Preliminary multidisciplinary study of the Miaobeihou zinc-smelting ruins at Yangliusi village, Fengdu county, Chongqing

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Abstract The Miaobeihou zinc-smelting site located at Yangliusi village in Fengdu county, Chongqing, was excavated between 2002 and 2004 in order to determine its date and the smelting techniques used. Slag, retort fragments and other materials were collected and analysed by chemical and metallurgical methods and dated by AMS-^{14}C radiocarbon. The results indicate that smithsonite and coal were used to produce zinc metal during the Ming dynasty. The zinc-smelting process found to have been carried out on this site closely matches the account given in the *Tian Gong Kai Wu*. The results of this excavation mark a major advance in our knowledge of the origins of zinc smelting in China: more field investigations, archaeological excavation and laboratory analysis work will be needed to take this further.

Keywords: zinc, smelting, China, metallurgy, archaeology, excavation.

Introduction

Despite the occasional very early occurrences of accidentally produced brass in China, deliberate metallic zinc production did not occur until the Jiajing period (AD 1552–1566) of the Ming dynasty, when zinc began to be produced on a large scale and used in the manufacture of brass. This late occurrence was due to the difficulty of the smelting process. The evidence comes from field investigations in Guizhou province (Zhou Weirong and Dai Zhiqiang 2002), although other researchers believe that zinc smelting began earlier than this date (Liu Guangding 1991; Xu Li 1986, 1998).

The *Tian Gong Kai Wu*, written by Song Yingxing at the end of Ming Dynasty (E-tu-Zen Sun and Shiou-Chuan Sun 1966) recorded zinc-smelting techniques (Fig. 1). Since the 1920s Chinese scholars have carried out systematic, text-critical research into the origins, development and technology of zinc smelting in ancient China (Liu Guangding 1991; Mei Jianjun 1990; Xu Li, 1986, 1998; Zhang Hongzhao 1955; Zhao Kuanghua 1984, 1996; Zhou Weirong and Dai Zhiqiang 2002, and see Zhou Weirong in this volume, pp. **xx–xx**). Others outside China have also researched this subject. Over the past 80 years, research into the origins of the zinc-smelting process has not shown great progress because of the lack of archaeological evidence. In the mid-1990s, Paul Craddock and Zhou Weirong (China Numismatic Museum) carried out field investigations into traditional zinc-smelting technology in southwest China to research its origin and development (Craddock and Zhou Weirong 1998, 2003).

Figure 1 Drawing of the zinc-smelting process recorded in *Tian Gong Kai Wu*.

In the 1980s, before the construction of the big dam of the Three Gorges of the Yangtze river, several smelting sites had been found on the southern bank of the Yangtze in Fengdu county, but no further investigation was carried out until 2002–04 when a site was excavated in Miaobeihou by the Henan Provincial Archaeology Institute (see Fig. 2). Many samples of furnaces, ore, slag and other smelting remains were unearthed, some of which were collected for analysis in our

Figure 2 Map showing the location of Miaobeihou zinc-smelting site.

laboratories. The results indicated that it was a zinc-smelting site. At the end of 2004, a research group with members from four institutions was established. More than 20 zinc-smelting sites were found in Fengdu county in the last year of field investigations and about 6000 square metres were excavated, of which the Miaobeihou site was just a small part. This paper reports on these new archaeological findings and the zinc-smelting technology seen at the Miaobeihou site.

Fieldwork

Located in southwest China in the southeast Sichuan basin, the Miaobeihou zinc-smelting site at Yangliusi village, Fengdu county is part of Chongqing, a municipality directly under the control of central government. It shares borders with the provinces of Hubei, Hunan, Guizhou, Sichuan and Shaanxi. The Miaobeihou site was located on the southern bank of the Yangtze river (Fig. 3). Almost all of the zinc-smelting sites found in Fengdu county were located on the lower terraces of the river at an altitude of about 150–170 m, convenient for transporting the ore and fuel to the site and to take away the zinc produced. A number of very important features were found during the excavation of the site including a furnace and unused smelting retorts (Figs 4 and 5). The retorts vary in size, with an average height of about 27 cm. Figure 6 shows a used retort excavated from the site. From this figure it can be seen that the pocket (see also Fig. 7) and the gas passage are preserved, and furthermore that some zinc metal, zinc oxide and zinc white still adhere to the pocket. A great deal of zinc ore together with some iron tools (Fig. 8), fragments of zinc ingots (Fig. 9), coal and other remains (Fig. 10) were also found.

Scientific examination

The debris of metal production was examined, in particular to discover the date and manufacturing technology, including the ores, fuel sources, smelting and processing techniques, the composition of the metal and its mechanical qualities. In order to determine smelting technologies, slag, retort fragments and other remains were collected from the site and analysed using metallographic microscopy, scanning electron microscopy with energy-dispersive spectrometry (SEM–EDS), X-ray diffraction (XRD) and inductively coupled plasma–atomic emission spectrometry (ICP–AES). The dates were provided using AMS-^{14}C radiocarbon methods.

Microstructural and chemical analyses

Compositional analysis of the alloys, slag and ores is significant to our understanding of the smelting techniques and the sources of ores. A scanning electron microscope (SEM) was used to observe the microstructures and compositions of polished sections of samples. An SEM with energy-dispersive spectrometer (EDS) was used to carry out the non-sampling quantitative analysis. This research was undertaken using a Japan Electron JEOM-850 SEM and a Philips PV9550 EDS. The excitation voltage was 20 kV. Since light elements such as carbon and oxygen whose atomic numbers are less than

Figure 3 View of the terrain of the Miaobeihou site on the banks of the Yangtze river.

Figure 4 The excavated foundation of No. 1 furnace.

Figure 5 Unused retorts excavated from the site.

Figure 6 Used retort excavated from the site.

Figure 7 The pockets for collecting the zinc at the top of the retorts.

Figure 8 An iron tool found at the site. Very similar iron tools were recorded by Xu Li (1998: pl. 7), still in use in the mid-20th century.

Figure 9 Part of a zinc ingot excavated from the Miaobeihou site.

Figure 10 A piece of by-product, mainly oxidised zinc.

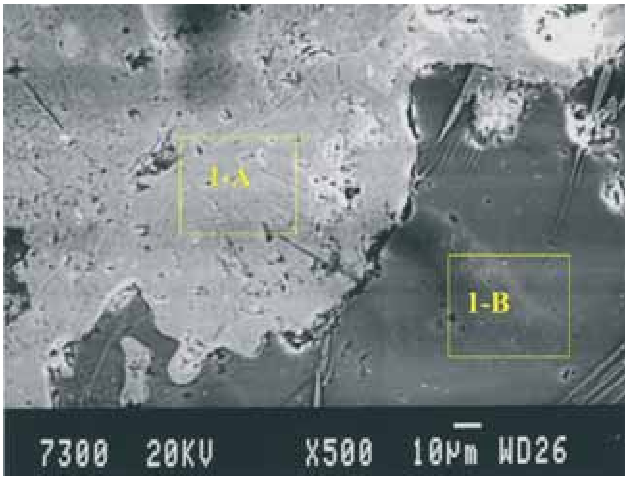

Figure 11 SEM image of polished section of slag No. 1 adhered to retort wall, high zinc content in white area 1A (see Table 1 for analyses).

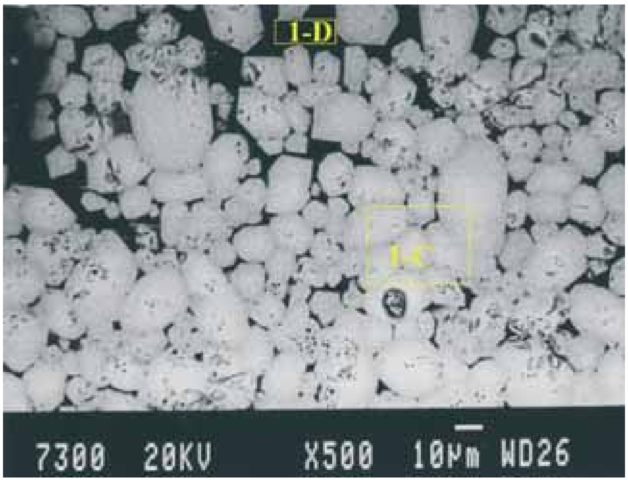

Figure 12 SEM image of slag No. 2 adhered to retort wall, high zinc content in white area 1C.

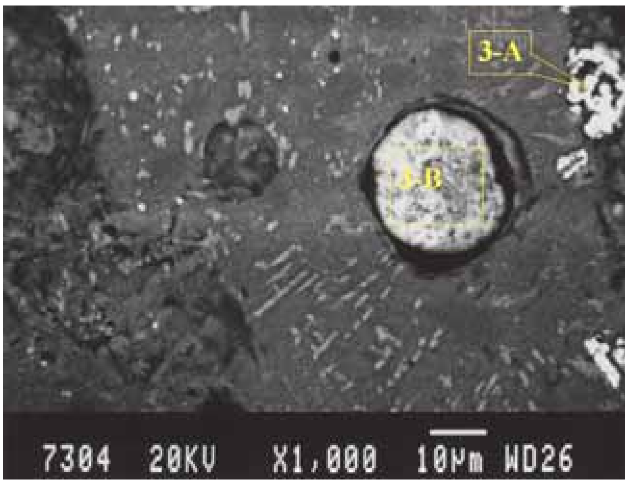

Figure 13 SEM image of slag No. 3 adhered to retort wall with zinc-rich area 3B.

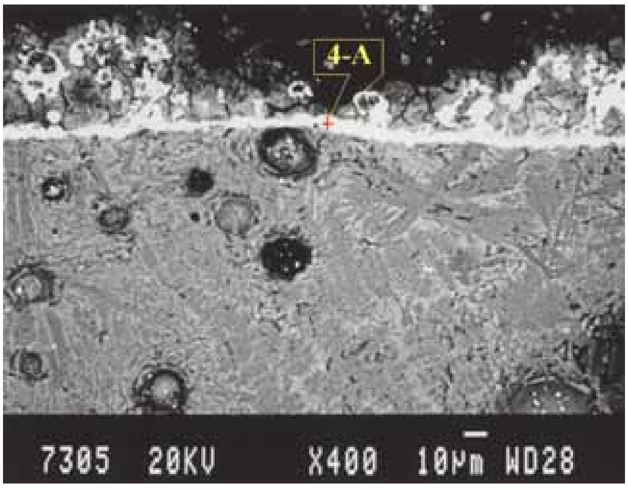

Figure 14 SEM image of the matrix of slag No. 4, high zinc content at position 4A.

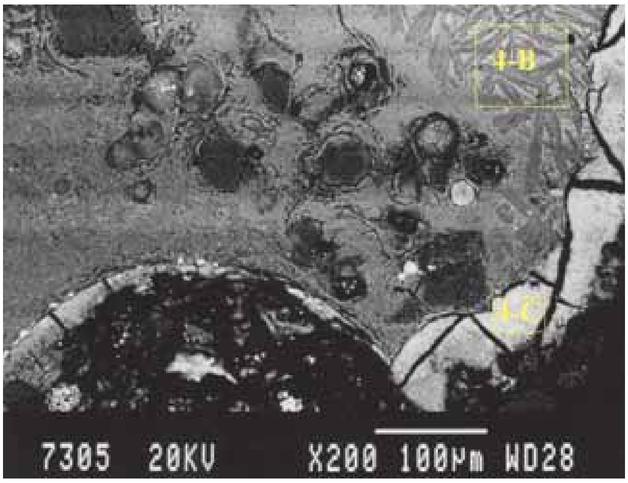

Figure 15 SEM image of the matrix of slag No. 4 with high zinc content at 4C.

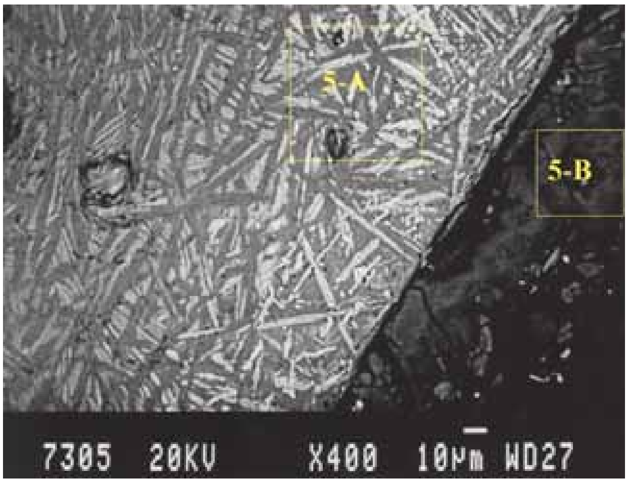

Figure 16 SEM image of the matrix of slag No. 5.

11 could not be detected, only a qualitative analysis of the corroded objects or occluded trace elements could be given. Oxidised components could not be determined. To determine the average components, surface scanning was used with multifaceted scanning on different parts of the samples to discover the precise composition of each sample. Based on previous analyses, the lower confidence limits for this instrument may be established at 0.3 wt%; values below this limit can be taken as indicative only. The analysis results of eight samples are shown in Table 1 and the SEM images are shown in Figures 11–17. Samples 1–8 are slag and sample no. 12 is a piece of by-product (shown in Fig. 10) which is a compound of zinc. In order to further elucidate their structure, other techniques were used such as metallography and XRD. Several were analysed with a Ricoh MD2/JADE 5 XRD apparatus carried out at the National Museum of Japanese History.

A total of eight samples of slag, by-product, zinc oxide, zinc ore and a zinc ingot were analysed quantitatively using ICP–AES. The instrument used was a Prodigy model (made by Leeman-Labs Inc., USA) at Peking University. The spectrometer had a wavelength coverage of 170–1010 nm and a resolution of 0.001 nm. The following analytical parameters

Table 1 Normalised composition analysed by SEM–EDS (wt%).

Sample no.	Analysis area	Mg	Al	Si	S	K	Ca	Ti	Mn	Fe	Cu	Zn	Figure no.
1	Average	1.2	14.1	50.5	0.1	5.3	6.2	1.8	0.2	9.3	0.1	7.8	11 and 12
	1-A	1.5	2.7	17.5	0.1	0.2	0.1	0.1	0.2	13.3	0.1	64.1	
	1-B	tr	0.3	1.4	0.1	tr	0.5	0.2	tr	95.2	tr	2.3	
	1-C	tr	tr	tr	0.1	0.1	0.1	tr	tr	13.5	0.1	86.1	
	1-D	0.2	7.6	54.7	0.2	5.3	6.5	0.4	tr	9.6	tr	15.6	
2		1.2	2.7	25.6	0.2	0.7	0.9	0.3	0.4	11.7	0.3	56.2	
		0.3	10.2	48.6	0.4	5.0	5.1	1.1	0.7	13.1	0.1	15.5	
		tr	0.2	1.2	0.4	tr	0.4	0.1	0.3	94.0	0.6	2.6	
3	Average	1.4	17.0	61.6	tr	5.7	1.9	1.4	tr	9.5	tr	1.7	13
	3-A	1.5	9.9	10.8	0.1	1.2	0.4	30.3	0.4	43.7	0.2	1.5	
	3-B	0.2	2.0	4.2	0.8	0.2	tr	0.1	0.2	1.6	1.0	89.7	
4	Average	0.8	22.1	64.4	0.2	5.2	0.5	1.2	tr	4.7	0.1	0.3	14 and 15
	4-A	2.3	19.5	18.5	0.1	1.3	1.0	0.7	0.2	17.0	1.4	37.9	
	4-B	2.1	16.5	54.3	tr	5.4	8.9	1.5	tr	10.5	tr	0.9	
	4-C	0.2	2.9	37.9	0.2	0.2	1.2	0.1	tr	1.0	0.4	56.1	
5	Average	1.7	20.4	52.8	0.5	4.8	6.2	1.4	0.2	11.3	0.1	0.3	16
	5-A	4.9	13.2	41.8	tr	4.0	2.6	1.7	0.2	18.6	0.1	12.8	
	5-B	0.4	25.2	47.3	tr	0.2	4.7	0.1	0.1	0.7	tr	21.4	
	5-C	6.5	38.8	17.1	tr	0.8	3.1	1.4	0.2	26.6	tr	5.5	
	5-D	tr	tr	tr	33.1	0.1	0.2	0.2	tr	65.2	0.6	0.1	
6	Average	1.5	12.1	51.7	tr	1.8	7.1	0.9	0.1	16.1	0.1	8.7	17
	6-C	2.5	15.8	31.4	0.1	2.9	8.6	0.9	0.8	15.8	0.5	20.6	
	6-D	1.6	10.3	25.6	0.1	2.8	16.0	1.0	0.7	18.4	tr	23.4	
8	Average	0.2	2.3	26.8	0.4	0.9	1.1	0.1	tr	13.2	0.3	54.3	
12	Average	tr	0.2	1.3	0.1	0.1	0.1	0.2	tr	tr	tr	98.0	

Average = averages of three or five measurements of different areas in cross-section at low magnification
tr = trace

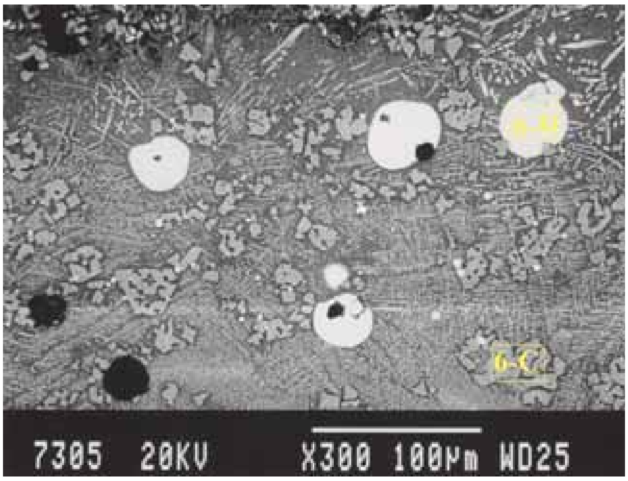

Figure 17 SEM image of the matrix of slag No. 6.

were used: coolant flow rate 14 L/min; atomisation air pressure 25 psi; high-frequency power 1.1 kW; rotation speed of peristaltic pump 1.2 ml/min and an integration time of 30s repeated three times. The analytical results obtained for zinc (Zn), lead (Pb), silver (Ag), cadmium (Cd), arsenic (As) and antimony (Sb) are shown in Table 2.

From the results given in Tables 1 and 2 it can be concluded that the process taking place at the site was distillation for zinc smelting. Of the metals used in the past, zinc was the most difficult to smelt because it volatilises at about the same temperature (around 1000 °C) that is needed to smelt the zinc ore. As a result it would form as a vapour in an ordinary furnace and immediately become re-oxidised and hence lost. Sample no. 12 (Fig. 10), which was collected from a slag pit, is an example of this phenomenon: the main component was smithsonite ($ZnCO_3$) with a little zinc oxide (ZnO).

Radiocarbon dating

Seven charcoal samples were taken from the various levels of the site and from the bottom of some of the retorts and furnaces for AMS-^{14}C dating. After acid-alkali-acid (AAA) treatment, charcoal samples were combusted by a Vario Elemental Analyser (Yuan Sixun *et al*. 2000). Pure carbon dioxide (CO_2) was collected and reduced to graphite on iron (Fe) powder by hydrogen gas in a vacuum system. Measurements of radiocarbon dates were performed by tandem accelerator mass spectrometry (AMS) at Peking University. All radiocarbon dates were converted to calibrated dates by OxCal v3.10 with the intcal104 calibration curve (Bronk Ramsey 2005). The results are shown in Table 3. Several retort and furnace wall samples were collected for dating by thermoluminescence (TL) and optically stimulated luminescence (OSL), the results of which will be discussed elsewhere, but it can be concluded that the Miaobeihou zinc-smelting site could date back about 400 to 500 years, somewhat earlier than the record in the *Tian Gong Kai Wu* published in 1637.

Discussion

Based on the archaeological excavations and the chemical analysis of the components of excavated retort, ore and slag samples, we conclude that the smithsonite was smelted with the local coal. The results are discussed below.

Raw materials used for zinc smelting

Many pieces of smithsonite ore were found during our excavations. There is evidence from geological investigation and

Table 2 Composition analysed by ICP–AES.

Sample no.	Sample	Zn (%)	Pb (%)	Ag (ppm)	Cd (ppm)	As (ppm)	Sb (ppm)
1	Slag adhered to retort wall	6.24	0.40	22		1838	30
2	Slag adhered to retort wall	8.16	0.42	10		2608	183
7	Slag	0.58	0.39	1	4	883	131
12	A piece of by-product	57.3	0.38	10	412	257	145
13	Slag adhered to retort wall	4.03	0.38	14		1604	78
14	Zinc oxide adhered to pocket	34.6	0.40	46	433	138	139
15	Zinc ore	16.1	0.39	9	527		9
16	Zinc ingot	99.2	0.72	21	125		

Table 3 Radiocarbon dates of the Miaobeihou site.

Lab code	14C age (BP, 1σ)	Calendar age AD (68.2% probability)
BA04196	400 ± 40	1440–1520 (57.6%) or 1600–1620 (10.6%)
BA04199	385 ± 40	1445–1520 (51.8%) or 1590–1620 (16.4%)
BA04200	345 ± 40	1480–1525 (24.4%) or 1555–1635 (43.8%)
BA04201	325 ± 40	1510–1605 (53.7%) or 1615–1640 (14.5%)
BA04203	385 ± 40	1445–1520 (51.8%) or 1590–1620 (16.4%)
BA04204	330 ± 40	1490–1530 (19.6%) or 1535–1605 (37.1%) or 1615–1635 (11.5%)
BA04206	330 ± 40	1490–1530 (19.6%) or 1535–1605 (37.1%) or 1615–1635 (11.5%)

field explorations that there are many large-scale smithsonite mines in Fengdu county and neighbouring areas. One mine is only about 50 km from the Miaobeihou site and the Longhe (Dragon river) could have been used for transporting the zinc ores. Coal was also found on the site and is still mined nearby today. The location of the site is thus very convenient for zinc production.

Structures of the furnace and retort

Furnace and retort structures are important to the study of zinc-smelting technology. The retorts are very similar to those depicted in the *Tian Gong Kai Wu* (Song Yingxing 1637): the majority are of earthenware with sand temper, but some are of earthenware with silt as filler. The average height of a retort is about 27 cm, the internal diameter of its mouth is 8 cm and the external diameter is 11 cm. The maximum diameter of the ventral part is 15 cm and the base is about 9 cm (Figs 5 and 6). The manufacture of the retorts involved a series of processes such as kneading the clay, modelling, forming and firing over a slow fire. The zinc ore was reduced in the retort with the coal acting as the reducing agent. The zinc vapours ascended to the low temperature region through the gas passage and condensed as molten zinc on the iron lid before dripping down into the pocket. The gas hole was essential to the control of air pressure and the discharge of waste gases during the process (Fig. 18).

It is instructive to compare the excavated No. 1 furnace foundation with the illustration in the *Tian Gong Kai Wu*. The excavation indicated that to build the furnace, a pit was dug about 55 cm deep with a 3–5 cm thick layer of coal powder and earth at the bottom to provide damp-proofing. The hearth was built on this. The interior of furnace 1 is about 305 cm long and 235 cm wide. The mouth and air vents were also found. This rectangular form of furnace found in the Miaobeihou site is similar to those depicted in the *Tian Gong Kai Wu* (the apparent triangular shape depicted is in reality no more than an attempt at perspective). A furnace with rectangular foundations was also excavated at the Jiudaoguai site not far away from the Miaobeihou site as shown in Figure 19. The Jiudaoguai furnace is about 550 cm in length and 100 cm in width. The structure of this furnace is the same as the *yan* (horse trough) furnaces described by Xu Li (1986) that operated in the mid-20th century in Guizhou province.

Smelting process

It is believed that the coal, generally broken and mixed with the smithsonite ore, was the main fuel and reducing agent for the smelting process at the site, and that the charcoal, which was found in small quantities confined to the bottom of the retorts, had been used only to ignite the charge.

Inferences concerning the smelting procedure can be made from the artefacts found on the site and also from recent and present-day smelting practice (Craddock and Zhou Weirong 2003; Xu Li 1986, 1998). After the smithsonite ore and coal were crushed and sifted, they were well mixed in the correct proportions. The ratio between ore and coal was correlated with the quality of the ore: the higher the ore quality, the larger the amount of coal. The mixture was packed into the retorts and a layer of fine-grained furnace ash with a little slurry was put on top of it. This was then carefully pressed down with a stone or iron hammer until the charge was packed tightly and a depression was created on the top. An iron plate was inserted to one side of the ashes on the top to keep a passage open through which the zinc vapour would pass to the top of the retort where it condensed, as illustrated in Figures 6 and 18. Clay was coiled around the rim of the retort to build up a pocket about 10 cm tall. Finally an iron lid was placed on top of the pocket and sealed with more mud, leaving only a small

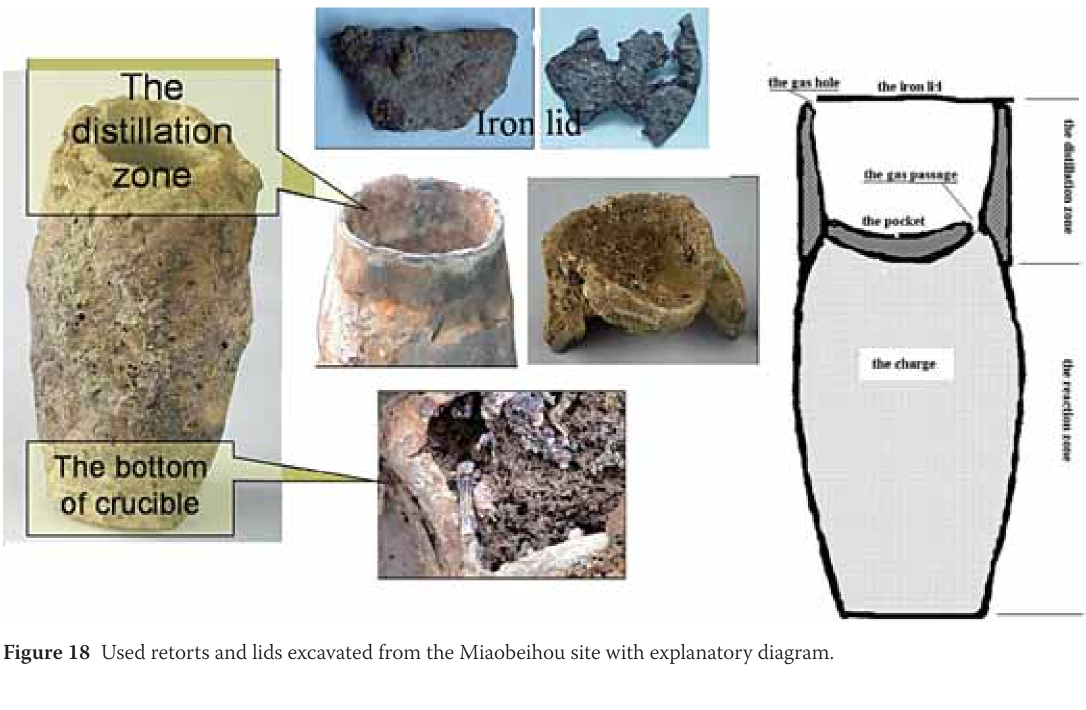

Figure 18 Used retorts and lids excavated from the Miaobeihou site with explanatory diagram.

Figure 19 A furnace with a rectangular foundation excavated at the Jiudaoguai site.

hole to act as a gas passage during the smelting process. The zinc condensed on the underside of the lid and dripped down into the collecting pocket.

The next step was to arrange the retorts in the hearths of the furnace. Based on the dimensions of the excavated hearths and retorts, there could have been about 60–80 retorts on a platform. Between the hearth and the top of the walls of retorts there would have been gaps which were filled with suitably sized slag lumps and mud. This sealing was important to keep the temperature of the pockets above the retorts at a lower level than that of the retort during the smelting process and also to physically stabilise the retort. During the distilling procedure the temperature of that part of the retort where the reaction took place would have been about 1200 °C but the temperature in the upper pocket of the retort would have been about 800 °C, which is essential for the rapid condensation of zinc vapour. It is estimated that it would have taken about 20 hours for the materials in the retorts to react completely after the lid was placed on the pocket. In practice it would generally have relied on the experience of the furnace master to decide when the reaction was complete. This was done by observing the flame during the night-time and the smoke during the daytime as it was emitted by the retorts through the small hole in the iron lid. After cooling the retorts for about 5–6 hours, the zinc ingots could be taken out of the pockets. Several fragments of zinc ingot, excavated in the 1970s at this site and now in the Institute of Cultural Relics of Fengdu county, were analysed by atomic absorption spectrometry (AAS) by the Chongqing Iron and Steel Company and found to contain about 95–98% zinc. A piece of zinc ingot was analysed by ICP–AES for this paper and found to contain 99.21% zinc – a high purity metal.

Date of the Miaobeihou site

The dating of the seven charcoal samples excavated from this site broadly agrees with the estimate by Zhou Weirong concerning the origin of zinc production in China (see Zhou Weirong, this volume, pp. **xx–xx**). It is very unlikely, however, that Miaobeihou is the earliest site of zinc production in China because of its relatively developed technique and the large scale of the industry in this area. It must surely have taken a long time for the smelting technique to develop to the large scale and high technical level seen at this site.

Conclusions

The Miaobeihou zinc-smelting site is the first Chinese early zinc-smelting installation to be excavated. By using SEM–EDS, XRD and radiocarbon dating, the artefacts from the Miaobeihou zinc-smelting site were investigated. The findings show that the techniques used at the site were similar to those recorded in the *Tian Gong Kai Wu* and thus can represent the zinc-smelting technology at least of the Ming period. This site is only one of a group of similar sites in the locality and as zinc-smelting techniques are unlikely to have become so highly developed during a short period, it is probable that the origins of zinc smelting in this area are much earlier. More field investigations, archaeological excavation and laboratory analysis will be needed to take this further.

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