SCIENCE CHINA
Technological Sciences

Special Topic: Cultural Heritage Conservation
•Article•

August 2023 Vol.66 No.8: 2297–2307
https://doi.org/10.1007/s11431-022-2363-y

Diversified manufacturing processes and multiple mineral sources: Features of Warring States bronze vessels excavated from Chutai Cemetery M1, Anhui Province

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Received November 28, 2022; accepted February 23, 2023; published online July 18, 2023

Northern Anhui was an important region for diverse bronze culture convergence and extensive metal resource circulation in the Pre-Qin Period. In this paper, metallographic microstructure analysis, chemical composition analysis, and lead isotope ratio analysis were conducted on 12 samples of 6 Warring States Period (476–221 BCE) bronze vessels excavated from Chutai Cemetery M1, Fuyang, Anhui Province, revealing the integrated application of diversified manufacturing processes, such as casting, forging, cold working, and welding and multiple metal minerals. The analytical results showed that 2 Ding vessels (鼎) were made by casting, and 2 He vessels (盒) and 2 Dui vessels (敦) were made by forging followed by cold working. These two types of bronze vessels made by different manufacturing processes have significantly distinct alloy ratios and mineral sources, among which the Cu and Sn contents of the 2 cast bronze vessels are lower and the Pb content is higher, while the Cu and Sn contents of the 4 forged bronze vessels are higher and the Pb content is lower. The lead minerals of the two types of bronze vessels might come from Western Henan and the middle and lower reaches of the Yangtze River, respectively. In addition, the 3 pieces of solder used to weld bronze vessels were all made of pure Sn, their metal minerals should come from the densely distributed area of tin ore in Southern China, and Sn solders were mainly discovered in the Chu culture area during the Eastern Zhou Period.

Northern Anhui, The Warring States Period, Chu culture, bronze vessels, manufacturing processes, alloying techniques, mineral sources

Citation: Luo Z, Yang M, Liu J S, et al. Diversified manufacturing processes and multiple mineral sources: Features of Warring States bronze vessels excavated from Chutai Cemetery M1, Anhui Province. Sci China Tech Sci, 2023, 66: 2297–2307, https://doi.org/10.1007/s11431-022-2363-y

1 Introduction

The Northern Anhui region refers to the area north of the Huai River in Anhui Province, which is a very special geographical unit in Eastern China (Figure 1). The region is close to the Central Plain to the north and adjacent to the middle and lower reaches of the Yangtze River to the south, which had been a strategic location for multiple forces to compete since ancient times. It was also a key channel for bridging the cultures of the North and the South in the Pre-Qin Period [1]. During the Warring States Period, the Chu State became one of the most powerful vassal states in Southern China. As the force of the Chu State continued to expand to the east, the Northern Anhui region was strongly influenced by Chu culture and gradually became the domination scope of the Chu State, and the Warring States bronzes excavated from this region also showed clear Chu-type styles [2,3].

Currently, Warring States bronzes in Northern Anhui were

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Figure 1 (Color online) Location of Chutai Cemetery M1, Fuyang, Anhui Province, and the main study area and related sites in this paper.

mostly discovered sporadically, and were mainly weapons and tools. Han and Feng [4], Zhou et al. [3], and Feng [5] briefly introduced and sorted out the types, forms, inscriptions, and cultural aspects of Warring States bronzes excavated from Northern Anhui; Li et al. [6] conducted analysis on several Warring States bronzes collected from Fuyang Museum and found that they were all lead-tin bronze and used lead ores from multiple sources. However, the academic community still has very limited knowledge about the manufacturing processes, alloying techniques, and mineral sources of Warring States bronzes excavated from Northern Anhui. This series of issues restrict us from exploring and discussing in greater depth the bronze manufacturing system and metal resource circulation network in Northern Anhui and the entire Eastern Chu State during the same period. Therefore, it is urgently needed to carry out systematic and comprehensive studies on the Warring States bronzes excavated from Northern Anhui, which have detailed archaeological backgrounds.

Chutai Cemetery M1 is an aristocratic tomb of Chu State in Northern Anhui. In this paper, metallographic microstructure analysis, chemical composition analysis, and lead isotope ratio analysis were conducted on Warring States bronze vessels and their solders excavated from this tomb, aiming to fully reveal its manufacturing processes, alloying techniques, and mineral sources. We will pay particular attention to the distinctions in manufacturing processes and alloying techniques between different types of bronze vessels, as well as the development and changes in the chemical composition characteristics of bronze vessels and metal solders made by nonmainstream techniques during the Chinese Bronze Age. Furthermore, the similarities and differences in metal mineral use between Chutai Cemetery M1 and other sites in Eastern Chu State and the metal resource circulation network of Eastern Chu State during the Warring States Period are also discussed.

2 Site context, sample information, and analytical methods

2.1 Site context

The Chutai Cemetery is located in northwestern Fuyang City, Anhui Province, and contains tombs dating from the middle and late Warring States Period to the Han Dynasty. At present, 29 tombs have been excavated in Chutai Cemetery, including M1, M3, and M26, dated to the middle Warring States Period, representing the highest grade of tombs in Chutai Cemetery and are high-grade Chu tombs of the Warring States Period. More than 40 bronzes such as Ding (鼎), Hu (壶), Dui (敦), Jian (剑), Ge (戈), Ji (戟), Jing (镜), Quanzhang (权杖) were excavated from M1; moreover, a larger number of lacquered wood artifacts and pottery artifacts were excavated. The archaeologist speculated that the identity of M1's owner should be a lower dafu (下大夫) [7].

2.2 Sample information

All our samples are from Chutai Cemetery M1, dating to the middle Warring States Period. In this study, 12 samples were extracted from 6 bronze vessels. The 6 bronze vessels include 2 He vessels (CT001, CT0010), 2 Ding vessels (CT007, CT008), and 2 Dui vessels (CT0013, CT0014). The 12 samples include 9 bronze vessel body samples and 3 solder samples. Among CT001, CT0013, and CT0014, 2 bronze vessel body samples were extracted, among CT007, CT008, and CT0010, 1 bronze vessel body sample was extracted, and the other 3 solder samples were extracted from CT0010, CT0013, and CT0014. Specific information of the bronze vessels and their solder samples are shown in Table 1, and photos of the bronze vessels are shown in Figure 2.

2.3 Analytical methods

(1) Metallographic microstructure analysis

The bronze body samples were inlaid in resin, then ground and polished to ensure that they met the conditions for metallographic observation. The samples were etched with ferric chloride hydrochloric acid ethanol solution, and then photographed and observed under the metallurgical microscope (ZEISS Axio Observer A1M) at the Archaeometry Laboratory of University of Science and Technology of China.

(2) Chemical composition analysis

All samples were inlaid in resin, then ground and polished to expose their metal layers. The chemical compositions of all samples were tested by the Energy Dispersive X-ray Fluorescence Spectrometer at the Archaeometry Laboratory of University of Science and Technology of China. The detecting instrument was EDX-8100 produced by Shimadzu Corporation of Japan.

(3) Lead isotope ratio analysis

All samples were pretreated before the lead isotope analysis. The samples were cleaned with acetone and put into ultrasonic vibration, then they were dried and dissolved with nitric acid, and finally, the lead was extracted from the samples by the electrolytic deposition method. In order to ensure that the lead concentration in the measurement was approximately 200 ppb, the element concentration was measured on the Agilent 7700 Plasma Mass Spectrometer (ICP-MS) at the Key Laboratory of Crust-Mantle Materials and Environments, Chinese Academy of Sciences. The lead isotope ratio was measured on Neptune Plus Multi-Acceptance Plasma Mass Spectrometer (MC-ICP-MS) at the School of Earth and Space Sciences of University of Science and Technology of China. During the test, the NBS-981 standard solution was repeatedly measured for calibration, and the standard error of each set of lead isotope ratios was less than ±0.001.

3 Results

3.1 Metallographic microstructure

As shown in Table 2 and Figure 3, the metallographic

Table 1 Basic information of the bronze vessel and solder samples excavated from Chutai Cemetery M1

Lab no.	Excavation no.	Bronze type	Excavation site	Period	Sampling position	Condition
CT-1	CT001	He	Chutai Cemetery M1	The Warring States	Lid	Metal
CT-2			Chutai Cemetery M1		Bottom	Metal
CT-3	CT007	Ding	Chutai Cemetery M1	The Warring States	Belly	Metal
CT-4	CT008	Ding	Chutai Cemetery M1	The Warring States	Foot	Metal
CT-5	CT0010	He	Chutai Cemetery M1	The Warring States	Solder	Metal
CT-6			Chutai Cemetery M1		Bottom	Metal
CT-7	CT0013	Dui	Chutai Cemetery M1	The Warring States	Lid	Metal
CT-8			Chutai Cemetery M1		Solder	Metal
CT-9			Chutai Cemetery M1		Bottom	Metal
CT-10	CT0014	Dui	Chutai Cemetery M1	The Warring States	Belly	Metal
CT-11			Chutai Cemetery M1		Bottom	Metal
CT-12			Chutai Cemetery M1		Solder	Metal

Figure 2 (Color online) Pictures of the bronze vessels excavated from Chutai Cemetery M1.

Table 2 Metallographic microstructure observation of the bronze vessel body samples excavated from Chutai Cemetery M1

Lab no.	Excavation no.	Metallographic microstructure	Manufacturing process
CT-1	CT001	Forging and cold working organization of Pb-Sn bronze. Cu-Sn α recrystallized grains and twins, irregular size grains, slip bands in some grains, small amounts of lead particles, and sulfides scattered at grain boundaries	Forging followed by cold working
CT-3	CT007	Cu-Sn α solid solution dendrites with obvious segregation, large amount of (α+δ) eutectic organization, small amount of lead particles, and sulfide inclusions scattered in the interstices of dendrites	Casting
CT-4	CT008	α solid solution grains, dendrite segregation disappears, a large number of lead particles and sulfide inclusions are scattered in the grain boundaries	Casting
CT-6	CT0010	Forging and cold working organization of Pb-Sn bronze. Cu-Sn α recrystallized grains and twins, irregular size grains, slip bands in some grains, small amounts of lead particles, and sulfides scattered at grain boundaries	Forging followed by cold working
CT-9	CT0013	Forging and cold working organization of Pb-Sn bronze. Cu-Sn α recrystallized grains and twins, irregular size grains, slip bands in some grains, small amounts of lead particles, and sulfides scattered at grain boundaries	Forging followed by cold working
CT-10	CT0014	Forging and cold working organization of Pb-Sn bronze. Cu-Sn α recrystallized grains and twins, irregular size grains, slip bands in some grains, small amounts of lead particles, and sulfides scattered at grain boundaries	Forging followed by cold working

microstructure of 6 samples can be divided into forging followed by cold working and casting categories. These 6 samples correspond to 6 bronze vessels, CT001 and CT0010 (He vessels), CT0013 and CT0014 (Dui vessels) made by forging followed by cold working, and CT007 and CT008 (Ding vessels) made by casting.

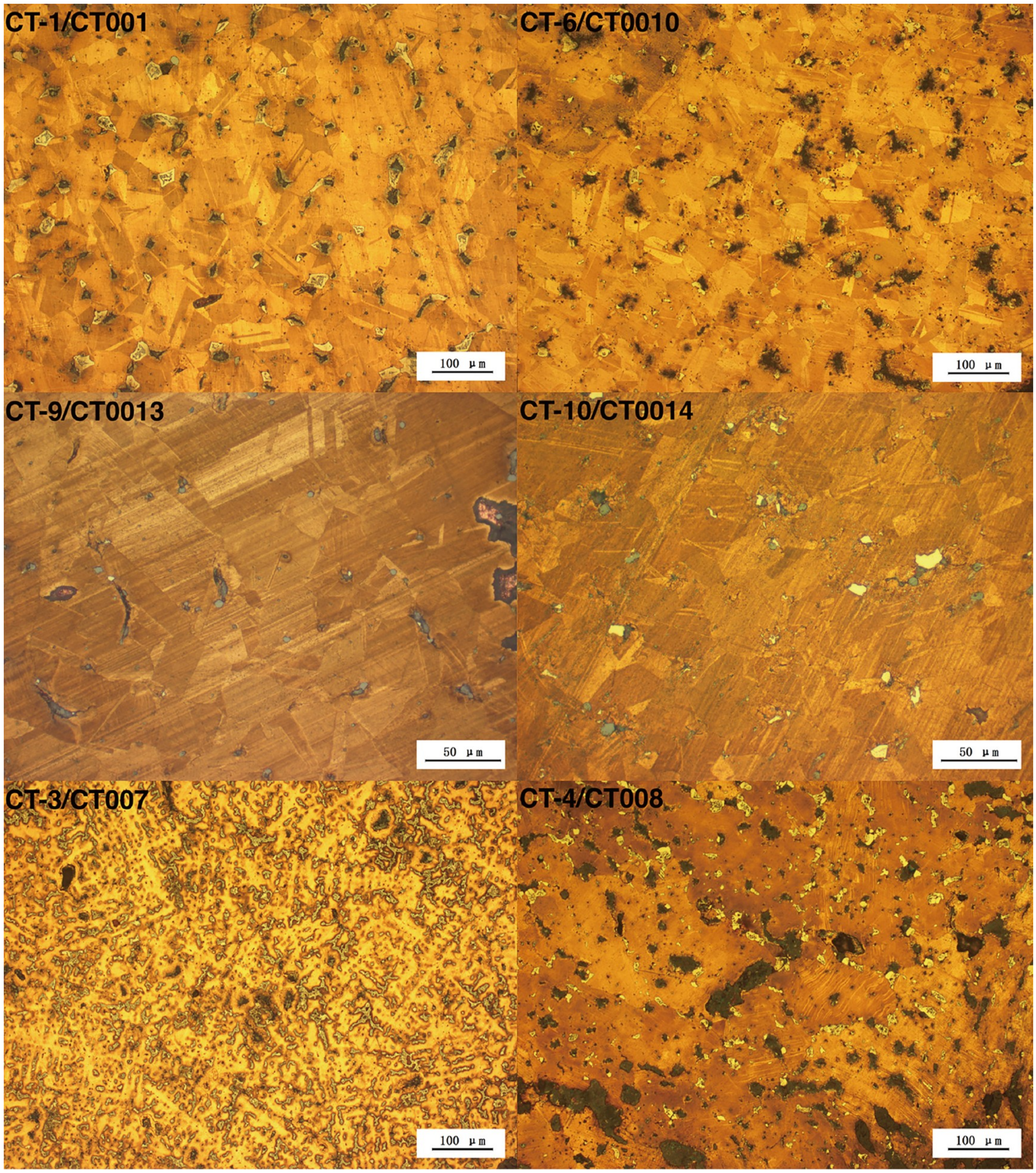

Figure 3 (Color online) Metallographic microstructure pictures of the bronze vessels excavated from Chutai Cemetery M1.

3.2 Chemical composition

The results of the chemical composition analysis of 12 samples are shown in Table 3. Using 2% as the limitation for judging metal type, 9 samples are Pb-Sn bronze, 3 samples are pure Sn artifacts. The 9 Pb-Sn bronze samples are bronze vessel bodies, and the 3 pure Sn samples are bronze vessel solders. The Pb contents of all 9 Pb-Sn bronze samples are higher than 2%, and their lead isotope ratios indicate the source of lead ore. The Cu and Pb contents of 3 pure Sn samples are lower than 1%, while their Sn contents are both higher than 96%, their lead isotope ratios should indicate the source of tin ore.

3.3 Lead isotope ratio

The results of the lead isotope ratio analysis are presented in Table 4 and Figure 4. The lead isotope ratios of 12 samples are as follows: $^{206}Pb/^{204}Pb$ is 17.5623–18.6057, $^{207}Pb/^{204}Pb$ is 15.5238–15.7400, $^{208}Pb/^{204}Pb$ is 38.2134–39.0181, $^{207}Pb/^{206}Pb$ is 0.8460–0.8839, $^{208}Pb/^{206}Pb$ is 2.0971–2.1759, and their lead isotope ratios are all consistent with the characteristics of common lead. The lead isotope data for all samples can be divided into three groups, where the first group includes data for 2 samples (CT-3 and CT-4) from 2 Ding vessels, the second group includes data for 7 samples (CT-1, CT-2, CT-6, CT-7, CT-9, CT-10, and CT-11) from 2

Table 3 Chemical composition of the bronze vessel and solder samples excavated from Chutai Cemetery M1

Lab no.	Excavation no.	Cu (wt%)	Sn (wt%)	Pb (wt%)	Total (wt%)	Alloy type
CT-1	CT001	80.4	15.0	2.9	98.3	Cu-Sn-Pb
CT-2		80.2	15.6	2.0	97.8	Cu-Sn-Pb
CT-3	CT007	73.4	11.1	13.8	98.3	Cu-Sn-Pb
CT-4	CT008	75.2	13.2	10.4	98.8	Cu-Sn-Pb
CT-5	CT0010	0.1	97.1	0.8	98.0	Sn
CT-6		80.8	14.0	3.6	98.4	Cu-Sn-Pb
CT-7		82.8	13.9	1.8	98.5	Cu-Sn-Pb
CT-8	CT0013	0.1	96.9	0.1	97.1	Sn
CT-9		81.5	12.8	4.2	98.5	Cu-Sn-Pb
CT-10		80.7	13.1	4.9	98.7	Cu-Sn-Pb
CT-11	CT0014	81.7	12.1	5.0	98.8	Cu-Sn-Pb
CT-12		0.0	97.5	0.1	97.6	Sn

Table 4 Lead isotope ratio of the bronze vessel and solder samples excavated from Chutai Cemetery M1

Lab no.	Excavation no.	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
CT-1	CT001	17.9350	15.6014	38.5010	0.8699	2.1467
CT-2		17.9742	15.6120	38.5409	0.8686	2.1442
CT-3	CT007	17.6994	15.5591	38.3284	0.8791	2.1656
CT-4	CT008	17.5623	15.5238	38.2134	0.8839	2.1759
CT-5	CT0010	18.6057	15.7400	39.0181	0.8460	2.0971
CT-6		18.2387	15.6773	38.7543	0.8596	2.1249
CT-7		18.0946	15.6359	38.6183	0.8641	2.1343
CT-8	CT0013	18.5064	15.7346	38.9364	0.8502	2.1040
CT-9		18.1561	15.6632	38.6625	0.8627	2.1294
CT-10		18.2206	15.6551	38.6980	0.8592	2.1238
CT-11	CT0014	18.2432	15.6610	38.7218	0.8584	2.1225
CT-12		18.4363	15.6963	38.8310	0.8514	2.1062

He vessels and 2 Dui vessels, and the third group includes data for 3 solder samples (CT-5, CT-8, and CT-12), and each group should point to different mineral sources.

4 Discussion

4.1 Alloying techniques of bronze vessels and their solders excavated from Chutai Cemetery M1

As shown in Figure 5, the chemical compositions of the bronze vessels excavated from Chutai Cemetery M1 can be divided into two categories. The first category includes 2 samples of 2 Ding vessels (CT-3 and CT-4), and their Cu-Sn-Pb variation ranges are as follows: Cu 73.4%–75.2%, Sn 11.1%–13.2%, and Pb 10.4%–13.8%. The second category includes 7 samples of 2 He vessels and 2 Dui vessels (CT-1, CT-2, CT-6, CT-7, CT-9, CT-10, and CT-11), and their Cu-Sn-Pb variation ranges are as follows: Cu 80.2%–82.8%, Sn 12.1%–15.6%, and Pb 2.0%–5.0%. The chemical compositions of these two types of bronze vessels are both concentrated and stable, but the Cu content of Ding vessels is significantly lower than that of He vessels and Dui vessels, and the Sn content is slightly lower than that of He vessels and Dui vessels, while the Pb content is significantly higher than that of He vessels and Dui vessels. The metallographic microstructure analysis shows that the Ding vessels were made by casting, while He vessels and Dui vessels were made by forging followed by cold-working, which shows that the Ding vessels excavated from Chutai Cemetery M1 are distinct from He vessels and Dui vessels in terms of alloying techniques and manufacturing processes, which is probably caused by the difference in function. The He vessels and Dui vessels, which were mainly regarded as food containers, need to be thin, light, and portable, therefore, the lower Pb content and the use of the forging process could reduce the weight and volume of the objects, and enhance the density, portability, and practical functions of the objects compared with those of Ding vessels, whose main function

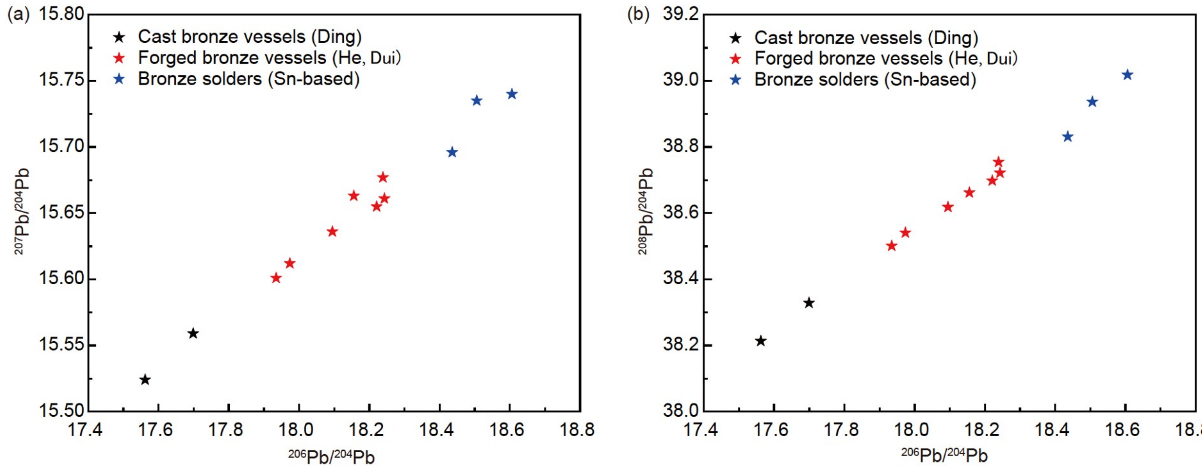

Figure 4 (Color online) Distribution chart of lead isotope data of the bronze vessels and their solders excavated from Chutai Cemetery M1.

was for cooking [8,9].

The 4 forged bronze vessels excavated from Chutai Cemetery M1 are worth highlighting. Compared with the mold-casting method, forging was not the mainstream method of making bronze vessels in China during the Pre-Qin Period [10]. Before the Zhou Dynasty, the forged bronzes found in China were mainly weapons and tools, and no forged bronze vessels were found. The 4 Pen vessels (盆), dating to the early Western Zhou Dynasty excavated from the Yujiawan site in Chongxin, Gansu Province, were the earliest forged bronze vessels ever found [11]. During the Eastern Zhou Period, the production of forged bronze vessels reached its peak in ancient China, and has been found in dozens of Eastern Zhou sites. They were mainly popular in Wu State, Yue State, Chu State, and Jin State during this period [12]. The chemical compositions of the 4 forged bronze vessels excavated from Chutai Cemetery M1, an aristocratic tomb of Chu State in the middle Warring States Period, fluctuate negligibly, showing a stable alloy ratio, and their chemical compositions are located exactly within the main distribution range of the chemical compositions of forged bronze vessels in the Eastern Zhou Period (Figure 6). Through simulation experiments, Zhang et al. [13] showed that the chemical compositions of forged bronze vessels have a suitable interval, in which the Sn content is between 9% and 15.8%, and the Pb content is lower than 5%. The Sn and Pb contents of the 4 forged bronze vessels excavated from Chutai Cemetery M1 are exactly within this interval. The above features all indicate that the alloy techniques of the forged bronze vessels excavated from Chutai Cemetery M1 are relatively mature. In addition, we should pay special attention to the 2 forged Dui vessels. The forged bronze vessels found in the Eastern Zhou Period are mainly Pan (盘), He (盒), Zhou (舟), Pen (盆), Zhi (枳), Xi (洗), Jian (鉴), Fu (釜), Fou (缶), and other vessels, while forged Dui vessels are rarely discovered. Similar findings can be seen in Dui vessels of the early-middle Warring States Period, excavated from LiuYue Cemetery M1, Huangmei, Hubei Province [14]. Related studies have shown that the middle Warring States

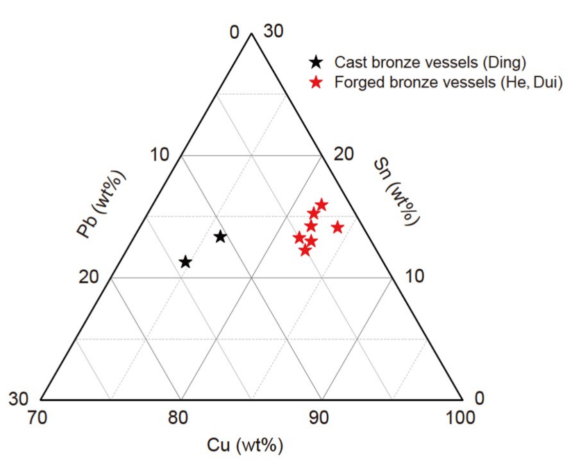

Figure 5 (Color online) Comparison chart of the chemical composition of two types of bronze vessels excavated from Chutai Cemetery M1.

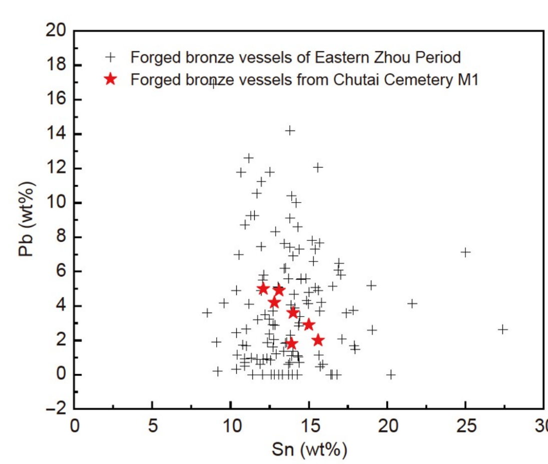

Figure 6 (Color online) Comparison chart of the Sn and Pb contents of forged bronze vessels excavated from Chutai Cemetery M1 and forged bronze vessels of the Eastern Zhou Period.

Period was a significant period in the transition from prosperity to decline for Dui vessels. Before the middle Warring States Period, the Dui vessels were beautifully decorated and highly skilled, while after this time, the number of Dui vessels decreased rapidly with their practical function gradually enhanced and the surface was mostly plain [15]. The forged Dui vessels excavated from Chutai Cemetery and Liuyue Cemetery are typical representatives of this transition phase.

Welding is a technical method of joining different positions of an object into shape, which is an important part of the bronze manufacturing process in ancient China [16,17]. The 3 pieces of Sn solder tested in this paper are crucial for understanding the alloy type of ancient Chinese bronze solders, because most solders found on Pre-Qin bronzes are made of Pb, Sn-Pb, and Cu-Sn-Pb materials, and Sn solders are found to be relatively less common [18,19]. At present, Sn solders are mainly found in bronzes of the Spring and Autumn Period, such as the bronze Ding (鼎) (M85:8) from Yidigang Cemetery, Suizhou [19]; the bronze Fu (簠) (M180:1) from Yugang Cemetery, Xiangyang [20]; the bronze Ding (鼎) (M2:34) from Xiashi Cemetery, Xichuan [21]; the bronze Jian (鉴) (M1:18) from Wenfengta Cemetery, Suizhou [22]; the bronze Zhan (盏) (M4:2) from Huangtupo Cemetery, Zhongxiang [19] and the bronze Zhan (盏) (M4) from the tomb of Xu duke in Yexian [23]. In addition, Sn solder was also found in the bronze JianFou (鉴缶) of the Cemetery of Marquis Yi of Zeng State, Suizhou in the early Warring States Period [24]. These bronze vessels, similar to the He vessels (CT0010) and Dui vessels (CT0013 and CT0014) excavated from Chutai Cemetery M1, are mainly found within the influencing terrains of Chu State during the Eastern Zhou Period and show obviously Chu-type style, which seems to suggest that Chu State already controlled rich tin resources during the Eastern Zhou Period.

4.2 The mineral sources of bronze vessels and their solders excavated from Chutai Cemetery M1 and the metal resource circulation in Eastern Chu State during the Warring States Period

The eastern part of Chu State was the core area of Chu's domination during the Warring States Period. In recent years, there have been several case studies on metal artifacts excavated from this region, but there is a lack of panoramic observations on the use patterns and circulation networks of metal resources in this region. Here we explore the possible mineral sources of the bronze vessels and their solders excavated from Chutai Cemetery M1. We focus on comparing their lead isotope data with the lead isotope data of Warring States metal artifacts (containing bronzes and other alloy-type artifacts) excavated from Eastern Chu State, aiming to further discuss the use and circulation of metal resources in Eastern Chu State during this period and the similarities and differences in mineral sources of different sites. It should be noted that almost all bronzes compared in this section have Pb contents higher than 2%, their lead isotope data mainly point to the source of lead ore, while the lead isotope data of the Sn artifacts, Pb artifacts, and Sn-Pb artifacts for comparison point to the source of tin ore and lead ore, respectively (Figure 7).

As mentioned earlier, the lead isotope data of Ding vessels excavated from Chutai Cemetery M1 are obviously different from those of He vessels and Dui vessels (referred to cast bronze vessels and forged bronze vessels below, respectively). The lead isotope data of the cast bronze vessels excavated from Chutai Cemetery M1, bronze excavated from Luan [25], and some Chu coins [26] are close to each other, and their $^{206}Pb/^{204}Pb$ ratios are clustered in the range of 17.5–17.9. The lead isotope data in this range overlap well with the lead isotope data from lead ores in Western Henan, previous studies also indicate that lead ores from Western Henan were widely used in Chu bronzes during the Eastern Zhou Period [27], so the cast bronze vessels excavated from Chutai Cemetery M1 might use lead ores from Western Henan. The lead isotope data of the forged bronze vessels excavated from Chutai Cemetery M1; bronzes excavated from Xijuan Cemetery M25 [28]; bronzes excavated from Shouxian [25]; bronzes excavated from Zongyang [29]; bronzes collected in Fuyang Museum [6]; and some Chu coins [26] are close to each other and are concentrated in the range of $^{206}Pb/^{204}Pb$=17.9–18.3. In fact, the mineral source situation indicated by this range of data is complex, these data partially overlap with lead isotope data from lead ores in the middle and lower reaches of the Yangtze River. Furthermore, it is possible that this range of data may be a result of mixing, especially in the case of the forged bronze vessels excavated from Chutai Cemetery M1, where 3 Sn solders are found. It appears that metal minerals from the tin-rich region of Southern China were introduced into the production of forged bronze vessels, accompanied by possible copper or lead material from adjacent regions (discussed in detail below). Therefore, compared with the cast bronze vessels, the increase in metal minerals with higher radiogenic in the south may lead to the data of the forged bronze vessels being in the middle of the data range.

The lead isotope data of metal artifacts represented by solders and horse-fittings (including three alloy types: Sn, Pb, and Sn-Pb) have higher radiogenic, with the $^{206}Pb/^{204}Pb$ ratios concentrated in the range of 18.4–18.7, which is clearly different from the lead isotope data of most bronzes mentioned above. In fact, the lead isotope data of the Sn solders excavated from Chutai Cemetery M1 and the Sn-based, Pb-based, and Sn-Pb-based horse fittings excavated from Xijuan Cemetery M25 are very close to each other. The tin ores and lead ores indicated by these data are likely to

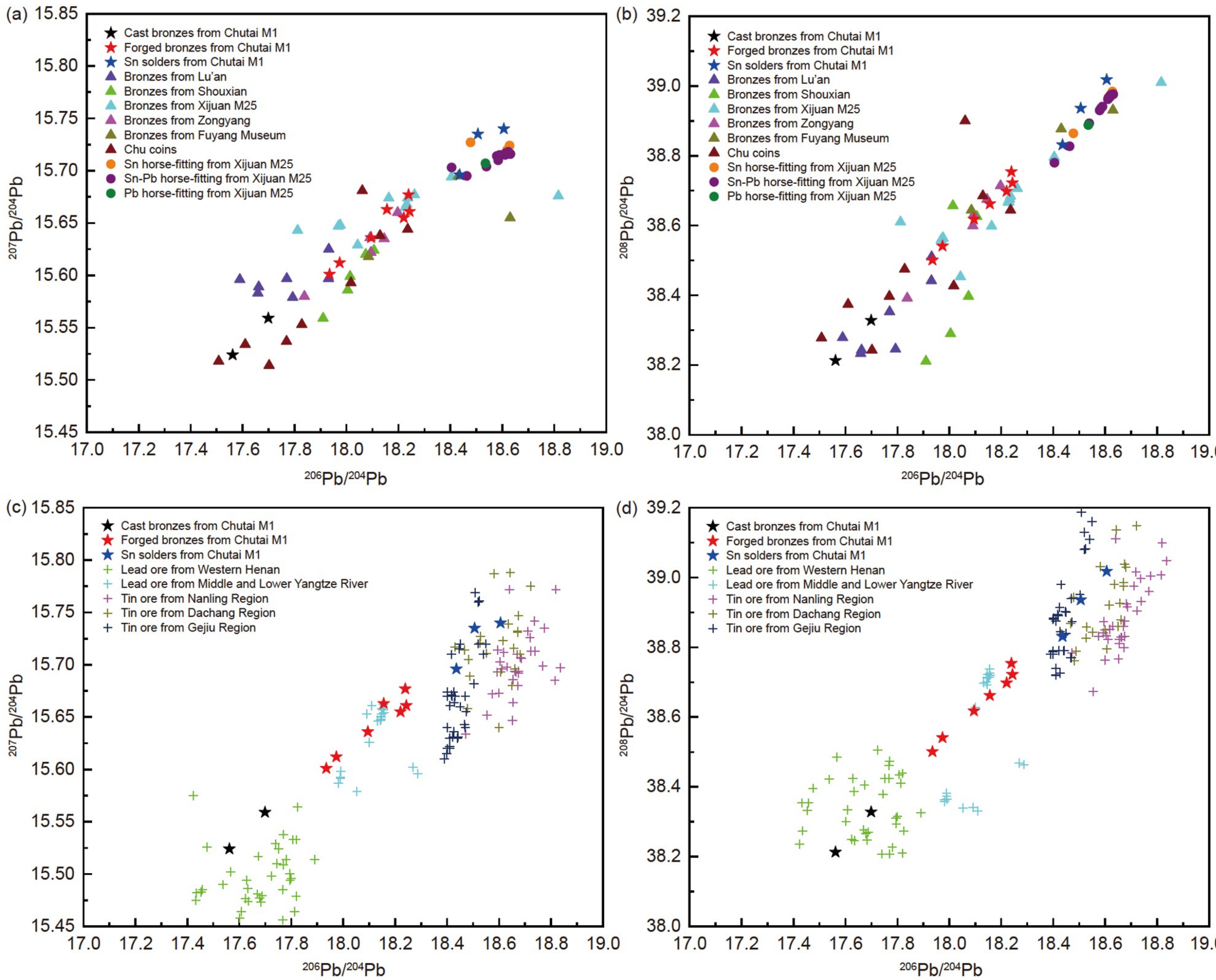

Figure 7 (Color online) (a), (b) Comparison chart of lead isotope data of Warring States bronzes and other metal artifacts excavated from Eastern Chu State; (c), (d) comparison chart of lead isotope data between the bronze vessels and their solders excavated from Chutai Cemetery M1 and metal ores in related regions.

come from polymetallic deposits of the same region. These data all partially overlap with the lead isotope data of tin and lead ores from the Nanling region, Dachang region, and Gejiu region in Southern China, but we consider that the minerals for these metal artifacts might come from the Nanling region for several reasons. First, the Nanling region, which spans Hunan, Guangxi, Guangdong, and Jiangxi, is an important primary tin ore distribution area in the world [30], and this region is also rich in lead mineral resources. Second, compared with the Dachang region and Gejiu region, the Nanling region is closer to the Anhui region, and these two regions were both strongly influenced by the power of the Chu State during the Warring States Period, which undoubtedly facilitated cultural exchange and metal resource circulation between the two regions. Third, recent studies have shown that the metal minerals of the Nanling region were widely used in the Xiangjiang Basin, Han-Huai Basin, and Nanyang Basin during the Eastern Zhou Period [31,32]. Currently, we cannot rule out that the Dachang region and Gejiu region are the possible mineral sources of these Sn-based, Pb-based, and Sn-Pb-based artifacts, but we can be sure that the minerals for these artifacts should come from tin-rich regions in Southern China, and their production was closely related to the large-scale mining, utilization, and circulation of tin resources during the same period.

In general, bronzes and other alloy artifacts from Eastern Chu State during the Warring States Period show different patterns and regularities in lead isotope data, which point to different kinds of minerals and contain a wide range of sources, including a series of potential regions in Western Henan, the middle and lower reaches of the Yangtze River and the Nanling region. The above features are certainly related to the special geographical location and frequent cultural interactions in this region, suggesting the existence of a large-scale and well-managed metal resource circulation network in Eastern Chu State during the Warring States Period.

5 Conclusions

In this study, the metallographic microstructure, chemical composition, and lead isotope ratio of 6 Warring States bronze vessels excavated from Chutai Cemetery M1, Fuyang, Anhui Province were analyzed. The results showed that among the 6 bronze vessels, 2 Ding vessels were casting, 2 He vessels and 2 Dui vessels were forging followed by cold working, 9 body samples of the 6 bronzes were all made of Cu-Sn-Pb materials, and 3 solder samples were made of pure Sn materials. In addition, the lead isotope ratios of all samples are consistent with the characteristics of common lead, and the lead isotope data of 2 Ding vessels, 2 He vessels, and 2 Dui vessels, as well as 3 Sn solders, are each grouped together.

The 2 Ding vessels, as well as 2 He vessels and 2 Dui vessels excavated from Chutai Cemetery M1, are Pb-Sn bronze. However, the alloy techniques and manufacturing processes are diversified, which may be related to the variation in object functions. The 2 forged He vessels and 2 forged Dui vessels have stable chemical compositions that are within the distribution range of the chemical compositions of forged bronze vessels in the Eastern Zhou Period, suggesting that their alloy techniques were quite mature. The 3 Sn solders on the bronze vessels excavated from Chutai Cemetery M1 were not commonly found during the Chinese Bronze Age, and similar material of solders on bronze vessels was mainly found in the Chu culture area, which was rich in tin ore resources during the Eastern Zhou Period.

The bronze vessels and their solders excavated from Chutai Cemetery M1 were from a wide range of mineral sources, among which the lead minerals of 2 Ding vessels could come from Western Henan, the lead minerals of 2 He vessels and 2 Dui vessels might come from the middle and lower reaches of the Yangtze River, or from a mixture of Western Henan lead ore and Southern China lead ore, and the tin minerals used in the 3 Sn solders might come from tin-rich regions in Southern China. Moreover, The Chutai Cemetery M1 was in an extensive metal resource distribution network of Eastern Chu State during the Warring States Period, the metal artifacts excavated from Chutai Cemetery M1 had mineral sources similar to those excavated from several sites in Eastern Chu State during the same period.

This work was supported by the National Natural Science Foundation of China (Grant No. 41303080), the Youth Promotion Association of the Chinese Academy of Sciences (Grant No. 2018499), and the National Key R&D Program of China (Grant No. 2022YFF0903700).

1 Zhang A B, Lu Q Y. The age and feature of Shang Dynasty bronze vessels unearthed from Southern Anhui (in Chinese). Archaeology, 2010, 6: 83–91
2 Liu H H. The Eastward Expansion of Chu Culture (in Chinese). Wuhan: Hubei Education Press, 1995
3 Zhou C Y, Lu Q Y, Zhu D H. Discovery and preliminary research on Shang and Zhou Bronzes in Northern Anhui (in Chinese). Historical Res Anhui, 2013, 6: 106–111, 118
4 Han Z Q, Feng Y T. The Warring States Period inscribed weapons excavated from Fuyang, Anhui Province (in Chinese). Southeast Culture, 1991, 2: 258–261
5 Feng Z J. Study on the bronzes of Shang and Zhou Periods in the north of Huaihe River in Anhui Province (in Chinese). Dissertation for Master's Degree. Hefei: Anhui University, 2016
6 Li Q, Huang H Y, Li L X, et al. Lead isotope ratio analysis of several Zhou Dynasty bronzes unearthed in Northern Anhui Province (in Chinese). Rock Mineral Anal, 2022, 41: 14–21
7 The Warring States tombs found in Chutai Cemetery, Fuyang, Anhui Province (in Chinese). Identif Appreciat Cultural Relics, 2018, 2: 91
8 Qin Y, Li S C, Yan D F, et al. Scientific analysis on hot-forged bronze vessels of the Eastern Zhou Dynasty to Qin and Han Periods excavated from Hubei and Anhui (in Chinese). Cultural Relics, 2015, 7: 89–96
9 Nan P H, Wang X Y, Chen X S, et al. The manufacturing processes of two bronze ladle dou unearthed from M30 at Wayaopo Cemetery in Xixian, Shanxi (in Chinese). Archaeology, 2020, 7: 107–116
10 Su R Y, Hua J M, Li K M. The Metal Technology of Early Ancient China (in Chinese). Shandong: Shandong Science and Technology Press, 1995
11 Zhang Z G, Ma Q L. Metallographical and element analysis on the bronzes of Western Zhou Dynasty excavated from Yujiawan, Gansu Province (in Chinese). Sci Conservat Archaeol, 2008, 1: 24–32, 76–77
12 Li Y. Between Furnaces and Hammers: Studies on Hot-Forged Thin-Walled Bronzes from the Pre-Qin Period to Han Dynasty (in Chinese). Shanghai: Shanghai Classics Publishing House, 2017
13 Zhang J, Liang C, Wang Z G, et al. Metallographic and component analysis of the bronze vessels excavated from Yugang Cemetery at Xiangyang City (in Chinese). Jianghan Archaeol, 2019, 3: 126–134, 102
14 Zhang J, Fan G D, Lin S R, et al. Scientific research of bronzes unearthed from tomb M1 at the Liuyue Cemetery in Huangmei County, Hubei Province (in Chinese). Jianghan Archaeol, 2021, 4: 126–133, 80
15 Gu Z X. Collection and Research on Ancient Chinese Bronzes—Volume of Dui Vessels (in Chinese). Beijing: Science Press, 2016
16 He T K, Jin F Y. A preliminary study on welding techniques in ancient China (in Chinese). Huaxia Archaeol, 2000, 1: 1–65
17 Zhang C P. The formation of the welding technology tradition in the casting of Shang and Zhou bronze rituals (in Chinese). Archaeology, 2018, 2: 88–98, 2
18 Sun S Y, Mei J J. Analysis on Pb-Sn solders in ancient China (in Chinese). J Univ Sci Tech Beijing, 2009, 31: 54–61
19 Zhang J. The research on the resource and technology of Eastern Zhou bronzes—Focusing on the Han-Huai region (in Chinese). Dissertation for Doctoral Degree. Beijing: Peking University, 2020
20 Institute of Cultural Relics and Archaeology of Xiangyang. Chu Tombs in Xiangyang (in Chinese). Beijing: Science Press, 2011
21 Henan Provincial Institute of Cultural Heritage and Archaeology, Archaeological Excavation Team of Henan Danjiang Reservoir, Xichuan Museum. The Chu Tombs of the Spring and Autumn Period in Xiasi, Xichuan (in Chinese). Beijing: Cultural Relics Press, 1991
22 Li Y, Hou J S, Fan Z W, et al. Materials characteristics of metal objects from tomb M1 and M2 of Wenfengta Cemetery in Suizhou (in Chinese). Jianghan Archaeol, 2014, 4: 91–108
23 Li Y Z, Zhang F T, Tan D R, et al. The decorative bronze with hollow symmetry nake patterns unearthed in the tomb of the Duke Linggong of Xu State—One of the cases of pre-Qin lost-wax method (in Chinese). Cultural Relics Central China, 2007, 1: 96–103
24 The Museum of Hubei Province. Tomb of Marquis Yi of Zeng State (in Chinese). Beijing: Cultural Relics Press, 1989
25 Wen J, Ling X, Zhao C C, et al. Primary analysis on lead isotope characteristics in Chu State bronzes in Eastern Zhou Period unearthed

from Luan District, Anhui Province (in Chinese). J Northwest Univ (Nat Sci Ed), 2013, 43: 1016–1020
26 Jin Z Y, Chase W T, Mabuchi H, et al. Study on the lead isotope ratio of the Warring States coins—Also on the lead in Lingnan, Guangdong during the same period (in Chinese). Cultural Relics, 1993, 8: 80–89
27 Zhang J, Chen J L. Preliminary lead isotopic study on Eastern Zhou Period bronzes (in Chinese). Cultural Relics Southern China, 2017, 2: 94–102
28 Chen D, Han Y, Wang Z, et al. The prestigious tin-lead horse fittings in the Warring States Period: Evidence from funerary artefacts of a Warring States Tomb at Shouxian, Anhui. Archaeometry, 2021, 63: 1290–1305
29 Wang Y, Wei G, Li Q, et al. Provenance of Zhou Dynasty bronze vessels unearthed from Zongyang County, Anhui Province, China: Determined by lead isotopes and trace elements. Herit Sci, 2021, 9: 97
30 Wang D H, Chen Y C, Chen Z H, et al. Assessment on mineral resource in Nanling region and suggestion for further prospecting (in Chinese). Acta Geol Sin, 2007, 7: 882–890
31 Luo Z, Fan A C, Jin Z Y, et al. Scientific analysis and research on the Warring States bronze mirrors unearthed from Changsha Chu cemetery, Hunan Province, China. Archaeometry, 2022, 64: 1187–1201
32 Zhang J, Wang D, Jia H Q, et al. Analysis of the Spring and Autumn bronzes excavated from Huangtupo Cemetery in Zhongxiang and research on related issues (in Chinese). Cultural Relics Southern China, 2019, 3: 104–113