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Primary research on the bronze technology of Lower Xiajiadian Culture in northeastern China

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Abstract

The site of Habaqila is located in the area between Inner Mongolia and Liaoning provinces and dated to the 13th–11th centuries BC. It was identified as a metal production workshop of the Lower Xiajiadian Culture and revealed abundant metallurgical remains, including ore fragments, slags, technical ceramics, and stone implements. Scientific analyses demonstrated that polymetallic ores were smelted to produce tin bronze and arsenical copper. Perforated furnaces might have been employed in this process. The site also revealed the first known field evidence of tin smelting in a Bronze Age site of northern China. Systematic investigation of this site increases our understanding of metallurgical processes of Bronze Age culture in northern China.

Keywords: Tin smelting, Cassiterite, Tin bronze, Arsenic bronze, Lower Xiajiadian Culture

Introduction

The archaeometallurgical studies in China can be traced back to the middle of the last century, and the exchanges between western academia and Chinese scholars have been increasing since 2000 [1]. The Eurasia steppe is considered as an important region of the introduction of bronze technology into ancient China, and our research is mainly focused on the early bronze cultures at the northern frontier of modern China [2]. To unveil the diachronic development of Bronze Age copper production technology in northern China, a series of archaeological reconnaissance and excavation activities were conducted in Chifeng, Inner Mongolia following the discoveries of the national archaeological survey. Although this region is not part of the ancient China proper, the understanding of Bronze Age cultures flourishing in this region could help to explain the origins of metallurgy in China [3] (Fig. 1). The scientific examination was applied in the archaeometallurgical study since the 1980s in China [4], which has provided a more detailed and accurate description of the materials for the discussion in a global perspective. The origins of metallurgical technology and the natural resource supply chain of Bronze Age northern China has been drawing more and more attention in tandem with archaeological studies [5]. The Lower Xiajiadian Culture (LXC from the 2nd millennium B.C to the 1st millennium B.C.) was one of the earliest cultures rising at the northeastern area of modern China and played an essential role in the early development of metallurgy in China during the 2nd millennium BC [6]. LXC's settlement pattern indicated a rather complicated social relationship involving intermarriage, defensive collaborations, resource exploration, and trade [7]. The bronze production technology of the LXC is represented by small artifacts, such as daggers and ornaments [8], and is considered closely related to the Zhukaigou Culture in central Inner Mongolia, and Qijia and Siba Culture in the Hexi Corridor [9], but sharply different from the Erligang Culture in the Central Plain [10]. The tin might have been deliberately added and varied in content for different types of artifacts [11]. The recent finds of mining and metallurgical remains in this region [12] suggested that local polymetallic mineral deposits might have been exploited by Bronze Age populations (Fig. 4). Based on pottery typology and radiocarbon analysis, several sites

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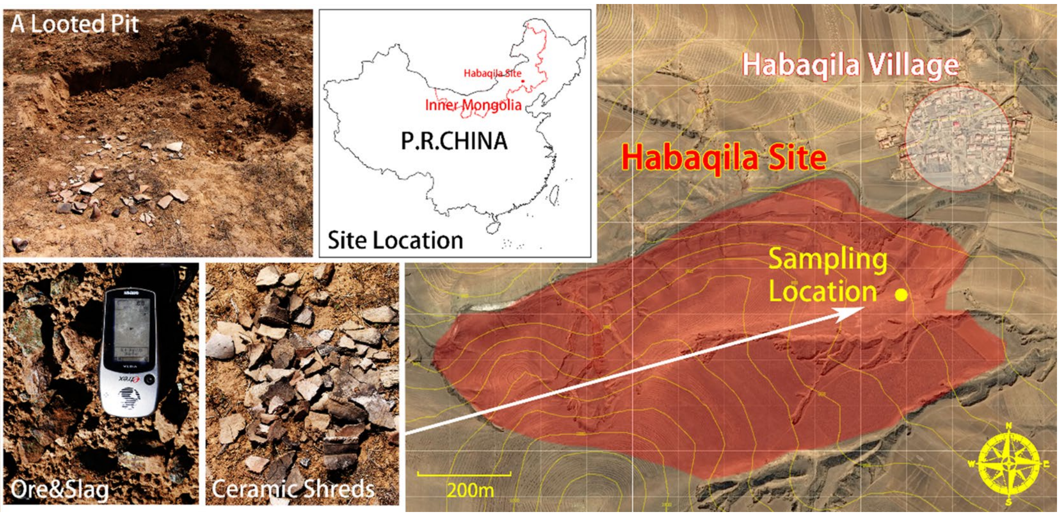

Fig. 1 The sampling and sites location

have been identified as active during the Bronze Age and are the main focus of this article.

Cassiterite has been considered as the only likely mineral resource used for tin production in antiquity all over the world, and cassiterite deposits are much rarer compared with the various and widespread copper mineral deposits [13]. According to modern geological databases, most of the substantial deposits of cassiterite are located in the south of China, so discussions about possible tin sources in northern China have never been systematically studied until researchers began to focus their attention on the tin-containing polymetallic deposits in the steppes of northern China, Mongolia, and Russia [14]. There are small scale cassiterite deposits that have been discovered in northern China by modern prospectors, but based on modern industrial assessments, most of the mineral veins in this region are too meager for cost-effective exploitation, and the scattered distribution without the benefit of a modern transportation network further reduces their commercial values [15]. However, the shallow depths of these deposits and cassiterite's high resistance to corrosion could endow certain lodes of cassiterite sand to form as sediments in the seasonal hydrographical system (alluvial ore) or surficial mineral vines (eluvial ore) with high potential for smelting. Short transport distances would have aided LXC prospectors and artisans in using these mineral veins for bronze production. Indeed, traces of ancient mining and smelting activities have been recorded in the region, In addition, the availability of poly-metallic minerals containing copper, tin, and arsenic provides the prerequisite conditions for the smelting of diverse bronze alloys, but the actual production techniques—which would be in part driven by efficiency, trading conflicts or other socioeconomic circumstances, or based upon the demands of certain political or religious purposes, would need solid evidence like that recovered from Habaqila site to reconstruct convincingly the full metallurgical repertoire.

Site background

This research was mainly focused on a Bronze Age sites called Habaqila named after the most nearby village. The village was administrated by the Yuzhoudi Town Government of Hexigtan Banner. The site was discovered during an archaeological investigation near the copper and stannous deposits recorded by modern prospection. There are three tin polymetallic mineral vein deposits around the Habaqila site, and in a bigger geo-range, this region should be considered as a mineral concentration zone (Fig. 4). Additionally, several contemporaneous sites with lithic mining tools and ancient mining relics (Fig. 4) have also drawn more attention to the potential for archaeometallurgical studies. These include the Xiqegou site, which has been systematically excavated and described as a seasonal mining settlement of LXC [16], and the Yihewomente site with dozens of mining pits, plenty of lithic mining tools, and surficial sediment of the tin mineral vein.

The Habaqila site is located aside the wadis of two major seasonal rivers, the Xar and Tsagaan Rivers. The core of settlement is located hundreds of meters southwest by the modern Habaqila Village, Hexigten Banner of Chifeng City. The archaeological remains are mainly distributed on the ridge of small hills (Fig. 1). Discovery of the site connected as a few pottery sherds and metallurgical wastes were unveiled during forest rehabilitation projects, followed by illicit looting in recent years by local grave robbers. After thoroughly cleaning several looting pits, followed by two archaeological surveys conducted at the site, pottery sherds, ore, slag, and animal bones were collected (Fig. 1). The depth of the looter pits was no more than 1.5 m, and no multiple cultural strata could be recognized by observing the cross-section of the pits. Most of the slag and ores were found from two of the pits, and few small pieces of slag and ore were found no more than 400 m away from the pits and almost all on the edge of the hillside. Diagnostic pottery sherds were collected for typological identification. The other relics such as the ore, slag, bones, and sinter refectory matter were all collected together for further examination in the laboratory. About twenty pieces of slag, dozens of animal bones, and pieces of burnt soil were found after the cleaning up of the looting pits. The greenish and bluish ores with dark brown minerals were all in handful sizes, most of the ore compositions were determined through qualitative analysis with portable XRF, while more than thirty ores were collected, and twelve samples of both slag and ore were picked up for further an alysis (Figs. 2, 3). Although the detailed context of the site could only be reconstructed after systematic excavation, the slag as metallurgical wastes should not be moved far from the smelting location. Additionally, the finding of the copper ore together with the slag was the most convincing evidence for the smelting activities which might suggest high-temperature metallurgical activities.

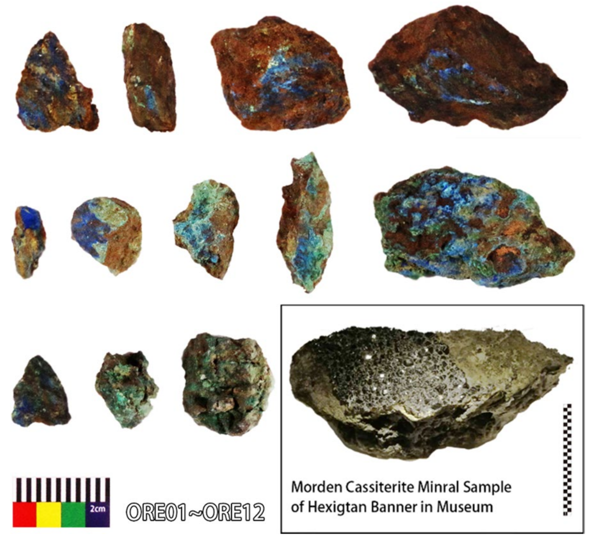

Fig. 2 The ore samples and modern cassiterite ore in the Habaqila region

Fig. 3 The excavated slag samples (no SLAG01 and SLAG09)

Analytical methods

26 samples were selected for analytical research. SLAG03 was identified as a vitrified furnace/crucible fragments without slag, and ORE01 and ORE11 contained too minimal mineral phases and therefore has been considered as gangue samples. Most of the samples were unearthed artifacts from the looting pits, whereas two slag and three ore samples were collected near the pits so therefore linked contextually to the looters' pits but without stratigraphic context.

The pottery sherds typology analysis was conducted by the Archaeology Institution of Jilin University. The bones associated with slag were sent to the School of Archaeology and Museology, Peking University for AMS (Accelerator Mass Spectrometry) ^{14}C dating (Laboratory No.: BA160698 and BA160699). Two well-preserved animal teeth were examined, and wood samples were subjected to radiocarbon calibration conducted using Oxford University Oxcal software v4.3 (Fig. 5). The slag and ore samples were mounted with epoxy resin and polished following standard archaeometallurgical procedure. Scanning electron microscopy coupled with energy X-Ray dispersive spectroscopy (SEM–EDS) analysis was conducted with a TESCAN VAGA3 XMU SEM equipped with a BRUKER XFlash Detector 610 M EDS Analyzer, in the Institute for Cultural Heritage and the History of Science & Technology, University of Science and Technology Beijing. Ten polymetallic ores samples (Table 1) were powdered for XRD (X-ray Powder Diffraction) and XRF (X-ray Fluorescence) analyses at the State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University. The crystallographic information was characterized by a RIGAKU powder X-ray diffractometer, D/

Table 1 Sample information

Sample	Method	Identified matter	Sample	Method	Identified matter
SLAG01	Unearthed	Refractory and slag	ORE01	Unearthed	Gangue
SLAG02	Collected	Slag	ORE02	Collected	Polymetallic ore
SLAG03	Unearthed	Refractory	ORE03	Unearthed	Polymetallic ore
SLAG04	Unearthed	Slag	ORE04	Unearthed	Polymetallic ore
SLAG05	Unearthed	Refractory and slag	ORE05	Unearthed	Polymetallic ore
SLAG06	Unearthed	Refractory and slag	ORE06	Unearthed	Polymetallic ore
SLAG07	Unearthed	Slag	ORE07	Unearthed	Polymetallic ore
SLAG08	Unearthed	Slag	ORE08	Collected	Polymetallic ore
SLAG09	Unearthed	Refractory and slag	ORE09	Unearthed	Polymetallic ore
SLAG10	Unearthed	Refractory and slag	ORE10	Unearthed	Polymetallic ore
SLAG11	Collected	Slag	ORE11	Unearthed	Gangue
SLAG12	Unearthed	Refractory and slag	ORE12	Collected	Polymetallic ore
CARB01	Unearthed	Animal molar	CARB02	Unearthed	Animal molar

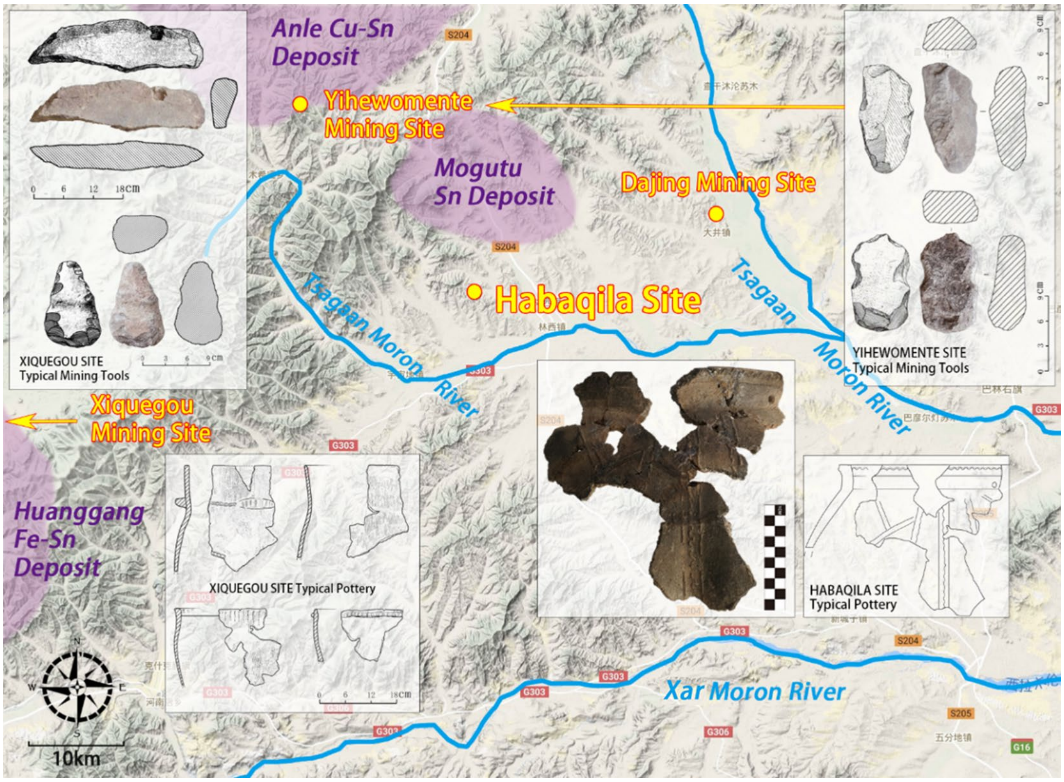

Fig. 4 Typical unearthed artifacts and mineral deposits around the Habaqila site

max 2500, with Cu Kα radiation (λ = 1.5418 Å) at 50 kV and 200 mA tube voltage and current, from 10 to 80° in 10°/min. Besides, the elemental composition was investigated by X-ray fluorescence using a PANalytical AXIOS wavelength dispersive advanced XRF spectrometer with a rhodium tube as the source of radiation at a 60 kV voltage and 50 mA current.

Results

Chronology

The pottery typology analysis has confirmed the Habaqila site was occupied by the Lower Xiajiadian Culture (LXC), similar to the Xiquegou mining site. The 'Snake Pattern' pottery (Fig. 4) found together with slag is characteristic for the final stage of the LXC contemporary with the

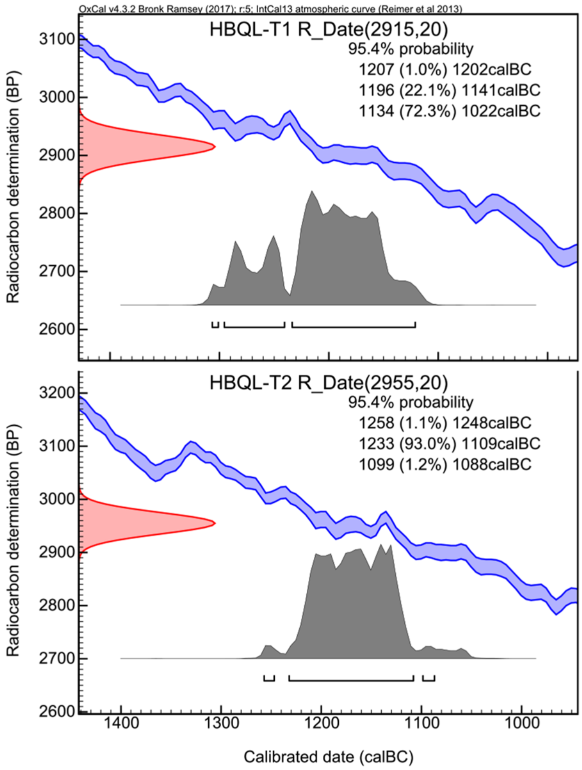

Fig. 5 Calibrated date of coexisting animal teeth with the oreand slag

Late Shang period in the Central Plain. Two bone samples have radiocarbon age between 13th and 11th centuries B.C. corresponding well with the pottery typology (1233 B.C.E to 1022 B.C.E Fig. 5). The pottery sherds at the site were rather simplex in typology aspect, especially the looted pieces which were identified as all belonging to the LXC.

Ore

All ore samples were mainly small with a greenish or blueish color with relatively high density. The sampling strategy was that of observing the semblance of the ore and picking up different pieces of samples by the approximated quantity of each category. P-XRF of the recovered ores showed Cu, Fe, and Sn content. The XRD analysis of ore samples showed the samples mainly consist of cassiterite, cuprite, bornite, marcasite, and other gangue minerals such as fluorite, quartz, mica, and feldspar (Table 2). According to the XRF results, most of the ore contents contain higher than 5% copper. Meanwhile, arsenic and tin were also commonly found with contents of both up to the level of 1%. In SEM–EDS images, the cassiterite particles in ore samples often inter-grew with paragenetic wolframite particles, and fluorite phases were found in almost all the ore samples (Fig. 6). This type of ore with cassiterite–wolframite intergrowth and fluorites were formed via mesothermal deposition and likely exploited by ancient workers for producing bronze [17]. SEM–EDS also revealed mineral phases rich in iron, copper, and arsenic in a mix with few pyrite phases (Fig. 6). These mix phases were found blended with different copper content but a similar iron and arsenic content phase. The higher copper content phases with lower oxygen level were deposited in mix texture forming heterogeneous patterns (Fig. 7). The morphology of the ore samples has indicated rather different features among them, but the elemental contents and combination thereof in the samples were relatively alike. So, the diversity of the semblance, especially in color, could be caused by weathering after mining.

Since there was hardly any primary mineral residual in the samples, all the ore samples could be considered as secondary enrichment sedimentation of copper, arsenic and stannic minerals. Copper and arsenic minerals were basically forming mixed oxides with heterogeneous texture. Cassiterite was the only stannic mineral with relatively even distribution and fractures filling with copper and arsenic minerals (Fig. 6). In general, the contexture of the ore was fragile and would have been susceptible to mechanical disruption.

Slag and vitrified furnace/crucible fragments

All 12 samples classified as “Slag” were combinations of slag and vitrified furnace/crucible fragments. But only the SLAG01 and SLAG09 could be directly recognized as two furnace/crucible fragments with sintering surface and a thin layer of slag (Figs. 8, 9). Other samples were divided into two types after the observation with SEM (Table 3). Type A slag was dark brownish little pieces with porous structure and the slag matrix phase was the dominant part of the sample. Type B samples, to the contrary, were mainly vitrified furnace/crucible fragments or other refractory materials with brown or pale grey sintering surface or a thin layer of slag.

The EDS data showed similar silica slag matrix with high aluminum, calcium, and iron contents. There was huge data fluctuation on silicon and iron contents, and both tin bronze and arsenical copper prills could be found within the matrix (Table 4). Arsenic bronze prills are the dominant alloy inclusion in most samples, and tin bronze could only be found in SLAG02 (Fig. 10). Apart from tin bronze prills, tin oxide particles were also identified in SLAG02. The arsenic content in prills varies from 5% to more than 30%, while the tin contents were mostly under 5% (Fig. 11). The bismuth and silver particles were found concentrated in particles and distributed in several bronze metal phases. The

Table 2 The XRF and SEM/EDS analysis of the ore samples

	Sample	ORE02	ORE03	ORE04	ORE05	ORE06	ORE07	ORE08	ORE09	ORE10	ORE12
XRF normalized data[a]	O	61.06	74.93	62.58	68.01	60.43	57.55	53.60	40.15	53.00	64.54
	F	3.59	0.00	1.56	0.00	0.00	1.47	0.00	3.27	0.00	0.00
	Al	1.50	3.63	3.28	0.41	0.88	2.25	3.72	0.64	4.01	1.73
	Si	3.97	6.89	11.18	6.48	2.63	8.30	11.19	2.99	9.13	3.77
	K	1.02	2.50	4.18	0.31	0.47	1.97	0.27	0.28	3.52	0.24
	Ca	10.90	0.22	3.72	0.18	2.40	3.60	0.88	12.97	0.79	0.75
	Fe	9.24	9.98	7.06	10.54	25.72	11.28	17.41	3.46	16.62	11.60
	Cu	6.14	0.99	5.69	7.08	5.05	6.16	9.77	30.67	6.60	7.65
	As	1.04	0.00	0.77	0.17	2.34	0.73	3.12	5.35	0.60	1.09
	Sn	1.54	0.87	0.00	6.82	0.09	6.69	0.04	0.21	5.75	8.61
	Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
SEM–XRD[b]	Sn + O	Cassiterite	Cassiterite		Cassiterite		Cassiterite			Cassiterite	Cassiterite
	Fe + W + O	Wolframite			Wolframite		Wolframite			Wolframite	Wolframite
	Ca + F	Fluorite		Fluorite			Fluorite		Fluorite		
	REE + P		Monazite				Monazite				Monazite
	Oxide	Fe + Cu + As	Fe + Cu	Fe + Cu+As	Fe + Cu	Fe + Cu+As	Fe + Cu + As	Fe + Cu + As	Fe + Cu + As		Fe + Cu + As
	Sulfide	Fe + Cu		Fe + As	Cu + As	Fe + As			Cu + As	Fe+Cu	

[a] Some elements had been eliminate considering the low contents and pollution

[b] Parts of minerals like Cassiterite and Fluorite could be characterized by XRD analysis others were determined by EDS data and morphology of SEM features

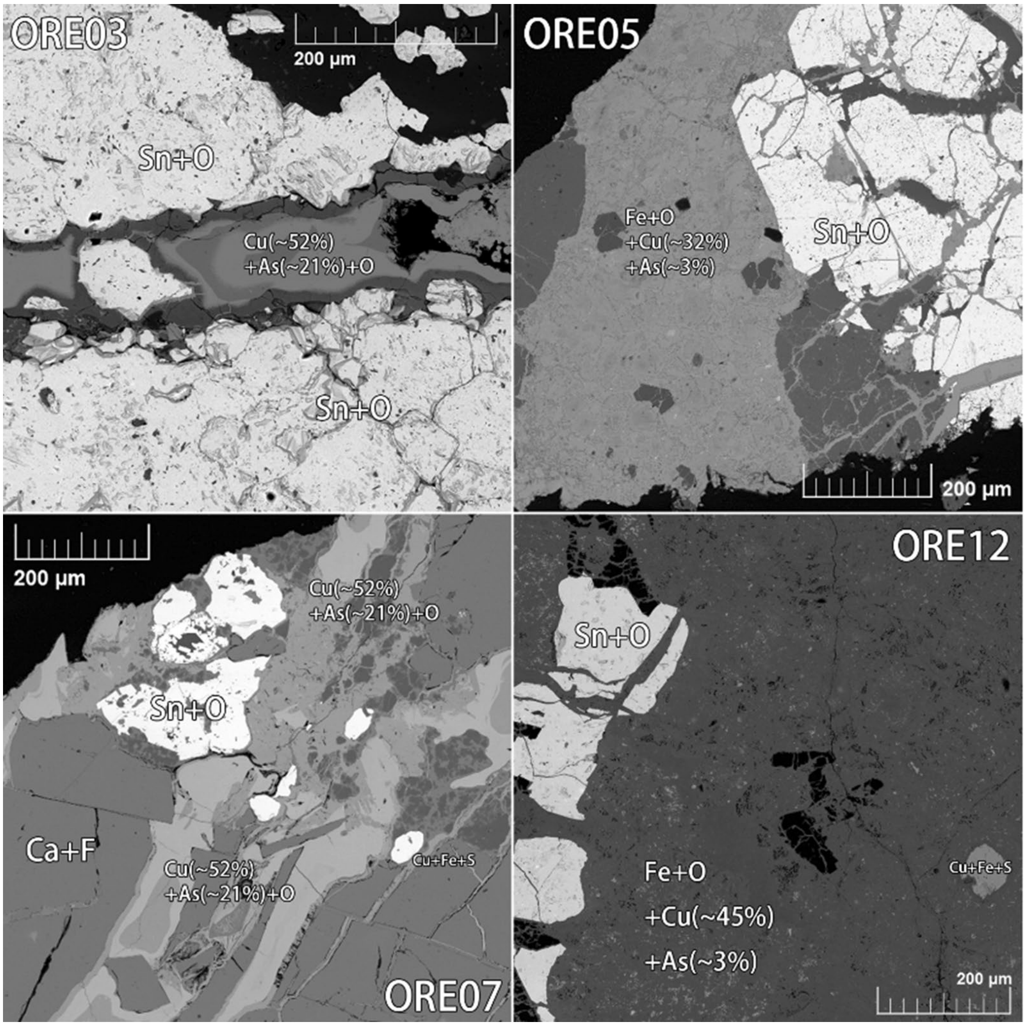

Fig. 6 SEM–EDS micrographs of ores

lead particles were not only found coherent within the Type A samples SLAG04 and SLAG08 but also in the adherent slag of SLAG06. The complex chemical concentration of metallic prills in these samples indicated that the polymetallic ore might be smelted to extract metal with varied tin and arsenic content (Table 3). These samples have demonstrated a bronze smelting process with roundish barely oxidized metal droplets and rather typical reducing slag matrix. The absence of unreacted particle and copper oxide phases suggests that the smelting was conducted in an ideal condition. Although it might be confusing that the roundish inclusion of SLAG07 (Fig. 11) contained relatively high levels of iron and tin in irregular morphology, there was no any other trace of this kind of slag in the following sampling and investigation, and thus it should be treated as an exception in this research. So, SLAG07 might be an exception since its texture is relatively heterogeneous and reflects a less successful smelting event.

Crucible/furnace (Type B) samples were made with non-refractory clay and tempered. Most samples were semi-vitrified at the side close to the lining while gently sintered at the other side, indicating they were heated from above/inside. The slag linings contain many tin oxide crystals and metallic tin prills but no Cu, Pb, or As in sharp contrast to slag samples. BSE images show fine rounded metallic tin droplets dispersing in a fayalite lattice (Figs. 8, 12) and occasionally wolframite crystals in tin oxide clusters (Fig. 8). Semi-reduced or recrystallized stannic oxides were also identified in slag, suggesting cassiterite might be the original ore charged into the crucible. The silicate matrix of slag lining is dominated by the low iron content (less than 5 wt% in weight percentage) and high calcium content (20 wt% in average content) glass but rather heterogeneously distributed (Table 3).

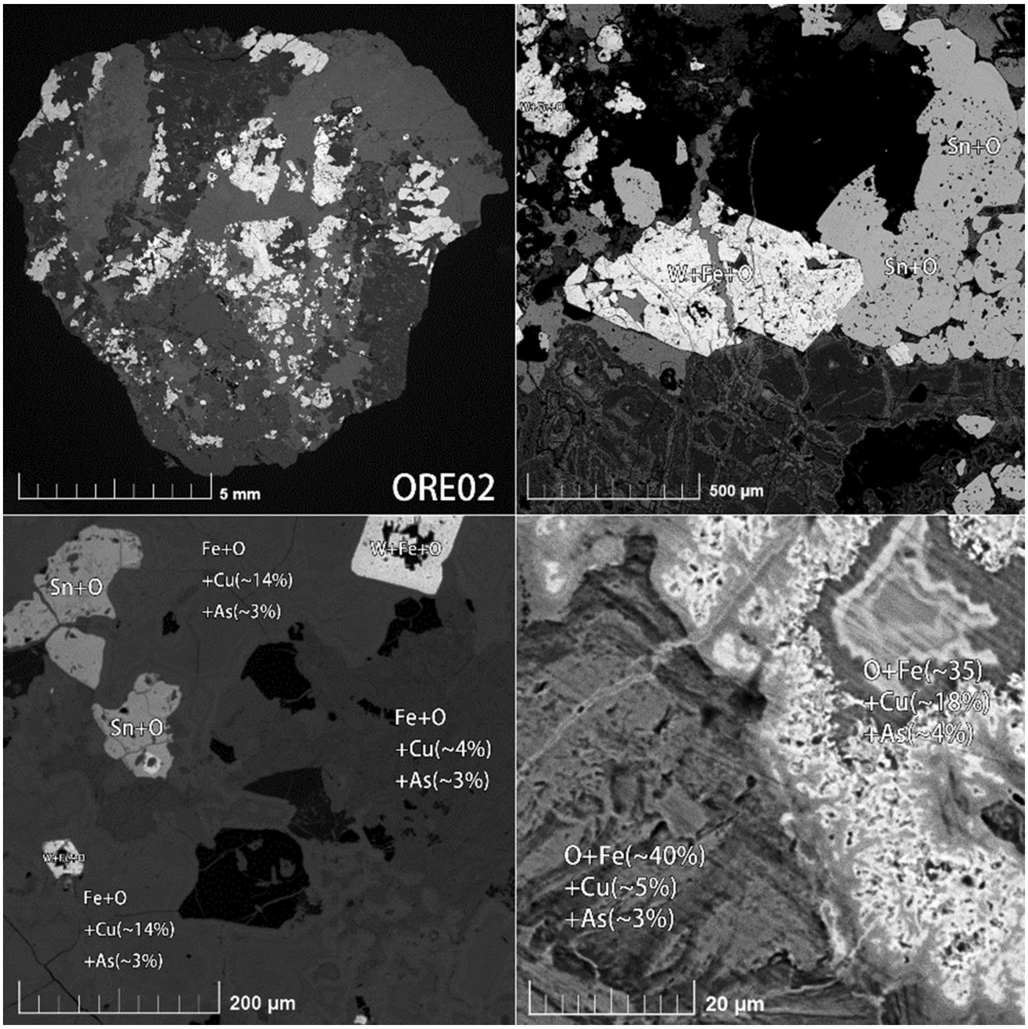

Fig. 7 SEM–EDS micrographs of ORE02

Lathe-shaped fayalite crystals and were also identified in a certain area of the lining. The ubiquity of metallic tin prills rather than tin oxide suggests these samples were involved in a reduction rather melting and oxidizing process. The find of wolframite is a strong indicator of cassiterite ore was employed since two minerals are commonly intergrown in ore deposits. The tin oxide formed by re-oxidizing tin metal would however not contain wolframite. The absence of Cu indicates that it was not a co-smelting or cementation process widely identified at bronze casting sites Tin ores were more likely smelted directly to produce metallic tin. No evidence for tin recycling in the furnace/crucible lining found in our samples [18]. The high content of calcium oxide could be related to the abundance of calcium minerals such as fluoride in the gangue which could provide a rather reasonable basicity, but without Sn-W-Fe metal phase found in the slags, the mild thermal circumstances under 1200 °C [19] could be the major factor affecting the heterogeneous distributions of the slag matrix. Some residual stannic oxide clusters were still in the shapes of cassiterite (Fig. 12), which could also infer high viscosity conditions of the smelting process.

The highly heterogeneous slags were commonly found in crucible smelting technologies, but whether the perforated ceramic was crucible or furnace fragments could not be determined since the pieces were too incomplete for reconstruction. Nonetheless, similar relics found at another important smelting site, Niuheliang [20], with perforated fragments considered representing the typical metallurgical techniques of the LXC, could be reconstructed into middle-scale furnaces (Fig. 9). The

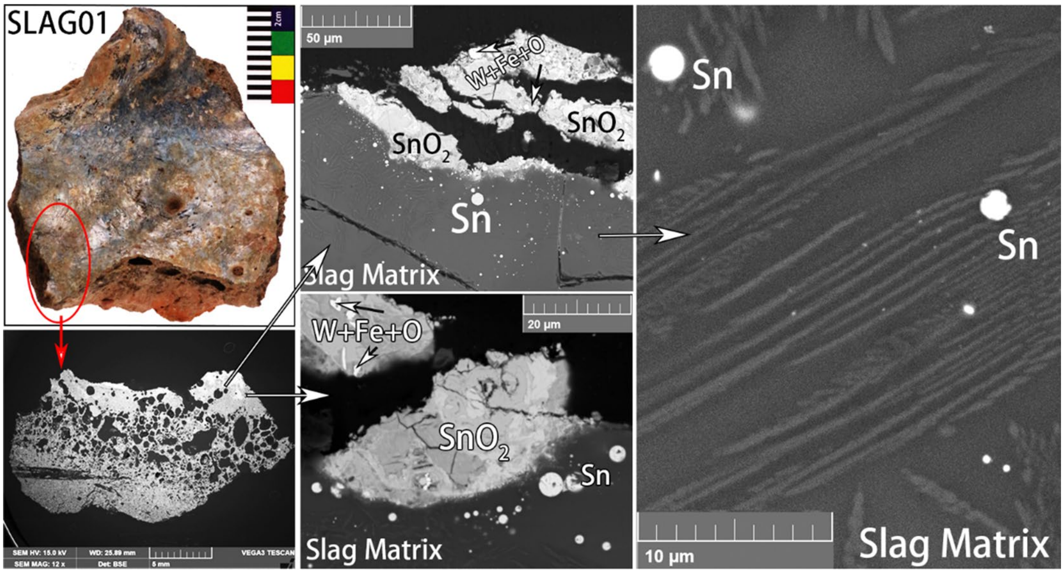

Fig. 8 SEM–EDS micrographs of SLAG01

perforated furnace was believed to be a deliberate design which reflected social and technical decisions [21] which was broadcast within the Mediterranean region at the Bronze Age [22]. The perforated furnace could be a cultural feature of the LXC metallurgical techniques and implied a universal technological designing tendency for the temperature and reaction atmosphere controlling.

Discussion

By reviewing the matrix data of the Type A slag samples, there were obvious differences in the contents of silicate and ferrous oxides, while the bronze prills distribution and morphology was different from each sample. However, according to the laboratory work conducted for this study, the metal particles containing arsenic and copper could be detected in all the slag samples, while tin was absent in most of the Type A slag, and the distribution of other trace elements like silver and lead demonstrated no different patterns. There was no deliberate alloy portion control or process differences that could be identified, therefore, these differences between the slag matrices could be caused by the time of slag discharge during similar procedures or different isothermal or reducing conditions in the furnace. Parts of the slag matrix composition reached a reasonable viscosity and melted into the liquefied phase which yielded out the samples with streamline patterns, while others might be attached to the furnace lining and formed under non-ideal thermal conditions. The highly varied composition of metal prills in slag samples suggest that the smelting charge and furnace conditions were not carefully controlled and the product would have a relatively wide range of compositions.

Comparing the data of ore samples with the slag, the high arsenic content of the bronze prills might correspond well with the Fe–Cu–As ores found at the site. The mass ratio between arsenic and copper in ore could reach as high as 28%. These slags reflect a production process in which tin was barely involved. Interestingly, the published data of the LXC bronze artifacts from the Dadianzi cemetery site contained only tin bronze and pure copper with no trace of arsenic. Based on these data [11], it is traditionally argued that the LXC people did not use arsenical copper in contrast to the contemporary cultures in northwest China and the Eurasian Steppe [23, 24]. The investigation of the Habaqila site presented here has further enriched our understanding of the metallurgical activities of the LXC people. Considering the LXC's relatively widespread geographical distribution and long chronological span, their metallurgical technology might be diversified and subject to change over time. Different technological choices between Dadianzi and Habiqila might be explained by the chronological gap (c. 3500 BP for Dadianzi) or varied metallurgical traditions within a single cultural complex.

Crucible/furnace fragments represent a tin metal smelting process based on rather pure cassiterite. The high tin metal and cassiterite contents indicate a rather rough single-stage smelting procedure [25], comparing with the modern two-step melting, in which a free-flowing silicate-based slag rich in tin oxide is first produced and later carbothermally reduced resulting in a full recovery of tin. However, with high-grade raw materials, the two-step method may not be necessary since the yield of slag would be very little, as would be the tin loss

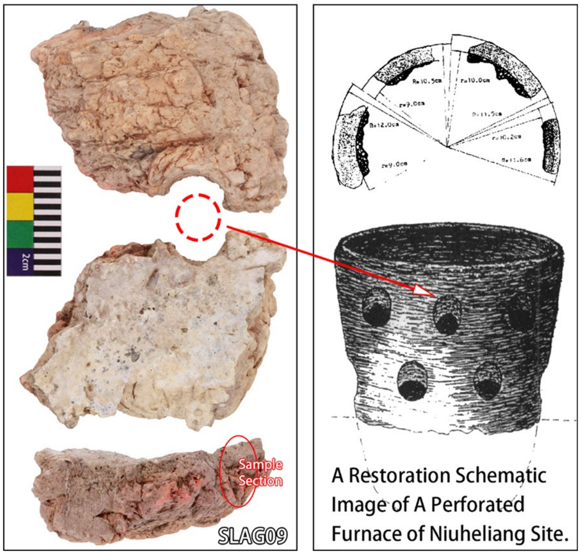

Fig. 9 The perforated sample SLAG09 and the restoration of the Niuheliangfurnace

in the whole smelting process [26]. Similar smelting technology could be able to reach a temperature over 1200 °C near the tuyere with a properly set-up blowpipe [27] connected by the holes on the furnace, theoretically [21]; but in practice, such temperature and atmosphere controls require very accurate operations and rich experience [28]. Also, a proper furnace lining, high-quality charcoal, and a well-beneficiated charge are crucial for the success of such a one-step smelting operation [26].

The absence of Cu and As suggest rather pure cassiterite was used in this process to produce pure tin metal. Type B slag attached to the crucible/furnace fragments would need such pure cassiterite deposits as the raw material recovered in our survey, or there could be natural methods, such like alluvial or eluvial deposits, or artificial methods to separate and purify the paragenetic ore for the smelting process. The residual wolframite particles and the cassiterite structure provide a connection between the polymetallic ore and the cassiterite smelting, which served as the first field evidence of tin smelting in the Bronze Age north China. Tin can be added to copper as tin metal or tin oxide. The latter way is also called cementation and tin oxide would be reduced simultaneously after being mixed with molten copper. Though dozens of Bronze Age copper smelting and bronze casting sites have been identified in China [29], none of them revealed clear evidence of how tin was added to copper. The importance of this new find is not only to prove that the technology of tin smelting had been mastered by the LXC people but has also suggested two different lines of metal production at this site. The directly reduced arsenical copper can be employed for casting objects at the site but the smelted tin might be alloyed with copper at other sites for tin bronze production. The separation of these two production lines indicates a rather complex production organization in the metallurgical industry. Different types of alloys might play varied social and economic roles, and therefore be produced in separated contexts. To further develop this argument, more analytical data of the LXC artifacts, especially those made with arsenical copper, is necessary.

The morphology analysis of the ore samples has shown the arsenic and copper minerals were tangled together, indicating that the separation of these two minerals would be almost impossible, but the cassiterite with independent mineral structure could be separated by mechanical crushing with lithic tools or natural corrosion and sediment. As observed in the ore, the wolframite and cassiterite were conjoined quite closely and their specific gravities (around 7) were alike, causing wolframite residue after the separation procedures in slag. Similar

Table 3 The EDS data of the slag matrix

Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	FeO	Total[a]	Type
SLAG02	1.4	0.6	10.9	58.2	0.0	2.7	6.1	0.0	20.1	100.0	A
SLAG04	3.4	1.4	9.9	56.8	0.0	2.5	11.8	0.0	14.3	100.0	A
SLAG05	1.1	0.0	12.4	35.7	0.3	1.3	6.8	0.0	42.3	100.0	A
SLAG07	0.1	0.4	7.7	35.0	0.0	1.1	12.4	0.0	43.0	100.0	A
SLAG08	1.5	0.7	10.3	58.9	0.0	2.5	7.5	0.0	18.6	100.0	A
SLAG11	1.9	1.1	12.2	51.1	0.0	1.9	10.3	0.0	21.6	100.0	A
SLAG01	2.7	1.7	13.5	64.2	0.0	4.6	8.9	0.7	3.8	100.0	B
SLAG06	3.9	1.4	9.6	50.0	0.9	2.2	24.1	0.0	7.9	100.0	B
SLAG09	2.7	1.9	13.6	60.9	0.1	2.9	14.3	0.0	3.6	100.0	B
SLAG10	2.1	1.4	12.2	72.0	0.0	3.5	4.9	0.0	3.8	100.0	B
SLAG12	2.0	1.5	12.5	66.6	0.0	3.5	8.9	0.3	4.6	100.0	B

[a] The oxides composition was converted from EDS data and normalized with experience

Table 4 The EDS data of the big bronze particles in type a slag

Sample	Bronze prill (wt%)							Total	Sample	Bronze prill (wt%)							Total
	O	Fe	Cu	Sn	As	Ag	Pb			O	Fe	Cu	Sn	As	Ag	Pb	
SLAG02	3.1	–	71.0	3.8	21.0	1.1	–	100.0	SLAG05	2.7	–	83.7	–	13.3	0.3	–	100.0
	7.0	–	67.6	4.2	21.1	–	–	100.0		2.9	–	66.9	–	30.2	–	–	100.0
	1.6	–	82.2	5.8	9.1	1.2	–	100.0		2.1	–	77.5	–	20.4	–	–	100.0
	2.3	–	73.5	1.3	22.9	–	–	100.0		4.1	–	72.6	–	23.3	–	–	100.0
	–	–	69.2	–	30.9	–	–	100.0		4.7	–	72.5	–	22.8	–	–	100.0
	1.2	–	70.9	1.2	26.7	–	–	100.0		2.0	–	93.0	–	5.0	–	–	100.0
	10.1	–	59.7	–	30.2	–	–	100.0		2.0	–	93.3	–	4.7	–	–	100.0
SLAG04	1.5	–	87.4	–	9.9	1.2	–	100.0	SLAG07	1.6	–	61.3	–	37.1	–	–	100.0
	10.5	–	86.8	–	2.6	–	–	100.0		1.5	–	59.7	–	38.8	–	–	100.0
	1.4	–	92.2	–	6.3	–	–	100.0	SLAG08	2.2	–	97.8	–	–	–	–	100.0
	2.5	–	85.7	–	10.4	0.8	0.7	100.0		1.5	2.0	71.4	–	24.1	–	1.0	100.0
	2.0	–	92.0	–	6.0	–	–	100.0		1.6	2.0	68.6	–	24.7	–	3.2	100.0
	0.9	–	93.4	–	5.2	0.5	–	100.0		1.7	3.3	91.6	–	–	–	3.4	100.0
	1.5	–	92.6	–	5.9	–	–	100.0	SLAG11	2.0	2.4	64.2	–	31.4	–	–	100.0
	12.2	–	86.7	–	–	1.1	–	100.0		1.6	1.4	66.2	–	30.8	–	–	100.0
	1.8	–	91.9	–	6.3	–	–	100.0		13.9	–	74.1	–	12.0	–	–	100.0
	2.0	–	90.9	–	7.1	–	–	100.0		1.2	5.1	55.4	–	38.3	–	–	100.0
	11.1	–	80.7	–	8.2	–	–	100.0		1.0	5.8	57.9	–	35.3	–	–	100.0

smelting strategy was found in Iron Age sites of Africa, utilizing similar ore resources with both cassiterite and arsenic-rich minerals [30]. As a result, the lithic grinding mortar (anvil) and other grinding tools, such as hammers, chisels and grinding balls (Fig. 4) unearthed from the Yihewoment and Xiquegou site could be rather crucial for these ore mining and refining activities.

The driving force behind this chosen strategy could be the demand for production of tin bronze, but there has been hardly any archaeological evidence for the tin metal, as none of the ingots [31], mining or smelting workshop sites were discovered before now. In this region, there has been no evidence for a sustainable pure tin source based on the large-scale tin mine exploitation in central Asia has been found [32, 33]. And the geological conditions and stannic ore sediment around Habaqila site were also quite different from the discovered mining sites [34]. So, the reason for the ore separation and tin smelting could be a compromise choice for the lack of pure cassiterite. The whole array of technical material culture, such as the lithic tools utilized for mining and grinding, and for the panning and beneficiation of the ore [35] could be an adaptation for this kind of polymetallic vein which even extended to the hinterland of modern Mongolia where more abundant mineral veins can still be found nowadays [36]. With sophisticated skills of ore treatments, both tin and arsenic bronze techniques could be developed with polymetallic ore. Production of handheld tools and small ornaments to assist in the resource extraction and metallurgical process would have been a high priority for LXC peoples, especially if pure tin or other metal products formed the basis for their desirability as a partner in long-distance exchange. The entire metallurgical process was likely embedded in technical and social decision-making of the LXC people in this region, just like the Shang people pursued high-efficiency mass production and enacted a mature supply system for the production of ritual bronze [37].

Conclusion

This primary research on the ore and slag unearthed at the Habaqila site has indicated different approaches to the bronze technology of the Low Xiajiadian Culture complex with dual processes of arsenic bronze production and pure tin smelting. The smelting slag proves that arsenic bronze could have been used and produced by the LXC people. Although to solve the puzzle of arsenic bronze technology systems in the northern fringe of China would need more data and evidence in future studies, but the analyzed samples had represented the assemble of sophisticated utilization of both arsenic and tin bronze technologies on polymetallic ore. This discovery could be a reasonable approach to enlight the following researches.

The exclusively tin smelting attaching slag of furnace/crucible fragment suggested there could be

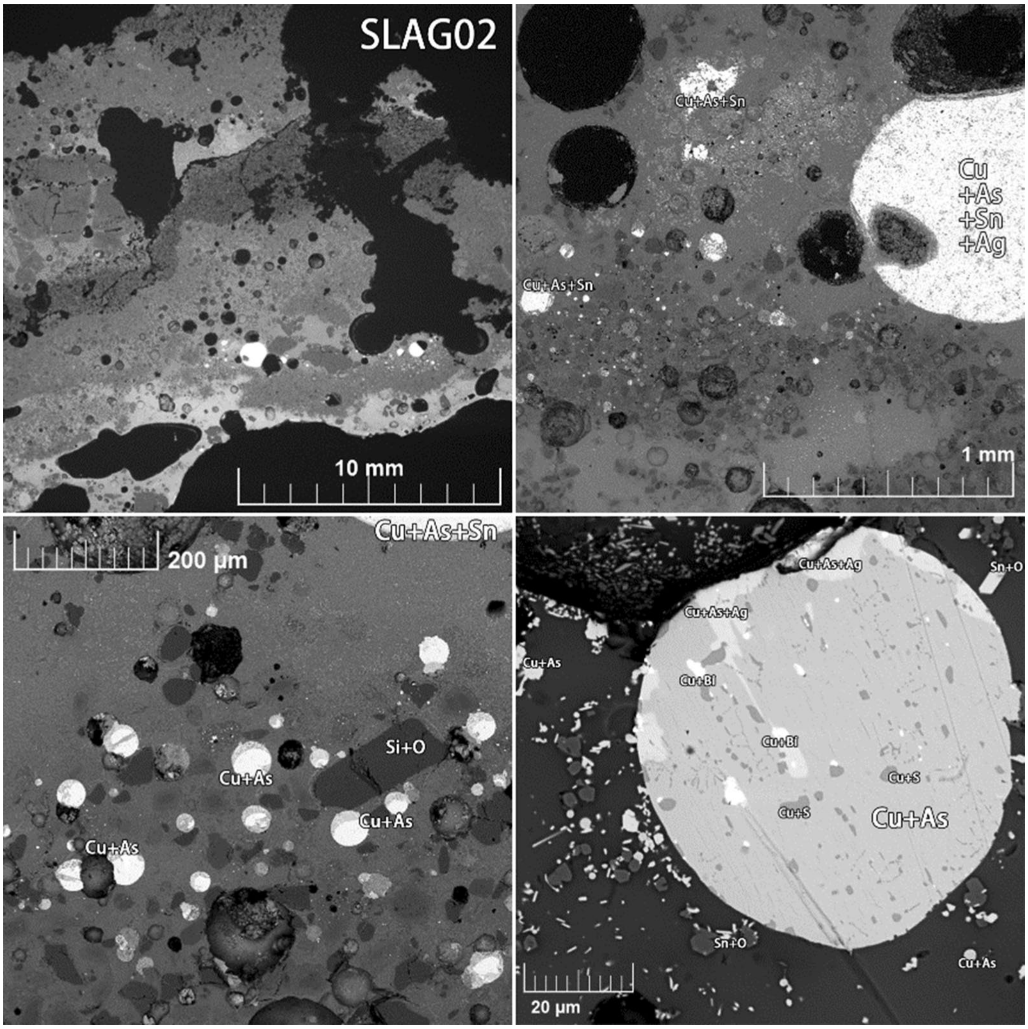

Fig. 10 SEM–EDS micrographs of SLAG02

undiscovered pure cassiterite resources in this region. Alternatively, the absence of pure stannic ore could indicate that pure tin metal was being smelted from polymetallic ores. And the polymetallic ore was separated by natural (alluvial and eluvial) or/and artificial process for cassiterite refinement and arsenic copper minerals beneficiation. The latter technique required recognition and mining of the tin, copper, and arsenic ore; the separation and beneficiation of the polymetallic ore; and the pure tin and arsenic bronze smelting of the whole technical package of bronze metallurgical activities. The features of each technique imply not only the technological preconditions but also socio-economic decision-making based on available sources and the cultural background. There would be two distinct lines of bronze production: one was for the production of arsenical bronze objects without alloy portion control, and the other was for a more compositionally tailored tin content in tin bronze objects based on the smelting of pure tin metal.

Considering the LXC has both a wide chronological and territorial span, to fully reconstruct the metallurgical technology of this culture would require a much more systematic survey and of metallurgical sites in this region. The technical diversity within a single culture could lead to many more processes being discovered. Understanding the social structure and hierarchy that underpins a given production chain, like the geological provenance of raw materials, the consumer and demand relationships, and choices behind given production strategies could also be addressed by further archaeological investigation. The encouraging findings from these poorly contextualized artifacts certainly invite future research into the LXC, situated in a crucial cultural and geographical region for

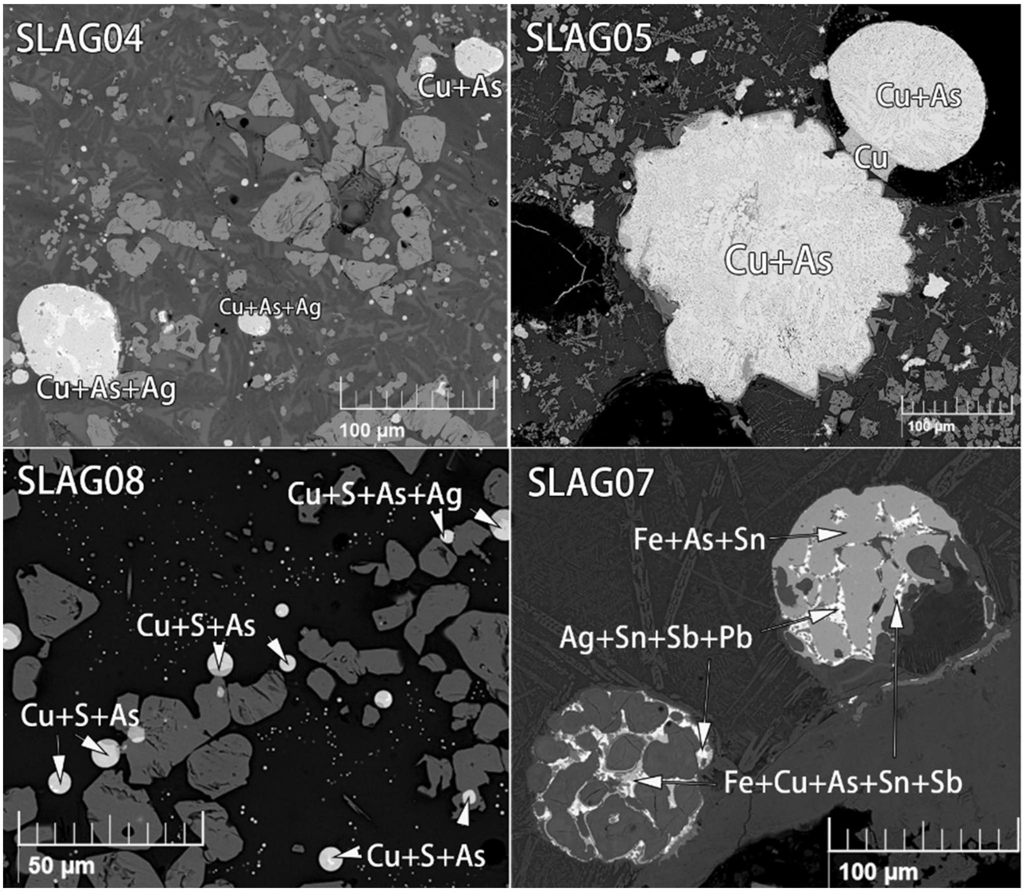

Fig. 11 SEM–EDS micrographs of arsenical bronze slag

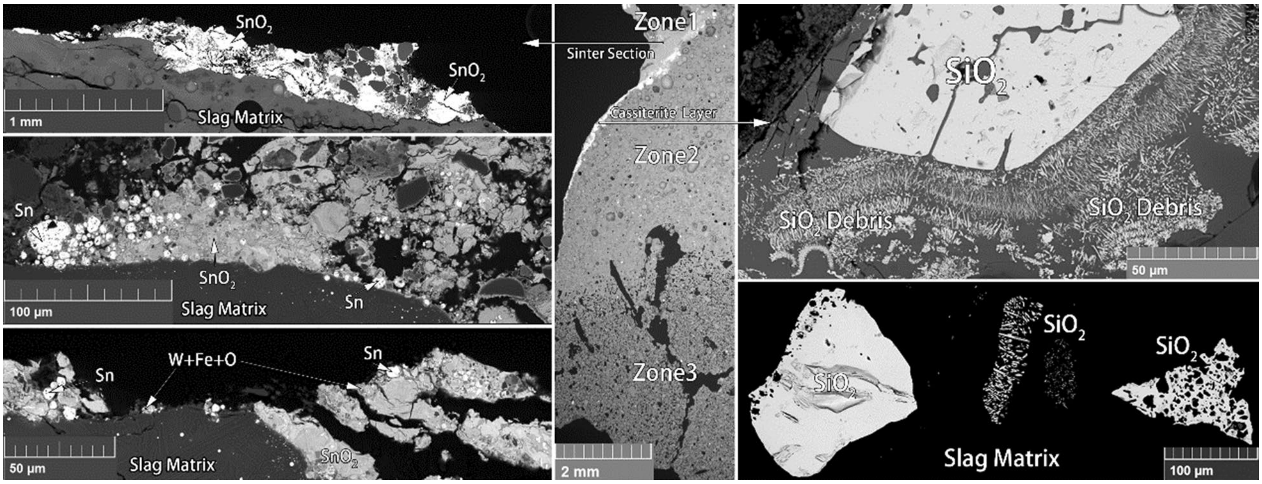

Fig. 12 SEM–EDS micrographs of SLAG09

understanding the spread and development of bronze metallurgy in the northern frontier of ancient China. We suggest that some of the former archaeometallurgical conclusions about the LXC should be reconsidered based on the evidence presented here, and also the huge special and chrono-span of Lower Xiajiadian Culture which could cause extra complexity of the issue. Additionally, the utilization of polymetallic ore, as well as the indications for the production of pure tin metal, could only be solved base on further fieldwork of the sites.

Abbreviations

LXC: The Lower Xiajiadian Culture; SEM–EDS: scanning electron microscopy coupled with energy X-ray dispersive spectroscopy; AMS ^{14}C: accelerator mass spectrometry, C14 dating; XRD: X-ray powder diffraction; XRF: X-ray fluorescence.

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Authors' contributions

YL is the leader of the programme and supervisor of CL. LW and YL are two of the major discoverers of the site. WL is also the chief archaeology counsel of this study. KC and SL have offered major aspects on the arsenic bronze and tin production, who are also supervisors of CL. CL is a major contributor in writing the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests.

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