Three Western Zhou bronze foundry sites in the Zhouyuan area, Shaanxi province, China

Wenli Zhou, Jianli Chen, Xingshan Lei and Tianjin Xu

ABSTRACT A large amount of Western Zhou bronzes and some Proto-Zhou bronzes have been discovered in the Zhouyuan area, the foremost region for the origin and development of Zhou culture. Since 2003, three bronze foundry sites have been located and excavated, providing new materials for investigating the bronze-making technology in this area. The Zhougongmiao site dates to the early Western Zhou period and even the Proto-Zhou period, while the other two sites have been dated to the middle and late Western Zhou period. This paper concentrates on the melting, refining and alloying aspects of metallurgical technology by examining small bronze artefacts, fragments and slags using a metallographic microscope and analytical techniques such as scanning electron microscopy with energy-dispersive spectroscopy (SEM–EDS) and energy-dispersive electron probe microanalysis (ED-EPMA). The results suggest that copper, tin and lead ingots and bronze scraps were probably brought to the foundry sites as raw materials. The Zhougongmiao site exhibits quite different characteristics from the other two sites with regard to the sources of copper ores, alloying and mould-making technology.

Introduction

The region of Zhouyuan, located in the Guanzhong Plain in Shaanxi province, north-west China, was the most important area for the origin and development of Zhou culture. Zhou people had already inhabited this region for many centuries before the establishment of the Western Zhou dynasty (mid-11th century BC–771 BC), an epoch called the Proto-Zhou period. The toponym 'Zhouyuan' is used to cover two geographical areas (Shi 1981): in a narrow sense, it refers to the main site, the Zhouyuan site, covering approximately 30 square kilometres and bordering a number of villages in Qishan and Fufeng counties; in a broad sense, it refers to the larger region, covering hundreds of square kilometres spanning from Wugong county in the east to Fengxiang county in the west, and from the Qishan Mountains in the north to the Wei River in the south. In this paper, the term Zhouyuan area refers to this latter region.

Since ancient times, numerous Western Zhou bronzes have been found, mostly from burials and hoards, in the Zhouyuan area, especially at the Zhouyuan site (Beida 2002). The huge number of these bronzes, together with the delicate craftsmanship and informative inscriptions are testament to the important status of the Zhouyuan area during the Western Zhou period. Most Chinese archaeologists have focused on the dating, inscription interpretation and artistic dimensions of the bronzes (Cao 1994); only a few unsystematic technical studies of bronzes have been carried out (Zhang 1997; Yang and Han 2007).

Before 2003, a limited number of moulds, slag and ingots had been found in the Zhouyuan area (Luo 1993: 22), implying that these bronzes were likely to have been manufactured locally. Since 2003, however, three important bronze foundry sites – Lijia, Zhougongmiao and Kongtougou (Fig. 1) – have been found and excavated in the region, yielding a wealth and variety of new materials that allow a more detailed study of the bronze-making technology. A joint team from Peking University and Shaanxi Provincial Institute of Archaeology carried out the field investigations and excavations. These are the only Western Zhou foundry

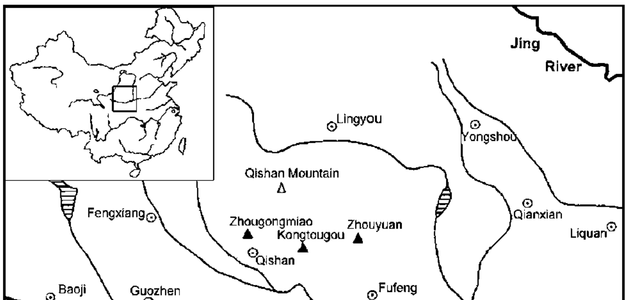

Figure 1 Map showing the distribution of the three bronze foundry sites in the Zhouyuan area.

sites to be excavated apart from the Beiyao foundry site of the early Western Zhou period in Luoyang, Henan province. Based on the typology of coexisting pottery, together with the styles and motifs of moulds (which can be related to those of extant bronze vessels), the Zhougongmiao foundry site can be dated to the early Western Zhou period and may even have been established as early as the Proto-Zhou period, while the Lijia and Kongtougou foundry sites date to the middle and late Western Zhou periods.

The Zhougongmiao site, located in the Fenghuang Mountains, Qishan county, yielded a number of bronze vessels of the Western Zhou and Proto-Zhou period. The discovery of high-status burial sites, a large number of inscribed animal bones and a bronze foundry in 2004 (Xu 2006) suggested that this site was an important arena of Zhou people. During field surveys, a small kiln was found on the bottom of which was a piece of a *luanling* (銮铃) mould showing typical early Western Zhou features. The kiln, apparently different from ordinary pottery kilns, is likely to have been used to bake the moulds. A small-scale excavation of the foundry site revealed hundreds of broken mould fragments with few motifs remaining. These moulds were identified to relate to vessels (*ding*鼎 and *gui*簋), weapons (knives and arrowheads), and chariot accessories (horse bit, *pao*泡, *luanling*), etc. In 2006, a waste pit (H27) of the late Proto-Zhou period was discovered, which contained a bronze knife, mould fragments, crucibles and metal (Chong and Lei 2007).

The Lijia bronze foundry site, located within the Zhouyuan site, west of Lijia village, Fufeng county, was first excavated in spring 2003 and then from September 2003 to January 2004 by the same team (Zhouyuan Archaeology Team 2004a,b). Thousands of moulds were excavated which had been used to cast a variety of bronzes, including vessels (*ding*, *li*鬲, *gui*, *hu*壶), musical instruments (*zhong*钟), weapons (*ge*戈), chariot accessories (*luanling*, *wei*軎, *xia*辖, *biao*镳, horse bits, *jieyue*节约), etc. Some of the well-preserved moulds had clear motifs on the inner surfaces (Fig. 2).

Figure 2 Mould fragments for a *ding* vessel (H66:95) from the Lijia site.

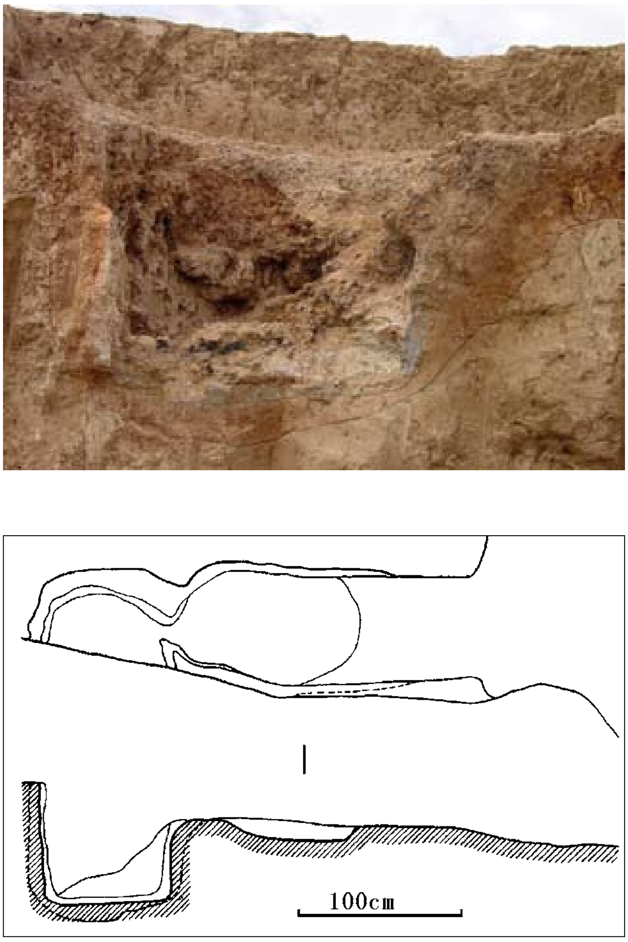

Figure 3 The furnace unearthed from Qizhen (above: section; below: drawing).

Later, the Kongtougou site, located between Zhougongmiao and Zhouyuan, was also excavated (Chong *et al.* 2007) and a third bronze foundry site was excavated in 2006. Moulds were identified to cast vessels (*ding* and *gui*), musical instruments (*zhong*), chariot accessories (*biao* and *xia*), etc. The motifs on the inner surfaces of moulds were less diverse than those of contemporary moulds from the Lijia site.

Many furnace fragments were found in the three foundry sites, typically mixed with mould fragments in large waste pits, particularly abundant in context H11 in the Kongtougou foundry site; all were made of coils of clay mixed with straw. From the largest fragments, diameters of furnaces are estimated to have ranged from 40 to 100 cm. Only one furnace was identified *in situ* (Fig. 3) (Wei and Li 2007), discovered when sectioned by a bulldozer digging clay at Qizhen village, about 1 km west of Lijia foundry in the Zhouyuan site. The preserved part was a pit dug into the soil, about 80 cm in diameter, 85 cm deep and with a wall thickness of 3–4 cm exhibiting clear evidence of exposure to high temperatures. Several pieces of moulds were discovered inside the furnace, while some slag and bronze fragments were found in nearby waste pits of the section. Local villagers reported the presence of two similar furnaces in the vicinity. Initially, it was expected that these furnaces had been used for bronze melting and casting, given their

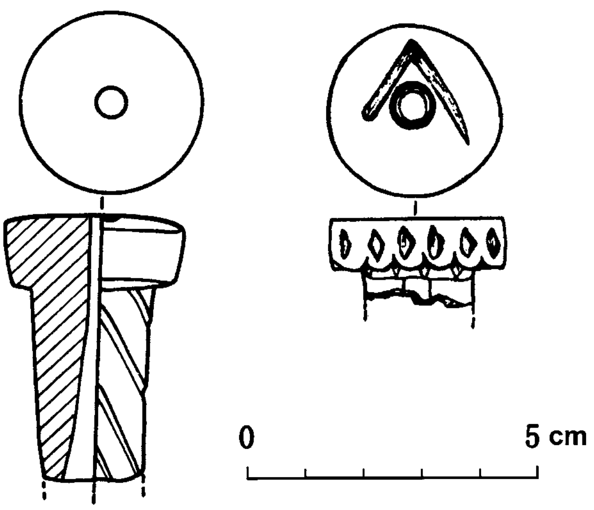

Figure 4 Ceramic tubes from the Lijia site (left: M2:19; right: H97: 10).

context and their overall structure. However, inductively coupled plasma atomic emission spectrometry (ICPAES) analyses of the slag found inside the furnace showed no obvious enrichment of copper, tin or lead, suggesting that the slag constituted only molten furnace clay. In addition, no clear evidence of crucibles or tuyéres was found in any of the foundry sites. On the contrary, some small columnar or mushroom-like ceramic tubes, whose functions remain unknown, were found in all sites (Fig. 4).

The most impressive finds from the three bronze workshops are the thousands of Western Zhou ceramic moulds employed for bronze casting. Chen Yang (2005) studied the mould-making technology of the Lijia and Zhougongmiao sites, reconstructed the mould-making process and discussed the technological changes from the early to the middle and late Western Zhou period. Some analytical studies were carried out on Lijia moulds and furnaces from the first excavation in the spring of 2003, providing some preliminary information on the choice of raw materials and mould-making process in the Zhouyuan area (Liu *et al.* 2007). There is no doubt these moulds deserve more detailed technical studies, and they will yield more information for our reconstruction of the piece-mould casting technology during the Western Zhou period (Nickel 2006).

This paper, however, will concentrate on other metallurgical remains, less abundant and perhaps less impressive at first glance, but also informative of the Western Zhou metallurgical technology. Based on analytical studies carried out on metal artefacts, metal fragments and slag, this paper examines the melting, refining and alloying technology of the three foundry workshops in the Zhouyuan area. Given that the samples from Zhougongmiao date to the early Western Zhou period while those from Lijia and Kongtougou date to the middle and late Western Zhou periods, an attempt will be made here to consider chronological changes by comparing the evidence from the different sites. Samples from Lijia, Zhougongmiao and Kongtougou sites are labelled SZY, ZGM and ZJT, respectively.

Methodology

Samples of metal and slag were mounted in phenolic resin and ground and polished following established procedures. Metallographic examinations were performed with a LEICA DM4000M optical microscope at the Archaeological Science Laboratory in the Department of Archaeology and Museology, Peking University. Chemical data were obtained according to two methods, depending on the availability of equipment during different stages of this research. Some samples had previously been analysed with a FEI QUANTA600F SEM and an Oxford Instruments EDS at the Chinese National Museum. Further samples were analysed by a JXA-8100 EPMA with an INCA-400 Oxford EDS at the School of Earth and Space Sciences, Peking University. The accelerating voltage was 20 KeV in both cases. Although the chemical results from these different instruments can be considered comparable, it should be noted that ED-EPMA analyses quantified the oxygen content, unlike the other technique (see tables below). In all cases, results are presented as weight percentages (wt%) normalised to 100%, and as stoichiometric oxides where relevant. Heavily corroded samples tend to have a higher content of oxygen and tin. Based on the chemical compositions, metals and alloys were classified as copper, bronze, etc., using conventional terminology. It should be noted, however, that only alloys containing lead in excess of 2% were identified as 'leaded'.

For metal artefacts and metal fragments, cross-sections were first investigated to identify inclusions and assess the degree of corrosion. They were subsequently carbon coated and studied in the backscattered electron mode of the SEM/EPMA. Several EDS area measurements were performed to obtain average bulk compositions and spot analyses were carried out on inclusions. After microanalysis, the carbon coating on the surface of the sections was removed, and samples were etched in alcoholic ferric chloride and observed under the metallographic microscope for microstructural studies. Similar analytical procedures were followed for the analysis of slag, although the phase structure was more complicated and thus required more detailed consideration.

Results

Metal artefacts

Only from the site of Lijia were artefacts obtained of recognisable shapes – all the other metals analysed for this study constituted smaller fragments of possible broken objects or casting spillage. Thirteen small metal artefacts from the Lijia site were collected for examination, including two awls, two chisels, five knives and three arrowheads.

It can be seen from the results of SEM–EDS/ED-EPMA (Table 1) that most of these artefacts were made of tin

Table 1 Chemical composition of bronze artefacts from the Lijia site (wt%).

Lab no	Type	Cu	Sn	Pb	Fe	S	O	Other	Alloy	Technology
SZY37	awl	62.4	22.2	3.7	–	0.5	10.1	Cl:1.0	Cu-Sn-Pb	cast
SZY38*	awl	84.4	15.0	0.3	0.3	0.1	na		Cu-Sn	cast, cold-worked
SZY53	awl	60.6	28.0	1.4	–	–	10.0		Cu-Sn	hot-worked
SZY50*	chisel	83.0	15.0	2.0	0.0	0.1	na		Cu-Sn-Pb	cast, cold-worked
SZY51*	chisel	77.6	21.9	0.3	0.1	0.1	na		Cu-Sn	cast, cold-worked
SZY39	knife blade	84.5	14.6	–	0.5	0.3	–		Cu-Sn	hot-worked, cold-worked
SZY42	knife blade	83.2	14.9	–	–	–	1.9		Cu-Sn	hot-worked, cold-worked
SZY43	knife handle	75.8	18.7	1.2	–	–	4.4		Cu-Sn	cast
SZY44*	knife blade	81.5	17.8	0.1	0.2	0.4	na		Cu-Sn	hot-worked
SZY45	knife blade	84.9	13.5	–	–	–	1.6		Cu-Sn	cast, annealed
SZY30	arrowhead	87.6	9.2	1.6	–	–	1.7		Cu-Sn	cast
SZY31	arrowhead	82.7	14.7	1.1	0.8	–	0.8		Cu-Sn	cast
SZY34	arrowhead	79.8	16.1	2.5	–	–	1.0	As:0.6	Cu-Sn-Pb	cast

Note: * = analysed by SEM–EDS; na = oxygen not analysed. The other samples were analysed by ED-EPMA including oxygen. Tin or lead exceeding 2% is regarded as an alloying component.

Table 2 Chemical composition of metal fragments from Lijia, Zhougongmiao and Kongtougou sites (wt%).

Lab no	Cu	Sn	Pb	Fe	S	O	Alloy	Technology
SZY22-1	84.6	15.0	–	–	0.4	–	Cu-Sn	cast
SZY22-2	73.3	26.7	–	–	–	–	Cu-Sn	cast
SZY55	81.3	13.1	3.9	–	–	1.0	Cu-Sn-Pb As：0.6%	cast
SZY56*	84.9	13.7	0.6	0.6	0.2	n.a.	Cu-Sn	cast
SZY62	80.0	15.6	1.3	–	–	3.2	Cu-Sn	cast
SZY63	88.2	9.0	1.2	0.4	–	1.2	Cu-Sn	cast
SZY64	88.7	9.2	1.0	–	–	1.1	Cu-Sn	cast
SZY65-6	82.2	13.5	2.0	–	–	2.2	Cu-Sn-Pb	cast
SZY65-17	72.2	17.3	–	1.0	0.9	8.6	Cu-Sn	cast, annealed
SZY66-2*	82.3	14.8	2.4	0.2	0.3	n.a.	Cu-Sn-Pb	cast, annealed
SZY66-4	67.7	21.3	–	1.3	0.7	8.9	Cu-Sn	cast, annealed
SZY67	79.5	20.5	–	–	–	–	Cu-Sn	quenched
SZY99	85.7	14.3	–	–	–	–	Cu-Sn	hot-worked
SZY100	84.9	14.6	–	0.4	–	–	Cu-Sn	cast
ZGM26	69.2	12.0	11.7	1.1	–	6.1	Cu-Sn-Pb	cast, annealed
ZGM29-1	83.6	15.1	–	–	0.2	1.1	Cu-Sn	cast
ZGM29-2	84.8	11.2	1.3	–	–	2.6	Cu-Sn	cast
ZGM30	84.5	15.2	–	–	–	0.3	Cu-Sn	cast
ZGM33-2	80.1	12.3	3.8	–	0.2	3.6	Cu-Sn-Pb	cast, annealed
ZGM36-1	54.8	29.2	0.6	0.5	0.2	14.7	Cu-Sn	cast, annealed
ZGM36-2	79.4	–	16.3	1.1	0.6	2.7	Cu-Pb	hot-worked
ZGM36-3	86.1	12.6	–	–	–	1.3	Cu-Sn	cast, hot-worked
ZGM37	84.3	11.5	–	2.1	0.4	1.8	Cu-Sn	hot-worked,then cold-worked
ZGM38-1	82.6	14.0	–	–	–	3.4	Cu-Sn	cast
ZGM39	79.3	12.7	5.8	–	–	2.3	Cu-Sn-Pb	cast
ZGM40	96.8	0.8	–	0.8	–	1.6	Cu	cast
	62.8	21.5	–	1.7	0.5	12.4	Cu-Sn	cast
ZGM41	75.1	17.0	4.4	–	–	3.5	Cu-Sn-Pb	cast
ZGM44	73.9	18.5	3.1	–	–	4.5	Cu-Sn-Pb	cast
ZJT10	89.8	0.8	–	6.8	0.8	1.7	Cu	cast
ZJT11	80.7	12.9	–	0.8	0.2	5.3	Cu-Sn	cast, annealed
ZJT14-1	82.2	8.2	–	0.7	0.6	8.3	Cu-Sn	cast
ZJT14-2	71.9	16.6	–	0.5	0.4	10.6	Cu-Sn	cast
ZJT15	82.0	10.9	1.6	1.0	–	4.5	Cu-Sn	cast, annealed
ZJT17	96.4	–	–	1.5	1.0	1.1	Cu	cast
ZJT19-1	82.6	13.9	0.4	–	0.2	2.9	Cu-Sn	cast
ZJT21-1	96.5	–	1.3	–	–	2.1	Cu	cast
ZJT21-2	85.5	9.2	–	0.6	0.6	4.0	Cu-Sn	cast
ZJT23-1	88.0	10.4	–	–	–	1.6	Cu-Sn	cast, annealed

Note: * = analysed by SEM–EDS; na = oxygen not analysed. The other samples were analysed by ED-EPMA including oxygen. Tin or lead exceeding 2% is regarded as an alloying component.

Table 3 Alloy types of metal fragments.

Site	Cu	Cu-Pb	Cu-Sn	Cu-Sn-Pb	Total
Lijia			11	3	14
Zhougongmiao	1	1	7	5	14
Kongtougou	3		7		10
Total	4	1	25	8	38

bronzes, seven of which contained a few percent of lead. Tin levels were around 15% in most cases. Only three objects showed higher tin levels, but these were heavily corroded bronzes whose remaining microstructures were not indicative of such high tin concentrations. Lead contents were typically low, rarely exceeding 2%. Most samples had many small copper iron sulphide inclusions; in two cases (SZY44 and 34), sulphide inclusions were found to contain nearly 1% selenium.

The metallographic study confirmed that all 13 artefacts were formed by casting. Nine samples showed normal casting dendrites and (α+δ) eutectoids. Among them, one awl and two chisels (SZY38, 50 and 51) were found to have some strain lines at the edges, which were probably caused by usage, while the handle of a knife (SZY45), with unobvious dendrites, seemed to have been slightly annealed after casting. The remaining four objects displayed clear evidence of working. The microstructures of a chisel (SZY53) and a knife (SZY44) showed equi-axed hexagonal grains, some of which were twinned. The middle part of the cross-section of the knife (SZY44) still preserved some dendrites, indicating that the annealing process was not extensive. Two other knives (SZY39 and 42) were cold-worked following hot-working. Their equi-axed grains showed bent twins and strain lines, while the sulphide inclusions and remaining (α+δ) eutectoids had become elongated along the orientation of the cold-working.

In summary, all 13 artefacts were made of quite similar copper alloys with around 15% tin but little lead. Such bronzes are of high tensile strength, hardness and some degree of extensibility, and some tools were worked to improve their mechanical properties.

Metal fragments

Many small metal fragments were excavated from the foundry sites, but it was difficult to identify their original functions or technological origins. They could either be metal raw materials (ingots or scraps for recycling), fragments of the products, or simply foundry spillage. Their analysis, however, yielded information about the types of alloys employed in the different foundries (Tables 2 and 3).

Lijia

Fourteen metal fragments from the Lijia foundry site were examined; most are tin bronzes containing 10–18% tin and little lead. Only samples SZY22-2 and SZY67 contained tin above 20%, while SZY55 was singled out as a leaded tin bronze with 0.6% arsenic. Overall, these compositions were consistent with those of the recognisable artefacts found at the site. Most of the fragments appeared as cast structures, although some seemed to have been annealed after casting. Only one sample (SZY99) was hot-worked, with sulphide inclusions aggregating and small iron-rich phases scattering. Sample SZY67, with a high tin content, showed acicular crystals indicative of quenching (Figs 5 and 6).

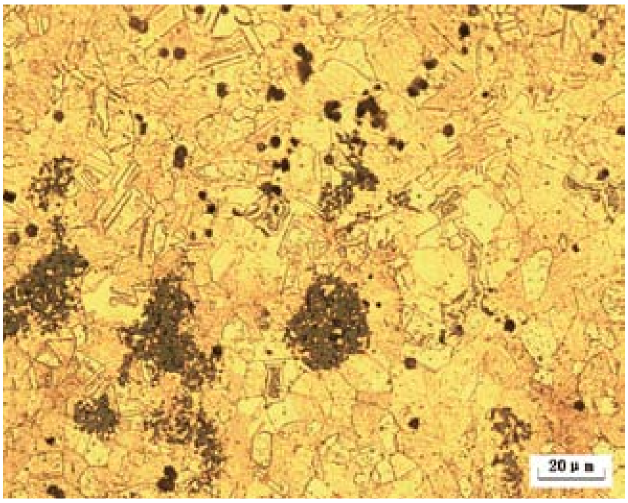

Figure 5 Sample SZY99 microstructure, etched, equi-axed and twinned grain with remnant (α+δ) eutectoids, aggregated sulphide inclusion and scattering

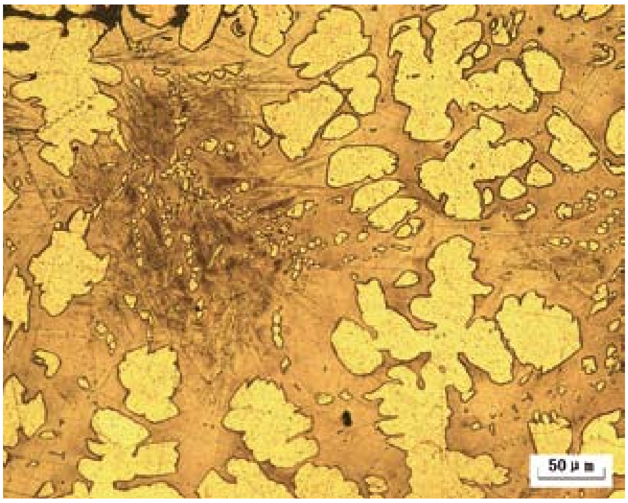

Figure 6 Sample SZY67 microstructure, etched, needle-like phase in (α+δ) eutectoids

Zhougongmiao

There are seven tin bronzes, five leaded tin bronzes, one leaded copper and one mixed metal (see below) among the 14 metal fragments from the Zhougongmiao foundry site. Four out of the five leaded tin bronzes had less than 6% lead, while the fifth contained as much as 11.7%. The only leaded copper sample (ZGM36-2) had a high lead content of 16.3% (Fig. 7). Overall, the presence of leaded alloys was much more frequent than at Lijia. Most of these objects exhibited cast or annealed structures, with few showing evidence of working.

Of particular interest is sample ZGM40, showing the mixture of two types of metal: pure copper and tin bronze (Fig. 8). The pure copper was embedded in a tin bronze matrix, with distinct boundaries. Although both metals appeared as

Figure 7 Sample ZGM36-2 microstructure, etched, equi-axed and twinned grain with intergranular lead prills and sulphide inclusions.

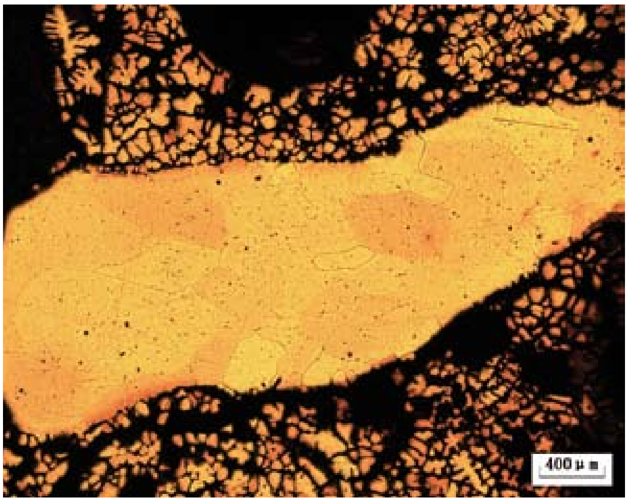

Figure 8 Sample ZGM40 microstructure, etched, two metals.

cast microstructures, the sulphide inclusions had different shapes and compositions: those in the pure copper were small prills of copper iron sulphides containing selenium, whereas those found in the intergranular ($\alpha+\delta$) eutectoids of the tin bronze were copper sulphides without detectable selenium. This piece of metal fragment probably formed when copper ingots and bronze scraps were mixed together and heated at too low a temperature to melt the copper completely.

Finally, it is notable that nine samples of these metal fragments have sulphide inclusions with selenium. Selenium is sometimes found as a trace element of copper ores, coexisting with sulphides, and it tends to remain with the sulphides when copper ores are smelted and refined (Rehren 1991). Therefore, the selenium in these sulphide inclusions of copper and bronze probably derived from the copper ores.

Kongtougou

Among the 10 samples analysed from Kongtougou are seven tin bronzes which were cast or annealed after casting. There are, however, two samples of unalloyed copper (ZJT17 and ZJT21-1). Interestingly, ZJT10 is a mixture of raw copper and slag (described and discussed in detail in the next section). Only one sample (ZJT17) was found to contain selenium-rich sulphide inclusions.

Slag

Some slag was found adhering to furnace wall fragments, while other samples were recovered as small lumps. Based on microanalytical results, most of the samples appear as typical copper-alloy melting slag, but a few are particularly rich in iron, making the interpretation more complicated. These two slag types will be discussed in turn.

Melting slag

Melting slag forms as the molten metal reacts with the furnace or crucible wall and fuel ash during the melting and alloying process. When exposed to air, the metal partly oxidises, thus forming diverse oxidic phases containing the alloying components – copper, tin and/or lead. Typical melting slag can be expected to contain silicates derived from the ceramic material, oxides of the alloying components, and a glassy matrix possibly enriched in alkali or alkali earth oxides from the fuel ash, but they rarely contain significant amounts of iron or other gangue-related elements. These are precisely the features noted in most of the Zhouyuan slag.

Sample ZJT7-3 from Kongtougou is presented here as a typical tin bronze melting slag, similar to those identified in other sites. It contains primary crystals of tin oxide, together with copper prills (sometimes with a rim of copper oxide) in a glassy matrix characterised by a high lime content. Exsolving from this matrix were also fine dendrites (probably of cuprite), together with very small globules, which were too small to be identified by EDS. Sample ZGM33-1 from Zhougongmiao was slag produced during the melting of leaded tin bronze. In this sample, the dominant phases were tin oxide, copper oxide and lead oxide, in a lead silicate matrix. Pure copper prills and heavily corroded leaded tin bronze prills were also found in this sample (Figs 9 and 10).

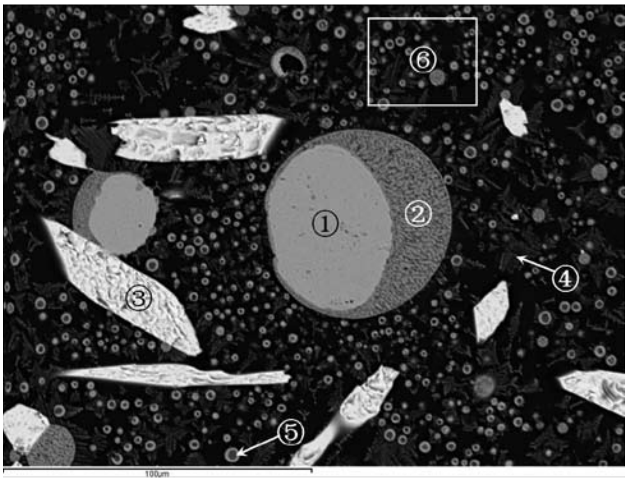

Figure 9 Backscattered electron (BSE) image of sample ZJT7-3, some copper prills (1) with a rim of copper oxide (2), tin oxide crystals (3), fine dendrites (4) and small globules (5) in a glassy matrix (6).

Figure 10 BSE image of sample ZGM33-1, some blocks of copper oxides (1), acicular tin oxide crystals (2) and lead oxides (3) in lead-rich silicate glassy matrix (4).

Table 4 Alloy types of melting slag.

Site	Cu-Pb	Cu-Sn	Cu-Sn-Pb	Total
Lijia		3	2	5
Zhougongmiao	1		1	2
Kongtougou		5	1	6
Total	1	8	4	13

The presence/absence of compounds of copper, tin and lead allows us to infer the alloys melted in each case (Table 4). In the case of Zhougongmiao, although only two slag samples have been analysed, they show particularly high lead concentrations, a feature in good agreement with the generally higher lead contents of the metal fragments from the site. It is more difficult, however, to determine whether these constituents entered the alloy as pure metals or scrap alloys, or whether tin entered the reaction as relatively pure mineral cassiterite that would be reduced and alloyed to the copper by cementation. A number of scholars (Dungworth 2000; Rostoker *et al.* 1983; Rovira 2005) have attempted to define analytical criteria for discerning these variable technological histories; however, given the lack of experimental data that can be used as a reference, these criteria must remain tentative. In our view, the abundance of tin oxide crystals in the slag cannot be taken as an indication of the addition of cassiterite to the melt; none of these phases seem residual minerals, but rather they are primary euhedral or acicular crystals formed from the slag melt. The free energy of the formation of tin oxide is much lower than that of copper and lead (cf. Ellingham diagram). Thus, all the tin in the alloy can oxidise, while part of the copper and the lead remain in the metallic state. As tin oxide is insoluble in other metals and it shows no reactivity with silica, it will tend to crystallise in a pure form. In some cases, however, relatively large islands of metallic copper are found within the slag, suggesting that this metal could have entered the charge in a relatively pure state, i.e. we would be dealing with bronze alloying rather than simply melting. Finally, where present, lead oxide will react heavily with the siliceous ceramic, resulting in the lead silicate glass identified in some slag. The proportions among the different alloying constituents, the temperatures reached, the duration of the process and the redox environment, will altogether add further variability to the crystallography and composition of the resulting slag, making technological interpretations even more difficult.

Altogether, at present we can only identify the Zhouyuan slag as products of melting (rather than smelting) and alloying of a range of alloys, without more precise technological identifications. In particular, there is no evidence of the use of mineral cassiterite; it seems that tin could have entered the reaction as a metal (see further discussion below).

Iron-rich slag

A few small black slag pieces from the site of Kongtougou (ZJT6 and 20) were more unusual, most notably in their high iron content. Samples ZJT6 and ZJT20 showed well-developed blocks of fayalite and globules of wüstite, with small prills of iron-rich copper (in ZJT6) or matte (in ZJT20), and no detectable levels of tin or lead (Figs 11 and 12). Sample ZJT10 was especially peculiar, as it exhibited a mixture of raw copper and iron-rich slag: the metallic part was composed of raw copper containing copper-iron-sulphide inclusions and globules of metallic iron, while the slag part was dominated by fayalite and wüstite crystals which were not fully developed; between them was a layer of copper-iron-sulphide (Figs 13 and 14).

Some of these features could appear more indicative of copper smelting, rather than melting, slag. However, considering the very low incidence of this type of slag at the site, we are reluctant to take these as indications that cop-

Table 5 Chemical composition of typical melting slag and iron-rich slag (wt%).

Lab no	Na_2O	MgO	SiO_2	Al_2O_3	SO_3	K_2O	CaO	FeO	CuO	SnO_2	PbO
ZJT7-3	1.0	3.8	49.2	11.1	–	1.2	20.1	6.6	5.0	–	2.1
	1.4	2.3	63.6	13.8	–	3.1	10.7	5.1	–	–	–
ZGM33-1	–	–	56.3	10.4	–	–	–	–	1.8	4.6	26.9
	0.8	1.4	32.3	6.4	–	1.5	7.5	6.2	–	–	43.9
ZJT6	–	1.0	20.9	2.5	0.7	0.6	5.4	68.9	–	–	–
	–	1.0	21.7	3.1	–	0.6	5.3	68.3	–	–	–
ZJT20	–	1.0	25.7	3.0	7.2	0.5	3.6	56.1	2.9	–	–
	–	0.9	28.3	2.5	5.0	0.7	0.9	56.8	4.8	–	–
ZJT10	–	0.7	23.0	3.5	4.8	–	2.2	43.9	21.8	–	–

Note: The chemical compositions of ZGM33-1 were spot compositions of the glassy matrix, while the others were area compositions of the samples. All the S, Fe, Cu, Sn and Pb contents are reported in their oxidic forms.

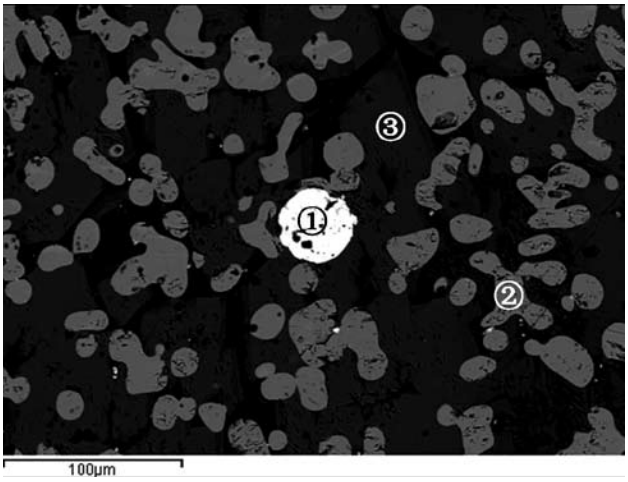

Figure 11 BSE image of sample ZJT6, a copper prill (1), wüstite globules (2) and blocky fayalite (3) in a glassy matrix.

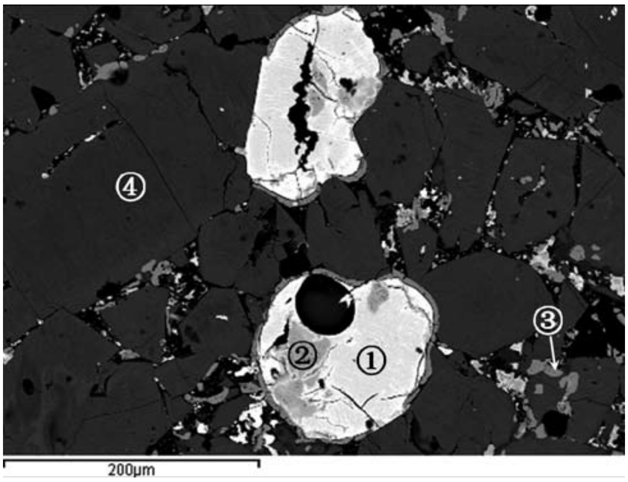

Figure 12 BSE image of sample ZJT20, some whitish copper iron sulphide prills (1) with some iron sulphide part (2), small wüstite globules (3) and blocky fayalite (4) in a glassy matrix.

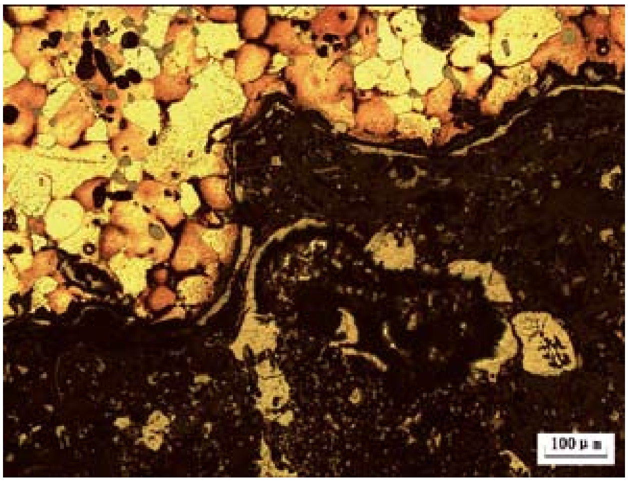

Figure 13 Sample ZGM40 microstructure, etched, a layer of copper-iron-sulphide between the raw copper and the slag.

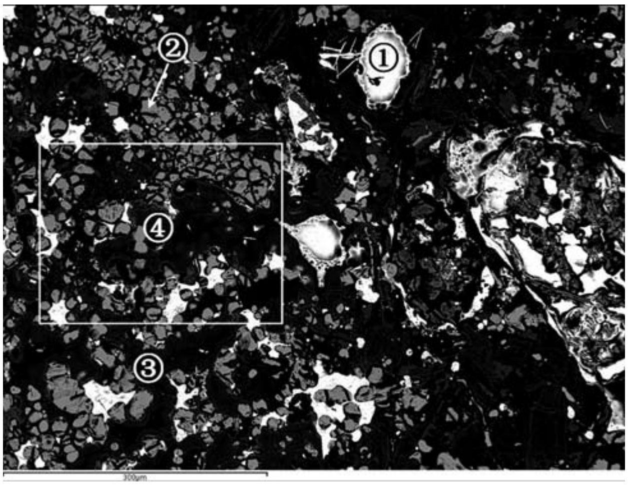

Figure 14 BSE image of sample ZJT10, some copper prills with a few percent of iron (1), wüstite globules (2) and fayalite (3).

per smelting took place in Kongtougou. If they truly were smelting slag, we would be inclined to regard them as accidental lumps that reached the foundry with the raw copper imported for the casting activities. However, it is also possible to interpret these as copper refining slag. If raw copper containing unduly high iron and/or sulphur reached the site, this could be refined by melting it in relatively oxidising conditions, so that these elements and any other slag inclusions present in the metal could float on the surface and be skimmed off. The result would be a slag or slag/matte layer similar to those documented here. In this sense, the presence of wüstite and fayalite would not be the result of a smelting reducing environment (where Fe^{3+} from the ore is reduced to Fe^{2+} or metallic iron), but rather the products of an oxidising atmosphere (where metallic iron contained in the copper could be oxidised to Fe^{2+}). Sample ZJT10 may be documenting exactly this process, preserving part of the raw iron-rich copper undergoing refining and forming slag. Arguing against the smelting scenario is also the predominance of Fe^{2+} in the form of wüstite, which would denote conditions unnecessarily reducing for the smelting of copper – iron oxide in copper smelting slag is typically present in the more oxidised forms, such as magnetite.

Discussion

Copper was an important commodity in the Western Zhou period. In the 1970s and 80s, two bun ingots were discovered at the Shaochen and Shaoli villages of the Zhouyuan site (Zhou 1972; Luo 1985). The one from Shaochen is 24 cm in diameter, 4.65 kg in weight and contains 97.7% copper and 2.3% lead; the other, from Shaoli, is 32.5 cm in diameter, 5 kg in weight and contains 97.6% copper, 0.6% iron and 0.6% sulphur (Fig. 15). These two ingots found not far from the Lijia foundry site provided strong evidence that copper ingots were used as raw materials. In addition, some of the pure copper and raw copper fragments described above were probably fragments of copper ingots. Together with the evidence provided by the iron-rich slag, it can be inferred that refined pure copper ingots, unrefined raw copper ingots and also leaded copper ingots (such as the Shaochen ingot) were introduced to foundry workshops for bronze-making. Although the precise provenance of the copper ingots has yet to be determined, it seems likely that a number of sources were supplying copper to the Zhouyuan workshops (see further discussion below). Different copper ingots have been discovered in other areas dated to the Western Zhou period. For example, several kilograms of diamond-shaped ingots were found in Muyu Hill, Tongling, Anhui province. Two of the three analysed ingots contain iron (2% and 9.5%). These iron-rich copper ingots were cast together with relatively unrefined raw copper, and are thus similar to some of the copper materials in the Zhouyuan area.

Another important source of copper could be bronze fragments, such as broken artefacts, and by-products generated during the melting and casting process. At the Zhouyuan site, fragments of large bronze vessels, sprues and even slag were found in bronze hoards, some of which were kept in bronze or pottery containers. These scraps might have been regarded as valuable metal materials by ancient people and deliberately preserved for recycling. More relevant evidence is provided by the newly excavated foundry sites. One piece of evidence is the large number of metal fragments found, some of which might have been collected from other places to be recycled; some generated during the melting and casting processes could have been used for local re-melting. Sample ZGM40 proves the use of bronze scraps as one kind of raw material. Another important piece of evidence is presented by some vitrified clay cores found in association with some slag in the three foundry sites. Clay cores are inner moulds of ears or legs of bronze vessels, so they usually remain inside bronze vessels after casting. If some broken bronze vessels were re-melted, the low-density clay cores would float to the surface of the molten metal and then be discarded, ending up as sintered lumps with some slag such as those recorded here (Fig. 16).

Tin was a more precious metal component for bronzes since tin ores were not as widespread as copper ores. In addition, ancient metallic tin rarely survived and few pure tin objects have been discovered to date. In ancient China, the earliest tin objects with reliable scientific analysis are one tin *ding*, one tin *gui* and eight tin fishes from Yu state cemeteries, dating back to the early and middle Western Zhou period (Su *et al.* 1988). One of the tin fishes, with 99% tin, indicates that contemporary workers were able to produce pure tin. More tin objects are known from the Eastern Zhou period (771–220 BC). Although neither metallic tin objects or fragments nor tin ores (usually cassiterite) were found in the Zhouyuan area, the availability of metallic tin in the period and the absence of residual cassiterite in the melting slag together suggest that bronzes were made with metallic tin.

Lead was easier to smelt and lead ores were more common. Many lead objects and fragments, dating back to the Western Zhou period and even earlier, have been found (Li 1984). No direct archaeological evidence for lead materials was found in the Zhouyuan area. However, metallic lead ingots or scraps were probably used as the lead source for the leaded copper and bronze, while in bronze objects with lower lead concentrations it might have been introduced as an impurity from copper ingots.

From the analyses of metallurgical debris in the Zhouyuan area, coupled with other relevant archaeological finds of the Shang and Zhou periods, it seems that generally similar metal materials, including ingots and scraps, were used at the Zhouyuan foundries. However, the metallurgical technology of the Zhougongmiao site is quite different from that of the other two sites. First, metal fragments and melting slag from Zhougongmiao generally displayed higher levels of lead than those from the other two foundries. Secondly, nearly two-thirds of the sulphide inclusions in the Zhougongmiao metal fragments contained selenium, whereas it was only found in a few cases in Lijia and Kongtougou metal artefacts

Figure 15 Copper ingots from Shaochen (top: 24 cm in diameter) and Shaoli (bottom: 32.5 cm in diameter). (Photo: Yang Junchang.)

Figure 16 Vitrified ceramic casting cores from Zhaojiatai.

and fragments. This strongly indicates that the copper materials at the Zhougongmiao foundry came from lead- and selenium-rich copper ores, which were no longer the main copper sources for the Lijia and Kongtougou foundries in the later period. A third difference is the relatively primitive mould-making technology in Zhougongmiao, which has been discussed elsewhere (Chen 2005; Zhou 2008). These technological differences might be explained partly by chronological changes, but the different characteristics of the settlements where these foundry sites were located should also be taken into consideration.

The Zhougongmiao site was identified by archaeologists to be a settlement of Zhou people from the Proto-Zhou to the Western Zhou period. The discovery of late Proto-Zhou casting remains in 2006 demonstrated that Zhou people could cast bronzes before the demise of the Shang dynasty. Their more rudimentary bronze-making technology was reflected in the restricted variety and number of Proto-Zhou bronzes in the Zhouyuan area, typically showing a relative rough craftsmanship. The bronze-making technology at the Zhougongmiao foundry in the early Western Zhou period can probably be considered an indigenous development from the Proto-Zhou period in this area, with little influence from Shang people. In the later period, however, Shang descendants in Lijia and Zhou people in Kongtougou must have inherited the more advanced casting technology from Shang people and also developed it from that of the Zhou people, thereby producing bronzes of higher quality.

Conclusions

These three bronze foundry sites, spanning the early, middle and late Western Zhou periods, are another important discovery following that of the Beiyao foundry site (dated to the early Western Zhou period) in Luoyang, Henan province. They give clues pertaining to the study of the technology of bronze casting, the sources of metal materials and the distribution of settlements in the Zhouyuan area during the Western Zhou period.

This paper has revealed aspects of bronze-casting technology in three Zhouyuan foundry sites by analysing bronze artefacts, bronze fragments and slag. It was found that the bronze tools and weapons were made primarily of tin bronze. Some of the bronze tools were hot-worked after casting and were of a good quality. Bronze fragments from the Zhougongmiao site were mainly made of tin bronze and leaded tin bronze, while those from the other two sites were mostly tin bronzes. A majority of the slag samples were typical melting slag or alloying slag, with phases containing oxidised alloying components. A few pieces of iron-rich slag from the Kongtougou site were interpreted as possible refining slag.

From the results of the analytical studies, it is estimated that copper, tin and lead ingots were brought to the foundry sites as raw ingredients, as well as scrap bronze fragments. The Zhougongmiao foundry (early Western Zhou period) is distinctive in its sources of copper ores, alloying and mould-making technology, which were different from those present at the later Lijia and Kongtougou foundries.

This paper focused primarily on the metallurgical activities of melting, refining and alloying by analysing metal artefacts, metal fragments and slag. It should be noted, however, that more work needs to be done. More bronze artefacts excavated from foundry sites and surroundings, especially vessels and chariot accessories, need to be examined further, particularly with a view to address the provenance of the different metals. In addition, furnace fragments call for future careful work and scientific examinations. The conspicuous lack of crucibles should also be considered.

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