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Beyond linear narratives: Complex copper ore exploitation strategies in Early Bronze Age China revealed by geochemical characterization of smelting remains

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ABSTRACT

Despite decades of efforts to reconstruct the bronze production and metal distribution systems of the Shang period in Bronze Age China, there remains limited understanding of the ore choices and smelting practices of the Shang people. This study addresses this research gap by conducting a detailed investigation of Shang period copper ores and smelting remains uncovered at the Tongling site in the Middle Yangtze River valley. The results of lead isotope, copper isotope, trace element, and rare earth element (REE) pattern help to classify the slags from this site into two groups, associated with smelting sulphidic (Group A) and oxidic (Group B) copper ores, respectively. This finding not only serves as the first physical evidence of the use of sulphidic copper ores in Early Bronze Age China but also provides pivotal details of the copper resource exploitation strategies of the Shang people. It challenges the traditional narrative that the Shang people moved to this area solely for the high-grade supergene deposits. The parallel use of both supergene and hypogene ores at the same site complicates the notion of a linear, technological evolution from simpler to more advanced copper sources. Despite the presence of hypogene ores, the study reveals that the Shang people maintained labour-intensive smelting practices, including crushing slag to recover trapped metallic prills, to meet the demands of large-scale bronze casting. This nuanced approach to copper resource exploitation reflects a complex, context-dependent strategy rather than a technological revolution. By highlighting these intricate metallurgical choices, this research contributes to a broader rethinking of early technological development, underscoring the diversity and adaptability of ancient craft industries and their role in shaping Shang society.

1. Introduction

The massive collection of bronze ritual vessels dated to the Shang period (16th-11th century BC, Table 1) represents a distinctive cultural characteristic of Bronze Age China (Bagley, 1999; Campbell, 2014). The Shang kingdom was built upon the domination of ceremonial rites, where bronze ritual vessels played a central role (Chang, 1986). A complex ritual practice emerged, involving combination of vessels with different functions, which were also used in sets as tomb objects to indicate the social status of their owners (Fig. 1b). The richest undisturbed Shang tomb found so far is that of *Fuhao* (a consort of the late 13th century BC King *Wuding*) in Anyang, which revealed 465 bronze artefacts with a total weight of more than 10 tons, demonstrating a massive bronze production industry in this period (Institute of Archaeology in Chinese Academy of Social Science, 1980). A range of other tombs and storage/sacrificial pits within and beyond the capital areas revealed similar finds with hundreds of ritual bronzes deposited in individual contexts (Sichuan Provincial Institute of Cultural Heritage and Archaeology, 1999; Jiangxi Provincial Museum et al., 1997). These bronzes weighing in tons could never be re-used or recycled and demonstrated the abundant metal supply for Shang people. One should also be reminded that the most magnificent tombs of the Shang period,

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Table 1
Chronological table of the Shang period.

Period	Period in Chinese Literatures	Capital site in the Central Plain	Date
Early Shang	Erligang Culture	Zhengzhou Shang City	c. 1540-1400 BC
Middle Shang	Baijiazhuang Huanbei (Huayuanzhuang) Culture	Xiaoshuangqiao Huanbei Shang City	c. 1400-1250 BC
Late Shang	Yinxu Culture	Yinxu/Anyang	c. 1250-1050 BC

the royal tombs at Xibeigang in Anyang, have been mostly looted and it is therefore not possible to reconstruct the full repertoire of Shang Kings' burial objects (Chang, 1980). However, their size towering over all aforementioned tombs and sacrificial pits makes one speculate that many more ritual bronzes had been deposited in them. Accordingly, a large number of publications have focused on the development of Shang-style bronze vessels and their reflection on the evolution of Shang ritual practices and regional interactions (Bagley, 1987; Liu, 2015; Liu et al., 2019; R. Liu et al., 2020a; Loehr, 1968; Mei et al., 2015; Zhang, 2004; Zhang et al., 2010).

These artefacts apparently indicate a massive scale bronze industry during the Shang period. Remains from bronze casting workshops, e.g. moulds, crucibles and slags, also received increasingly more scholarly

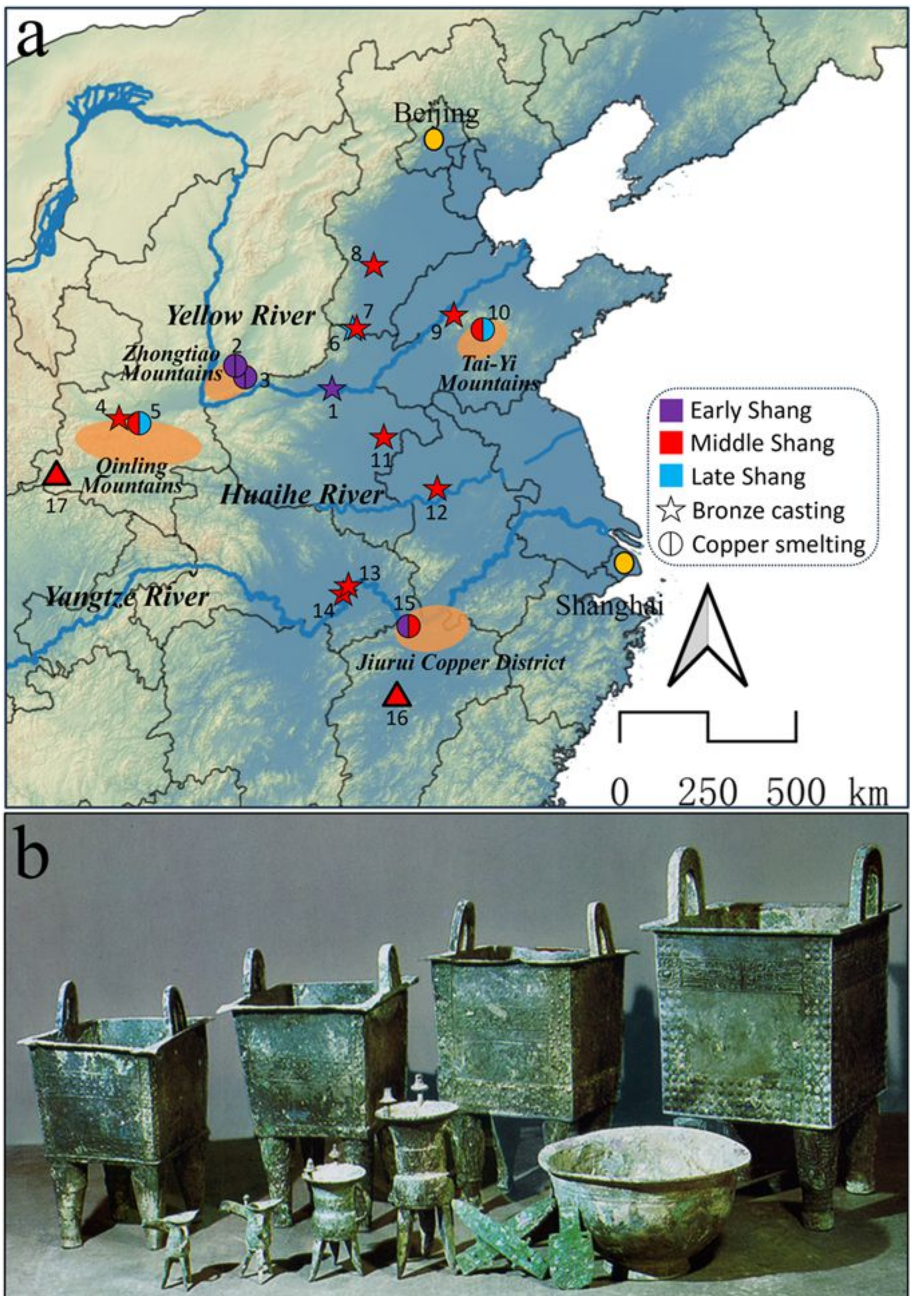

Fig. 1. a: Map of the copper smelting and bronze casting sites dated to the Shang period. The location of Tongling is marked with the number 15. 1-Zhengzhou Shang City, 2-Xiwubi, 3-Yuanqu Shang City, 4-Laoniupo, 5-Huanzhenfang, 6-Yinxu, 7-Huanbei Shang City, 8-Buyao, 9-Daxinzhuang, 10-Yingcheng, 11-Mengzhuang, 12-Taijiasi, 13-Guoyuanzui, 14-Xiaozui (Panlongcheng), 15-Tongling, 16-Dayangzhou, 17-Longtou (Hanzhong). b: The assemblage of bronze ritual vessels found at the Nanshunchengjie storage/sacrificial pit of the Zhengzhou Shang City (Henan Provincial Institute of Cultural Heritage and Archaeology, 2001).

attention as it has been proven to be a rich source of information for discussions concerning bronze processing and casting technology (S. Liu et al., 2020b; Liu, 2009; Sun et al., 2022, 2023a) and the provenance of metals (Sun et al., 2023b; He et al., 2024). However, until now, there has been little attention paid to the primary stage of this industry, namely mining and smelting activities. Shang period copper smelting sites have been identified in the Zhongtiao Mountain (Li, 2011; Dai et al., 2020), the Guanzhong Plains (Liu, 2002), and the middle range of the Yangtze River Valley (Cui and Liu, 2017; Liu and Lu, 1998) (Fig. 1a). However, their metallurgical remains have only been subjected to limited technical investigations. Li (2011) analysed copper smelting remains from the Zhongtiao Mountain dated to the Erligang period, and found sites in this area mostly produced pure copper. Chen et al. (2017) revealed evidence of arsenical copper production at the Laoniupo site in Guanzhong Plains through scientific analyses of metallurgical ceramics and slags. They proposed that complex ores consisting of arsenic-bearing minerals may have been used as the source of alloying element and smelted together with raw copper/high purity copper minerals to produce arsenical copper. Zhangsun et al. (2020) also examined copper smelting slags found at Laoniupo and Huaizhenfang in the Guanzhong Plains and proposed that pure copper and arsenical copper had been produced at these sites. Li et al. (2019) analysed copper smelting remains of the Late Shang period, and revealed that arsenical copper and tin bronze were produced together. Pang et al. (2024) recently reported a copper smelting workshop at Daye in the Middle Yangtze River valley potentially dated to the Late Shang period, which seems to produce copper as well as tin bronze at the same time. Apart from these preliminary characterizations which mainly confirm the existence of copper smelting

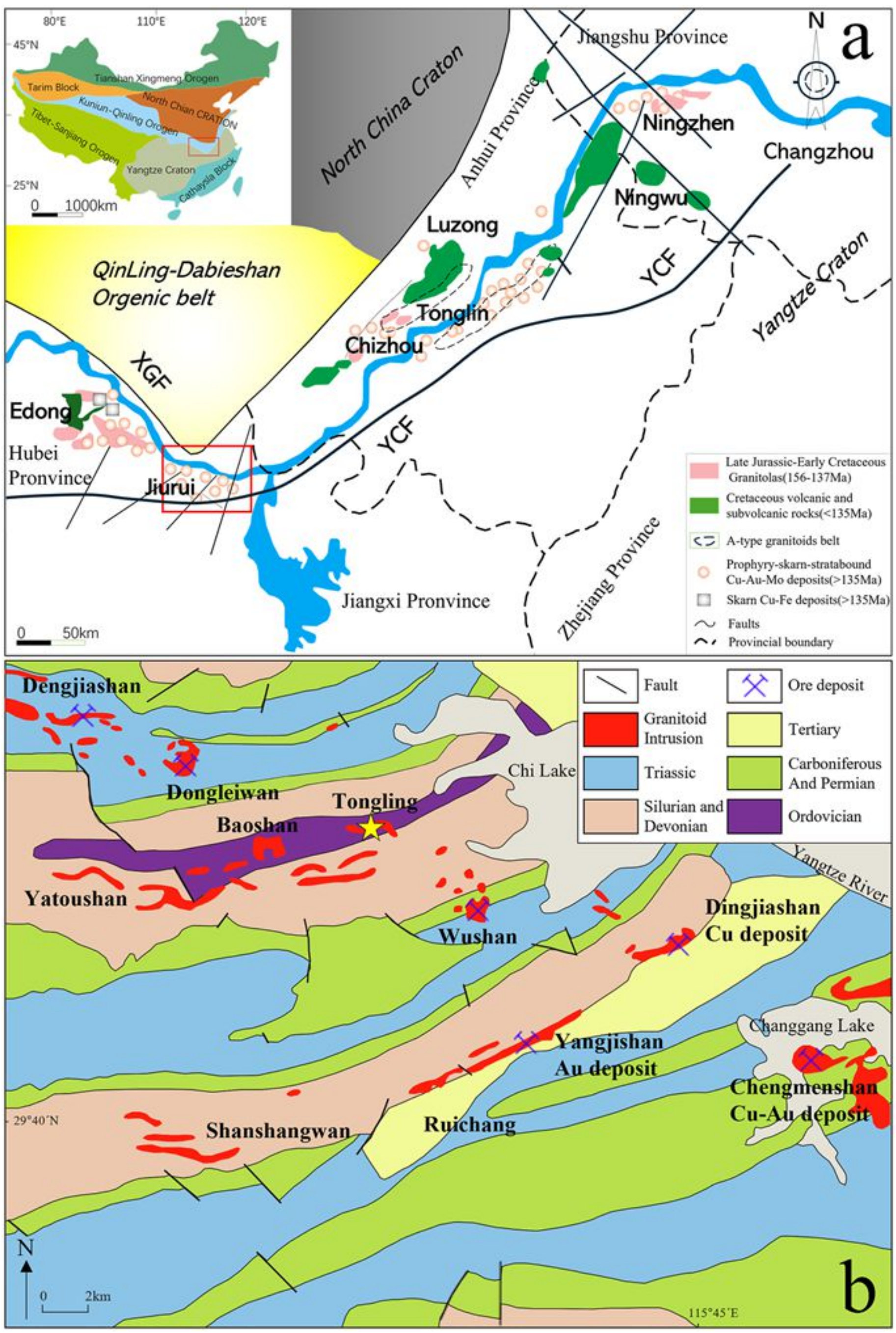

Fig. 2. Geological map of the Middle-Lower Yangtze River polymetallic belt (a) and the Jiurui metallogenic district (b) (After Wen et al., 2019).

activities at these sites, there is little in-depth discussion about ore choice and detailed metal production strategy of Shang people. There is still limited knowledge about the ore types, potential flux, smelting installations and post-smelting processing methods employed by the Shang people. It is unclear how the material basis for a magnificent bronze casting industry evidenced by the rich bronze vessel collections was provided.

This paper aims to address this research lacuna by presenting a detailed metallurgical and geochemical investigation on copper production remains from the site of Tongling in northwestern Jiangxi province, the most well-known copper production site in the Yangtze River valley established during the Early to Middle Shang period. The first excavation at Tongling was in the 1980s and revealed a splendid Middle Shang period copper mining site with well-preserved ancient mining shafts and beneficiation implements (Liu and Lu 1998). However, until recently, there was little understanding of copper smelting at this site. A new archaeological expedition (2014–2016) altered this situation and provided an important opportunity to gain insight into the technological features of copper smelting in the Yangtze River Valley (Cui and Liu 2017). This technological reconstruction also provides a new facet of the Shang metallurgical industry, different from the traditional impression of a large scale and highly centralized ritual vessel production system.

1.1. Geological context

The site of Tongling is located at the Jiujiang-Ruichang (Jiurui) metallogenic district, part of the Middle Yangtze River metallogenic belt (Fig. 2). The V-shaped Middle Yangtze River metallogenic belt is bounded by the Tanlu fault to its north and the Yangxin-Changzhou fault to its south, and regarded as one of the most important copper metallogenic belt in south China (Zhou et al., 2015). Copper mineralization in the Jiurui district mainly took place as responses to Yanshanian tectono-thermal events (148-138 Ma; Yang et al., 2011). Skarn-, strata bound- and porphyry-type deposits are identified in this district. The strata bound deposits are mainly hosted in Silurian sandstone and shale strata with orebodies having lateral extension of several hundreds, sometimes over two thousand meters (Qiu et al., 1989). The principal Cu-bearing ore minerals in strata bound deposits are chalcopyrite and bornite, with minor amounts of covellite and tennantite. It is also noticed that its supergene high-grade copper ores are widely developed and characterized by high arsenic concentrations (Qiu et al., 1989). The skarn-type mineralization was developed in alteration zones surrounding porphyritic granitoids. This type of deposits shares similar ore mineral assemblages with those of strata bound deposits, but is characterized by more common occurrence of coarser-grained sulphides. Typical gangue minerals of skarn-type deposits include grossular-andradite garnet, diopside and calcite (Qiu et al., 1989). Many lead isotope analyses have been carried on chalcopyrite, pyrite, galena and feldspar from several deposits in the Jiurui metallogenic belt, showing that minerals from various deposits are characterized by consistent and narrow ranges of lead isotope ratios, with $^{206}Pb/^{204}Pb$ ranging from 17.8 to 18.2, $^{207}Pb/^{204}Pb$ from 15.55 to 15.58, and $^{206}Pb/^{204}Pb$ from 38.0 to 38.4 (Hsu and Sabatini, 2019). This tight cluster of lead isotopic ratios shows that lead in these deposits likely originated from a homogeneous source (Qiu et al., 1989). The rare earth element (REE) patterns of ore-hosting porphyries in the Jiurui district are consistently characterized by enrichment in light rare earth elements (LREE) and depletion of heavy rare earth elements (HREE) (Zhou et al., 2015).

The most intensively studied copper deposit in this region is the Wushan deposit with both skarn and strata bound mineralization, located about 15 km to the east of Tongling (Wang, 1989; Wen et al., 2019). The skarn-type mineralization is spatial-temporarily related to a porphyritic granitoid intrusion dated at 146-145 Ma. Li et al. (2019) reported that chalcopyrite from ores hosted in skarn, limestone and dolomite have Cu isotopic values of $\delta^{65}Cu_{NIST\ SRM\text{-}976}$ ranging from −0.38 to 0.82 per mil with an average of 0.26 per mil. The limited characterization of ore deposits at Tongling shows that it was also formed around a granitoid intrusion during the Yanshanian event with hydrothermal strata bound ore deposits in a fracture belt and scattered skarn deposits in the contact zone (Wang, 1989). Near-surface remobilization of copper took place along fracture zones and led to formation of supergene copper ores characterized by mineral assemblage of limonite, haematite, pyrolusite, hollandite and malachite. In addition, Cu-bearing gossan also formed during weathering of primary copper ore bodies. It is speculated that the Bronze Age people chose these locations to set up a mine since gossans and soft clayish ores in fracture zones are relatively easy to mine (Liu and Lu, 1998).

1.2. Archaeological context

Tongling is currently the only known copper mining and smelting site in the Middle Yangtze River Valley that can be securely dated to the Early-Middle Shang period. The style of *li* (鬲) tripods and *Pen* (盆) vessels suggest that Tongling had a direct link with thePanlongcheng site in the Jianghan Plain (Cui and Liu, 2017) (Fig. 1a), which was strongly influenced by the Central Plain Shang culture (Bagley, 1977; Liu and Chen, 2012). The site of Tongling played a fundamental role in the network of Shang settlements in the Yangtze River valley and the Central Plain. The expansion of Shang culture to the south is normally associated with the exploration of rich copper sources in the Yangtze River metallogenic belt (Liu and Chen, 2000; Sun et al., 2023b) while Tongling was the major copper production center dominated by Shang people in the south. Despite its important social-economic status, little attention has been given to the metallurgical remains found at this site more than 30 years after its first identification. The archaeological expedition (2014–2016) finally unveiled a major Shang period smelting camp named Jiaotanchang site (焦碳厂) on the northern slope of the mine found in the 1980s (Fig. 3a). Though it has been severely disturbed by later human activities, abundant evidence of human occupation and metallurgical activities was still revealed from an area of approximately 20,000 m^2. More than 20 Shang period ash pits and a rammed earth platform were identified at this site (Fig. 3b) (Cui and Liu, 2017). Pottery typology dated this site to the Middle Shang period. Radiocarbon dating of charred seed samples anchor the site between 1500-1200 BC (Reimer et al., 2020), corresponding well to the pottery typology and covering the complete chronological span of the Middle Shang period (Fig. 4, Table 1, OSM Table S1).

Slags from this site are mostly sand-like small pieces less than 1 cm in diameter. A floatation, wet-sieving and hand-picking method has been used to retrieve these highly fragmented slags from soil samples (see also S. Liu et al., 2020b for description of methodology). In total, 93.5 L of soil from 18 different units were processed with this method. Each soil sample was collected from an individual archaeological context (a stratum or an ash pit) and all well dated to the Middle Shang period by associated pottery sherds. Microscopic examination of a heavy portion of each soil sample revealed a large number of slag fragments. This process is still going on and our research team is developing a more efficient way to differentiate slag pieces from rock, bone and soil pieces. Fifty-six samples including ore, slag, and furnace fragments have been analysed for their geochemical and mineralogical compositions. Six archaeological ore samples were recovered from one ash pit (2015RJH5) in the central platform and another five in the western part of the excavation area (2018RJH1) (Fig. 3b). In addition, six pieces of ore samples directly collected from the mining shaft excavated in 1980s were also analysed (Fig. 5). The ceramic bodies of two furnace fragments were analysed to get baseline trace element values of technical ceramics. Slag fragments were discovered and sampled from contexts all over the site. Thirty-seven slag samples were analysed including 32 with SEM-EDS for chemical composition (excluding un-reacted inclusions), 21 for trace element concentration, 36 for lead isotope ratios and 10 for

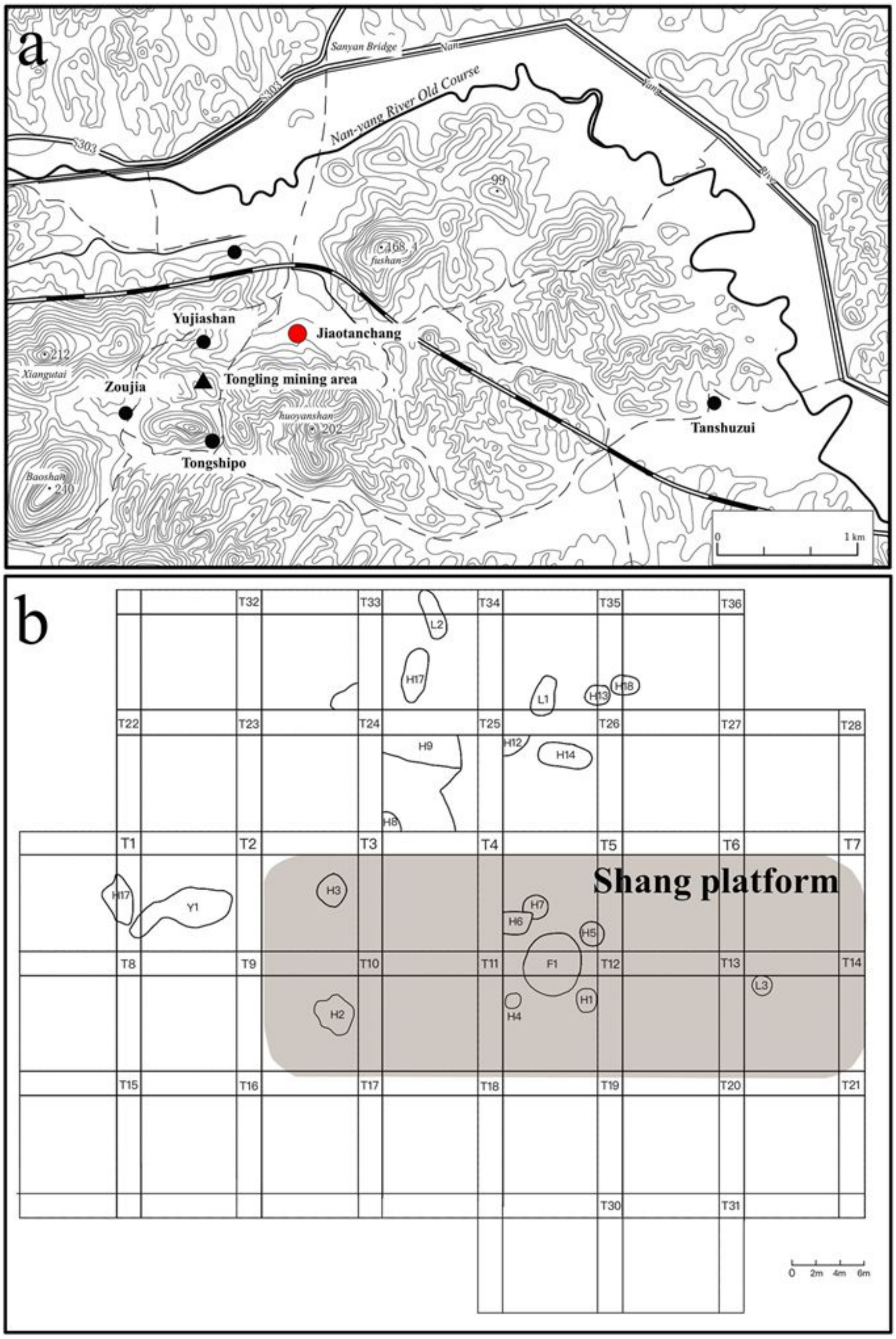

Fig. 3. The plan of Tongling (a) and Jiaotanchang site (b).

copper isotope ratios (OSM Table S2).

2. Methodology

The selected slag and ore pieces were first mounted with epoxy resin and a thin slice sample (c. 1 mm) was removed from the block's upper surface with a Buehler precision saw to expose fresh sample, and to save material for further isotopic and trace element analysis. The blocks were then processed following standard procedure of preparing polished blocks for reflected light and scanning electron microscopic examination. A Leica DM4500 reflected light microscope was used to investigate mineral composition of each sample. A Tescan Vega III scanning electron microscope equipped with Bruker energy dispersive spectrometer was used to analyze individual phases and obtain bulk chemical composition. The accelerating voltage was set to 20 kV and the live collecting duration was 60 s. A Horiba XploRA confocal Raman microspectrometer equipped with an Olympus microscope was used to characterize the unreacted minerals embedded in the slag samples. The excitation wavelengths were 532 nm. The spectra spanned from 200 to 1500 cm^{-1} using a grating with 1200 gr/mm and the spatial resolution was not more than 1 cm^{-1}. The acquisition time is 60 s with five acquisitions per spectrum. The power on samples was kept to no more than 5 mW. The spectrometer is calibrated by monocrystalline silicon.

Based on preliminary results of the SEM-EDS and Raman investigation, slag and ore samples were then selected for copper and lead isotope and trace element analyses. The thin slice of sample removed before polishing was used for these analyses. The analyses were measured in Beijing Createch Testing Technology Co., Ltd. All chemical preparations

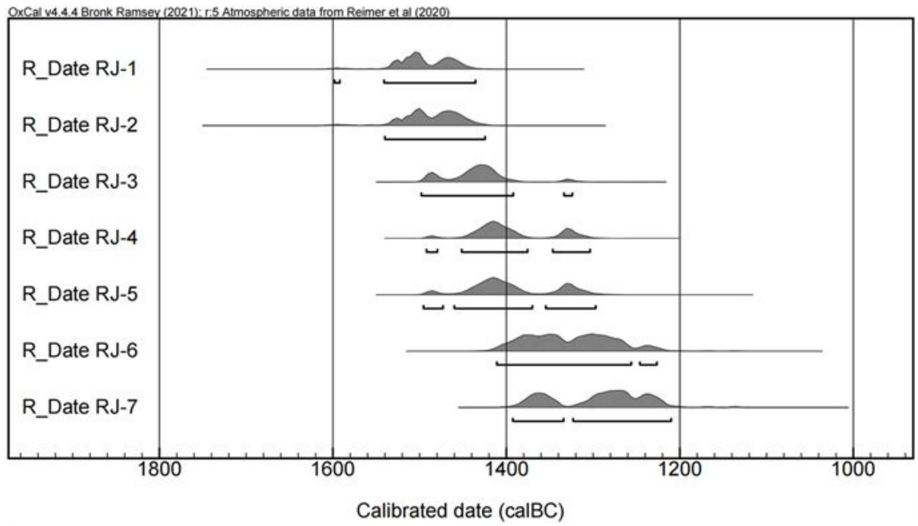

Fig. 4. Calibrated radiocarbon dates of charred seeds from the Jiaotanchang site (OSM Table S1).

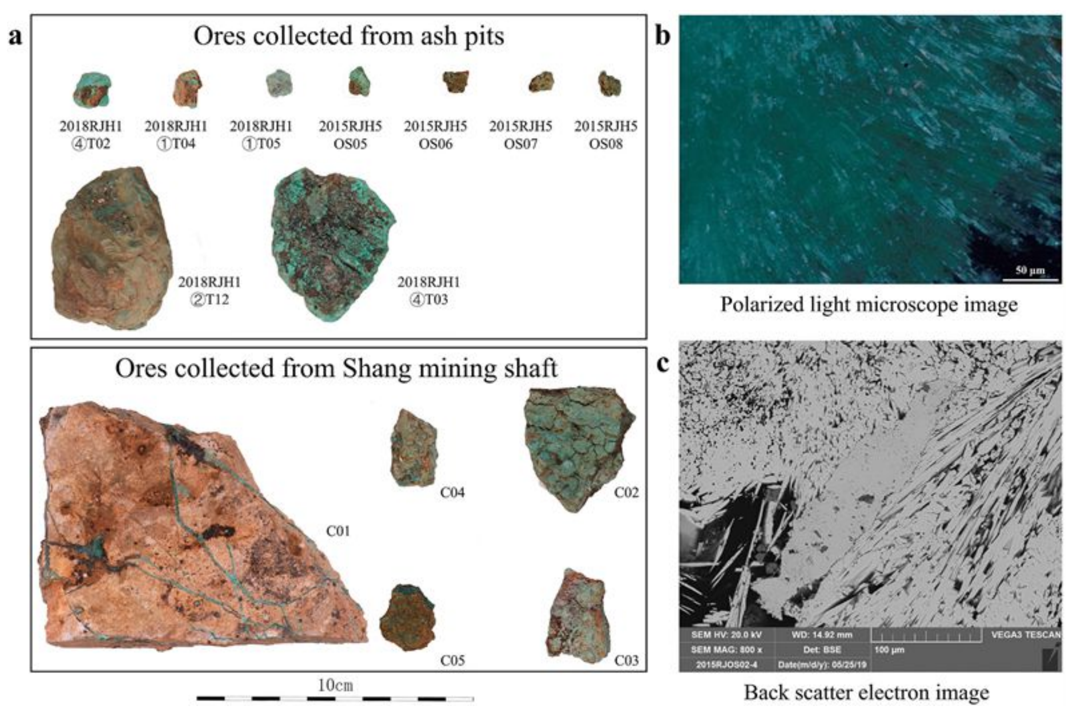

Fig. 5. Images of ore samples recovered from the site of Tongling (a). Polarized light microscope image (b) and BSE image (c) both show feather like malachite crystals.

were conducted on Class 100 work benches within a Class 1000 clean laboratory. The standard sample pre-processing and testing procedures for the lead isotope and trace element analyses can be found in Chen et al. (2021) and Sun et al. (2022), respectively. In the process of copper isotope analysis, about 150 mg of sample powder was weighed into a 15 mL SavillexTM PFA screw-top beaker. Concentrated HNO_3 and HF (1 mL and 2 mL) were added to the samples and the sealed beakers were heated on a hotplate at 150 °C for 1 week. After digestion, acids were evaporated on the hotplate and residues were dissolved in 1 mL of concentrated HNO_3. This procedure was then repeated 3 times. Finally, the samples were dissolved in 1 mL of 7 M HCl for Cu purification. Copper was separated and purified by 7 M HCl using AG MP-1 (Bio rad, 100–200 mesh) anion resin. Copper isotope analyses were performed on a Thermo Fisher Scientific Neptune Plus MC-ICP-MS. Sample analyses were bracketed by the analyses of 400 ng/mL Cu standard solution (CAGS Cu) in order to normalize isotopic compositions of a sample. In addition, the in-house standard Alfa-Cu was repeatedly tested for accuracy monitoring, and errors for each measurement were calculated to be near ±0.03‰ (2σ). The fractionation is described with δ^{65}Cu value (Fujii et al., 2013; Mathur et al., 2009).

3. Results

3.1. Ores

Optical microscopic observation indicates that ores from the Tongling site are mainly composed of feather-shaped malachite crystals with quartz, limonite and clay as gangue minerals (Fig. 5). Pseudomorphic crystals of primary chalcopyrite or other sulphide minerals are not observed, suggesting that malachite and limonite were directly crystalized from surface or underground water during weathering, rather than products of replacement of primary sulphides. Bulk chemical analysis of 15 samples shows that most of the ores are rich in Cu (>20 wt %) and have varied amounts of Si, Al, and Fe. None of them shows significant contents of Ca (below detection limit). Eleven ore samples were selected for ICP-MS trace element analysis. The result shows that they commonly contain elevated amounts of Mn (740 ppm in average) and Zn (1417 ppm in average) while elements that are commonly applied to provenance studies, such as Co and Ni, are in low concentrations (<50 ppm). The Pb content of these samples are mostly below 100 ppm with a Pb/Cu ratio in the order of 10^{-5} level. The Sn contents of all analysed samples are below 2 ppm.

Lead isotope ratios of ore samples scatter in a wide range with $^{206}Pb/^{204}Pb$ ratio between 18.6 and 20.5, and four of them can be classified as highly radiogenic lead ($^{206}Pb/^{204}Pb > 19$) (Jin et al., 2017). They form a good linear array in the $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ plot but not in the $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ plot. The $\delta^{65}Cu$ values of ore samples fall between 1 and 4.9 with only one outlier ($\delta^{65}Cu = 0.2$).

Fig. 6 demonstrates a significant geochemical variation between the Tongling ores and the hypogene ores from the Jiurui Metallogenic district (Li et al., 2019; Hsu and Sabatini, 2019; Zhou et al., 2015). The ores from Tongling have systematically higher $^{206}Pb/^{204}Pb$ ratios than Jiurui ores while their $^{208}Pb/^{204}Pb$ ratios fall in the same level. The $\delta^{65}Cu$ values of Tongling ores are distributed in a wider range but consistently higher than hypogene ores from the Wushan skarn-dominated copper deposit. In chondrite-normalized REE patterns (Sun and McDonough, 1989), the Jiurui ores are much more enriched in LREE compared to HREE, while Tongling ores do not show significant differentiation between LREE and HREE.

These variations reflect different ore-forming processes. Since most copper deposits in the Jiurui metallogenic district formed in the same geological event with similar source materials, the primary hypogene ores tend to have highly similar geochemical signatures, forming tight clusters in lead isotope and copper isotope plots. On the other hand, Tongling ores are exclusively of supergene origin, bearing no residual chalcopyrite and gangue minerals such as garnet and diopside. Copper isotope value has been widely accepted to be sensitive to weathering processes since the heavier ^{65}Cu tends to concentrate in water solution and later translates into reprecipitated oxidic minerals (e.g. malachite and azurite) with higher $\delta^{65}Cu$ (Albarède, 2004). The average of geological ore samples collected from different regions shows that oxidic ore, supergene sulphidic ore and primary sulphidic ore would have positive $\delta^{65}Cu$, negative $\delta^{65}Cu$, and $\delta^{65}Cu$ around 0‰ respectively (Mathur et al., 2009). It is therefore not surprising to find that all Tongling ores fall in the more positive side to the Jiurui ores.

In addition, supergene ores of this region seem to have elevated HREE concentrations compared to hypogene ores. It may be due to enrichment of HREE in carbonates, and the recrystallized copper oxide minerals tend to have a more even distribution between LREE and HREE (White, 2013, p. 265). It is also found that supergene ores also tend to have low Pb, W and Mo contents. Pb is less soluble in water and would not move together with Cu in weathering process, resulting relatively low Pb content in newly crystallized oxidic ores. W and Mo are both incompatible elements and might not crystalize together with Cu into oxidic minerals (White, 2013, p. 271–272). The depletion of Pb during weathering likely influences Pb isotope ratios of supergene ore as it would be easily contaminated by lead from other minerals (in this case mainly quartz and minerals in soil) associated with malachite. The extraneous lead introduced from associated minerals show a highly radiogenic feature ($^{206}Pb/^{204}Pb > 19$). However, this type of highly radiogenic lead has a low $^{208}Pb/^{204}Pb$ value (<39) and does not form linear array in the plot of $^{208}Pb/^{204}Pb$ against $^{206}Pb/^{204}Pb$. It has been suggested this feature was associated with U-bearing minerals precipitated from hot water (Killick et al., 2020). As uranyl ion $(UO_2)^{2+}$ has higher solubility in hot water than Th complexes, this type of deposit tend to generate high $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ values but relatively low $^{208}Pb/^{204}Pb$ values. This highly radiogenic lead dominated Pb isotope fingerprints of supergene ore due to its low Pb concentrations. In opposite, its influence on hypogene ore is negligible as the sulphidic copper mineral has much higher Pb content. Similar features were indeed identified in oxidic copper ores from copper mining and smelting sites in Hexi corridor dated to the late 3rd millennium BC (Chen et al., 2020; Liu et al., 2021). If more oxidic copper minerals with depleted Pb content are analysed, this type of highly radiogenic should be more frequently identified. It is apparently different from the highly radiogenic lead found in Shang bronzes which has much higher $^{208}Pb/^{204}Pb$ value and Pb content (see Jin et al., 2017; Liu et al., 2018). Geochemical analyses of ores demonstrate that supergene and hypogene ores from this region can be neatly separated via their different geochemical fingerprints. These geochemical proxies are therefore also useful to characterize archaeological slag unearthed from the site of Tongling and enhance our understanding about the ore exploration strategy of Shang

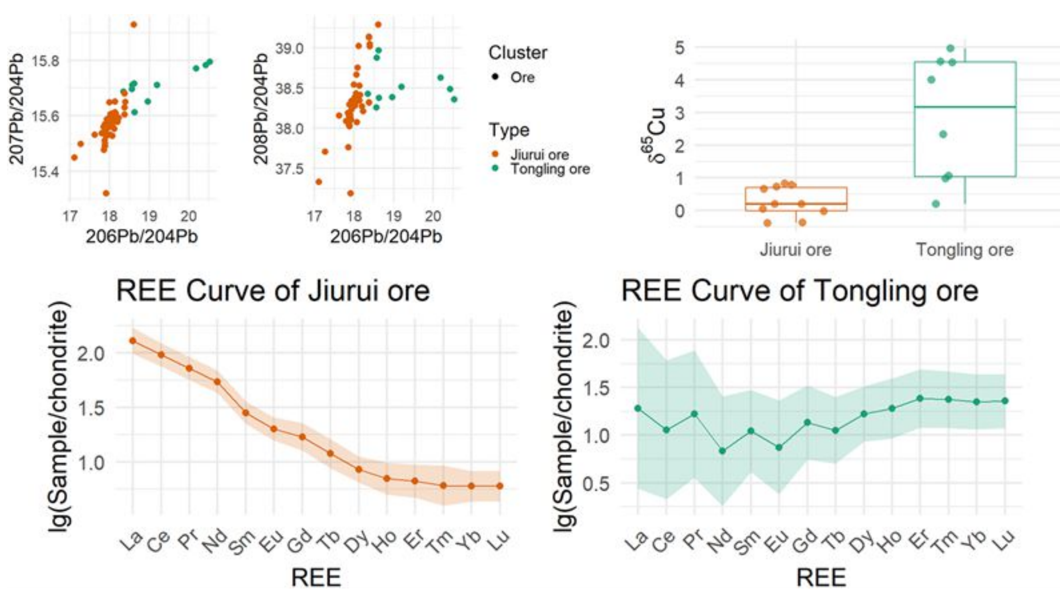

Fig. 6. Geochemical variation between Tongling and Ores from Jiurui metallogenic district.

people at this site.

3.2. Slag

Microscopic analysis shows that slags of Tongling are highly heterogeneous with numerous unreacted inclusions, cavities, and embedded metal prills (Fig. 7). Slag matrices are mostly dominated by angular magnetite and rounded wüstite. Fayalite and pyroxene are less frequently identified. Iron oxides are distributed highly unevenly and can sometimes gather into large clusters. Bulk chemical analysis of the originally molten part of the slags, i.e. avoiding all unreacted particles, shows these samples to have highly varied FeO, CaO, MnO and SiO_2 contents (see online supplementary material for detailed results). Most samples are rich in FeO with its concentration as high as 68 wt%. The copper content of these slags (shown as CuO) is also quite high. The average is about 3.4 wt% and one sample (2018RJH2①S005) revealed more than 17 wt%. Most copper presents as metallic prills while cuprite (Cu_2O) was identified in rare cases. The combination of these phases suggests the redox condition in the smelting installations was close to the QFM buffer (Liu and Rehren, 2024) with probably a high variation even across the same smelting event. Micro-area chemical analysis on individual copper prills shows that they are all pure copper with no alloying elements. About half of them have significant Fe content (>1 wt %). Many samples reveal copper sulphides (mainly Cu_2S) as collars around copper prills or even forming independent globules. However, bulk sulphur content has been found above detection limit of SEM-EDS (c. 0.1 wt%) in only one sample (2015RJL1②S005) though where it reaches as high as 2.6 wt% (presented as SO_3).

Microscopic and Raman analyses were conducted on unreacted inclusions trapped in these samples to provide more information regarding the original ore charges. The result shows that apart from quartz, garnet and diopside were also identified in these samples. Chemical and Raman analyses show that most garnet are andradite dominated with high CaO and FeO contents. Diopside forms solid solution with hedenbergite, causing elevated FeO content (Fig. 8). It is noted that andradite and diopside are also reported as main gangue minerals in skarn deposits at Wushan (Wen et al., 2019). The heterogeneous nature and abundance of unreacted inclusions suggest that Tongling slags had never reached a fully molten state. The high viscosity of slags would undoubtedly cause a poor separation between slag and copper, rendering high Cu concentration in most samples. This also explains why most slags recovered from this site are sand-like fragments with a size of only around 1 cm. They were likely crushed after smelting to retrieve copper lumps and globules still trapped in them (Zou, 2020). A similar practice has been observed in many other Chalcolithic and Bronze Age smelting sites (see Bourgarit, 2019, 2007; Golden et al., 2001; Shugar, 2003).

An interesting find is that the Tongling slag samples can be divided into two groups based on their CaO and MnO contents. The CaO-rich slags (Group A) generally have an MnO content lower than 2 wt% and CaO content over 2 wt%. They frequently reveal unreacted garnet and diopside fragments as well as copper sulphide prills. As andradite garnet and diopside are both CaO-rich minerals linked to hypogene skarn deposits, they likely account for the high CaO in this type of slag. On the contrary, the MnO-rich slags (Group B) mostly have less than 2 wt% CaO and much higher MnO content than Group A. They only have embedded quartz rather than andradite and diopside, linking them more likely to supergene deposits.

The division of Group A and Group B slags is also evident in other types of data. The correlation matrix of trace element data (Fig. 9) shows a relatively strong correlation for a large group of elements from Ni to Rb. Among them, Mn-Zn-Sr, Ni-Co-Tl, and Nb-Zr-Hf are strongly associated with each other, reflecting their close geochemical similarity. It may suggest each of these groups originated from the same material in smelting charge. Lead and copper are also strongly associated, presumably due to concentrating of lead in copper melt. PCA analysis shows that Group A and Group B are well separated in terms of trace elements pattern. The three strongly associated elemental groups Mn-Zn-Sr, Ni-Co-Tl, and Nb-Zr-Hf are all concentrated in Group B slags, while Group A slags tend to be more concentrated with W and Mo (Fig. 9), again linking them to hypogene skarn and porphyry-type deposits. The chondrite normalized REE curve of Group A slags tilts to the right, with high LREE/HREE ratios. On the contrary, Group B slags show a "V" shape REE curve

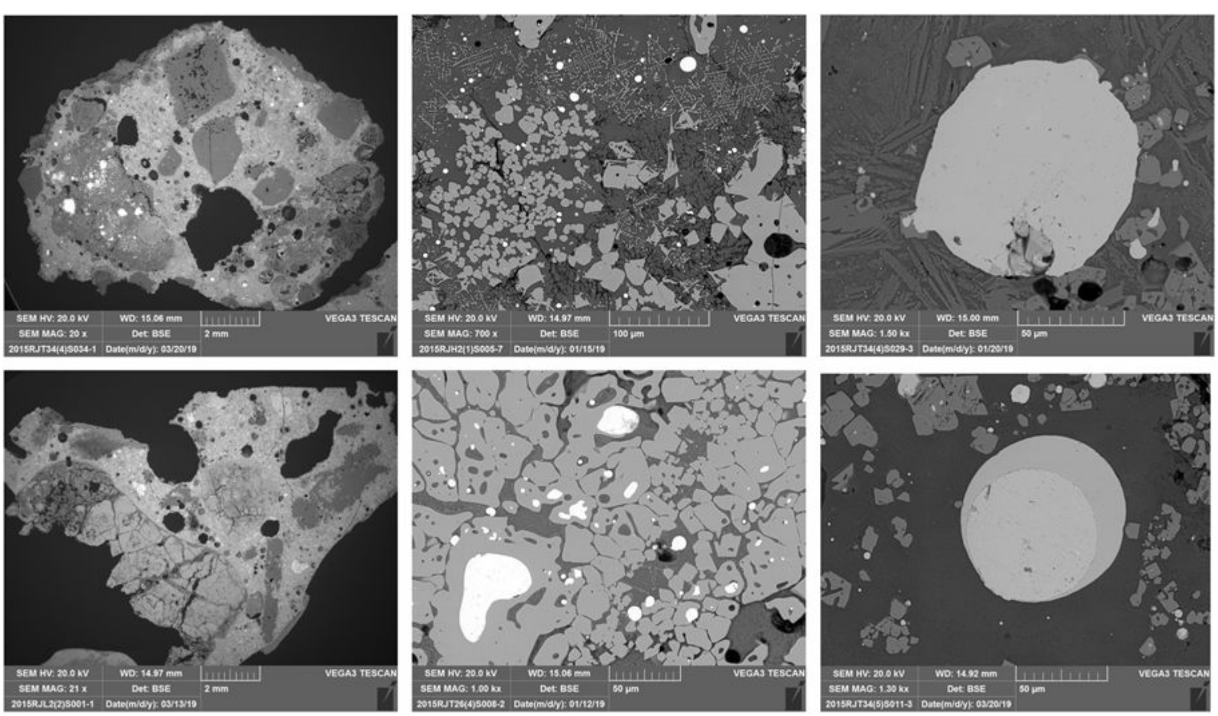

Fig. 7. BSE images of Tongling slag samples. The upper images belong to Group B slag samples and lower images are of Group A slag samples. It is noted that Group A sample commonly show unreacted garnet and diopside inclusions while Group B sample only have quartz inclusions.

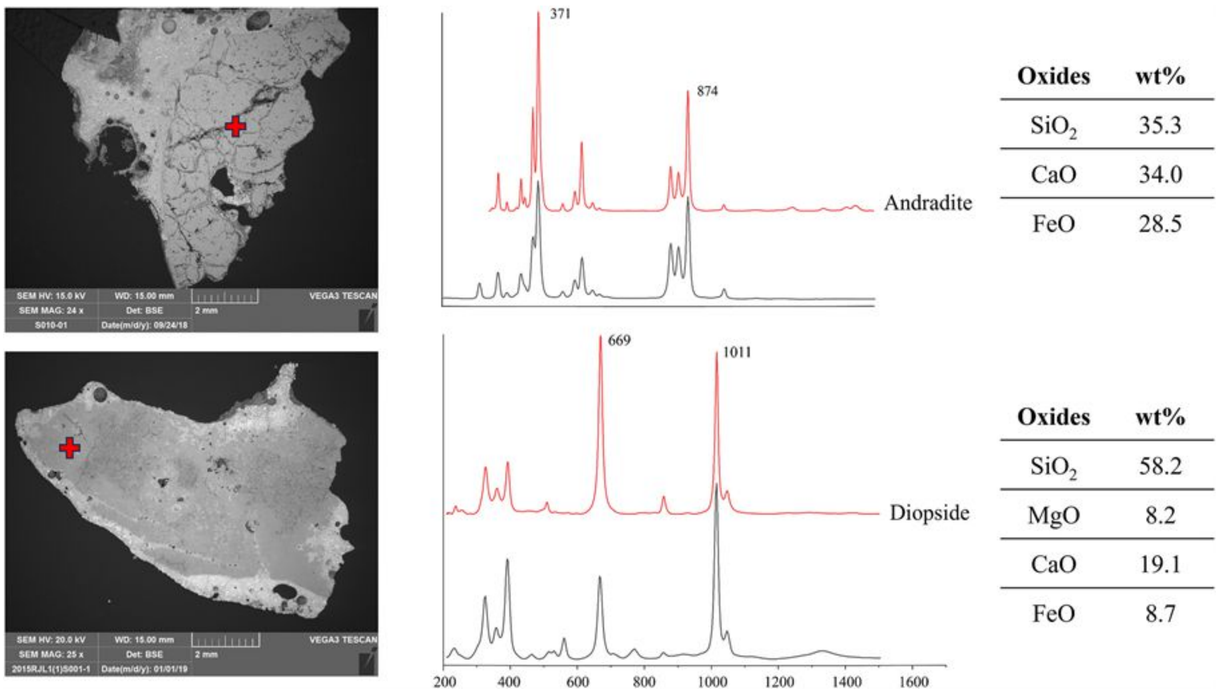

Fig. 8. Unreacted inclusions found in Tongling slag and their Raman and SEM-EDS analytical results. The reference Raman spectra are from RRUFF database (Downs, 2006).

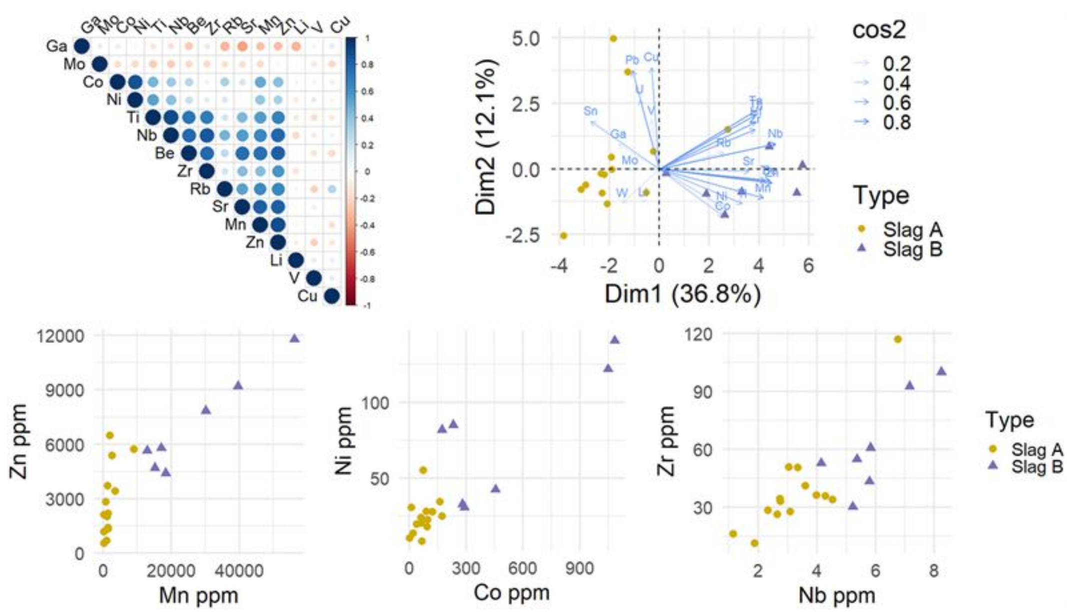

Fig. 9. The correlation matrix and PCA analysis results as well as binary plots of trace element data of Group A and Group B slags.

and are significantly enriched with HREE (Fig. 10).

In lead isotope plots, Group A slags form a relatively tight cluster with $^{206}Pb/^{204}Pb$ between 17.8 and 18.2 while samples of Group B extend from $^{206}Pb/^{204}Pb \approx 18.5$ to the highly radiogenic end ($^{206}Pb/^{204}Pb > 19$) (Fig. 11). They show a linear relationship in the graph of $^{207}Pb/^{204}Pb$-$^{206}Pb/^{204}Pb$ but not in $^{208}Pb/^{204}Pb$-$^{206}Pb/^{204}Pb$, and have $^{208}Pb/^{204}Pb$ values lower than 40. The $\delta^{65}Cu$ value of Group A and Group B samples concentrated around 0.5 and 2.3 respectively (Fig. 11). As the isotopic ratios of copper and lead have both been experimentally shown to not fractionate significantly in metallurgical processes (Cui and Wu, 2011; Klein and Rose, 2020), they should both be considered as useful proxies to associate anthropogenic items with geological ore sources. A comparison of these values between slags and ores shows that Group A slags match well with Jiurui ores reported in the geological literature, while Group B slags are quite consistent with the supergene Tongling ores analysed in this research (Fig. 11). Additionally, Group A slags also show a REE curve similar to hypogene Jiurui ores with high LREE/HREE values. The REE curves of Group B slags and Tongling ores do not match perfectly, but they both have relatively enriched HREE (Figs. 6 and 10). If contamination from technical ceramics during slag forming process is considered, the similarity of REE curves between Group B slags and Tongling ores is also significant.

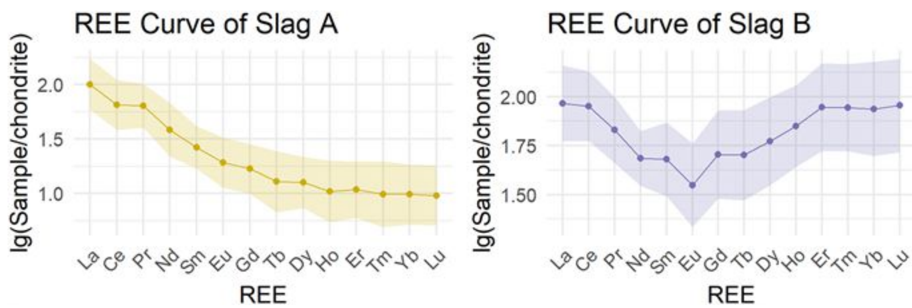

Fig. 10. The chondrite normalized REE curve of Group A and Group B slag samples.

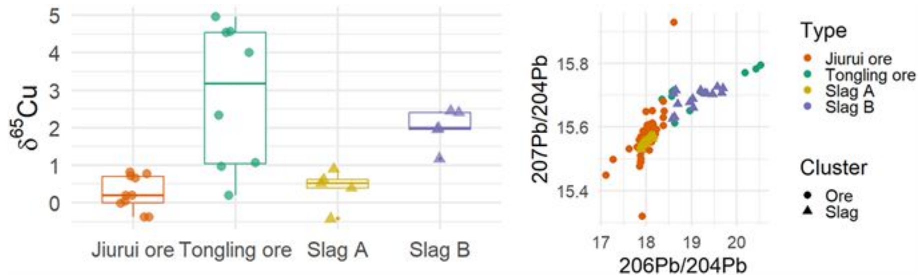

Fig. 11. Lead isotope ratios and $\delta^{65}Cu$ value of Group A slag, Group B slag, Jiurui ore and Tongling ore.

4. Discussion

4.1. The use of hypogene ore in Bronze Age China

The analyses of ores have demonstrated that copper and lead isotopes as well as trace element data are reliable proxies in differentiating ore types from this region. Thus, it can be contended that the differentiation between Group A and Group B slags is due to the utilization of hypogene and supergene ores, respectively. Although remains of hypogene ore have not yet been identified at this site through archaeological excavations, the presence of such ore can be firmly proved by the analysis of slags. The brief geological report of the Tongling deposit mentioned scattered skarn deposits in contact zone between granitoid intrusion and host deposit (Wang, 1989). A recent expedition at the adjacent Baoshan area also identified a skarn deposit (Li et al., 2015). There are probably many other small deposits around the site that could have been explored by Bronze Age miners for this type of ore. It is however not possible to pinpoint its exact origin, as most hypogene ore deposits from the Jiurui metallogenic district bear similar geochemical features.

The site of Tongling reveals so far the earliest evidence of hypogene ore exploration in Bronze Age China. Previous studies have identified sporadic copper smelting slag with matte globules rich in Fe and S from the context of Middle-Late Western Zhou (10th-8th century BC) (Mu, 1990; Cui et al., 2020) and Spring & Autumn (8th-5th century) (Li 1999) in the Middle Yangtze River Valley. These finds have long served as evidence for the initial stage of using sulphidic ores to complement oxidic ones due to the high demand of copper in these periods. Most scholars believed that hypogene copper ores were not used in large scale until quite late since people had not mastered techniques such as deep underground mining and desulfurization of copper sulphide minerals. It was even hypothesized that the impetus of Early Shang expansion (15th-14th century BC) and abandonment of Zhongtiao Mountain copper mines adjacent to the Central Plain during this period is associated with the exhaustion of supergene ores from these mines (Liu and Chen, 2002). It was argued that as the supergene belt of the strata bound and porphyry copper deposits in the Zhongtiao Mountain (for ore geology of the Zhongtiao Mountain copper deposits see The writing group of geology of Zhongtiaoshan copper mine, 1978) is relatively thin and could not sustain the long term copper mining of the Erlitou and Early Shang period, ancient miners had been forced to explore new sources of copper and finally established new copper mines in the Middle Yangtze River valley, specifically the site of Tongling.

The detailed characterization of slags and ores from Tongling now provides a novel perspective for this discussion. As slag samples involved in this investigation were from various contexts across the site and sampled randomly, the high proportion of Group A slags (>50 %) suggests smelters at the site of Tongling had been able to use hypogene ore in a quite frequent manner. In pyrometallurgy, there are generally two approaches to deal with S and Fe in copper minerals such as chalcopyrite in this type of ore, namely roasting-smelting and matte smelting. In matte smelting, an intermediate product of Cu-Fe-S (matte) is created while gangue and part of the iron in chalcopyrite are removed into slag. Matte is then repeatedly roasted and smelted to lose most iron and finally be converted to copper (1) (Davenport et al., 2002). The multi-stage style of this technology would leave various types of slags with different types of sulphidic inclusions in the field. If slag with Fe-rich matte inclusions is identified, it is a strong argument that matte smelting was carried out. This type of remains has been identified in the late second millennium BC Alpes and Cyprus (Addis et al., 2016; Hauptmann, 2011; Van Brempt and Kassianidou, 2016). Most previous evidence of hypogene ore smelting found in China are also associated with this type of find. However, matte smelting is arguably at an advanced stage in a technological developing sequence, and earlier use of hypogene ore might be more commonly associated with the roasting-smelting approach (2).

$$
\begin{aligned}
2CuFeS_2+3O_2 &= 2CuS + 2FeO + 2SO_2 \\
2CuS + 3O_2 &= 2CuO + 2SO_2 \\
CuO + CO &= Cu + CO_2
\end{aligned} \tag{1}
$$

$$
\begin{aligned}
CuFeS2 + 2O2 &= CuO + FeO + SO2 \\
CuO + CO &= Cu + CO_2
\end{aligned} \tag{2}
$$

It has been experimentally shown that chalcopyrite can be reduced to copper metal in relatively oxidizing crucibles and furnaces of Chalcolithic and Early Bronze Age smelters (Burger et al., 2010a, 2010b; Hanning et al., 2010). The sulphide anion in chalcopyrite can be a reducing agent and positively contribute to the reduction of copper. The archaeological evidences of this process have also been identified in Chalcolithic southern France (Bourgarit et al., 2003), the Chalcolithic site of Akladi Cheiri in Bulgaria (Rehren et al., 2020) and Early Bronze site of Shahr-i Sokhta in eastern Iran (Hauptmann et al., 2003). A later development of this process might be removing sulphur from ores first via a dead roasting before charging to smelting furnaces (2). As sulphur cannot be completely removed, residual sulphur in ores would result in Fe-free sulphide collars around copper prills. However, quite similar slags could also be identified in smelting supergene ore with residual sulphide impurities or mixture of oxidic and sulphidic ores (naturally or intentionally). Thus, it might inevitably create a confusion in the classification of slag with these prills. Many slags of this type had been "cautiously" classified as remains from smelting oxidic ore with minor sulphide impurities.

The clear distinction between Group A and Group B slags, coupled with the high consistency observed between Group A slags and Jiurui ores, suggests that hypogene ore was exclusively utilized without mixing with oxidic ore at the site of Tongling. As almost every context (a stratum or a ash pit) involved in this research revealed both Group A and Group B slags, both types of ores were probably used in parallel at this workshop during the Shang period. This practice is different from the technological approaches documented in some later Chinese literature, emphasizing mixing ore of different grades (Pollard and Liu, 2024). A re-examination of previously published data reveals that similar slag has been identified at a range of other Shang period copper smelting sites such as Xiwubi (Cui et al., 2022), Laoniupo (Chen et al., 2017) and Yingcheng (Wang et al., 2023), and a piece of pure matte was even identified at the site of Dongxiafeng close to Zhongtiao Mountain dated to the pre-Shang period (Li et al., 2018). Therefore, with more detailed analyses, it would be highly possible to find more wide-spread evidence of using hypogene copper ores during the 2nd millennium BC in China.

This finding not only challenges but decisively refutes the longstanding, linear evolutionary model of copper ore exploitation in Bronze Age China, which assumes a straightforward transition from easily accessible supergene ores to deeper hypogene deposits. Instead, the evidence from Tongling reveals a more flexible and context-specific approach, in which supergene and hypogene ores were exploited concurrently, depending on local resource availability and the technological demands of the time. This dual exploitation strategy persisted well into the 1st millennium BC (see Li, 1999 and Yang et al., 2024 for the site of Tonglvshan), demonstrating the enduring importance of supergene ores despite the development of more complex smelting technologies. The recognition that Bronze Age metallurgists employed both ore types in tandem, rather than in a successive evolutionary manner, forces a rethinking of broader narratives in the history of technology. This pattern suggests that technological change was not driven by a simple linear deterministic progression from 'primitive' to 'advanced' techniques. Instead, it reflects a non-linear, adaptive strategy shaped by a range of socio-economic, environmental, and resource-based factors (Montes-Landa et al., 2024). In light of these findings, future studies should revisit other early metallurgical sites with fresh attention to the possibility of hypogene ore use, thereby enriching our understanding of the diversity and sophistication of early metal production systems in China and beyond.

4.2. The style of Shang copper metallurgy

This research not only provides fresh evidence of using hypogene ore in central China during the mid-second millennium BC but also renders a more comprehensive understanding about copper smelting industry of the Shang period. A review of prior investigations shows that Shang metallurgy was exclusively characterized by large-scale operations and highly advanced technology, as evidenced by the substantial number of bronze vessels featuring complex decorative motifs uncovered from Shang burial sites and settlements (Bagley, 1987, 1990, 1999; Liu, 2003). The bronze casting remains from Shang capitals at Zhengzhou and Anyang underscored this argument. The manufacturing of mould pieces could have been a highly technically demanding and time-consuming operation as it is revealed to be made with specialized silt-rich material (Cheng et al., 2023; Stoltman et al., 2009, 2018) and frequently employed complex multi-layer structures to ensure a flawless patterned surface of finished objects (Sun et al., 2023a; Tan et al., 1999; Liu and Yue, 2004). The piece-mould casting itself was also considered to be a strategy to enhance labour specialization to meet a high demand on production efficiency (Franklin, 1992; Lddderose, 2001; Li, 2007).

The massive scale bronze casting of the Shang period was naturally assumed to be supported by an equally magnificent copper production industry. The identification of hypogene ore smelting at Tongling seems to evidence a highly developed technical capability of Shang metal workers. However, a cross-comparison of Tongling slag with its contemporary hypogene ore smelting slags from the Mediterranean and Europe shows some significant differences. Furnace smelting and slag tapping have been a common practice in both the Alps and Cyprus, evidenced by large slag heaps found at Torino and Kition (Addis et al., 2016; Van Brempt and Kassianidou, 2016; Hauptmann, 2011). The site of Tongling however revealed no slag fragment larger than 5 cm in length, and most slag samples investigated in this research are too small to be identified without wet-sieving of soil samples. Their semi-reacted nature and high Cu concentration suggest the slag was not tapped and its separation from copper was quite poor. As argued previously, this type of slag evidently needed to be crushed to retrieve copper globules trapped in the slag. Slag-crushing was a common practice for metal workers from the earlier part of the Bronze Age (Bourgarit et al., 2003). Sand-sized slags similar to those of Tongling have been identified in many different parts of the world (Golden et al., 2001; Hauptmann et al., 2009; Shugar, 2018). The extracted metal prills would later be remelted in crucibles (e.g. Levy et al., 2002). If this reconstruction reflects the technical reality of the Tongling site, it represents a relatively low efficiency but highly labour-intensive process of copper production. It should be noted that slag crushing has turned out to be a common practice for Shang metal workers, since a recent campaign of investigating micro-slag at other Shang sites has revealed similar remains in a range of Early to Middle Shang copper smelting (Cui et al., 2022; Wang et al., 2023) and bronze casting workshops (S. Liu et al., 2020b; Hu et al., 2021).

All these finds together suggest that Shang copper production relied on relatively simple smelting installations without slag-tapping, and the production scale was mainly promoted by high labour investment rather than technical advances. To contextualize hypogene ore exploration in this background, we argue that it is a scenario considerably different from what Powell et al. (2018) proposed, in a study of Balkan Bronze Age copper production, that the exhaustion of supergene ores caused a hiatus of copper production in the region and its resurrection would become possible only after the introduction of hypogene ore mining and smelting techniques (see also Jansen, 2018 for comments on this research). As hypogene ore was utilized in parallel with supergene ones without mixing, they should be attributed to independent smelting operations, even to different production units inside this site. It testifies that smelters' choice of ore was a complex decision-making process, probably depending on various technical and social-economic factors. Li (2019) synthesized that archaeological data from the Late Shang capital Anyang indicate a large scale of production was supported by multiple bronze casting workshops operating at the same time, each of which uncovered hundreds of thousands of casting mould pieces as well as furnace and crucible fragments (see also He, 2019). Li (2019) pointed out that these precinct workshops were not centrally controlled by the Shang kings or high elites from the temple and palace complex at Xiaotun, but probably independently managed by secondary elites in individual settlements since the workshops were scattered in a wide area across and even beyond the Late Shang capital at Anyang (Fig. 12) (see Kong et al., 2022 for a new find of a bronze workshop outside the traditional Yinxu area). The archaeological evidence from the Early

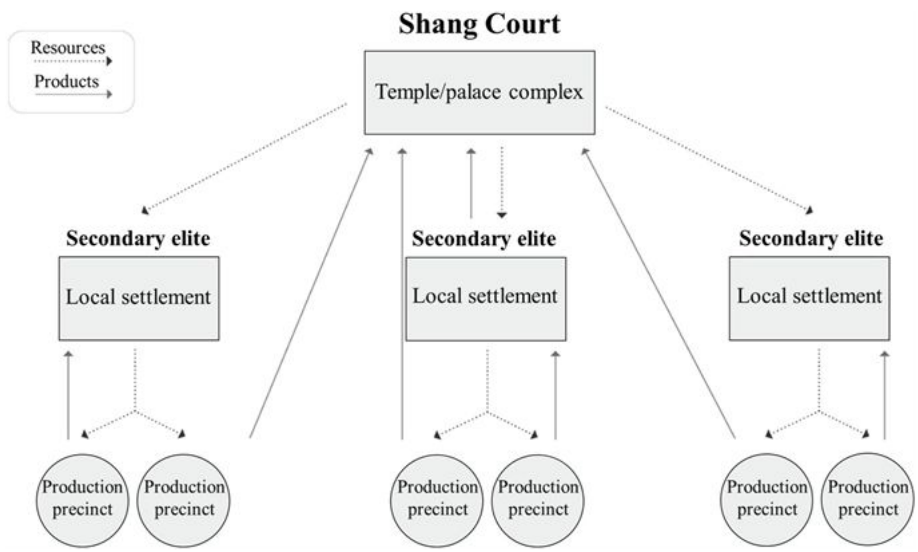

Fig. 12. Organizational model of metal production in the Late Shang capital Anyang (after Li, 2019, p. 184).

Shang capital at Zhengzhou revealed a similar scenario. Two bronze casting workshops, Nanguanwai (南关外) and Zijinshanbei (紫荆山北), were found to the south and north of the inner city, both operating during the Lower Erligang II to Upper Erligang I period (16th-15th century BC) and revealing moulds for implements, weapons and ritual vessels (Henan Provincial Institute of Cultural Heritage and Archaeology, 2001; Liu and Chen, 2012). A recent excavation inside the inner city revealed a third workshop active in more or less the same period. It is admitted that there are fundamental differences in terms of production organization between primary (smelting) and secondary (casting) productions but it should still be highlighted that running an industry in a number of parallel and separate production units at the same site seems to be a common practice of Shang people (see Campbell et al., 2011 for bone workshops). It is perfectly possible that these separately organized production units followed different technological choices. This style of production featured in many craft industries of the Shang period, and potentially points to a more commercialized production, instead of a redistribution-based one controlled by a central power (Campbell et al., 2022). Each of these production units might form based on kinship and served their own customers and were coordinated by the Shang court via exchanging their products for crucial subsistence and resources of production (Campbell et al., 2022; Li, 2019).

5. Conclusion

This research addresses a facet of the Shang bronze industry which was not properly examined in most previous research. The detailed geochemical and mineralogical characterization of copper ores and slags from the middle Shang site of Tongling revealed that both oxidic and sulphidic copper ores were employed at this site. The smelting of these two types of ores happened in parallel at the site both with a relatively low efficient process, generating semi-molten slag with high residual copper and many unreacted mineral inclusions. These primitive slags are in stark contrast to the tap slag produced in sulphidic ore smelting sites in contemporary Europe and had to be mechanically crushed for retrieving copper trapped in it. These finds evidenced that the exploration of sulphidic copper ores does not necessarily indicate an advanced stage of copper smelting technology, and the choice of ore could also be diversified at one smelting site. It is indicated that the Middle Shang copper production industry was organized in a multi-linear and labour intensive style, which is principally in accordance the bronze casting and other craft production industries of Shang culture.

CRediT authorship contribution statement

Siran Liu: Writing – review & editing, Writing – original draft, Visualization, Supervision, Methodology, Investigation, Formal analysis. **Zhenfei Sun:** Writing – review & editing, Visualization, Methodology, Investigation, Formal analysis. **Tao Cui:** Writing – review & editing, Supervision, Investigation, Formal analysis. **Guisen Zou:** Writing – review & editing, Visualization, Supervision, Methodology, Investigation, Formal analysis. **Richen Zhong:** Writing – review & editing, Visualization, Supervision, Methodology, Investigation, Formal analysis. **Thilo Rehren:** Writing – review & editing, Supervision, Methodology, Investigation, Formal analysis.

Declaration of competing interest

The authors declare that there is no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jas.2024.106092.

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