Metallurgy at the Crossroads: New Analyses of Copper-based Objects at Tianshanbeilu, Eastern Xinjiang, China



LIU Cheng¹, LIU Ruiliang^{2, 3, *}, ZHOU Pengcheng⁴, LU Chun⁵, YANG Zengxin⁶, A. Mark POLLARD³, Peter HOMMEL⁷, MA Jian¹, CUI Jianfeng⁸, Peter BRAY^{9, 10}, TONG Jianyi¹ and Jessica RAWSON³

¹ School of Cultural Heritage, Northwest University, Xi'an 710069, China

² Research Center of Material Science and Archaeology, NPU Institute of Culture and Heritage, Northwestern Polytechnical University, Xi'an 710072, China

³ School of Archaeology, University of Oxford, Oxford, UK (OX1 3TG)

⁴ Xi'an Museum, Xi'an 710068, China

⁵ Shandong University of Finance and Economics Library, Jinan 250012, China

⁶ School of Electronic Engineering, Xidian University, Xi'an 710068, China

⁷ Department of Archaeology, Classics and Egyptology, University of Liverpool, Liverpool, UK (L7 7BD)

⁸ School of Archaeology and Museology, Peking University, Beijing 100871, China

⁹ British Museum, London, UK (WC1B 3DG)

¹⁰ Department of Archaeology, University of Reading, Reading, UK (RG6 6AB)

Abstract: Tianshanbeilu is the largest Bronze Age site in eastern Xinjiang, China. Stretching across the entire second millennium BC, it performed a prominent role in connecting the Hexi corridor, Central China and the steppe. A further insight into the metallurgical tradition and the metal supply network is of vital importance to improve our understanding of its multi-connected nature. This paper offers a new set of chemical and isotopic data on the copper-based objects at Tianshanbeilu, including alloying elements, trace elements (impurities) and lead isotopes. Combining the concentrations of arsenic and antimony reveals that arsenic was introduced to copper partially due to the use of specific minerals tethrahedrite -tennantite. Lead isotopes demonstrate that multiple sources of copper were employed at Tianshanbeilu and a majority of them are characterized by common lead, which appears rather different from those of the Central Plains and the Hexi corridor, but highly consistent with local ores. Surprisingly, one object at Tianshanbeilu contains the well-known highly radiogenic lead. This object undoubtedly marks the westernmost boundary of the distribution of the highly radiogenic lead. We also anticipate that more lead isotopic analyses in NW China will further contribute to the study of the highly radiogenic lead in Central China.

Key words: highly radiogenic lead, chemical and isotopic analysis, metallurgy, Tianshanbeilu

Citation: Liu et al., 2020. Metallurgy at the Crossroads: New Analyses of Copper-based Objects at Tianshanbeilu, Eastern Xinjiang, China. Acta Geologica Sinica (English Edition), 94(3): 594–602. DOI: 10.1111/1755-6724.14531

1 Introduction

Over the last fifty years, the excavations and investigations focussed on the eastern part of Xinjiang province in China have significantly advanced our understanding of the complex processes of interaction and exchange among the prehistoric communities of eastern Eurasia (Millard, 2007; Han, 2007). The rapidly increasing database of copper-based objects discovered in this area has not only aroused research interest in the technological traditions of prehistoric Xinjiang, but also provided critically important data to compare and contrast with analytical work conducted in Central China and the Eurasian steppe (Mei, 2000; Qian, 2006; Linduff, 2004). Such comparative studies are leading us towards a more complete picture of the processes by which metallurgical innovations were adopted and transformed within different local contexts, as well as their wider impact on contemporary society (Li, 2005; Mei, 2003; Kuzmina, 2007; Chernykh, 1992, 2017; Sherratt, 2006).

This paper presents a new set of chemical and isotopic measurements of the copper-based objects from the site of Tianshanbeilu in eastern Xinjiang, dating to the second millennium BC (Fig. 1). It fills an important gap in discussions of the introduction and uptake of metallurgy in eastern Eurasia and provides the first opportunity for scholars to combine data on lead isotopes, alloying elements and trace elements from the same objects in the study of archaeometallurgy in eastern Xinjiang. The overarching question in the current study is to explore the sources and the types of metal (particularly copper and lead) and the alloying technology employed at Tianshanbeilu. By combining new analytical results with

© 2020 Geological Society of China

http://www.geojournals.cn/dzxbcn/ch/index.aspx; https://onlinelibrary.wiley.com/journal/17556724

^{*} Corresponding author. E-mail: ruiliang.liu@arch.ox.ac.uk



Fig. 1. General distribution of the main Bronze Age archaeological cultures/culture-historical communities of the steppedesert zone showing possible typological relationships with the material from TSBL. (a-c) 2000–1500 BC: i) sites and materials attributed to the Andronovo culture; ii) sites and materials attributed to the Okunev/Okunev type cultures; iii) Main sites discussed in this paper (distributions collated from Mei and Shell, 1999; Kuzmina, 2007; Vadetskaya, et al., 2014); (a-c) 1500 BC: i)

iii) Main sites discussed in this paper (distributions collated from Mei and Shell, 1999; Kuzmina, 2007; Vadetskaya, et al., 2014); (a–c) 1500 BC: i) sites and materials attributed to the Karasuk and Irmen cultures; ii) general distribution of deerstone monuments with depictions of Karasuk-style artefacts; iii) sites and materials attributed to the Cordoned Ware horizon (distributions collated from Agapov et al., 2014).

existing data from the published literature (Mei, 2000; Qian, 2006; Han and Sun, 2004), it is clear that multiple alloy compositions were employed at Tianshanbeilu. The variation in both lead isotopic data and trace element impurity patterns suggest that the copper used in the production of the artefacts recovered from Tianshanbeilu was derived from multiple sources. This diversity, in both the alloying practices and sources of raw materials. helps to reinforce the interconnected nature of the site, already suggested in previous scholarship based primarily on typological analysis. A particularly significant result of the new analytical programme is the identification of a copper sample containing highly radiogenic lead (HRL) at Tianshanbeilu. This find at Tianshanbeilu marks the westernmost edge of the distribution of HRL in China, and significantly contributes to the puzzle of the use of HRL in China.

The Tianshanbeilu site is located in the modern Hami city, eastern Xinjiang (E 92°50'31", N 42°53'23"). It occupies a geographically important location as the next stop after Hami on the eastward journey is the well-known Hexi corridor. Tianshanbeilu was initially called the Linya Cemetery or Yanmansu Kuanglinchang Banshichu Cemetery. A series of excavations were carried out between 1988 and 1997 by local institutions, revealing 706 tombs and recovering more than 3000 artefacts, including pottery, copper-based objects, gold, silver, bones, stones, cowries, turquoise and glass (Gong, 1997; Shui, 1993; Chen, 1990). All of these materials are being recorded and characterized by Northwest University of China since 2016. Its chronological span is usually assigned to the second millennium BC. The importance of this site for our understanding of the archaeology of Eurasia is captured by Mei (2003) who describes it as 'pivotal... in bridging the early bronze cultures to the east and west.'.

The material culture at Tianshanbeilu consists of two major bodies of artefacts, pottery and copper-based objects. The repertoire of pottery, particularly the painted wares, provides a clear typological connection to those of the contemporary Siba and Qijia cultures in the Hexi

Corridor, strongly implying an eastern connection (Mei, 2000; Li, 2005; Han, 2007; Mei et al., 2015). An initial study of the metalwork from the site also supported this connection. The personal adornments and small implements which dominate the assemblage-earrings, bracelets, mirrors, beads, plaques, buckles, knives, awls, axes and tubes-show close similarities in typology to those recovered from Siba and Qijia sites (Qian, 2006; Mei, 2000). Similar alloying practices are also widely shared across these regions. Careful archaeometallurgical examination has attested the simultaneous employment of pure copper, tin-bronze, leaded bronze, arsenic copper and arsenic bronze, together with the techniques of casting, forging, annealing and cold-working in both eastern Xinjiang and the Hexi Corridor (Mei, 2000; Li and Shui, 2000; Li, 2002; Li, 2009; Jaang, 2015). However, the metalwork at Tianshanbeilu also shows connections stretching out to the north and west into the Eurasian steppe. Typologically speaking, the closest ties with neighbouring areas of the steppe are seen in the Late Bronze Age, associated with the late Andronovo and Corded Ware horizons in Eastern Kazakhstan and southern Siberia (Kuzmina, 2007: 265). In their initial review of this material evidence for contact between western Xinjiang and the steppe, Mei and Shell (1999) concluded that the eastern boundary of 'Andronovo cultural influence' may have reached as far as the Hami region. The finds from Tianshanbeilu may suggest a somewhat broader chronological pattern of contact. It has been suggested that general material categories seen at Tianshanbeilu find parallels with both the earlier Middle Bronze Age communities of the Sayan-Altai and the characteristic material of the Karasuk culture (Zhang, 2017). Except for the pottery and metals, other sorts of remains, though in much smaller quantities, illustrate some cultural communication with the similar nature. One carnelian bead discovered at Tianshanbeilu may indicate a connection to Central or even Western Asia (Rawson, 2010). Still wider networks, attested in the presence of numerous cowry shells-whose ultimate origins lie either in the Indian or Pacific Ocean-underline complexity and

extent of contemporary chains of exchange and communication (Bin, 2001; also see Vadetskaya et al. (2014) for a note of caution).

In addition to the material culture, archaeobotanical and isotopic analysis also places Tianshanbeilu, and Xinjiang more generally, as a point of contact between east and west (Dong et al., 2017; Wang et al., 2017; Liu et al. accepted). The introduction of millet (C_4 plant) as a major dietary staple has been identified in Late Bronze and Early Iron Age communities in many parts of the Eastern steppe zone from the distinctive isotopic signature it left behind in the bones of people who consumed it. In southern Siberia, this major transformation in diet is seen clearly from the late second millennium BC onwards, at a time when material connections with northwestern China and the Central Plains are also increasingly apparent (Svyatko et al., 2013). Wang et al. (2017) situate Tianshanbeilu at the centre of this process of agricultural exchange on the basis of 110 new stable isotopic data (carbon and nitrogen) of human bones and describe an "isotopic millet road" across Eurasia.

A critical obstacle that keeps us from further understanding how the networks centred on Tianshanbeilu were gradually established and expanded is the relatively low chronological resolution of the site. Unlike chronological studies in the Central China, which can rely not only upon pottery typology, stratigraphy and radiocarbon dating, but also on various textual evidence such as oracle bones or bronze inscriptions, very few techniques apart from typology and radiocarbon can be employed to date a steppe culture site in Xinjiang. It is even more challenging in the context of Tianshanbeilu since the stratigraphic sequence of the cemeteries is extremely difficult to establish. For a rather long period, the discussion of the absolute chronology of Tianshanbeilu has been based on only six radiocarbon dates published in the 1990s, amongst which one is probably beyond the time span of interest (ZK2790, 7176±110 BCE, IA CASS, 1996). Another four radiocarbon dates are published in Wang et al. (2017). Using Bayesian modelling in OxCal (Bronk Ramsey, 1998), the start and end boundary falls

into 1943–1763 BCE and 1127–931 BC (95.4% probability), respectively (Yang, 2018; Ma et al. submitted). Further analysis by kernel density estimation and summed function in OxCal agrees that the major body of Tianshanbeilu ranges from around 1800 BCE to 1000 BCE (Bronk Ramsey, 2018). This date range is consistent with the chronological range reflected by the broad material culture (Fig. 1a and b), but does not, at present, allow us to explore more precisely the chronology of contact between China and the steppe in eastern Xinjiang.

2 Materials, Methods and Results

Forty-six metal objects were selected for analysis in this project, which is part of a larger conservation project on Xinjiang bronzes organized by Northwest University of China (Online supplementary material I). Due to heavy corrosion, only sixteen objects yielded reliable compositional results (see discussion below), while thirtyeight objects yielded lead isotope results (Fig. 2; Tables 1 and 2).

2.1 Alloying composition and impurity elements

The compositional analysis was conducted in the Conservation Laboratory of Shaanxi Provincial Institute with scanning electron microscopy and energy dispersive spectrometry (SEM: ZEISS EVO MA25; EDS: X-Max 20 of Oxford UK). All of the samples were measured under the parameters of 20 KeV, live time 120s (dead time around 30%) and calibrated using the default standardless mode. The minimum detectable limit for the majority of elements is estimated to be 0.1% (Cu, Sn, Pb, Sb, Ag, Ni, Fe, Co) but it increases to 0.15% for As and Bi and 0.2% for Zn due to the overlap in the energy spectrum. More details of the operational process can be found in (Liu, 2016).

A series of pilot analyses were conducted before the main analytical sequence in order to assess the degree of corrosion of the samples and its likely effects on the analysis. It is well known that the corrosion of metal is a complex process and that corrosion products often show



Fig. 2. Some of the objects selected for chemical and isotopic analysis (a full list of sampled objects can be found in the online supplementary materials associated with this article).

 Table 1 Compositional results based on SEM-EDS

Object type	Arch. Num	Cu	Sn	Pb	As	Sb	Bi	Ag	Zn	Ni	Co	Fe	0	S	Total	Number of measurements	Elements over 1%
Plaque	M1:2-2	90.3	4.40	0.19	2.85	0.26	0.00	0.12	0.12	0.03	0.03	0.01	1.73	0.00	100.0	4	Cu-Sn-As
Plaque	M34:7	96.0	1.26	0.09	1.32	0.34	0.02	0.06	0.01	0.30	0.05	0.07	0.52	0.00	100.0	5	Cu-Sn-As
Tube	M37:2-1	90.5	7.33	0.18	0.15	0.11	0.01	0.08	0.03	0.10	0.03	0.10	1.36	0.00	100.0	5	Cu-Sn-As
Ornament	M53:1	78.1	12.20	0.23	0.11	0.04	0.00	0.04	0.00	0.02	0.04	0.19	8.99	0.00	100.0	2	Cu-Sn
Knife	M59:5	89.5	8.09	0.37	0.48	0.26	0.00	0.04	0.10	0.03	0.04	0.07	1.00	0.00	100.0	5	Cu-Sn
Earring	M64:5	88.1	5.33	1.09	0.48	0.34	0.00	0.18	0.00	0.05	0.06	0.14	3.74	0.50	100.0	4	Cu-Sn-Pb
Tube	M80:5	87.1	7.65	0.22	0.63	0.02	0.00	0.26	0.05	0.00	0.03	0.07	3.93	0.00	100.0	4	Cu-Sn
Bead	M93:3	84.8	9.43	0.98	0.06	0.03	0.00	0.03	0.06	0.03	0.01	0.00	4.54	0.00	100.0	4	Cu-Sn
Pao	M145:8	68.5	20.90	0.31	0.05	0.41	0.00	0.24	0.05	0.04	0.04	0.08	9.07	0.28	100.0	4	Cu-Sn
Tube	M202:3	96.8	0.65	0.24	0.07	0.03	0.00	0.04	0.00	0.06	0.06	0.10	1.94	0.00	100.0	5	Cu
Earring	M261:2	90.6	7.08	0.33	0.34	0.17	0.01	0.15	0.00	0.01	0.01	0.15	1.20	0.00	100.0	5	Cu-Sn
Ring	M298:6	79.9	11.80	0.67	0.27	0.10	0.00	0.09	0.06	0.05	0.03	0.28	6.31	0.54	100.0	4	Cu-Sn
Plaque	M376:7	91.9	4.97	0.13	1.90	0.17	0.03	0.10	0.09	0.00	0.02	0.06	0.61	0.00	100.0	5	Cu-Sn-As
Plaque	M571:2	73.8	14.70	0.28	2.23	0.07	0.00	0.36	0.09	0.03	0.11	0.18	8.13	0.00	100.0	2	Cu-Sn-As
Pao	M81:6	85.2	6.98	0.41	0.48	0.38	0.00	0.06	0.11	0.14	0.00	0.03	6.20	0.00	100.0	3	Cu-Sn-As
Plaque	M198:7	87.9	9.28	0.08	0.60	0.27	0.04	0.10	0.07	0.01	0.05	0.07	1.54	0.00	100.0	5	Cu-Sn

Table 2 Results of lead isotopic analysis

Arch.	Object	²⁰⁸ Pb/	²⁰ /Pb/	²⁰⁶ Pb/	²⁰⁸ Pb/	²⁰ /Pb/
Number	type	²⁰⁴ Pb	²⁰⁴ Pb	²⁰⁴ Pb	²⁰ 6Pb	²⁰⁶ Pb
M1:1	Knife	38.079	15.542	18.244	2.087	0.852
M1:2-2	Plaque	37.975	15.558	18.026	2.107	0.863
M13:4-A	Circle	38.106	15.529	18.095	2.106	0.858
M27:2	Tube	38.576	15.627	18.570	2.077	0.842
M34:3	Plaque	38.068	15.551	18.131	2.100	0.858
M34:7	Plaque	37.881	15.558	17.980	2.107	0.865
M37:2-1	Tube	37.861	15.535	17.927	2.112	0.867
M45	Bracelet	37.651	15.495	17.881	2.106	0.867
M48:10	Tube	36.261	15.157	17.488	2.073	0.867
M50:4	Arrow head	38.043	15.571	18.262	2.083	0.853
M53:1	Ornament	37.590	15.502	17.803	2.111	0.871
M59:5	Knife	37.825	15.540	17.931	2.110	0.867
M64:5	Earring	38.328	15.612	18.390	2.084	0.849
M80:5	Tube	37.994	15.546	18.200	2.088	0.854
M81:6	Disc	37.633	15.440	18.043	2.086	0.856
M81:7	Mirror or Plaque	37.762	15.564	17.925	2.107	0.868
M82:3	Earring	37.918	15.555	18.158	2.088	0.857
M93:3	Bead	38.034	15.567	18.070	2.105	0.861
M99:3	Ornament	38.197	15.544	18.234	2.095	0.852
M110:4	Tube	38.058	15.566	17.895	2.127	0.870
M126:8	Knife	37.892	15.554	18.064	2.098	0.861
M183:5	Ornament	36.593	15.148	17.782	2.058	0.852
M197:3	Plaque	37.595	15.485	17.851	2.106	0.867
M202:3	Tube	38.231	15.617	18.144	2.107	0.861
M261:2	Earring	38.185	15.603	18.285	2.088	0.853
M261:8	Buckle	37.524	15.490	17.770	2.112	0.872
M317:9	Circle	37.783	15.529	17.979	2.101	0.864
M329:1	Knife	37.623	15.480	17.925	2.099	0.864
M361:9	Ornament	37.860	15.549	18.049	2.098	0.861
M437:7	Ornament	38.181	15.553	18.513	2.062	0.840
M479:7	Ornament	37.583	15.562	17.713	2.122	0.879
M520:3	Bead	38.080	15.540	18.228	2.089	0.853
M554:7	Buckle	38.170	15.580	18.195	2.098	0.856
M571:2	Plaque	40.620	15.800	20.209	2.010	0.782
M580:3	Earring	37.830	15.529	17.971	2.105	0.864
M640:11	Plaque	36.473	15.102	17.779	2.051	0.849
M652:5	Tube	38.142	15.545	18.155	2.101	0.856
M683:7-1	Spiral tube	37.900	15.537	18.122	2.091	0.857

significant enrichment/depletion of elements with respect to the original chemistry of the metal alloy. During this process, particular attention was paid to the total of each analysis, as this serves as the primary index of data quality. Generally speaking, totals from this SEM-EDX analysis should fall within 98–102%. A second indicator of data quality and no less important is the concentration of oxygen. A high percentage of oxygen within the analytical total strongly indicates the presence of corrosion products. After careful examination of the whole sample, five areas of each sample were selected for full measurement using the parameters listed above. However, even if after the first run of filtering a few measurements still show rather high percentage of oxygen (> ~10%, see online supplementary material), which have to be abandoned. The rest measurements are subsequently averaged and normalize the average (Table 1; See online supplementary material II for all the individual analysis).

The major issue is that the copper objects from Xinjiang are invariably heavily corroded, and the most likely explanation for the high but variable oxygen is that the analysis is including a variable proportion of oxidized metal. Where the oxygen is high, therefore, the remainder of the analysis does not necessarily represent the core metal, but an unknown combination of core metal and oxidized corrosion product. It is tempting to simply remove the oxygen by normalizing the other components to 100%, but this is unlikely to give a representative analysis, since the corrosion product may contain elements scavenged from the local environment, and the corrosion process can lead to the selective loss of certain elements, thus apparently enriching the others. This is also the case for the previously published data from this area. Mei (2001) published the analyses of 19 objects from Tianshanbeilu, with oxygen recorded as between 0 and 42.3% (average c. 13.5%). Qian (2006) published data from 89 objects: oxygen was not reported, but the analytical totals were systematically low, suggesting that between 0 and 6.64% could have been oxygen. The chemical analysis of such objects presents a significant challenge. In this paper, we have taken 10% oxygen to be the maximum acceptable value. Where the five spot analyses all record < 10% oxygen we have simply averaged all five. Where one or more of the five spot analyses record > 10% oxygen, we have averaged the remaining analyses (and recorded the number of analyses in the average. Where all five analyses have >10% oxygen we have rejected the whole analysis.

2.2 Lead isotopic analyses

The lead isotopic measurements were carried out at the laboratory of Earth and Space Sciences at Peking using VG Elemental Multicollector-University, Inductively Coupled Plasma Mass Spectrometer (MC-ICP -MS). Each time it was calibrated by measuring the internationally agreed standards NBS 981 to minimize the standard deviation of the measurements (less than 0.02%). About 50 mg of each sample was dissolved in a nitric acid solution after washing and drying. Lead was then separated electrochemically by deposition onto a platinum electrode under weak nitric acid conditions. The lead on the platinum electrode was dissolved using a few drops of 2% nitric acid into a polyethylene bottle. The purified lead solution was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and then diluted by adding deionized water to 400-1000 ppb. The international standard T1 SRM997 was also added as internal calibration. All of the samples were subsequently moved to MC-ICP-MS for isotopic measurements and the final results are shown in Table 2.

4 Discussion

4.1 Chemical data

The alloving technology in eastern Xinjiang has been extensively discussed in the existing literature (e.g. Mei, 2000: Oian. 2006). So far. a total of 107 analyses of metal have been published. Based on the commonly used cut-off of 1% for "deliberate alloving" (Pollard et al., 2018), the alloying technology at Tianshanbeilu involves pure copper, arsenical copper, arsenic bronze (Cu-Sn-As), tin-bronze, leaded bronze (Cu-Sn-Pb), leaded copper and leaded arsenic bronze (Cu-Sn-Pb-As). This wide range of alloy types is quite typical of steppe metal assemblages (Chernykh, 1992; Hsu, 2016; Pollard et al., 2017). Patterns of mobility associated with pastoralism would likely result in varied or fluctuating supply of metal, leading to a more diverse spectrum of alloy compositions. Re-use and recycling old objects is an obvious strategy to maintain the amount of metal in circulation, resulting in dispersed distributions of the alloving metals in the overall assemblage.

Relative to the huge number of leaded bronzes discovered in Central China, the particular feature of Steppe metallurgy is often considered to be the presence of arsenic in copper-based objects. In this project, many objects have been found to contain arsenic up to 2.71%. One bead reported in Qian (2000) has the highest percentage of arsenic so far seen in Tianshanbeilu, at 9.58%. For most objects arsenic is below 3%. As shown in Fig. 3, one distinctive feature of this assemblage is the cooccurrence of arsenic and antimony in the metal, a feature seen as particularly typical of metal production in the Bronze age of the northern Savan (Bobrov et al., 1997). Plotting antimony against arsenic (both over 1%: Fig. 3) reveals two clear correlations - one with essentially low but constant antimony, and the other in which the arsenic and antimony are positively correlated. These two elements are often associated with one another in the form of minerals of the tennantite-tethrahedrite series, in which arsenic and antimony form a complete solid substitution



Fig. 3. Plotting arsenic and antimony of the Tianshanbeilu metals.

series from the end members tennantite ($Cu_{12}As_4S_{13}$) and tetrahedrite ($Cu_{12}Sb_4S_{13}$). Therefore, the correlation presented in the data of Group I can be potentially explained by the use of tennantite-tethrahedrite or tennantite as part of the ore charge (Krismer et al., 2011). Being different from Group I, the four objects in Group II show distinctive concentrations of arsenic but not antimony. One likely explanation is the addition of arsenic ores during the process of smelting, which has been attested in a number of studies focused on the probably most well-known Bronze Age mining and smelting site, Nulasai (Fig. 1, Mei, 2000; Li, 2001).

4.2 Lead isotopes

Figure 4 shows a conventional pair of lead isotope diagrams for the data in Table 2. Clearly, the lead isotopic data are distributed into three groups. The majority of the data falls into a group with $17.7 > Pb^{206}/Pb^{204} > 18.6$, which represents common lead (CL). A smaller group of three objects is also clearly distinguished at lower values of Pb^{207}/Pb^{204} and Pb^{208}/Pb^{204} . The most interesting 'group', however, is the first, consisting of only one data point (sample M571: 2), but showing highly radiogenic lead (HRL, for which our definition is $Pb^{206}/Pb^{204} > 19$). This is so far the first object presenting a highly radiogenic signature found in Xinjiang. It was discovered in tomb M571, tentatively dated to Phase III of Tianshanbeilu (ca. 1500-1300 BC, Yang, 2018; Ma et al. submitted), which corresponds to the Shang period (ca. 1500–1045 BC). It is too fragmented to be typologically diagnostic (Fig. 2), but is described as a plaque, which means that it is a Steppe-type object rather than a fragment of imported central Chinese bronze ritual vessels.

Figure 5 shows the available lead isotope data for modern copper or lead ores in Xinjiang. There is a good overlap between the majority of the common Tianshanbeilu lead (Group II in Fig. 4) and the ore data, suggesting that a local source of lead is possible. The smaller group in Figure 4 (Group III) is not as yet matched by any known Xinjiang source. Apart from one bornite (Cu₅FeS₄) sample from western Xinjiang containing highly radiogenic lead, so far there is little evidence to suggest a local mine which is capable of producing the 'Tianshanbeilu' type of HRL (Group I). Of course, this does not preclude such a source, since the bornite sample



Fig. 4. Lead isotopic groupings at Tianshanbeilu.



Fig. 5. Comparison of lead isotopic data between the Tianshanbeilu objects and the modern ores of Xinjiang (sources of data are in the online supplementary materials).

shows that HRL does exist in Xinjiang. More detailed archaeological and geological investigations into local ancient mines needs to be conducted around Xinjiang.

Figure 6 compares the common lead isotopic data between Tianshanbeilu and the data from the Shang Sackler collection (Bagley, 1990), which reflects the lead in circulation in Central China. The slopes of the two isochrons are inconsistent, especially in Pb²⁰⁸/Pb²⁰⁴ vs



Fig. 6. Comparing common lead isotopic data between Tianshanbeilu and Central China.

Pb²⁰⁶/Pb²⁰⁴. This suggests that the ore bodies which these two groups of lead derive from may have different geological ages or have followed a different evolutionary line. This difference is sufficient to suggest that the metal in Tianshanbeilu does not represent recycled metal from Central China.

Previous work by many scholars has accumulated over one thousand measurements of lead isotopic data for bronzes distributed across Central China and the Yangtze River area (Jin, 2008; Liu et al., 2015, 2018; Jin et al., 2017; Chen et al. 2019). The primary concern of most researchers has been centred on the provenance of HRL, but no consensus has yet been reached, and there is still uncertainty about whether this lead is the result of exploitation of a single source of lead, or many. However, these data show that approximately half of the bronzes recovered from Anyang contain HRL, and that bronzes containing HRL are widely spread over Central China. The work of Cao (2014) has significantly extended the distribution of HRL towards the north, where he has discovered a substantial number of such bronzes in the highlands of Shaanxi and Shanxi. Based on the chemical compositions and typological analysis, he argues that the reason for the appearance of Anyang-composition leaded bronze in these regions is a result of exchanging Anyang bronzes for horses, with some objects being recycled into local forms (Cao, 2014).

A further issue to consider therefore is whether HRL was locally available in Tianshanbeilu. New analytical work has shown the appearance of HRL in the west, such as in the Hexi Corridor. At the Gansu Mogou site, a considerable number of objects have been discovered containing HRL (Wang, 2019). Likewise, copper ores and

objects excavated from the Bronze Age sites in the Hexi Corridor show clear radiogenic signatures (Chen et al.2020, Dodson et al., 2009). Figure 7a-b plots the data from the Hexi Corridor and Tianshanbeilu for comparison, and Figure 7c-d shows a comparison between the data from the Shang Sackler collection (representing the objects at Anyang) and all of the data from Tianshanbeilu, including the HRL sample. This is obviously inconsistent with the reported values from the Hexi corridor (Fig. 7b), particularly in terms of Pb²⁰⁸/Pb²⁰⁴, suggesting a difference in the thorium environment between the ore sources of the two sets of samples. Figure 7c-d shows that the Tianshanbeilu HRL sample is consistent with the isotopic pattern from the objects in the Shang Sackler Collection (representing the metal in circulation in Central China), suggesting that this sample may represent an object remade from metal originating in the Shang centre. However, the low lead content of this object (0.34%)indicates that is unlikely to simply be recycled Central Chinese metal, which tends to contain much more lead (~ 2 -30%). In the light of this, we suggest that this sample represents the use of a source of lead containing HRL, from a source as yet unknown, but most likely in Xinjiang.

5 Conclusions

The new analyses of copper-based objects at Tianshanbeilu have revealed a number of interesting points regarding the metallurgy during the second millennium BC around eastern Xinjiang. The new chemical data presented here illustrates a problem which can also be seen in other similar datasets – the metal objects tend to be small and thin, and are often corroded all through. This is most easily seen when the percentage oxygen is reported, since uncorroded copper contains

dissolved oxygen at less than a fraction of a percent. Further work is required to understand how best to use such data, but the approach adopted here is to simply eliminate samples which contain more the 10% oxygen.

The general paucity of metal objects suggests that the Tianshanbeilu people did not enjoy an abundant supply of metal. Even so, the metals they employed clearly derived from more than one source, as evidenced by the range of alloy types represented, and also the lead isotope data. Although tin-bronze is the most ubiquitous local alloying type, a variety of other combinations of metals have also been identified, including the use of ores from the tennantite-tetrahedrite series. The lead isotope data reveals the most significant finding of this paper - the occurrence of a single sample of heavily corroded Cu-Sn-As alloy in the form of a plaque, containing highly radiogenic lead $(Pb^{206}/Pb^{204} = 20.209)$. This is currently the furthest west that such lead has been found, and is currently the only example from Xinjiang. The widely discussed issue about the source of highly radiogenic lead in Shang dynasty bronzes is further complicated by the discovery of such lead in bronzes from Gansu and now from Xinjiang. This wide distribution must surely strengthen the view that there were multiple sources or different types of HRL used in Bronze Age China. This does not of course imply that Anyang itself received such lead from more than one source - simply that more than one source supplied HRL to the many bronze-producing regions of China.

Acknowledgements

This work is funded by ERC advanced project FLAME (Flow of Ancient Metal Across Eurasia, 670010), Social Science Research Fund of Shaanxi Province China (2014H02) and academic fund of Wolfson College



Fig. 7. Comparison of lead isotopic data of Tianshanbeilu, the Hexi Corridor and the Shang Sackler Collection (Data from Chen et al., 2020; Dodson et al., 2009).

(University of Oxford).

Manuscript received Feb. 21, 2020 accepted Apr. 2, 2020 associate EIC: CHEN Fahu edited by FEI Hongcai

References

- Bagley, R., 1990. Shang ritual bronzes: casting technique and vessel design. Archives of Asian Art, 43: 6-20.
- Bobrov, V.V., Kuzminykh, S.V., and Teneyshvili, T.O., 1997. Drevnyaya metallurgiya srednego Yeniseya (Lugavskaya Kul'tura). Kemerovo: Kuzbassvuzizdat, 1-12.
- Bronk Ramsey, C., 1998. Probability and dating. Radiocarbon, 40: 461-474.
- Bronk Ramsey, C., 2018. Methods for summarizing radiocarbon datasets. Radiocarbon, 59: 1809-1833.
- Cao, D., 2014. The loess highland in a trading network (1300-1050BC). Unpublished PhD Thesis. Princeton University, 1-380
- IA CASS (Institute of Archaeology, Chinese Academy of Social Science), 1996. Report of radiocarbon dating (23). Kaogu, 7: 66-70 (in Chinese).
- Chen, G., 1990. Bronze Age and early Iron Age culture at Xinjiang. Kaogu, 4: 366–374 (in Chinese).
- Chen, G., Cui, Y., Liu, R., Wang, H., Pollard, A.M., and Li, Y., 2020 (online available). Lead isotopic analyses of copper ores in the early Bronze Age Central Hexi Corridor, Northwest China. Archaeometry
- Chen, K., Mei, J., Rehren, T., Liu, S., Yang, W., Martinon-Torres, M., Zhao, C., Hirao, Y., Chen, J., and Liu, Y., 2019. Hanzhong bronzes and highly radiogenic lead in Shang period China. Journal of Archaeological Science, 101: 131-139
- Chernykh, E.N., 1992. Ancient metallurgy in the USSR: the early metal age. Cambridge: Cambridge University Press, 1-359
- Chernykh, E.N., 2017. Nomadic cultures in the megastructure of the Eurasian World (Trans. I. Savinetskaya and P. Hommel).
- Moscow: LRC Press, 1–696. Dodson, J., Li, X., Ji, M., Zhao, K., Zhou, X., and Levchenko, V., 2009. Early Bronze in two Holocene archaeological sites in Gansu, NW China. Quaternary Research, 72: 309-314.
- Dong, G., Yang, Y., Han, J., Wang, H., and Chen, F., 2017. Exploring the history of cultural exchange in prehistoric Eurasia from the perspectives of crop diffusion and consumption. Science China Earth Sciences, 60: 1110-1123.
- Gong, G., 1997. Preliminary discussion of early coppers at Xinjiang. Kaogu, 9: 7-20 (in Chinese).
- Han, J., 2007. Bronze Age and early Iron Age cultures at Xinjiang. Beijing: Wenwu Press, 1–125 (in Chinese).
- Han, R., and Sun, S., 2004. Preliminary studies on the bronzes excavated from the Tianshanbeilu cemetery, Hami, Xinjiang, in Linduff K (eds.). Metallurgy in ancient eastern Eurasia from the Urals to the Yellow river. Lampeter, Ceredigion, Wales: The Edwin Mellen Press, 157-172.
- Hsu, Y.-K., 2016. The dynamic flow of copper and copper alloys across the prehistoric Eurasian steppe from 2000 to 300 BCE. Unpublished PhD thesis. University of Oxford, 1–130.
- Jaang, L., 2015. The landscape of China's participation in the Bronze Age Eurasian Network. Journal of World Prehistory, 28: 179-213.
- Jin, Z., 2008. Lead isotopic archaeology in China. Beijing: Press of University of Science and Technology, 1-233 (in Chinese).
- Jin, Z., Liu, R., Rawson, J., and Pollard, A.M., 2017. Revisiting lead isotope data in Shang and Western Zhou bronzes. Antiquity, 91: 1574-1587.
- Krismer, M., Vavtar, F., Tropper, P., Kaindl, R., and Sartory, B., 2011. The chemical composition of tetrahedrite-tennantite ores from the prehistoric and historic Schwaz and Brixlegg mining areas (North Tyrol, Austria). European Journal of
- Mineralogy, 23: 925–936. Kuzmina, E.E., 2007. The Origin of the Indo-Iranians and the Prehistory of the Silk Road. Leiden: Brill, 1–763.

- Li, S., 2002. The interaction between northeast China and Central Asia during the second millennium BC: an archaeological perspective. In: Boyle K, Renfrew C, and Levine, M. (eds.), Ancient interactions: east and west in Eurasia. Cambridge: McDonald Institute for Archaeological Research, 171-181.
- , S., 2005. Trans-regional interaction of early metallurgy between northwest China and the Central Plains. Kaogu Li, Xuebao, 3: 239-278 (in Chinse with English abstract).
- Li, S. 2009. Study of the archaeological Tianshanbeilu mudi yiqi vicun yanjiu. In: Chinese National Museum, and School of Archaeology and Museology Beijing University (eds.). Essay Collection of Yuweichao. Beijing: Wenwu Press, 193–202 (in Chinse with English abstract).
- Li, S., and Shui, T., 2000. The study of the Siba cultural copper objects. Wenwu, 3: 36–44 (in Chinse with English abstract).
- Li, Y., 2001. Study on smelting technology of the Nulasai site in Nileke county, Xinjiang. Nonferrous Metals, 53: 64-66 (in Chinse with English abstract).
- Linduff, K.M., 2004. Metallurgy in ancient eastern Eurasia from the Urals to the Yellow River. Lewiston, New York: Edwin Mellen Press, 1–315.
- Liu, R., 2016. Capturing changes: applying the Oxford system to further understand the movement of metal in Shang China. Unpublished PhD thesis. University of Oxford, 1-278
- Liu, R., Bray, P., Pollard, A.M., and Hommel, P., 2015. Chemical analysis of ancient Chinese copper-based objects: Past, present and future. Archaeological Research in Asia, 3: 1 -8
- Liu, R., Rawson, J., and Pollard, A.M., 2018. Beyond ritual bronzes: identifying multiple sources of highly radiogenic lead across Chinese history. Scientific Reports, 8: 11770.
- Liu, R., Pollard, A. M., Rawson, J., and Schulting, R., accepted Dietary Changes Across Chinese History: Synthesis of Stable Isotopic Data for Human Bone Collagen. Holocene.
- Ma, J., Tong, J., Liu, G., Li, W., Chang, X., Yu, J, Ma. Y., Tian, Y. Mu, L. and Liu, R., submitted. Chronology of Tianshanbeilu cemetery and early development of Hami oasis during the 2nd millennium BC. Radiocarbon.
- Mei, J., 2000. Copper and bronze metallurgy in late prehistoric Xinjiang: its cultural context and relationship with neighbouring regions. Oxford: Archaeopress, 1-93.
- Mei, J., 2003. Cultural Interaction between China and Central Asia during the Bronze Age. Proceedings of the British Academy, 121: 1–39. Mei, J., and Shell, C., 1999. The existence of Andronovo cultural
- influence in Xinjiang during the 2nd millennium BC. Antiquity, 73: 570–578.
- Mei, J., Wang, P., Chen, K., Wang, L., Wang, Y., and Liu, Y., 2015. Archaeometallurgical studies in China: some recent developments and challenging issues. Journal of Archaeological Science, 56: 221-232.
- Millard, J.A., 2007. Eurasian crossroads: a history of Xinjiang.
- New York City: Columbia University Press, 1–352. Pollard, A.M., Bray, P., Hommel, P., Hsu, Y.-K., Liu, R., and Rawson, J., 2017. Bronze age metal circulation in China. Antiquity, 91: 674-687.
- Pollard, A.M., Bray, P., Hommel, P., Liu, R., Pouncett, J. Saunders, M., Howarth, P., Cuénod, A., Hsu, Y. -K., and Perucchetti, L., 2018. Beyond Provenance: New Approaches to Interpreting the Chemistry of Archaeological Copper Alloys. Leuven: Leuven University Press, 115-144.
- Qian, W., 2006. The Prehistoric Copper and Bronze of Hami Region in Xinjiang and Their Contexts of Neighboring Cultures. Beijing: Zhishi Chanquan Press, 1-168 (in Chinse with English abstract).
- Rawson, J., 2010. Carnelian beads, animal figures and exotic vessels: traces of contact between Chinese states and Inner Asia, ca 1000-650 BC. In: Wagner, M., and Wang, W. (eds.), Bridging Eurasia. Mainz: Von Zabern, 5-12.
- Sherratt, A., 2006. The trans-Eurasian exchange: The prehistory of Chinese relations with the West. In: Mair, V.M. (eds.), Contact and exchange in the ancient world. Honolulu: University of Hawaii Press, 32-53.
- Shui, T., 1993. Comparison of archaeological cultures in Bronze

Age Xinjiang. Guoxue Yanjiu, 01: 1–13 (in Chinese).

- Svyatko, S.V., Schulting, R.J., Mallory, J., Murphy, E.M., Reimer, P.J., Khartanovich, V.I., Chistov, Y.K., and Sablin, M.V., 2013. Stable isotope dietary analysis of prehistoric populations from the Minusinsk Basin, Southern Siberia, Russia: a new chronological framework for the introduction of millet to the eastern Eurasian steppe. Journal of Archaeological Science, 40: 3936–3945.
- Vadetskaya, E.B., Polyakov, A.V., and Stepanova, N.F., 2014. Svod Pamyatniki Afanasievskoy Kul'tury. Barnaul: Azbuka, 1 –45.
- Wang, T., Wei, D., Chang, X., Yu, Z., Zhang, X., Wang, C., Hu, Y., and Fuller, B.T., 2017. Tianshanbeilu and the Isotopic Millet Road: reviewing the late Neolithic/Bronze Age radiation of human millet consumption from north China to Europe. National Science Review, 00: 1–16.
- Wang, Y., 2019. Scientific study on copper and bronze artefacts of the Lower Xiajiadian Culture. PhD thesis. University of Science and Technology Beijing, 1–72.
- Yang, C., 2018. Scientific study on The Bronzes From Tianshanbeilu cemetery. Unpublished Master thesis. Northwest University China, 1–96.
- Zhang, L., 2017. The transmission of the Karasuk metallurgy to the northern zone of China. Shidi, 1: 100–124.

About the first author



LIU Cheng, male, born in 1964 in Shanghai; Master; graduated from Northwest University, China; associated professor of the School of Cultural Heritage, Northwest University, China. He is now interested archaeological and conservation science. Email: liucheng@ nwu.edu.cn; phone: +86 13772137915.

About the corresponding author



LIU Ruiliang, male, born in 1988 in Ji'nan City, Shandong Province; Ph.D, graduated from the University of Oxford; Junior Research Fellow in Wolfson College and postdoctoral researcher in the School of Archaeology, University of Oxford. He is interested in archaeometallurgy, radiocarbon dating and east-east communication in antiquity. Email: ruiliang.Liu@arch.ox.ac. uk, phone: +44 01865 285219