Chemical analysis of ancient Chinese copper-based objects: Past, present and future

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Abstract

The primary aim of this paper is to track the history of quantitative chemical analysis on Chinese copper-based metal objects and suggest a future outlook. The beginnings of this subject can be traced to the 1770s. Its overall history can be divided into five stages. By considering the different interpretational contexts in each of these stages, we show that all have made a significant contribution to our knowledge of the chemistry of copper alloy objects in China, and in broader terms to understanding the archaeology of China. Thanks to the sustained efforts of our predecessors, a substantial database of chemical and isotopic information has been created for present scholars, which we summarize here. We suggest, however, that this database contains a great deal of invaluable information which has yet to be fully explored. Moreover, given the scale of the Bronze Age in China, we also suggest that there is a great deal of more analytical work required before we can truly interpret the role of metal in Bronze Age Chinese society. This historical review also suggests that dialogue between related disciplines is a crucial factor in this area, and one which is vital in capitalizing the work already achieved.

Introduction

A staggering number of copper–alloy objects have been unearthed in China since the first scientific excavation of the Bronze Age sites in Yinxu (殷墟, the capital city late Shang dynasty, ca. 1250–1046 BC) of modern Anyang (安阳) in the year 1928. Nowadays, Yinxu, or Anyang has been widely regarded as one of the peak periods in Chinese Bronze Age (ca. 1900–200 BC, dates related to Chinese Bronze Age sites below are from Liu and Chen, 2012). As we show, however, the chemical analysis of Chinese copper-based artefacts considerably preceded these excavations. Those carried out in Europe and North America since the Second World War are well-known but there are some which are much earlier. Overall very little has appeared in the English language literature on the history of chemical analyses carried out in Asia. The aim of this paper is therefore to review the different stages in this research, to reflect on the differing motivations over time for such work in the East and West, and to consider the future potential of further analyses of ancient Chinese copper alloy objects.

The past

Early European analyses of Chinese metal

The earliest published chemical analysis of metal from China appears to be that of Gustav Von Engeström, 1775, Von Engeström, 1776, a Swedish mineralogist and chemist, who became 'Assessor of Mines' in Sweden. In 1776 he published a paper on the chemical analysis of a Chinese white metal, which he found to contain copper and nickel (with some cobalt), and gave the proportion of nickel to copper as 5 or 6 parts to 13 or 14 (i.e., approximately 29% Ni) (von Engeström, 1776). He also described how this raw alloy of copper and nickel was transported to Canton, where a third metal — zinc — was added, to give 'Pak-fong'. His paper in Swedish is translated in full into English (Bonnin, 1924). The method of quantitative analysis appears to have been his own invention using 'Hepar sulphuris' (von Engeström, 1775), in addition to the use of the blow-pipe, for which he is also well known. His method is praised by Kirwan (Kirwan, 1810), who states: "Where several metals are contained in an alloy, Engeström has used much laudable industry in promoting and improving a general method of separating them successively". Hepar sulphuris ('liver of sulfur') was a compound produced by heating potassium carbonate and sulfur, which evidently fluxes the metal, allowing it to be taken into solution with nitre (potassium nitrate). This is not the method of chemical analysis which became well established in Europe by the end of the 18th century (Pollard, 2013). Von Engeström's publication of, 1776 is remarkable for two reasons — it appears to be one of the earliest reported quantitative chemical analyses of any metal alloy, and it is dated only 25 years after the first isolation of nickel (also in Sweden, in 1751, by Axel Fredrik Cronstedt, of whom von Engeström was a student), but certainly before the widespread recognition of nickel as a separate metallic element. It is likely, however, that the metal he analysed was of contemporary manufacture, and therefore 1776 does not mark the true beginning of the analysis of archaeological Chinese metal.

Further analytical work followed on Chinese white metal, starting with Fyfe (1822), but continuing throughout the 19th century, as documented by Bonnin (1924) and Mei (1995), motivated by a desire to understand (and replicate) this remarkable unknown material which was being imported into Europe from China via the various East India companies. Analysis of other Chinese copper alloys was motivated more by curiosity than commercial forces, and also a desire to compare oriental copper alloys with the emerging data on prehistoric European metals. This included the work of Klaproth (1810) who analysed 'Gong-gongs and tam-tams' (musical instruments or bells), finding them to have approximately 78% copper and 22% tin, with some bismuth. Onnen (1848), in addition to analysing two pieces of white copper, reported on a further seven irregular pieces cut from copper cakes, two of which were brass (17.6 and 35.8% zinc), and the rest impure coppers. Genth (1858), in Philadelphia, reported the analyses (by Pöpplein) of eight Chinese copper alloy coins (plus two Roman), showing that most of the Chinese coins were largely alloyed with zinc (26–32%). Morin (1874) reports the analyses of seven bronze vases exhibited at the 1869 Paris Exposition of Chinese and Japanese objects at the Palais de l'Industrie. Unfortunately, because Morin gives no details of the bronzes other than a brief description, it is not possible to cross-check these analyses against the catalogue, but it seems more than likely that these represent the first analyses of ancient Chinese bronzes. The objects were all leaded bronzes, with 2.6–7.3% tin and 9.9–20.3% lead. The most thorough pre-modern European work on Chinese copper alloys is that of Collins (1931), who reports the chemical analyses of 20 (photographed and dated) objects, dating from the Shang to the Tang (618–907 AD). Most are leaded bronzes.

The early stage in Asia: 1911–1932

It would appear that Asian chemical studies of Chinese copper-based objects probably started between 1910 and 1920, e.g. (Chikashige, 1918). The most important characteristic for this stage was that in general the samples were unprovenanced and the burial context was therefore unknown. In order to overcome this problem, scholars suggested that chemistry was the key to link typology, chronology, and historical texts. The section named the Record of Diverse Technology (Kao Gong Ji, 考工记) in the book Rites of Zhou (Zhou Li, 周礼, dated to late Eastern Zhou, 东周, 770–221 BC, Chen, 1954) was mentioned in an overwhelmingly large number of papers in this stage. This work contains several formulae or recipes for alloy production. Therefore, as suggested by Liang (1925), the chemistry of copper-based objects with typical Zhou style would enable scholars to ascertain whether the Rites of Zhou was created in the Zhou dynasty (周, 1046–221 BC) or a later period. If these written records closely correlated with the chemistry of well-dated Zhou objects it was further argued that 'standards' could be defined to establish the chronology of otherwise undated bronzes. Utilizing this process Liang contended that the Rites of Zhou was quite accurate (Liang, 1925).

The Record of Diverse Technology was and continues to be referenced in an enormous number of publications concerned with the relationship between the typology of a vessel and the proportions of major elements in the metal, from Chikashige (1918) to Sun (2011). Two principal formulae, Ye Shi (冶氏) and Zhu Shi (筑氏), were recorded. The former one incorporated a lower proportion of tin whilst the latter one normally contained a higher quantity. Under each formula there were three sub-formulae indicating more specific proportions of alloying components for six specific types of objects. Together they are known as the "Six Formulae" (Table 1). However, the character Jin was mentioned in every formula but its exact meaning remained ambiguous (in modern Chinese it means gold). One interpretation was that Jin was equal to the total composition, which leads to the results in the Interpretation I column in Table 2. For example, the first formula in this case would translate as six parts of the overall alloy being divided so that tin occupies one part whereas copper occupies five parts (copper:tin = 5:1, or copper = 5/6 (83.3%), tin = 1/6 (16.7%)). The other interpretation argues that Jin in fact stands for copper, which leads to the alternative translation of the first formula as the overall alloy being divided into seven parts. In this case, copper comprised six parts (6/7 = 85.7%) and tin one part (1/7 = 14.3%). This second calculation gives the compositions in the Interpretation II column in Table 2. All the proportions according to the differing interpretations have been compiled in Table 3.

The existence of these formulae has been extremely important in the interpretation of chemical data from Chinese bronzes, but has prompted the question of how much credence should be given to this historical text. The multiple-layered nature of historical texts has been stressed in many independent critiques, e.g. von Falkenhausen (1993). A key issue to take into consideration is the background and context of the text whilst attempting to link it to real chemical analyses. It is therefore important to investigate questions such as to whom the book was presented, how much technical knowledge the author(s) may have had, whether or not various components of the same book were written at the same time, and under what socioeconomic circumstances the book was created. In the Near East, we come across similar issues of understanding historical texts on ancient metallurgy. Comparing the figures recorded in Mesopotamian recipes and the actual chemistry from contemporary objects provides us with the recurring pattern that the final level of tin in the bronze is consistently lower than that recorded in the texts. Cuénod and her colleagues consider two models to explain these results. One is that the oxidative loss of tin in high-temperature processes led to lower final levels of tin compared to the starting conditions. The other possibility is that the texts were actually referring to cassiterite (a principal tin oxide and ore), not metallic tin (Cuénod et al., accepted for publication). Alongside these chemical factors, the social context of these texts is also debated, for example whether they are palace records, or represent more descriptive technical works. Overall it is best to exercise caution and avoid the over-interpretation of these historical texts.

Despite the complicated relationship between historical texts and real chemistry, between 1911 and 1932 an increasing number of analyses demonstrated that the technologies of binary (copper–tin bronze or leaded copper) and ternary (leaded bronze) alloying were commonly employed in early dynastic China (Shang and Zhou dynasties). Discussion was thus directed towards understanding the function of each element in the casting process and in the final properties of the finished objects. Underpinning this work was the assumption that the alloy composition was achieved by deliberate design. It is clear that a certain amount of tin and lead would radically lower the melting point of the alloy and increase the fluidity for easier casting. Furthermore, the mechanical properties, such as hardness, colour, or toughness, would be significantly changed by alloying with tin and lead. The major impact of these early Chinese archaeometallurgical studies was the development of an analytical protocol combining chemical measurement with metallography which continues to this day, whereas in European work the chemical study of metals soon far outstripped the number of metallographic studies.

The lack of scientific excavation was an important limitation in this stage of Chinese archaeology. Without any information on stratigraphy and absolute dating, chemistry was often considered as an indicator of chronology. Wang (1923) attempted to reconstruct the chronological sequence between six inscribed coins, ranging from the Han (汉, 206 BC–220 AD) to the Sui (隋, 581–618 AD) dynasty. Based on significant variations of lead concentration, he suggested that coins with lower levels of lead should be earlier than the more heavily leaded ones. This viewpoint was primarily attributed to the Book of Han (Hanshu Shihuozhi, 汉书 · 食货志) in the Han dynasty, who recorded that the addition of lead into coins was illegal at the beginning of the Han dynasty but widely done in later periods (Wang, 1923). Whilst this lends credence to the observation that the lead content of coins might well be related to date, it does not necessarily mean that there is a strict chronological relationship between the two.

Early Chinese analyses showed that lead was present in early Chinese bronzes, at least by the Erlitou period (二里头, ca.1900–1500 BC, Liu and Chen, 2012). It was also shown that the content of lead could be highly variable, which could in part be an artefact of the technical challenge of measuring of lead in copper alloy objects. In the early period (before the end of the Second World War), chemical analysis was usually done by wet chemistry (gravimetric analysis). Generally speaking, wet chemistry is good for the measurement of lead in copper–alloy objects because the whole sample is dissolved, the lead is precipitated from solution, and weighed. It does, however, require rather a large sample which is completely destroyed. Although requiring less material for analysis, modern instrumental analytical tools can be less accurate in the measurement of lead, for several reasons. In X-ray fluorescence (XRF), the characteristic peaks of lead and arsenic are generally overlapping so that it is difficult to separate them. Neutron activation analysis (NAA) is even worse because it is incapable of detecting lead. Even where such problems do not present themselves, the existence of lead segregation — the uneven distribution of lead-rich phases within the microstructure of the alloy — is also problematic for micro-analysis (Hughes et al., 1982). Techniques which combine imaging with chemical analysis, such as scanning electron microscopy (SEM), allow the problem of segregation to be identified, without necessarily solving it. It is therefore necessary to exercise considerable caution when analysing copper objects containing more than around 1% lead.

To summarize, intense efforts in the early stages of metallurgical research in China were largely channelled towards determining the proportion of alloying elements in the objects and understanding the chronological sequence of metal objects. It was assumed that chemical variation in objects was mostly attributable to deliberate design. Unfortunately, as none of the objects were recovered from scientific excavations, it was not easy to draw broader conclusions by positioning these chemical characteristics within a wider chronological or socio-economic context. To a certain extent, historical texts provide some of this context along with guides to ancient metallurgical practice and chronology, but should not be over-interpreted. It is also worth noting that in early Chinese research we barely see any influence of the traditional European Culture–Historical and later Functionalist framework of the metallurgical ‘industry’ and the inevitability of technological progress as proposed by Childe (1930). The central argument of this framework is the linear evolution of metal technology from pure copper, arsenical copper, tin bronze and finally to leaded bronze, as an inevitable consequence of increasing technological development. This was largely based on the assumption that competition between different metallurgical industries would eventually force technologically inferior ones to be gradually replaced by superior ones — an approach now considered to be overly technologically deterministic. Although absent in the early Chinese interpretations, Childe's idea can often be encountered in the more recent research, as shown below. In conclusion, these early publications undoubtedly addressed the fundamental question of the composition of alloys. As a whole, they created an important foundation for further studies once professional archaeological excavations were widely conducted across China.

The Anyang stage: 1930s

The 1930s is often seen as a milestone of Chinese archaeometallurgy, not only because series of chemical analyses were continuously published (Chikashige, 1930, Chikashige, 1936, Collins, 1931, Dono, 1930, Dono, 1932a, Dono, 1932b, Dono, 1932c, Dono, 1932d, Dono, 1933, Dono, 1934a, Dono, 1934b, Dono, 1935a, Dono, 1935b;), but also, for the first time, archaeologists were able to determine the composition of objects from scientific excavations (Carpenter, 1933). Based on the observation of metallographic structures, Carpenter lists the likely proportions of copper and tin for four samples. He also made a comparison between these estimates with The Six Formulae (Table 4). Meanwhile, because such large quantities of bronze objects were being repeatedly uncovered in the metal-ore poor region of Anyang, Chinese archaeologists began to seriously engage with the question of copper provenance (Liu, 1933). It was, however, a question not easily approached due to the fact that the locations of the copper mines in the Shang dynasty were only rarely and vaguely recorded in any historical texts.

The Second Sino–Japanese War and the Chinese Civil War from 1937 to 1949 progressively halted any further excavations and laboratory measurements. Subsequently, the People's Republic of China began to provide sponsorship for various unfinished archaeological projects and launched a great number of new studies.

From metallurgy to archaeometallurgy: 1950s–1980s

The defining characteristic of this forty year period is an increasing awareness of interpreting the chemistry of copper-based objects in a wider archaeological context. This stage can be further divided into two periods. In the first twenty years, scholars remained focused on two main questions. One was concerned with the extent to which ancient Chinese craftsmen appreciated the influence of alloying on the mechanical properties of the finished objects. The other one was how to correlate the Record of Diverse Technology with the chemistry of archaeological artefacts. This phase was essentially a continuation of the work done before the Second World War. Chen (1954) classified 32 objects into four groups (pure copper, bronze, leaded copper, leaded bronze) based on the presence or absence of tin and lead (Table 5). Inspired by this new characterization, he accepted the fact that the addition of tin and lead would affect mechanical properties and the casting process. A striking result of his work was the discovery that many weapons of the Shang dynasty were leaded copper. The low hardness of this alloy precludes their practical use in warfare. Chen therefore suggested that the addition of lead was to save tin. More importantly, these leaded-copper objects were interpreted as being designed for deliberate deposition, which was a crucial interpretive break with the past tradition of seeing alloy design as solely functional. Regarding the Record of Diverse Technology, scholars like Chen began to accept a more limited view; that the text may reflect merely a specific type of alloying technique that was implemented only at a certain time and place. Chen and others also reaffirmed the view that simple mathematical calculations between chemistry and texts are unable to reveal the whole picture (Barnard, 1961, Yuan 袁翰青, 1954, Zhang 张子高, 1958, Zhou 周则岳, 1956, Zhou 周始民, 1978). Although this discussion is still mentioned in many current publications, as discussed below, views of the historical texts have changed since the 1970s.

Chemical analysis on dynastic coins was also carried out during this period. Scholar Wang Jin (who had focused on this subject since the 1920s) found that the concentration of copper and tin constantly dropped off, to be replaced by other metals such as lead and zinc in later periods, possibly in order to reduce the expense of producing coins. Lead in specific periods may substitute for tin but the overall pattern from the Tang (618–907 AD) to Qing dynasties (1644–1912 AD) appeared to be quite random. Zinc, in contrast, showed a clear and striking pattern in the dynastic coinage. As indicated below, brass (copper containing zinc as the major alloying element) had been reported from Neolithic sites but these results are now regarded as very dubious. Wang showed that it was not until the Ming and Qing dynasties that zinc could be confirmed as a deliberate addition. In stark contrast to the very low concentration of zinc found in the earlier-period coins, zinc levels of over 20% were found in the coinage of these two dynasties (Wang 王琎, 1959, Wang 王琎 and Yang, 1959).

The work of Tang (1979) marked the beginning of the second half of this stage. A huge effort was channelled towards exploring the question of the origins of Bronze Age China, in terms of both when and where it began. The central aim was to reconstruct the sequence through which metallurgy developed in prehistoric China. Inspired by the model of pure copper to arsenical copper to tin–bronze developed by Childe and others to explain the evolutionary sequence of metal use in Europe, several Japanese and Chinese scholars attempted to link the chronology of the development of copper alloying to reveal a similar pattern. As far as we know, Dono appears to be one of the earliest researchers interested in the existence of a Copper Age (i.e., a period when unalloyed smelted, not native, copper was used). He proposed the identification of a Copper Age of China, but one that was possibly intertwined with the beginning of the Anyang Bronze Age (Dono, 1932a, Dono, 1932c, Dono, 1932d, Dono, 1933, Dono, 1934a, Dono, 1934b). This argument was not convincing due to the fact that the chronology he based it upon was not determined independently. In fact the existence of a Copper Age in China was completely rejected by Tang (1979). He contended that the Chinese first made tin bronze roughly 6000 years ago and not until very late did pure copper come into use (ca. 4000 years ago). The archaeological evidence included the fragments of metal found in the Jiangzhai (姜寨) site (copper 65%, zinc 25%, tin 2%, lead 6%) and Banpo (半坡) sites (copper with a large amount of nickel (20%) and zinc). Both sites belong to the Neolithic Yangshao culture (仰韶, ca. 5000–3000 BC, Liu and Chen, 2012). Although these were obviously not bronze, he further quoted the Soviet archaeologist Artemiy Artsikhovsky and suggested that brass (Cu–Zn) could be a parallel to tin–bronze in the very early period. He also noted that metal was initially made into weapons according to mythology. Pure copper was too soft and only copper–tin alloy would have been suitable.

Disagreement was subsequently expressed by An Zhimin, noting that the contexts of the two pieces of metal cited by Tang were very suspicious (An, 1981). They could be a result of accidental mixing from the upper stratigraphy. More importantly, evidence from only two pieces of metal was far from sufficient to draw an outline for the initial stage of the Chinese metal age. Scholars gradually focused their attention on four main regions, Gansu, Inner Mongolia, the Central Plain and Shandong, in which a majority of early copper-based metal objects (before the 16th century BC) had been unearthed. Thanks to chemical analysis on this early material, it was possible to plot alloying chemistry against chronology

(University of Science and Technology Beijing, 1981). The argument was made that ancient China may have experienced a similar sequence of metal use as in other parts of the world, i.e., accidental bronze—pure copper—bronze. In the very earliest period when smelting was not well controlled, copper and its natural co-existing elements could not be completely separated; it therefore produced so-called “accidental bronze”. This logic had been used in Europe to explain the existence of arsenical copper alloys before the appearance of tin bronze, but there is still a continuing debate about whether these were ‘deliberate’ or ‘accidental’ alloys. The argument continues that with the improvement of smelting techniques pure copper came to dominate. However, as pure-copper objects were unable to satisfy various requirements (hardness, appearance, etc.), craftsmen continued to experiment and finally invented the technique of alloying copper and tin to make bronze. This trajectory was widely accepted in the Chinese literature (Bai 白云翔, 2002, Du 杜廼松, 1992, Hua 华泉, 1985, Li 李学勤, 1984, Li 李京华, 1985, Sun 孙淑云 and Han, 1997, Zheng 郑德坤, 1987). Nevertheless, two issues should be further considered. Teng noted that the quality of chemical analysis was rather poor and insufficient for discerning a sequence. Many analyses were vaguely recorded as high, low or absent. Meanwhile, trace elements and lead isotopes were inaccessible for those important objects (Teng, 1989). Chronology was also problematic (Linduff and Mei, 2014). Radiocarbon dates of various key sites have wide ranges and thus often overlapped with one another. Due to this the chronology of early metal objects was routinely illustrated in terms of archaeological cultures, such as Majiayao (马家窑, ca. 3300–2000 BC) or Longshan (龙山, ca. 2600–1900 BC, Liu and Chen, 2012). Both ambiguities contributed to the disagreement on the origins of Bronze Age China, as either indigenous invention or outside stimulation.

We should bear in mind that this framework of technological progress is not the only way in which Chinese scholars have addressed the problem of the origin of the Bronze Age. For example, based on the work of Tong (1987), Rawson has developed the idea of the Arc (a variety of regions surrounding the Central Plain, including modern Sichuan, Shaanxi, Inner Mongolia, North Shanxi, and Northeastern China). She proposed that the Arc people, dwelling outside the central Chinese zone, played a salient role in the communication between the Central Plain and the Steppe. This communication may be visualized by movement of technology, such as metallurgy, horse riding and many others (Rawson, 2013). Therefore, it is important to say that a great deal of research independent of chemistry must also contribute to our knowledge on the subject of the origin of Bronze Age China.

In the second period of this stage, examination of the correlation between alloying proportions and related technology was continued in parallel to the work on Bronze Age origins. In particular, measurements of the average value and the range of the alloying elements attracted scholars' attention. A ‘proper’ average (i.e., one consistent with historical sources) and a narrow range were often considered as the indicators of advanced metalworking. Scholars also routinely used metallography to investigate the techniques of production, such as casting, annealing, cold working and so on. A typical example can be found in the work of He and Ou (1994). They analysed 13 copper–alloy objects unearthed from two late Shang sites (Luoshan 罗山 and Gushi 固始) in Henan province. They contended that some objects were of poor quality because their hardness and toughness was not ideal as a result of ‘improper’ alloying. One spear was alloyed with merely 0.553% tin and 4.330% lead. For good physical properties in practical use, it is often stated that the tin level “should” be over 10%. Furthermore, He and Ou also compared Luoshan and Gushi with Yinxu and suggested that they were less developed in terms of metallurgy. One piece of evidence for this was the higher frequency of pure-copper objects (characterized by a percentage of tin and lead below 3%), which were rarely found in Yinxu. At the same time, the range of tin and lead was not well controlled, implying insufficient knowledge about the relationship between alloying and mechanical properties. Equally, mixing and recycling may have contributed to this wide distribution of alloying elements.

The present: classical provenance

In Europe, the provenance question for copper alloys can be traced back to the 1840s (Pollard, 2013), but it was not until after the Second World War that modern analytical instruments, such as optical emission spectroscopy, were widely employed for the chemical analysis of archaeological metal artefacts, thus vastly increasing the number of analyses produced. Despite the increasing quantity of data, its quality and therefore usefulness can vary considerably. Few publications report what calibration standards were used, or give any meaningful estimates of limits of detection or analytical precision. The absence of such information makes it very difficult to evaluate data quality since most instruments obtain results by comparing unknown (samples) with known (primary standards), and estimate precision and limits of detection from multiple measurements of secondary standards (Pollard, 2007).

The main goal of using trace elements in provenance studies is to establish a connection between objects and specific mines, or between the objects themselves. The best-known databases of the trace element chemistry of Chinese bronzes are those of the Freer and Sackler collections in western academia (Bagley, 1987, Pope et al., 1967, Rawson, 1990, So, 1995). They provided chemical analyses of unprecedented quality for future study. More trace element measurements have been carried out by Chinese scholars, particularly for the sites in Yinxu, Qianzhangda (前掌大, ca. 1250–1046 BC), later phases of Panlongcheng (盘龙城, ca. 1400–1250BC) and Hanzhong (汉中, ca. 1400–1046 BC). However, the behaviour of trace elements throughout the life cycle of copper alloy objects from extraction through smelting and casting to mixing and recycling is complicated. It is therefore not possible to definitively associate any given copper alloy object with an ore source without a thorough understanding of the biography of the object and the behaviour of the trace elements in the copper The team at the University of Science and Technology of China lead by Wang Changsui selected a specific set of trace elements in copper which are preferentially attached to copper rather than slags during smelting and processing (Au, Ag, As, Sb, Bi, Se, Te, Co, Ni, etc.) (Li 李清林, 2010, Qin 秦颖 et al., 2004, Qin 秦颖 et al., 2006, Wei 魏国峰, 2007). Clearly, the key step after analysis is to find out how these numbers should be interpreted archaeologically. Many statistical approaches were applied, including cluster analysis, principal components analysis and discriminant analysis. Obviously, the resulting chemical groups are only meaningful provided these methods are used critically and properly. The choice of statistical method employed can have a dramatic effect on the resulting definition of clusters of artefacts that archaeologists must then interpret. Minor changes in parameters or procedures can result in a significantly different outcome. In order to address this ambiguity, Pollard made the suggestion that we should only accept interpretations which are supported by structures reproduced using multiple independent statistical methods, and details of the analysis undertaken should be fully recorded and published (Pollard, 1982). As described below, we would now dispute the analytical usefulness of techniques that aim to identify clusters within metal chemistry datasets. Recycling, mixing, and differential oxidation would stretch out and smear signatures rather than lead to isolated clusters of data.

In China the first attempt to tackle the provenance of copper alloys found at Anyang can be attributed to Shi (1955). He plotted all the copper mines mentioned in local chronicles on a map (124 counties, within a radius of 3000 km from Anyang), and assumed that 400 km was likely to be the maximum distance for ancient people to transport metals. Beyond this distance, Shi argues it would be too labour-intensive and financially over-burdening to guard the route, but this must now be seen as an arbitrary figure. As a result, 26 copper mines, distributed in modern Henan, Shanxi, Shandong, and Jiangsu, came into contention as sources. However, it remains unclear how far local historical chronicles are representative of mining areas in the earlier Shang and Zhou dynasties, although it is now known that mines exist in these areas which can be possibly dated to these dynasties, such as recent excavation of the Shigudun site (Provincial Institute of Archaeology in Anhui, 2013). Also, river systems may have played an important role in ancient transportation, rendering the reliance on a simple distance metric unrealistic.

Subsequent research shifted to using the bronze inscriptions of the Western Zhou (西周, 1046–771 BC) for further information. In the early 1980s, Wen called for archaeologists to focus more on central China as the source of the metal based on a translation of the bronze inscriptions and later historical texts (Wen 闻广, 1980a, Wen 闻广, 1980b, Wen 闻广, 1983). Tong et al. (1984) made a strong critique that the translations by Wen were erroneous. It must be concluded that the inscriptions on Chinese bronzes can offer vital information on the provenance and movement of metals, but they are also rather fragmented so that interpretation must proceed with caution.

The use of lead isotopes is well known for tracing copper sources, and has been used archaeologically since the 1960s. The first lead isotopic analysis of a Chinese bronze is that of a ritual vessel from the Western Zhou reported by Brill and Wampler (1967), in what was also the first paper on the lead isotope analysis of any archaeological metals and glass. Much larger-scale projects were subsequently carried out in co-operation between Chinese, Japanese and western scholars. Jin published the first paper applying lead isotope ratios to investigate the provenance of Anyang metals (included in Jin, 2008). A group of lead isotope ratios stand out immediately (highly radiogenic lead isotope ratios, with 207Pb/206Pb < 0.8). By comparing with a geological database of lead isotope ratios, Jin suggested that such lead isotopes are likely to originate in the area where modern Yunnan, Sichuan and Guizhou administrative borders meet, in southwestern China. Obviously, in a heavily leaded bronze object, the measured lead isotope ratio will be dominated by the signal in the added lead, rather than the relatively minor amount of lead associated with the source of the copper. Hence, in leaded bronzes, the lead isotope signal is an indicator of the source of lead, not copper. Jin suggested however that some metal found in Anyang was likely to originate in southwestern China, where copper and lead naturally co-existed and are characterized by highly radiogenic lead isotopes. This argument radically pushed the research area further towards the south–west (Jin, 2008). Highly radiogenic lead isotopes were also subsequently found in the early Bronze Age sites of Sanxingdui (三星堆) (Jin et al., 1995) and Jinsha (金沙) (Jin et al., 2004) on the Chengdu Plain, the Hanzhong metal assemblage in Southern Shaanxi (Jin et al., 2006), Panlongcheng (Peng 彭子成 et al., 2001, Sun 孙淑云 et al., 2001) and Xin'gan (新干) (Jin et al., 1994) in the Lower Yangzi river valley. All these sites are dated to the later Shang or early Western Zhou.

Despite the apparent ubiquity of highly radiogenic lead isotopes, the interpretations have varied dramatically. Saito and his colleagues suggest Qinling mountains as another source for this peculiar group of lead isotope ratios (Saito et al., 2002). Based on geochemistry and the overlapping of lead isotope signals between Shang objects, modern mines, and later Eastern Zhou and Han objects including metals and glasses, it was suggested that a multiple-source model in which objects with different 207Pb/206Pb values could originate in a variety of regions from Northern China to the Middle and Lower Yangzi river valley (Peng et al., 1999). A controversial issue emerges which is how to define a locally-produced object or how to characterize the range of lead isotopes from a single mine. No one is certain about the extent to which data from later objects such as Eastern Zhou metals or Han glass can represent the local range of lead isotopes applicable to the Shang or Western Zhou, and how many samples are required to define a range for any particular mine. Even systematic sampling by geologists may not be adequately representative because modern geologists prefer unweathered minerals but ancient craftsmen may have more readily encountered weathered ones as they were close to the ground surface. Moreover, many ancient mines are likely to be exhausted and thus not available for study in the present time.

Another framework for lead isotopic provenancing was introduced by Cui and Wu (2008). It was based on the methodology invented by Zhu (1995), who essentially standardized the three isotope ratios against crustal average values (ostensibly to remove age effects), and then reduced these three variables to a pair of values by a process which is similar to principal components analysis. Using these two coordinate parameters, Cui and Wu re-characterized the lead isotopes of the bronzes of the Shang and Western Zhou Dynasties. Applying this new characterization to the Sackler collection database showed that the Shang people may have extracted metal from two mines, one of which was abandoned in the Western Zhou period. But the exact locations of these two mines remain unclear.

Retrospect and prospect

As far as we are aware, around 3300 chemical analyses and 1300 lead isotope measurements have been published on Chinese copper-based objects ranging from the Erlitou to Western Zhou periods, which cover about half the range of the Chinese Bronze Age. These are summarized in Appendices 1 and 2 (online supplement). Many of these chemical analyses are, however, not as comprehensive as we would like in order to apply newly-developed techniques to follow the flow of metal (Bray and Pollard, 2012, Bray et al., 2015, Needham, 1998). As a minimum, we recommend that analyses of copper-based alloys should report Cu, Pb, Sn, Zn, As, Sb, Ni, Sb, Fe, Co and Bi, plus lead isotope data on the same samples. Moreover, since a variety of analytical techniques have been applied in obtaining the existing data, one concern is the difficulty of comparing data from different techniques In the long run, it may be essential to reanalyze old as well as new samples with standardized protocol, which is ultimately the best way to resolve this issue. Although 3300 analyses are a considerable body of data, when compared to Early Bronze Age Europe (25–30,000 chemical analyses and between 1–2000 lead isotope values, late third to mid second millennium BC, Pernicka, 2014, Pollard and Bray, 2014), it is clear that this can only be the beginning of systematic archaeometallurgy in China. Moreover, Fig. 1, which shows how these analyses are distributed across modern China, clearly indicates that there are large areas from where we urgently need new data before further discussion on, for example, the role of alloys, patterns of impurities or interactions among various central or local metal industries. However, acquiring new data can only be the beginning of the next stage of Chinese archaeometallurgy. Summarizing the history of chemical analysis on Chinese copper-based objects reveals the fact that dialogue between archaeologists, metallurgists and historians is an absolutely essential component of this subject. Although nowadays scientific analyses of copper-based objects have become a routine component of archaeological excavation reports, it must be appreciated that archaeological and historical information also plays a major role in understanding these chemical analyses. The existing database has helped archaeologists to solve many critical issues, such as the variation in alloying techniques. More and better-quality data will encourage dialogue between archaeologists and metallurgists as it enables us to explore many other interesting questions, such as metal flow, interaction between people and metal, and, of course, communication between people. This dialogue beyond the borders of disciplines and nationalities significantly contributes to our knowledge on Bronze Age China.

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Table 1. Original text of the Six Formulae.

	Objects	**Original text in Chinese**
冶氏	钟鼎	六分其“金”而锡居其一
	斧斤	五分其“金”而锡居其一
	戈戟	四分其“金”而锡居其一
筑氏	大刃	三分其“金”而锡居其一
	削杀	五分其“金”而锡居其二
	鑑燧	金锡半

Table 2. Translation of the Six Formulae.

Ye Shi	**Type of objects**	**Interpretation I**	**Interpretation II**
Ye Shi	Type of objects	Interpretation I	Interpretation II

	钟鼎 Zhong Ding (Bells and tripod vessels)	Six parts of the overall alloying was divided and tin to occupy one part	The overall alloy was divided into seven parts which copper occupied six and tin occupied one
	斧斤 Fu Jin (Axes and hatchets)	Five parts of the overall alloying was divided and tin to occupy one part	The overall alloy was divided into six parts which copper occupied five and tin occupied one
	戈戟 Ge Ji (Daggers and halberds)	Four parts of the overall alloying was divided and tin to occupy one part	The overall alloy was divided into five parts which copper occupied four and tin occupied one
Zhu Shi	大刃 Da Ren (Large knives)	Three parts of the overall alloying was divided and tin to occupy one part	The overall alloy was divided into four parts which copper occupied three and tin occupied one
	削杀 Xiao Sha (Swords)	Five parts of the overall alloying was divided and tin to occupy two parts	The overall alloy was divided into seven parts which copper occupied five and tin occupied two
	鑑燧 Jian Sui (Reflective mirrors and concave mirrors)	Two parts of the overall alloying were divided and tin to occupy one part	Two parts of the overall alloying were divided and tin to occupy one part

Table 3. Two differing proportions between copper and tin in the Six Formulae.

	Types of objects	**Chemistry I**			**Chemistry II**		
		Cu	**Sn**	**Ratio**	**Cu**	**Sn**	**Ratio**
Ye Shi	钟鼎 Zhong Ding	83.33	16.67	5:1	85.71	14.29	6:1
	斧斤 Fu Jin	80.00	20.00	4:1	83.33	16.67	5:1

	戈戟 Ge Ji	75.00	25.00	3:1	80.00	20.00	4:1
Zhu Shi	大刃 Da Ren	66.67	33.33	2:1	75.00	25.00	3:1
	削杀 Xiao Sha	60.00	40.00	3:2	71.43	28.57	5:2
	鑑燧 Jian Sui	50.00	50.00	1:1	50.00	50.00	1:1

Table 4. Carpenter's (1933) analyses on Anyang excavated metals (The number in the brackets is from the Record of Diverse Technology).

Specimen	Copper %	Tin %
1562	85	15 (40)
1161.1	83	17 (40)
1359.2	80	20 (25)
1161.2	Heavy corrosion	10–20 (17)

Item	Cu average%	Sn %	Pb %	Hardness	Number of objects
Bronze (Cu–Sn)	82.08	5–20	< 0.6	94	11
Leaded Bronze (Cu–Sn–Pb)	79.71	> 10	> 5	80	9
Leaded Copper (Cu–Pb)	82.83	< 1	> 10	45	8
Pure Copper (Cu)	92–98	< 1	< 2	36	5

Fig. 1. Summary of database of trace elements in Shang and Western Zhou (total analyses, a less than 15, b 16–30, c 31–100, d 100–200, e 200–400, f more than 400; i more than 1500, ii 200–250, iii less than 50).