Micro-slag and "invisible" copper processing activities at a Middle-Shang period (14^{th}-12^{th} century BC) bronze casting workshop

Liu, Siran,[1] He, Xiaolin,[2] Chen, Jianli,[3] Zou, Guisen,[4] Guo, Shijia,[3] Gong, Xicheng,[5] Rehren, Thilo[6]

1. Institute for Cultural Heritage and History of Science & Technology, USTB
2. School of History, Wuhan University
3. School of Archaeology and Museology, Peking University
4. Institute for History and Culture of Science & Technology, Guangxi University for Nationalities
5. Anhui Provincial Institute of Archaeology
6. STARC, The Cyprus Institute

Abstract

Micro-slag artefacts from ancient bronze casting workshops were largely ignored in previous research despite their rich information potential. Current research demonstrates they could significantly enhance our understanding about past metallurgical activities but their identification requires careful in-situ analysis and a well-designed sampling strategy. Here we present an innovative methodology combining in-situ geochemical survey, wet-sieving of soil samples and detailed microscopic study, employed to investigate an important Middle-Shang site, Taijiasi, in the Huaihe River valley. The micro-slags from this site revealed that in addition to bronze alloying and casting, raw copper refining was also practiced. Material evidence for the refining process was not immediately visible in the archaeological excavation since most slag was mechanically crushed to retrieve any copper trapped in them, leaving only micro-slag fragments typically smaller than 3000 µm (3 mm). The fact that most micro-slag was recovered from one sector (H234) of a small building (F16) located on the same platform as the elites' long houses suggests that mechanical processing of refining slag was conducted in a confined area and closely supervised. It might reflect people of this site valuing copper as a highly

precious material and making all effort to recover copper otherwise lost in slag. This find will potentially shed new light on a range of important issues of Shang archaeology, including the regional variation of Shang metallurgical styles and the provenance of copper in the Shang period. This research also encourages researchers to look into archaeological soil samples with abnormally high copper content and understand the particles in them causing these high readings.

Key words

Micro-slag, bronze casting workshop, in-situ analysis, microscopic analysis, refining

1. Introduction

Metal smelting and processing in the pre-modern period generated a range of material remains such as slag, metal spillage, crucible/furnace fragments, tuyères and casting moulds. The detailed analysis of these remains can provide crucial information about ancient metallurgical technology and facilitate the study of function and spatial organization of metal workshops. Many authors have published research on the scientific characterization of metal processing remains (e.g. Rovira, 2002, Rehren, 2003, Hauptmann, 2014, Liu, et al., 2015, Murillo-Barroso, et al., 2017, Rademakers and Farci, 2018). However, little attention has previously been paid to the sample collection strategy (but see Rademakers and Rehren, 2016). It has been known that metal smelting at the dawn of metallurgy may leave little material evidence due to the high purity of raw materials and relatively small production scale (Craddock, 2000, O'Brien, 2004, Radivojevic, et al., 2010). Additionally, workers may sometimes further process smelting slag for embedded metallic inclusions. In sharp contrast to the massive slag mounds in many Late Bronze Age sites, a range of Chalcolithic and Early Bronze Age sites only revealed nut-sized or smaller slag fragments (less than 1 cm), which are believed to be intentionally crushed after smelting in order to retrieve metallic prills trapped in them (Epstein, 1993, Montero-Ruiz, 1993, Golden, et al., 2001, Shugar, 2003, Bourgarit, 2007, Burger, et al., 2010). To recover these micro-slags in the field, a careful sample collection strategy involving geochemical survey and wet-sieving of soil samples is needed during the excavation.

This article demonstrates that it is equally important to investigate micro-slag from bronze casting workshops, using as a case study a Middle-Shang period (14th-13th century BC) bronze casting workshop at Taijiasi in Anhui province, China. The systematic analysis of various types of metallurgical remains created a significantly more comprehensive view of bronze processing activities at this important settlement in Central China than would have been otherwise possible.

1.1 Archaeological Background

The site of Taijiasi is located at Funan county, northwestern Anhui province, more than 500 km away from the Shang capitals in the Central Plains, and about 200-300 km from the copper belt in the Yangtze River valley (Figure 1). The site is at the north bank of the Runhe River (润河), a branch of the Huaihe River (淮河). In the 1930s to 1950s, a number of important Shang bronze ritual vessels had been discovered as chance finds in the old course of the Runhe River (Ge, 1959), indicating the residence of Shang elites in this area. However, it had not been clear whether these ritual artefacts were locally produced or imported from the Central Plains. Since 2014, the site of Taijiasi was excavated by a joint archaeological team of Anhui Provincial Institute of Archaeology and Wuhan University. The site consists of five mounds. The largest one is around 4000 m^2, surrounded by a moat about 10 m wide. The mound was mostly excavated and revealed rich material remains demonstrating Shang people lived at this site and conducted metallurgical craft-production.

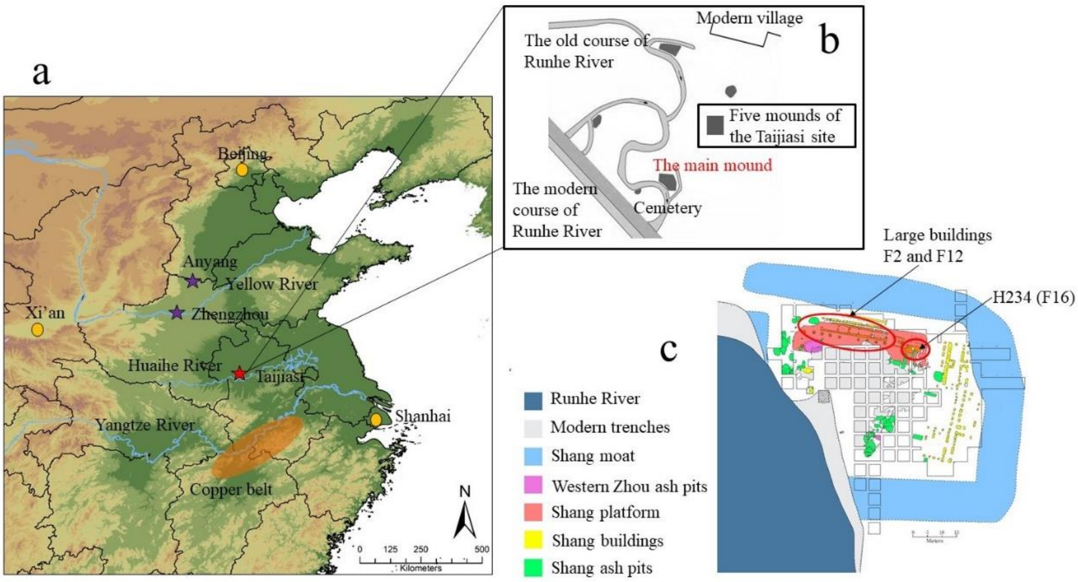

Figure 1 The site of Taijiasi. The geographic distance between the Taijiasi site and Shang capitals in the north is shown in (a). Its five mounds are shown in dark grey colour in (b). (c)

is the plan of the Taijiasi major mound. The metallurgical workshop H234 is located on the same platform as the large buildings F2 and F12.

Based on stratigraphic association and pottery typology, the Shang occupation of this site is divided into two phases. The first phase is from the Upper Erligang to the Early Huanbei Period (Middle Shang I-II). The second one is dated to the later Huanbei period or Yinxu I stage (Middle Shang III) (see Table 1 for a chronological framework of the Middle Shang). Three seasons of excavations revealed many important features including 16 building foundations and 262 ash pits, which mostly dated to the later period of this site. To the west of this mound, 7 tombs of the second phase were excavated, revealing a number of ritual bronze vessels and jade objects. A rammed earth platform was identified in the northern part of the main mound with four buildings (F2, F12, F14, F16) on it. The rammed earth platform is arguably a strategic feature of the site and its current surface is still about 1m above the ground. Both F2 and F12 were large long houses with a significant size (over 20m in length), and are thought to be elite residence or ritual places, due to their size and special location (He and Gong, 2018).

Table 1 Chronological table of the Middle Shang period and its major sites

Period	Date	Major sites
Middle Shang I	c. 1400-1350 BC	Xiaoshuangqiao site
Middle Shang II	c. 1350-1300 BC	Huanbei Shang City
Middle Shang III	c. 1300-1250 BC	Huanbei Shang City

The most prominent craft production at this site was bronze casting, indicated by a great number of metallurgical remains such as slag, furnace/crucible fragments, and moulds that were found in the moat and ash pits. The majority of them were dated to the later stage of the site (13^{th} century BC). This article focuses on this period while the remains found in the earlier contexts suggest there was already metallurgical production taking place then. The mould fragments of Taijiasi suggest that ritual vessels were the major products of the site (He and Gong, 2018). It is the first Shang period bronze casting workshop identified in the Huaihe River valley, demonstrating that the production of ritual vessels was not confined to the capital sites in the Central Plain.

Bronze casting remains of the later stage were found in three types of contexts. The first one is the foundations of buildings, where the metallurgical remains were likely introduced accidentally during the construction process. The majority of metallurgical remains were found in ash pits and the moat, the second context type. More than 30 ash pits revealed slag, crucible/furnace fragments and/or mould pieces. Two trial trenches in the east part of the moat also yielded many slags in the sediment. Metallurgical remains found in this context type were most likely waste dumped during the production, or secondary deposits formed after the production. The third context type is the fill of building F16 on the rammed earth platform. It has an area of approximately 48m^2 with two sectors H234 and H241; metallurgical remains were mainly found in sector H234. Remains of other crafts (such as bone tool manufacturing or pottery making) were absent from this context. The wall foundation was not found but 26 column bases around this building indicate it was roofed. It was dated to the later phase of this site based on pottery sherds recovered from the fill of this feature. The excavation revealed its first locus containing mainly podzolic sediment, in which green and black particles (< 1 cm) were found embedded. There were, however, only one copper fragment (H234①:5) and a few pieces of moulds, slag and crucible/furnace fragments revealed during the initial excavation.

An investigation of Shang metallurgical activities at this site was conducted jointly by the Institute for Cultural Heritage and History of Science & Technology (ICHHST), University of Science and Technology Beijing (USTB), the School of History, Wuhan University and School of Archaeology and Museology, Peking University. An innovative sampling strategy was employed to collect not only macro-metallurgical remains but also soil samples from geochemically abnormal strata and units. These samples were processed by wet-sieving to retrieve micro-artefacts, which were then subjected to detailed lab-based analyses leading to much new information concerning the nature of metallurgical activities at this site.

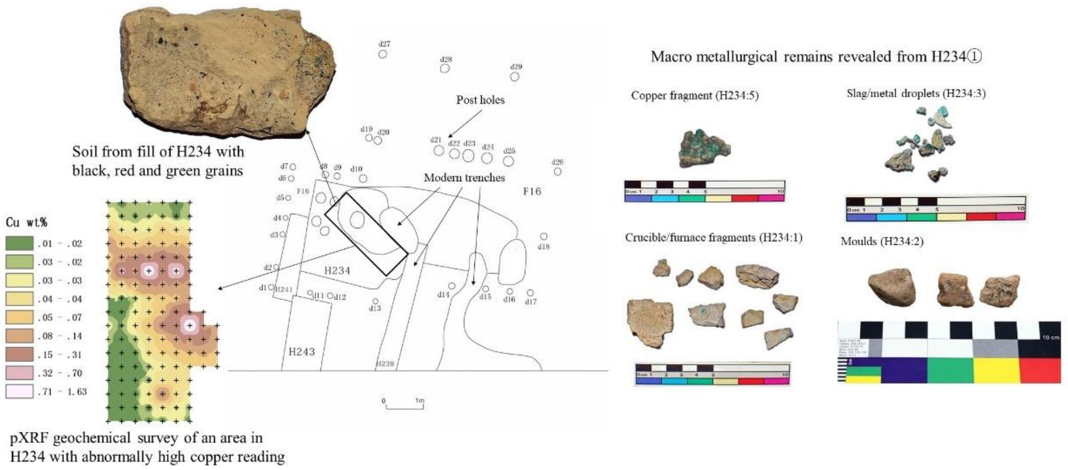

Figure 2 Plan of F16 and metallurgical remains including slag, crucible, and mould fragments found in sector H234. The northwestern corner of H234 shows elevated Cu and Ca reading during pXRF survey. The fill of this part contains many black, red and green particles.

2. Methodology

A Thermofisher Niton XL3t pXRF was used to conducted systematic in-situ soil analyses at the site. Soil mode was used and the collection time was 90 s. Profile soil samples from H234 were collected and analysed with X-ray powder diffraction (XRD) and Fourier Transformed Infrared (FTIR) spectrometry to study their mineralogical composition and thermal history. A Rigaku D/max-rb X-ray diffractometer with Cu-Kα radiation and an operating voltage of 30-45 kV was used for XRD analysis. FTIR measurements were performed with a Thermofisher IS5 spectrometer in transmission mode. Soil samples were collected for floatation and wet-sieving from the area with abnormally high Cu content identified by in-situ pXRF analysis. The heavy fraction of the samples was wet-sieved with an 80 mesh sieve to recover fine remains. This was followed by a careful examination under the stereo-microscope, picking out fragments with features of copper processing remains (e.g. green/black colour, porous/glassy texture, metallic lustre). The soil samples were obtained from ash pits, the moat and sector H234. In total, 161.5 litre of soil were treated by this method.

Macro-metallurgical samples, including slag, crucible, and metal fragments as well as micro-artefacts were subjected to detailed characterization at the archaeometry lab of ICHHST, USTB. Optical microscopy and a Tescan Vega III SEM equipped with a Bruker XFLASH 6|10 energy dispersive spectrometer (EDS) was used to investigate the microstructure and chemical composition of soil, slag and metal samples. The accelerating voltage was set to 20 kV and the live collecting duration was 60 s. Bulk compositions of micro-slags were determined by analysing the area of a polygon fitted into the slag fragment, including all metal prills and residual mineral inclusions. The data quality of the instrument was monitored with glass (Corning B) and tin bronze standards (CHARM set).

3. Results

3.1. Metallurgical activity at Taijiasi

Workshop H234

Macro metallurgical remains from H234 were analyzed for their chemical composition and microscopic structure. The copper fragment H234①:5 was identified as a piece of pure copper with impurities of less than 1 wt%. The crucible/furnace fragments (H234①:1) are associated with alloying and casting processes with abundant bronze prills, tin oxide and copper oxide in them (Figure 3).

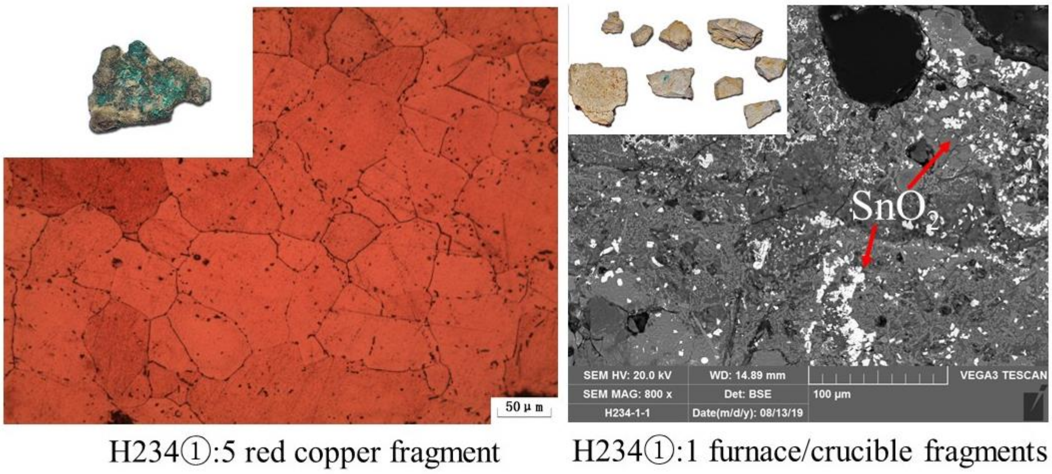

Figure 3 Microscopic images of the H234①:5 copper fragment and H234①:1 furnace/crucible fragments. H234①:5 has a typical metallographic structure of pure copper with αgrains and Cu-Cu2O eutectic structure. H234①:1 contains many SnO_2 particles in its slag lining.

The sampling interval of the in-situ geochemical survey was first set to 50 cm, and 80 points in total were analysed. A small area in the northwestern corner of sector H234 shows significantly elevated Cu and Ca contents. A more focused survey with a sample interval of 10 cm was then conducted in this area. The result shows that most Cu and Ca abnormal points concentrate in an irregular area of this part.

A modern trench cutting through the central part of the building exposed a profile of six loci (Figure 4). Locus 1 (H234①) is the podzolic soil with green and black inclusions. Locus 2 (H234②) is a hard greyish-whitish material. Loci 3-4 (H234③, H234④) are clay-rich yellow soil. Locus 5 (H234⑤) is podzolic soil containing ash and charcoal fragments. Level 6 (H234⑥) is the natural soil beneath the foundation of building F16.

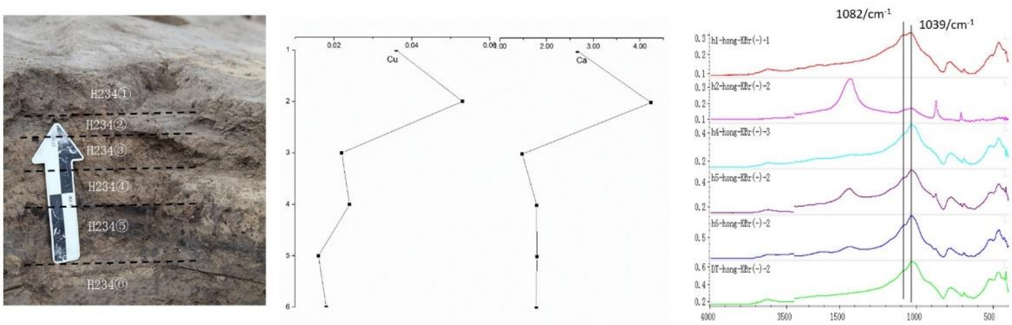

Figure 4 Profile of Cu and Ca rich area inH234. In-situ pXRF analysis shows that H234①-② are rich in Cu and Ca. FTIR analysis shows H234① has an additional absorption band around 1080/cm^{-1} and H234② has a strong absorption band around 1470/cm^{-1}.

The microscopic analyses show that H234③-⑥ are loess-like soil. H234① is also loess-like but contains much higher Cu and Ca than H234③-⑥. Its IR spectrum shows a stronger absorption band around 1082/cm^{-1}. According to previous FTIR investigation of archaeological sediments (Berna, et al., 2007), the major absorption band of fired clay tends to move from 1030/cm^{-1} to 1080/cm^{-1}. It is therefore suggested that H234① contains more fired clay than H234③-⑥. H234② is chemically and mineralogically different from the rest of the samples. Chemical analysis with SEM-EDS shows it contains mainly CaO with a small amount of silica. Its IR spectrum shows a strong absorption band around 1470/cm^{-1}, corresponding with carbonate minerals (Monnier, 2018). XRD analysis proves H234② contains mainly calcite ($CaCO_3$) as well as a small amount of quartz (SiO_2) and albite ($NaAlSi_3O_8$) (Figure S2). It was probably a lime-lined floor of this workshop. Its surface has a high Cu content, demonstrating the metallurgical activities that took place on it.

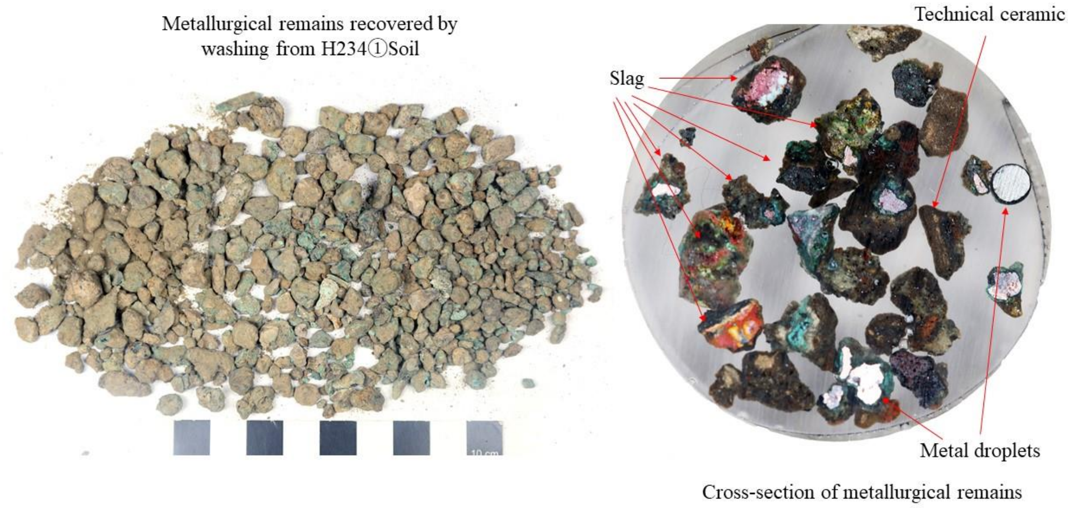

Figure 5 Micro-artefacts recovered from the H234① soil samples. The diameter of the resin block is 3 cm. Many of the fragments in the left picture are conglomerates of many slag pieces, bound by clay matrix. The actual particle size of slag can only be measured by microscopic analysis.

Though there was only a limited quantity of macro-metallurgical remains from H234①, wet-sieving of soil samples revealed many microscopic remains. The heavy portion mounted in epoxy resin was examined by OM and SEM. A considerable number of slag fragments and metal prills were identified in these polished blocks. Many of them were still coated with a clay shell or embedded in clay matrix, and could not have been identified without microscopic examination in cross-sections. The diameters of slag pieces were measured in SEM images and their chemical compositions were analysed using SEM-EDS. Among 84 fragments randomly selected for analysis, the average particle size is 1210 μm, with a considerable number of them below 1000 μm (Table S1, Table S2). Microscopic examination shows they are mostly slag fragments and metal prills, while technical ceramic is also occasionally identified (Figure 6).

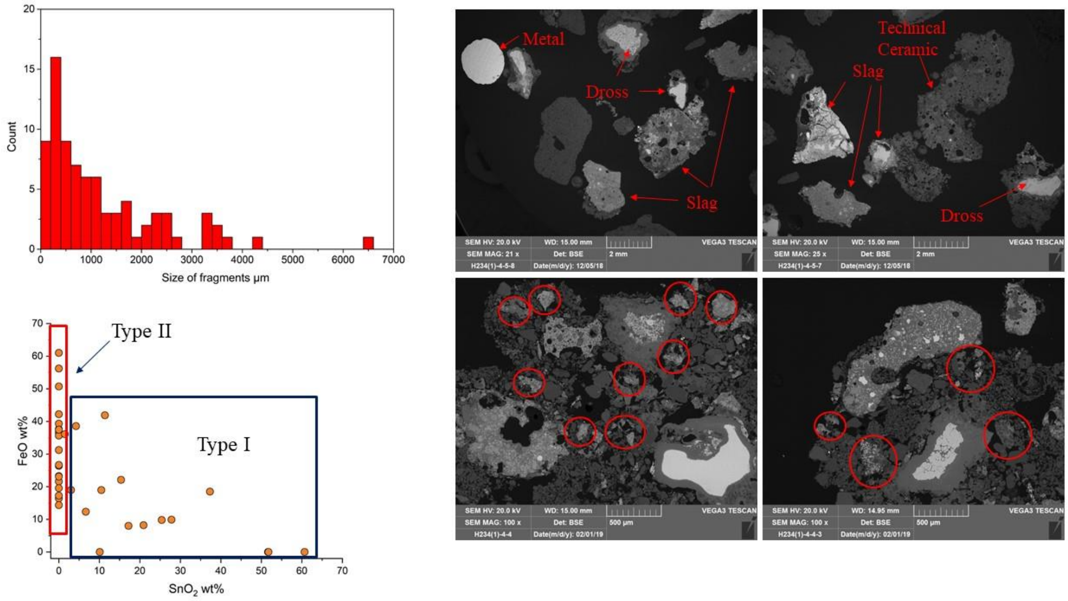

Figure 6 Size distribution and chemical composition of metallurgical remains found in H234① soil samples. Images are microscopic photographs of metallurgical remains. Two images at the lower row show many small slag fragments (labelled by red circles) embedded in the soil matrix. All analysed samples can be divided into two groups (Type I and Type II) on the basis of their tin content.

Two chemical groups were identified in these samples (Figure 6, Table S1, Table S2). Type I remains, including slag, dross and metal prills, are characterized by their high SnO_2 content (23.9 wt%) in average. Typically, these fragments are dominated by diamond and needle shaped tin oxide, cuprite and sometimes malayaite crystals. These Sn-rich phases are usually associated with metallic copper globules with varied Sn content (0-52 wt%). Free-standing bronze prills found in polished blocks typically have a spherical morphology. Other alloying elements such as As, Sb and Pb were found to be below the detection limit (c. 0.1 wt%) in Type I samples, suggesting the final product was tin bronze. Many dross fragments were arguably associated with high temperature metal 'burning' processes, that is the oxidation of metal at high temperatures during working, indicated by the presence of a relatively large metal core and diamond shaped tin oxide in the matrix (Figure 7:a,e). On the other hand, extraordinarily high-tin globules (>40 wt% Sn) (Figure 7:b and f) suggest fresh tin-rich raw materials such as metallic tin or cassiterite were involved in an active alloying process (Rehren 2001; Rovira, 2002, Liu, et al., 2015, Rademakers and Farci, 2018). Rounded metal prills might have spilled out from crucibles and moulds during melting and casting.

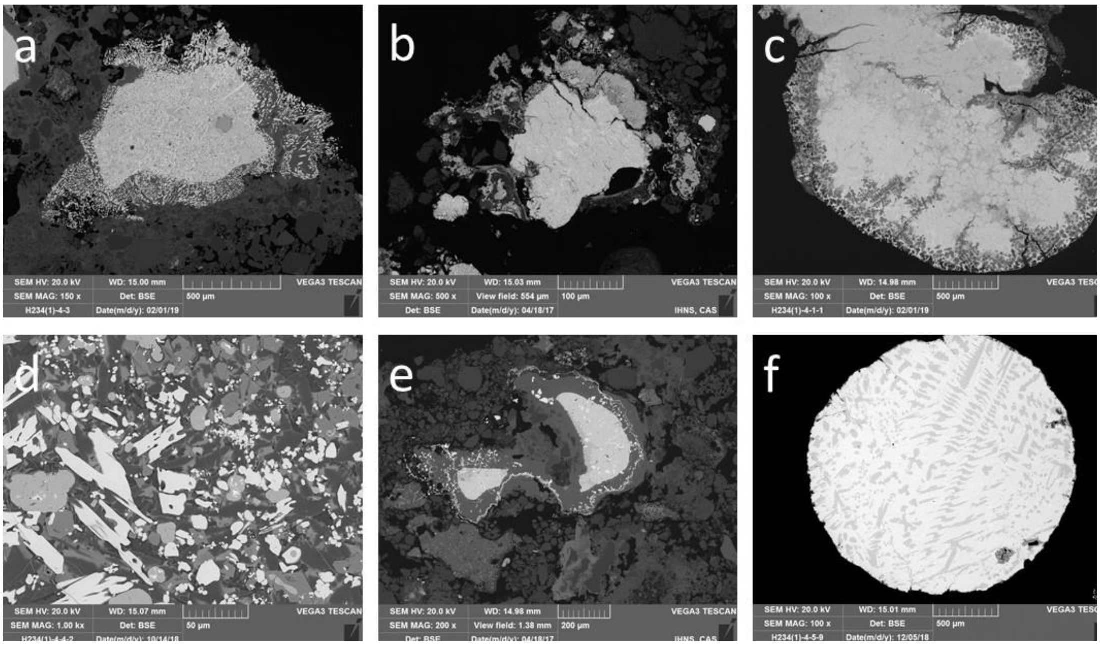

Figure 7 Micrographs of Type I slag, dross and metal prills. a,e: Typical burnt metal with a large metal core surrounded by tin oxides. d: matrix of Type I slag with many tin oxide and copper oxide crystals. b,c,f: Metallic prills/fragments with varied tin content.

In contrast, Type II remains contain no tin (Sn below detection limit); they account for c. 70% of the analysed fragments (Figure 6). They are mostly slag fragments, while their CuO and FeO contents are highly varied and have a general negative correlation with each other (Figure 8; note that any metallic copper prills in these fragments were included in the bulk analyses, expressed in the total as CuO). This type might be further separated into two subgroups based on their CuO and FeO contents. A tentative line could be drawn between a copper-rich (Type II-a) (CuO > 40 wt%, FeO < 10 wt%) and an iron-rich group (CuO < 30 wt%, FeO > 10 wt%) (Type II-b). The iron-rich slag fragments can have as much as 60 wt% FeO and are dominated by angular magnetite (Fe_3O_4) crystals and sometimes even wüstite (FeO), while the iron-poor and copper-rich ones contain mostly globular and dendritic cuprite (Figure 8). Delafossite lathes were frequently identified in slag with intermediate CuO and FeO contents (Figure 8). However, it has to be borne in mind that these slag particles are generally below 3 mm in size and the chemical separation between the two subgroups might be attributed to the varied metallurgical practices or highly varied nature of early bronze processing slag (Müller, et al., 2004, Rademakers and Rehren, 2016). There are also generally a few percent of CaO, K_2O and P_2O_5, which were likely from fuel ash. The SiO_2/Al_2O_3 ratio of these samples varied between c. 3-4 and c. 10-13 with an average of 6.8, while the value of technical ceramics from this site are generally 5-6. It indicates that the major source of SiO_2 and Al_2O_3 in the slag particles was likely technical ceramics. A few relatively large slag fragments contain unreacted quartz, which could be either residual material from technical ceramics or added flux (Figure 9).

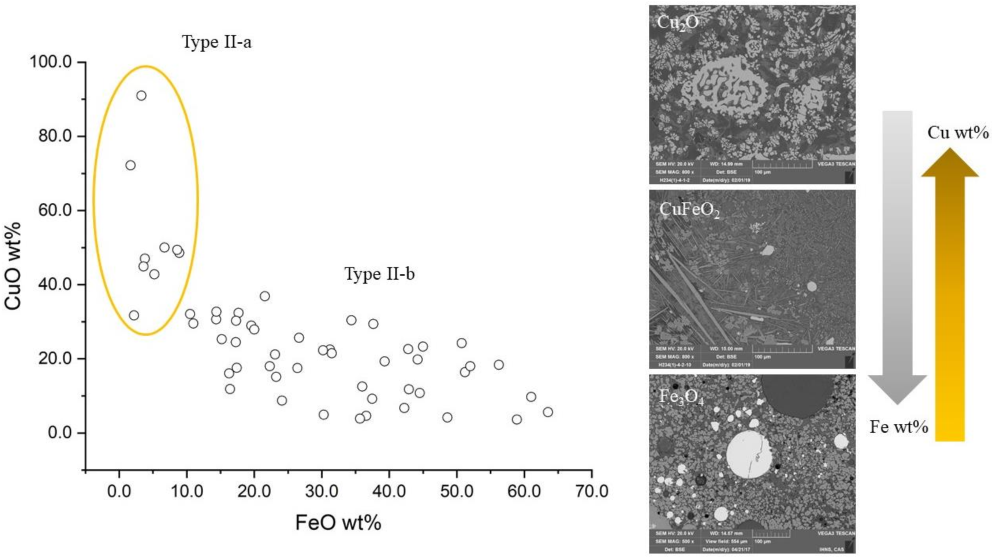

Figure 8 Chemical and mineralogical composition of Type II slag samples. Their typical microstructure changes along with Fe and Cu content. Type II-a slag are rich in Cu but poor in Fe. Type II-b slag are rich in Fe.

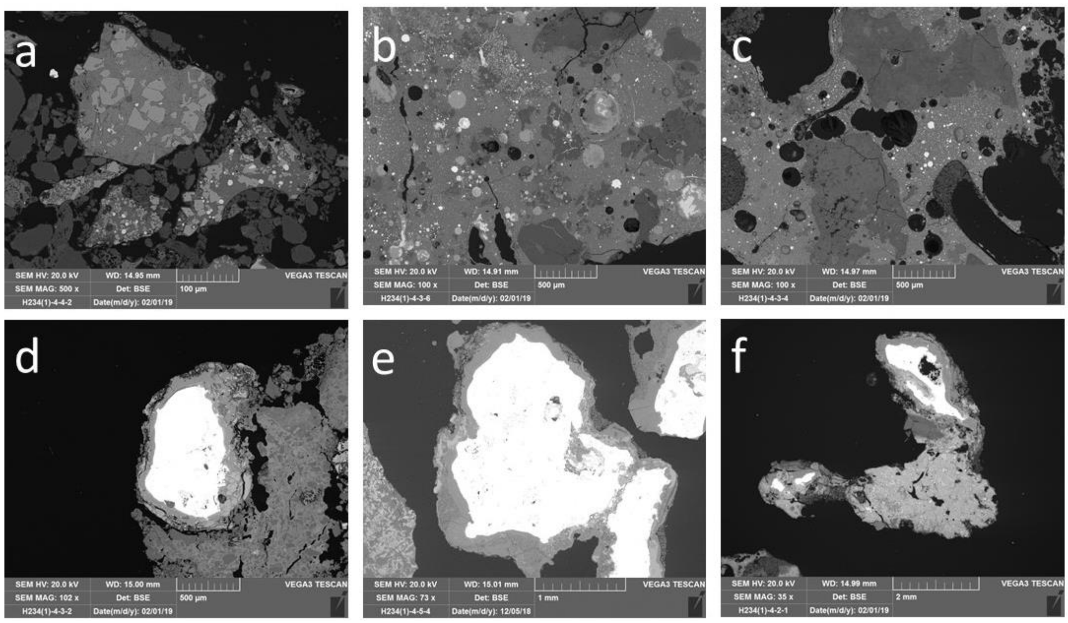

Figure 9 Micrographs of Type II slag. a: slag fragments with angular magnetite crystals. b, c: relatively large slag fragments containing unreacted quartz particles. d, e, f: metallic prills embedded in Type II slag.

Metallic prills embedded in Type II slag are all identified as non-alloyed copper with a few percent of Fe as impurity (average 1.5 wt%, see Table S3 for full dataset). The relatively large (>500 μm) metal prills usually have an irregular shape and are generally Fe free. They have the typical Cu-Cu_2O eutectic structure of pure copper and are either free-standing or combined with slag pieces (Figure 9).

3.2. Metallurgical remains from other contexts

Apart from H234, slag, dross, metal fragments and technical ceramics dated to the same period were also recovered from the foundation of building F12, F14 and F18, the ash pits located all over the mound, and the sediment in the moat surrounding the mound. Most of these samples are significantly larger than those found in H234. Wet-sieved soil samples did not reveal micro-slag fragments like those from H234① from any of these contexts in a considerable quantity. Nineteen slag and crucible/furnace lining samples, and five metal artefacts/fragment samples were selected for analysis (Table S3, Table S4). Fifteen of the slag samples contain abundant tin oxide crystals and tin bronze prills. The technical ceramic sample H291:3-2 does not have developed slag lining but the bronze prills trapped in its interior surface indicate it was associated with tin bronze processing. The other four samples have high CuO content (15-57 wt%) but no Sn. One slag sample recovered from the foundation of building F18 (F18JC:5) shows significant FeO content (18.8 wt%) and bears many iron-rich phases such as rounded wüstite and angular magnetite (Figure 10:e). The remaining three samples are all rich in CuO and relatively poor in FeO (<10 wt%), similar to Type II-a slag from H234①. Five artefacts including one arrow head (F15JC:1) and four metal fragments (H291:1, G1③:3-2, H323:2) were found to be tin bronze (Sn 4.5-19.0 wt%) and only the H321:4 bronze fragment contains 3.6 wt% Pb. All five samples have an as-cast metallographic structure and show no signs of hot or cold working.

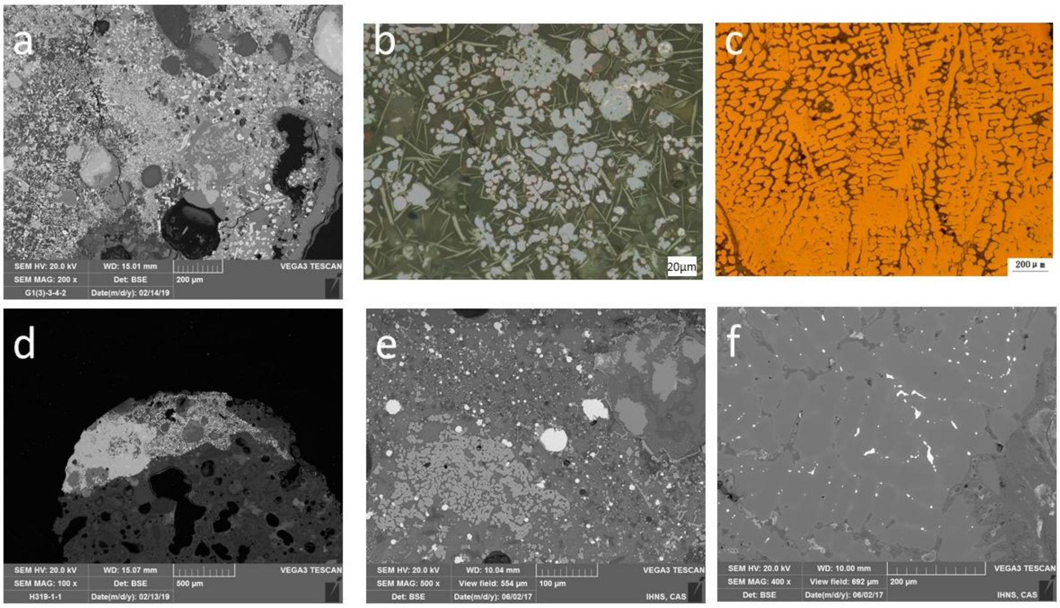

Figure 10 Micrographs of samples from contexts other than H234. a: much tin oxide in slag matrix of G1③:4. b: matrix of H311②:1. Needle-like crystals are delafossite while pale rounded ones are cuprite. c: as-cast metallographic structure of bronze fragment H291:2. d: slag lining of H319:1. e: F18JC:5 slag matrix with much wüstite, magnetite and pure copper prills in it. f: BSE image of H321:4. Lead particles in as-cast bronze structure.

The scatter plot of Figure 11 shows the comparison between slag of H234① and other contexts. A general observation is that samples from these contexts have lower FeO content than those from H234①.The Sn-bearing slag from these contexts have similar SnO_2 content but the relatively iron-rich ones found in H234① (indicated by dashed oval in Figure 11) were not identified elsewhere. Apart from F18JC:5, the Sn-free slag fragments of these contexts also have relatively low FeO content, corresponding to Type II-a slag of H234①. F18JC:5 shows similar chemical and mineralogical compositions to the Type II-b slag of H234①.

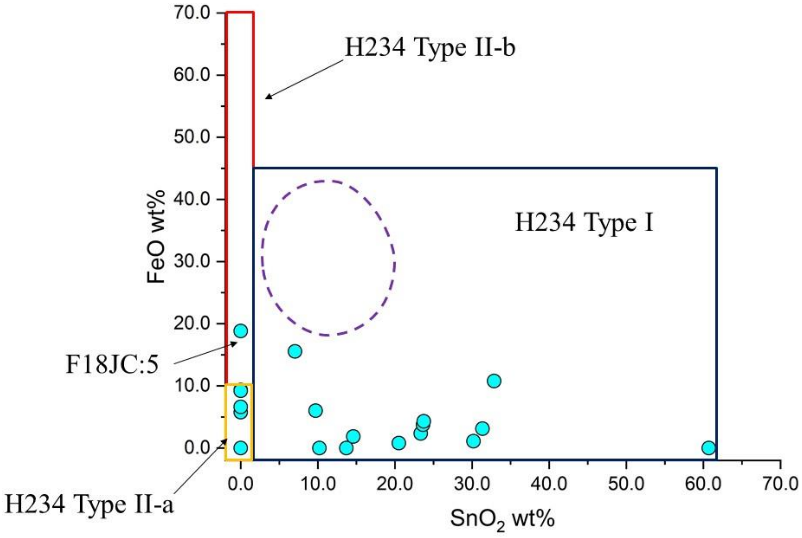

Figure 11 Chemical composition of slag samples from other contexts. The compositional range of H234 Type I and Type II slags are indicated with blue and red / yellow rectangles, respectively.

4. Discussion

4.1. The metallurgical nature of Taijiasi slag

The three main metallurgical processes in an ancient bronze casting workshop are alloying/casting, copper melting, and copper refining, particularly for the removal of iron from raw copper, while copper smelting could also be conducted at certain contexts. The tin-rich Type I slag can be safely associated with the bronze alloying/casting process. The extraordinarily high-tin prills indicate that metallic tin or tin oxide was freshly added to the melt. The interpretation of the Type II slag and prills is more complicated since copper melting, smelting and refining processes can all generate iron- and copper-rich slag free from alloying elements. During melting, metallic copper can turn into cuprite due to poorly controlled redox conditions, and form delafossite if the metal contained iron, as often is the case for raw copper. It is argued the relatively copper-rich but iron-poor slag fragments found in both H234① (Type II-a) and other contexts were more likely associated with copper melting practice. The pure copper fragment found in H234① (H234①:5) was likely the outcome of such an operation and lost during the remelting/alloying process.

A refining process in which iron and other impurities in copper were oxidized would generate slag with much iron oxide (e.g. magnetite, wüstite) as well as some copper oxides, differentiating them from melting and alloying slags (Craddock, 1995, 203). However, in a Chalcolithic/Early Bronze Age context, copper smelting slag could also bear similar features of high copper content and mixed copper and iron oxides, due to locally highly varied redox conditions in a crucible or primitive furnace (Müller, et al., 2004, Burger, et al., 2010, Radivojevic, et al., 2010, Rehren, et al., 2016).

For the case of Taijiasi, it is less plausible if not impossible that primary smelting was conducted. A few relatively large scale copper smelting workshops of the Shang period have been identified in the Zhongtiao Mountain (Li, 2011), the Guanzhong Plains (Chen, et al., 2017), and the middle range of the Yangtze River Valley (Cui and Liu, 2017). Geographically, all these sites are located relatively close to major copper ore deposits. The analyses of their smelting slag show a copper content generally lower than 10 wt% (Li, 2011; Zou et al. in preparation, Zou, 2020). Given that copper smelting workshops had been established close to the mines, it makes little sense that ores were also brought to somewhere 200-300 km away for smelting.

Instead, a major part of Type II-b slag could be associated with refining. Three fourths of them have a copper content (combined metallic copper and copper oxide) higher than 10 wt% with an average of 20 wt% total copper reported as CuO. The elevated copper content serves as an indicator of refining since in such a less-controlled oxidizing process iron and copper can both turn into oxides (Tylecote, et al., 1977). Copper refining had previously been identified in workshops at Zhouyuan dated to the Western Zhou period (11^{th}-8^{th} century BC), based on the analyses of slag and raw copper found at the bronze foundries (Zhou, et al., 2009). The raw copper from those sites contains up to 9 wt% Fe and the refining slag is dominated by iron oxides and fayalite. Currently available analytical results of Shang period slag show no evidence of refining (Liang, et al., 2005, Huang, et al., 2011, Zhou, et al., 2015, Li, et al., 2018), even though analyses of bronze artefacts from the Late Shang period capital in Anyang have shown a trend of increasing iron content over time (Zhao, 2004). The ongoing investigation of the Middle Shang period copper smelting slag from the site of Tongling in Ruichang, Jiangxi province shows a significant iron content in embedded copper prills (frequently over 4 wt%) (Zou, 2020). The iron-rich raw copper therefore might have needed to be refined before alloying and casting.

About one-fourth of Type II-b slag fragments have a copper content of less than 10 wt%.

They could certainly be a product of varied redox conditions inside the refining vessel. An alternative scenario is, however, also worth consideration. The recent investigation of the Middle Shang Tongling site revealed a significant amount of mechanically crushed smelting slag fragments (c. 0.5-1 cm in diameter), which are quite heterogeneous and typically rich in magnetite (Figure 12) (Zou 2020; Zou et al. in preparation). Due to the chronological gap, the Tongling site would not have been the copper source of Taijiasi, but it might reveal the general features of Middle Shang copper smelting slag.

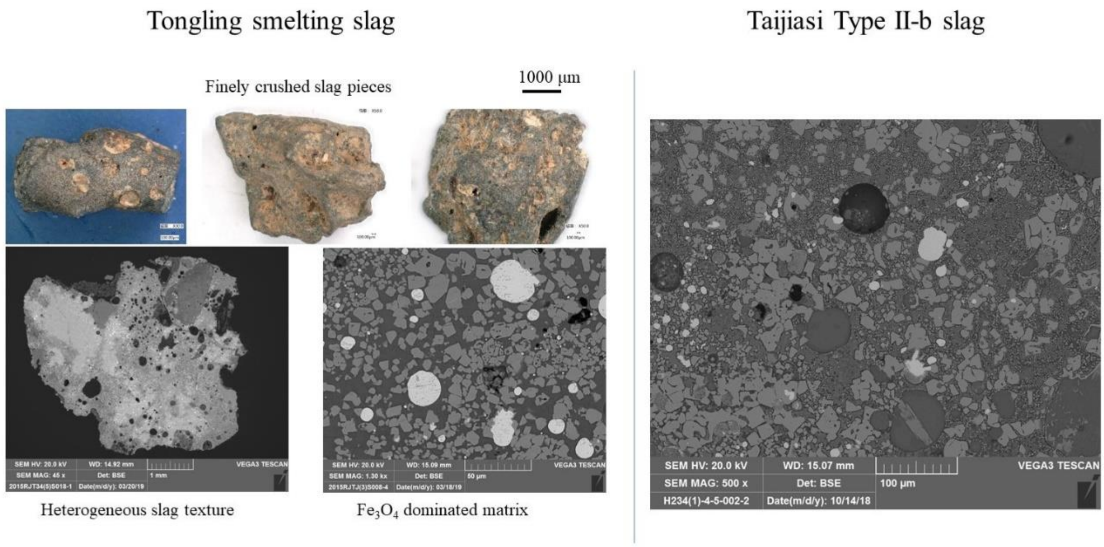

Figure 12 The comparison between Tongling and Taijiasi Type II-b slag. Their mineralogical compositions and heterogeneity are quite similar to each other.

The striking similarities between the Middle Shang smelting slag and Taijiasi Type II-b slag drive us to think that some Type II-b slag could also be derived from crushing of smelting slag (Figure 12). The heterogeneous nature of the smelting slag indicates it was quite viscous and could trap copper easily. A preliminary mechanical processing at the smelting sites might not be efficient enough in retrieving all copper prills, meanwhile leaving many copper lumps containing still some adhering slag crumbs. These slag-copper composite pieces could have been intentionally kept and shipped to the casting workshop for further cleaning and refining. It was important to avoid them entering alloying/casting crucibles since their slag part was difficult to melt (T>1200℃). The semi-solid slag fragments could cause metal loss or compromise casting (e.g. by jamming the mould sprue). These composite fragments thus needed to be first crushed, sorted, and even occasionally re-melted, leaving remains mineralogically similar to smelting slag.

The copper processing activities at the site of Taijiasi are summarized as Figure 13. The original materials could be iron-rich raw copper as well as a slag-copper composite from a remote smelting site, and were refined at Taijiasi to relatively pure copper. The pure copper was then mixed with fresh tin/tin oxide to make bronze and cast artefacts including ritual vessels, weapons and many other items.

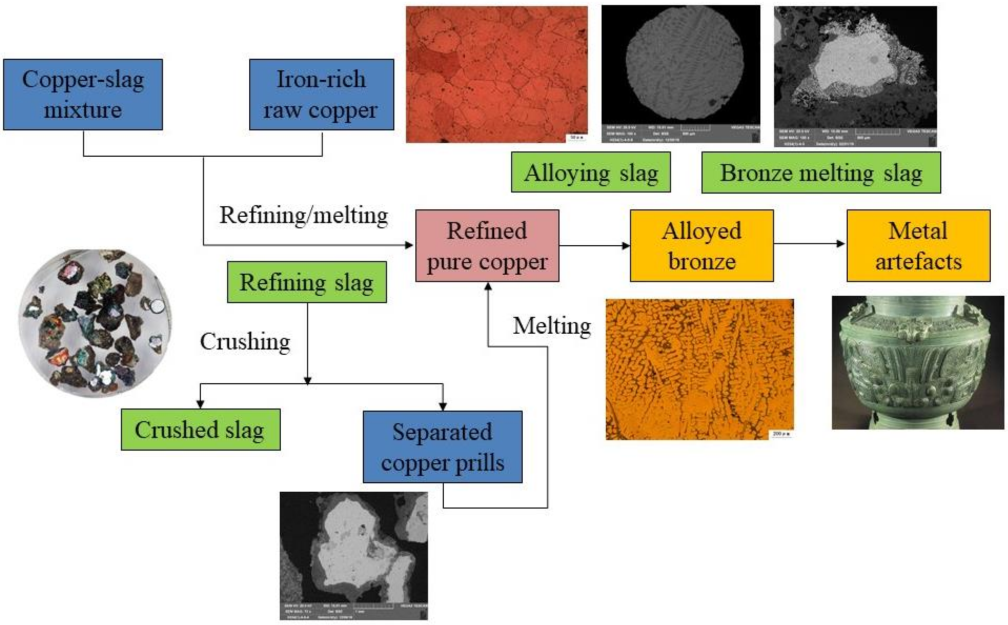

Figure 13 The reconstructed metallurgical *Chaîne opératoire* at the site of Taijiasi.

5. New perspectives in the study of Shang metallurgy

The micro-slag analysis does not only reveal the raw copper processing practices at Taijiasi, but also indicated that most related slag remains were carefully collected and crushed before being discarded within H234. It suggests that all activities of handling raw copper were constrained to a single place, and all related slag was re-processed as much as possible until down to quite fine fragments. In contrast, bronze alloying/casting slag was commonly found in all areas of the site and apart from those in H234, they were discarded without much reprocessing, as indicated by their size which is usually larger than 1 cm in diameter. The presence of relatively iron-rich alloying/casting slag mostly in H234① strengthens this point. It indicates that iron-rich raw copper was only available in H234 and could occasionally be alloyed with tin without much refining. In other contexts, the copper used for making alloy had all been refined, most likely at H234. The location of H234 suggests it was probably under close supervision by people from the major buildings on the platform. The unalloyed copper is thus argued to be a strategic resource for the elite of this site and was not allowed to be accessed unsupervised. The alloying/casting slag, though rich in copper as well, was not collected for crushing, probably because the copper in them was mainly present in oxide form, making it much less accessible by physically processing. They were dumped with much less care and were more likely to be re-distributed to a much wider area of the site via secondary disturbances.

The question then arises whether workers from other Shang period sites conducted similar practices, or was what we saw at Taijiasi a local tradition of people living in the Huaihe River Valley. This is arguably an important new facet of investigation since it reflects people's varied attitudes to copper. Most likely, people who had better and easier access to copper resources would be less careful in terms of slag processing. So far, published analytical results of other Shang period metal workshops did not show evidence for copper refining and slag crushing practice. However, these were from privileged Central Plain sites, and since micro-slag samples were never actively collected from these sites, it is not yet possible to reach any meaningful conclusion regarding their management of this resource. More controlled excavations with careful sampling of micro-remains are much needed in future excavations of these sites.

Another important perspective is the provenancing of copper used during the Shang period. There have been decades of discussions surrounding the geological origin of copper, tin and lead in the Shang period (Jin, et al., 2017, Liu, et al., 2018a, Liu, et al., 2018b, Chen, et al., 2019 and references therein). Most previous discussions were based on elemental pattern and lead isotope ratios of finished artefacts, which contained a mixture of copper, lead and tin from various sources which would obviously render it more difficult pinpointing origins for each specific metal. Copper ingots were rarely found in Shang contexts and only a few of them have been analysed (Han and Ko, 2007, 221). Until now, though a number of Shang period copper mining and smelting sites have been identified, the geological origin(s) of much of the copper for Shang bronze is still not clear. While these copper mines mainly bear ores with common lead isotopic signatures ($^{206}Pb/^{204}Pb<20$), their signature had been largely masked in artefacts containing highly radiogenic lead (Liu, et al., 2018b). The identification of refining slag at

Taijiasi offers a new hope to provenancing Shang copper, since the copper in the Type II slag was not yet alloyed and likely still preserves the geochemical features of its geological origin. Thus, these micro-slags are the best proxy in the Shang archaeological context for tracing the source(s) of copper supply. It is expected that in due course more refining slag will be identified in other Shang period bronze casting foundries, and cross-comparison of their isotopic data should shed new light on the discussion about the source and distribution network of copper in the Shang period.

5.1 Invisible copper processing activities

The detailed study of micro-slag from Taijiasi does not only enhance our understanding about Shang period metallurgy but also demonstrated the importance of micro-artefacts in the study of an ancient metallurgical workshop. Indeed, it has become common practice to carefully searching for hammer scale (iron oxide) with a magnet when excavating iron smithing workshops (e.g. Veldhuijzen and Rehren, 2007, Birch, et al., 2015, Lam, et al., 2018). However, a similar detailed sampling strategy has not yet been employed in the excavation of copper casting workshops. Commonly, lab-based researchers conducted their sampling on the metallurgical remains collected by excavators. These remains are typically large (>1cm in length/diameter) and bear metal corrosion or highly vitrified slaggy parts, making them readily identifiable in the field. However, considering the high value of copper, mechanical processing of copper smelting and refining/melting slag could arguably have been a common behaviour among early metallurgists. Without a careful excavation strategy, the potentially rich information retained in these micro-artefacts would have been lost.

The combination of pXRF survey, wet-sieving of soil samples and lab-based analysis has been shown to be an effective method for investigating a bronze casting workshop. Geochemical survey with pXRF can help excavators quickly locate interesting areas and loci based on their abnormally high concentration of copper, and has been utilized in many excavations of metallurgical workshops (Cook, et al., 2005, Cook, et al., 2010, Eliyahu-Behar, et al., 2012, Carey, et al., 2014) and even landscapes (e.g. Hanks, et al., 2015). However, little attention had been paid to the specific causes of these high readings. Various types of remains including ore and its tailings, slag, crucible lining, bronze prills, and corroding artefact fragments could cause elevated copper content in soil. Identifying these different sources via detailed analyses could lead to quite different archaeometallurgical interpretations. Therefore, it is important in future excavations to collect copper-rich soil samples and study micro-artefacts in them, which would not only enhance our understanding about the metallurgical activities at workshop themselves but also provide a new facet for cross-comparative studies among varied workshops.

Acknowledgements

We owe a lot of thanks to students and colleagues who participated in the field excavation of Taijiasi and the micro-slag sampling. We would like to particularly thank Professor Chen Bingbai of Wuhan University, the PI of the Taijiasi project. We thank Mr. Yan Bichen for conducting FTIR analyses of soil samples. We appreciate the precious advice from and discussion with Professor Lei Xingshan of Peking University and Professors Qian Wei and Chen Kunlong of USTB. This research is supported by the National Natural Science Foundation of China (No. 51704023, 51850410507), the National Social Science Foundation of China (No. 17ZDA178) and Fundamental Research Funds for the Central Universities (No. FRF-DF-19-007, No. FRF-TP-18-033A2).

References

Berna, F., Behar, A., Shahack-Gross, R., Berg, J., Boaretto, E., Gilboa, A., Sharon, I., Shalev, S., Shilstein, S., Yahalom-Mack, N., Zorn, J.R., Weiner, S., 2007. Sediments exposed to high temperatures: reconstructing pyrotechnological processes in Late Bronze and Iron Age Strata at Tel Dor (Israel), Journal of Archaeological Science 34, 358-373.

Birch, T., Scholger, R., Walach, G., Stremke, F., Cech, B., 2015. Finding the invisible smelt: using experimental archaeology to critically evaluate fieldwork methods applied to bloomery iron production remains, Archaeological and Anthropological Science 7, 73-87.

Bourgarit, D., 2007. Chalcolithic copper smelting, in: La Niece, S., Hook, D., Craddock, P.T. (Eds.), Metals and Mines: Studies in Archaeometallurgy, Archetype Publications, London, pp. 3-14.

Burger, E., Bourgarit, D., Wattiaux, A., Fialin, M., 2010. The reconstruction of the first copper-smelting processes in Europe during the 4th and the 3rd millennium BC: where does the oxygen come from?, Applied Physics A 100, 713-724.

Carey, C.J., Wickstead, H.J., Juleff, G., Anderson, J.C., Barber, M.J., 2014. Geochemical survey and metalworking: analysis of chemical residues derived from experimental non-ferrous metallurgical process in a reconstructed roundhouse, Journal of Archaeological Science 49, 383-397.

Chen, K., Liu, S., Li, Y., Mei, J., Shao, A., Yue, L., 2017. Evidence of arsenical copper smelting in Bronze Age China: A study of metallurgical slag from the Laoniupo site, central Shaanxi, Journal of Archaeological Science 82, 31-39.

Chen, K., Mei, J., Rehren, Th., Liu, S., Yang, W., Martinón-Torres, M., Zhao, C., Hirao, Y., Chen, J., Liu, Y., 2019. Hanzhong bronzes and highly radiogenic lead in Shang period China, Journal of Archaeological Science 101, 131-139.

Cook, S.R., Clarke, A.S., M.G., F., 2005. Soil geochemistry and detection of early Roman precious metal and copper alloy working at the Roman town of Calleva Atrebatum (Silchester, Hampshire, UK), Journal of Archaeological Science 32, 805-812.

Cook, S.R., Banerjea, R.Y., Marshall, L.-J., Fulford, M., Clarke, A., van Zwieten, C., 2010. Concentrations of copper, zinc and lead as indicators of hearth usage at the Roman town of Calleva Atrebatum (Silchester, Hampshire, UK), Journal of Archaeological Science 37, 871-879.

Craddock, P.T., 1995. Early Metal Mining and Production, Edinburgh University Press, Edingburgh.

Craddock, P.T., 2000. From hearth to furnace: Evidences for the earliest metal smelting technologies in the eastern Mediterranean, Paléorient 26, 151-165.

Cui, T., Liu, W., 2017. The new finds and research on the Tongling copper mining and smelting site in Ruichang, Jiangxi (江西瑞昌铜岭铜矿遗址新发现与初步研究), Cultural Relics from South (南方文物) 4, 57-63 (in Chinese).

Eliyahu-Behar, A., Yahalom-Mack, N., Shilstein, S., Zukerman, A., Shafer-Elliott, C., Maeir, A.M., Boaretto, E., Finkelstein, I., Weiner, S., 2012. Iron and bronze production in Iron Age IIA Philistia: new evidence from Tell es-Safi/Gath, Israel, Journal of Archaeological Science 39, 255-267.

Epstein, S.M., 1993. Cultural choice and technological consequences: Constraint of innovation in the late prehistoric copper smelting industry of Cerro Huaringa, Peru, Unpublished PhD Thesis, University of Pensylvania

Ge, J., 1959. Finding of Yin-Shang period bronze artefacts at Funan, Anhui province (安徽阜南发现殷商时代的青铜器), Cultural Relics (文物), 2 (in Chinese).

Golden, J., Levy, T.E., Hauptmann, A., 2001. Recent discoveries concerning Chalcolithic metallurgy at Shiqmim, Israel, Journal of Archaeological Science 28, 951-963.

Han, R., Ko, T., 2007. History of Science and Technology: Mining and Metallurgy (中国科学技术史•矿冶卷), Science Press (科学出版社) (in Chinese).

Hanks, B., Doonan, R.C.P., Pitman, D., Kupriyanova, E., Zdanovich, D., 2015. Eventful Deaths – Eventful Lives? Bronze Age Mortuary Practices in the Late Prehistoric Eurasian Steppes of Central Russia (2100-1500 BC), in: Renfrew, C., Boyd, M., Morley, I. (Eds.), Death Rituals, Social Order and the Archaeology of Immortality in the Ancient World, Cambridge University Press, Cambridge, pp. 328-347.

Hauptmann, A., 2014. The investigation of archaeometallurgical slag, in: Roberts, B.W., Thornton, C.P. (Eds.), Archaeometallurgy in Global Perspective, Springer, New York, Heidelberg, Dordrecht, London, pp. 91-105.

He, X., Gong, X., 2018. The excavation report of the Taijiasi site at Funan county, Anhui province (安徽阜南县台家寺遗址发掘简报), Archaeology (考古), 3-13 (in Chinese).

Huang, J., Wei, G., Song, G., Li, S., Wang, C., 2011. Analyses on remains of smelting and casting copper at Xiaoshuangqiao site (小双桥遗址出土冶铸遗物的科技分析), Nonferrous Metal (有色金属) 63, 147-152 (in Chinese).

Jin, Z.Y., Liu, R., Rawson, J., Pollard, A.M., 2017. Revisiting lead isotope data in Shang and Western Zhou bronzes, Antiquity 91, 1574-1587.

Lam, W., Chen, J., Chong, J., Lei, X., Tam, W.L., 2018. An iron production and exchange system at the center of the Western Han Empire: Scientific study of iron products and manufacturing remains from the Taicheng site complex, Journal of Archaeological Science 100, 88-101.

Li, J., 2011. Investigation and study on early copper mining and smelting sites in the south of Shanxi province, central China (晋南早期铜矿冶遗址考察研究), Unpublished PhD Thesis, University of Science and Technology Beijing (in Chinese)

Li, J., Li, Y., Tian, J., 2018. The study of metallurgical remains from the site of Dongxiafeng (东下冯遗址冶铸遗存研究), Archaeology and Cultural Relics (考古与文物), 116-123 (in Chinese).

Liang, H., Li, Y., Sun, S., Tong, W., 2005. Analyses on As-containing slag unearthed from Shang Dynasty city site in Yuanqu country of Shanxi China (垣曲商城出土含砷渣块研究), Nonferrous metals (有色金属) 57, 127-130 (in Chinese).

Liu, R., Rawson, J., Pollard, A.M., 2018. Beyond ritual bronzes: identifying multiple sources of highly radiogenic lead across Chinese history, Sci Rep 8, 11770.

Liu, S., Rehren, Th., Pernicka, E., Hausleiter, A., 2015. Copper processing in the oases of northwest Arabia: technology, alloys and provenance, Journal of Archaeological Science 53, 492-503.

Liu, S., Chen, K.L., Rehren, Th., Mei, J.J., Chen, J.L., Liu, Y., Killick, D., 2018b. Did China Import Metals from Africa in the Bronze Age?, Archaeometry 60, 105-117.

Monnier, G.F., 2018. A review of infrared spectroscopy in microarchaeology: Methods, applications, and recent trends, Journal of Archaeological Science: Reports 18, 806-823.

Montero-Ruiz, I., 1993. Bronze Age metallurgy in southeast Spain, Antiquity 67, 46-57.

Müller, R., Rehren, Th., Rovira, S., 2004. Almizaraque and the Early Copper Metallurgy of Southeast Spain: New Data, Madrider Mitteilungen 45, 33-56.

Murillo-Barroso, M., Martinón-Torres, M., Massieu, D.C., Socas, D.M., González, F.M., 2017. Early metallurgy in SE Iberia. The workshop of Las Pilas (Mojácar, Almería, Spain), Archaeol Anthropol Sci 9, 1539-1569.

O'Brien, W., 2004. Ross Island. Mining, Metal and Society in Early Ireland, National University of Ireland, Galway.

Rademakers, F.W., Rehren, Th., 2016. Seeing the forest for the trees: Assessing technological variability in ancient metallurgical crucible assemblages, Journal of Archaeological Science: Reports 7, 588-596.

Rademakers, F.W., Farci, C., 2018. Reconstructing bronze production technology from ancient crucible slag: experimental perspectives on tin oxide identification, Journal of Archaeological Science: Reports 18, 343-355.

Radivojevic, M., Rehren, Th., Pernicka, E., Sljivar, D., Brauns, M., 2010. On the origins of extractive metallurgy: new evidence from Europe, Journal of Archaeological Science 37, 2775-2787.

Rehren, Th., 2003. Crucibles as reaction vessels in ancient metallurgy, in: Craddock, P.T., Lang, J. (Eds.), Mining and Metal Production through the Ages, Archetype, London, pp. 207-215.

Rehren, Th., Leshtakov, P., Penkova, P., 2016. Reconstructing Chalcolithic copper smelting at Akladi cheiri, Chernomorets, Bulgaria, in: Nikolov, V., Schier, W. (Eds.), Der Schwarzmeerraum vom Neolithikum bis in die Früheisenzeit (6000-600 v.Chr.), Leidorf, Rhaden/Westfalen, pp. 205-214.

Rovira, S., 2002. Early slags and smelting by-products of copper metallurgy in Spain, in: Bartelheim, M., Pernicka, E., Krause, R. (Eds.), The Beginnings of Metallurgy in the Old World, Verlag Marie Leidorf Rahden, Westf, pp. 83-98.

Shugar, A.N., 2003. Reconstructing the Chalcolithic metallurgical process at Abu Matar, Israel, in: Proceedings of Archaeometallurgy in Europe I, Milano, pp. 449-458.

Tylecote, R.F., Ghaznavi, H.A., Boydell, P.J., 1977. Partitioning of trace elements between the ores, fluxes, slags and metal during the smelting of copper, Journal of Archaeological Science 4, 305-333.

Veldhuijzen, H.A., Rehren, Th., 2007. Slags and the city: early iron production at Tell Hammeh, Jordan and Tel Beth-Shemesh, Israel, in: La Niece, S., Hook, D., Craddock, P.T. (Eds.), Metals and Mines:

Studies in Archaeometallurgy, Archetype Publications, London, pp. 189–201.

Zhao, C., 2004. Chemical analysis of bronze artefacts unearthed in Yinxu, Anyang (安阳殷墟出土青铜器的化学), Collected Papers on Archaeology (考古学集刊) 15, 243-268 (in Chinese).

Zhou, W., Chen, J., Lei, X., Xu, T., Chong, J., Wang, Z., 2009. Three Western Zhou bronze foundry sites in the Zhouyuan area, Shaanxi province, China, in: Mei, J., Rehren, Th. (Eds.), Metallurgy and Civilisation: Eurasia and Beyond, Archetype, London, pp. 62-72.

Zhou, W., Liu, Y., Yue, Z., 2015. Scientific study on two types of copper processing containers from the Xiaomintun site in Anyang (安阳殷墟孝民屯出土两类熔铜器具的科学研究), Cultural Relics from South (南方文物), 48-57 (in Chinese).

Zou, G., 2020. Archaeometallurgical Investigation of the Tongling Site at Ruichang in Jiangxi Province (江西瑞昌铜铃遗址商代冶金考古综合性研究),Unpublished PhD Thesis, University of Science and Technology Beijing (in Chinese)