

Article

Preliminary Discussion on the Highly Radiogenic Lead in Unalloyed Copper Artifacts of the Eastern Zhou Dynasty: Starting from the Huili Copper Spearheads

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Abstract: The debate about the highly radiogenic lead in Chinese archaeology has never ceased. However, previous studies have mainly focused on high leaded bronzes and lead materials, and with little specific discussion on the unalloyed copper artifacts and the sources of copper materials in China. In this work, a trace of highly radiogenic lead was found in ten copper spearheads unearthed from Huili County, Sichuan Province, southwest China, which inspired our research on this issue. The pXRF results showed that their lead content is extremely low, so the lead isotope ratios can indicate the source of copper, and the data correspond to the local copper deposits. Combined with other relevant highly radiogenic lead isotope data of unalloyed copper artifacts, the results indicate that there were multiple sources of copper ores used in the Shang Dynasty, and copper mines were continuously used in Southwest China until the Eastern Zhou Dynasty.

Keywords: unalloyed copper; lead isotope; China; bronze age

1. Introduction

The long period of the Bronze Age in China (c.2000–500 BCE) saw the growth and maturity of a civilization. For archaeometallurgical research, metal sources, supply management, and trade systems are always the core content. However, when involving China, highly radiogenic lead that mainly appeared in the Shang Dynasty (c.1600–1046 BCE) is a very special and important discovery. Since its recognition, it has attracted a great deal of attention, and many studies have been conducted around it over the past four decades [1].

Lead has four stable isotopes, of which ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb are produced by the radiogenic decay of uranium and thorium, while the total amount of ²⁰⁴Pb does not change with time. Lead isotopic

composition of different deposits varies with the geological age and geochemical environment of the metal deposits, thus can be used as a “fingerprint” [2]. According to the composition of different lead isotopes, they can be divided into normal lead and highly radiogenic lead (also known as abnormal lead, $^{206}\text{Pb}/^{204}\text{Pb} > 19.5$) [3]. The latter is more special because of their rarity and tend to be more characteristic and indicative when tracing the source of lead-containing materials in any archaeological context.

Ancient bronze products were always made from a mixture of some raw materials in a certain proportion, and lead is a widely distributed element in various minerals and ores. It is generally believed that when the content of lead in copper-based artifacts is high (more than 2 wt%), it is artificially added. In this case, the isotopic composition of lead directly reflects the geochemical information of the lead ore raw materials (represented by galena) used for the metalwork [4]. During a few decades, the bronzes containing highly radiogenic lead were subsequently identified in many places of China, such as Henan, Sichuan, Jiangxi, Shanxi and Shaanxi [5–9]. In the Chinese Bronze Age, the casting of bronzes with high lead content was a common practice. As a result, the controversy over highly radiogenic lead, especially around lead-rich bronzes, has been raging in Chinese archaeology. Since the application of lead isotope analysis to trace the raw materials of Shang bronzes in the 1980s, Jin has first put forward the famous view that the highly radiogenic lead was originated from the northeast Yunnan [7], whereas some scholars have proposed different viewpoints. For example, the Qinling Mountains, the middle and lower reaches of the Yangtze River, and other places are possible sources of radiogenic lead ores. The recently published papers have gained wide attention in China and internationally. Sun et al. compared the lead isotope data of Shang bronzes with tin ingots, tin grains, and bronze products in Africa, and argued that the lead materials for the bronzes of Yinxu originated in Africa. Liu et al. thereupon refuted this conclusion from the result of lead content in the Central Plains bronzes, which was much higher than that in African tin ingots, that there was no archaeological evidence to prove the connection between the Central Plains and Africa in the Shang Dynasty [9–11].

However, among the highly radiogenic copper-based artifacts from China, there are not only many high-lead bronzes but also a number of unalloyed copper wares. For example, the copper sickle unearthed from the Haimenkou site in Yunnan Province contain evident abnormal lead [4]. Some unalloyed copper sickle-shaped objects and Zhang sceptres, which are recognized as characteristic products of the Hanzhong community, hold a highly radiogenic lead composition [8]. In addition, several artifacts, turquoises, and smelting slags with low lead contents from other regions such as Sichuan and Jiangxi have similar isotopic features [12,13]. It is generally believed that if a copper-based artifact has a low lead concentration, its lead isotope data should reflect the source of copper ore. Therefore, the lead content needs to be used as a criterion to determine whether lead material was intentionally added to the metal artifact. Archaeologists hold different views on the threshold for excluding interference from lead impurities in other ores. When the content is below a certain level, e.g., 1 wt% is a relatively low value among all proposals, lead isotope should be considered to reflect the source characteristics of other ores [14]. In addition, it has been suggested that lead isotopes reflect the origin of tin minerals even for low-lead copper ware in Southern Africa [15]. There is much evidence that the lead in cassiterite and tin ingot is highly radiogenic. However, Qin proposed that it is difficult for lead in cassiterite or tin ingot to have an effect, as the copper content in Chinese bronze ware products is much higher than the tin content [16]. Liu et al. put forward that several artifacts with low lead contents (<1 wt%) and malachite samples from various sites also showed similar lead isotope ratios, suggesting that the source of highly radiogenic lead in alloys is indeed copper ores with variable lead content [10]. Therefore, in order to eliminate the influence of additional tin and lead on the lead isotopic studies for copper, this paper focuses on unalloyed copper artifacts with very low lead and tin content. Moreover, the lead in these ancient unalloyed copper wares is supposed to be an impurity in the copper ore, reflecting the source of the copper ore.

As the main raw material for manufacturing copper alloys, copper minerals have an important relationship with the Bronze Age civilization. The acquisition of large-scale copper-based alloys was

premised on large-scale mining and mineral smelting, which also implied the enhancement of social organizational capacity and the emergence of a new social order [17]. According to Zhang Guangzhi, copper and tin ores were the main political resources in the history of the Xia, Shang, and Zhou dynasties, and one of the biggest motives for the repeated migration of the capital may have been the pursuit of copper and tin deposits [18]. In a word, in ancient China, the mastery of copper minerals was not only a matter of resource utilization but also a matter of dynastic scope and the exploitation and the circulation of copper minerals. Therefore, tracing the source of raw copper minerals is an issue that deserves special attention. More importantly, copper ores with highly radiogenic lead are even more intriguing. To date, there has been relatively little lead isotopic research about copper minerals in unalloyed copper artifacts. Many issues such as the following remain unsolved. Where else were the copper ores with highly radiogenic lead utilized during the Bronze Age? Was there any exchange between regions that appear highly radiogenic lead in copper artifacts? Will these data shed new light on the use of metals in ancient China? Therefore, it is quite necessary to investigate them specifically to uncover the potential archaeological significance.

Southwest China is considered by some scholars as one of the possible sources of highly radiogenic lead [19]. More importantly, unalloyed copper artifacts are widespread in the bronze culture of Southwest China. Under this line, the trace of highly radiogenic lead was again found in copper spearheads from a cemetery of the Eastern Zhou Dynasty (770–221 BCE) in Huili, Southwest China. On this basis, and combined with the data on highly radiogenic lead isotopes in Bronze Age copper products, this paper attempts to provide insight into these issues.

2. The Archaeological Context and Samples

Huili County is situated in the southwestern part of Liangshan Prefecture in southern Sichuan Province. The Jinsha River encircles the western and southern boundaries of Huili (Figure 1). The river valley basin of Huili County is fertile, with a pleasant climate and abundant metal resources. In terms of copper resources, Huili's reserves account for up to 82% of Sichuan Province according to a modern geographical survey [20]. Judging from the appearance of the Huili bronze culture, it developed slowly on the basis of local primitive culture. The stone weapon mold unearthed in Washitian, the large number of bronze artifacts unearthed in Guojiabao, and the relevant records in the historical documents of the Han Dynasty (202 BCE–220 CE) all indicate that bronze metallurgy in this area emerged no later than the Eastern Zhou Dynasty [21].

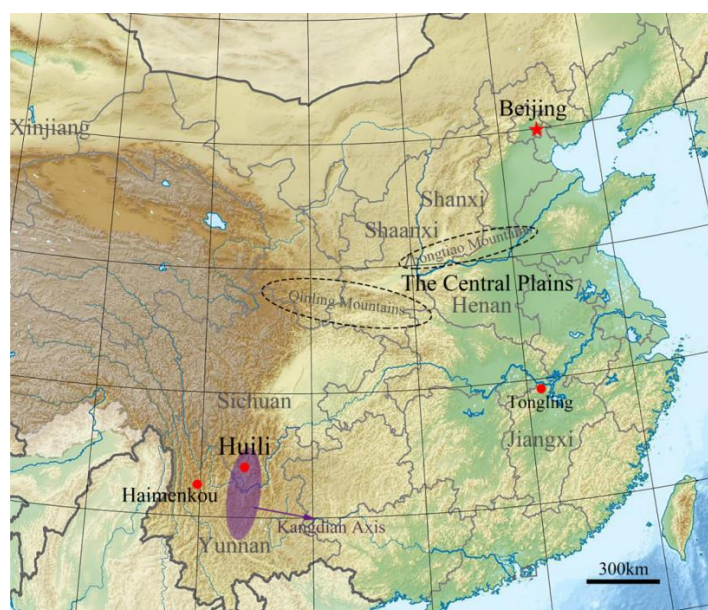


Figure 1. The geographical location of Huili County and other places mentioned in this paper.

Ten spearheads from the Guojiabao site were provided by the Cultural Relic Administration Center of Huili County to support this study. The Guojiabao cemetery is located in Xinfu Township, Tong'an Town, southeast of Huili County. The cemetery was destroyed due to the development of modern agriculture and infrastructure. According to the only surviving burials, there are two types of tombs, vertical shaft tombs and stone masonry graves. The metal objects are mainly coarse and utilitarian, including spearheads, dagger-axes, and swords. In addition, there is a small amount of pottery and turquoise. According to the excavators' inferences, the cemetery belongs to the Warring States Period (475–221 BCE) [22].

The spearheads are of the same overall style, with a leaf-shaped blade, elliptical socket, without decoration and loops (Figure 2). They are significantly different from the spearheads from other regions (or even neighboring areas) of the same time. For example, in the Eastern Zhou Dynasty, the spearheads of the Shu culture north of Huili are usually fitted with a pair of symmetrical bow-shaped loops on the socket and decorated with cicadas, tigers, birds, and other patterns [23]. However, the spearheads of Dian culture south of Huili are of various shapes and mainly the nonleaf-shaped [24]. Usually, they are decorated with extremely complicated and exquisite ornamentation on the socket. In the Central Plains, the spearheads often have willow leaf-shaped or trefoil leaf-shaped blades, and the socket is often studded with holes [25]. From the typology of the Huili spearheads, the possibility of introduction from other cultures can be ruled out. Additionally, a spearhead stone mold highly consistent with these spearhead samples was found in Huili Washitian cemetery. These indications testify to the local characteristics of these Huili spearheads.



Figure 2. The spearheads analyzed in this study.

3. Analytical Methods and Results

3.1. Elemental Analysis

In order to minimize the damage to objects, a portable Energy Dispersive X-ray Fluorescence device (Niton XL3t 950He, Thermo Fisher Scientific Inc., Waltham, MA, USA) was used to analyze the elemental composition and indicate the alloy type. The observed area of the spearhead was polished to expose a bright metal base surface with sandpaper first. The main filter operates at a voltage of 50 kV and a current of 10 μ A. The diameter of the detection spot is 3 mm. The metal mode was selected and used throughout the data-gathering phase. Elemental data were collected with the acquisition time set to 60 s. The limits of detection (LODs) of the Niton XL3t 950He (Thermo Fisher Scientific Inc., Waltham, MA, USA) were 70 ppm for Sn and 35 ppm for Pb. The copper alloy standard sample ETM-EB375 (EU copper alloy standard sample) was selected to determine the alloy composition, which was compared with the standard value [26]. Final detected results were obtained by averaging three analyses which were then normalized. Only conventional alloying elements (Cu, Sn, Pb) were considered (Table 1) in this paper. The pXRF analysis of the Huili spearheads revealed a high content of Cu (99–100 wt%), accompanied by low amounts of Sn (below 0.039 wt%), and Pb (between 0.01 and 0.26 wt%). Such results are consistent with previous research. The elemental analysis of the copper-based artifacts unearthed in the Fanjiawan site in Huili County showed that the use of high purity copper with few impurities is the main feature of the bronze culture in Huili area. Metal-ware with high purity copper has the defects of low hardness and strength, which means a relatively primitive technique, regardless of the use of alloys. Compared with the Central Plains at the same period, this kind of technology was backward, which can be regarded as the consequence of the underdevelopment of local culture and a relatively closed geographical environment.

Table 1. Composition and lead isotope ratios of the spearheads of Huili.

Lab No.	Cu	Sn	Pb	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
HL01	99.97	-	0.03	20.109	15.688	40.713	0.7802	2.0247
HL02	99.93	-	0.07	19.924	15.739	40.578	0.7899	2.0366
HL03	99.98	-	0.02	20.324	15.699	41.015	0.7724	2.0180
HL04	99.35	0.39	0.26	19.672	15.741	40.294	0.8002	2.0483
HL05	99.99	-	0.01	20.482	15.733	41.238	0.7682	2.0134
HL06	100	-	-	20.442	15.748	41.155	0.7704	2.0132
HL07	99.93	-	0.07	20.303	15.789	41.089	0.7777	2.0238
HL08	99.93	-	0.07	20.217	15.719	40.894	0.7775	2.0228
HL09	99.99	-	0.01	20.418	15.722	41.151	0.7700	2.0155
HL10	99.96	-	0.04	20.24	15.716	40.935	0.7765	2.0225

3.2. Lead Isotope Analysis by MC-ICP-MS

The lead isotope ratios were measured by a MC-ICP-MS (VG Elemental Axiom, Thermo Fisher Scientific Inc., Waltham, MA, USA) in the School of Earth and Space Sciences of Peking University. The specific experimental operation process for each sample was as follows: 10 mg sample was dissolved with aqua regia (Beijing Cemical Works, Beijing, China) and heated appropriately to accelerate dissolution. After the sample was completely dissolved, high purity deionized water was added to dilute the solution volume to 100 mL. The liquid was measured to detect the lead content by using ICP-AES (PHD, Leeman Labs Inc., Hudson, NH, USA), and then deionized water was added until the lead content was diluted down to about 500ppm. After the thallium (Tl) standard solution (NCS Testing Technology Co., Ltd, Beijing, China) (SRM997) was added into each sample solution, the sample was measured on the MC-ICP-MS. SRM981 standard was run with the samples yielding the following values ($n = 4$): $^{206}\text{Pb}/^{204}\text{Pb} = 16.942 \pm 0.001$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.497 \pm 0.001$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.718 \pm 0.001$ (see Table S1). The results are in good agreement with the published standard value [27].

During the analysis of one sample, the standard deviations of the five lead isotope ratios (measurement times = 20) were all less than 0.02%.

Ten spearhead samples covered a range of lead isotope ratios from 19.672 to 20.482 for $^{206}\text{Pb}/^{204}\text{Pb}$, 0.7682 to 0.8002 for $^{207}\text{Pb}/^{206}\text{Pb}$, and 2.0132 to 2.0483 for $^{208}\text{Pb}/^{206}\text{Pb}$ (Table 1). These isotope data are relatively uniform (the variance of $^{206}\text{Pb}/^{204}\text{Pb}$ is 0.0639). As can be observed, highly $^{206}\text{Pb}/^{204}\text{Pb}$ isotope ratios are obtained for the Huili spearhead samples, showing the clear radiogenic lead signature. Moreover, all spearhead samples are typical unalloyed copper artifacts, and it can be concluded that the lead isotope ratios of Huili spearheads reflect the copper ore source.

4. Discussion

4.1. Identification of the Copper Ores of Huili Spearheads

The lead isotope data of the copper spearheads are the starting point for discussion. One of the primary concerns is whether these spearheads were made using local copper materials from Huili. As recorded in the Book of Geographical Records of Han Dynasty, which was completed around 105 AD, Huili was rich in copper resources. The initial incentive for the contact between Huili and the surrounding region may have been the abundant local metal quarries, and the people buried at Guojiabao may be involved in the exchange of raw metal materials [28]. In addition, the style of the Huili spearhead samples is significantly different from other cultures, indicating that the metalworking was conducted in Huili. The copper deposits in Huili territory are volcano-sedimentary metamorphic deposits, which were formed in about 1950–1700 Ma [29]. The main types of copper deposits are chalcopyrite, bornite, and chalcocite.

Geological data show that the Kangdian Axis, where Huili is located, is a place where copper deposits are concentrated. According to geologists, the isotopic composition of copper deposits in the Precambrian strata of the Kangdian Axis varies widely, and some of the copper deposits have highly radiogenic lead as well as a linear relationship. The copper mines in Huili and its surrounding areas, such as the Lala copper mine and Dahongshan copper mine, appear to have similar lead isotope characteristics [30]. For example, the lead isotopic composition of the Huili Lala copper deposit has remarkably high values of $^{206}\text{Pb}/^{204}\text{Pb}$, ranging from 18.636 to 192.150. The $^{206}\text{Pb}/^{204}\text{Pb}$ of Xinping Dahongshan copper deposit varies from 17.434–20.640 [31]. The reason for this is that the stratum of the Kangdian Axis underwent metamorphism during the Jinning Movement (800–900 Ma). The copper ores were metamorphosed, causing the lead in the original copper ore body or stratum contaminated with uranium-derived lead, and here, there is a large amount of radiogenic lead copper material. Meliksetian et al. suggested that the ore-bearing solutions of some mineralization stages of the deposits remobilized the lead from the geologically older rocks and that the lead isotope fingerprints of these ores inherit the specific lead isotope signature of substrata. Additionally, the lead isotope composition is an important geochemical characteristic of ore deposit, and it remains unchanged during metallurgical processes [32]. In this way, the direct comparison can be made between the raw materials and artifacts. We did not analyze the samples which have very abnormal lead isotopic data as similar values have never been present in the copper assemblage. Detailed data are listed in Table S2. As shown in Figure 3, although there is little analytical lead isotope data from local copper mines, the data clearly showed the characteristics of highly radiogenic lead in Huili local copper mines. Moreover, the data of Huili spearheads fall within the range of lead isotopes of local copper deposits; thus, it is more likely that the spearheads were made from local copper ores in the Kangdian Axis.

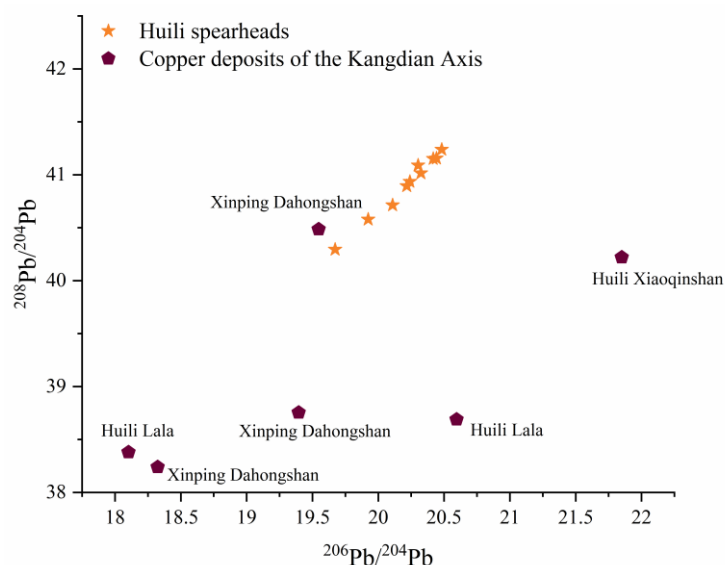


Figure 3. Lead isotope ratios of Huili spearheads and copper deposits of the Kangdian Axis.

4.2. The Highly Radiogenic Lead in Unalloyed Copper Artifacts of the Eastern Zhou Dynasty

Highly radiogenic lead bronzes are found mainly in the Shang Dynasty, and rarely in the later period. The discovery of ten unalloyed copper spearheads containing highly radiogenic lead in this paper led to a preliminary discussion of the exploitation and utilization of these special copper ores during the Eastern Zhou Dynasty (770–221BCE). Were there any connections and differences in the use of copper materials within the two eras? Therefore, for the sake of prudence, we followed the criterion of lead and tin content both less than 1 wt% in selecting data on highly radiogenic lead copper-based artifacts from China (Table S2). Most of the relevant copper artifacts collected belonged to the Shang and the Eastern Zhou dynasties, and were unearthed from various regions including Henan, Shaanxi, Jiangxi, Hunan, Sichuan, and Yunnan (Figure 4).

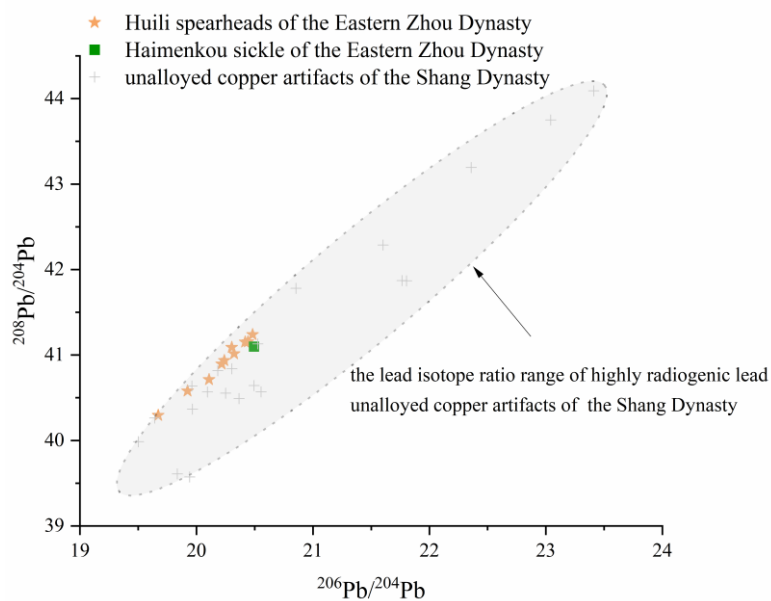


Figure 4. Lead isotope ratios of the highly radiogenic lead copper artifacts in the Eastern Zhou Dynasty and the Shang Dynasty (the range of the highly radiogenic lead of Shang copper artifacts was drawn based on the analyzed data, and the related information is summarized in Supplementary information, Table S2).

Among all the data, an unalloyed copper product belonging to the Eastern Zhou Dynasty was found at the Haimenkou site in northwestern Yunnan. According to the latest research result, the date of the Haimenkou site is tentatively set as the Spring and Autumn Period (770–467 BCE) [33]. Coincidentally, the lead isotope data of the copper sickle unearthed from the Haimenkou site are consistent with those of the Huili spearheads (see Figure 4). Based on previous studies of metal and ceramic artifacts, there is a close connection between Huili and northwest Yunnan. This is mainly due to the fact that during the pre-Qin period, tribal ethnic groups such as *Xi* and *Kunming* in northwest Yunnan were already very strong, whereas the tribal ethnic groups scattered across the Jinsha River Valley (e.g., people in Huili) were relatively weak, and their productivity levels were still in a relatively low stage of development. The powerful ancestors of northwest Yunnan waged war in order to seize wealth from these weak tribes [21]. In the process, these small and scattered tribes were plundered economically and integrated culturally. Therefore, it is not surprising that the lead isotope data of these two nearby areas are similar. The similarity implies that the copper from Huili and Haimenkou copper artifacts may have come from the same set of deposits, and that highly radiogenic lead products were still circulating in southwest China at that time.

The lead isotope values of the copper products from the Eastern Zhou and the Shang dynasties in China are summarized in Figure 4. Comparing the two, there are obvious differences, and the results further illustrate the chronology variation in resource selection and supply. The highly radiogenic lead isotope data of copper artifacts of the Eastern Zhou Dynasty are very concentrated in a small range, falling within the lower left corner of the range of Shang unalloyed copper products, while the data of the Shang Dynasty are scattered over a larger span. In historical documents such as *Shanhaijing* and *Yugong* (the ancient geography books completed around the third century BC), it is recorded that different locations once provided copper ores for the Shang Dynasty. In addition to artifacts, traces of highly radiogenic lead have been found in smelting slags from the mining–smelting site in Jiangxi and copper ore samples in Xinjiang of the Shang Dynasty [13,34]. Additionally, traces have also been found in the copper mines in modern copper deposits of Zhongtiao Mountain and Qinling Mountain [35,36]. Thus, various highly radiogenic copper mines were probably utilized during the Shang Dynasty. This study also suggests that the ancestors in Southwest China may have continued to use some copper ores with highly radiogenic lead during the Eastern Zhou Dynasty, while most of the highly radiogenic copper sources of the Shang Dynasty were not further utilized.

5. Conclusions

The discovery of highly radiogenic lead in ten unalloyed copper spearheads unearthed from Huili in the Warring States Period started a discussion of the use of copper materials with highly radiogenic lead in the Eastern Zhou Dynasty. Compared with the lead isotopic composition of copper ores from Huili, the copper materials of Huili spearheads are likely from the local area. This paper also discussed the highly radiogenic lead in unalloyed copper products of the Shang Dynasty and of the southwestern region in the Eastern Zhou Dynasty. The results suggest that a variety of sources of copper ores which contain highly radiogenic lead were exploited in ancient China, and the special copper ores were still accessed and used by the ancestors in the Southwest during the Warring States period. Although the number of samples is limited, this discovery will undoubtedly form a preliminary progress for the discussion on the mining and utilization of copper ores in the Eastern Zhou Dynasty.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-4701/10/9/1252/s1>, Table S1: The results of four runs for the SRM981 determination and published values; Table S2: The lead isotope data of unalloyed copper artifacts of the Shang and Eastern Zhou dynasties, and copper ore samples of modern copper deposits in Huili.

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