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RESEARCH

Bronze technology and metal resources in the Zhouyuan area before and after the replacement of Shang and Zhou Dynasties

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Abstract
The Zhouyuan site was the largest central settlement in the western Guanzhong Plain during the Shang and Zhou periods; it was once the capital of the Zhou people before the establishment of Western Zhou. The archaeological culture used by the Zhou people before they destroyed the Shang Dynasty is called "pre-Zhou culture." In this work, bronzes excavated in the Zhouyuan area from the pre-Zhou period to the Western Zhou period were analyzed via a field emission electron probe microanalyzer for chemical compositions and MC−ICP−MS for lead isotope ratios. The results show that various alloy types were used in pre-Zhou, whereas more stable alloy recipes and materials with better performance were used in Western Zhou. The pre-Zhou bronzes contain highly radiogenic lead and common lead, and the Western Zhou bronzes are all common lead. The alloying techniques and metal resources of the Zhouyuan area both changed significantly from pre-Zhou to Western Zhou, which could be related to the great transformation of the bronze industry pattern after the Zhou people replaced the dominance of the Shang Dynasty. Zhouyuan also participated in the circulation network of metal resources centered on Yin Ruins during the late Shang. The highly radiogenic lead metal resources were probably obtained from Yin Ruins through the Shang culture in the eastern Guanzhong Plain (Laoniupo). It can be inferred that the Zhou people acquired bronze smelting and casting techniques from Shang after they conquered Laoniupo; then, their military equipment, as well as sacrificial vessels, improved considerably, which provided resources and technical support for the forthcoming war against the Shang capital.

Keywords Zhouyuan site · Pre-Zhou period · Bronze alloy technology · Lead isotope analysis · Replacement of Shang and Zhou

Introduction

The Shang and Western Zhou dynasties were the heyday of Chinese bronze culture. The replacement of Shang by Western Zhou was a very important dynasty change in the early history of China because the politics, economy, culture, military, ethics and other aspects of ancient China underwent great changes and profoundly influenced later generations. Therefore, the study of the origin and early stage development of the Zhou people has been extremely important in Chinese history for a long time. According to ancient documentary records, Zhou was a small tribe in the west of the Central Plains before the destruction of the Shang Dynasty; the Zhou people originated in the west of the Guanzhong Plain, then migrated around it, finally settled in Zhouyuan at the southern foot of Qi Mountain and began to flourish. By the time of King Wen (文王), the Zhou people had begun to overthrow the Shang Dynasty and moved the capital to Feng (丰). King Wu (武王), the son of King Wen, ultimately destroyed the Shang Dynasty, established the Western Zhou Dynasty and founded the capital Hao (镐). The capital of Western Zhou changed from Zhouyuan to Fenghao. Chinese scholars began to explore early Zhou history archaeologically in the 1930s. The archaeological culture used by the Zhou people before King Wu destroyed the Shang Dynasty is called "pre-Zhou culture," which was a regional bronze culture during the

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Shang period. After the establishment of the Western Zhou Dynasty, on the basis of inheriting pre-Zhou culture, the Zhou Dynasty absorbed Shang culture and other cultures and formed the unique Western Zhou culture. According to historical documents, archaeological work on pre-Zhou culture has been carried out mainly in the west of the Guanzhong Plain and the northern loess tableland. Many important sites, such as Zhouyuan, Fenghao, Zhengjiapo, Nianzipo, Beilyu, Zhougongmiao and Xitou, have been excavated (Fig. 1). Although scholars have different opinions about each site, the age of the remains of pre-Zhou culture that has been discovered thus far is roughly the same as that of the late Shang culture (Yin Ruins), and the upper limit may be as early as the early and middle Shang culture (Zou 1980; Liu 2003; Zhang 2004; Lei 2010). However, the archaeological cultures in the Guanzhong area during the Shang period were quite complicated. The area east of Xi 'an city was the distribution area of Shang culture, and the western area had not only pre-Zhou culture but also the Jingdang type of Shang culture, which disappeared in Yin Ruins phase II (ca. 1255–1195 BC) and Qiang Rong culture. Therefore, it is very difficult to identify which type of archaeological remains belongs to the pre-Zhou culture. Scholars have debated this topic for many years, but it is still inconclusive (Liu 2003; Zhang 2004; IA, CASS 2007; Lei 2010; Sun 2015). Among these sites, the historical records of the Zhouyuan and Fenghao sites, which were once the capitals of the Zhou people, are clearer and constitute the basis for confirming pre-Zhou culture. The Zhouyuan site, in particular, has been used for a long time, and many archaeological remains have remained.

The archaeological site of Zhouyuan is located at the junction of Fufeng and Qishan Counties, Baoji City, Shaanxi Province, China. This site covers an area of approximately 30 square kilometers and was the largest central settlement site in the western Guanzhong Plain during the Shang and Zhou Dynasties. As early as the Han Dynasty, Shang and Zhou bronzes were found in the area of Zhouyuan. In the late Qing Dynasty, a number of Western Zhou bronzes were discovered in Zhouyuan. Since the 1940s, archaeologists began to carry out archaeological investigations and excavations in the Zhouyuan area, finding many bronze cellars, ash pits, tombs, and large architectural foundations, as well as workshops on copper casting, bone making and stone making. In particular, the Western Zhou building groups found in the Fengchu, Yuntang-Qizhen, and Zhaochen sites were quite large in scale and were believed to be palaces or ancestral temples. From 2020 to 2021, a massive rammed earth building in the pre-Zhou period was found at the Wangjiazui site in Zhouyuan, with a total area of more than 2200 square meters, which was believed to be a palace or ancestral temple, providing key evidence confirming that the Zhouyuan site was the capital of Zhou in the pre-Zhou period (EBCCRN 2022). At the same time, the city walls of a small city, which were built from the late Shang period to the early Western Zhou period, and a large city built in late Western Zhou were confirmed (Fig. 2). The small city was

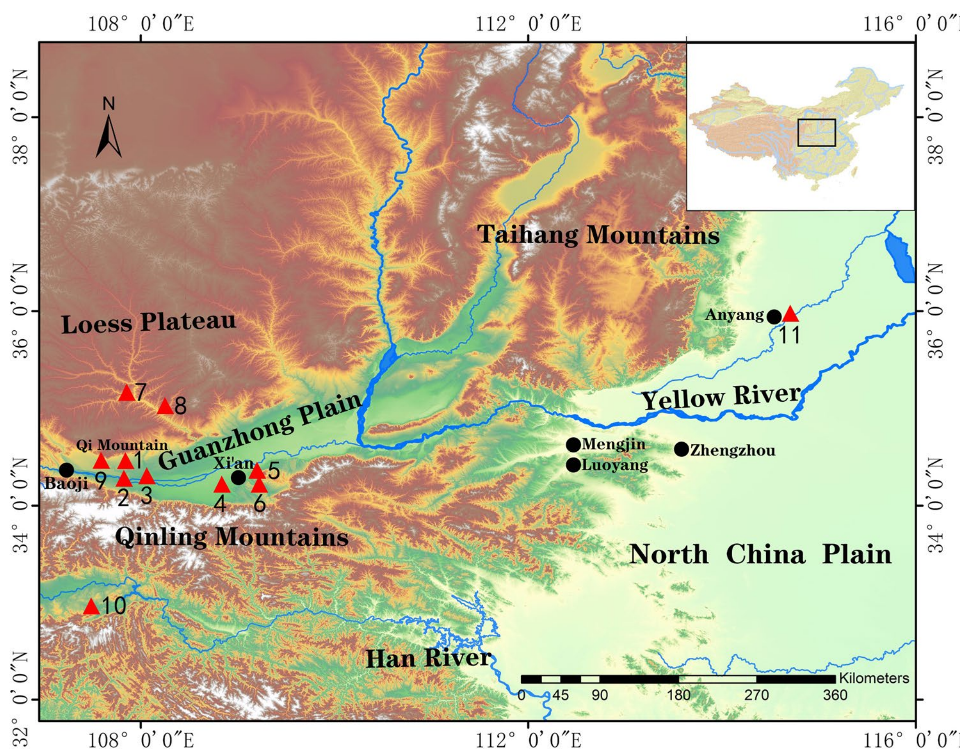

Fig. 1 Locations of the Zhouyuan site and related sites. 1. Zhouyuan 2. Beilyu 3. Zhengjiapo 4. Fenghao 5. Laoniupo 6. Huaizhenfang 7. Nianzipo 8. Xitou 9. Zhougongmiao 10. Hanzhong 11. Yin Ruins

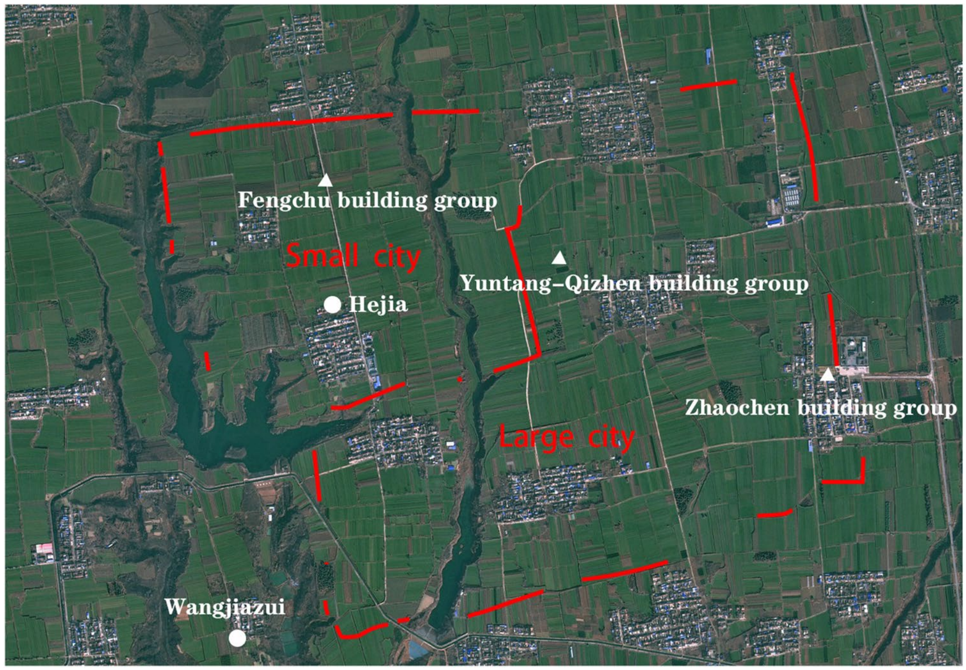

Fig. 2 Zhouyuan city and the locations of the Wangjiazui and Hejia sites. The shape of the city walls is based on ZAT (2023)

much larger than all known city sites in early Western Zhou, and the large city was basically the same size as the capital Luoyang in the late Western Zhou period (ZAT 2023). In the past, scholars generally believed that Zhouyuan was the place where the Zhou people built ancestral temples and nobles settled in Western Zhou. On the basis of the large city newly founded in Zhouyuan, a new point of view was put forward that Zhouyuan was the capital of Western Zhou after the time of King Kang (康王) (Cao 2023).

Owing to the unique historical status of Zhouyuan, archaeologists have focused on the Shang and Western Zhou bronzes unearthed there. A considerable amount of research on the decorations, shapes, inscriptions and combinations of objects has been conducted (Cao 2004, 2005; Xu 2002; Xu and Duan 2017; Pei 2019). Scholars have also analyzed the alloy compositions, metallography structures and casting technologies of copper wares from the Zhouyuan area during the pre-Zhou and Western Zhou periods and have focused on bronze technologies (Zhang et al.1999; Yang 2002; Zhou et al. 2009; Yang et al.2011; Liu et al. 2017; Wang et al.2017; Sun et al. 2022). However, few scientific analyses of bronzes from the pre-Zhou period have been performed, especially lead isotope and trace element analyses. In addition, there is still a significant lack of research on the metal circulation patterns between Shang and pre-Zhou bronze cultures. In this work, we report the analysis results of the alloy compositions and lead isotope ratios of copper wares excavated at the Wangjiazui and Hejia sites in Zhouyuan and at the nearby Zhengjiapo site in Wugong County and the Beilyu site in Fufeng County (Fig. 1) from the pre-Zhou period to the early and middle Western Zhou periods. Combined with previous studies, we explore the production and circulation of pre-Zhou copperwares in the Zhouyuan area and further discuss the replacement of the Shang and Zhou Dynasties from the perspective of bronze technology and metal circulation.

Materials and methods

Materials and chronology

The types of pre-Zhou bronzes unearthed in the Zhouyuan area vary and include vessels, weapons, tools, chariot and horse fittings, as well as ornaments. During the Western Zhou period, both the quantity and type of bronze objects excavated in Zhouyuan increased substantially. Since this paper is concerned mainly with alloying technology and metal resources from pre-Zhou to early Western Zhou in the Zhouyuan area, different types of objects from this period were selected and sampled for analysis. It was also influenced by the preservation status of the artifacts, as intact artifacts could not be sampled. A total of 30 bronze artifacts unearthed in the Zhouyuan area were analyzed in this work, including vessels, weapons, tools, ornaments, and chariot fittings (Fig. 3). Detailed information on these samples is shown in Table 1. Among them, 19 bronzes were unearthed from Wangjiazui, 7 from Hejia, 12 from Beilyu, and 1 from Zhengjiapo. Weapons, including dagger axes and halberds, are bent or broken intentionally, which was a special burial custom of the Zhou people (Zhang 2005). The Wangjiazui and Hejia sites in Qishan County are located

Fig. 3 Bronze wares unearthed in the Zhouyuan area during the pre-Zhou and Western Zhou periods

in the core area of the Zhouyuan site and face each other across the Wangjiagou ditch (Fig. 2). A number of archaeological investigations and excavations have been carried out there over the years, revealing that this area has the densest distribution and richest accumulation of archaeological remains at the Zhouyuan site during the Shang Dynasty (ZAT 2003). Recently, the discovery of the large rammed earth building in the north of Wangjiazui village revealed that the Wangjiazui area was the center of the Zhouyuan settlement during the pre-Zhou period (EBCCRN 2022). The Wangjiazui site is roughly equivalent to the late Shang period (ca. 1320–1040 BC) (Lei 2010), and the artifacts analyzed in this work are mainly from the pre-Zhou tomb 19 excavated in 1996–1997 (Yang et al.2003; Lei 2010), which is a medium-sized tomb with numerous burial goods; the owner was likely an aristocrat. On the basis of the stratigraphy and shape of burial objects, Lei (2010) claims that tomb 19 is roughly dated to the period between Zhou's migration to Feng and the destruction of the Shang Kingdom. The Hejia bronzes are mainly from tomb 1 and tomb 5, which were excavated in 1973 (SPM and SPCRMC 1976), and the Western Zhou tomb, which was excavated in 1966 (Chang 1972). Among them, 1973 tomb 1 is a medium-sized tomb, which is the highest grade pre-Zhou burial found thus far at the Zhouyuan site. The bronze group unearthed is a typical unit of pre-Zhou culture and can be dated to Yin Ruins phases III and IV (ca. 1205–1040 BC) (Li 2017). The 1973 tomb 5 and 1966 Western Zhou tomb can be dated to the early Western Zhou period. The Zhengjiapo site in Wugong County is nearly 30 km southeast of Zhouyuan. The bronze tripod analyzed in this study was collected at Shangjiapo within the Zhengjiapo site (BCAWT 1984) and was dated to Yin Ruins phase II by typology research (Zhang 2004). The Beilyu cemetery in Fufeng County is approximately 20 km south of the Zhouyuan site. On the basis of burial customs, burial objects, and bronze inscriptions, excavators believe that tomb owners were soldiers guarding the capital of Zhouyuan (BCZM and Luo 1995). The Beilyu cemetery lasted for a long time and was divided into 6 phases by the excavator. The bronzes analyzed are mainly from phases I, III and VI, and their ages are equivalent to those of Yin Ruins phase III (ca. 1205–1080 BC), the transition between Shang and Zhou, and middle Western Zhou, respectively. For some objects from the transition period, it was difficult to determine whether they belonged to late Yin Ruins Phase IV (ca. 1090–1040 BC) or the beginning of Western Zhou. Thus, all the samples could be divided into three major stages, namely, the pre-Zhou period, the transition period between Shang and Zhou, and the Western Zhou period. The sampling site was chosen to be at the broken stubble of the artifact or a hidden area avoiding the main decoration, and a small piece that was approximately 3 mm^3 was cut. Most samples contained a metal body, except for ZY-XA039, which was severely rusted.

Analytical methods

The chemical compositions of the samples were analyzed to reveal the alloy techniques used. The tests were carried out using a field emission electron probe microanalyzer (JEOL JXA-8530F Plus) at the Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China (USTC), Chinese Academy of Sciences. The experimental conditions included a 15 kV

Table 1 Sample information of the bronzes from the Zhouyuan area

Site	Object	Lab No	Archaeological No	Relative Date	Late Shang or Western Zhou Kings	Absolute Date	Remarks	Reference
Zhengjiapo	Tripod	ZY-2274		Phase II of Yin Ruins	Wu Ding (late phase), Zu Geng, Zu Jia	1255–1195 BC		BCAWT 1984
Beilyu	Dagger-axe	Y19	IV M93:7	Phase III of Yin Ruins	Lin Xin, Kan Ding, Wu Yi, Wen Ding	1205–1080 BC	Phase I of the cemetery	BCZM and Luo 1995
	Dagger-axe	Y17	I M7: 4	Phase IV of Yin Ruins to Early Western Zhou (transition period)	Di Yi, Di Xin (Shang Kings), King Wu, King Cheng (Western Zhou Kings)	1090–1021 BC	Phase III of the cemetery	
	Pao	Y27	II M4:1	Phase IV of Yin Ruins to Early Western Zhou (transition period)	Di Yi, Di Xin (Shang Kings), King Wu, King Cheng (Western Zhou Kings)	1090–1021 BC	Phase III of the cemetery	
	Dagger-axe	Y13	II M3:2	Phase IV of Yin Ruins to Early Western Zhou (transition period)	Di Yi, Di Xin (Shang Kings), King Wu, King Cheng (Western Zhou Kings)	1090–1021 BC	Phase III of the cemetery	
	Dagger-axe	Y20	IV M210	Phase IV of Yin Ruins to Early Western Zhou (transition period)	Di Yi, Di Xin (Shang Kings), King Wu, King Cheng (Western Zhou Kings)	1090–1021 BC	Phase III of the cemetery	
	Bell chariot fitting	Y25	IV M145:3	Phase IV of Yin Ruins to Early Western Zhou (transition period)	Di Yi, Di Xin (Shang Kings), King Wu, King Cheng (Western Zhou Kings)	1090–1021 BC	Phase III of the cemetery	
	Fish	Y22	VM25	Middle Western Zhou	King Yi, King Xiao	899–886 BC	Phase VI of the cemetery	
	Fish	Y23	VM25	Middle Western Zhou	King Yi, King Xiao	899–886 BC	Phase VI of the cemetery	
	Wei chariot fitting	Y24	VM25	Middle Western Zhou	King Yi, King Xiao	899–886 BC	Phase VI of the cemetery	
	Tripod	Y29	VM148: 2	Middle Western Zhou	King Yi, King Xiao	899–886 BC	Phase VI of the cemetery	
	Dagger-axe	Y26		Unknown				
	Fish	Y28		Unknown				

Table 1 (continued)

Site	Object	Lab No	Archaeological No	Relative Date	Late Shang or Western Zhou Kings	Absolute Date	Remarks	Reference
Wangjiazui	Chisel	Y30	H3	Pre-Zhou (Late Shang)		1320–1040 BC		Yang et al.2003 ; Lei 2010
	Chisel	Y31	H14③:2	Pre-Zhou (Late Shang)		1320–1040 BC		
	Ring	Y32	M19:006–1	Phase IV of Yin Ruins	Di Yi, Di Xin	1090–1040 BC		
	Fragment	Y33	M19:006–2	Phase IV of Yin Ruins	Di Yi, Di Xin	1090–1040 BC		
	Fragment	Y34	M19:006–3	Phase IV of Yin Ruins	Di Yi, Di Xin	1090–1040 BC		
	Dagger-axe	YN1	M19:001	Phase IV of Yin Ruins	Di Yi, Di Xin	1090–1040 BC		
	Halberd	YN2	M19:006	Phase IV of Yin Ruins	Di Yi, Di Xin	1090–1040 BC		
	Dagger-axe	YN3	M19:3	Phase IV of Yin Ruins	Di Yi, Di Xin	1090–1040 BC		
	Halberd	YN4	M19:1	Phase IV of Yin Ruins	Di Yi, Di Xin	1090–1040 BC		
	Bell	YN5	M19:7	Phase IV of Yin Ruins	Di Yi, Di Xin	1090–1040 BC		
Hejia	Arrowhead	YH1	七五 55	Phase III-IV of Yin Ruins	Lin Xin, Kan Ding, Wu Yi, Wen Ding,Di Yi, Di Xin	1205–1040 BC	1973M1	SPM and SPCRMC 1976
	Dou vessel	YH2	七五 17	Phase III-IV of Yin Ruins	Lin Xin, Kan Ding, Wu Yi, Wen Ding,Di Yi, Di Xin	1205–1040 BC	1973M1	
	Chisel	YH5	七五 34	Phase III-IV of Yin Ruins	Lin Xin, Kan Ding, Wu Yi, Wen Ding,Di Yi, Di Xin	1205–1040 BC	1973M1	
	Dagger-axe	YH7	七五 27	Phase III-IV of Yin Ruins	Lin Xin, Kan Ding, Wu Yi, Wen Ding,Di Yi, Di Xin	1205–1040 BC	1973M1	
	Arrowhead	YH9	七五 53	Phase III-IV of Yin Ruins	Lin Xin, Kan Ding, Wu Yi, Wen Ding,Di Yi, Di Xin	1205–1040 BC	1973M1	
	Dagger-axe	YH4	七五64	Early Western Zhou	King Cheng, King Kang	1042–996 BC	1973M5	
	Gui vessel	ZY-XA039	七二 193	Early Western Zhou	King Kang	1020–996 BC	1966 Western Zhou tomb	Chang 1972

Absolute Date according to Group of Experts on the Xia-Shang-Zhou Chronology Project 2022. Report of Xia-Shang-Zhou Chronology Project. Beijing: Science Press voltage, 15 nA current, and 30 μm diameter test point. BRONZE 32X SN7B (certified and supplied by MBH Analytical Ltd.) was used for quality control in the tests (Heginbotham et al. 2015). The error in the analysis of the main elements was less than 1%. The final result was the average of two to three measurements for each sample. The main elements of sample ZY-XA039, which was severely rusted, was analyzed via X-ray fluorescence (XRF). The lead isotope ratios were analyzed utilizing MC-ICP-MS. A portion of the samples was analyzed at the School of Earth and Space Sciences, University of Science and Technology of China, and the remaining samples were analyzed at the State Key Laboratory of Continental Dynamics, Department of Geology, Northwestern University, Xi'an, China. The NBS-981 lead standard samples were repeatedly measured for calibration during the test so that the data could be compared.

ICP-OES and ICP-MS were used for the analysis of the main and trace elements of ZY-2274, respectively. The element analysis was completed in the Physical and Chemical Science Laboratory Center, USTC. The lead isotope ratio was analyzed via TIMS at the Beijing Research Institute of Uranium Geology of China.

Results and discussion

Alloying techniques

The main element and trace element analytical results are shown in Table 2. Most of the main elements in the samples were analyzed by Yang (2002) via SEM−EDS previously, and the data are basically consistent with our results reported in this paper. With 2% as the boundary of the alloy element division, the alloy materials of these samples are relatively diverse. The bronze tripod from Zhengjiapo is a leaded copper alloy with a high lead content of 13.1%. The 12 samples from Beilyu contain 4 alloy types, including 5 copper-tin–lead alloys, 4 tin bronzes, 2 copper-lead alloys, and 1 copper-lead-arsenic alloy. The 10 Wangjiazui samples contain 5 leaded tin bronzes and 5 tin bronzes. There are 4 alloy types in the 7 Hejia samples, namely, 3 leaded coppers, 2 tin bronzes, 1 leaded tin bronze, and 1 copper-lead-arsenic alloy. Samples YH1 and YH7 also contain some amount of arsenic, between 1 and 2%. Because the arsenic content of only two copper-lead-arsenic alloys is less than 3%, it is more like unconscious smelting of the paragenic ores. On the other hand, the smelting of arsenic-copper at the Laoniupo site in Xi'an was confirmed (Chen et al. 2017), which is closely related to Zhouyuan, as described in the following manuscript, so the possibility of intentional addition of arsenic cannot be completely ruled out. The alloy types of the Beilyu and Hejia samples are more varied, whereas those of the Wangjiazui samples are more homogeneous, with copper-tin–lead ternary alloy technology dominating overall.

In the past, many scholars have carried out compositional analyses of bronze wares unearthed in the Zhouyuan area (Zhang et al. 1999; Yang 2002; Mei and Han 2007; Zhou et al. 2009; Liu et al. 2017; Wang et al.2017; Sun et al. 2022). Figure 4 shows the alloying type distribution of bronzes unearthed in the Zhouyuan area from the pre-Zhou period to the Western Zhou period. As shown in the figure, various alloy materials were used in the pre-Zhou period, with a slightly higher proportion of leaded tin bronze and tin bronze, as well as a variety of other alloys, such as leaded copper, copper-lead-arsenic, and pure copper. Moreover, some leaded copper wares contain more than 1% arsenic. During the transition period between Shang and Western Zhou, copper-tin–lead ternary alloys were the main alloy type, accounting for approximately 80%, and very few other alloy types were present. However, it should be noted that the number of pre-Zhou copper artifacts found thus far in the Zhouyuan area is relatively low, and even fewer samples have been analyzed; more data are still needed for further research. Moreover, the quantities and types of bronze artifacts unearthed in the Zhouyuan area increased substantially in Western Zhou, and more than 100 sets of analytical data are available at present. Our statistical analysis of these data revealed that tin bronze was absolutely dominant, accounting for approximately 81%, followed by leaded tin bronze, which accounted for approximately 15%. There were only three pieces of pure copper and one piece of leaded copper, but these 4 samples were probably all copper ingots rather than the final products (Yang 2002; Liu et al. 2017). Thus, the alloying technology used in the Zhouyuan bronzes underwent a major shift from pre-Zhou to Western Zhou. The alloy types of pre-Zhou bronzes are diverse, and materials with poorer mechanical performance, such as pure copper, leaded copper, and lead-arsenic copper, were used, demonstrating that the Zhou people were still in the stage of exploring the bronze casting process during the pre-Zhou period. In the time of Western Zhou, large numbers of tin bronzes with excellent performance were used, while other alloy types rarely emerged, except for a few leaded tin bronzes. The alloy recipe became more stable, and the alloy technologies were greatly improved, reflecting that the Zhou people quickly absorbed the advanced bronze technologies from the Shang Kingdom and mastered high-quality metal resources after the establishment of the Western Zhou Dynasty.

As shown in Fig. 5, this batch of samples has higher contents of As, Ag, and Fe and lower contents of Ni, Co, and Au, and some of the samples also contain more Sb, Zn, and Bi. The trace elements As, Sb, Ag, Ni, Co, Zn, Bi, and Au, which are related to the source of the copper ores, were used to construct a spider diagram and perform principal

Table 2 Analysis results of the chemical compositions of bronzes from the Zhouyuan area

Site	Object	Lab No	Cu wt%	Sn	Pb	As	Sb	Ag	Ni	Fe	Co	Zn	Bi	Au	Method	Alloy type
Zhengjiapo	Tripod	ZY-2274	75.000	0.060	13.100	-	0.004	0.172	0.005	-	0.001	0.013			ICP-OES/ICP-MS	CuPb
Beilyu	Dagger-axe	Y19	93.254	0.645	3.198	2.008	0.203	0.091	0.120	0.002	0.003	0.075	0.014	0.003	EPMA	CuPbAs
	Dagger-axe	Y17	78.061	13.117	6.160	0.070	0.010	0.059	0.028	0.266	0.011	0.225	0.062	0.014	EPMA	CuSnPb
	Pao	Y27	82.673	9.099	5.158	0.265	0.152	0.374	0.037	0.158	0.012	0.123	0.082	0.008	EPMA	CuSnPb
	Dagger-axe	Y13	91.006	4.261	3.976	0.200	0.129	0.135	0.049	0.006	0.008	0.063	0.123	0.005	EPMA	CuSnPb
	Dagger-axe	Y20	85.118	0.037	13.667	0.226	0.061	0.090	0.047	0.036	0.000	0.045	0.169	0.003	EPMA	CuPb
	Bell chariot fitting	Y25	78.531	8.896	11.279	0.193	0.105	0.106	0.059	0.193	0.023	0.056	0.099	0.004	EPMA	CuSnPb
	Fish	Y22	79.910	13.839	1.882	0.149	0.045	0.044	0.039	0.469	0.009	0.079	0.054	0.000	EPMA	CuSn
	Fish	Y23	79.202	12.982	1.365	0.115	0.061	0.041	0.037	0.458	0.014	0.049	0.042	0.000	EPMA	CuSn
	Wei chariot fitting	Y24	88.361	8.203	2.568	0.064	0.030	0.054	0.054	0.076	0.013	0.085	0.037	0.003	EPMA	CuSnPb
	Tripod	Y29	78.165	18.972	0.620	0.548	0.160	0.102	0.029	0.156	0.009	0.229	0.199	0.015	EPMA	CuSn
	Dagger-axe	Y26	93.480	0.034	5.724	0.043	0.009	0.135	0.038	0.000	0.000	0.069	0.123	0.002	EPMA	CuPb
	Fish	Y28	90.731	5.846	0.871	0.029	0.026	0.068	0.043	1.157	0.012	0.152	0.211	0.020	EPMA	CuSn
Wangjiazui	Chisel	Y30	91.788	6.609	1.033	0.047	0.019	0.042	0.165	0.004	0.012	0.089	0.000	0.000	EPMA	CuSn
	Chisel	Y31	85.691	13.276	0.071	0.089	0.024	0.024	0.039	0.049	0.005	0.115	0.037	0.002	EPMA	CuSn
	Ring	Y32	82.969	12.689	2.056	0.335	0.051	0.176	0.115	0.882	0.068	0.280	0.003	0.000	EPMA	CuSnPb
	Fragment	Y33	70.235	19.986	7.615	0.364	0.066	0.121	0.032	0.463	0.006	0.201	0.076	0.000	EPMA	CuSnPb
	Fragment	Y34	72.118	24.619	0.972	0.135	0.017	0.074	0.020	1.010	0.011	0.061	0.012	0.000	EPMA	CuSn
	Dagger-axe	YN1	88.844	10.461	0.012	0.095	0.136	0.065	0.019	0.026	0.005	0.086	0.000	0.007	EPMA	CuSn
	Halberd	YN2	81.165	11.980	4.485	0.467	0.284	0.207	0.030	0.812	0.015	0.092	0.162	0.000	EPMA	CuSnPb
	Dagger-axe	YN3	78.304	13.623	6.878	0.238	0.119	0.083	0.038	0.190	0.010	0.075	0.047	0.000	EPMA	CuSnPb
	Halberd	YN4	92.313	6.864	0.104	0.034	0.005	0.023	0.012	0.024	0.006	0.064	0.000	0.015	EPMA	CuSn
	Bell	YN5	72.280	19.338	7.066	0.216	0.098	0.070	0.041	0.221	0.002	0.048	0.040	0.002	EPMA	CuSnPb
Hejia	Arrowhead	YH1	76.691	0.061	6.645	1.789	0.119	0.290	0.027	1.041	0.022	0.346	0.335	0.043	EPMA	CuPb(As)
	Dou vessel	YH2	82.260	12.808	4.009	0.053	0.008	0.066	0.041	0.058	0.001	0.070	0.077	0.008	EPMA	CuSnPb
	Chisel	YH5	95.022	0.769	2.049	0.669	0.029	0.139	0.044	0.028	0.004	0.093	0.097	0.005	EPMA	CuPb
	Dagger-axe	YH7	78.839	1.878	17.583	1.090	0.027	0.094	0.037	0.030	0.009	0.060	0.151	0.000	EPMA	CuPb(As)
	Arrowhead	YH9	88.995	0.056	5.019	2.916	0.139	0.281	0.033	0.466	0.017	0.096	0.348	0.000	EPMA	CuPbAs
	Dagger-axe	YH4	88.664	6.986	1.246	0.015	0.013	0.061	0.039	0.160	0.003	0.308	0.000	0.040	EPMA	CuSn
	Gui vessel	ZY-XA039	84.149	11.972	0.223										XRF	CuSn
Standard sample	32X SN7B	Certified values	81.21	12.45	2.31											
	32X SN7B	Measured values	81.28	12.42	2.29										EPMA	

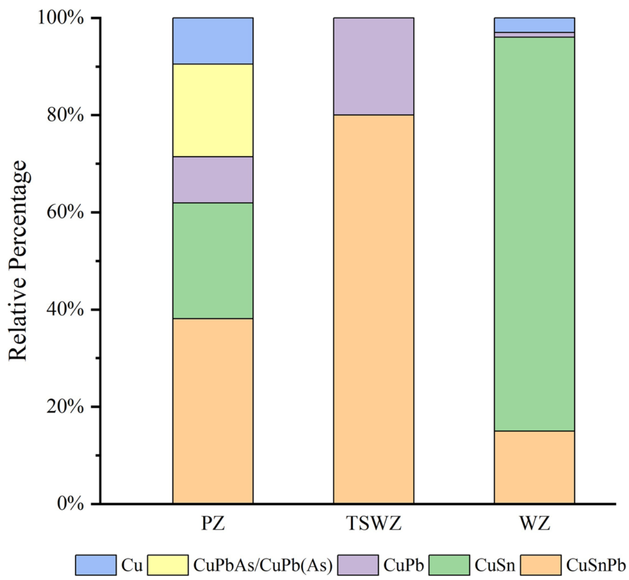

Fig. 4 Alloying type distribution of bronzes unearthed in the Zhouyuan area from pre-Zhou to Western Zhou. PZ: Pre-Zhou; TSWZ: Transition period between Shang and Western Zhou; WZ: Western Zhou

component analysis (Fig. 6). The results show that there is no clear distinction between different samples from different sites.

Lead isotope analyses

The lead isotope analytical results are shown in Table 3. The lead isotope ratios of these copper wares are quite scattered. As shown in Fig. 7a, b, with $^{206}Pb/^{204}Pb = 19$ as the boundary, all the data can be categorized into two parts: highly radiogenic lead and common lead. The variation range of $^{206}Pb/^{204}Pb$ values of highly radiogenic lead is 19.392–22.212, whereas that of common lead is 17.082–18.947. In the range of highly radiogenic lead, the data represent different distribution trends, among which sample YN1 from Wangjiazui and sample YH5 from Hejia have slightly lower $^{206}Pb/^{204}Pb$ values, ranging from 19 to 20; however, other samples (bronze tripod from Zhengjiapo, Y17 from Beilyu, Y30, Y33 from Wangjiazui, YH2 and YH7 from Hejia) contain more radiogenic lead, with $^{206}Pb/^{204}Pb$ values ranging from approximately 21 to 22. Within the range of common lead, the data on bronzes from Beilyu, Wangjiazui and Hejia are all distributed evenly. The two

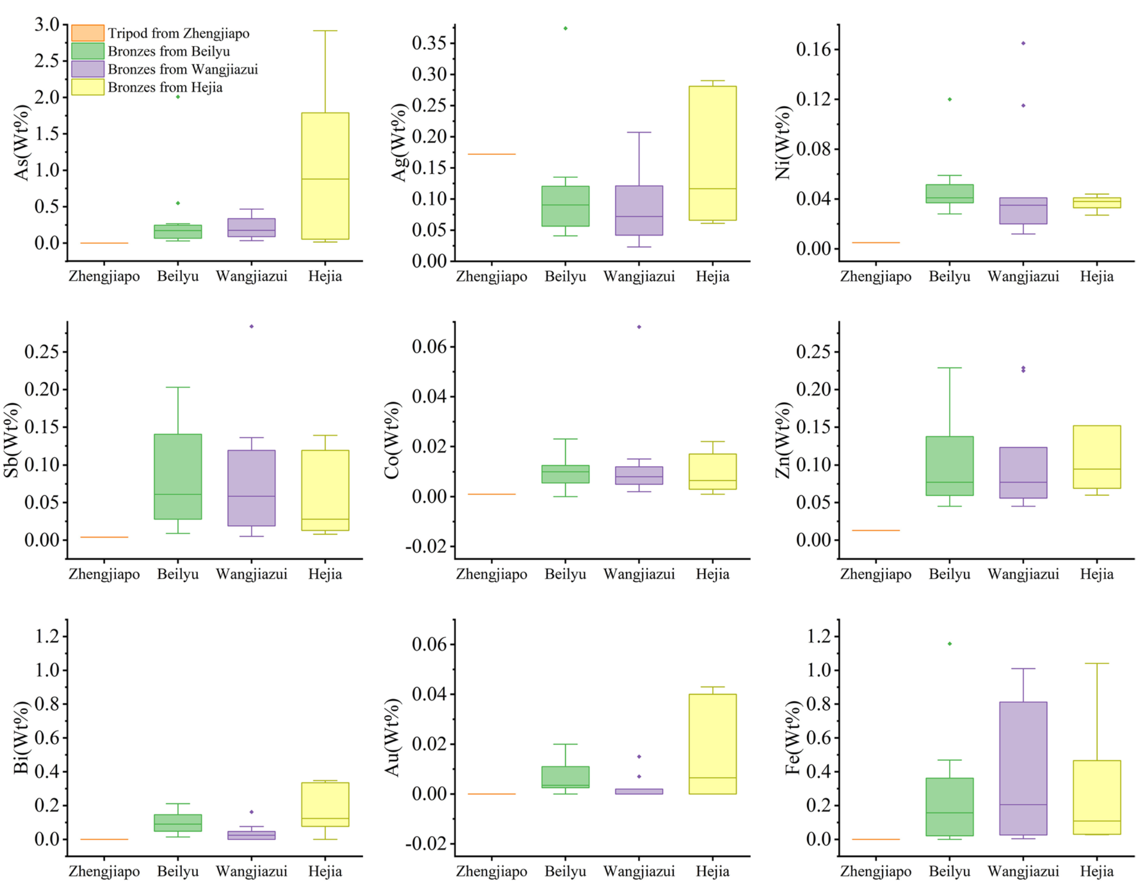

Fig. 5 Comparison of impurity variations in bronzes from different sites

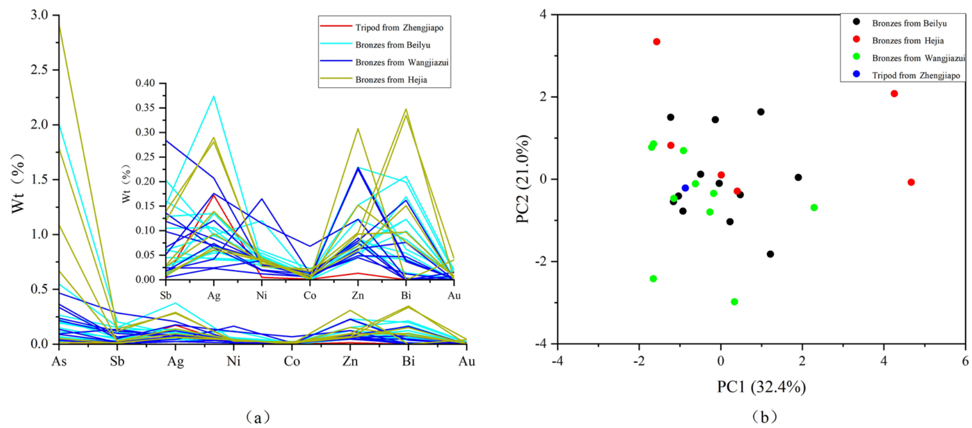

Fig. 6 Spider diagram (**a**) and principal component analysis (**b**) for trace elements

Table 3 Analysis results of the lead isotope ratios of bronzes from the Zhouyuan area

Site	Object	Lab No	$^{206}Pb/^{204}Pb$	2SD	$^{207}Pb/^{204}Pb$	2SD	$^{208}Pb/^{204}Pb$	2SD	Method
Zhengjiapo	Tripod	ZY-2274	22.212	0.002	16.057	0.001	42.277	0.004	TIMS
Beilyu	Dagger-axe	Y19	18.947	0.0002	15.697	0.0002	39.314	0.0006	MC-ICP-MS
	Dagger-axe	Y17	22.066	0.0003	16.136	0.0002	42.495	0.0006	MC-ICP-MS
	Pao	Y27	17.676	0.0006	15.557	0.0004	38.060	0.0007	MC-ICP-MS
	Dagger-axe	Y13	17.981	0.0006	15.623	0.0004	38.440	0.0009	MC-ICP-MS
	Dagger-axe	Y20	17.488	0.0006	15.536	0.0004	37.870	0.0010	MC-ICP-MS
	Bell chariot fitting	Y25	17.480	0.0007	15.534	0.0004	37.858	0.0008	MC-ICP-MS
	Fish	Y22	18.025	0.0002	15.615	0.0004	38.375	0.0009	MC-ICP-MS
	Fish	Y23	18.025	0.0003	15.613	0.0004	38.383	0.0010	MC-ICP-MS
	Wei chariot fitting	Y24	18.025	0.0003	15.594	0.0003	38.292	0.0011	MC-ICP-MS
	Tripod	Y29	18.368	0.0004	15.671	0.0003	38.662	0.0008	MC-ICP-MS
	Dagger-axe	Y26	17.493	0.0003	15.540	0.0004	37.906	0.0008	MC-ICP-MS
	Fish	Y28	18.067	0.0003	15.602	0.0003	38.424	0.0015	MC-ICP-MS
Wangjiazui	Chisel	Y30	21.214	0.0003	16.018	0.0003	42.102	0.0006	MC-ICP-MS
	Chisel	Y31	18.041	0.0006	15.600	0.0004	38.391	0.0009	MC-ICP-MS
	Ring	Y32	17.082	0.0004	15.455	0.0004	38.635	0.0009	MC-ICP-MS
	Fragment	Y33	21.549	0.0005	15.994	0.0003	41.704	0.0009	MC-ICP-MS
	Fragment	Y34	18.758	0.0004	15.655	0.0003	38.957	0.0005	MC-ICP-MS
	Dagger-axe	YN1	19.392	0.0004	15.743	0.0003	39.687	0.0026	MC-ICP-MS
	Halberd	YN2	18.151	0.0004	15.606	0.0003	38.467	0.0010	MC-ICP-MS
	Dagger-axe	YN3	17.514	0.0005	15.541	0.0003	37.897	0.0007	MC-ICP-MS
	Halberd	YN4	17.423	0.0004	15.493	0.0003	38.577	0.0011	MC-ICP-MS
	Bell	YN5	17.510	0.0005	15.539	0.0003	37.891	0.0009	MC-ICP-MS
Hejia	Arrowhead	YH1	18.442	0.0002	15.621	0.0002	38.552	0.0006	MC-ICP-MS
	Dou vessel	YH2	21.924	0.0003	16.042	0.0002	42.107	0.0005	MC-ICP-MS
	Chisel	YH5	19.943	0.0002	15.802	0.0002	40.096	0.0005	MC-ICP-MS
	Dagger-axe	YH7	22.044	0.0003	16.046	0.0002	42.175	0.0007	MC-ICP-MS
	Arrowhead	YH9	18.332	0.0002	15.600	0.0002	38.468	0.0005	MC-ICP-MS
	Dagger-axe	YH4	18.371	0.0001	15.566	0.0001	38.265	0.0003	MC-ICP-MS
	Gui vessel	ZY-XA039	17.559	0.0010	15.538	0.0017	37.906	0.0069	MC-ICP-MS

bronze fishes excavated from Beilyu (Y22, Y23) have very similar alloy compositions and nearly identical lead isotope ratios, suggesting that they were cast from the same batch. From the perspective of the social status of the owners, there is no significant distinction in the metal sources of the copper wares used by the aristocrats residing in Zhouyuan's core

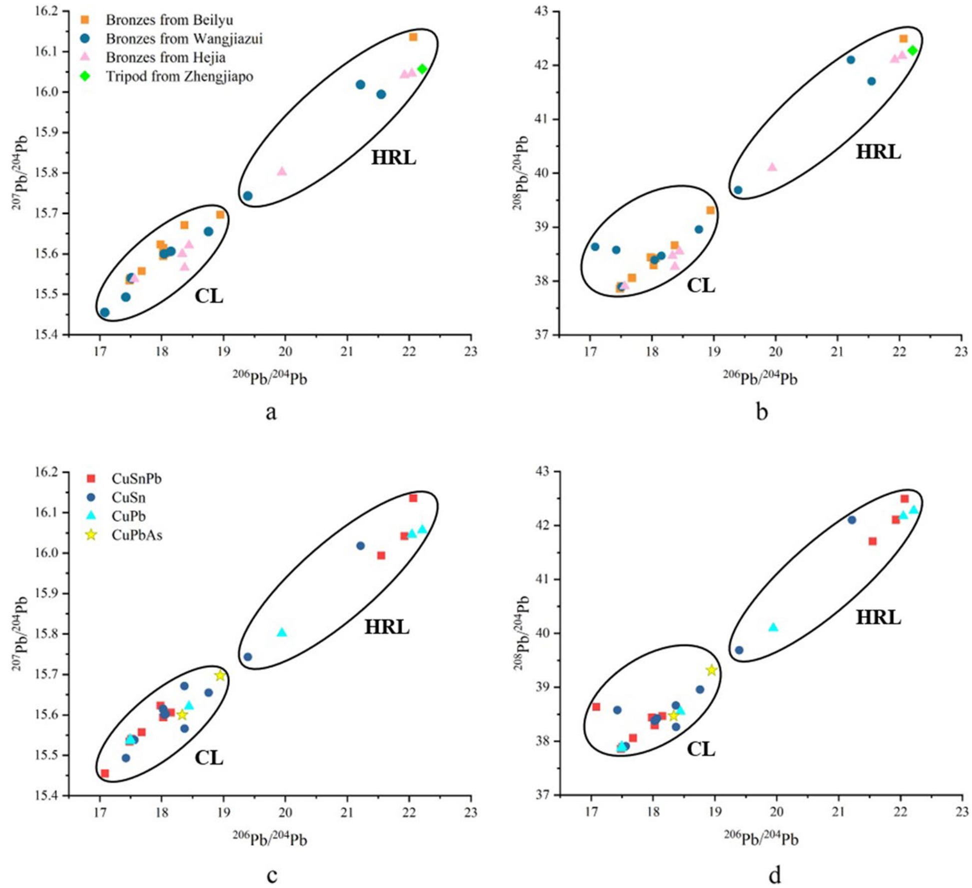

Fig. 7 **a**, **b** Lead isotope ratios of bronzes unearthed in the Zhouyuan area. **c**, **d** Lead isotope ratios of different alloy types (HRL: highly radiogenic lead, CL: common lead)

area (Hejia and Wangjiazui) and the commoners living in areas far from the capital city (Beilyu). Compositional analyses reveal that there are 4 alloy materials in these samples. The lead isotope ratios of leaded bronze, leaded copper, and copper-lead-arsenic alloys should indicate the source of lead ores, whereas the lead isotope data of tin bronze should be the result of mixing copper and tin ores. As shown in Fig. 7c, d, there is no significant difference in the lead isotope ratios between leaded and nonleaded artifacts, either in the highly radiogenic lead range or in the common lead range.

As a regional bronze groups formed during the Shang Dynasty, pre-Zhou bronzes were strongly influenced by Shang culture. Zou (1980) categorized copper wares from pre-Zhou culture into three main groups, namely, Shang-style objects, Shang-Zhou mixed-style objects and Zhou-style objects, among which Shang-style objects have the most varieties and quantities, followed by Shang-Zhou mixed-style and Zhou-style artifacts. The tripod collected in Zhengjiapo resembles those from tomb 1 (M1:2 and 3) in Wuguan, Anyang (Zhang 2004). The Dou vessel unearthed in Hejia 73M1 is similar to those from the western district of Yin Ruins (M907:12 and 28) (AWT, IA, CASS 1979), and the decorations on the top of the handle are exquisite; therefore it is more likely that it was imported from Yin Ruins. The dagger axes, arrowheads and chisels analyzed in this study also resemble objects from Shang culture. On the other hand, the joint halberds and bell unearthed in Wangjiazui have never been found in Shang culture and should be Zhou-style objects. Lead isotope analyses revealed that the Shang-style wares contain both highly radiogenic lead and common lead, whereas the Zhou-style objects are all common lead. Zou (1980) emphasized that both the Shang-Zhou mixed style and Zhou-style bronzes were cast by the Zhou people (or captive Shang people), and most Shang-style bronzes were also cast by the Zhou people (or captive Shang people) according to inscriptions rather than being imported directly from Yin Ruins or other Shang cultural regions. The Zhengjiapo tripod is poorly made and the alloy type is leaded copper, which is distinct from tin bronzes and leaded tin bronzes widely used in contemporary Yin Ruins (Zhao 2004). Thus, it is more likely that the tripod was cast locally, indicating that the Zhou people also used highly radiogenic lead metals in the production of bronzes.

As mentioned above, these bronzes are from different ages. Figure 8 shows the relationship between the lead isotope ratios and the ages of the copper wares. Only the Zhengjiapo tripod belongs to Yin Ruins phase II, whose lead isotope ratios conform to the characteristics of highly

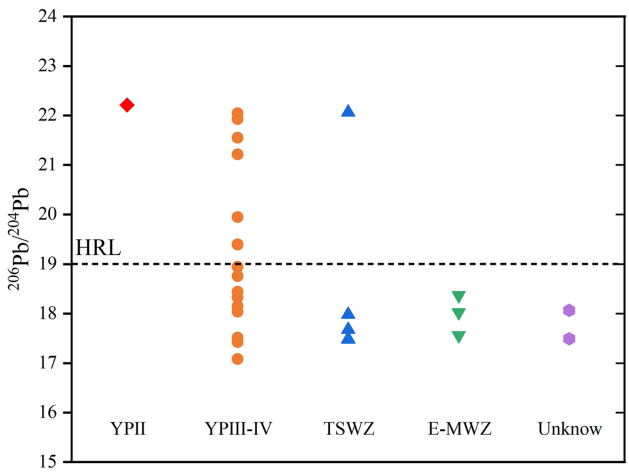

Fig. 8 Relationships between the lead isotope ratios and ages of the bronzes. YPII: Yin Ruins phase II; YPIII-IV: Yin Ruins phase III-IV; TSWZ: Transition period between Shang and Western Zhou; E-MWZ: Early and middle Western Zhou

radiogenic lead. The lead isotope data of the bronze wares of Yin Ruins phases III–IV include both highly radiogenic lead and common lead, and the proportion of bronzes with highly radiogenic lead is nearly 40%. Among the 5 bronzes in the transition period between Shang and Zhou, one contains highly radiogenic lead, and the remaining 4 bronzes are common lead. All the Western Zhou samples contain common lead, and highly radiogenic lead has not been used since then. To comprehensively understand the transition of metal resource origin from pre-Zhou to Western Zhou in the Zhouyuan area, published lead isotope data (Wang et al. 2017; Sun et al. 2022) are compared in Fig. 9. As shown in the figure, the lead isotopic compositions of bronze wares from pre-Zhou to Western Zhou vary widely, indicating that the provenance of the ores is quite complex. The data distribution of pre-Zhou copper ware is the most scattered, including essentially a 50/50 split between highly radiogenic lead and common lead. The highly radiogenic lead then declined considerably during the transition period. During the entire Western Zhou Dynasty, all bronzes were common lead. This clearly indicates that highly radiogenic lead ores were used more frequently during the Shang Dynasty and almost disappeared after the establishment of Western Zhou in the Zhouyuan area. According to previous lead isotope research on bronzes excavated from sites in the Yellow River and Yangtze River Basins during the Shang period, copper wares containing highly radiogenic lead first appeared on the lower Erligang floor (early Shang) in Zhengzhou and emerged in large quantities from the upper Erligang floor to Yin Ruins phase II, accounting for approximately 80% in the Shang capital area (Zhengzhou and Anyang) and large proportions in other peripheral regions; then decreased dramatically to 38% in phase III of the Yin Ruins. In Yin Ruins phase IV and later, the highly radiogenic lead metals almost disappeared and were used only sporadically, except at the Jinsha site in Chengdu (Southwest China) (Jin et al. 2017). The ages of the objects with highly radiogenic lead analyzed in this paper are equivalent to Yin Ruins phases III and IV, which account for approximately 40% of the contemporary samples. This is very close to the proportion of Yin Ruins phase III bronzes with highly radiogenic lead unearthed in Anyang, indicating that the use pattern of highly radiogenic lead metal resources in the Zhouyuan area was basically the same as that in Yin Ruins during the Shang (pre-Zhou) period. The data for the Zhouyuan copper wares from early to mid-late Western Zhou basically overlap. Overall, the lead isotope ratios of the pre-Zhou and Western Zhou copper wares in the Zhouyuan area are obviously different. The data from the pre-Zhou period are more scattered, whereas the data from the Western Zhou period are more concentrated. In particular, highly radiogenic lead was no longer used in the Western Zhou, indicating that the metal origin and supply pattern changed significantly with the replacement of the Shang and Zhou Dynasties. However, there is a certain overlap in the data, suggesting that some of the mineral sources of pre-Zhou may have been inherited by Western Zhou (mainly common lead). The alloying techniques and metal resources of the Zhouyuan area both changed significantly from pre-Zhou to

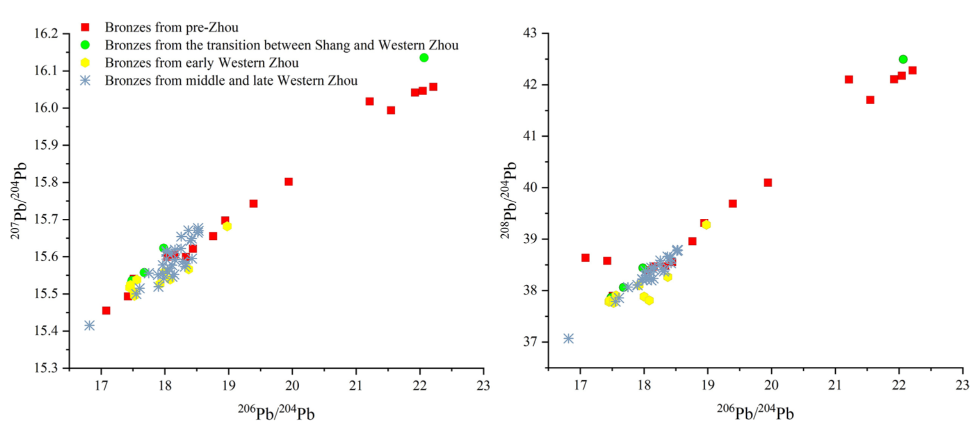

Fig. 9 Comparison of bronzes unearthed in Zhouyuan from pre-Zhou to Western Zhou periods

Western Zhou, which could be related to the great transformation of the bronze industry pattern after the Zhou people replaced the dominance of the Shang Dynasty.

Another issue to consider when interpreting lead isotope data is mixing and recycling. Although historical and archaeological evidence is quite limited, mixing and recycling are likely to have occurred in Shang and Western Zhou bronze production. Chemical compositional analysis of bronzes can provide clues as to whether they were mixed or recycled and remelted, and two clearly distinguishable patterns can be recognized in both the alloying and impurity data (Liu et al. 2020). As shown in Fig. 10, it shows a symmetric distribution (approximately normal) around a specific value of tin content and can be interpreted as the result of deliberate control of the alloying process, which is referred to as primary alloying. Moreover, most objects contain lower levels and tighter distributions of multiple trace elements (cobalt, zinc, antimony, and nickel) (Fig. 5), suggesting that copper may be obtained from one or a limited number of very pure copper sources (Liu et al. 2020). Both the alloying and impurity data indicate that mixing and recycling are relatively unlikely here. Of course, since the samples analyzed come from a variety of archaeological contexts, mixing and recycling in individual samples cannot be completely ruled out. Mixing and recycling have a greater effect on common lead ores, as Hsu et al. (2021) suggested that values for common lead between Group I and Group II are likely the result of mixing of the two types of ores. However, for lead ores with highly radiogenic lead, we believe that the effects of mixing and recycling, if any, are not significant. The data compositions of this kind of lead ores themselves are extremely specific and wide-ranging, making it difficult to erase highly radiogenic lead signals even with common lead copper materials. Moreover, no clear tendency of mixing highly radiogenic lead metals and common lead metals was observed in the plots of lead isotope ratios versus lead content (Fig. 11).

Relationship between Pre-Zhou and Shang from the perspective of metal resources

According to historical documents, the Zhou people had a close relationship with the Shang people before the destruction of the Shang Kingdom. Archaeological observations indicate that the pre-Zhou bronze culture originated mainly from Shang culture and that most pre-Zhou bronzes have cultural factors from Yin Ruins. Figure 12 shows a comparison of the lead isotope ratios of pre-Zhou bronzes and Yin Ruins bronzes. As shown in the figure, except for two common lead bronzes, which have slightly higher values of $^{208}Pb/^{204}Pb$, all the pre-Zhou bronze data plot within the range of Yin Ruins objects. Previous studies have revealed that highly radiogenic lead is the main characteristic of Shang cultural bronze; moreover, this kind of metal resource, although rare geologically, was widely used in bronzes excavated from sites in the middle and lower reaches of the Yellow River and Yangtze River in China during the Shang period; all sites unearthed highly radiogenic lead bronzes that had close connections with Shang culture, especially in the late Shang period (Sun et al. 2001; Peng et al. 2001; Jin 2008; Tian 2013; Cao 2014; Liu 2015; Xiao et al. 2016; Liu et al. 2016; Ma et al. 2016; Chen et al. 2019; Zhangsun et al. 2021; Wang et al. 2021). In addition, bronzes containing highly radiogenic lead from all sites during the Shang Dynasty showed almost identical trends of temporal change over a staggering spatial range, suggesting that there is likely only

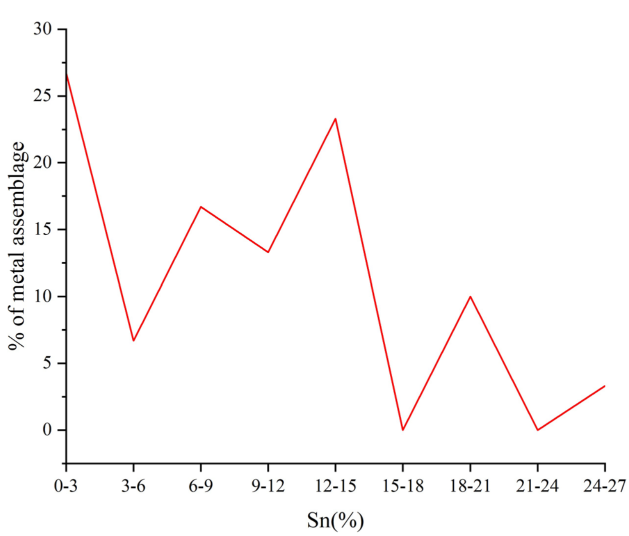

Fig. 10 Tin distributions of bronze assemblages at Zhouyuan

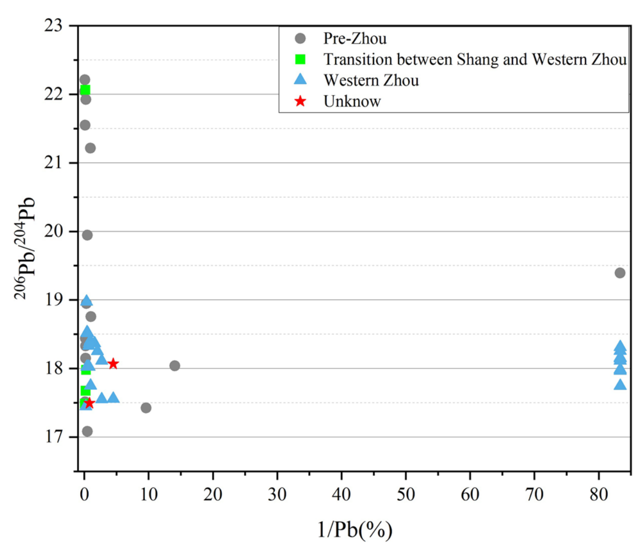

Fig. 11 A plot of Zhouyuan bronzes data, showing 1/Pb (%) against lead isotope ratio $^{206}Pb/^{204}Pb$

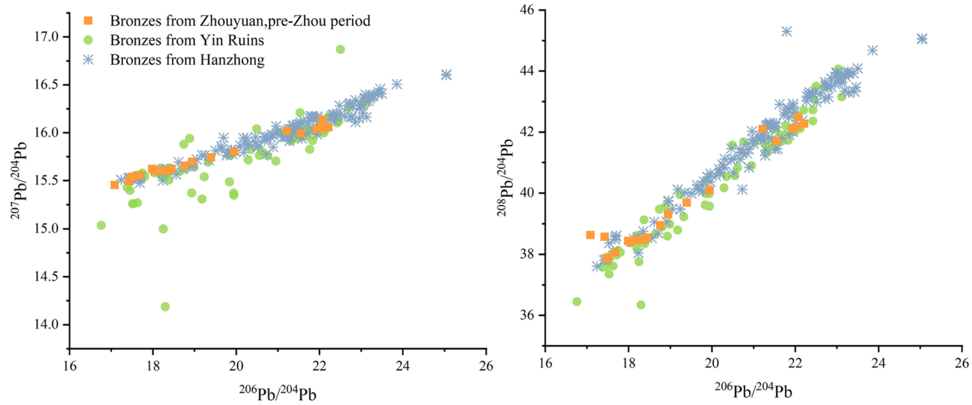

Fig. 12 Comparison of pre-Zhou bronzes from Zhouyuan with Shang bronzes from Yin Ruins and Hanzhong

one origin for these highly radiogenic lead metal resources (Jin 2008). The compositional and temporal features of pre-Zhou bronzes with highly radiogenic lead are also consistent with those of Yin Ruins objects, demonstrating that the origins of the highly radiogenic lead metal resources used in Zhouyuan and other sites should be the same. The compositional analyses revealed that the highly radiogenic lead copper wares were made of different alloy materials, including both leaded and unleaded objects, indicating that this kind of metal resource should contain both lead and copper ores (Jin 2008), which is also consistent with the situation reflected by pre-Zhou bronzes.

In the case of common lead, there are two lead sources during the Yin Ruins phase IV and early Western Zhou periods: Group I had $^{206}Pb/^{204}Pb$ ratios between 17.4 and 17.6, which probably originated from Xiaoqinling, Tongbai-Dabie or Luanchuan in North China. The $^{206}Pb/^{204}Pb$ ratios of Group II vary between 17.9 and 18.2, and the possible provenances may be Edong and Jiurui in the middle and lower Yangtze River valley or Qinling Mountains (Hsu et al. 2021). As shown in Fig. 13, some of the Zhouyuan bronzes are concentrated in Group I, indicating that the Group I lead were also the main resources used at the Zhouyuan site from pre-Zhou to the early Western Zhou periods. The Zhouyuan Group I bronzes overlap with the Anyang bronzes from Yin Ruins Phase IV, suggesting that the Zhou people were also closely connected to Yin Ruins in terms of common lead metal resources and that they probably continued to control the Shang metal resource supply network after the destruction of the Shang and into the early Western Zhou period (Hsu et al. 2021). Its possible sources, Xiaoqinling, Tongbai-Dabie or Luanchuan, are also very close to the Guanzhong area and may be sources of contemporary Zhouyuan common lead bronzes. However, no significant aggregation of data has been observed within Group II, and although some of the Zhouyuan objects fall within the Group II data range, Group II lead was not used in large quantities until the mid-Western Zhou to the early Spring and Autumn periods and are thought to be related to Zhou's military and cultural contact with the southern states (Hsu et al. 2021). The Group II lead may have originated from the middle and lower reaches of the Yangtze River (especially from Edong and Jiurui, Jiangxi) or the Qinling Mountains, and a comparison of galena from these regions with Zhouyuan objects (Fig. 14) shows that the data are indeed very close to each other. However, the middle and lower reaches of the Yangtze River are relatively far from the Guanzhong area, and there is not much archaeological evidence for a close connection between Zhouyuan and the middle and

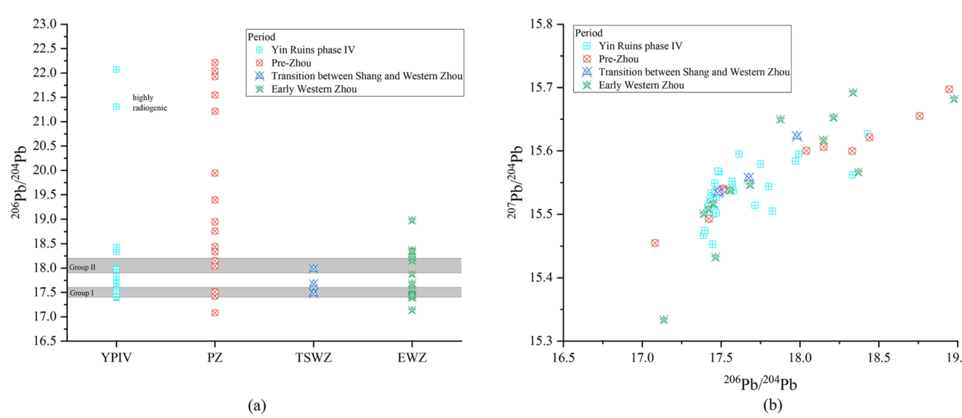

Fig. 13 Comparison of Zhouyuan bronzes from pre-Zhou to early Western Zhou and Yin Ruins phase IV bronzes. The range of common lead Group I and II is based on Hsu et al. (2021)

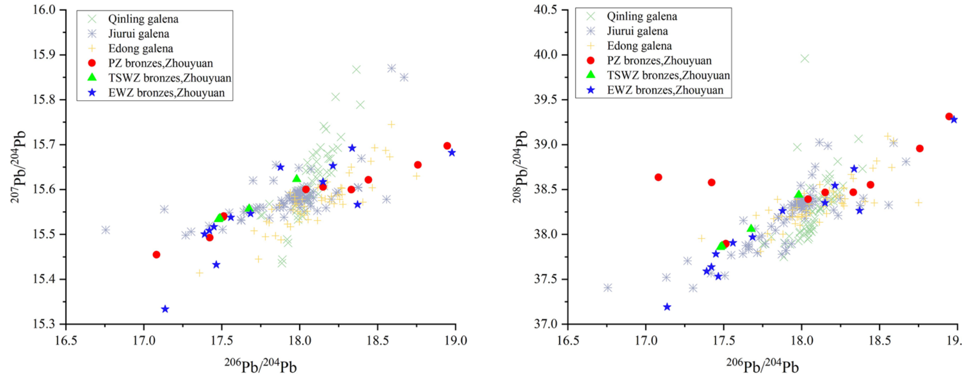

Fig. 14 Comparison of Zhouyuan common lead bronzes from pre-Zhou to early Western Zhou and galena from Qinling, Jiurui and Edong

lower reaches of the Yangtze River in the pre-Zhou period, suggesting that the more probable origin is still the Qinling Mountains.

There have been extensive debates about the origin of highly radiogenic lead metal resources in the Shang Dynasty, but no firm conclusion has been reached yet. Different hypotheses have emerged successively, supporting the origin in the Southwest region (Jin 1984, 2008; Zhu and Chang 2002), the middle–lower reaches of the Yangtze River (Peng et al. 1997, 1999, 2001), and the Qinling Mountains (Saito et al. 2002; Chen et al. 2019). The Qinling Mountains, located just south of the Guanzhong Plain, are rich in metal resources. However, by studying Shang bronzes unearthed in Hanzhong, which lies at the southern foot of the Qinling Mountains, we suggest that the Qinling Mountains are unlikely to be the origin of highly radiogenic lead ores used in the Shang Dynasty, especially lead ores (Zhangsun et al. 2021). Figure 12 shows the absolute identity of highly radiogenic lead from Zhouyuan, Hanzhong and Yin Ruins. Therefore, it can be inferred that the highly radiogenic lead metals used in Zhouyuan were unlikely to be locally smelted but were imported from other places. Moreover, the other regional bronze groups in the Shang period, such as Sanxingdui, Xingan, Hanzhong, Northern Shaanxi and Hunan bronzes, especially objects with local styles, also contained a large amount of highly radiogenic lead, demonstrating that in addition to the direct circulation of the finished bronze products between the Shang capital and peripheral regions, there was also a unified distribution of metal resources to local copper production workshops for casting (Zhangsun et al. 2021). Owing to its unique fingerprinting characteristics, the highly radiogenic lead outlines a network of metal resource circulation centered on the Shang Dynasty. Analyses of the Zhouyuan copper artifacts suggest that the western Guanzhong Plain was also involved in the late Shang metal resource circulation network and that the highly radiogenic lead ores used by the Zhou people were obtained from the Shang Dynasty. A recent study also suggested that highly radiogenic lead may have originated from western Henan Province (Jin et al. 2020), although this hypothesis needs to be further proven.

However, Zhouyuan is too far from Yin Ruins, and the connection between them may not be direct. We also found copper artifacts containing highly radiogenic lead at the Laoniupo site in Xi'an City, Shaanxi Province (Zhangsun 2017), indicating that the Zhouyuan and Yin Ruins may have been indirectly linked through the Shang culture sites in the eastern Guanzhong Plain. The sites of Laoniupo in Xi'an City and Huaizhenfang in Lantian County are two important Shang cultural sites in the eastern Guanzhong Plain. In particular, Laoniupo, which is a large settlement site, was initially a stronghold of Shang forces in the west and developed rapidly into a feudal state in the late stage (Liu 2002). Notably, metallurgical remains such as slags, charcoals, and burnt soil were found at both sites, indicating that there might have been a copper production center in the eastern Guanzhong Plain during the Shang period (Zhang 2004). These sites are the only two copper smelting workshops found in the Guanzhong Plain so far and are quite rare outside the core area of Shang culture. Scientific analyses of the slags from Huaizhenfang and Laoniupo have demonstrated that the smelting products of Huaizhenfang are pure copper and that those of Laoniupo are pure copper and arsenic copper (Chen et al. 2017; Zhangsun 2019). The copper ores smelted are common lead and probably originated from the northern foot of the Qinling Mountains, and the copper metal produced there might have been exported to the Shang capitals; therefore, the acquisition of copper metals should be one of the driving forces for the Shang people to continue their reign in the west of the kingdom (Zhangsun et al. 2020). A comparison of the unleaded bronzes from Zhouyuan with the copper ores and slags from the Huaizhenfang and Laoniupo sites reveals that the data of some common lead samples are almost identical (Fig. 15). Even though common lead has overlapping effects, the origins of the copper resources are probably the same because these sites are very close in time and space. Nevertheless, it is less likely that the Zhou people mined and smelted the copper ores from the northern foot of the Qinling Mountains by themselves during the pre-Zhou

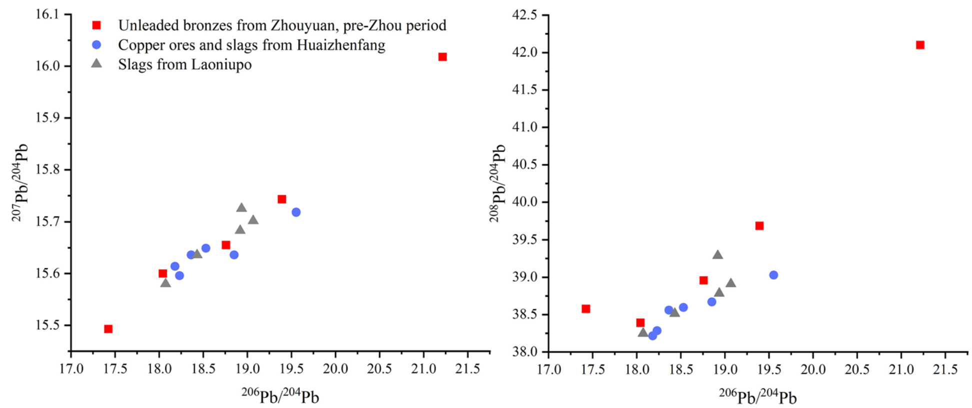

Fig. 15 Comparison of unleaded pre-Zhou bronzes from Zhouyuan with copper ores and slags from Laoniupo and Huaizhenfang

period. The only metallurgical remains of the pre-Zhou culture were found at the Zhougongmiao site, which is very close to Zhouyuan. Ceramic models, crucibles, slags, copper blocks, and small pieces of bronze wares were discovered at the Zhujiaxiang site in Zhougongmiao; most of the pottery models were broken, and it was difficult to recognize the shape of the finished product; only one arrowhead model was identified, and the small copper blocks were speculated to be related to copper ingots (Chong and Lei 2007). Judging from the pre-Zhou metallurgical remains discovered at the Zhougongmiao site, the bronze casting industry of the Zhou people was not well developed before the destruction of the Shang Dynasty, and it is uncertain whether the pre-Zhou people were able to mine and smelt metal ores. More likely, the Zhou people acquired the common lead copper smelted by the Shang people at Laoniupo, which may also be the reason why some of the pre-Zhou bronzes contain a certain amount of arsenic. As the relationship between Shang and Zhou changed from subordinate to hostile, the method of obtaining metal resources was bound to change dramatically.

According to the oracle bone inscriptions, historical documents and archaeological discoveries, it is believed that Laoniupo was the Chong State, which was the largest state governed by the Shang people in the west and was undoubtedly the greatest obstacle for the Zhou people to exterminate the Shang Dynasty in the east (Liu 2002). 《Shiji. Zhoubenji史记.周本纪》 recorded the process of Zhou destroying Shang: Earl Xi (King Wen) adjudicated the lawsuit between Yu and Rui States and claimed the throne in the first year; subsequently, he conquered 4 little neighboring tribes continuously from the second year to the fifth year; in the sixth year, King Wen destroyed the Chong State eventually and moved the capital to Feng; then, he passed away in the seventh year. King Wu affected a junction with vassals in Mengjin in the ninth year and destroyed the Shang Kingdom in the eleventh year. Thus, the conquest of the Chong State was the key victory for the Zhou people in the process of destroying Shang. The unleaded bronzes unearthed in Zhouyuan are all from Wangjiazui tomb 19. The date of this tomb is approximately equivalent to the period between King Wen's relocation to Feng and the fall of the Shang Dynasty (Lei 2010), after the conquest of the Chong State. It can be inferred that the Zhou people had full control of the copper resources in the eastern part of Guanzhong after destroying the Chong State. In addition to large quantities of copper smelting remains, bronze casting pottery models have also been unearthed in the late Shang strata of the Laoniupo site, many of which are complicated models of vessels, suggesting that the Shang people from Laoniupo possessed a high level of bronze production technology and were able to produce bronze wares independently. It is not difficult to surmise that the Zhou people also acquired bronze smelting and casting techniques from Shang after they conquered the Chong State, and the military equipment, as well as sacrificial vessels of Zhou, improved considerably, which provided resources and technical support for the forthcoming war against the Shang capital.

Conclusion

The Zhouyuan site has an important historical status and is the key point for exploring pre-Zhou and Western Zhou culture. Over the years, many archaeological studies have been conducted, especially on bronze wares, which have always been valued by the academic community. However, scientific analysis of the Zhouyuan bronzes, especially pre-Zhou bronzes, has been relatively limited. In this work, the chemical compositions and lead isotope ratios of bronzes excavated from Wangjiazui and Hejia in Zhouyuan, as well as nearby Zhengjiapo and Beilyu sites, were analyzed using multiple methods.

The results show that the alloy types of bronzes from Beilyu and Hejia are more diverse, whereas those of Wangjiazui bronzes are relatively unitary, and the copper-tin–lead ternary alloy techniques are dominant overall. Combining these results with published data, we found that the Zhouyuan area has a variety of bronze alloy types in the pre-Zhou period, and alloy materials with poorer performance, such as pure copper, lead copper, and lead-arsenic copper, have been used, demonstrating that the Zhou people were still exploring the bronze casting process during the pre-Zhou period. In Western Zhou, large numbers of tin bronzes with excellent performance were used, whereas other alloy types, with the exception of a few leaded tin bronzes, barely emerged. The alloy recipe became more stable, and the alloy technologies were greatly improved, reflecting that the Zhou people quickly absorbed the advanced bronze technologies of the Shang Dynasty and mastered high-quality metal resources after the establishment of Western Zhou. The lead isotope data of the Zhouyuan copper wares can be divided into two groups: highly radiogenic lead and common lead. There is no obvious difference in the data of bronzes with different alloy materials. In terms of age, the bronzes from phase II of the Yin Ruins to the transition period between Shang and Zhou contain both highly radiogenic lead and common lead, whereas the Western Zhou copper wares are all common lead. The alloying techniques and metal resources of the Zhouyuan area both changed considerably from pre-Zhou to Western Zhou, which could be related to the great transformation of the bronze industry after the Zhou people replaced the dominance of the Shang Dynasty.

The use pattern of highly radiogenic lead metal resources in the Zhouyuan area is basically the same as that in Yin Ruins and other areas, and some of the Zhouyuan common lead objects have lead isotope ratios identical to those of Anyang Yin Ruins phase IV bronzes, suggesting that the Zhouyuan area also participated in the circulation network of metal resources in the late Shang Dynasty. The source of Zhouyuan common lead metal (primarily lead) from the pre-Zhou to the early Western Zhou mainly originated from the Xiaoqinling, Tongbai-Dabie, Luanchuan, Qinling, Edong and Jiurui regions. The highly radiogenic lead metals used were obtained from Shang; however, the provenance of these metal resources is still unclear. The connection between Zhouyuan and Yin Ruins was probably not direct but indirect through the Shang culture in the eastern Guanzhong Plain (Laoniupo). The lead isotope data from Wangjiazui tomb 19 bronzes and Huaizhenfang and Laoniupo copper ore and slags overlap greatly, suggesting that the Zhou people might have acquired the copper smelted by the Shang people from Laoniupo in some way. The Chong State, located in Laoniupo, was the greatest obstacle for the Zhou people to head east; thus, the conquest of the Chong State was a key victory for Zhou in the process of exterminating the Shang Dynasty. After occupying the Chong State, the Zhou people had a comprehensive grasp of the copper resources in eastern Guanzhong and acquired advanced bronze smelting and casting techniques from the Shang people of Laoniupo, which provided the resources and technological support for the forthcoming wars of exterminating the Shang capital.

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Declarations

Competing interests The authors declare no competing interests.

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