Coal-fuelled crucible lead-silver smelting in 12th-13th century China: a technological innovation in the age of deforestation

Siran Liu[a]; Thilo Rehren[b,c]; Dashu Qin[d]; Jianli Chen[d]; Wenli Zhou[e]; Marcos Martinón-Torres[f]; Xin Huang[g]; Wei Qian[a]

a. The Institute of Cultural Heritage and History of Science & Technology, University of Science and Technology Beijing, Beijing, Beijing, China
b. STARC, The Cyprus Institute, Nicosia, Cyprus
c. UCL Institute of Archaeology, London, UK
d. School of Archaeology and Museology, Peking University, Beijing, China
e. Institute for the History of Natural Sciences, Chinese Academy of Sciences, Beijing, China
f. Department of Archaeology, University of Cambridge, Cambridge, the United Kingdom
g. Cultural Relics Institute Hebei Province, Shijiazhuang, China

Abstract:

Silver was an important metal in the economy of imperial China. However, until now, research on silver production technology in its social-economic and environmental contexts has been limited. Here we present a unique silver-lead production site in Hebei province, north China, dated between the 12th and 13th century AD, yielding vast numbers of slag-filled tubular crucibles and coal-ash slag chunks. Microstructural and chemical analysis reveals the crucibles were manufactured from refractory clays and that the slag inside contains lead-silver particles, un-reacted ore and numerous fragments of metallic iron. These finds indicate that the crucibles were used for smelting argentiferous sulphidic lead ores, which were reduced to metal by desulphurization using metallic iron. Mineral coal was employed to fuel this process from outside the crucibles. The use of mineral coal and externally-fired crucibles for smelting was an important technological innovation, but not one that could be adopted by all industries. We argue that it was most likely associated with rampant deforestation and the fuel crisis historically documented for the early second millennium in northern China. Contrary to received wisdom, this study demonstrates that the early adoption of coal was not as widespread as typically assumed, as it required a range of technological innovations. Crucible smelting, as one of the solutions, was embraced by lead-silver smelters, while most iron smelters in this period still persisted with the charcoal-fired furnace smelting tradition.

Key words: Imperial China, Coal, Crucible, Silver smelting, Deforestation, Innovation

Highlights:

- Systematic analyses of crucible lead-silver smelting remains from Yanchuan
- Reconstruction of coal-fired iron reduction process (IRP) in crucibles based on analytical data and experimental smelting
- An ingenious crucible smelting process and early use of coal at a time of fuel crisis
- Rethinking the development of coal-fuelled metallurgy in China

1 Introduction

Silver played a significant role in the economy of imperial China, and since the Tang (7th-10th century AD) and Song periods (10th-13th centuries AD) was widely used for official rewards, gift-giving, bulk transactions, and paying taxes and tributes (Katō 2006 [1926])· Historical texts record a large number of silver production sites in China and their tremendous outputs (Golas 1999). With much previous research focussing on the consumption of this important metal (e.g. von Glahn 1996), very little work has addressed the production end of the line, including questions such as how so much silver was produced, or how this massive scale of production interplayed with the social-economic and environmental contexts.

In the pre-modern period, silver was usually extracted from its ores using charcoal-fired furnaces with lead metal as a collector, producing argentiferous lead bullion. Silver was then retrieved from this through an oxidative process known as cupellation. By the 7th century AD, Chinese craftsmen had started to use the iron reduction process (IRP) to smelt argentiferous galena in furnaces (Liu et al. 2015). In Europe, this technology was only known for the small-scale assay of lead ores during the medieval period, and was not used for lead-silver smelting until the 18th century AD (Dube 2006). In this process, metallic iron or iron oxide-rich material was charged as reductant and desulphurizing agent to release lead from its sulphide (galena) in the smelting furnace, avoiding the need to first oxidize galena by roasting to lead oxide before then reducing this with carbon monoxide. This ingenious smelting method could be used under mildly reducing conditions and separated lead effectively (Liu et al. 2015).

$$\mathrm{PbS\ (Ag) + Fe = FeS + Pb\ (Ag)}$$

A recent archaeological expedition in Quyang county of Hebei province in north China has provided the first archaeological evidence that IRP was also practiced with externally-fired refractory crucibles fuelled by mineral coal. The objective of this paper is to characterize the metallurgical technology of the site in its broader context. We note that the technology is contemporary to a well-documented deforestation crisis and scarcity of charcoal in the region, and discuss the possible environmental pressure on the evolution of technology.

2 Archaeological Background and Materials

Quyang county, located in the eastern range of Taihang Mountain (Figure 1), is known for its Ding Kilns (定窑) producing high quality white porcelain wares. The area is rich in deposits of kaolinite-rich refractory clay. White porcelain wares started to be produced in this area in the Late Tang period (9th century AD) and became famous in the Song and Jin period (10th-13th centuries AD) (Kerr and Wood 2004, 192). Apart from kaolinitic clay, the area is also known for its coal deposits. Liu and Shang (1957) and Wang (1927) identified three major Permo-Carboniferous deposits, Lingshan (灵山), Taoli (套里) and Micheng (迷城). Lingshan is the largest one with an estimated coal seam thickness of more than 6 m, and contains mainly bituminous coal. Coal production of the Quyang county during the Northern Song period (10th-12th century AD) has been recorded in the local gazetteer (Wu et al. 1986, 76). There is also archaeological evidence showing that since approximately this period, the local porcelain kilns were fired with mineral coal (Lin 1965; Qin 1999). Interestingly, neither historical documents nor modern geological reports record major lead and silver ore deposits within Quyang county.

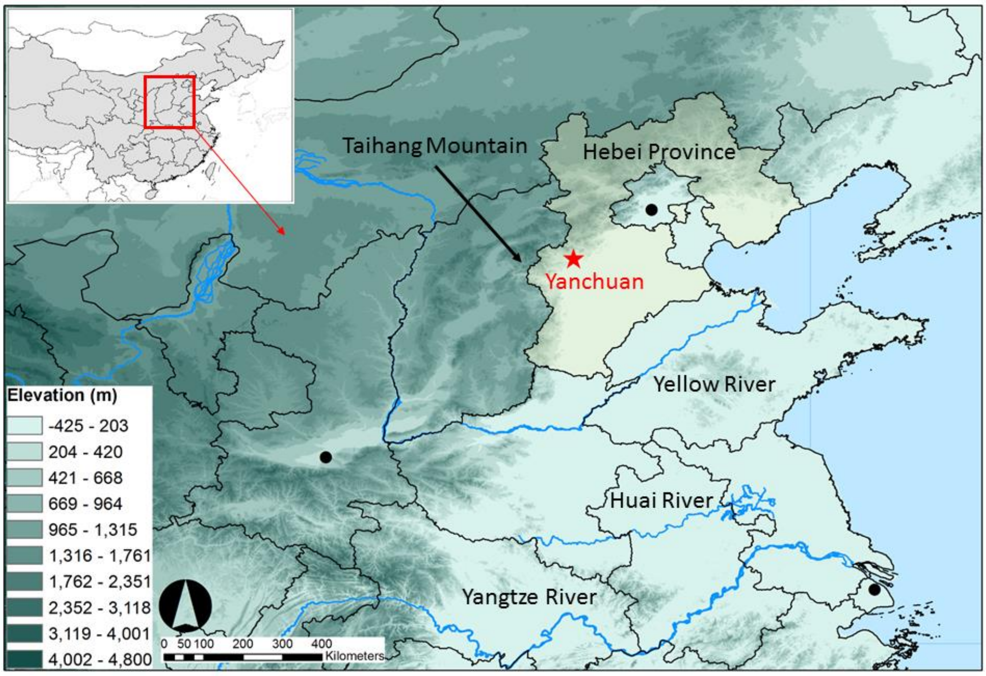

Figure 1 Location of the site of Yanchuan in Hebei province, north China. The site is on the east slope of the Taihang mountain where abundant kaolinitic clay and mineral coal deposits are located.

In 2009, a joint archaeological project excavated four sectors (Jianci, Jianxi, Beizhen and Yanchuan) of the Ding Kilns production region (Qin et al. 2014). Apart from abundant evidence of porcelain making, the excavation team identified in Yanchuan village slag-filled metal production crucibles (Figure 2). A test pit of 10 m×10 m yielded more than 100 kg of crucible fragments, and the associated porcelain sherds date the metal production activity at this site to the 12th-13th century AD, a time when Quyang county along with most other areas of north China was under the control of the Jin state.

Figure 2 Satellite map showing the landscape of the Yanchuan site and the excavation area that yielded tubular crucibles and other production remains.

The excavated remains include slag-filled crucible bodies, bowl-shaped crucible bases and fuel-ash slag with crucible fragments embedded (Figure 3). The tubular crucibles fragments are typically 10-20 cm in height (the original height might be c. 5cm more) and c. 8 cm in diameter. The total volume is approximately 1-1.5 L. The wall thickness is typically 1-2 cm. Their uniform vitrification, glaze on the exterior surface, tubular shape and relatively thin walls indicate that these crucibles were heated from the outside (Bayley and Rehren 2007). Occasionally, the crucible bases are found attached to each other (Figure 3), showing that the reaction vessels were densely packed in the furnace during firing. Coal-ash slag was also identified in the porcelain kilns at Jianci village (Lin 1965), and therefore it is necessary to examine whether the Yanchuan coal-ash slag is indeed associated with the metallurgical production. In many broken samples, crucible sherds were found trapped in the semi-molten coal-ash slag (Figure 3). Interestingly, in coal-fired 19th-century crucible smelting furnaces, crucible sherds were frequently used to line the furnace base (Read 1934; Zhou et al. 2014). Presumably, they acted as simplified furnace bars, facilitating the separation of the coal-ash slag from the firing chamber, supporting the fuel column, and creating ventilation channels. Thus, through the similarities between the 19th century material and the excavated coal-ash slag and sherds, we associate the coal-ash slag found at Yanchuan with the crucible metal production process rather than porcelain production.

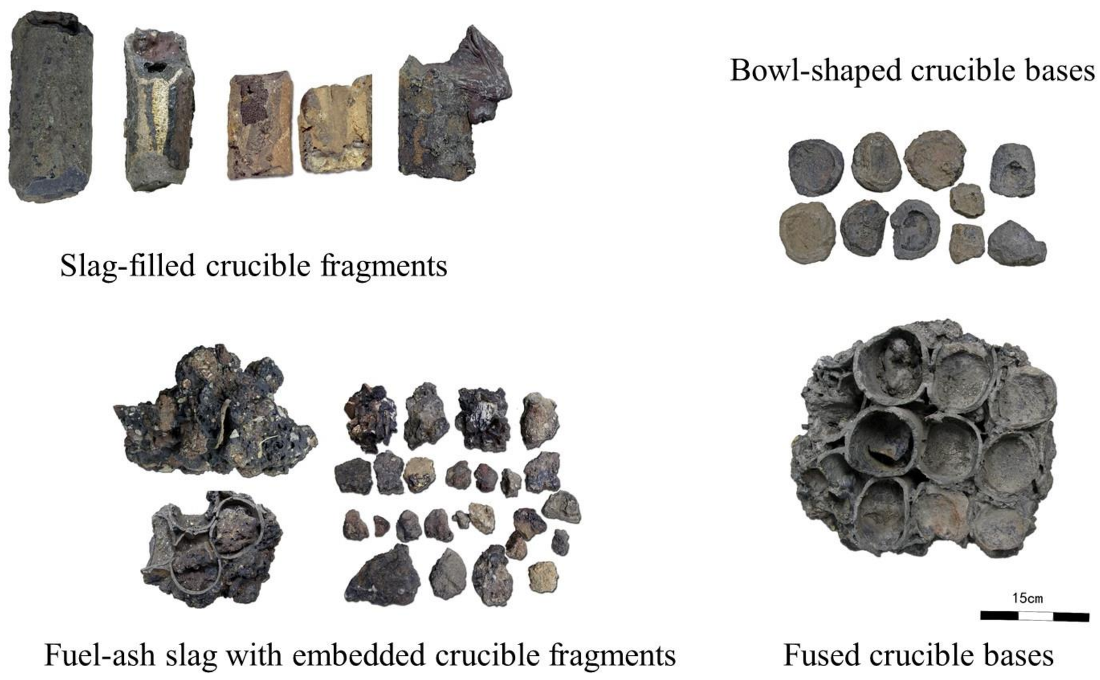

Figure 3 Metallurgical crucibles, crucible bases and fuel ash slag found at the site of Yanchuan.

3 Materials and methods

Twenty crucible slag samples, including nine attached to their ceramic bodies, five crucible base samples and five coal-ash slag samples were analyzed. Detailed information and pictures of these samples are provided in Supplementary Information (SI). Cross-sections were mounted in epoxy resin and polished down to a 0.25 μm finish with diamond paste. Following optical microscopy, a JEOL JXA 8600 electron microscope equipped with Oxford Instruments X-sight Energy Dispersive Spectrometer (EDS) was used to conduct chemical analysis, using an acceleration voltage of 20 kV, a beam current of 50 nA and a working distance of 11 mm. The bulk chemical composition of slag and ceramic samples was determined by averaging 3-5 area analyses of 1 mm by 0.8 mm each. The beam stability of the machine is monitored by repeated analyses of a cobalt standard. The EDS data quality was tested by analysing USGS BHVO-2 basalt, NIST 1412 glass and Corning B glass. The precision and accuracy tests of SEM-EDS used for analysis is provided in SI Table 1. The result shows that for elements present at concentrations above 0.5 wt%, the accuracy of the machine is good and the analytical error margin is less than 10%. When the concentrations are between 0.1 wt% and 0.5 wt%, the data are less reliable. All data presented in the following part of this article are normalised to eliminate the error caused by the temporary fluctuation of the beam current. The ceramic fabrics of the Yanchuan crucibles contain a significant amount of inclusions. They were analysed together with the clay matrix for bulk chemical composition since both of them are likely to be the natural components of local clay. The bulk chemical composition of slag was analysed avoiding un-reacted quartz fragments since they did not contribute to the melting behaviour of the slag. The 3-5 area analyses show relatively small variability within each sample. The difference between the maximum and minimum values is usually under 2 wt% for major components (>10 wt%) and under 1 wt% for minor components (<10 wt%), hence only mean values are reported.

4 Results

Most crucibles were completely filled with glassy slag. The cross-sections show that there was little interaction between slag and ceramic, demonstrating the refractory nature of the ceramic material. The crucible bases generally have similar material characteristics to the bodies but are usually much thicker. Their interior part typically has a layer of glassy and porous vitrification. The slag column inside crucibles usually contain a significant proportion of angular quartz particles with varied size. The large ones are over 1 cm in diameter while the small ones are less than 1 mm. In a few cases, it is observed that the bottom part of the slag column has fewer particles than the upper part, presumably due to the relatively low specific gravity of quartz. Metallic particles are frequently identified inside the slag, e.g. an oval shaped metal bead with a long axis of 1.3 cm shown in Figure 4. The chemical and microscopic analyses presented later found it was a metallic iron bead with much sulphur and phosphorus impurities. The coal-ash slag is highly heterogeneous with abundant quartz and rock fragment inclusions. Mineral coal and coal gangue inclusions were also frequently observed. The detailed analytical results for crucible body, slag, and fuel-ash slag are presented in the following sections.

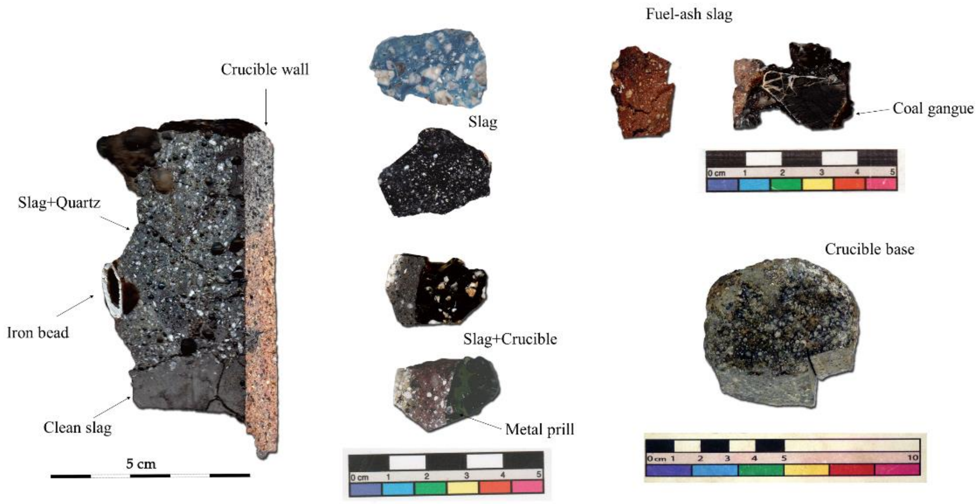

Figure 4 Cross-sections of crucible, base, slag and fuel-ash slag samples.

4.1 Crucible body

Kaolinitic clay with high alumina (26-31 wt%) and medium iron oxide (1.9-5.3 wt%) contents was employed to manufacture these crucibles (see SI for full dataset). The matrices show a high degree of vitrification and numerous argillaceous inclusions of irregular shape ranging in size between 0.1 mm and 1.0 mm (Figure 5). Mineral coal and coal gangue fragments between 0.1 mm and 1.0 mm in size were also identified in almost all samples, reaching up to approximately 5 vol%. They show a distinctive yellow colour under the optical microscope (Figure 5). This find may indicate that original clay sources are associated with coal strata. Compared to the white porcelain sherds from the Ding Kilns and dated to the Jin period (Cui et al. 2012), the Yanchuan crucibles are significantly richer in TiO_2 and FeO, while two analyzed saggar samples from the site show chemical compositions closer to those of the crucibles (You et al. 1987) (Figure 6). The firing temperature of the Ding Kilns was determined as around 1300 ºC (Li 1998, 167), and a similar 偶 or slightly lower operational temperature might be assumed for the crucibles.

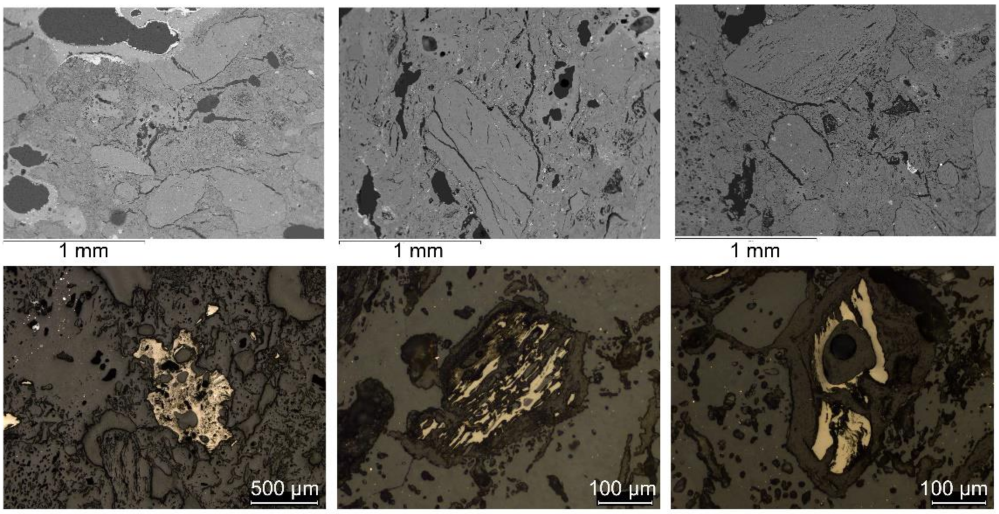

Figure 5 Argillaceous inclusions (top) and coal fragments (bottom) identified inside the crucible ceramic matrices.

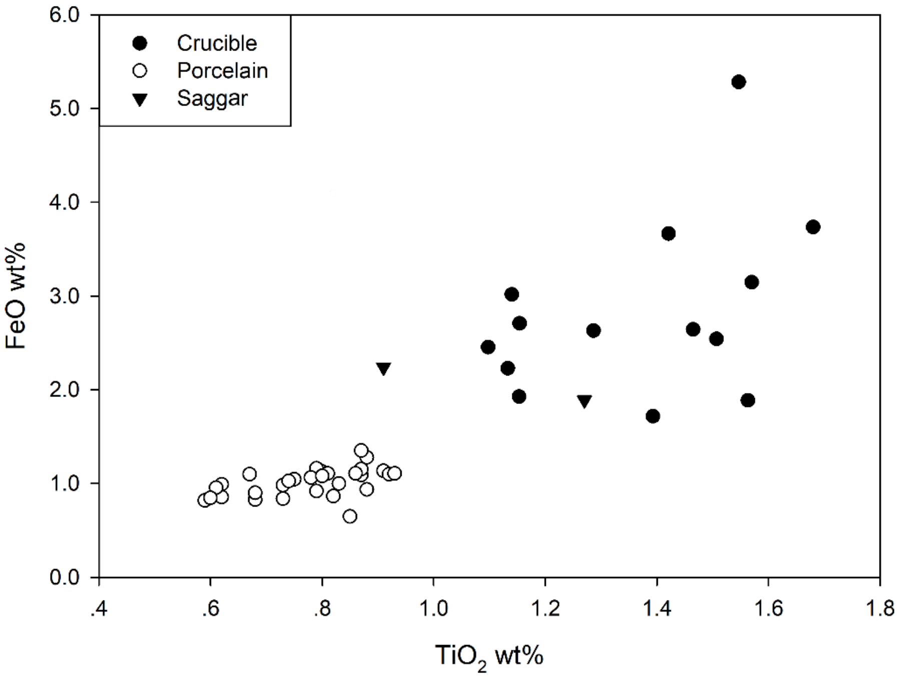

Figure 6 Comparison of the bulk chemical composition of the Yanchuan crucibles, Jin Dynasty Ding Kilns white porcelain sherds (Cui et al. 2012) and the Ding Kilns saggars (You et al. 1987). The porcelain is clearly separated from crucible and saggar in the FeO-TiO2 diagram.

4.2 Slag

The crucible slag is predominantly silica-rich glass with lead-rich metallic globules and metal sulphide (matte) inclusions (Figure 7). The average PbO and SO_3 contents of slag are 2.2 wt% and 0.7 wt% (globules included). The glassy slag mainly consists of SiO_2 (46-62 wt%), Al_2O_3 (6-16 wt%), CaO (5-26 wt%), and FeO (1-30 wt%). The concentrations of ZnO, MgO and MnO are relatively low (< 4 wt%). The significant variation of these components suggests the composition of the crucible charges was not standardized. Numerous un-reacted quartz grains from the ore, and occasionally large Fe and Pb-Ag metallic fragments were identified in the slag. Re-melting experiments demonstrated that crushed slag could become fully fused at 1200 °C (SI), suggesting the working temperature might be around or higher than this figure. The major contributors for the formation of this glassy slag are likely to have been gangue, ore and iron-rich material charged inside the crucible. Considering that lead/silver ore deposits are not identified in this region, and that ore fragments were not recovered from the site, it is difficult to determine the exact contribution of each source. Given the local limestone-rich geological setting (Liu and Shang 1957), the high CaO content of slag might be attributed to gangue and flux. The high FeO content is likely to derive from the added iron-rich material and gangue.

Table 1 Bulk chemical composition of the crucible slag from the site of Yanchuan.

Code	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	FeO	ZnO	BaO	PbO
QYS-1	0.4	1.6	6.0	47.6	0.8	1.8	1.7	5.7	0.4	1.0	29.5	0.9	bdl	2.5
QYS-2	bdl	2.0	6.7	51.7	0.4	1.2	1.7	7.5	0.4	bdl	23.3	1.3	bdl	3.8
QYS-3	0.1	1.7	6.1	47.5	0.7	1.6	1.8	5.7	0.3	1.2	30.0	0.9	bdl	2.3
QYS-4	0.2	1.3	15.7	51.3	0.3	0.4	1.9	6.0	0.3	bdl	16.1	0.2	3.5	2.7
QYS-5	0.4	1.3	7.1	51.7	0.3	1.0	1.9	6.6	0.4	bdl	26.1	0.9	bdl	2.3
QYS-6	0.6	1.4	14.0	51.6	bdl	0.5	1.9	6.6	0.2	bdl	17.3	bdl	3.5	2.4
QYS-7	bdl	3.1	8.5	53.0	1.0	1.1	3.2	12.2	0.4	0.7	12.9	3.5	bdl	0.3
QYS-8	bdl	2.5	15.1	48.4	0.7	0.8	4.1	4.0	0.6	2.0	19.6	1.4	bdl	0.7
QYS-9	0.4	3.6	9.4	56.0	0.5	bdl	2.4	13.1	bdl	bdl	5.8	0.7	4.8	3.3
QYS-10	0.2	0.9	8.6	58.7	bdl	1.0	2.5	26.0	0.3	bdl	1.9	bdl	bdl	bdl
QYS-11	bdl	2.2	7.5	62.0	bdl	0.2	1.3	16.6	0.6	bdl	5.7	2.9	bdl	1.0
QYS-12	bdl	1.4	9.2	48.5	bdl	bdl	1.8	13.9	0.2	bdl	19.5	0.3	bdl	5.2

QYS-14	1.0	3.3	13.1	48.2	1.6	bdl	4.8	23.1	0.7	bdl	3.6	bdl	bdl	0.5
QYS-15	bdl	3.6	13.3	57.9	bdl	0.4	2.9	17.5	0.6	bdl	3.8	bdl	bdl	bdl
QYS-16	bdl	3.6	12.3	48.6	bdl	1.3	1.5	26.0	0.6	bdl	1.0	bdl	5.1	bdl
QYS-17	bdl	3.5	7.3	62.1	bdl	bdl	1.9	16.8	0.6	bdl	4.2	1.8	bdl	1.7
QYS-18	bdl	1.7	6.4	46.4	bdl	bdl	1.6	15.4	0.5	bdl	23.4	1.1	bdl	3.5
QYS-19	bdl	1.0	9.4	47.6	0.1	0.8	1.8	4.9	0.7	0.1	25.6	0.3	bdl	7.6
QYS-20	0.1	1.7	6.1	51.4	0.7	1.2	1.8	6.5	0.5	0.1	26.6	1.3	bdl	2.0

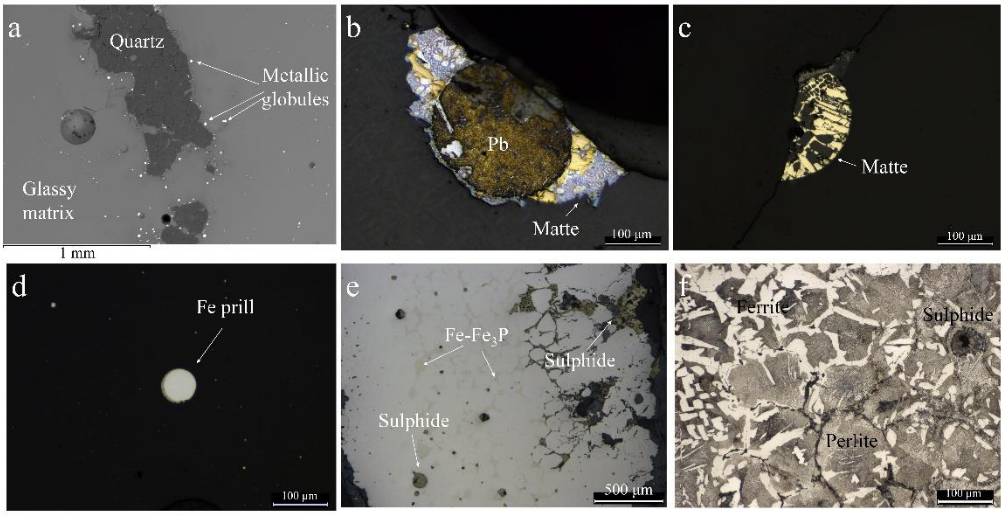

Figure 7 Micrographs of crucible slags. a: Glassy slag matrix, unreacted quartz inclusion and suspended metallic globules. b: Lead particle embedded in Pb-Fe-Cu matte matrix. c: Iron rich matte particle. d: Metallic iron prill suspended in slag matrix. e,f: Metallographic structure of large iron bead shown in Figure 4. A large number of sulphide inclusions were found in this sample (e). The sample is etched with 2 % nital. The iron-rich grain is mainly pearlite and the exterior part of this sample is dominated by Widmanstätten ferrite (f).

Metallographic analysis of the large iron bead shown in Figure 7 reveals a microstructure of low-carbon steel with significant P (4.0 wt%), S (0.4 wt%) and Cu (1.0 wt%) contents. The dominance of pearlite in its inner part indicates that the fragment originally had a relatively high carbon content but was decarburised in the smelting process, creating a low-carbon exterior part. Numerous sulphide inclusions were identified in this iron fragment, while at one side of it, a large band of sulphide was found penetrating into the metal, indicating the fragment was in contact and probably reacting with a sulphide melt in the smelting process.

Most metallic globules are lead with various amounts of silver. Out of 33 globules we analyzed, most contain more than 1 wt% silver (SI) (Figure 8). Additionally, small globules trapped within un-reacted quartz inclusions are also silver-rich, indicating the ore used at this site was silver-bearing (Figure 8). These finds demonstrate that silver-rich lead bullion was the major product of the site. This intermediate product would most likely be subjected to cupellation to retrieve the silver, but there is no relevant evidence at the site and this process may have taken place elsewhere.

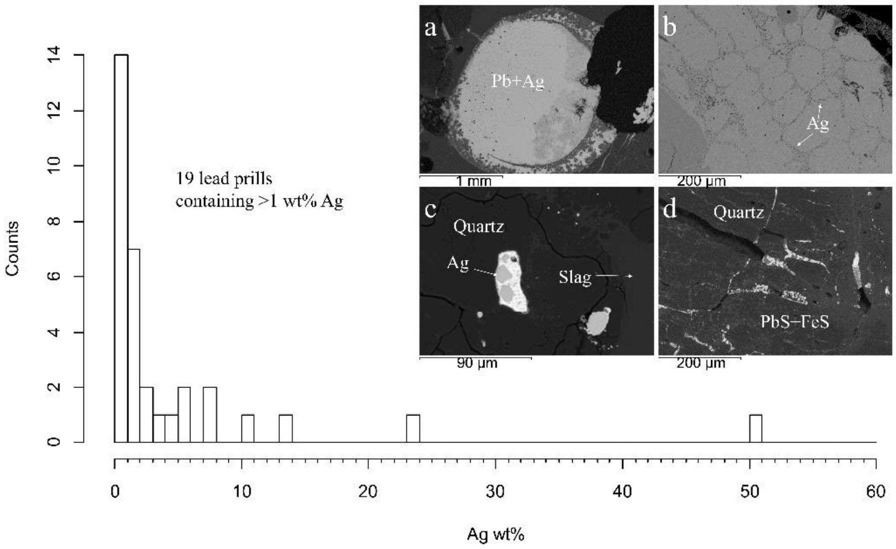

Figure 8 Silver content of lead prills. More than half of the prills have Ag content higher than 1 wt%. a-b: BSE image of a metallic lead globule in crucible slag matrix. Intergranular dark particles are metallic silver and the bulk silver content of this globule is about 2 wt%. c-d: Silver-rich particles trapped in the quartz matrix of unreacted inclusions.

4.3 Coal-ash

The coal-ash slag associated with the crucibles contains a large quantity of semi-reacted coal fragments and coal gangue, while its matrix is mainly composed of alumina-rich silicate minerals and glass (Figure 9). The five analyzed samples are all rich in SiO_2 (52.7 wt%) and Al_2O_3 (21.1 wt%) with varied amounts of FeO, CaO and SO_3 (SI), demonstrating the major ash component in coal was clay minerals and iron sulphides.

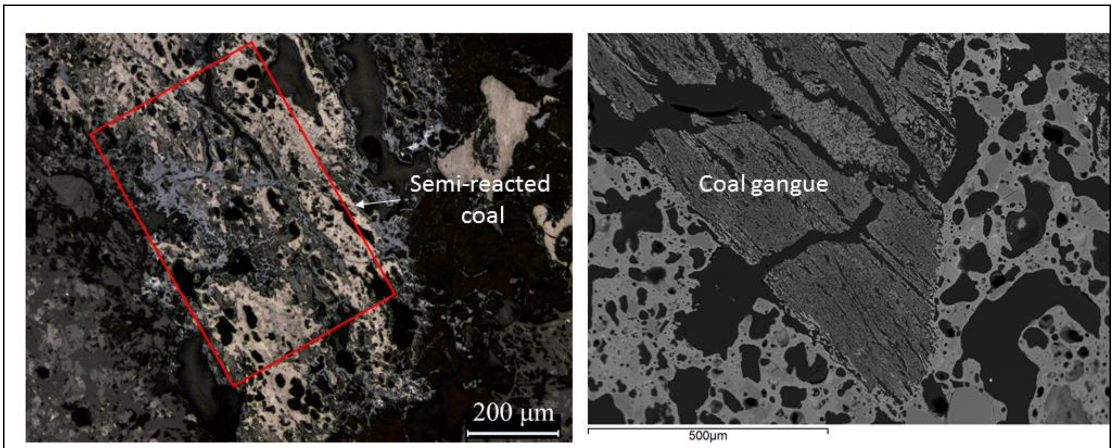

Figure 9 Mineral coal and coal gangue fragments found in the coal-ash slag samples.

5 Experimental smelting

The analysis of the archaeological finds indicated that a lead-silver ore with quartz gangue was smelted inside crucibles. No fully-molten slag formed and, in most cases, considerable amounts of gangue were left in the crucible charge. The identification of a large metallic iron bead and iron prills in the slag suggests that the iron reduction process (IRP) might have been employed to reduce the ore. To test the viability of this hypothesis, an experiment was conducted in a clay-bound graphite-tempered crucible, melting a mixture of sulphide ores with metallic iron, slag and free silica, but no carbonaceous component (Table 2).

Table 2 The crucible charge of experimental smelting, mixed before charging.

Material	galena	pyrite	metallic iron	iron slag	flint
Weight (g)	70.0	30.1	17.0	120.0	60.1

We used commercially available galena and pyrite to simulate the ore, both containing a minor amount of quartz as gangue. Iron bloomery slag was used to simulate self-fluxed gangue, containing only fayalite and a small amount of metallic iron (see Liu *et al*. 2015, 161). The crushed flint was added to simulate the unreacted quartz inclusions found in the Yanchuan slag. Small pieces of metallic iron (<1cm) were added to react with the galena, forming lead metal and iron sulphide. Based on the re-melting test of Yanchuan slag, the smelting temperature was set at 1200 °C with a process duration of 1 hour.

During the experiment, the reaction between iron metal and the sulphides resulted in the formation of cakes of iron-rich matte and lead metal beneath an inclusion-rich slag layer. The similarities between the experimental and archaeological slag columns are striking (Figure 10). Both of them have an inclusion-rich upper part and a thinner inclusion-free lower part. A thin slag layer was found at the crucible base underneath the lead metal (Figure 10), corresponding to the thin glassy layer observed in archaeological crucible bases. Despite the short smelting time and the high viscosity of the inclusion-rich slag, the separation between slag and smelting products was good and no large metallic particles remained in the slag. Matte and lead collected at the bottom of the crucible as two separate cakes. These would have formed in the past as well, to be collected by smelters after breaking the crucible. The matte might have been further processed (e.g. roasted and re-charged into crucibles) to recover any silver and lead trapped in it, while the lead bullion cakes were subjected to cupellation. The slag-filled crucible body fragments and empty crucible bases were discarded; the archaeological finds are consistent with this argument.

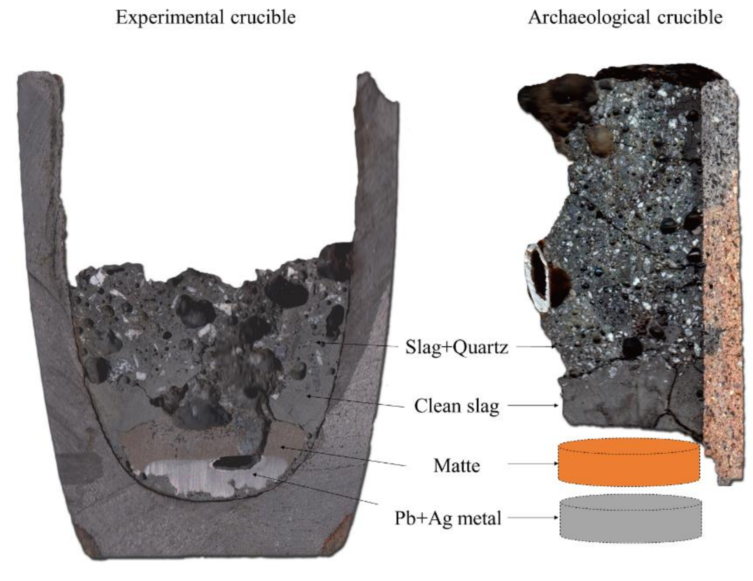

Figure 10 The result of experimental smelting (left) and the cross-section of archaeological crucible (right). Both slag columns have an inclusion-rich upper part and an inclusion-free lower part. Matte and lead cakes similar to the ones seen in the experimental smelting likely formed in the archaeological case as well but would have been removed for further processing. A thin layer of slag forms along the crucible wall at the crucible base also in the experimental smelting.

6 Discussion

6.1 IRP in crucible

Silver-bearing lead bullion was produced at the site of Yanchuan by smelting argentiferous galena with metallic iron and no need for charcoal or carbon monoxide in the reaction vessel. Based on the analysis of a large iron bead in the slag, it is argued that the original iron charge was steel or even cast iron rather than low carbon wrought iron. During the smelting process, three liquid layers would form inside the crucible: slag (top), matte (middle), and metallic argentiferous lead (bottom) as indicated by the experimental smelting (Figure 11). Mineral coal was burnt outside the crucibles to provide energy for the metallurgical reactions inside, and formed coal-ash slag.

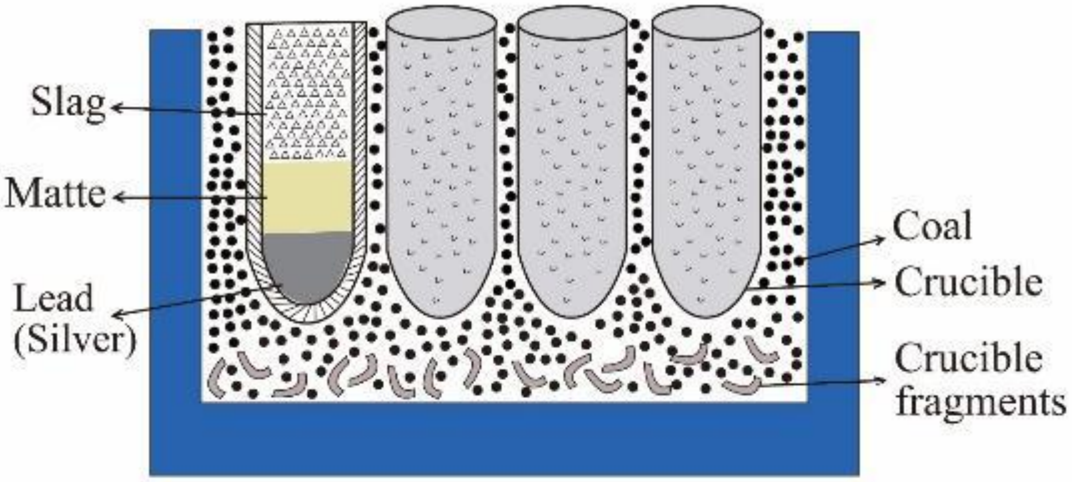

Figure 11 Graphic illustration of crucible smelting process identified at the site of Yanchuan.

Lead-silver smelting using externally-fired crucibles has been recorded by ethnographic studies in many areas in China as an alternative to the large-scale furnace production involving modern machineries (Zhou et al. 2014). A 14th-century text documented a similar technology in India (Dube 2006). Currently, the earliest known Chinese report of crucible lead smelting is from report to the throne concerning a lead production site at Xiqueling (喜鹊岭), Lingzhou (灵州) (nowadays Wuzhong city (吴忠市) in Ningxia Hui Autonomous Region (宁夏回族自治区)) dated to the 18^{th} century (Institute of Qing History 1983, 381). This record provided a detailed cost breakdown for the production (Table 3).

Table 3 Cost breakdown of 18th-century lead smelting in Lingzhou.

Type	Cost per batch (silver taels)	Note	Percentage in total cost (%)
Mining	5.06	450 jin (approx. 16.6 kg)	53.5
Transportation	0.80	140 li (approx. 70 km) from the mining site to the smelting site	8.4
Crucibles	0.38	100 crucibles	4.0
Cast iron	2.66	192.7 jin (approx. 7.1 kg)	28.1
Coal	0.37	675 jin (approx. 25 kg)	3.9
Coal for ‘cleaning’ lead	0.02	40 jin (approx. 1.5 kg)	0.2
Bellow worker	0.10	2 workers	1.1
Smelter	0.06	1 smelter	0.6
Others	0.02	firewood, straw, water	0.2
Lead product	-	225 jin (approx. 8.3 kg)	

*After text from Institute of Qing History, RUC 1983, 381-382.

*All weights in Chinese historic mass units. One jin is c. 37 g.

Several important points in this breakdown are worth noting. First, the inclusion of metallic iron in the list demonstrates that the IRP was used for smelting. For an ideal reaction about 1/4 of the weight of galena is needed in iron metal. However, the recorded ore/iron weight ratio was approximately 2.3:1, indicating a significant over-charging of iron metal. The excess iron may have been necessary to react with pyrite (FeS_2) in the ore and saturate the FeS rich matte, ensuring complete lead recovery. Second, the amount of lead produced in this process is only 1.2 times that of the iron used, and only half of the ore weight, even though pure galena contains more than 85 wt% lead. If it is assumed that all lead in the ore had been converted into lead metal, the galena weight is only c. 60 wt% of the ore weight. This indicates that relatively low grade mixed-sulphide ores with a significant amount of gangue minerals were used at this site, which is also consistent with the lack of recorded ore dressing cost. Third, mineral coal was the only fuel used to fire the furnace since charcoal is not mentioned in the bill. However, the cost of coal was only around 4% of the total cost. Fourth, mining and smelting were geographically separated (c. 70 km), and approximately 8% of the production cost was on transporting the ore to the smelting site. There is no record of transporting mineral coal in this bill, indicating that smelting was practiced close to the coal mine. Finally, even in such a late period, the metallic iron used to reduce lead was still one of the major costs for this process (28.1%).

The crucible lead smelting technology at the site of Yanchuan seems to be not significantly different from that recorded in this report. The abundant quartz gangue particles in the slag indicate a relatively low quality ore was used as well, and residual iron fragments show that an excessive amount of iron was charged in the crucible. The site of Yanchuan is located next to the coal deposits but relatively far from silver deposits. The local mineral coal and refractory clay resources were fundamental for the success of this metal production industry but the transportation of these bulky materials was much more expensive than transporting ores (See Chen 2014; Zhou et al. 2014 for the coal-fired zinc smelting). The association between crucible smelting and IRP is expected since iron can efficiently reduce lead while not taking up much of the precious space inside the vessel, allowing more ore to be charged and hence giving a higher yield. On the other hand, compared to furnace or hearth smelting, crucible technology requires more labour and capital input on manufacturing the highly refractory tubular crucibles (especially as crucibles could only be used once), relatively long distance transportation of ore, and purchasing cast iron. Making an estimation based on the 18th century bill, these three items together account for c. 40% of the total cost. Additionally, even though multiple crucibles could be used in one furnace, the limited volume of each vessel and the need for batch processing rather than continuous smelting limited the production scale so that only silver-rich ore could be smelted economically. The advantage of crucible smelting is, however, that low quality mineral coal could be used instead of wood charcoal (Rostoker and Bronson 1990, 66). Thus, we argue that this innovative technology was embraced at this site primarily because it enabled the use of coal instead of charcoal, without compromising the quality of the product.

6.2 Rethinking of early coal-fuelled metallurgy in China

China was one of the earliest areas in the world to utilize mineral coal. Textual and archaeological evidence show that mineral coal was used for heating and potentially metal production as early as the Han period (2nd century BC-2nd century AD) (Read 1939, 119-133). The Song period (10th century AD-13th century AD) has long been linked to a considerable expansion of coal consumption due to the shortage of charcoal supply in north China (Golas 1999, 195). Since the Iron Age (5th century BC), north China witnessed large scale deforestation due to the increasing population and environmental decline (Elvin 2004; Marks 2012), which finally created a fuel crisis during the early second millennium AD, forcing people to look for alternative energy sources. According to historical records, the metal production industry became one of the major consumers of coal (Hartwell 1962). From this period onward, some analyzed iron artefacts show a significant sulphur content and peculiarly old radiocarbon ages (Han and Ko 2007, 589; Huang et al. 2005; Qiu and Cai 1986), both indicative of mineral coal as fuel for iron smelting. In spite of this general agreement, there has been little discussion of precisely how coal was used in metallurgy. Coking was not widely used in China until the Ming (15th-17th century AD) or even the Qing period (17th-20th century AD) (Liu et al. 2014), and most smelters in the early second millennium AD had to deal with raw mineral coal. Bituminous coal and lignite, which are the dominant coal types in China, are not considered a suitable fuel by modern standards, due mostly to their high sulphur, tar and ash contents. Their relatively low strength under high temperature limits the height of the furnace stack they can be used in, while softened coal can block the airflow inside the furnace or even collapse it (Wagner 2003). Thus, the widespread use of coal as a fuel for iron smelters in the Song period has been questioned already (Wagner 2008, 317).

So far, contrary to common assumptions based largely on textual references, there is still no clear archaeological evidence for the widespread use of mineral coal directly in iron smelting furnaces in China from the 10th-13th century. More than 20 iron smelting sites in north China dated to this period have been subjected to investigation but most of them revealed no solid evidence of using coal instead of charcoal as the main fuel (Han and Ko 2007, 566-580; He 2012; Hua 1999, 421-423; Huang 2014; Liu 2015a; Wang and Qian 2014; Wang 2018 and references therein) (Figure 12). The excavation of the Shuiquangou (水泉沟) site (9th-12th century AD) at the northern suburb of Beijing revealed four iron smelting furnaces, massive slag deposits and a large amount of charcoal fragments but no sign of mineral coal or coal-ash slag (Liu 2018). The study of a large scale state-monitored iron smelting workshop at Zunhua, Hebei province revealed that even in the 16th-17th century, charcoal was still used as the main fuel in iron-smelting blast furnaces (Chen et al. 2017). Only recently, slag with embedded coke (not coal) fragments was found at two iron smelting sites in Handan city, Hebei province, and are potentially dated to the Yuan dynasty (13th-14th century AD)

(Wang 2018). In this light, the use of mineral coal in the metal industry recorded in historical documents might still not be a nation-wide practice and at least partially related to the "processing" of metals (e.g. melting, smithing, puddling), rather than smelting.

The finds at Yanchuan thus provide rare archaeological evidence for the use of mineral coal directly in a metal smelting process during the early second millennium AD. The ingenious crucible smelting technology was employed to cope with the aforementioned problems of using low quality mineral coal. Separated by the crucible wall, impurities in the fuel would not affect the metallurgical reactions, and the furnace used to fire the crucibles would have had a relatively low height, thus a lower burden of coal and less likely to collapse. It is interestingly observed that all crucible-based lead-silver smelting sites currently identified and broadly dated to the imperial period are located in north China while shaft furnace sites are all found in the south (Figure 12) (Liu 2015b).

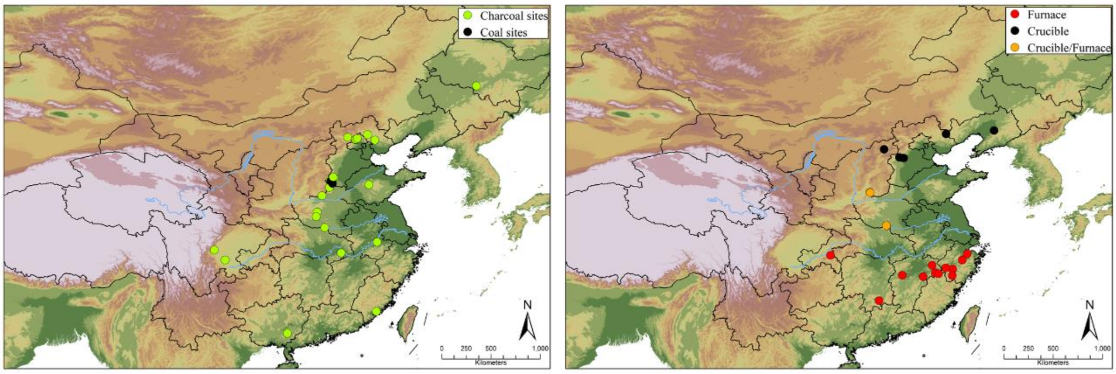

Figure 12 Left: Map of currently investigated 10th-13th century iron smelting sites. Charcoal was found to be the main fuel in most sites (green dots) while only two sites in Hebei were found using coke (black dots). Right: Map of currently known lead-silver smelting sites dated to the imperial period (Liu 2015b). Crucible lead-silver smelting sites are located in the northern, drier part of China while the furnace smelting sites characterized by tap slag remains are exclusively found in more humid southern China. Two sites which reveal both furnace slag and crucibles are found in between these two regions.

In contrast to the north, south China had a more humid weather and much lower population density in the early period (Hartwell 1982), which resulted in a better preservation of its forest resources and a faster regeneration of consumed woodlands. Even after the fleeing of large numbers of northern Chinese from their tumultuous homelands to the south during the 4th-13th century AD, south China still maintained a significantly better forest coverage than the north (Zhang 2016). Historical records also show that in south China charcoal was continuously used for metal production throughout the second millennium AD (Xu 1994).

Due to the lack of textual records and archaeological finds, the origin and early history of crucible lead-silver IRP smelting technology is not clear. Sporadic evidence shows that coal-fuelled crucibles might have been used as early as the Eastern Han period (1st-3rd century AD) (He et al. 1985; Needham 1958) and IRP had been used since the Tang Dynasty (7th-10th century AD). However, we still did not find substantial field evidence of using IRP with coal-fuelled crucibles before the Song and Jin periods (10th-13th century) (Liu 2015b; Zhou et al. 2014). Thus, the invention of this smelting method might have taken place before but its widespread adoption (hence higher archaeological visibility) likely happened only in the Song period. We need to separate the “inception” from the “adoption” (Torrence and Van der Leeuw 1989) and it has been argued that only after becoming cost-effective, safe and reliable, do new technologies become widely accepted (Killick 2001; Kingery et al. 1986). A number of factors might have influenced the adoption of coal by lead/silver smelters in the north, and the scarcity of charcoal should be considered as a critically important one. Though a detailed palaeoenvironmental reconstruction of the local area is not yet available, the historical documents have provided a general background that north China had been substantially deforested and charcoal was in short supply by the 11th century AD (Marks 2012, 144). Xu and Huang (1988) studied the change of fuel source from charcoal to coal in the capital of Northern Song Dynasty, Kaifeng (开封), in the central Henan province. Their work shows that by the early 11th century, Kaifeng suffered a serious fuel crisis due to the lack of charcoal supply and the situation only got better when coal was widely used for domestic purposes in the 11th century. More specifically, the Ding Kilns are known to use coal since the Northern Song period despite its relatively short flame, stronger oxidizing atmosphere and the bulky amount of combustion ash (Kerr and Wood 2004, 328), strongly indicating the local charcoal resources had been exhausted (Li 1983). Additionally, the influence from the porcelain kilns also deserves consideration. The Ding Kilns had been using coal prior to the Yanchuan crucible smelting activities (Lin 1965; Qin 1999). Some degree of knowledge transfer between craftsmen should be expected in terms of the fuel choice, but in the context of metal production this shift required significant adaptations to the broader technological set up.

The combination of crucible smelting and mineral coal illustrated an important technological choice of north Chinese lead-silver smelters during the fuel crisis in the early second millennium

AD. This technology survived until the modern period and remains an important part of the traditional Chinese lead-silver industry. It is interesting to notice that though this technology was widely embraced by lead-silver smelters, iron smelters did not show much interest on it. Despite a few cases from earlier contexts, coal-fuelled crucible iron smelting was not widely used in the Chinese iron smelting industry until the Qing period (Hua 1999, 429), and most archaeological evidence shows that charcoal was still the main fuel throughout the first half of the second millennium AD. This adherence to the old tradition might be partially due to concerns about sulphur contamination, since iron smelting would require coal to be charged inside crucibles as reductant. Furthermore, a range of additional social-economic and cultural factors, e.g. production scale and persistence of technological traditions, also deserve consideration. Iron was the most commonly used metal in this period, and crucible smelting might not have been an efficient choice for the massive scale iron production. Additionally, the centuries-long tradition of using large blast furnaces at smelting sites set up close to charcoal sources may have acted as a further hindrance preventing smelters from a holistic change to coal-fired crucible smelting. In turn, the requisition of precious charcoal resources by iron smelters may have driven other charcoal users, such as lead-silver smelters, to explore the possibilities of using mineral coal instead, thus leading to the adoption the crucible smelting method.

This research therefore demonstrates that the switch from charcoal to coal in the metallurgical industry was a complex process, potentially involving a series of technological innovations, and not easily transferrable to all metals. Mineral coal could not directly replace charcoal in furnace smelting systems due to a number of technical reasons. Charcoal-fired furnaces continued to be used for a quite long period by iron and lead/silver smelters (especially in south China), even after recurrent mentions of mineral coal in historical records.

7 Conclusion

In summary, the study of the lead-silver smelting industry at the site of Yanchuan revealed the use of a peculiar lead-silver smelting technology, employing externally-fired tubular crucibles to hold the charge, the iron-reduction process to produce lead metal from galena, and mineral coal as the main fuel. While we await additional results from palaeoenvironmental and archaeometallurgical studies, we propose that the adoption of this technological innovation was likely encouraged by the fuel crisis in north China during the early second millennium AD. The technical challenge of using mineral coal could be successfully tackled by the crucible technology. Conversely, iron smelters of this period still persevered with the charcoal-fired furnace smelting tradition. This study has demonstrated the complex process of the adoption of mineral coal for metallurgical uses in China, while more generally illustrating the combination of environmental and socio-cultural parameters that both trigger and constrain innovation processes.

Acknowledgement:

This research was part of SRL's PhD work at UCL, supervised by ThR and MMT. It was further developed while SRL was working at the Institute of Cultural Heritage and History of Science & Technology, USTB with great contributions of colleagues from Peking University. The Hebei Provincial Institute of Cultural Relics and the Institute of the Ding Kilns site management provided great help in the field investigation and sample collection. We gratefully acknowledge the help of Mr. Kevin Reeves, Dr. Harriet White and Dr. Patrick Quinn with sample preparation and analyses. Dr. Pira Venunan and Dr. David Larreina-Garcia are specially thanked for their significant help with the experimental work. Dr. Haifeng Liu and Dr. Hongjiao Ma offered invaluable advice. We also appreciate Ms. Wei Liu's help with preparation of illustrations. Detailed comments from five reviewers have helped us strengthen the text; any remaining shortcomings are ours. SRL's doctoral studies were supported by grants from the Sino-British Fellowship Trust, the Institute for Archaeo-Metallugical Studies, and Rio Tinto Ltd. This ongoing research is further supported by a grant from the National Natural Science Foundation of China (No. 51704023).

References:

Bayley, J. and Rehren, Th. 2007. Towards a functional and typological classification of crucibles. In: La Niece, S., Hook, D. & Craddock, P. T. (eds.) Metals and Mines: Studies in Archaeometallurgy. London: Archetype Books, 46-55.

Chen, H. 2014. Fueling the boom: coal as the primary source of energy for processing zinc in China and comparison with Europe, ca. 1720-1820. Journal of the Economic and Social History of the Orient, 57, 76-111.

Chen, H., Liu, H. and Qian, W. 2017. The last state monopoly iron works in imperial China: the Zunhua iron works of the Ming Dynasty. JOM, 69, 1093-1099.

Cui, J., Qin, D., Li, X. and Zhou, L. 2012. Chemical analysis and comparative study of some white porcelain sherds from the Ding, Xing and Gongyi Kiln sites (定窑、邢窑和巩义窑部分白瓷的成分分析及比较研究). Science of Conservation and Archaeology, 24, 1-10 (in Chinese).

Dube, R. K. 2006. The extraction of lead from its ores by the iron-reduction process-a historical perspective. JOM, 58, 18-23.

Elvin, M. 2004. The Retreat of the Elephants: An Environmental History of China. New Haven and London: Yale University Press.

Golas, P. J. 1999. Science and Civilisation in China Volume 5: Chemistry and Chemical Technology; Part XIII: Mining. Cambridge: Cambridge University Press.

Han, R. and Ko, T. 2007. History of Science and Technology: Mining and Metallurgy (中国科学技术史•矿冶卷). Science Press (科学出版社) (in Chinese).

Hartwell, R. 1962. A revolution in the Chinese iron and coal industries during the Northern Sung, 960-1126 A.D. The Journal of Asian Studies, 21, 153-162.

Hartwell, R. 1982. Demographic, political, and social transformations of China, 750-1550. Harvard Journal of Asiatic Studies, 42, 365-442.

He, F. 2012. New archaeological discoveries of iron smelting sites at Wuan, Hebei province (河北武安冶铁考古及新发现). Wenwu Chunxiu (文物春秋), 5, 21-25 (in Chinese).

He, T., Lin, Y., Wansong., Y. and Yu, F. 1985. Preliminary study of crucible steel from Luoyang (洛阳坩埚附着钢的初步研究). Studies in the History of Natural Sciences (自然科学史研究), 4, 59-63 (in Chinese).

Hua, J. 1999. Ancient Metallurgical Technologies in China-A Civilization Forged by Copper and Iron (中国古代金属技术-铜和铁造就的文明). Zhengzhou: Daxiang Press (in Chinese).

Huang, W., Li, Y., Zhou, W. and Liu, Y. 2005. The sulphur content of iron coins from Sichuan, Shaanxi and Shanxi provinces and its implication of using coal for iron smelting (川陕晋出土宋代鉄钱硫含量与用煤炼铁研究）. China Numismatics (中国钱币), 4, 38-44 (in Chinese).

Huang, X. 2014. A Study on hte Profiles of Iron Smelting Shaft Furnaces in Ancient China (中国古代冶铁竖炉炉型研究). Unpublished PhD thesis, University of Science and Technology Beijing (in Chinese).

Institute of Qing History, R. 1983. Mining industry of the Qin Dynasty (清代的矿业). Beijing: Zhonghua Book Company (in Chinese).

Katō, S. 2006 [1926]. Study of Gold and Silver in Tang and Song: Based on the Currency Function of Gold and Silver (唐宋金银之研究--以金银之货币机能为中心) Translated from Japanese version published in 1926 by Zhonghua Book Company. Beijing: Zhonhua Book Company (中华书局) (in Chinese).

Kerr, R., And Wood, Nigel., 2004. Science and Civilization in China, vol5: Chemistry and Chemical Technology. Cambridge: Cambridge University Press.

Killick, D. 2001. Science, speculation and the origins of extractive metallurgy. In: Brothwell, D. R. & Pollard, A. M. (eds.) Handbook of Archaeological Sciences. Chichester: John Wiley.

Kingery, W. D., Vandiver, P. B. and Prickett, M. 1986. The beginnings of pyrotechnology, Part II: production and use of lime and gypsum plaster in the pre-pottery Neolithic Near East. Journal of Field Archaeology, 15, 219-244.

Li, H. 1983. The history of the Ding Kilns and its relationsihp with the Xing Kilns (定窑的历史以及与邢窑的关系). Palace Museum Journal (故宫博物院院刊), 3, 70-77 (in Chinese).

Li, J. 1998. A History of Science and Technology in China: Ancient Pottery and Porcelain (中国科学技术史：陶瓷卷). Beijing: Science Press (in Chinese).

Lin, H. 1965. Investigation of the Ding Kiln site at Jianci village, Quyang county, Hebei province (河北曲阳县涧磁村定窑遗址调查与试掘). Archaeology (考古), 8, 394-412 (in Chinese).

Liu, H. 2015a. Preliminary research on furnace materials of historical ferrous metallurgy in China (中国古代制铁炉壁材料初步研究). Unpublished PhD thesis, University of Science and Technology Beijing (in Chinese).

Liu, L. and Shang, G. 1957. Geological report of the Lingshan coal field and its surrounding area at Quyang county, Hebei province (河北省曲阳县灵山煤田附近地质概查报告书) National Gelogical Archives of China, 11662 (in Chinese).

Liu, N. 2018. The excavation of the Shuiquangou iron smelting sites in the Dazhuangke metallurgical complex at Yanqian, Beijing (北京市延庆区大庄科辽代矿冶遗址群水泉沟冶铁遗址). Archaeology (考古), 6, 38-50 (in Chinese).

Liu, P., Li, Y. and Qian, W. 2014. Pre-modern Chinese Coke Iron-making as seen from textual records (从文献记载看我国古代焦炭炼铁). The Chinese Journal for the History of Science and Technology (中国科技史杂志), 35, 41-48 (in Chinese).

Liu, S. 2015b. Gold and silver production in imperial China: Technological choices in their social-economic and environmental settings. Unpublished PhD thesis, University College London.

Liu, S., Rehren, Th., Chen, J., Xu, C., Venunan, P., Larreina-Garcia, D. and Martinón-Torres, M. 2015. Bullion production in imperial China and its significance for sulphide ore smelting world-wide. Journal of Archaeological Science, 55, 151-165.

Marks, R. B. 2012. China: Its Environment and History. Plymouth, UK: Rowman&Littlefield Publishers.

Needham, J. 1958. The Development of Iron and Steel Technology in China. London: Newcomen society.

Qin, D. 1999. The mutual influence between the Cizhou and the Ding Kilns (论磁州窑与定窑的联系和相互影响). Palace Museum Journal (故宫博物院院刊), 86, 43-56 (in Chinese).

Qin, D., Li, X. and Gao, M. 2014. The brief archaeological report for the excavation at district A in Jianciling, Quyang county, Hebei province (河北曲阳县涧磁岭定窑遗址 A 区发掘简报). Arcahaeology 2, 3-25 (in Chinese).

Qiu, S. and Cai, L. 1986. Use of radiocarbon dating to determine the fuel used in ancient Chinese iron-smelting (我国古代燃料的碳 14 鉴定). In: Wang, Z. & An, Z. (eds.) Archaeological Research in China: A Collection of Papers in Commemoration of the Fifieth Year of Prof. Xia Nai's Work in Archaeology (中国考古学研究：夏鼐先生考古五十年纪念论文集). Beijing: Science Press (科学出版社), 359-363 (in Chinese).

Read, T. T. 1934. The early casting of iron: a stage in Iron Age civilization. Geographical Review, 24, 544-554.

Read, T. T. 1939. The earliest industrial use of coal. The International Journal for the History of Engineering & Technology, 20, 119-133.

Rostoker, W. and Bronson, B. 1990. Pre-Industrial Iron: Its Technology and Ethnology. Philadelphia: privatedly published.

Torrence, R. and Van Der Leeuw, S. 1989. Introduction: what's new about innovation? In: Torrence, R. & Van Der Leeuw, S. (eds.) What's new? A closer look at the process of innovation. London: Unwin Hyman, 1-15.

Von Glahn, R. 1996. Fountain of Furtune: Money and Monetary Policy in China, 1000-1700. London: University of California Press.

Wagner, D. B. 2003. Chinese blast furnaces from the 10th to the 14th century. Historical Metallurgy, 37, 25-37.

Wagner, D. B. 2008. Science and Civilization in China Vol5, 11: Ferrous Metallurgy. Cambridge: Cambridge University Press.

Wang, Q. and Qian, W. 2014. Preliminary investigation and research of several iron smelting sites of Liao Dynasty in Yanshan region (燕山地带部分辽代冶铁遗址的初步调查). Journal of Guangxi University for Nationalities (Natural Science Edition) (广西民族大学学报（自然科学版）), 20, 44-52 (in Chinese).

Wang, R. 2018. Primary Investigation on Ancient Iron Smelting Sites in Handan of Hebei Province (邯郸地区冶铁遗址初步调查研究). Unpublished PhD Thesis University of Science and Technology Beijing (in Chinese).

Wang, Z. 1927. Geology of Lingshan coal field at Quyang county and Micheng coal field at Tang county in Hebei province (河北曲阳县灵山及唐县迷城煤田地质). National Gelogical Archives of China, x00000329 (in Chinese).

Wu, X., Qi, S. and Zhao, X. 1986. The history of coal exploration in ancient China (中国古代煤炭开发史). Beijing: China coal industry publishing house (煤炭工业出版社) (in Chinese).

Xu, H. 1994. Coal use in the Southern Song period (南宋时期煤炭的开发利用--兼对两宋煤炭开采的总结). Social Sciences in Yunnan (云南社会科学), 6, 68-76 (in Chinese).

Xu, H. and Huang, C. 1988. The fule problem in Kaifeng area during the Northern Song period (北宋时期开封的燃料问题--宋代能源问题研究之二). Social Sciences in Yunnan (云南社会科学), 6, 79-95 (in Chinese).

You, E., Zhou, D. and Gao, L. 1987. Kiln furniture and firing method of the Yaozhou Kiln in Shaanxi and the Ding Kiln in Hebei (陕西耀州窑、河北定窑窑具与装烧方法的研究). Journal of University of Science and Technology in Shaanxi (陕西科技大学学报), 0, 1-7 (in Chinese).

Zhang, Q. 2016. The forest coverage in the Southern Song and the reasons for its changes (南宋森林覆盖率及其变迁原因研究). International Social Science Journal (Chinese edition), 3, 98-115 (in Chinese).

Zhou, W., Liu, S., Liu, H. and Chen, J. 2014. A preliminary study of traditional Chinese crucible lead smelting technology (中国传统坩埚炼铅技术初探). Studies in the History of Natural Sciences, 33, 201-215 (in Chinese).