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Received 20 June 2018; accepted 28 February 2020

doi: 10.18520/cs/v118/i9/1436-1442

## Source change of lead materials for mirror-making industry in Western Han, China: evidence from Nanyang bronze mirrors

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**The circulation of lead materials has always been a major concern in the Bronze Age archaeology. The source of lead materials for mirror-making industry during the Han Era in China is still not comprehensible. In particular, the change of raw material sources from Western to Eastern Han has not been well explained. In this study, five bronze mirror samples that were excavated from Nanyang City, Henan Province, Central China, were analysed using optical microscope, scanning electron microscope-energy dispersive spectrometer and multi-collector inductively coupled plasma mass spectrometry methods. Further data on Han mirrors from Chang'an and Linzi in China and Japan were collected for a comparative study. The results show that lead ore sources in Western Han were multiple and complex, while those in Eastern Han were dominated by the Lower Yangtze. This type of change had begun to take place in Western Han, not in the transitional period as revealed in previous studies. The present study indicated that Nanyang played a pivotal role as a resource hub in this process.**

**Keywords:** Bronze mirror, lead isotope ratio, mirror-making industry, source change.

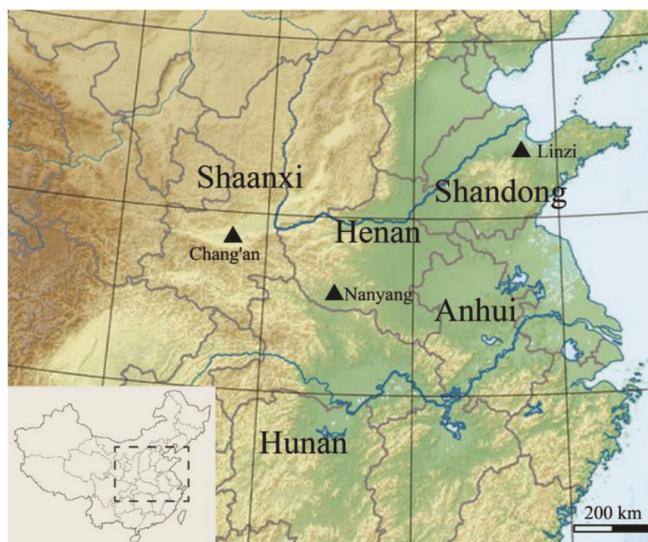
THE history of the bronze mirror industry in China can be traced back to the Qijia culture (c. 4000 BP). In the early stage, bronze mirrors functioned more as religious objects than as reflectors of images<sup>1</sup>. As the first highlight in the history of ancient Chinese bronze mirrors, the Han Dynasty witnessed unprecedented production and use of such mirrors<sup>2</sup>. They became an indispensable part of the daily life of the Chinese, from emperors to the common people<sup>3</sup>. These mirrors have consequently become important representatives of the material culture at that time.

The initial decoration of the Western Han (WH: 202 BC–AD 8) mirrors was inherited from the Warring States period (475–221 BC); soon afterwards, the kaleidoscopic patterns emerged. Researchers have done a detailed analysis of various types and subtypes of these mirrors, and

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**Table 1.** Burial units and types of analysed bronze mirrors from Nanyang, China

Lab no.	Ornament type	Burial unit	Burial age
N1	Plain	2000NCQB M9	Late Western Han Dynasty
N2	Plain	2000NCQB M95	Early Western Han Dynasty
N3	Plain	2005NCJ M60	Early Western Han Dynasty
N4	Linked-arc, Pan Chi	2007NFBC M285	Middle Western Han Dynasty
N5	Four mountain lines	2009NTX M60	Early Western Han Dynasty

**Figure 1.** Geographical locations of Nanyang, Chang'an and Linzi, China.

established a style chronology<sup>4</sup>. An important fact revealed was that another great transition occurred from the WH style to the Eastern Han (EH: AD 25–220) style. Moreover, Japanese researchers carried out scientific detection of Han mirrors unearthed in Japan and found that WH mirrors were clearly different from EH ones in terms of lead isotope ratios<sup>5–7</sup>. It is well known that lead isotope data could effectively reveal the provenance information of ancient metals. Therefore, further inference was made that lead source for the mirror-making industry could probably have also changed between WH and EH; specifically selection of raw materials may have shifted from northern to southern China<sup>6,7</sup> (the boundary between the North and the South is based on the Qinling Mountain–Huaihe River line).

However, the Han bronze mirrors unearthed in China do not fit this model well. For example, some lead isotope data of the WH mirrors from Chang'an and Linzi in China fall into the region of the EH mirrors unearthed in Japan<sup>8,9</sup>. Considering that both Chang'an and Linzi were then metropolis in northern China (Figure 1), it is difficult to understand that the influx of southern lead raw materials was due to simple regional differences. Does this indicate that the change of lead ore source was earlier than previously considered?

On the other hand, the sources of bronze raw materials are complex during different periods in China. Recent research has demonstrated that Nanyang area was a resource distributing centre receiving lead ores from Southern China during the early WH Dynasty<sup>10</sup>. Hence, if there were any metal resources transported to northern China from the south, they would most probably pass by Nanyang. More importantly, Nanyang was not only a metallurgy centre but also a prosperous metropolis at that time, and there were frequent exchanges with multiple regions. Under such conditions, are the WH mirrors from this area same as those in Chang'an and Linzi or just like in Japan? Clarifying this will help us understand the raw material circulation and thus shed light on the above issues.

The Nanyang basin lies in the southwest of Henan Province between the Yellow River and the Yangtze River. It is an intermountain basin between northern and southern China with transitional characteristics (Figure 1). From the Neolithic Age to the Zhou Dynasty, the Nanyang basin became the zone of competition between northern and southern political powers. During the Warring States period, Nanyang had already become the most famous metallurgical centre in China<sup>11</sup>. During the WH Dynasty, industrial and commercial activities were already present in Nanyang, whose level of economic prosperity ranked first in China. Besides, Nanyang linked many other areas by at least five traffic arteries on land as well as numerous waterways as a transportation hub<sup>12</sup>.

At that time, Nanyang had jurisdiction over 42 counties in China, among which Tongbai, Fangcheng, Neixiang, Zhenping, Nanzhao, Xixia, Xichuan, Biyang, Lushan were abundant in iron and copper ores<sup>13</sup>. Moreover, modern geological exploration indicates that the Nanyang basin is rich in galena<sup>14</sup>. Some copper casting relics of the Middle Shang period and the Western Zhou period were unearthed near Nanyang City. Archaeological evidence has confirmed that metallurgy, as seen in the bronze industry in Nanyang, had been developed since ancient times<sup>13</sup>.

The present study is based on five archaeological bronze mirrors that were provided by the Nanyang Municipal Institute of Cultural Relics and Archaeology, China. Table 1 and Figure 2 provide information about the samples. All the mirrors were excavated from various places in the urban district of Nanyang City (Figure 3).

They have varying degrees of damage and are suitable for sampling and further scientific analysis.

Due to its geographical location, Nanyang was affected by both the Central Plains culture and the southern culture. The bronze mirror style of the Warring States period lasted up to the early WH period in Nanyang, but it was mainly influenced by the Chu Culture<sup>15</sup>. In addition, the patterns appearing on these samples, such as Linked-arc, Pan Chi, and mountain, were common in the state of Chu<sup>2,4</sup>. On the one hand, judging from the pattern style, these mirrors are undoubtedly products of the WH Dynasty and even earlier. On the other hand, according to their burial age, none of them is later than the Late WH Dynasty.

Although the copper industry gradually declined following the expansion of the iron industry, many metallurgical sites and mining remains of the Warring States period and the WH Dynasty have been found in Nanyang, such as in Nanzhao County, Tongbai County and Wancheng<sup>16</sup>. Moreover, according to the inscription of some unearthed bronze mirrors of the EH Dynasty in Nanyang,



Figure 2. Bronze mirrors analysed in this study.

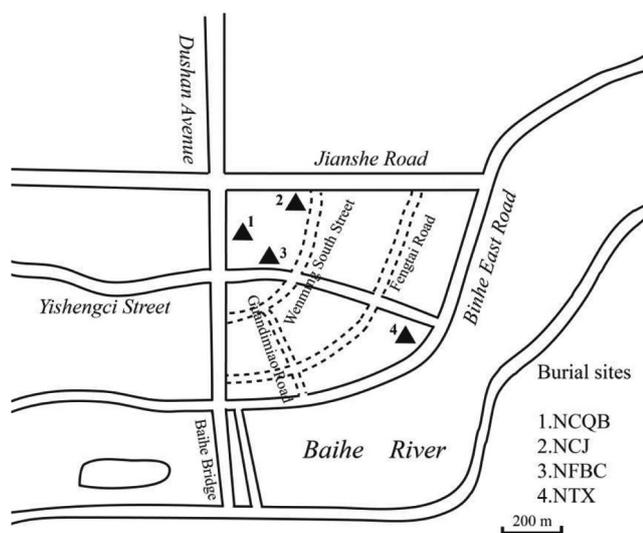


Figure 3. Discovery sites of Nanyang mirrors.

this area hosted a flourishing mirror-casting industry during the Han Dynasty<sup>13</sup>. Hence, most of the bronze mirrors were considered to be locally made.

First, small pieces of bronze mirror samples were polished using silicon carbide paper to remove the corroded parts. Then, these polished pieces were inserted into bakelite cylinders using a metallographic inlaying machine (XQ-1, SMEC Ltd, Shanghai, China). Next, the samples were polished and etched with ferric chloride alcohol solution. Finally, a polarizing microscope (BX51; Olympus Ltd, Beijing, China) was used to visualize the microstructures of the samples.

A small piece of each sample was removed and inserted into a bakelite cylinder using a metallographic inlaying machine. Then, the elemental compositions of the fresh section were determined by SEM-EDS (HITACHI, TM3030, Japan). The acceleration voltage was set at 20 kV, acquisition time as 90 sec, and the working distance kept at 12–15 mm. To reduce errors, each of these samples was obtained by averaging three random analyses of areas of 870 μm × 1270 μm.

This analysis was carried out at the School of Archaeology and Museology, Peking University in Beijing, China. First, 2 mg of small bronze pieces was chipped-off. The pieces were then dissolved in 3 ml of HCl and 1 ml of HNO<sub>3</sub>. Subsequently, the clear solution was leached and diluted with deionized water to 10 ml. The solutions were then measured to detect lead content by ICP-AES (PHD, Leeman Labs Inc, California, USA). According to the results representing lead content, the solutions were diluted to 1000 ppb. The thallium (Tl) standard SRM997 was added to the solutions. Lead isotope analyses were carried out using MC-ICP-MS (VG AXIOM, Thermo-Elemental Inc, England, UK). This is a double-focusing magnetic sector spectrometer equipped with an array of ten variable Faraday collectors. Further, it has a fixed Faraday and an electron multiplier detector. Based on repeated analysis of SRM981, the overall analytical 2σ error for all lead isotope ratios was less than 0.238% (ref. 17) (Table 2).

Metallography is a useful and efficient tool for studying manufacturing processes, thermal history of an object and nature of corrosion products<sup>18</sup>. Figure 4 shows representative images taken using a polarizing microscope. Figure 4a and c shows images before etching with the

Table 2. Results of two runs for SRM981 determination, analytical 2σ error and published values<sup>17</sup>

ICP-MS Number	SRM981		
	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>207</sup> Pb/ <sup>204</sup> Pb	<sup>208</sup> Pb/ <sup>204</sup> Pb
1	16.941	15.496	36.718
2	16.945	15.498	36.716
Cattin <i>et al.</i> <sup>17</sup>	16.942	15.496	36.720
Analytical 2σ error (%)	0.238	0.047	0.072

ferric chloride alcohol solution, while Figure 4b and d shows those taken after corrosion.

The photomicrographs show distinct dendrites with segregation. The microstructures are presented with  $(\alpha + \delta)$  eutectoid and  $\alpha$  phases as well as small lead globules spread as uncombined black spots. However, we could not find any evidence of hot-working or quenching microstructure, such as equiaxial grain with twin crystal or  $\beta$ -needles<sup>19</sup>. The result indicates that these mirrors were consistent with the WH mirrors from Chang'an and Linzi<sup>8,9</sup>.

Table 3 gives the elemental concentration of the bronze samples. Some studies have proposed that if the lead content is more than 2%, it can be considered as an intentional alloy component, and introduced by lead ores<sup>20</sup>. Other studies have demonstrated that the limit can be as low as 1% (ref. 21). Moreover, some experts have proposed that if lead is absent from the original copper ore, it could be considered an intentional alloying addition even at low amounts<sup>22</sup>. From a technological point of view, craftsmen of that time were aware that addition of lead could reduce the porosity caused by crystallization kinetics and increase the mould-filling capacity<sup>23</sup>.

Based on this, bronze mirrors are all Cu–Sn–Pb ternary alloys. According to the total amount of copper, tin and lead, samples N1 and N3 in the present study shaved severe

corrosion. The alloy ratios still varied although the deviation of the data due to corrosion was eliminated as much as possible. The lead content of three other uncorroded bronze mirrors was lower than those from Chang'an, but similar to mirrors from Linzi<sup>8,9,24</sup>.

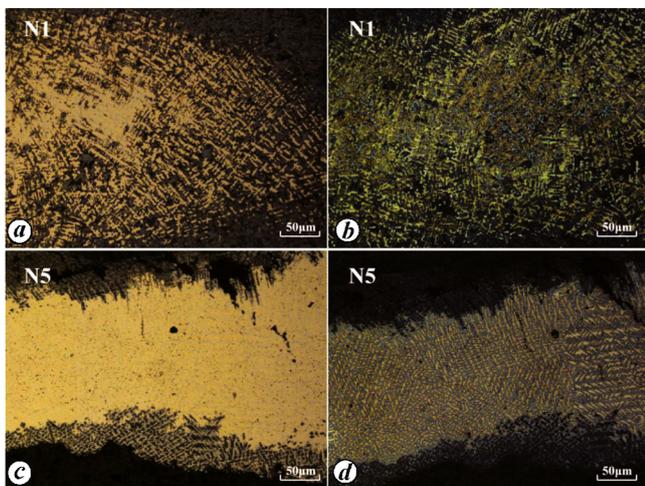
Table 4 shows that the lead isotope ratios conform to the characteristics of common lead<sup>25</sup>. As all the samples are leaded bronzes, isotopic data of the mirrors indicate the lead-ore source. According to the geochemical provinces theory and the latest summary of lead isotope distribution in China, there are at least two lead-ore sources for Nanyang bronze mirrors. In terms of tectonic terrains, NCC and Qinling-Dabie fold belt are potential sources for the northern group, while Upper Yangtze, Lower Yangtze, Cathaysia and Sanjiang are likely sources for the southern group<sup>26,27</sup>.

The published lead isotope data of Han mirrors from Japan as well as Chang'an, Linzi and Nanyang in Chinese were collected for comparative study<sup>6,8–10,24</sup>. Considering the similarity of local production technology, related data of Nanyang bronze vessels of the early WH period were also referred as background. The Han mirrors were divided into three periods based on typology: WH, TP (from late WH to early EH) and EH. Figure 5 illustrates the provenance relationship between them.

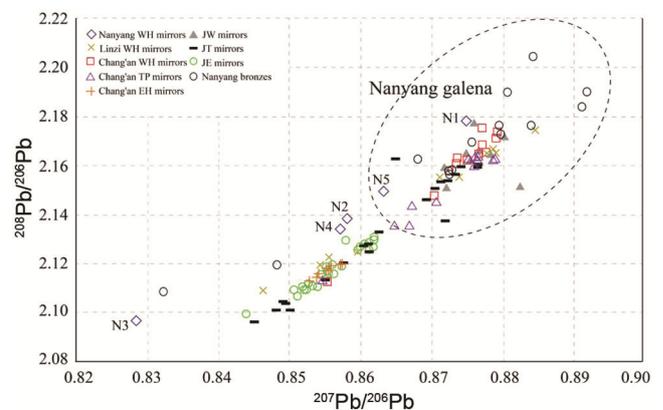
In general, the deviation of all data from their regression lines is not large, which indicates that they come from the same geographical unit. In Figure 5 part of the data of WH mirrors falls into scope of EH mirrors. Although only one of Chang'an WH mirror's data falls into this range, nearly half of Linzi WH mirrors have the same performance, which definitely shows that this is a common feature. On the contrary, data of EH mirrors do not blend into the range of WH mirrors. This indicates that much fewer sources of raw materials were used for mirror-casting industry in EH than before. Moreover, the isotopic data of TP mirrors, both unearthed from China and Japan, stretch across two areas. This fact demonstrates that

**Table 3.** Elemental composition of bronze mirrors

Lab no.	Elemental concentration (wt%)			
	Cu	Sn	Pb	Total
N1	58.53	26.49	7.89	92.91
N2	66.81	28.92	1.32	97.05
N3	49.25	38.86	5.06	93.17
N4	71.86	24.74	2.58	99.18
N5	75.65	22.43	0.76	98.84



**Figure 4.** Metallographic images of bronze mirror samples (100X).



**Figure 5.** Lead isotope ratios of Han bronze mirrors from Nanyang, Linzi and Chang'an in China, and Japan (JW, JT and JE represent Western Han, Transitional Period and Eastern Han mirrors unearthed in Japan respectively).

**Table 4.** Lead isotope ratios for the bronze mirrors studied

Lab no.	Lead isotope ratios				
	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
N1	17.7311	0.8748	2.1782	15.5128	38.6223
N2	18.1944	0.8581	2.1383	15.6137	38.9074
N3	18.9821	0.8284	2.0966	15.7254	39.7989
N4	18.2286	0.8571	2.1338	15.6246	38.8984
N5	18.0657	0.8632	2.1494	15.5961	38.8320

there were not only changes in style, but also likely multiple selections of mineral resources. Furthermore, data of JW mirrors and JE mirrors (JW and JE represent Western Han and Eastern Han mirrors unearthed in Japan respectively) do not overlap, which may imply that Han mirrors flowing into Japan were not so comprehensive that there existed a gap in the middle time.

However, isotope data of Nanyang mirrors were more scattered than those of other regions, especially sample N3 as an outlier, containing a unique significance. In addition, one data point of Nanyang bronzes appears similar (in the lower left corner of Figure 5). The two data show little tendency to the characteristics of anomalous lead in southern China. In fact, anomalous lead has been often detected in bronze ware of the Yin ruins and Sanxingdui site of the Shang dynasty, which was thought to exist only in southwest China<sup>28</sup>. Not only galena, but some WH bronze drums in southern China also show similarities to these two data<sup>29</sup>. Previous studies suggest that their lead isotope ratios are consistent with lead deposits in Hunan and Yunnan Provinces in China<sup>10,30,31,32</sup>.

As for typical lead source in EH, all of the related data clustered closely together and possibly originated from a single ore deposit. The Han mirror inscriptions may provide some evidence, e.g. ‘Danyang produced high quality copper during Han period’. Danyang was located in today’s Anhui Province and lead was also produced nearby<sup>33</sup>. Therefore, the single source was considered probably to be in the range of the Lower Yangtze metallogenic belt<sup>8</sup>. The results of this study also support the same.

The isotopic data of a lead deposit in Zhaoye region of Shandong Province is almost the same as those in Qinling Dabie belt, which shows that the fact of typical lead sources in WH is more complicated<sup>27</sup>. It was recorded as early as the Warring States period that mining of lead ores occurred in Linzi. And based on the geographical proximity, lead source for Linzi was considered from the local areas or neighbourhood<sup>9</sup>. However, data of Nanyang galena offer greater variations which can include all of WH mirrors and Chang’an TP mirrors<sup>10</sup>. Both Chang’an and Nanyang are located near or in the Qinling-Dabie belt and hence they have used their nearby raw materials.

The major anomaly about the data on these Nanyang mirrors and bronzes is that they seem to represent the lead sources of three places rather than two<sup>33</sup>. One is

from the local region, another may be from Lower Yangtze such as Danyang, and yet another from further southwest. In addition, coupled with the source of Linzi bronze mirrors, it can be concluded that there are multiple sources of raw materials for casting mirrors in WH. From this point of view, it is too simple and vague to describe the use of raw materials from WH to EH only applying the word ‘change’. The lead sources gradually tend to be consistent and unitary. This transformation can be regarded as ‘resource integration’. The trend shows gradually unitary and the reality may be ‘integration’. The lead ores from Lower Yangtze were used for bronze making as early as WH, the proportion become heavier in TP and finally became dominant in EH. Based on the present study, it can be inferred that Nanyang played a pivotal role in this process.

After the Qin state occupied Nanyang in the late Warring States period, a large number of immigrants moved into Nanyang, among which many were merchants and those from the handicraft industry. As a result, several materials and technologies were brought to Nanyang<sup>12</sup>. Later, the WH Dynasty implemented a policy of recuperation (socio-economic rehabilitation and recovery) in the early days. The power of resource utilization was extended to the public. Hence many individual workshops, including metallurgical workshops, emerged in metropolitan areas such as Nanyang. Prosperous economic interactions and frequent commodity circulation attracted the resources of southern China into the Central Plains and even abroad. The lead materials along with copper ores from that Lower Yangtze entered the northern markets through Nanyang by water route, because the rivers in Nanyang are tributaries of the Yangtze and the Huaihe<sup>12</sup>. Maybe due to stable production, low price and other factors, they gradually dominated and became the largest, and almost the only source of supply for the mirror-making industry in EH Dynasty.

Five WH bronze mirrors from Nanyang have been analysed in this study. All mirrors were Cu–Sn–Pb ternary alloys, and all the samples seem not to have been subjected to hot-working or quenching. The lead contents of Nanyang bronze mirrors were lower than those of WH mirrors from Chang’an, but similar to mirrors from Linzi.

The lead isotopic results showed that like the Chang’an and Linzi mirrors, the raw materials of these five bronze

mirrors from Nanyang had different sources. Three potential sources include the Nanyang Basin, Lower Yangtze such like Anhui, and further southwest areas like Hunan or Yunnan.

The lead ore sources for mirror-making industry in WH were multiple and complex in the metropolis of that time. When lead materials from the Lower Yangtze entered the market in WH, they gradually replaced the others and became the largest source of supply for the mirror-making industry in the EH Dynasty. In this process, Nanyang seems to have played a pivotal role as a transfer station for resource transportation.

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ACKNOWLEDGEMENTS. This research is supported by the University of Chinese Academy of Sciences (no. 2019-Y954026XX2), the Youth Innovation Promotion Association of CAS, China (no. 17XKG003), China Scholarship Council (CSC no. 201904910738), and National Natural Science Foundation of China (Grant no. 41471167). We thank the anonymous reviewers for useful comments that helped improve the manuscript.

Received 26 March 2019; revised accepted 24 January 2020

doi: 10.18520/cs/v118/i9/1442-1447