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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.

1. 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.

2. The past

2.1. Early European analyses of Chinese metal

The earliest published chemical analysis of metal from China appears to be that of Gustav von Engeström (1775, 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.

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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.

2.2. 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.

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

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