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# Early bronze metallurgy at Guniushan City site in the lower Yangtze River, Anhui Province, China

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This paper is the scientific analysis of metallurgical relics from a city site in the mining and smelting heritage area of Southern Anhui during the Bronze Age. The samples from the Guniushan city site have been collected from archeological excavations and field surveys, with two types products of copper and tin-bronze. The significance of the metallurgical history of the Guniushan city site was also examined to deepen insights into local technology dissemination and culture interaction, acquisition and circulation of raw materials, and regional administration and industry pattern through the exploration of intrinsic connections between the city site and metallurgical civilization in Southern Anhui. Not only does this study reflect bronze metallurgy at the site, but it also proves essential for reconstructing the relationship between city sites in the lower Yangtze River and the flourishing mining and metallurgical industry in Southern Anhui during the Zhou Dynasty (ca. 1100 BC ~ 300 BC).

The southern Anhui Province of China, which is centered on the Dagongshan-Fenghuangshan Mountain ancient mining area in Tongling City and Nanling County<sup>1</sup>, contains the highest concentration of mining and smelting heritage sites in the lower Yangtze River. This region has attracted the attention of numerous Chinese archeologists who have conducted extensive research there, and their work has significantly advanced our understanding of the scientific and historical value of mining and smelting heritage throughout the Yangtze River Basin. In accordance with the literature records of the pre-Qin period (before 221 BC) and the inscriptions on early bronze vessels, the lower Yangtze River, where the Southern Anhui mining and smelting heritage area resides, consistently supplied metal raw materials to early Central China through tributes of metal, trade, or military conquests. This supply fulfilled the substantial demand for copper required used in casting bronze vessels during the Shang and Zhou dynasties, thereby making a significant contribution to the prosperity of the Chinese bronze civilization. The Guniushan city site in Nanling County, located on the eastern periphery of Southern Anhui ancient mining and smelting heritage area, is recognized as a key heritage monument under national protection (Fig. 1). Its principal occupation spans from the Western Zhou Dynasty to the Spring and Autumn Period (ca. 1100 BC ~ 500 BC). Numerous scholars have emphasized its direct association with the early mining and smelting activities controlling the Dagongshan Mountain area in Southern Anhui<sup>1,2</sup> and its archeometallurgical study is crucial for understanding the relationship

between early city civilizations and the development of mining and metallurgy in Southern Anhui.

Southern Anhui along the Yangtze River is endowed with abundant copper mineral resources, predominantly in the form of skarn deposits<sup>3</sup>. Within the oxidation zone, copper minerals chiefly comprise malachite, azurite, and cuprite, whereas in the primary zone, the principal copper minerals include chalcopyrite, chalcocite, bornite, and tetrahedrite. Since 1986, the Ancient Copper Mine Research Group, established by the Anhui Provincial Institute of Cultural Relics and Archeology, has identified over one hundred mining and smelting sites dating from the Western Zhou Dynasty to the Tang and Song dynasties (ca. 1100 BC ~ 1200 AD) across the Southern Anhui<sup>4</sup>, covering an area approaching 2000 km<sup>2</sup>. Notably, four major clusters of ancient mining and smelting sites exist: Fenghuangshan Mountain, Tongguanshan Mountain, Shizishan Mountain, and Dagongshan Mountain (Fig. 1 and Fig. 2). Between 2013 and 2015, collaborative surveys by the University of Science and Technology Beijing and local cultural heritage organizations revealed a new series of early metallurgical sites, including Shendun in Tongling City, Xiaojiaoyuan in Nanling County, and Chuanxingshan in Guichi City<sup>5</sup>. Field surveys suggest that Southern Anhui developed a radiating ancient mining and smelting network centered on Tongling City. Additionally, broadleaf forests dominated by species such as *cyclobalanopsis glauca* and Chinese cork oak are widely observed in this region, and their charcoal yields high thermal energy<sup>1</sup>, rendering them an optimal fuel source for copper smelting.

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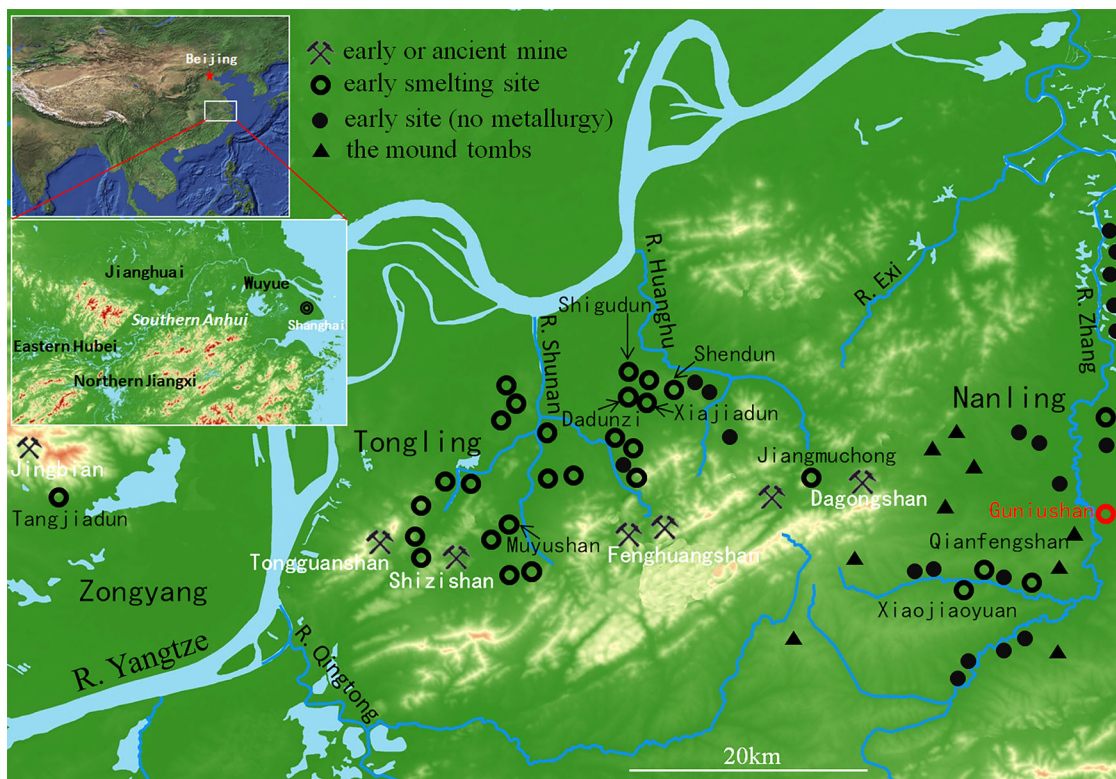


Fig. 1 | Topographic map depicting Guniushan city site in Nanling County and Southern Anhui mining and smelting heritage area.



Fig. 2 | Early mining pit and stone hammers in Southern Anhui ancient mining area.

The early metallurgical heritage in Southern Anhui primarily included two major activities: mining and smelting<sup>1</sup>. Early mining operations employed both open-pit and underground techniques. The underground mining methods include three types of excavations: vertical shafts, inclined shafts, and horizontal tunnels. Common mining tools include stone hammers and wooden shovels. At present, at least thirty to forty pre-Qin period

(before 221 BC) metallurgical sites have been identified in Southern Anhui<sup>4</sup>, predominantly in hilly or flat agricultural regions approximately ten to several dozen kilometers from mining sources. These sites typically span areas of 5000 to 20,000 m<sup>2</sup> and are associated with cultural artifacts such as sand-tempered pottery, hard pottery with printed patterns, and primitive porcelain. Diamond-shaped copper ingots are representative of local



**Fig. 3** | Aerial perspective showing the northern section of the Guniushan city site.

metallurgical products. Sites such as Jiangmuchi in Nanling County, Muyushan in Tongling City, and Huijiachong in Chizhou City have yielded hundreds of kilograms of these ingots, dating from the Western Zhou Dynasty to the Spring and Autumn Period<sup>14</sup> and they exhibit a surface rust colouration attributable to iron oxidation. Chemically, they consist of crude copper with a high iron content; thus, further melting and purification are needed before being cast into bronze vessels. Southern Anhui has also produced numerous bronze casting artifacts. For example, refs. 4,6 stone molds of the Western Zhou Dynasty for casting small objects were discovered at the Jiangmuchi site in Nanling County and the Muyushan site in Tongling City, whereas a ceramic mold of the Western Zhou for casting ritual vessels was unearthed at the Shigudun site in Tongling City. Collectively, along with frequent early literature records or inscriptions on bronze vessels, these findings underscore Southern Anhui as one of the most significant copper sources in China during the pre-Qin period. The thriving early mining and smelting industry served as a strong driver of the advancement of local bronze civilization and the increasing social complexity within the lower Yangtze River.

Among the early bronze smelting sites subjected to archeological excavation in Southern Anhui, the Shigudun site in Tongling City stands out as the earliest, where metallurgical artifacts associated with the late Erlitou culture (1770 BC–1610 BC) have been uncovered<sup>5</sup>. Radiocarbon dating of three metallurgical sites—Muyushan, Jiangmuchi, and Shigudun—has further substantiated that the principal phase of early bronze smelting activity in Southern Anhui extends from the Western Zhou Dynasty to the Spring and Autumn Period. The charcoal from Layer 7 at the Muyushan site in Tongling City yields a calibrated radiocarbon date of 3015 BP<sup>1</sup>, which corresponds to the early Western Zhou Dynasty. Charcoal from a smelting furnace at the Jiangmuchi site in Nanling County has a calibrated dendrochronological age of  $2815 \pm 115$  BP<sup>3</sup>, corresponding to the late Western Zhou Dynasty. At the Shigudun site in Tongling City, bamboo charcoal from House No. 1 dates between 1000 BC and 920 BC<sup>6</sup>,

aligning with the early Western Zhou Dynasty, whereas the ash layer in Layer 13 dates between 760 BC and 530 BC, corresponding to the early to middle Spring and Autumn Period.

The Guniushan city site is located in Tangxi village, Nanling County, approximately 40 km south of the Yangtze River and about 2.5 km east of the Zhang River. It dates back from the Western Zhou Dynasty to the early Spring and Autumn Period<sup>2</sup>. The city site is encircled by a moat approximately 20–30 meters in width, which is indicative of its robust defensive features. The Guniushan city site spans approximately 900 meters in length and 750 meters in width (Figs. 3 and 4), covering nearly 700,000 m<sup>2</sup>, and five elevated platforms, delineated by waterways, are found in the northern section.

Between 1997 and 1998, the Anhui Provincial Institute of Cultural Relics and Archeology conducted surveys and excavations at the Guniushan city site<sup>1,6</sup>. The work uncovered an area exceeding 200 m<sup>2</sup> and yielded valuable data concerning the city layout, cultural stratigraphy, and chronological framework. The findings indicated that the cultural deposits within the city measured approximately 2–3 meters in thickness, with the upper strata dating to the early Western Zhou Dynasty and the lower strata corresponding to the early Spring and Autumn Period. More than one hundred cultural artifacts, including pottery, hard pottery, primitive porcelain, stone tools, and metallurgical slag, were recovered. On the basis of the distinctive regional characteristics of the pottery styles, the excavation team posits the existence of a localized cultural typology, designated as the “Guniushan type,” represented by the Western Zhou Dynasty relics at the site, which exhibited extensive interactions with the neighboring Wuyue culture region, Jianghuai region, and Central China. In terms of subsistence and economy<sup>6</sup>, the city site was covered with substantial quantities of red-baked soil, copper smelting slag, and pottery production debris, as well as remains of rice grains, rice straw, and sinkers, indicating that the inhabitants of the Guniushan city site possessed advanced copper smelting and pottery manufacturing technologies and engaged in agricultural practices as well as fishing and hunting.

Fig. 4 | Remote view of the Guniushan city site.



The Guniushan city site, the ancient mining and smelting area in Southern Anhui, and the mound tombs collectively constitute an integrated complex, exhibiting a close interrelation in terms of era, culture and function<sup>2</sup>. Approximately 15 km west of the city site lies the core zone of the southern Anhui ancient mining and smelting zone (Fig. 1). The scale of mining and smelting activities in this region necessitated the presence of an administrative center responsible for operation, production, and distribution. While strategically positioned overlooking the Jianghuai region to the north, the Guniushan city site occupies a critical transportation nexus controlling access from Southern Anhui mining and smelting zone to the core of the Wuyue cultural region, thereby likely fulfilling such administrative roles. This perspective further implies that investigations into early mining and metallurgy should incorporate an analysis of the underlying factors driving their development. The Zhang River Basin, where Guniushan is located, is also characterized by a high density of mound tombs, numbering in the thousands<sup>1</sup> (Fig. 1). The nearest mound tomb to the Guniushan city site is the Qianfengshan mound tomb, which is approximately 1 km to the southwest. Excavations of certain tombs within Qianfengshan have uncovered tools associated with mining and smelting activities<sup>6</sup>, as well as copper fragments, suggesting that the interred individuals were likely miners, smelting craftsmen, or supervisors of bronze casting operation with a certain social status. To some extent, underpinned by early mining and smelting activities, the Guniushan city site, the Southern Anhui ancient mining and smelting zone, and the mound tombs collectively functioned as the administrative center, production base, and burial ground for Southern Anhui's mining and smelting industry from the Western Zhou Dynasty through the Spring and Autumn Period, while the establishment of such an administrative center was of considerable significance to the sustained development and stability of local early mining and metallurgy.

## Methods

### Slag samples

Six slag samples were procured from the archeological excavation at the Guniushan city site between 1997 and 1998 (Fig. 5), originating from Layer © of Unit T1428, and dating to the early Western Zhou Dynasty (ca. 1100 BC ~ 900 BC). These slag are generally more than 20 cm in length, characterized by a grayish-brown, non-glassy state and a loose texture with numerous gas pores visible on the cross-sections, and some surfaces show patches of copper oxidation, presenting as both green patina and azurite-like blue colouration. An additional six slag samples were obtained during a

2015 field survey at the Guniushan city site (Fig. 6). These slag measured from 1.8 cm to 4.8 cm in length, characterized by a black-brown or black-gray, non-glassy state and a hard texture, with gas pores on the cross-sectional surfaces, and green patina colouration on the surface. The field survey of the Guniushan city site also found numerous pottery fragments dating from the Western Zhou Dynasty to the Spring and Autumn Period, some of which featured decorative animal-face motifs.

### Component analysis

After being sectioned, embedded, polished and sprayed with carbon, the samples were used for phase observation and composition determination under a ZEISS EVO18 scanning electron microscope equipped with a BRUKER Nano XFlash Detector 5010 X-ray spectrometer. The compositional analysis of the samples was performed on their cross-sectional areas using a standardless quantitative approach via scanning electron microscopy for 90 s. These tests were carried out at the State Key Laboratory for New Metals and Materials, University of Science and Technology Beijing.

## Results

### Slag classification of excavated samples

The six slag samples excavated from Layer © of Unit T1428 can be classified into two categories based on whether they are mixed with metal prills containing Sn (as shown in Table 1). Category 1 comprises five samples (24490, 24491, 24492, 24493, and 24494) linked to the smelting of red copper, with no tin-containing inclusion particles detected, and mainly copper particles visible in the matrix, as shown in Fig. 7. Notably, sample 24493 has a matrix containing 15.48% copper, with copper enrichment also identified within the iron olivine crystallites, as well as traces of chromium-containing iron-copper minerals. It is postulated that the copper enrichment within the matrix and various phases of this slag results from early slag discharge during copper smelting or from instability in the furnace atmosphere. Category 2 includes only sample 24489, which is potentially associated with the smelting of tin bronze. This sample matrix contains tin-bearing inclusions (Fig. 8), copper particles, and magnetite phases.

### Slag classification of surveyed samples

The six slag samples from the field survey can also be classified into two categories based on whether they are mixed with metal prills containing Sn (as shown in Table 1). Category 1 comprises five samples (24495, 24496, 24497, 24498, and 24500) linked to the smelting of red copper, with no tin-

Fig. 5 | Slag samples from excavation of Guniushan.



Fig. 6 | Slag samples from field survey of Guniushan.



containing inclusion particles detected, and mainly copper particles and matte particles visible in the matrix. Category 2 includes only sample 24501, which is associated with the smelting of tin bronze. Analysis revealed a predominance of tin bronze and numerous Sn-Fe mineral particles (Fig. 9), and notably, some of the tin bronze particles were larger than 100  $\mu\text{m}$  in diameter (Fig. 10).

On the basis of the present excavated and surveyed samples, the metallurgical products at the Guniushan city site predominantly include two types: red copper and tin bronze, with the potential presence of lead-tin bronze as well. The detection of tin-iron (Sn-Fe) minerals in the tin bronze slag indicates that the tin materials may be related to the tin sand being rich in iron.

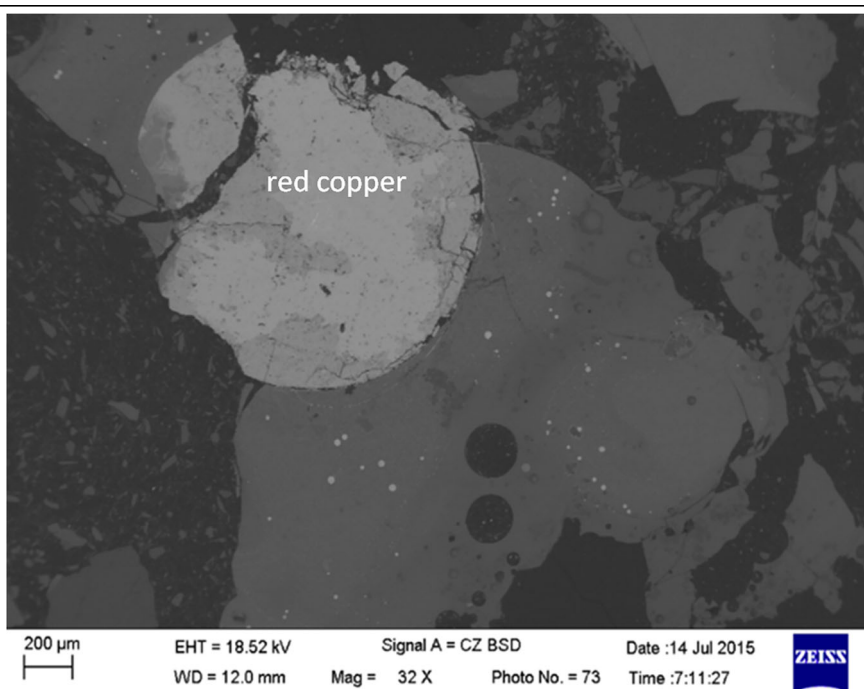
## Discussion

Initially, this batch of slag was categorized into two groups based on their association with tin bronze smelting (see Table 1 for classification and matrix composition): Category 1 involves copper metallurgy and comprises of ten samples, including excavated samples (24490, 24491, 24492, 24493, 24494) and field surveyed samples (24495, 24496, 24497, 24498, 24500). Category 2 involves tin bronze metallurgy and includes two samples: excavated sample 24489 and field survey sample 24501. On the basis of the variation in matrix composition, Category 1 can also be further subdivided into two slag types: system FeO-SiO<sub>2</sub> and system SiO<sub>2</sub>-FeO (Al<sub>2</sub>O<sub>3</sub>). The system FeO-SiO<sub>2</sub> slag includes samples 24490, 24496, 24497, 24498, and 24500, with FeO contents ranging primarily from 40% to 60%. The system

**Table 1 | Matrix composition of metallurgical relics from the Guniushan city site (Wt%)**

Sample source	Category	Lab no.	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	FeO	S	Cu	Attribute
Layer ③ of Unit T1428 (Excavation)	1	24490	1.17	2.96	39.60	0.97	12.75	42.55	-	0.61	Cu
		24491	1.14	12.22	61.47	2.08	1.83	21.26	0.02	9.93	
		24492	1.36	11.48	54.46	2.93	6.03	23.75	-	3.53	
		24493	1.07	18.30	68.77	2.58	0.67	8.61	0.06	15.48	
		24494	2.18	6.94	42.26	2.61	20.49	25.53	0.04	5.81	
	2	24489	0.51	1.01	36.27	0.18	2.38	59.66	0.13	3.88	Cu-Sn(Pb)
Field survey	1	24495	0.84	7.24	58.04	3.83	4.41	25.64	0.10	19.63	Cu
		24496	0.93	2.43	40.83	1.25	9.12	45.44	0.18	0.80	
		24497	1.81	6.69	50.04	0.51	0.43	40.53	0.17	2.61	
		24498	0.38	0.87	39.28	0.15	0.29	59.03	-	9.27	
		24500	0.76	4.37	37.64	0.83	4.53	51.87	-	0.69	
	2	24501	-	2.16	32.51	2.12	13.6	49.61	0.51	2.76	Cu-Sn

**Fig. 7 |** Copper particles in the 24491.



SiO<sub>2</sub>-FeO (Al<sub>2</sub>O<sub>3</sub>) slag includes samples 24491, 24492, 24493, 24494, and 24495, with SiO<sub>2</sub> contents ranging primarily from 40% to 70%. In addition, calcium oxide (CaO) constitutes a significant component of the slag, and its content in slag from the Guniushan city site exhibits considerable variability, with excavated samples ranging from 0.67% to 20.49% and field surveyed samples ranging from 0.29% to 13.6%. Given that malachite samples unearthed around the Dagongshan Mountain ancient mining and smelting area during the Western Zhou Dynasty contain no calcium<sup>5</sup>, it is inferred that the calcium present in the slag mainly originates from physical and chemical erosion of the furnace walls by copper and iron oxides in the ore.

For the following two reasons, the system FeO-SiO<sub>2</sub> slag and the system SiO<sub>2</sub>-FeO slag from the Guniushan city site could belong to the same metallurgical process:

(1) Influence of refractory materials. In the study of copper smelting slag at the Arisman site in Iran<sup>7</sup>, Thilo(2012) proposed two potential explanations for the low FeO content (averaging approximately 25%): first, the furnace walls and tuyere pipes both with low refractoriness are prone to erosion, resulting in a significant impact of refractory components on the slag; second, the gangue constituents in the ore are not fully melted. Given

that the system SiO<sub>2</sub>-FeO (Al<sub>2</sub>O<sub>3</sub>) slag at the Guniushan city site contains relatively high amounts of aluminum (Al<sub>2</sub>O<sub>3</sub> > 10%) and is characterized by a loose and porous structure, the formation of these slag should be greatly influenced by the refractory components.

(2) Influence of the metallurgical atmosphere. Ambert(2013) conducted analyses on more than ten slag samples from the La Cappitelle site in France<sup>8</sup>, dating to the 3<sup>rd</sup> millennium BCE, which revealed that their SiO<sub>2</sub> content predominantly ranged between 40% and 50%. Within the same slag sample, both silicon-rich zones with a mixed assemblage of olivine, feldspar minerals, pyroxene minerals, magnetite, or fayalite phases, and iron-olivine zones with a relatively balanced presence of Fe-Si phases were found. This uneven distribution is likely attributable to the metallurgical atmosphere and reducing power inside the furnace, which led to a non-uniform material distribution in different zones of the same slag.

Principal component analysis (PCA) was used to achieve a more comprehensive understanding of the chemical composition and technological property of the present excavated and field surveyed slag samples. The application of PCA in ancient slag has recently emerged in some Western case studies and serves as a valuable tool for investigating ancient

Fig. 8 | Tin alloying particles in the 24489.

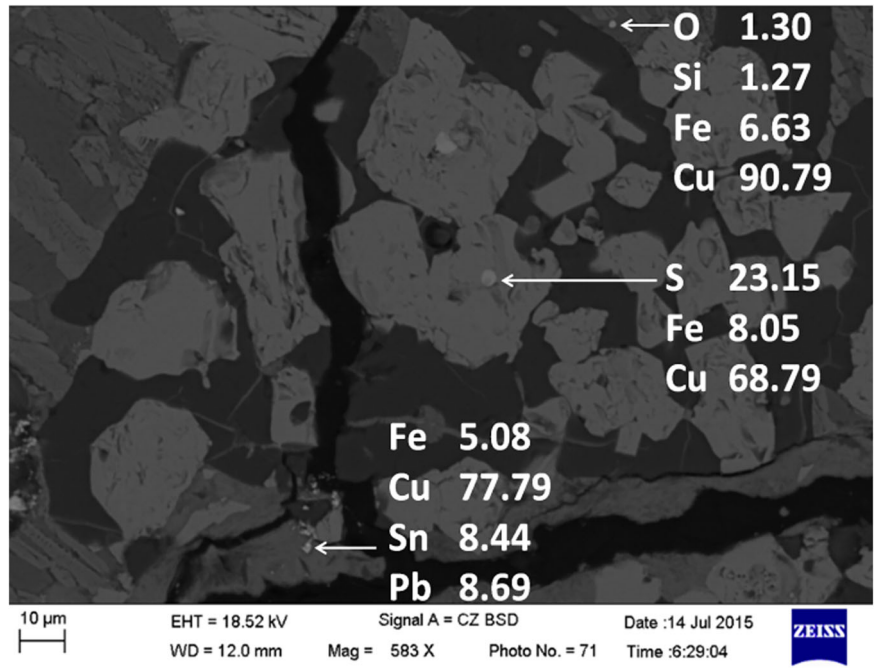
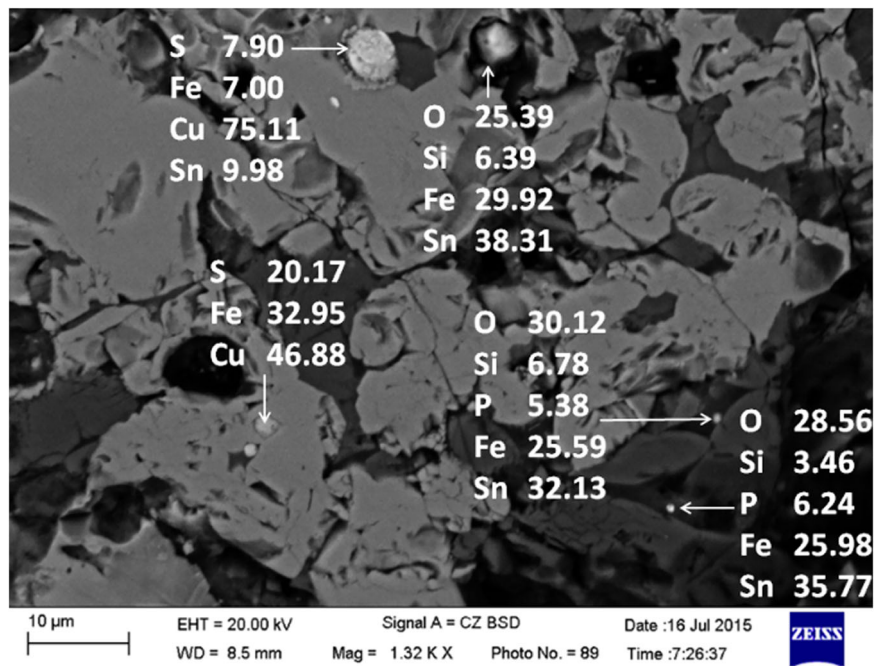


Fig. 9 | Particles of tin bronze and tin-iron minerals in the 24501.



metallurgical processes, slag classification, and the influence of refractory materials or ore (fluxing agents). For example, Ilaria(2023) conducted a comparative analysis of the matrix compositions of copper smelting slag alongside refractory and ore components at the Taldysai site in central Kazakhstan<sup>9</sup>, dating to the 2<sup>nd</sup> millennium BCE. Similarly, Veldhuijzen(2006) compared the matrix compositions of iron smelting slag and wrought iron slag with refractory components at the Hammeh site in Jordan and the Beth-Shemesh site in Israel during the early 1<sup>st</sup> millennium BCE<sup>10</sup>. Also, Iles (2014) examined the matrix compositions of iron smelting slag with and without added flux at the Mwenge site in Uganda during the 14th century AD<sup>11</sup>. As shown in Fig. 11, the cumulative contribution rate of the excavated and field surveyed slag samples from the Guniushan city site

reached 80.2%. For the first principal component (PC1), FeO has the highest loading coefficient, followed by SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, indicating that these oxides have the greatest impact on PC1. For the second principal component (PC2), CaO and MgO demonstrate the highest loading coefficients, suggesting their predominant impact on PC2. Furthermore, although the red copper slag from both the excavation and field survey show a certain extent of overlap, the excavated samples display greater dispersion and greater impact by refractory-related elements such as Ca, Mg, Al, and K, whereas the field surveyed samples suffer greater impacts from ore-related elements, particularly Fe. FeO, which is associated with ore formation, exhibits positively or negatively correlations with Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O (both refractory-related) as well as SiO<sub>2</sub> (related to refractory or ore). Thus, the above results

Fig. 10 | Tin bronze particles in the 24501.

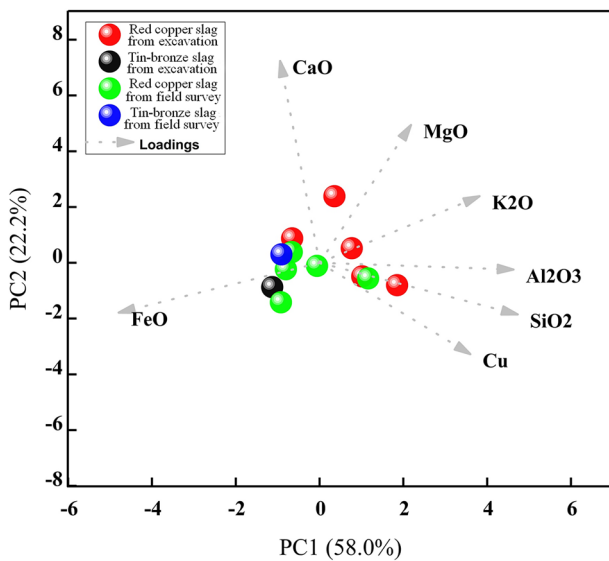
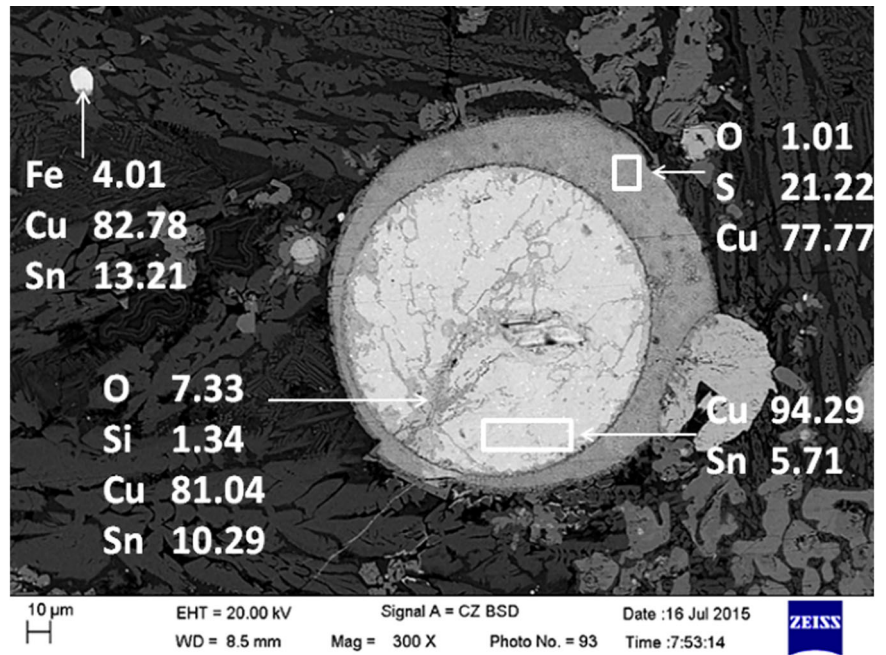


Fig. 11 | Principal component analysis of metallurgical relics from the Guniushan city site.

indicate that the system FeO-SiO<sub>2</sub> slag from the Guniushan city site was influenced primarily by the ore component, whereas the system SiO<sub>2</sub>-FeO (Al<sub>2</sub>O<sub>3</sub>) slag was more significantly affected by the refractory components, with potentially limited samples from both excavation and field survey. Similarly, the Xiajiadun site (see Fig. 1), located near Guniushan, also yielded the system FeO-SiO<sub>2</sub> slag, and the lead isotope analysis indicates that the raw materials were sourced from local copper deposits<sup>5</sup>.

Notably, within the Category 1 slag samples from the Guniushan city site, copper-rich phases and magnetite phases, which are commonly found in both copper smelting and copper melting slag matrices, can be observed. Archaeometallurgical studies conducted in the Central China, the middle and lower Yangtze River, and the Qurayyah site in Saudi Arabia have discussed the technical differences between copper smelting slag and copper melting slag<sup>5,12,13</sup> and their findings indicate that copper melting processes generally occur in crucibles, producing slag characterized not only by relatively elevated levels of calcium, silicon, aluminum, and copper but also

by distinctive matrix phases. The partial slag samples from the Guniushan city site (24491, 24493, 24495) belong to the system SiO<sub>2</sub>-FeO (Al<sub>2</sub>O<sub>3</sub>) with comparatively high copper contents; however, their classification as copper melting slag remains inconclusive: (1) Although magnetite (Fe<sub>3</sub>O<sub>4</sub>) and copper-iron phases associated with the oxidizing atmosphere are evident in the slag matrix, the polular phases of copper melting slag, such as copper ferrite (CuFeO<sub>2</sub>) and hercynite (FeAl<sub>2</sub>O<sub>4</sub>), have not been identified. (2) The entrapped copper particles are predominantly rounded, with no irregularly shaped copper particles in typical copper melting slag or cuprite (Cu<sub>2</sub>O) phases formed under strongly oxidizing conditions. The Category 1 slag from the Guniushan city site should be linked primarily to smelting activities.

For the bronze metallurgical process at the Guniushan city site, which draws upon archaeometallurgical research conducted in the middle and lower Yangtze River<sup>5</sup>, it is posited that the red copper slag obtained from excavation and field survey (see Table 1) are considered products of the same smelting process: first, after the copper liquid formed during smelting, a large quantity of Category 1 slag was removed; subsequently, tin was added into the furnace holding the copper liquid to produce bronze, resulting in the discharge of a small amount of Category 2 slag, which contains particles of tin bronze or lead-tin bronze.

The discovery of the Yejiashan site in Hubei Province offers valuable archeological evidence for understanding how the regional cultural center operated and administrated copper, tin, and other metal resources by the Western Zhou Dynasty (ca. 1100 BC ~ 800 BC) in the middle Yangtze River<sup>14</sup>. In the lower Yangtze River, numerous large-scale early mining and smelting sites are found in Southern Anhui, indicating a relatively complete bronze industry chain, characterized by distinctive local metallurgical techniques. Multiple lines of evidence indicate that the Guniushan city site, as a significant stronghold or regional center of local bronze culture in Southern Anhui, is closely associated with the prosperity and advancement of local metallurgical civilization. Well, how could we transcend the technical analyses and integrate a city perspective to understand the significance of metallurgical history for the Guniushan city site in depth? In other words, what were the mechanisms that enabled the large-scale bronze production system in Southern Anhui to maintain consistent and sustained operation? This will be analyzed from the following three perspectives:

The first perspective is concern about city site and metallurgy diffusion. Early city sites played a crucial role in facilitating the exchange and

promotion of metallurgical techniques among small to medium-sized settlements and across wider regions. Beyond the Guniushan city site, numerous small and medium-sized settlements in Southern Anhui engaged in household-scale production of tin bronze and arsenic bronze<sup>5</sup>. At some sites<sup>5,6</sup> such as Shigudun and Xiajiadun in Tongling City, Tangjiadun in Zongyang County, and Tianningzhai in Qianshan County, ceramic molds for casting ritual vessels have been found. The bronze industry pattern in Southern Anhui contrasts with that in Central China<sup>15,16</sup> where bronze casting technology was predominantly centralized within major city centers. In Southern Anhui, however, small and medium-sized settlements were also able to produce tin bronze and ritual vessels. Additionally, local craftsmen also recognized the metallurgical properties of copper, tin, and lead, enabling them to regulate the ratios of tin and lead according to the intended vessel type. For example, during the Western Zhou Dynasty to the Spring and Autumn Period<sup>17,18</sup> weapons typically comprised copper-tin binary alloys, whereas ritual vessels often incorporated Pb to the casting of intricate decorative patterns. The relevant cases include Spear No. 86006 (20.7% tin) and Vessel No. 86025 (21.7% tin, 1.8% lead) from the Qianfengshan mound tombs in Nanling County of Southern Anhui; also include Spear No. 28 (20.1% tin, 3.4% lead) and Basin No. 51 (18.5% tin, 2.8% lead) from the Wangjiashan tomb in Zhenjiang City, Sickle No. 2 (17.0% tin, 6.2% lead) from the Bingxisheng site in Kunshan City, and Tripod No. Z14 (22.2% tin, 5.9% lead) from the Qinglongshan tomb in Dantu City, in the Wuyue culture region. These artifacts exhibit consistent technical characteristics, with a tin content of approximating 20% (even higher than the 10% of Andronovo culture<sup>19</sup>) and a relatively low lead content. This high-tin alloy tradition in the lower Yangtze River not only reflects the advanced manufacturing levels of local bronzes but also indicates the presence of an extensive technological exchange network built by the city sites. Entering the Spring and Autumn Period (ca. 800 BC ~ 500 BC), metallurgical technology in the lower Yangtze River almost reached its peak, underpinned by abundant local mineral resources, especially weapon techniques and alloy preparation, such as stripes, high tin contents, double hoops, or composite techniques of swords<sup>20,21</sup> which had been absorbed by other regional cultures such as Chu and Qi through the Yangtze River and Huai River Basins.

The second perspective is concern about city site and copper-tin resources assignment. The redistribution and reproduction of metal resources to areas of scarcity, facilitated by early city centers, was a critical mechanism in local social complexity. More and more metallurgical relics<sup>22</sup>, coupled with lead isotope analyses of bronze artifacts, provided a deeper understanding of the circulation of copper sources from Southern Anhui. These findings revealed that early copper materials in Southern Anhui not only met the local needs for bronze metallurgy but were also transported to the Wuyue cultural region in the eastern lower Yangtze River, as well as the Jianghuai region to the north (see Fig. 1). This form of material cultural interaction flowed in both directions<sup>1,6</sup>. In Southern Anhui, printed pottery or primitive porcelain from the Wuyue culture region, as well as handled vessels or angular-shouldered jars from the Jianghuai region are also common. Beyond that, the lead isotope analyses also revealed that copper materials from Southern Anhui during the Zhou Dynasty were supplied to early Central China and passed through the Jianghuai region<sup>22–24</sup>. The role of such a transfer station in the Jianghuai region was similar to that of the Zeravshan River Basin in Uzbekistan during the BMAC period (ca. 2300 BC ~ 1700 BC), which facilitated the flow of bronze resources from the Eurasian steppe to the oases in southern Central Asia and even as far as Mesopotamia<sup>25</sup>.

Tin is a crucial alloying component that enhances both the mechanical properties and the castability of bronze artifacts. Although bronze production occurs both inside and beyond the Guniushan city site, a technical difference may exist: the tin-bronze production prevails within the Guniushan from current evidence, whereas in the Shunan River and Huanghu River of Tongling City (see Fig. 1), the production of both tin bronze and arsenical bronze has been found among small to medium-sized settlements<sup>5</sup>. Combined with recent related research on the Kuro-Araks Culture in Caucasus and the Godin Tepe site in Iran<sup>26,27</sup> owing to the

relatively independent of culture, the lack of tin minerals and the pressing need for bronze in Southern Anhui, the addition of arsenic alloy materials for smelting arsenical bronze during this period may well be a conscious act, locally sourced, and its composition was effectively managed. Current research indicates that the arsenic bronze smelting or melting technology in Southern Anhui involved a two-step process<sup>5</sup>: first, smelting copper ores or melting copper materials, and then adding arsenic alloy materials to the furnace holding the copper liquid to yield arsenic bronze. In relative terms, the production feature of Guniushan, focusing on tin bronze, was likely based on its control over the core smelting and casting technologies, which roughly means that the early city site balanced the tin materials needed for bronze production in Southern Anhui. Situated more than 300 km from Southern Anhui, the tin mine area of northern Jiangxi Province plays a significant role in tracing the tin sources for the lower Yangtze River<sup>28,29</sup>. In Northern Jiangxi, the ancient copper mine of Ruichang City dates to the Mid-Shang Dynasty (ca. 1500 BC ~ 1300 BC), while early ceramic molds have been found at the Shihuishan site in De'an County and the Chenjiadun site in Gongqing City, which all indicate a good archaeometallurgy foundation<sup>16</sup>. Together, these findings point to a close connection between the tin sources for bronze vessels in the Yangtze River and the tin mining area in Northern Jiangxi, with the various waterways of the Yangtze River serving as crucial links. Recent scientific studies on bronze artifacts from sites such as Dahuzui in Hubei Province and Gaoshaji in Hunan Province have revealed early connections between tin materials used in the Yangtze River and tin deposits in Southern Hunan<sup>30</sup>. Since the current limited scope of tin archaeometallurgy work in southern China, more in-depth research needs to be carried out, particularly in Southern Hunan.

The third perspective is concern about city site and regional metallurgy administration. Although the early metallurgical sites in the ancient mining and smelting area of Southern Anhui were numerous and large-scale, the boundaries between living and production zones within them were blurred<sup>5,6</sup> featuring an immature social division of labor, highly concentrated technical processes, and a low degree of specialization. In other words, the personal attachment relationship of craftsmen was not strict, and they could engage in frequent technical interaction between settlements through personnel mobility, such as mining and exchange. Moreover, many small and medium-sized settlements, such as the Shigudun and the Xiajiadun, both in Tongling City, have discovered bronze casting or ritual vessel production, and the complex alloy compositions (including Sn bronze, As bronze, As-Sn bronze, Pb-Sn bronze, As-Pb bronze, and Pb bronze) are clearly different from those of typical government workshops in early Central China, which comprehensively demonstrate the local popularity of household-based metallurgy and imply that the city sites have relatively relaxed supervisory awareness of metallurgical production planning and bronze metallurgy.

In comparison, bronze metallurgy and ritual vessel production in early Central China were often monopolized at central sites or city sites located some distance from copper mines, such as the Erlitou site in Yanshi City, the city site of Shang Dynasty in Zhengzhou City, and the Beiyao site in Luoyang City<sup>15,31,32</sup> which were bronze casting sites in the pre-Qin period (before 221 BC). These sites were approximately 100 km away from the production base of copper materials in Zhongtiao Mountain during the Bronze Age<sup>33</sup>, reflecting that the level of bronze industry pattern in early Central China was more advanced than that in Southern Anhui. This phenomenon parallels that found in southwestern Iran around the late 3<sup>rd</sup> millennium BCE, where many tin-bronze artifacts were discovered at the Elamite capitals of Susa and Anshan<sup>34</sup>. As noted by Lesley (2010)<sup>27</sup>, this association is linked to tin-bronze's identity with a "high-status alloy", which was primarily utilized for elite settlements. Nevertheless, with the rise of indigenous culture and the permeation of Wuyue culture since the Western Zhou Dynasty, the mining sites, smelting sites, settlement sites, mound tombs, and the city site have been densely distributed in the ancient mining and metallurgical area of Southern Anhui. This is undoubtedly linked to the rapid development of the local metallurgical industry. From the macro-perspective, the Guniushan city site, which represents an interregional resource exchange center, may

have primarily played supervisory and coordinating roles in production operation, labor management, and product distribution. Furthermore, the widespread involvement of small and medium-sized settlements of Southern Anhui engaged in bronze smelting and casting indicates relaxed control of the mining and metallurgy industry by the early city, and the flow of metal resources to areas such as the Wuyue culture region and Jianghuai region shows improvement and development of commodity exchange. These factors collectively reflect more of the social nature and commercial characteristics of early metallurgical civilization in this region, which stands in contrast to the political property and insignia of power embodied in Central China's bronze industry pattern, which was shaped based on the maintenance of ritual hierarchies and consolidation of ties with the central royal region.

In Conclusion, the scientific research of bronze metallurgical relics unearthed from the Guniushan city site holds considerable scholarly significance for the study of early bronze metallurgy in the lower Yangtze River, where Southern Anhui lies. This study also provides a unique perspective for deepening our understanding of the relationship between the “mining-smelting-casting” bronze production chain and the management of metallurgical handicraft in this region. Furthermore, although the samples in this study are limited, they were obtained from formal excavation and field survey; the repeated detection of tin-bronze particles indeed confirms the existence of bronze metallurgical activities within the city site. Given the archaeometallurgy significance of this site, it is also recommended that relevant institutions conduct further excavation in the future. Briefly, the existence of the “city site” discussed in this paper should be intrinsically and closely linked to the establishment of an administrative center in the prosperous mining and metallurgical area by early states in the lower Yangtze River, and it also embodies the highest tier of the local complete bronze production chain, substantially enhancing the understanding of bronze metallurgy civilization in the lower Yangtze River.

### Data availability

The data is provided within the manuscript.

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### Author contributions

C.C.: analysis, field survey, conceptualisation, and manuscript writing; Y.L. (corresponding author): resources, manuscript review, and supervision; H.L.: field survey and manuscript revision; C.L.: field survey and manuscript revision; X.G.: sample collection and supervision; L.W.: sample collection. All authors reviewed the manuscript.

### Competing interests

The authors declare no competing interests.

### Additional information

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