

Manufacture technique of bronze-iron bimetallic objects found in M27 of Liangdaicun Site, Hancheng, Shaanxi

CHEN JianLi^{1†}, YANG JunChang^{2,3}, SUN BingJun² & PAN Yan¹

¹ School of Archaeology and Museology, Peking University, Beijing 100871, China;

² Shaanxi Provincial Institute of Archaeology, Xi'an 710054, China;

³ Key Scientific Research Base of Conservation on Stone and Brick materials, State Administration Bureau of Cultural heritage, Xi'an 710061, China

Analysis of the fabrication technology of a bronze knife with an iron blade and a bronze Ge with an iron blade, two copper-iron bimetallic wares, unearthed in M27 of Liangdaicun Site, Hancheng of Shaanxi, is performed in this paper by using metallographic, EPMA and AMS-14C dating methods. The microstructures of the two samples are typical wrought bloomery iron containing a substantial amount of carbon, which is also called carburized steel, made from bloomery iron by cementation in the solid state. The objects can be dated back to the early Spring and Autumn period. This study provides new evidence for understanding the beginning of iron smelting in China. Most of the early known iron wares of the period between the late Western Zhou Dynasty and the early Spring and Autumn were unearthed in the region at the junction of Henan, Shanxi and Shaanxi, at the middle reaches of the Yellow River, suggesting that this region may likely be one of the earliest centers of iron smelting technology in China and deserves further archaeological research. As early iron products were also discovered in the area of the upper reaches of the Yellow River and in Xinjiang, appropriate attention also should be paid to the relationship between these two areas in terms of the origin of iron smelting.

archaeometallurgy, Liangdaicun, AMS-¹⁴C dating, bimetallic object, ironworking

1 Introduction

The beginning of iron smelting is a research topic of high interest to archaeologists, archaeometrists and also scholars from various disciplines. Unfortunately few remains of early iron and steel have been discovered and almost no reliable records can be found in the historical literature. This paper will report our study on two early iron objects unearthed from a cemetery site in the village of Liangdaicun, near Hancheng city in Shaanxi province.

Hancheng city is located in the eastern part of Guanzhong plain, Shaanxi province, neighboring with Shanxi and Henan provinces (Figure 1). In April 2005, a collaborative archaeological team, consisting of the Shaanxi Provincial Institute of Archaeology, the Weinan

Municipal Institute of Archaeology and Preservation of Cultural Heritage, and the Hancheng Municipal Bureau of Heritage and Tourism, carried out the excavation of the Liangdaicun Cemetery Site^[1-3].

In this excavation, among a great number of archaeological discoveries, three big tombs (M19, M26 and M27) received attention, especially the Tomb No. 27 (M27). The tomb M27 consists of a chamber of vertical rectangular shape (9.3 m long, 7.1 m wide and 13.2 m deep) and attached to the chamber are both a northern ramp and a southern ramp with lengths of 33.8 m and

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[†]Corresponding author (email: jianli_chen@pku.edu.cn)

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17.8 m, respectively. The finds in M27 were extremely rich, including 24 bronze ritual vessels, 140 jade and 48 gold items, and a bronze Gui with inscriptions. The discovery of the inscribed Gui proved the existence of the Rui State during the early Spring and Autumn period (SAP, 770–476 BC) in East Shaanxi. The most important fact is that a bronze knife with iron blade (M27: 391) and a bronze Ge with iron blade (M27: 970) were unearthed from M27 (see Figure 2). The inscriptions of “Rui State” were also found on other bronze wares in M19 and M26. Therefore both the bronze knife and bronze Ge with iron blade mentioned above should be considered among the earliest non-meteoritic iron products in China.

The other earliest known non-meteoritic iron products are the iron Ge, sword and spear unearthed from the cemetery of the Guo State in Sanmenxia, Henan Province^[4], and a piece of cast iron found in ruins at the village of Qucun, Quwo County, Shanxi Province^[5]. They are dated back to around 800 BC. Hancheng, Sanmenxia and Quwo are all located at the conjunctive region of Henan, Shaanxi and Shanxi, which are in the middle reaches of the Yellow River. Based on these facts and the recent discoveries, we suggest that this region might likely be the cradle of iron smelting in China.



Figure 1 The location of the village of Liangdaicun.

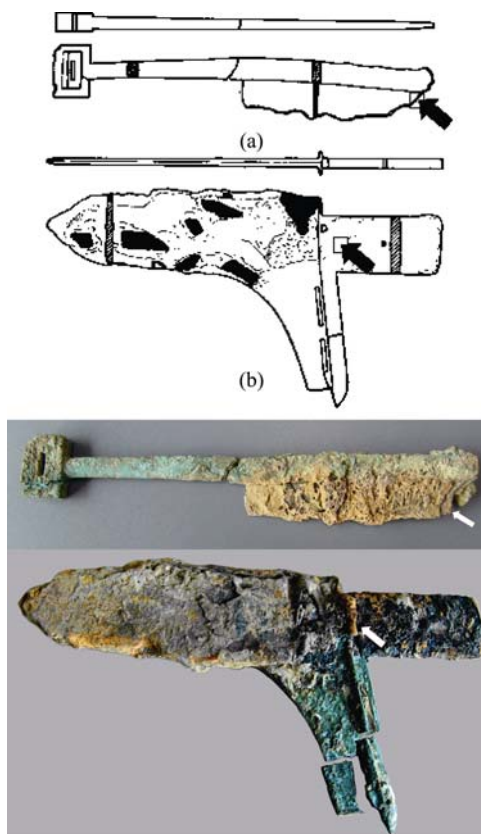


Figure 2 The iron objects unearthed from No.27 tomb. (a) Bronze knife with iron blade; (b) bronze Ge with iron blade.

2 Sampling and experimental methods

Two small samples were cut from the iron objects for metallographic examination. They were almost entirely composed of iron oxyhydroxide corrosion products. After grinding and polishing, microstructures were studied using metallographic techniques and EPMA, and chemical compositions were analyzed using JXA-8100 EPMA and an INCA-400 energy dispersive X-ray spectrometer. The excitation voltage was 15 kV, electric current was 1×10^{-8} A. The analysis results are shown in Table 1.

For radiocarbon dating, wood and lacquer were collected from M26 and M27. After standard acid-alkali-acid (AAA) treatment, the samples were vacuum-sealed in pre-baked quartz tubes with CuO and sulfur, and combusted at 850°C for about 3 h. Then the resulting CO₂ was purified and reduced to graphite on Fe-powder by hydrogen. Measurements of radiocarbon dates were performed by the National Electro 1.5SDH-1 accelerator mass spectrometry. The dating results are shown in Table 2. The work was completed at the AMS-¹⁴C Laboratory at Peking University.

Table 1 Compositional data for the iron blades of the two objects (wt%)

Object	Analysis area	Mg	Al	Si	S	K	Ca	Mn	Fe	Cu	Ni
M27: 391	average 1	0.4	3.8	17.4	0.9	1.2	1.2	0.8	74.2	–	–
	average 2	0.1	0.6	3.5	0.5	0.2	0.3	–	28.1	66.6	–
	average 3	–	–	0.2	0.6	0.1	0.1	0.2	44.9	53.9	–
	point 1	0.1	0.1	1.3	0.4	0.2	0.3	–	44.3	53.2	–
	point 2	0.5	0.4	0.4	1.1	0.2	1.6	–	86.9	8.9	–
	point 3	0.1	0.1	0.8	0.1	–	0.0	0.1	98.7	–	–
	point 4	0.2	0.4	0.6	0.7	–	0.2	–	91.5	6.2	0.1
	point 5	0.1	0.1	0.9	0.3	–	0.2	–	91.0	6.5	0.6
	point 6	0.1	0.1	0.7	0.1	0.2	–	0.1	91.5	6.9	–
	point 7	–	1.1	2.5	0.6	0.3	0.1	–	42.7	52.8	–
M27: 970	point 8	0.5	0.7	1.5	–	0.2	0.2	–	91.4	5.5	–
	average	0.2	0.1	0.3	–	0.1	–	–	98.9	0.3	–
	point 1	1.1	16.7	53.7	–	9.4	11.3	0.6	7.2	–	–
	point 2	1.1	22.3	45.8	–	9.4	13.5	0.7	7.0	–	0.2
	point 3	1.1	16.7	53.0	0.3	8.9	11.6	–	7.6	–	0.9
	point 4	1.4	16.1	49.1	–	9.6	10.2	–	11.3	1.5	0.9
	point 5	1.1	16.1	37.4	–	4.3	7.0	–	34.1	–	–
	point 6	0.1	0.1	0.2	–	–	–	–	99.4	–	–
	point 7	0.2	0.3	0.1	0.2	0.1	–	–	99.0	–	–

Table 2 Radiocarbon dates of M26 and M27

Sample	Lab code	¹⁴ C age (bp, 1σ)	Calibrated age (BC, 95.4%)
M26	BA07354	2500±35	789—509 (94.2%), 436—420 (1.2%)
M27:143	BA07355	2575±35	812—746 (66.1%), 689—664 (12.4%), 644—552 (17.0%)
M27:146	BA07356	2570±35	809—745 (61.4%), 689—663 (13.5%), 645—551 (20.5%)
M27:469	BA07357	2455±40	755—683 (23.6%), 669—410 (71.8%)
M27:972	BA07358	2470±35	762—680 (27.7%), 672—482 (58.0%), 466—415 (9.8%)

3 Results

The bronze knife with iron blade (M27: 391) might have been used for cutting. It is 18.5 cm long, 2.8 cm wide and 0.5 cm thick, with a slightly curved back, straight iron blade, long handle, and a rectangular ring head. The sample for analysis was cut from the blade as shown by the arrow (Figure 2). This sample was completely corroded and only mineralized remnants of its microstructure remained. What could be seen were vague traces of a pseudomorph laminated structure, perhaps due to the welding of steel strips, which was heavily disrupted by alteration to iron oxyhydroxides. Vague traces of ferrite and pearlite in hypoeutectoid steel also remained, but the carbon content was difficult to estimate (Figure 3). Microscopic examination revealed a number of laminated slag inclusions in the corrosion, scattered in different regions, a few of which can be seen to be two-phase (Figure 4), strongly suggesting that this iron blade

was made of iron extracted by the bloomery process. EPMA results also showed that the iron blade was made of bloomery iron, for its Ni content was very low (Table 1).

The bronze Ge with iron blade (M27: 970) was used as a weapon in ancient China. It is 19.5 cm long and 3.3 cm wide. The sample for analysis was cut from the blade (or in Chinese Yuan) as shown by the arrow (Figure 2). This sample was also completely corroded and only mineralized remnants of its microstructure remained. It had a ferrite and pearlite hypoeutectoid steel structure, with around 0.2% C (Figure 5), and a number of laminated slag inclusions in the corrosion (Figure 6). EPMA results also showed that the Ni content was very low (Figures 7–9 and Table 1). It was suggested that this iron blade was made of carburized steel, while its iron was extracted by the bloomery process. The microstructure of the bronze part of M27: 970 was $\alpha + (\alpha + \delta)$ dendrites and re-deposited free copper particles (Figure 10).

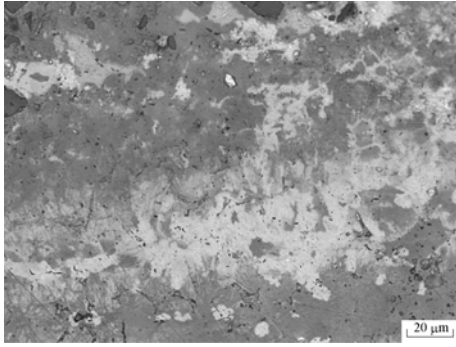


Figure 3 Completely corroded microstructure of M27: 391, some evidence for ferrite and pearlite remains (unetched).



Figure 4 Laminated two-phase slag inclusions of M27: 91 (unetched).

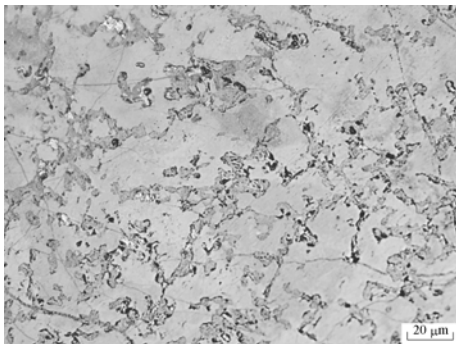


Figure 5 Completely corroded microstructure of M27: 970, some evidence for ferrite and pearlite remains (unetched).

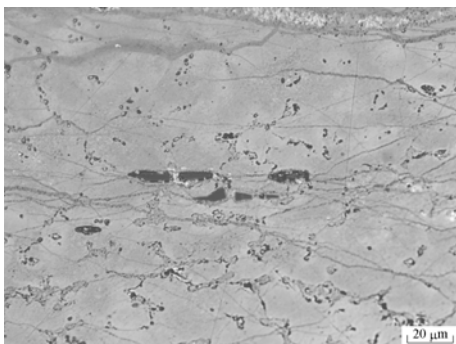


Figure 6 Laminated slag inclusions and ferrite and pearlite remains of M27: 970 (unetched).

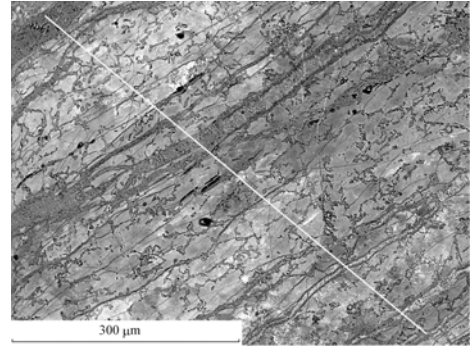


Figure 7 The location of the line distribution of Fe and Ni of the iron blade of M27: 970.

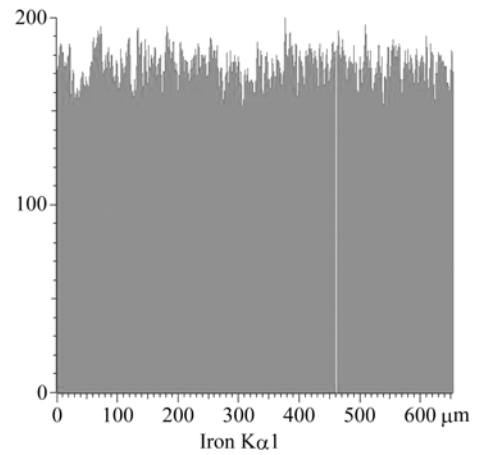


Figure 8 The line distribution of Fe.

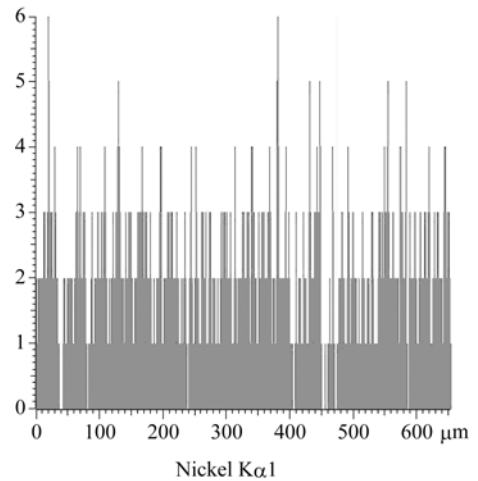


Figure 9 The line distribution of Ni.

The date of M27 is one of the key points in this research. Based on the fact that many vessels inscribed with Rui were unearthed at M19, M26 and M27, archaeologists concluded that the cemetery site of the Rui

State should be of the early SAP, about the 8th century BC. In order to prove it, one piece of lacquer taken from the coffin of M26 and four wood samples selected from small objects unearthed in M27 were analyzed by the AMS-¹⁴C dating method. The results are listed in Table 2, which confidently supports the archaeological argument.



Figure 10 Bronze microstructure of M27: 970 showing $\alpha + (\alpha + \delta)$ dendrites (unetched).

4 Discussion

4.1 The manufacturing techniques of the objects

Due to the poor preservation, the two iron objects under study were almost completely corroded without residual metal. Careful observation of the corrosion for vestiges from the original microstructure must be carried out to determine the materials and fabrication technology accurately. The process of iron corrosion in soil burial environments is complicated with different rates of corrosion due to the differences in the various phases of the microstructure. This allows us to infer the original microstructure based on the appearance of the remnant slag inclusions and the vestiges of the original microstructure in the corrosion. Moreover, combining this information with the elemental composition can be a good method to

determine the materials and fabrication technology of corroded iron objects. For instance, the evidence of a ferrite + pearlite microstructure was found in the corrosion of the knife M27: 391 (see Figure 3), moreover, in the corrosion, the silicate + ferrous oxide eutectic mixture can be seen to have elongated deformation along the direction of forging (See Figure 4). This shows that the sample was made from a carburizing steel. The Ge M27: 970 was also completely corroded, without residual of the metal matrix, but the ghost of a ferrite + pearlite microstructure can be found in the corrosion as well as the fayalite + ferrous oxide eutectic inclusions among block smelting iron (See Figures 5 and 6). This shows that the sample also came from the forging of carburized steel. In order to prove our judgment, we performed an experiment to determine the elemental composition of both samples as shown in Table 1. The results show that the nickel content of the samples is very small. This is significantly different from the Ni content of meteoritic iron products unearthed in China as shown in Table 3. Therefore, both samples can be identified as bloomery iron with high confidence.

4.2 Usage of bimetallic objects

Bimetallic techniques use metals of two different alloys to make one object through secondary casting. Two bronze-iron bimetallic wares unearthed in M27 provided important cultural evidence of the early stages of the use of iron. So far, many bimetallic wares such as iron swords (Yue, knives, spears, daggers) with bronze (gold, silver and jade) handles have been found by the archaeologists at many places in China, and there have been also bronze-iron bimetallic weapons of various ages unearthed in Iran, some areas of the former Soviet Union, the Korean Peninsula and Japan, so further research is deserved concerning the fabrication technology, development and spread of bimetallic weapons of this kind.

Table 3 Meteoritic iron objects found in China^[6]

Name	Unearthed site	Date	Ni content
bronze Yue with iron blade	Gaocheng, Hebei Province	middle Shang period, 14th century BC	0.8%–2.8%
bronze Yue with iron blade	Pinggu, Beijing	middle Shang period, 14th century BC	1.9%–18.4%
bronze Yue with iron blade	Junxian, Henan Province	late Shang—early Zhou period, 10th century BC	6.7%–6.8%, 22.6%–29.3%
bronze dagger with iron blade	Junxian, Henan Province	western Zhou period, 9th century BC	5.2%
iron Ben with bronze hilt	Sanmenxia, Henan Province	western Zhou period, 9th century BC	5.8%–47.7%, 12.5%–14.8%
iron dagger	Sanmenxia, Henan Province	western Zhou period, 9th century BC	6.0%–27.4%
iron knife with bronze hilt	Sanmenxia, Henan Province	western Zhou period, 9th century BC	5.8%–13.4%, 31.4%–35.6%

Bimetallic techniques ensure good mechanical properties of the objects. Other than combining jade and bronze, bimetallic techniques also include the creation of bronzes composed of two different alloys, i.e., bronze and iron. There have been many archaeological discoveries of bronze from late Shang period and meteoritic iron composite weapons. During the SAP, man-made iron was invented. This caused development in the techniques for casting bronze and iron composite objects, not only for weapons but also for vessels.

After the inspection and analysis of some of the samples unearthed domestically, such as the bronze Yue with iron blade in Gaocheng and others listed in Table 3, the material of those was found to be meteoritic iron. While the iron sword with jade handle in Guo cemetery, Sanmenxia^[4], the iron sword with gold handle from the early SAP unearthed in Yimencun, Baoji City of Shaanxi^[7] and the iron sword with copper handle from the period between 8th and 5th century BC unearthed in Longshan area^[8] had ferruginous blades of bloomery iron or carburized steel. All of these wares are bronze-(gold-, jade-) iron composite wares, with iron forge welding in the blade by using a cast-on method. All of these were the earliest evidence of using iron. These showed that the artisans already understood the difference in performance between copper and iron to some extent at that time. These also showed that iron was relatively scarce and valuable in the early stages of using ferrous metals and reflected people's regard of iron as a precious material.

Bronze-iron bimetallic wares of the Shang and West

Zhou periods were also found in archaeological excavations, showing that cast-on technology had a long history. However, the early bronze-iron bimetallic wares were made of meteoritic iron (see Table 3). The invention of bronze-iron bimetallic technology was of great significance for iron wares and metallurgy. Table 4 lists the excavation sites, dates, fabrication technologies and other information for 14 pieces of bloomery iron and steel, which are dated before the early Warring States period. Of those wares dated earlier than the SAP, the other four wares are all bimetallic except for a piece of residual iron slice found in Qucun, Quwo County. The blades of these wares are all made from high strength iron, which is consistent with the fabrication technology of meteoritic iron products in the early stages. The excavation of the two bronze-iron bimetallic wares of M27 from the early SAP in Liangdaicun provided new evidence for the study of the problem.

The origin of bimetallic techniques can be traced back to the separate casting method and the technology of embellishing bronze with inlays used from the Shang times or earlier. The separate casting method involved casting the minor parts of an object and then placing them in a bigger mould for the main body so that all components could be casted into a whole. Sometimes the main body was casted first and its minor parts were fitted onto it by another casting, such as the famous Ram Zun unearthed in Ningxiang, Hunan Province, and the earliest object, the head of a wand that was decorated with four ram's heads and unearthed in Yumen, Gansu Province^[10]. Turquoise-inlaid bronzes found at Erlitou in

Table 4 Pieces of bloomery iron and steel dated before 5th century BC^[9]

Unearthed site	Objects	Number	Date	Material
Tombs of Guo State at Sanmenxia, Henan	dagger	1	late Period of Western Zhou Dynasty	bloomery iron
	sword	1		carburized steel
	spear	1		
Qin Tombs at Jingjiazhuang, Lingtai, Gansu	sword	1	early SAP	carburized steel
Jiangdu of Jin State at Qucun, Quwo, Shanxi	fragment	1	early SAP	bloomery iron
No.2 tomb at Yimen, Baoji, Shaanxi	sword	1	late SAP	bloomery iron
Qi Tombs at Langjiazhang, Linzi, Shandong	knife	1	late SAP	bloomery iron
No.65 tomb of Chu state at Yangjiashan, Changsha, Hunan	sword	1	early SAP	carburized steel
No.2 tomb at Chengqiao, Liuhe, Jiangsu	iron bar	1	late SAP	bloomery iron
No.7 tomb at Zhannishan, Wuxian, Jiangsu	shovel	1	late SAP	bloomery iron
Xiji, Ningxia	sword	1	5th century BC	carburized steel
Guyuan, Ningxia	sword	2	5th century BC	carburized steel
Pengyang, Ningxia	sword	1		

Yanshi showed that inlaid technique had already reached a fairly advanced stage before its use there. The Guan Fou owned by the Marquis Yi of the State of Zeng was decorated with inlays of red copper^[11]. Jade was also used as decorative element on certain bronze objects. This was done by inserting the jade in the mould before pouring the molten metal into it. Bronze weapons with iron blades were made in the same way. According to the metallographic analysis, the earliest iron objects in the Central Plains area were made of wrought iron or carburized steel. Most of these objects form part of a bronze-iron combination object.

4.3 The beginning of the use of man-made iron in China

At present, there is no conclusion regarding the time and place of origin of China's iron smelting. In recent years, a number of early iron objects were unearthed in Sanmenxia, Henan, Quwo City, Shanxi, and the area at the junction of Henan, Shanxi and Shaanxi, adjacent to Liangdaicun Site. Three meteoritic iron products and three bloomery iron products were unearthed in the Guo State cemetery of the late Western Zhou Dynasty, Sanmenxia. Two shapeless remnant pig iron slices and a triangle-shaped iron slice dated to the middle SAP were unearthed in Qucun in Quwo. The bronze knife with iron blade and bronze Ge with iron blade, unearthed in M27 and dated to the early SAP in Liangdaicun, were identified as bloomery iron products. This shows that the middle reaches of the Yellow River, the area of Henan, Shanxi and Shaanxi that takes Zhong Tiao Mountain as its center, is earlier than other areas of China in the unearthed age of ironwares. After entering the late SAP, smelting iron industry in this area developed rapidly. For instance, Han Rubin who studied the fabrication technology of about 4000 ironwares created before the 3rd century BC in China found that the area of Shanxi province was the area where most of the ironwares between the 3rd and 5th century BC. were unearthed. It became the center of iron smelting in the Warring States period. The nearby area of Western Henan also had a large number of excavated ironwares^[12]. So the important evidence for the origin of iron smelting technology is the man-made ironwares produced between the late Western Zhou Dynasty and the early SAP that were unearthed in this area. More early SAP ironwares may be unearthed in this area, so further archaeological excavations and future laboratory research may

be necessary

At present, there are more than 50 ironwares that dated before the 5th century BC. unearthed in Baoji, Shaanxi and the neighboring Gansu, Ningxia. It is worth exploring the relationships between ironwares unearthed in the area at the junction of Henan, Shanxi and Shaanxi. Among the 50 ironwares, nine of them belong to the early SAP^[13-17], and the remaining samples belong to SAP and Warring States Period^[18-20]. One carburized steel sword with gold handle unearthed in No. 2 cemetery in Yimencun, Baoji City has been analyzed by metallographic methods^[7]. Therefore, in the production technology, there was no difference between the early ironwares in this area and those unearthed in Sanmenxia, Quwo or Liangdaicun. The dates of the ironwares from these two areas were almost the same, so the communication and transportation of the iron wares and the smelting technologies between the two areas should be the focus of further research.

In recent years, the early ironwares unearthed in Xinjiang have caused great concerns for scholars, as they hold some clues for the study of the beginning of the use of man-made iron in central China. Some scholars believe that the iron smelting technology of China's central region comes from the Xinjiang, but there are still multiple views about the date of early ironwares unearthed in Xinjiang^[21-25]. According to the analysis of the authors, the ironwares in the Xinjiang did not see large-scale development before the Han Dynasty. Ironwares of Yanbulake, Subeixi, Chawuhugoukou, Ili river and other areas of Xinjiang included small iron knives, swords, sickles, finger rings, the residual iron blocks, arrowheads, thimbles, needles and other small tools and weapons, which conformed to the economic situation of Xinjiang at that time. As to the tombs where ironwares were excavated, the details of these tombs are generally not fully released. The tombs where iron objects were found have few ¹⁴C dates. So far, there are only six ¹⁴C dates on samples taken directly from tombs where ironware was found, and the dating error is significant. Therefore, the establishment of a framework of ¹⁴C dates for the early ironwares in Xinjiang needs further research.

5 Conclusion

Studies on two copper-iron bimetallic wares, a bronze knife with iron blade and a bronze Ge with iron blade,

unearthed in M27 of Liangdaicun Site, Hancheng of Shaanxi reveal that the iron blades of both samples are of carburized steel produced from bloomery iron, that both the bimetallic wares were manufactured by using the cast-on method to connect the iron with the copper, and that both archaeological evidence and AMS-¹⁴C dating support an age of early SAP for these two bimetallic wares.

Based on this study and other known early man-made iron wares we believe that the region at the junction of Henan, Shanxi and Shaanxi, located at the middle reaches

of the Yellow River might be the center of the earliest iron smelting technology in China. The relationship between this region and the region of the upper reaches of the Yellow River where early bloomery iron products have also been discovered is also discussed in this paper.

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