is indicated by a dot (as opposed to a line for the median in a boxplot). The box encloses a 50% confidence interval for the mean, and the whiskers a 95% confidence interval. (upper left) log(Pb/Zn), (upper middle) log(Sb/(Cu + Sn)), (upper right) log(Pb/(Cu + Sn)), (lower left) log(Au/(Cu + Sn)), (lower middle) log(As/(Cu + Sn)), and (lower right) log(Pb/Ag), are for the six groups: Shang Groups A, B and C, Western Zhou (W) and Eastern Zhou (E). Note the differences in scales

suggest different geological sources of lead. However, these compositional differences may also reflect differences in copper and tin sources and the methods of measurement.

Figure 6 shows that the arrows of Cu and Sn lie together and their logratios are correlated. Correlations between other elements with copper and tin are high, for example, log (Sb/Cu) vs. log (Sb/Sn) and log(As/Cu) vs. log (As/Sn) are $r = 0.90$ and $r = 0.89$, respectively. This suggests strongly that Cu and Sn were introduced into the bronzes in a fixed ratio of amounts. Because Cu and Sn are likely to vary together (and, therefore, difficult to separate), these elements were amalgamated

Table 2 Numbers of vessels and compositional measurements used in the analyses of the Shang dynasty bronzes

	Shang dynasty bronzes—Compositional data				
Analyses	Compositional elements	No. of compositional measurements	No. of compositional measurements removed	No. of objects with compositional measurements	No. of compositional measurements used in analyses
1st	Cu, Sn, Pb, Fe, Zn, Au, Ag, Hg, As, Sb, Co, Ni	113 from 99* objects, i.e. 14 duplicates	19 (1: modern; 1: only major elements measured; 17: *na* data in minor elements such as Hg)	86	94 (8 duplicates) Groups A: 44; B: 19; C: 31
2nd	Cu&Sn, Pb, Zn, Au, Ag, As, Sb		2 (1: modern; 1: only major elements measured)	97	111 (14 duplicates) Groups A: 48; B: 25; C: 38

*104 catalogued objects (five objects not sampled) for the subsequent analyses. Interestingly, the Pb arrow does not lie with the arrows of Cu and Sn. This is discussed in the following sections.

Figure 6 also shows that arrows for cobalt, iron and nickel lie close together which, like Cu and Sn, suggests that they form logratios which are proportional. Although this could be related to the metal ore sources (i.e. all three elements may have come in together from the copper, tin and lead), it could also be related to the sampling procedure.

It is proposed here that variation may have been introduced to the system from drill bit(s) used for the NAA sampling; that is, drill bits can include levels of cobalt and nickel, as well as iron. In fact, some issues had been noted previously when the measurements were first conducted (Bagley, 1987): cobalt was highlighted as being particularly problematic (with some measured values being discarded) and nickel had not been included in later measurements of the Eastern Zhou bronzes (So, 1995). Furthermore, NAA concentrations for nickel were based on the intensities of a cobalt isotope formed by the reaction with a nickel isotope.

Cobalt and nickel were removed from subsequent analyses presented here. Iron was removed for reasons of possible contamination but also because it had been measured using two methods (AAS and NAA), with only averaged results being recorded in the catalogues. Iron also had the largest errors in repeat measurements (22.8%). Mercury was removed because many of measurements of this element were below the detection limit and, like nickel, this element had not been included in the suite of elements measured in the Eastern Zhou bronzes (presumably because the variation it introduced reflected its volatility).

Removal of these elements may seem unduly conservative. Nonetheless, they may have introduced variation into the system which is potentially unrelated to either the materials or the methods used in the manufacture of these ancient bronze vessels. This could be particularly problematic for analyses which use elements such as nickel as discriminators for copper sources, such as the FLAME method (e.g. Pollard et al., 2018). Moreover, removing these elements had the benefit of reducing the numbers of compositional measurements that had '*na*' values and values classified as being below the detection limit, thereby increasing the numbers of Shang compositional measurements included in subsequent analyses from 94 to 111 (and the number of Shang objects from 86 to 97).

The number of components used in the analyses is now seven (i.e. the amalgamation (Cu + Sn), Pb, Zn, Au, Ag, As and Sb) with each being available in compositional datasets of the Shang, Western Zhou and Eastern Zhou dynasty bronzes.

Second Analysis: Shang, Western and Eastern Zhou Bronzes

Table 3 shows the number of measurements comprising each dataset and the mean, median and standard deviation values of raw compositional values. All data are given in Supplementary Materials.

The groups used in the second analyses were the three Shang Groups (A, B and C) described in the previous section, the Western Zhou Group (W) and Eastern Zhou Group (E). The Western and Eastern Zhou groups were not delineated by A,

Table 3 Numbers of vessels and compositional measurements used in the analyses of the bronzes: mean values, standard deviations (sd) and median values of raw compositional data (not normalised) measured in per cent and parts per million (ppm). n denotes the number of analyses

		Shang (Bagley, 1987)			**Western Zhou** (Rawson, 1990)		**Eastern Zhou** (So, 1995)		
Objects in catalogue		104 (5 not sampled + 1 major elements only + 1 modern)			129 (4 modern)		86 (7 not sampled)		
Compositional measurements		111 (from 97 objects)			160 (from 125 objects)		98 (from 79 objects)		
		Cu	**Sn**	**Pb**	**Zn**	**Au**	**Ag**	**As**	**Sb**
		%			ppm				
Shang (A) n = 48	mean	77.17	12.08	8.34	129	15	575	3014	129
	sd	6.62	4.99	6.45	251	13	342	9467	119
	median	76.45	13.15	6.10	62	11	550	730	95
Shang (B) n = 25	mean	80.42	11.18	6.82	126	14	670	3783	367
	sd	8.83	6.00	7.98	291	13	565	7657	497
	median	78.90	12.90	3.30	37	10	500	1130	134
Shang (C) n = 38	mean	75.81	11.28	9.98	267	41	1094	4721	1646
	sd	6.88	3.95	8.58	644	106	764	6385	2579
	median	76.80	12.05	7.70	96	20	880	3345	595
Western Zhou (W) n = 160	mean	79.77	11.79	5.68	350* (207)	35	816	3200	900
	sd	7.18	4.06	5.99	1929 (691)	47	490	3969	1841
	median	80.60	12.50	4.25	74	24	725	2000	405
Eastern Zhou (E) n = 98	mean	69.65	10.83	15.57	610**(111)	33	1288	4528	1463
	sd	9.28	5.23	7.73	4957 (430)	17	511	5168	2912
	median	69.60	10.60	15.55	20	31	1210	3650	1065

High mean values dominated by single measurements of *2.3%Zn and **4.9%Zn. The values with these measurements removed are in parentheses

B and C because relatively few of their objects fell in Groups A and B in Fig. 4, thereby affecting the sample size for statistical analyses. It was decided to include all bronzes from the Western and Eastern Zhou dynasties in the W and E groups; that is, no data were removed from the Western Zhou and Eastern Zhou bronzes even though a few vessels fell in Groups A and B.

Figure 7 is a plot of the LRA after Co, Fe, Ni and Hg were removed and Cu and Sn were amalgamated for all three datasets: Shang (111 measurements from 97 objects), Western Zhou (160 measurements from 125 objects) and Eastern Zhou (98 measurements from 79 objects). The LRA ratios account for 63.1% of the total variance.

The logratio variances for each group are similar before and after the amalgamation (in parentheses): Shang Group A: 0.620 (0.557); Shang Group B: 1.094 (0.913); Shang Group C: 0.875 (0.825); Western Zhou W: 0.804 (0.798); and Eastern Zhou E: 0.590 (0.541). The LRA from the second analysis exhibits similar patterning to the first analysis for the Shang groups; that is, there is overlap of the 95% confidence ellipse around the mean between Shang Groups A and B and Shang Groups B and C. As expected from the LRA (Fig. 7), the ANOVA test for three groups, that is, Shang (combining Shang A, B and C), Western Zhou and Eastern Zhou are significantly different ($p=0.001$). Applying the test to Shang Groups B and C and the Western Zhou group (W), Shang Group B and the Western Zhou are significantly different ($p=0.002$). Shang Group C and Western Zhou are also significantly different ($p=0.045$). Because this p-value is very close to the $p=0.05$, it is difficult to draw any conclusions regarding differences in the compositions of bronzes from the end of the Shang period (i.e. Shang Group C) and those of the Western Zhou (W). However, Shang Groups B and C, which were significantly different ($p=0.035$) in the first analysis, are no longer significantly different in the second analysis ($p=0.078$). This change is potentially driven by the removal of proportional elements (i.e. Ni, Co, Fe) that may have been introduced during the sampling procedure. Nonetheless, it is interesting that there is no statistical difference between Shang Groups B and C because vessels in Shang Group B were made using radiogenic lead, while those of Shang Group C used common lead sources. This would cast doubt on whether there was any change in the lead source during the Shang dynasty, despite differences in the isotopic signatures of the two groups.

As with the LRA for the Shang dynasty dataset (Fig. 6), the rays of Pb and (Cu + Sn) in Fig. 7 do not lie together. This was unexpected as presumably lead had been introduced with the copper and tin to improve the castability of the bronze as part of the compositional recipe. Figure 7 also shows that Sb/Pb and Zn/Pb provide almost orthogonal rays suggesting that the two logratios, that is, log(Sb/Pb) and log(Zn/Pb), are only slightly correlated. A weak association ($r=0.56$) is found if these ratios are plotted together. This could suggest that antimony and zinc in the bronze system have different origins; that is, if antimony is predominantly associated with copper, then zinc is predominantly associated with lead.

The following analyses investigate the drivers for the compositional variations of the groups.

Figure 7 represents the analysis of all pairwise logratios (numbering 21 combinations if Cu and Sn are separated, but 15 when they are amalgamated). However, a smaller set can be determined, which explains most of the variance while approximating closely the geometric structure of the compositional data. Since several logratios compete for being chosen at similar levels of explained variance, it is preferable that selection is assisted by expert knowledge, in order to explain as much variability as required to reveal the underlying structure of the data using logratios that are meaningful to the archaeological scientist.

The stepwise selection for the formation of logratios conducted here uses the amalgamation of Cu and Sn, and individual values of Cu and Sn were removed. However, it was considered that the logratio variance to be explained should remain that of the original data set of eight elements, that is, the data set without amalgamation.

The following stepwise process was followed (details of the steps are given in Table 4):

The original compositional data are replaced by a set of carefully selected ratios, with the following requirements: (1) the ratios are easily interpretable by the practitioner, i.e. the archaeological scientist; (2) the set of ratios, after log-transformation, explains either all or a very high percentage of the variability contained in the original data set and defines a geometry that comes measurably close to that of the original data set and so preserves its essential multivariate structure; and (3) the ratios can be validly reported as univariate statistics, with conventional summary measures and plots, which can be compared with the same ratios in similar studies. The benefits of this approach become particularly apparent when investigating the sources of elemental and isotopic variation in these objects.

Step 1: The automatic procedure produced a list of candidate logratios in descending order of explained variance. Table 4 presents the top five ratios in terms of the percentage of variance that each explains. The first logratio, (Pb/Zn), in the list for the first step explains the most variance (31.8%) and was also the preferred choice. From an archaeological science perspective, this ratio could relate to the lead source. Zinc is found in the mineral sphalerite (ZnS) which is often associated with the sulphidic lead ore galena (PbS), a potential source of lead used in the bronzes. This could suggest that part of variation between groups (i.e. Groups Shang (A, B and C), Western Zhou (W) and Eastern Zhou (E)), might be explained by compositional variation in the lead sources.

Step 2: The second column in Table 4 shows the list of candidates after log(Pb/Zn) has been forced in, after which the same stepwise procedure was performed on all the remaining ratios. The percentages are now the cumulative ones, additional to that of the log(Pb/Zn) chosen previously. The logratio of Sb/(Cu + Sn) explains the most variance and was selected because copper can be associated with antimony in fahlore ores such as tetrahedrite $Cu_{12}Sb_4S_{13}$. The selection of log (Sb/(Cu + Sn)) means that 51.8% of the total logratio variance in the data set is accounted for; that is, more than half of the total logratio variance can be explained by two logratios.

Step 3: Now that log(Pb/Zn) and log(Sb/(Cu + Sn)) have been forced in, the top of the list of ratios became dominated by ratios with gold. For example, either selection of log(Zn/Au) or log(Pb/Au) would bring the explained variance up to

Table 4 Stepwise process of analysis. The table shows the top five ratios and the associated cumulative percentage of the total variance explained at each step. The ratios in bold and underlined were those selected based on expert knowledge. These six ratios account for 92.1% of the total logratio variance

STEP 1		STEP 2		STEP 3		STEP 4		STEP 5		STEP 6	
Ratio	%	Ratio	%	Ratio	%	Ratio	%	Ratio	%	Ratio	%
Pb/Zn	**31.8**	**Sb/(Cu+Sn)**	**51.8**	Zn/Au	71.4	**Au/(Cu+Sn)**	**82.7**	Au/As	89.4	Au/Ag	92.1
Pb/(Cu+Sn)	30.4	Zn/Au	51.4	Pb/Au	71.4	Au/Sb	82.7	**As/(Cu+Sn)**	**89.4**	Ag/As	92.1
Pb/Au	27.1	Pb/Au	51.4	Pb/Sb	68.1	Zn/Au	82.7	Pb/As	89.4	**Pb/Ag**	**92.1**
Zn/Sb	27.0	As/(Cu+Sn)	51.0	Zn/(Cu+Sn)	68.1	Pb/Au	82.7	Zn/As	89.4	Zn/Ag	92.1
Pb/Ag	26.1	Pb/Sb	49.4	**Pb/(Cu+Sn)**	**68.1**	Au/As	79.8	As/Sb	89.4	Ag/Sb	92.1

71.4%. Although Au can be associated with silver in lead ores (and zinc can be associated with lead ores, see *Step 1*), the absolute concentrations of gold in the bronze vessels are much higher than gold usually associated with silver in lead ores: that is, the bronzes have gold to silver ratios that are generally an order of magnitude higher than that usually found in argentiferous galena (Wood et al., 2021). This could suggest that gold enters the system from more than one source. In effect, although these ratios are statistically high, they are difficult to interpret. The logratio of Pb/(Cu + Sn) was selected to investigate variation in the recipe of adding Pb to (Cu + Sn) in the manufacture of the bronzes, despite being 3.3% below the optimal value. The explained variance became 68.1%.

Step 4: After selecting the logratio of Pb/(Cu + Sn), ratios that included gold continued to dominate the top of the list. The logratio of Au/(Cu + Sn) was selected because it explained the most variance and because gold can be associated with copper in fahlore, particularly Sb-fahlore (Kucha et al., 1997). The explained variance increased to 82.7%.

Step 5: The top of list of ratios became dominated by ratios that included arsenic. The logratio of As/(Cu + Sn) was selected, bringing the explained variance to 89.4%, as arsenic can be associated with copper ores, such as tennantite ($Cu_{12}As_4S_{13}$). In fact, copper minerals tetrahedrite ($Cu_{12}Sb_4S_{13}$) and tennantite ($Cu_{12}As_4S_{13}$) often form a solid solution (i.e. pure endmembers are rarely found in nature, with arsenic replacing antimony) (Pernicka et al., 2016).

Step 6: Although a high percentage of variance had been already explained by the previously selected logratios, a ratio with silver was included as this has been used previously an indicator to investigate provenance (Liu et al., 2020b). The logratio of Pb/Ag was selected, bringing the explained variance to 92.1%.

The six logratios identified from the stepwise procedure described above (i.e. logs of Pb/Zn, Sb/(Cu + Sn), Pb/(Cu + Sn), Au/(Cu + Sn), As/(Cu + Sn) and Pb/Ag) representing 92.1% of the variance of the dataset, are both high statistically and meaningful to the archaeological scientist. Figure 8 shows the PCA using the six selected logratios. Since $61.6 + 21.2 = 82.8\%$ of the variance is explained by the two dimensions, this means that $0.828 \times 92.1 = 76.26\%$ of the total logratio variance is explained by this two-dimensional solution.

The PCA (Fig. 8) shows that a lot of variation between the groups (Shang A, B and C and Western Zhou (W) and Eastern Zhou (E)) lies along dimension 2. It also shows that the confidence ellipse of the Eastern Zhou (E) on the PCA is separate from the others along dimension 1. To demonstrate this one variable at a time, Fig. 9 presents 95% confidence plots for the logratio means of the groups, using bootstrapping—see Greenacre, (2016); Wood and Greenacre, (2021). As with the confidence ellipses, confidence intervals that do not overlap suggest that there will be a significant difference between the respective groups (Krzywinski & Altman, 2013).

As expected from the PCA plot (Fig. 8), the confidence interval plot (Fig. 9) for the logratio of (Pb/Zn) shows that Shang Group A is higher than Western Zhou group (W) and that Shang Groups B and C overlap with both Shang A and Western Zhou (W). The logratio for the Eastern Zhou group (E) is significantly higher than the other groups. The confidence interval plot for log(Pb/Zn) suggests that lead ores were increasingly associated with zinc minerals (such as sphalerite) until the Eastern Zhou dynasty. Examination of the raw data supports this view (Table 3), with the mean, median and standard deviation of zinc concentrations doubling for Shang Group C compared with Shang Groups A and B. Large spikes were noted in zinc concentration for the vessels in the Western and Eastern Zhou groups.

The confidence interval plot (Fig. 9) for the logratio of (Pb/Ag) suggests that Shang B, Shang C and the Western Zhou groups (W) have lower ratios than those of Shang A and the Eastern Zhou (E). This could suggest that the lead used in the Shang A and Eastern Zhou periods was less argentiferous. However, as will be discussed below, silver can be also associated with copper ores (Pernicka et al., 2016).

The logratio of Pb/(Cu + Sn) should best reflect the compositional recipe used in the manufacture of the bronzes. The overlapping confidence ellipses in the confidence interval plot (Fig. 9) highlight high variation in the mean values. The higher mean value for the Eastern Zhou (E) reflects the higher measured lead concentrations for these vessels and the concomitant lower concentrations of copper and tin (Table 3).

The logratios of As/(Cu + Sn), Sb/(Cu + Sn) and Au/(Cu + Sn) exhibit similar patterns for the groups on the confidence interval plots (Fig. 9). This strongly suggests that these ratios not only have a common origin but that there is also a step change from Shang Groups A and B to Shang Group C, Western Zhou (W) and Eastern Zhou (E). Furthermore, these ratios are potentially associated with the source of copper, as antimony, arsenic and gold are often associated with fahlore ($Cu_{12}Sb_4S_{13}$) (Kucha et al., 1997; Pernicka et al., 2016).

Exploring the Analyses

The analyses conducted here aim to identify patterns in the chronologies (as determined from typological assessments), lead isotopic measurements and the compositional data of the Shang, Western Zhou and Eastern Zhou ritual bronzes.

Figures 3 and 4 show that the lead in the bronzes from the different dynastic periods has different isotopic signatures. Radiogenic lead was used for about two-thirds of the Shang bronzes and common lead was used predominantly for the remainder of the Shang bronzes and for the Western Zhou and Eastern Zhou vessels. A reasonable, *but not definitive*, interpretation is that the changes in the isotopic signatures (and the Pb crustal ages) are due to changes in the geographical location of the lead sources exploited during the different dynastic periods. If this is the case, however, then changes should be reflected in the compositional analyses; that is, compositional variation attributable to the lead source would be presumably dependent on the geographical location of the source. However, there are a few issues that need to be considered before conclusions can be drawn on the role of lead in the manufacture of the bronzes, including finding an explanation for the arrows of lead not aligning with those of copper and tin on the LRA plots (Figs. 6 and 7).

Variation of lead concentrations in the compositional recipe could be for two reasons:

- Lead was not added in a fixed recipe with copper and tin but was added almost arbitrarily.
- Lead was added in fixed proportions with the copper and tin, but this is somehow not reflected in the compositional measurements.

The first explanation may suggest that lead entered the system with the copper and/or tin ores; that is, leaded bronzes were produced by either smelting polymetallic copper–lead ores or co-smelting copper and lead ores which, unlike making alloys by mixing pure copper and lead, would not usually have uniform chemical compositions. However, a recently discovered cache of 293 lead ingots at Anyang, dated to Yinxu phase IV (c. 1101–1046 BCE) (Y. Liu et al. 2018; Anyang Team, 2021) would suggest that lead was deliberately added in the form of metal. This could suggest that lead metal may have been added been added as a cheap alterative to tin and copper; that is, low amounts of lead were added to improve castability, but excess lead was added arbitrarily because it was economically prudent. However, this does not seem to be an appropriate explanation for the high-status ritual bronzes intended for ceremonial purposes or burial with the dead.

The view taken in the current article is that lead was not added arbitrarily and that the second explanation is more likely; that is, the compositional measurements do not reflect the bronze recipe accurately. There are several reasons to support this view:

a) Copper–tin ratio

The arrows for copper and tin lie together, which suggests that they are proportional (Fig. 6). Figure 10 presents overlapping histograms of the raw data for the three dynastic periods under investigation. The ratio of Cu/Sn is on average around 6:1, with occasional outliers probably reflecting inhomogeneity in the samples rather than any deliberate change in recipe. There is no statistical difference between the logratios of (Cu/Sn) for the three sub-data sets (Shang, Western Zhou and Eastern Zhou), with each contributing to the almost normal distribution. Because it is unlikely that the same polymetallic ore source was exploited for over 1200 years producing copper–tin alloys with almost constant composition, the histogram in Fig. 10 suggests that copper and tin ores were mined separately and that tin was added to copper in measured proportions according to an empirically derived and long-lasting recipe.

The arrows for lead in the LRA plots (Figs. 5 and 6) do not lie with the arrows for copper and tin. The point being made here is that if ancient bronze producers used a standard recipe for the amounts of copper and tin used to make bronzes, why would not they apply similar rigour to the amounts of lead added?

b) Lead migration

Because lead does not dissolve in copper or bronze but remains as discrete globules, increasing concentrations can result in these globules joining up and forming

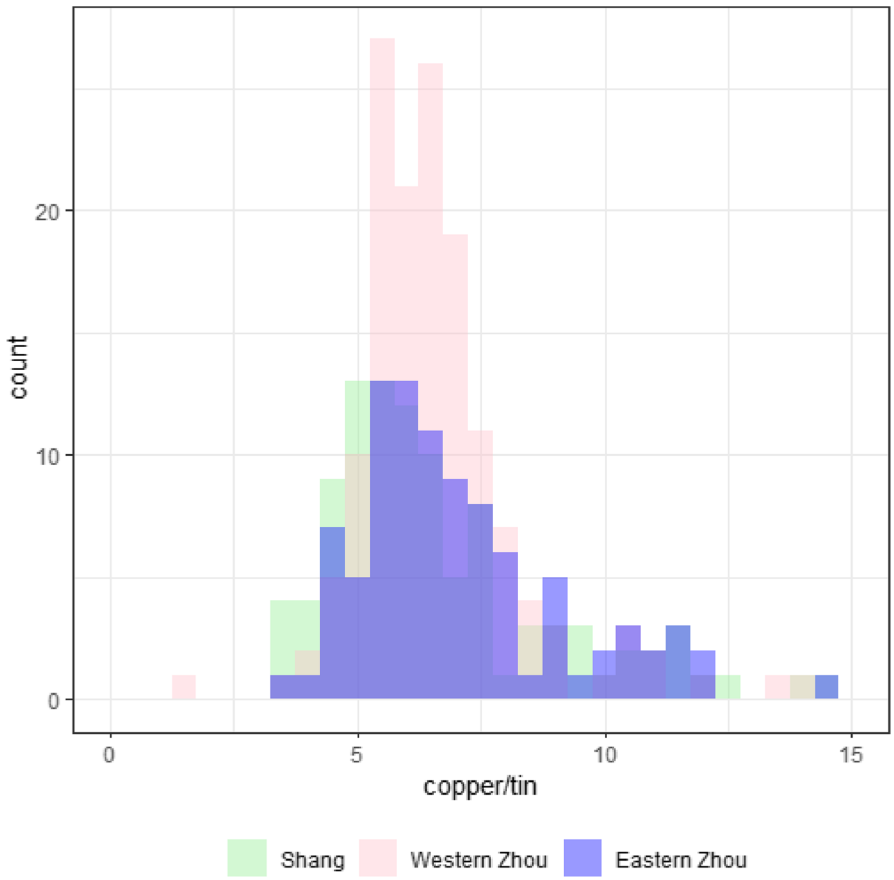


Fig. 10 Histograms of the copper-to-tin ratio (Cu/Sn) from the raw data for bronzes with compositional measurements. Outliers are not plotted for clarity

macroscopic 'lakes' of lead within bronze (Craddock & Giumlia-Mair, 1988: 319). Furthermore, lead can migrate to the surface of bronzes. Figure 11 provides an example of this phenomenon (Chen, 2010: Fig. 4.21). Lead, now in the form of lead carbonate, is found at the surface of a Shang bronze from Hanzhong, Shaanxi Province (c. thirteenth-century BCE). This suggests that compositional analyses based on measurements conducted at the surface will exhibit high levels of variation in lead and are unlikely to represent the bulk composition of the bronze (Fig. 11).

The experimental method used for the ritual bronzes was to drill into the object to remove samples for subsequent analysis (Bagley, 1987; Rawson, 1990; So, 1995). The compositions of these samples would be clearly influenced by the presence of surface layers. This is evidenced by the few repeat measurements which had been carried out that used the same hole as the original measurement but with a deeper core. Table 5. shows that there are large differences in the concentrations of lead

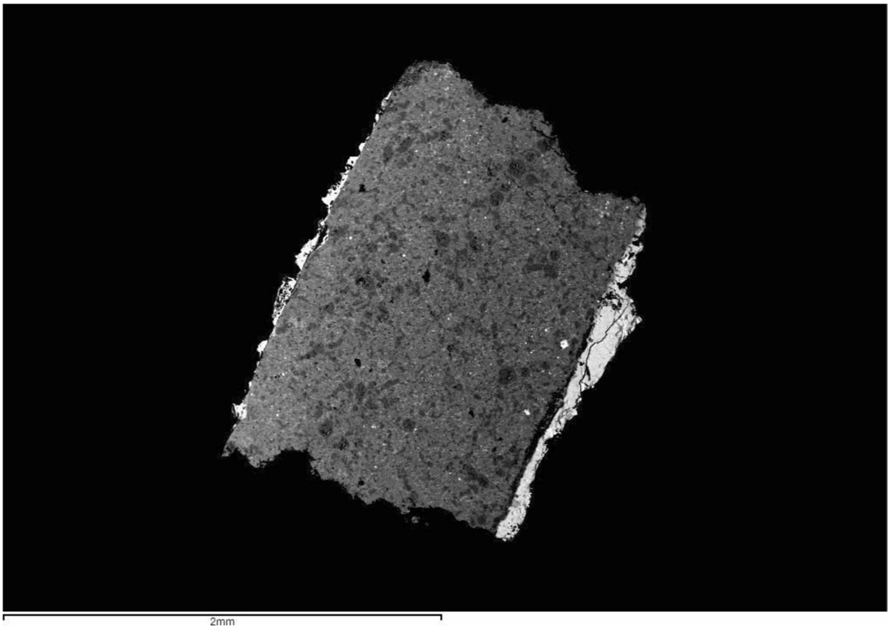


Fig. 11 Migration of lead from a Shang Dynasty bronze sample unearthed from Hanzhong, dating to about the thirteenth-century BCE. The outer layer is mainly lead carbonate. Permission from K. Chen (2010)

present; that is, in some instances, deeper holes have lower concentrations of lead (and tin). This supports that the surface, at least in some cases, had become enriched with lead either during manufacture, perhaps because of the cooling profiles caused by the moulds or because of corrosion during deposition. Furthermore, differences in the lead isotope values for different core depths could suggest that, for low concentrations of lead, it is the lead associated with copper source that dominates the LIA signal. This might suggest a new procedure to determine the copper source in bronze objects.

The repercussions of surface enrichment are that *absolute* values of lead cannot be trusted to identify the bulk composition of the bronzes when surface measurement techniques are used, and therefore, the 'true' bulk recipe cannot be determined. In fact, the differences in values between deep and shallow cores (Table 5.) cross the typical 1–2 weight% empirical boundary that is often used to differentiate between alloyed and unalloyed artefacts. This would cast doubt on studies which have attempted to relate changes in the bronze recipes to vessel type, chronologies, technological determinism and social status (Gettens, 1967; Barnard & Satō, 1975; Linduff, 1977; Bunker et al., 1997:309–318; Caley et al., 1979; Li et al., 1984), especially for studies focussing on a few objects in isolation.

c) Absolute values

Regardless of whether the surface has been enriched with lead or not, the application of absolute values presents challenges. For example, silver has been long

Table 5 Repeat measurements from raw compositional data from three Shang vessels (Bagley, 1987) using the same hole but with a deeper core. *Note that the LIA values were different for the shallow and deep measurements, with each placing in different groups

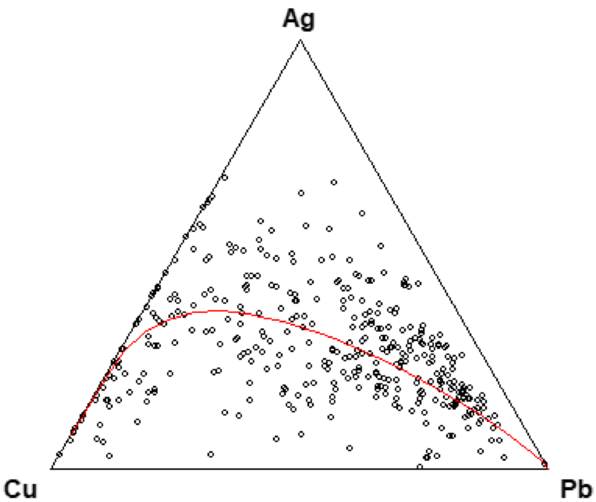
	Cat. No	Core depth	Cu	Sn	Pb	Zn	Au	Ag	As	Sb	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$	Group
			%			ppm								
Shang (ding)	82	shallow	83.8	9.5	3.33	54	11.2	1190	860	116	1.9255	0.7331	21.8484	A
		deep	98.8	0.309	0.95	115	2.83	326	540	38	1.9405	0.7424	21.5471	A
Shang (ding)	83*	shallow	83.9	12.6	1.21	47	24.8	254	4900	100	1.9822	0.7565	21.1595	B
		deep	96.4	<0.2	0.61	128	11	257	540	65	1.9330	0.7359	21.7818	A
Shang (ding)	87*	shallow	80.8	12.7	2.3	33.6	31.3	520	1320	221	1.9349	0.7414	21.5657	A
		deep	98.4	0.14	<0.05	76	44	164	144	35	2.0061	0.7877	20.0965	B

hypothesised to offer an independent proxy to characterise lead minerals. Recently, however, the silver concentration in bronze artefacts has been used to identify the numbers of lead sources of the Shang Dynasty bronzes. Liu et al., (2020b) proposed that correlations between silver and lead content, in conjunction with the lead isotope signature, suggest that bronzes found in south China and the Central Plains had different lead sources during the late Shang period. But the same method could *not* distinguish from the levels of silver the highly radiogenic and common lead used at Anyang (Liu et al., 2020b), even though the differences in lead isotopes are quite stark (Figs. 3 and 4).

The fundamental premise behind Liu et al., (2020b) analysis may supply the reason for this method working in some instances but not in others. In effect, Liu et al., (2020b) assume that lead ores contribute most of the silver to the bronze system; that is, because correlations on plots between *absolute* amounts of Ag and Cu were found to be negative and those between Ag and Pb were positive, it was considered that silver in bronzes mainly resulted from the addition of lead, with no connection to the base copper. However, this line of reasoning is flawed, primarily because changes in the concentration of lead in the bronze system will necessarily result in changes in the absolute values of the other components, including copper.

This issue is best visualised by plotting a ternary diagram (Fig. 12) using centred values of the compositional data for Ag–Cu–Pb from the Shang, Western Zhou and Eastern Zhou legacy datasets. The data appear to follow a one-dimensional pattern joining the vertices Cu and Pb. This suggests that ratios involving Ag have almost a constant value and that most compositional variance is due to variation in Pb/Cu (note: a similar pattern is obtained if the Cu + Sn amalgamation is used instead of copper). In effect, plots of absolute values of Ag vs. Cu and Ag vs. Pb (Liu et al., 2020b) can result in correlations that are compelled (i.e. as the proportion of one component increases, the proportions of other components *must* decrease) and therefore *cannot* be used to conclude that silver is solely attributable to the addition

Fig. 12 Ternary diagram for the subcompositions Cu–Pb–Ag from the Shang, Western Zhou and Eastern Zhou legacy data, exhibiting a one-dimensional pattern joining the vertices Cu and Pb. The red line displays the direction of the principal component of the subcomposition



of lead. In fact, the concentrations of silver in the bronzes are higher than the few tenths of a per cent usually associated with lead from galena ores (Wood et al., 2021), and copper sources such as tetrahedrite (fahlore) are well known to be associated with silver (Cronshaw, 1921: 12; Pernicka et al., 2016). Nonetheless, regardless of whether the silver derives from the lead and/or the other components, its variation is dominated by fluctuations in the compositional recipe.

These fluctuations in the recipe are evident in the confidence interval plots (Fig. 9) investigated here for the logratio of (Pb/Ag), which show similar patterning to the confidence interval plot of the logratio of Pb/(Cu + Sn). The logratio of (Pb/Ag) suggests that the vessels in Shang Group A and Eastern Zhou Group (E) generally have either more lead and/or less silver than Shang Groups B and C and Western Zhou (W). However, a cursory inspection of the raw data (Table 3) shows that Shang Group A has more lead and less silver than Shang Group B, less lead and less silver than Shang Group C, and more lead and less silver than Western Zhou (W). Although some lead sources inevitably are more argentiferous than others, non-systematic differences are difficult to interpret, even before overlaps in confidence intervals are considered.

Essentially, analyses based on correlations between absolute concentrations of silver and lead content (Liu et al., 2020b) are unable to distinguish between the lead sources, which means that they are unlikely to be able to differentiate between compositions of bronzes found in south China and those from the Central Plains.

Logratios as Indicators

The analytical approach conducted in the current article is focussed less on absolute amounts of each component, but on relative amounts (i.e. log*ratios*). Nonetheless, examination of the raw data shows that the variation of the amalgamation (Cu + Sn) that comprises the main components of the bronze system is relatively constant. This could suggest that differences between groups for the confidence plot of log(Pb/(Cu + Sn)) reflect the variation in the lead concentration (Fig. 9). For example, an examination of the raw data (Table 3) confirms that the Eastern Zhou bronzes (Pb%: mean = 15.57, median = 15.55, s = 7.73) have two to three times as much lead as a combination of the other groups (Pb%: mean = 6.86, median = 4.80, s = 6.84). This could be useful parameter to identify Eastern Zhou bronzes. However, it must be restated that these lead values were measured by drilling and sampling material that may have been enriched with lead (Fig. 11; Table 3) and therefore do not necessarily reflect the compositional recipe of the bulk bronze.

A lot of between-group variance can be explained from the logratios of Sb/(Cu + Sn) and As/(Cu + Sn) (Figs. 8 and 9). Plotting log(Sb/(Cu + Sn)) vs. log(As/(Cu + Sn)) on a bivariate plot indicates a relationship with the groups (Fig. 13). At higher values, the logratios appear to exhibit a correlation for Shang Group C, Western Zhou (W) and Eastern Zhou (E), suggesting concomitant increases in Sb and As with increasing (Cu + Sn). As many copper ores have naturally occurring arsenic and the copper minerals tetrahedrite ($Cu_{12}Sb_4S_{13}$) and tennantite ($Cu_{12}As_4S_{13}$) often form a solid solution, this correlation potentially reflects that fahlore was

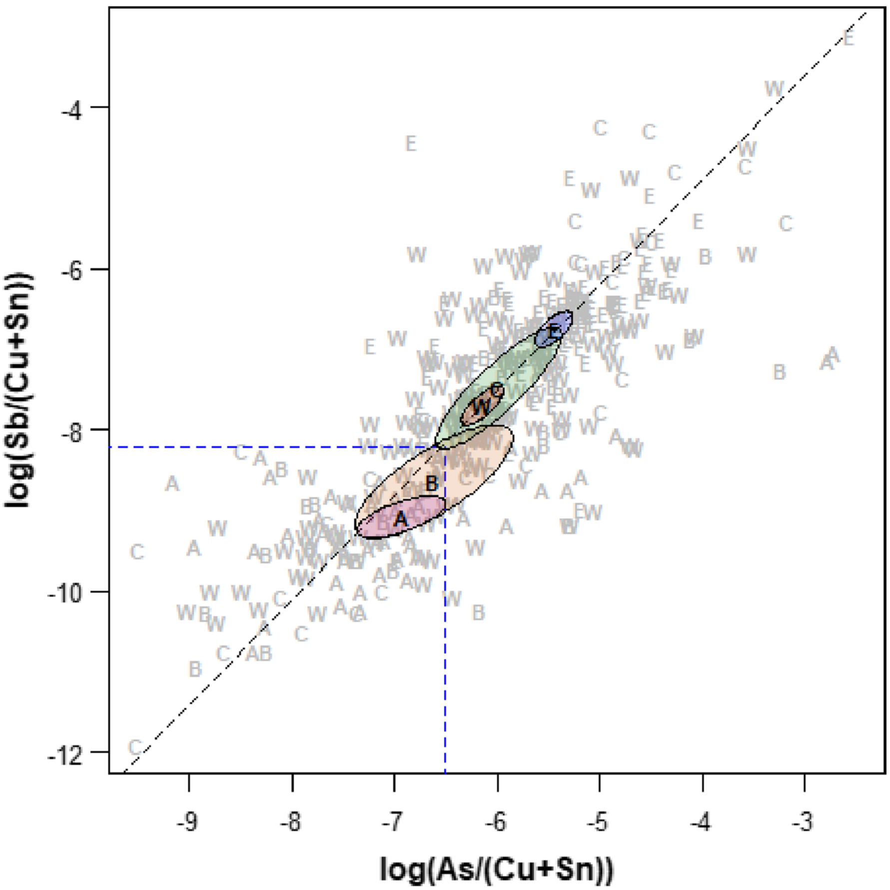


Fig. 13 Scatterplot of the two logratios log(Sb/(Cu + Sn)) and log(As/(Cu + Sn)) for bronzes, using the same bootstrapping approach to obtain 95% confidence ellipses around the means (large symbols: Shang A, B and C; Western Zhou (W) and Eastern Zhou (E)) of the three groups. The grey dashed line is drawn through the three mean values for Shang Group C, Western Zhou (W) and Eastern Zhou (E). The data show a possible deviation from linearity at lower values of the two logratios, that is, log(Sb/(Cu + Sn)) ≈ -8.2 and log(As/(Cu + Sn))≈ -6.5

exploited to acquire copper. At lower values, the orientation of the confidence ellipses of Shang Groups A and B indicates that these groups are less associated with both antimony and arsenic, that is, the deviation from the dashed line at progressively lower values of these ratios (approximately log(Sb/(Cu + Sn)) = -8.2; log(As/(Cu + Sn) = -6.5).

Figures 14 plots the data for log(Sb/(Cu + Sn)) with respect to the chronologies of the vessels determined from typological assessments. The increase around 1100 BCE suggests a sudden transition to using fahlore to source copper, that is, values higher than approximately log(Sb/(Cu + Sn)) = -8.2 (denoted by the dashed line in Fig. 14). These higher values consist mainly of vessels from Shang Group C, the Western Zhou (W) and Eastern Zhou (E) and indicate that copper sources

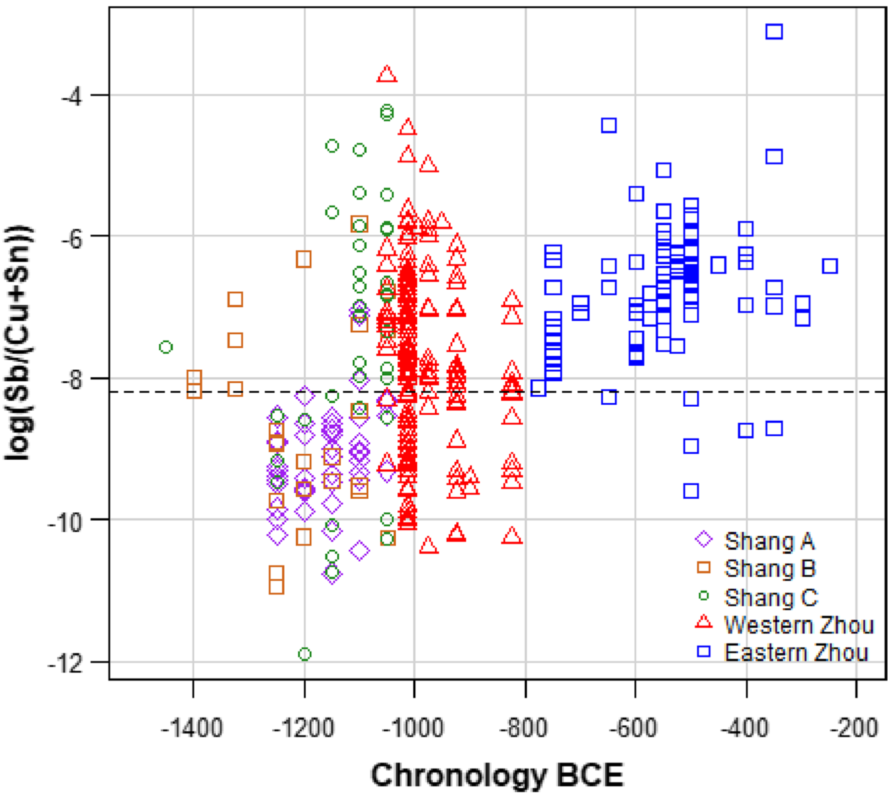


Fig. 14 Plot of log(Sb/(Cu + Sn)) against chronologies of vessels determined from typological assessments delineated by groups (Shang A, B and C; Western Zhou (W) and Eastern Zhou (E). The dashed line is a threshold determined from the step change (log(Sb/(Cu + Sn)) = -8.2). Note that this threshold is similar to the change in slope at lower values of this ratio in Fig. 13

associated with antimony were increasingly exploited, thereby supporting that fahlore ores were increasingly targeted for copper from around the eleventh-century BCE.

Arsenic and gold plotted on the same type of plot as Fig. 14 exhibit similar relationships, although the changes in values for the logratio that includes gold are much smaller (as indicated in the scales on the confidence interval plots in Fig. 9). Nonetheless, as gold can be associated with fahlore (Kucha et al., 1997), this would support that copper was acquired from fahlore from c. eleventh-century BCE.

In effect, Fig. 14 suggests that the majority of Chinese ritual bronze vessels manufactured:

- between 1300 and 1100 BCE were made using copper from oxidised copper ores.
- between 1100 and 800 BCE were made using copper from both oxidised copper ores and fahlore.

- after 800 BCE (i.e. the bronzes of the Eastern Zhou dynasty), were made almost exclusively from copper derived from fahlore.

The few bronzes from earliest times, prior to and through the Erligang Period (c. 1500–1300 BCE) (Watson, 1977), that is, the fifteenth-century (Style I) and the late fourteenth-century BCE (Styles II and III) vessels, display values of log(Sb/(Cu + Sn)) which lie on or above the dashed line. This could suggest that these few early vessels were made in locations where oxidised copper sources had already been exhausted, presumably to make copper objects.

The confidence interval plot (Fig. 9) shows that the logratio of (Pb/Zn) appears to decrease between the Shang and Western Zhou dynasties, with the Western Zhou exhibiting significantly lower values than the Shang Group A. This suggests that, despite the transition from radiogenic to common lead in c. eleventh-century BCE, the change in log(Pb/Zn) is gradual until the Eastern Zhou dynasty (over 200 years later). This can be observed in a histogram for log(Pb/Zn), which highlights that

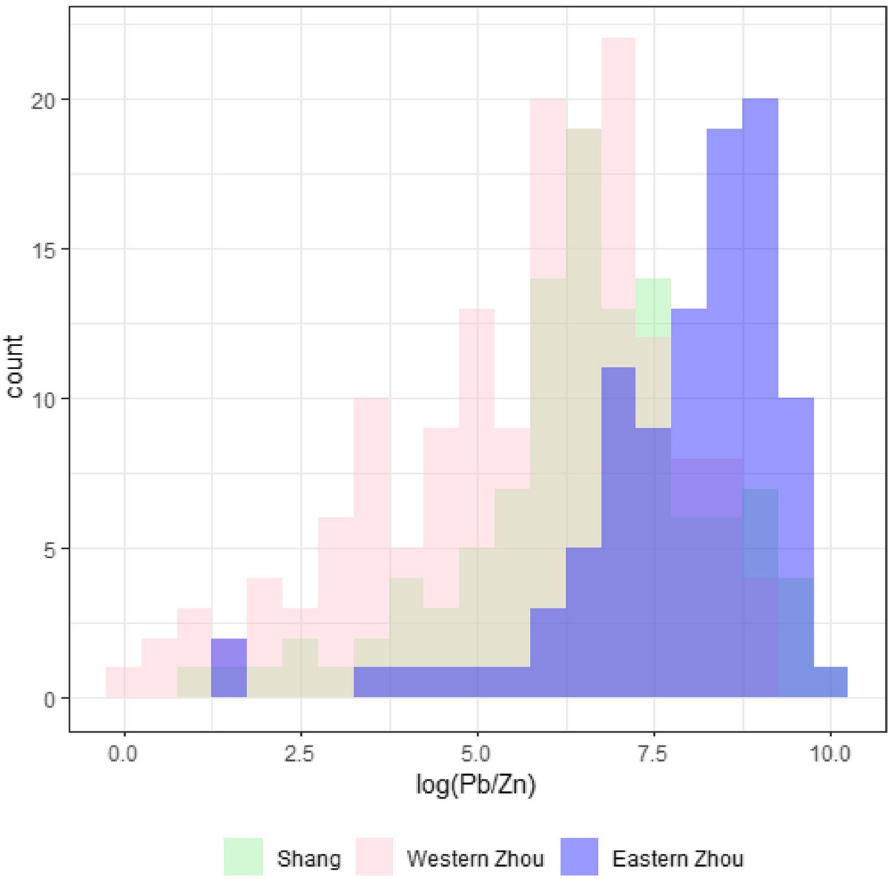


Fig. 15 Histograms of log(Pb/Zn) for the Shang, Western Zhou and Eastern Zhou dynasties

vessels from the Shang, Western Zhou and some from the Eastern Zhou overlap (Fig. 15). In fact, the spread in the logratio of (Pb/Zn) appears to be greater for the Western Zhou vessels than those of the Shang dynasty. This could suggest that lower-grade ores were exploited in later periods; that is, miners tried to acquire pure lead ores but were increasingly impeded by the presence of unwanted zinc ores.

Figures 16 uses the empirical threshold of log(Sb/(Cu + Sn)) = -8.2 from Fig. 14 to plot log (Sb/(Cu + Sn)) vs log(Pb/Zn), that is, the ratios that explain the greatest proportions of compositional variance in the bronzes. In fact, these two logratios can explain most of the compositional variation in the ritual bronzes and distinguish between the groups of vessels.

For clarity, plots of (Sb/(Cu + Sn)) vs log(Pb/Zn) are presented for the different groups. These plots are interpreted as follows:

- The vertical axis (log(Sb/(Cu + Sn)) reflects predominantly differences in the copper source. Values below the dashed line suggest low concentrations of antimony in the bronzes and the use of oxidised copper ores. Values above the dashed line suggest high concentrations of antimony in the bronzes and the use of fahlores.
- The horizontal axis (log(Pb/Zn)) reflects predominantly differences in the lead source. High values of the logratio reflect low concentrations of zinc in the bronzes and the application of high purity lead ores, such as galena. Low values reflect high concentrations of zinc in the bronzes and lead ores associated with high amounts of zinc mineral, such as sphalerite.

The narrative that emerges from these bivariate plots is that the drivers for the compositional variation between groups are that near-surface oxidised copper ores were exploited in the thirteenth–twelfth-century BCE (i.e. vessels from Shang Groups A and B with log(Sb/(Cu + Sn) < -8.2) until the sudden introduction of copper from deeper ores with higher concentrations of antimony (i.e. vessels from Shang Group C and Western Zhou with log(Sb/(Cu + Sn) > -8.2). It is not until the Eastern Zhou dynasty that fahlore was used almost exclusively.

The reason for the variation in the logratio of (Pb/Zn) in Fig. 16 is more difficult to identify. One possible explanation would be that the variation in zinc concentration is due to variation in smelting and manufacturing processes. However, decreases in log(Pb/Zn) during the Shang and Western Zhou dynasties indicate that lead ores with more zinc were used to make bronzes in later periods; that is, the logratio of (Pb/Zn) decreases from the Shang and throughout the Western Zhou dynasties (Fig. 9). This would suggest that the processes used to make the ritual bronzes were less efficient in later periods than at their inception. While possible, the patterns shown in Fig. 16 suggest a trend opposite to most technological systems and would require an alternative sociocultural explanation.

An alternative interpretation is that these bivariate plots (Fig. 16) indicate that the lead source *did not change* from the Shang to Western Zhou dynasties and that there was variation in the same lead deposit; that is, the spread in the logratio of (Pb/Zn) suggests that high- and low-grade lead ores were exploited and that the transition from lead ores with low to high levels of zinc was gradual. In effect, the majority of

Fig. 16 Plots of log(Sb/(Cu + Sn)) against log(Pb/Zn) delineated by groups (Shang A, B and C; Western Zhou (W) and Eastern Zhou (E). (Fig. 16a: upper) Shang Groups A, B and C; (Fig. 16b: lower) Western Zhou (W) and Eastern Zhou (E). The dashed line is the threshold from the step change in Fig. 14. Increases in the vertical axes potentially reflect deeper mining of copper ores, and decreases in the horizontal axes potentially reflect deeper mining of lead ores

vessels in Shang Groups A and B that have values for log(Pb/Zn) ≥ 6 could suggest that lead used to make these bronze vessels derived mainly from lead ores associated with relatively low levels of sphalerite. Conversely, the numbers of vessels with lower values (i.e. log(Pb/Zn) ≤ 6), which appear to increase during eleventh-century BCE (i.e. Shang C) and particularly during the Western Zhou dynasty, suggest lead ores with more associated sphalerite. This patterning would be indicative of lead deposits that were increasingly mined at progressively lower depths for lower grades of lead ore in later periods (i.e. the lead ore mined became increasingly associated with zinc minerals). Essentially, the high variation in log(Pb/Zn) supports strongly that a lead deposit was thoroughly exploited.

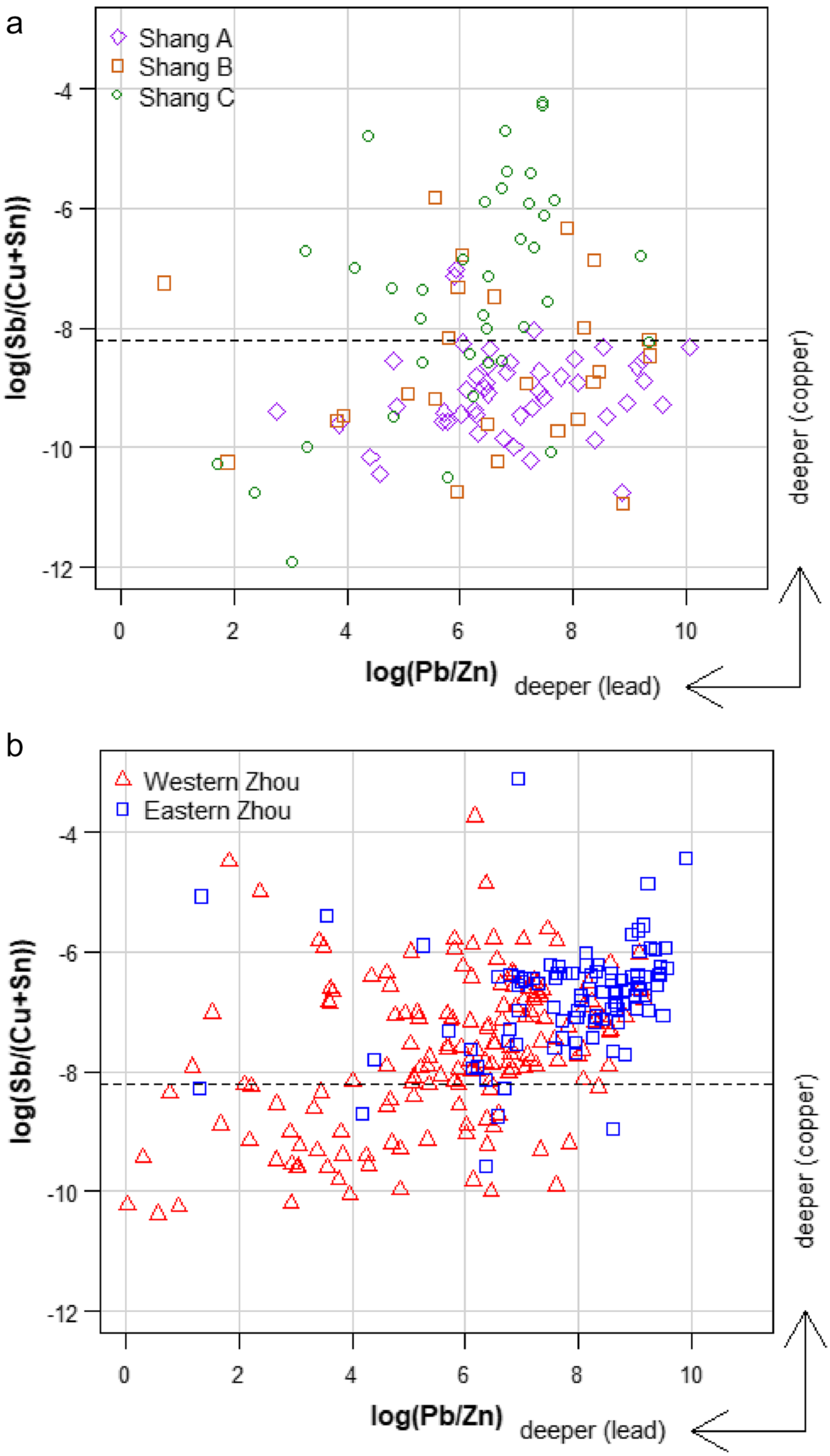
The Eastern Zhou bronze vessels indicate exploitation of a different lead deposit (i.e. significantly higher values of log(Pb/Zn) in Figs. 9, 15 and 16). This could suggest that during the Eastern Zhou period another lead deposit was deliberately sought out that was not associated with zinc minerals (and/or that there were technological advances such as the roasting of ores prior to smelting). However, although the majority of the Eastern Zhou vessels have these higher values, many Eastern Zhou vessels have log(Pb/Zn) values that overlap with those of the earlier vessels (Fig. 15). This could suggest that even during the Eastern Zhou the same lead deposits were worked as those in the Shang and Western Zhou dynasties.

Essentially, the compositional analyses suggest that sudden increases in log(Sb/(Cu + Sn)) reflect deeper mining of copper ores in a typical copper deposit as oxidised ores became exhausted and fahlores were exploited. Possible decreases (or at least significantly increased variation) in log(Pb/Zn) from the Shang to the Western Zhou could reflect progressive mining of lower-grade ores until the Eastern Zhou dynasty. This indicates thorough (and perhaps increasingly deeper) mining of lead ores in a typical lead deposit.

Applying the Indicators

This section applies the indicators that represent the most compositional variation in the legacy data set to unearthed objects in the Chinese archaeological record, that is, the logratios of Sb/(Cu + Sn) and Pb/Zn.

Only a small number of tombs have been found intact at Anyang. Of those with bronzes (weapons and ritual vessels) found in situ, some have compositional analyses. Compositional data have been collated from several sources by Liu et al., (2020a) and include bronzes from higher and lower 'elite' tombs. Figures 17 and 18 present compositional data from unearthed objects at Anyang that had numerical elemental measurements for copper, tin, lead, antimony and zinc (85 objects). These samples had been delineated according to the following chronologies (Liu


a
Shang A
Shang B
Shang C
log(Sb/(Cu+Sn))
log(Pb/Zn)
deeper (lead)
deeper (copper)
b
Western Zhou
Eastern Zhou
log(Sb/(Cu+Sn))
log(Pb/Zn)
deeper (lead)
deeper (copper)

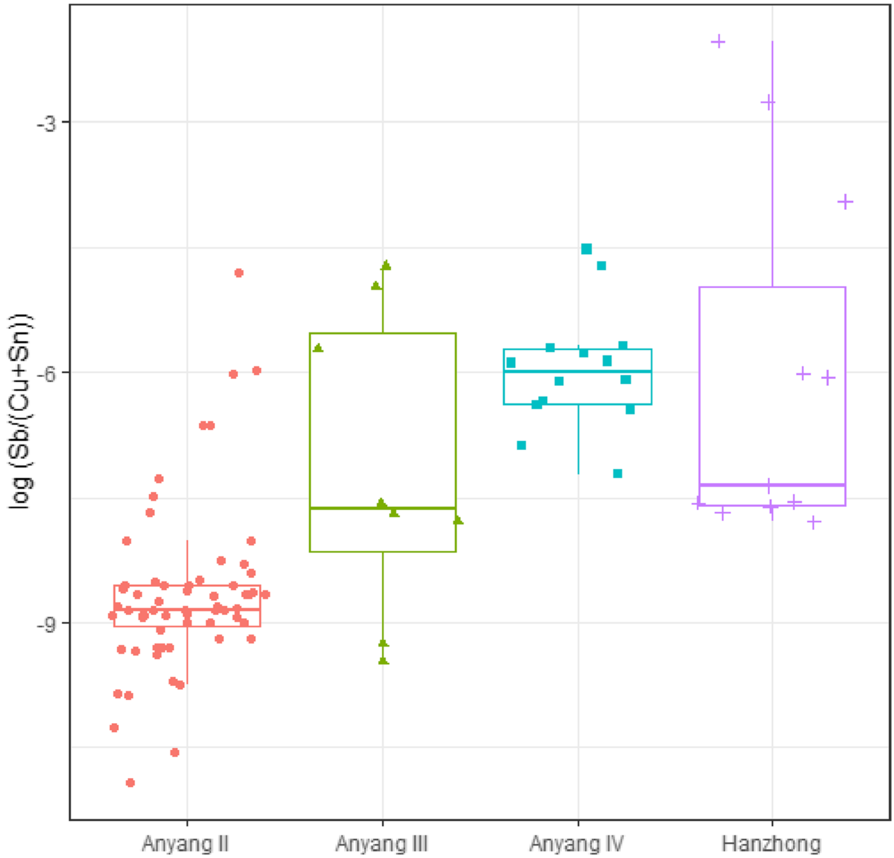


Fig. 17 Boxplots of log(Sb/(Cu + Sn)) for unearthed bronze objects from Anyang and Hanzhong. Data sources listed in ANYANG_HANZONG.csv file in supplementary materials. The boxes indicate the medians and interquartile ranges (IQR). The whiskers indicate points that fall within 1.5 × IQR. Jitter has been applied to the points to prevent obscuring values due to overlaps. Notice that for the unearthed Anyang objects there is an increase in log(Sb/(Cu + Sn)) with later chronologies. This is consistent with the increase exhibited by the legacy data (Fig. 14)

et al., 2020a): Anyang Phase II (1243 BCE–1157 BCE), Phase III (1197 BCE–1108 BCE) and Phase IV (1177 BCE- 996BCE). Figures 17 and 18 also show compositional data for sceptre- and sickle-shaped copper-based objects from Hanzhong (Chen et al., 2009) that had values above the detection limit for copper, tin, lead, antimony and zinc (11 objects). This site has been considered contemporary with the late Shang (c. fourteenth–twelfth-century BCE), with the presence of dozens of typical Shang-style ritual vessels among the bronze finds indicating a correlation between the Hanzhong bronzes and the Shang culture in the metropolitan areas (Chen et al., 2009).

The logratio of Sb/(Cu + Sn) increases from Anyang II to Anyang IV (Fig. 17). This supports the proposition presented earlier that there was a change in the type of copper

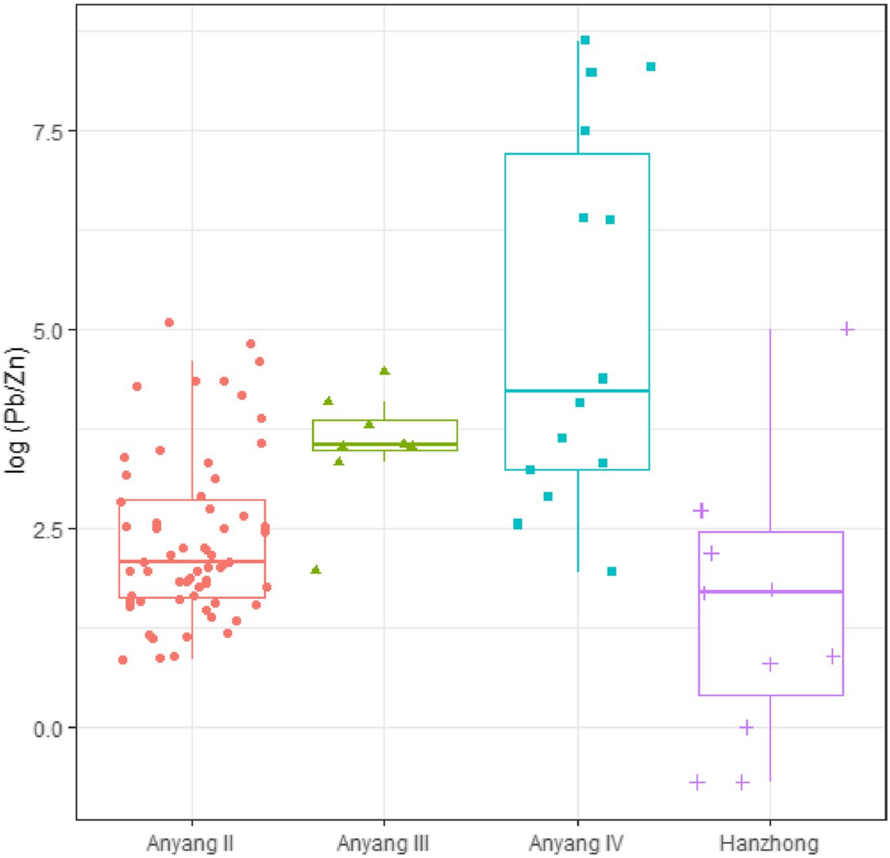


Fig. 18 Boxplots of log(Pb/Zn) for unearthed bronze objects from Anyang and Hanzhong. Notice that six ritual vessels from Anyang phase IV have values (ranging between 6.4 and 8.6) which are consistent with Shang ritual vessels from the legacy data (Figs. 15 and 16)

ore towards the end of the Anyang period, from oxidised copper ores to fahlore. These unearthed objects also indicate that the majority of the unprovenanced Shang dynasty bronzes in the legacy data set derived from Anyang. Furthermore, the copper-based objects from Hanzhong are consistent with the later Anyang bronzes, particularly those objects from Anyang Phases III and IV. This suggests that these Hanzhong objects were made using copper derived from fahlore, that is, antimony-rich ores. This makes the Hanzhong objects consistent with those unearthed at Anyang as well as those in Shang Group C in the legacy dataset. In effect, the composition of these ceremonial implements, although distinctive in typology from other object categories of Hanzhong bronzes, such as vessels and weapons (Chen et al., 2009: Fig. 9) whose materials match the widely used tin–lead bronze system in the Shang period (Chase & Ziebold, 1978), exhibits similar log(Sb/(Cu + Sn)) values to bronze objects unearthed at Anyang and to those of the legacy data presented earlier. This could suggest that although there may have been the existence of indigenous metalworking traditions at Hanzhong (Chen et al. 2009), the bronze metal was potentially derived from the same location as that of the Anyang bronzes and was reworked at Hanzhong. In effect, the Hanzhong sickle-shaped and sceptre-shaped objects were most likely local creations made from the same copper metal used to make bronze objects at Anyang. This suggests that metal was transported from Anyang and/or there were recycling and recasting of Anyang objects at Hanzhong, perhaps mixed with local copper objects, to make these endemic ceremonial implements.

Figure 18 shows that the logratio of (Pb/Zn) exhibits a high degree of overlap between the four unearthed groups, which could suggest that the same lead ore deposit was exploited. Any patterning regarding chronology, however, is less evident here than in the legacy datasets, potentially due to the low levels of lead in these unearthed objects. These low lead levels could be because differences in sampling and measurement methods play a much more significant role for any indicator that includes lead (due to the migration of lead to the surface of bronzes—Fig. 11; Table 5.), and/or because many of the unearthed objects are bronze weapons rather than ceremonial vessels. A cursory examination of the compositional data of these unearthed objects (see the ANYANG_HANZHONG data file in supplementary materials) suggests that lead was not added as part of the compositional recipe to many of these unearthed objects (perhaps to retain their mechanical properties); that is, the logratio of (Pb/Zn) reflects the intrinsic lead found in the copper (and tin) rather than lead that was mined and deliberately added to improve castability of the large ceremonial vessels in the legacy datasets. Conversely, the elemental analysis conducted on the unearthed Anyang ritual vessels by Zhao et al. (2008) (i.e. six ritual vessels with high levels of lead from Anyang IV) has log(Pb/Zn) values that range from 6.4 to 8.6 (Fig. 18). These values are consistent with the Shang ritual vessels in the legacy datasets (Figs. 15 and 16). In effect, the variation in the indicator log(Pb/Zn) in Fig. 18 reflects the category (vessels, weapons and so forth) of bronze objects and whether exogenous lead was added. Nonetheless, as with the legacy dataset, there is no evidence of any sudden change in the composition of the lead source for the unearthed Anyang data (Fig. 18) that can be associated with the transition from radiogenic to common lead sources (Fig. 4). Moreover, the high variation of log(Pb/Zn) for the Hanzhong sceptre- and sickle-shaped artefacts is consistent with the use of recycled bronze- or copper-based objects from Anyang to make these implements, perhaps mixed with local copper objects, rather than Hanzhong having its own bronze-making tradition.

In summary, Figs. 17 and 18 not only demonstrate the utility of the indicators log(Sb/(Cu + Sn)) and log (Pb/Zn) for comparing bronzes from different sites, chronologies and object categories, but also for analysing compositional data generated by different experimental instruments from different research groups.

Discussion

There has been a lot of debate regarding the locations of the copper, tin and lead sources used to make the ritual bronzes of the Chinese Bronze Age. Lead isotope research has suggested that, for at least the first half of the Late Shang, a significant portion of the Anyang bronzes contained radiogenic lead, a feature they share with contemporaneous bronzes found along the Yangtze from Sichuan to Jiangxi (Jin et al., 2003: 594–602; Jin et al., 2017). However, ancient lead miners had no way of differentiating between radiogenic and common lead deposits, which would suggest that the move to common lead ores near the end of the Shang dynasty was simply part of the process of mining for appropriate lead sources to make bronze. An appropriate lead source would have been one that was easy to smelt to produce lead that could be cast with copper and tin in multicomponent moulds to make bronze vessels.

It is difficult to comment on the tin source using the analyses presented here because tin and copper are intimately connected in the compositional recipe. However, because tin very rarely occurs naturally with copper (Jettmar, 1971), it is likely that tin was acquired separately but mixed with copper in a prescribed recipe. However, the compositional analyses suggest that the bronzes were produced using different types of copper ore. Initially, it appears that the ores mined were copper oxides—probably colourful ores such as malachite ($Cu_2CO_3(OH)_2$). Towards the end of the Shang Dynasty (c. eleventh-century BCE), copper also appears to have derived from sulphidic fahlores ($Cu_{12}Sb_4S_{13}$). Both oxidised and fahlore copper ores continued to be used during the Western Zhou dynasty, followed by an almost exclusive use of fahlore in the Eastern Zhou period. As oxidised copper ores are often found in the near-surface weathered horizon of typical copper deposits and fahlores are found deeper and close to the primary sulphide ore body, these compositional changes could suggest that a single copper deposit, perhaps with many mines, was exploited throughout the Shang, Western Zhou and Eastern Zhou Dynasties. This mining trajectory is supported by the compositional data from the legacy datasets and from the objects unearthed at Anyang, both of which indicate that later bronzes contain more antimony. Furthermore, this signature is found in the copper-based objects of Hanzhong, which alongside the dozens of typical Shang-style ritual vessels recovered at the site suggest that either bronze metal was transported from Anyang or that Shang bronzes were recycled at Hanzhong to make objects that were desirable to the local population.

Regarding the mining of lead ores, there does not appear to be any sudden change in composition when the transition from the radiogenic to common sources of lead occurred (c. eleventh-century BCE). In fact, the increased association of zinc in the legacy datasets could suggest that lower-grade lead ores were exploited from the Shang dynasty onwards and that zinc minerals, such as sphalerite, reflect the mining of deeper ores; that is, that same lead deposit was mined progressively until the grade of the ore mined was too low to smelt lead of sufficient quantity or quality to manufacture the ritual bronzes. In fact, there only appears to be a significant change in the lead source during the Eastern Zhou dynasty. This chronological trajectory is less apparent in the unearthed objects because not all categories of objects appear to have had exogenous lead added (such as weapons). Nonetheless, the indicator log(Pb/Zn) does not suggest any change in the composition of the lead source with the change from radiogenic to common lead at the end of the Shang dynasty for both the legacy data and unearthed objects.

In effect, the compositional analyses conducted here suggest that differences between groups, which are not apparent if only lead isotope data are used to investigate the vessels, can be explained by the high proportion of compositional variation of two logratios: log(Sb/(Cu + Sn)) and log(Pb/Zn). The variation in these ratios potentially reflects a trajectory from the Shang dynasty onward for deeper mining of copper and lead ores. This trajectory fits well with a sociocultural explanation of development in technological systems that enabled miners to exploit ores in the contact zone, at levels close to the water table.

Interpretations of the compositional analyses appear to be in direct conflict with the analyses based on lead isotopes. In fact, the compositional analyses suggest that the transition from radiogenic to common lead is *not* a consequence of exploiting new lead deposits in different locations but simply exploitation of lower-grade (and probably deeper) lead ores in the *same* deposit. The mechanism to reconcile the elemental and lead isotopic datasets is as follows:

1. Ancient miners were unable to distinguish radiogenic from common lead sources, and even if they had been able to do so, it would not have informed their choice about which lead ores were worth exploiting to make bronze. What appears to have informed ancient lead miners, however, were zinc minerals. Zinc minerals, such as sphalerite (ZnS), which are often avoided due to the volatility of zinc during smelting and casting, can be found in typical lead ore deposits. Despite zinc being an unwanted and chemically complex partner in smelting operations (Wertime, 1968), ancient miners would have been increasingly unable to dig around brown sphalerite to get at the speckled galena. Therefore, lead and zinc minerals from the *same* deposit were increasingly smelted together. A change in lead deposit only appears to have occurred during the Eastern Zhou dynasty.
2. Without the need for a change in location of the source of lead to explain the compositional changes, suggests that heterogeneous lead deposits were mined; that is lead deposits were exploited that comprised both common and radiogenic lead. Zhu and Chang, (2002) have proposed the Mississippi type of lead–zinc mineralisation or uranium rich lead mines at the edge of late archaic shield, which are potential radiogenic sources in China. The four regions they identified for such sources include the regions of Northeast Yunnan, Qinling, the middle and lower Yangtze River and Northeast China. These disparate regions do not particularly narrow down the archaeological regions proposed for the sources of lead (and copper) to make the bronzes. However, what they do highlight is that lead deposits near these sources could exhibit systematic zoning of radiogenic and common lead within what would normally be classified as a common lead deposit; that is, common lead deposits that underwent the genetic process of progressive modification of the composition of common lead by the incremental addition of radiogenic lead.

This mechanism would provide an explanation for the sudden change from radiogenic to common lead in the manufacture of the ritual bronzes after about 300 years—miners started to dig out ores in a different zone of the same lead deposit around the eleventh-century BCE. It would also suggest that vessels with intermediate values in Fig. 4 may not be a consequence of mixing bronzes or lead metal, or the exploitation of numerous discrete lead deposits, but are due to variation in the ore-bearing horizons from the numbers of mines that exploited the lead deposit. The mechanism also provides an explanation as to why the source of radiogenic lead for the bronzes has not been located—the radiogenic zone was exhausted during the Shang Dynasty (i.e. Shang Groups A and B) before the continued exploitation of the same deposit in the common lead zone (i.e. Shang Group C) throughout the Western Zhou Dynasty (W). Although the compositional analyses suggest that there was a change in the lead ore deposit during the Eastern Zhou dynasty (771–256 BCE), probably instigated by high levels of zinc minerals, some of the Eastern Zhou vessels overlap those of the earlier vessels. In other words, the cessation of radiogenic lead at the end of the eleventh-century BCE does not necessarily require any change in location of the lead source, and its location is probably in a region where only archaeological evidence of mining a common lead deposit would now be found.

The change from radiogenic to common lead ores (Fig. 4) and the exploitation of fahlore would support that Shang mining technology advanced around the eleventh-century BCE; that is, Shang miners began to dig shafts and horizontal galleries sufficiently large for workers to follow veins of galena and fahlore. In fact, sporadic (and inadvertent) use of radiogenic lead for bronze vessels (Fig. 4) and for non-metal objects such as pigments, leaded glaze and glass in later periods (R. Liu. et al. 2018) appears to reflect that any change from predominantly radiogenic to common lead sources simply signals that lead deposits were thoroughly exploited. In effect, once it is recognised that radiogenic and common lead signatures can be found in the same ore deposit, any change in isotopic signature could simply mark the expansion of mining in the same deposit rather than signalling changes in geographical location. This suggests that the metals used for the ritual bronzes of the Chinese Bronze Age were acquired by digging deeper rather than seeking out new sources, at least until the Eastern Zhou dynasty.

It is perhaps important to note that only around 1,000 tons of metal over 200 years were required to manufacture the bronzes buried in tombs at Anyang (Campbell, 2014: endnote 8); that is, a combined weight of 14 kg per day of copper, tin and lead. That one metalliferous region had sufficient resources to manufacture these ritual bronzes and those of the Zhou dynasties seems quite plausible. Although the location of this region is still up for debate, it needs to be considered that a region should not be discounted simply because radiogenic lead signatures or oxidised copper ores are now absent. In fact, since it is likely that these copper and lead sources would have been exhausted in the Bronze Age, it is perhaps time to reinstate southern Shanxi province, an area rich in copper and tin (Shih Chang-ju in Barnard & Satō, 1975: fig. 13) and the birthplace of the legendary Xia (the first Chinese Bronze Age dynasty), as the main candidate that supplied the metals for the ritual bronzes.

Concluding Remarks

There is no doubt that the bronze vessels of the Shang, Western Zhou and Eastern Zhou dynasties fulfilled multiple social, political and ritual roles for different groups of people. However, before modes of production, circulation and consumption of metal can be used to inform on sociocultural patterns, it is necessary to interrogate the scientific data and their analyses that allow such inferences to be made. Many investigations into Chinese bronzes have focussed primarily on analysing lead isotope measurements from bronze artefacts. These analyses have been considered to provide evidence that distant regions around China and beyond supplied metals to manufacture the bronze vessels, and, in turn, this evidence has been used to inform on the wider social and cultural contexts of the Chinese Bronze Age. The analyses conducted in this article incorporated lead isotope, elemental and chronological data from over 300 bronze vessels from legacy data sets and nearly 100 copper-based unearthed objects from Anyang and Hanzhong. The issue addressed here is not whether lead isotope and compositional data can identify changes in archaeometallurgical signatures—they can—but whether these changes are meaningful to determine the sources of metals that can inform on the societies and cultures of the Chinese Bronze Age.

It is proposed that radiogenic and common lead signatures are a distraction to determination of the provenance of bronze objects from the Chinese Bronze Age and that the conclusions derived from the compositional data are more parsimonious than those based predominantly on lead isotopes. Essentially, the analyses indicate that typical deposits of copper and lead were exploited throughout the Shang, Western Zhou and part of the Eastern Zhou dynasties by mining progressively deeper ores, as reflected in the objects of legacy data sets and the unearthed objects from Anyang. Furthermore, it appears that copper-based objects found at Hanzhong have similar compositional signatures to those unearthed at Anyang. This could suggest that either metal was transported from Anyang to Hanzhong or that some Shang objects were acquired and recast at Hanzhong.

In terms of the social and cultural implications, these analyses make it difficult to conclude that the knowledge required to make bronze vessels was widely distributed by the Late Shang period or that there was integration of smaller, peripheral sites based on the circulation of technological capital far beyond the limits of Shang hegemony. A more probable interpretation is that the ritual bronze vessels of the Chinese Bronze Age, at least until the Eastern Zhou dynasty, were manufactured in the Shang and Zhou heartland from metals mined in these regions and that at some point bronze objects travelled to locations beyond these spheres of influence.

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Declarations

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