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Not so efficient, but still distilled: the technology of Qing Dynasty zinc production at Dafengmen, Chongqing, southwest China

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ABSTRACT

The technology of zinc distillation at three large-scale production sites in Chongqing, southwest China, dated to the Ming Dynasty (AD 1368–1644), has recently been reconstructed from the analysis of production remains (Zhou et al. 2012). This paper presents the study by OM and SEM-EDS of zinc production remains from the later site of Dafengmen, in the same region, dated to the Qing Dynasty (AD 1644–1912). The main aims are to add to our characterisation of the Chinese technological tradition of zinc distillation, and to use a comparative approach to explore adaptations to different geological and sociopolitical contexts. The results reveal that at Dafengmen zinc-makers employed a broadly similar technology to those at the Ming sites, based on distillation by ascending in ceramic retorts, but they used lower grade oxidic zinc ores, a lower proportion of reducing agents, and elongated retorts of inferior performance, leading to greater losses of zinc. This is in spite of Dafengmen's ideal location near the necessary raw materials. The reasons for the lower technical efficiency at the later site are explained in terms of different social, political and economic constraints.

1. Introduction

Zinc made a relatively late appearance in the metallurgical history of China. As a volatile metal, its production required sophisticated distillation installations. The production of this metal played a special role in both the technological and economic history of Ming and Qing China: as a key constituent of the copper alloy brass, zinc was employed for coinage (Zhou, 2004; Wang et al. 2005) and also exported via long-distance maritime trade (Bonnin, 1924; de Ruette, 1995; Souza, 1991; Craddock and Hook, 1997).

Our understanding of Chinese zinc distillation technology has traditionally been limited by a lack of studies of production remains. The discovery of nearly 20 zinc smelting sites dated to the Ming Dynasty (AD 1368–1644) along the Yangtze River in Fengdu, Chongqing, southwest China since 2002 has allowed the first high-resolution, contextualised technological reconstruction of zinc distillation (Fig. 1). Zinc production remains from three of these sites, Miaobeihou, Puzihe and Muxiexi, have been analysed and the technology employed has been reconstructed in great detail. The analytical results revealed the use of large-scale installations for zinc distillation with retorts made of jar-shaped pots, condensers, pockets and lids, all well designed with formal and material properties that optimised performance during zinc distillation by ascending. The retorts were charged with iron-rich oxidic zinc ores, coal and charcoal; a high temperature of around 1200 °C and highly reducing atmosphere were achieved to reduce the zinc ores; the zinc vapour formed within the pots was cooled and collected in the condensers. The mass production of zinc in Fengdu was probably set up to supply government mints (Liu et al., 2007; Zhou et al., 2012; Zhou, 2012).

A search was made for the possible ore sources which supplied these zinc smelting sites in Fengdu. The nearest lead-zinc deposits, at Laochangping in Shizhu (Fig. 1), about 50 km southeast of the Fengdu sites, were investigated during several field trips from 2004 to 2010. These exploratory surveys revealed large amounts of tap slag from lead/silver or copper smelting (Xie and Rehren, 2009) as well as old zinc mine workings in the Laochangping region. The minerals found inside Yushi Cave, one of the largest old zinc mines,

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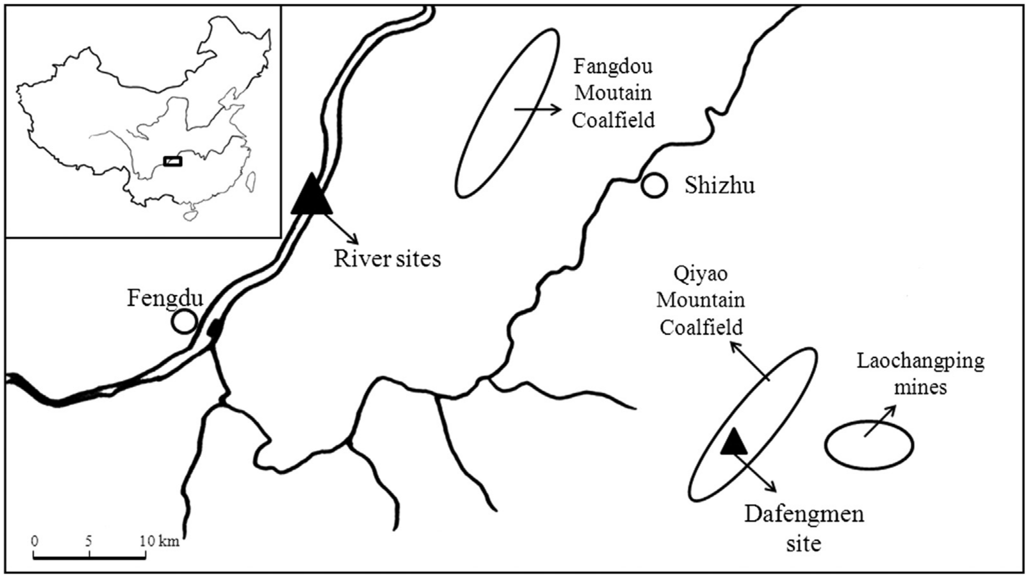

Fig. 1. Map showing the locations of the Ming production sites in Fengdu ('River sites'), Dafengmen site in Shizhu, the Laochangping mines, and the Fangdou and Qiyao Mountain Coalfields.

were mainly iron-rich zinc carbonates, similar to those excavated at Miaobeihou, one of the Fengdu sites (Zhou et al., 2012), indicating that the Fengdu sites could have used zinc ores from this region. Four zinc smelting sites were also found a few kilometres west of the Laochangping mines. Several rectangular furnace foundations were found and some were excavated. One of these zinc smelting sites, Dafengmen (Fig. 1), was investigated in August 2010, and various types of production remains were collected and analysed to reconstruct the technology employed. With dates indicating a production peak during the Qing Dynasty (AD 1644–1912), and a location broadly in the same region but with significantly different topography and resource environment, the site offered an excellent comparison with the earlier Ming sites, characterised previously.

This paper presents the analytical study of the Dafengmen remains as the basis for a technological reconstruction and a comparison with the Ming technology. Factors considered include retort design, raw material selection and processing, performance and efficiency, and environmental and sociopolitical constraints. It is shown that, in spite of a seemingly ideal location in close proximity to the zinc ores, fuel and refractory clay needed for the industry, the Qing zinc production technology appears technically less efficient. These differences are explained in terms of different sociopolitical constraints.

2. Site description

Dafengmen is about 7–8 km west of the Laochangping region, situated in a long narrow valley between mountains. Dafengmen literally means 'large wind gate', and it is thus named because it is very windy. Abundant retorts fragments and slag were scattered all over the valley area. Trees and plants are rarely visible in this area, probably because of the severe pollution caused by the metallurgical debris. The size of the site has been estimated by a modern mining and smelting company who planned to re-process these smelting remains to extract zinc for the production of zinc oxide. They estimated that the Dafengmen site is around 2 km in length, 250 m in width; the heaps of retorts and slag are 1.5–3 m thick, weighing approximately 250,000 tonnes.[1]

Radiocarbon dating of charcoal samples from the site indicates that the production mainly dates to the Qing Dynasty (AD 1644–1912) (Table 1). There is also literary evidence from *Local Gazetteer of Shizhu* saying that mass production of zinc began from 1770 and continued until the 1840s in the Laochangping region (RGALHS, 2009). One charcoal sample (BA07558) was dated to the Song Dynasty (AD 960–1279), but it is highly unlikely that this date corresponds with the zinc smelting activity, since it would predate any evidence of zinc production in China by several centuries; perhaps the charcoal was made from an old tree or simply derived from earlier activities in the area.

3. Methods

The methods and instrumentation employed are exactly the same as for the previous study of Ming remains (Zhou et al., 2012), and they are repeated here for convenience. Different parts of retorts and slag from Dafengmen were selected for analysis. Several samples were chosen from each category of material in order to assess their internal variability. Samples were named with three capital letters followed by a number. The first two letters SD refer to the Dafengmen site, while the third letter B or T denotes bottom or top parts of retorts respectively. The samples were mounted in epoxy resin and polished to 1 μm for optical microscopy (OM) and scanning electron microscopy-energy dispersive spectrometry (SEM-EDS) examinations.

The OM used was a Leica DM LM. Microphotographs were taken in plane polarised reflected light (PPL) and cross polarised reflected light (XPL).

The SEM used was a Philips XL30 environmental SEM with an Oxford Instruments spectrometer package. The polished blocks were carbon coated. They were observed in secondary electron (SE) and backscattered electron (BSE) modes, and analysed using the EDS system. The acceleration voltage applied to all analyses was 20 kV, the working distance 10 mm, the spot size 5.0–5.6, the beam current adjusted to a deadtime of 35–40% and the livetime 50 s. Given the heterogeneous nature of most of the samples studied, the bulk compositions of the samples were obtained by averaging five measurements of large areas of ~2 by ~2.5 mm. It is accepted that analysing such large areas of heterogeneous and often porous materials may compromise accuracy, but this was still deemed the

[1] Online source: http://wenku.baidu.com/view/cef1ff3f5727a5e9856a61bb.html.

Table 1
AMS radiocarbon dates of charcoal samples from Dafengmen by Peking University AMS lab, calibrated by OxCal 4.1 and IntCal 09.

Lab code	^{14}C date (BP, 1σ)	Calibrated date (AD)	
		68.2% probability	95.4% probability
BA07558	810 ± 30	1215 (68.2%) 1261	1175 (95.4%) 1271
BA101496	155 ± 30	1669 (13.3%) 1694, 1728 (32.1%) 1781, 1798 (8.0%) 1812, 1919 (14.7%) 1945	1666 (16.6%) 1709, 1718 (33.7%) 1785, 1795 (27.3%) 1890, 1910 (17.8%) 1953
BA101497	235 ± 30	1645 (42.0%) 1668, 1782 (26.2%) 1798	1528 (2.3%) 1544, 1633 (48.3%) 1683, 1737 (2.6%) 1756, 1761 (32.6%) 1804, 1936 (9.6%) 1955
BA101499	280 ± 30	1523 (38.3%) 1571, 1630 (29.9%) 1660	1499 (0.4%) 1502, 1513 (54.2%) 1601, 1616 (38.4%) 1666, 1784 (2.3%) 1796
BA101500	160 ± 25	1669 (12.4%) 1689, 1730 (36.1%) 1780, 1798 (7.4%) 1809, 1926 (12.3%) 1944	1665 (16.5%) 1700, 1721 (39.5%) 1785, 1793 (10.8%) 1819, 1832 (9.9%) 1880, 1915 (18.8%) 1954
BA101501	160 ± 25	1669 (12.4%) 1689, 1730 (36.1%) 1780, 1798 (7.4%) 1809, 1926 (12.3%) 1944	1665 (16.5%) 1700, 1721 (39.5%) 1785, 1793 (10.8%) 1819, 1832 (9.9%) 1880, 1915 (18.8%) 1954
BA101502	110 ± 35	1691 (19.0%) 1729, 1811 (41.2%) 1892, 1907 (8.0%) 1924	1680 (31.3%) 1764, 1800 (64.1%) 1939

most suitable way of obtaining a reliable quantification of the composition of different components that often appear fused together. The ceramic matrices of the pots were analysed as areas of ~100 by ~150 μm, avoiding large inclusions; the glassy phases of the slag were studied at areas of ~400 by ~600 μm; individual phases were probed by measuring spots of a few micrometres in diameter. Results were combined with oxygen by stoichiometry where appropriate. Sulphur is reported as an oxide, but it is acknowledged that it may also be present in other forms, such as zinc sulphide in slag samples. The accuracy of SEM-EDS decreases for values below 0.3%, but values below this threshold are reported for indicative purposes. Sodium was omitted in the analyses of samples rich in zinc (pots, condensers and slag), because both Na Kα and Na Kβ peaks overlap with the Zn Lα peak.

4. Results

4.1. Retorts

Numerous retorts were identified in the 2004 field survey; the best preserved pot was about 40 cm in height, with a volume

Fig. 2. Left: a nearly complete pot from Dafengmen collected during the 2004 fieldwork; right: Reconstruction of a Dafengmen retort, which was composed of pot, condenser, pocket and lid.

estimated at about 2 L (Fig. 2 left). As with the Ming examples (Zhou et al., 2012), the retorts from Dafengmen were made of pots, condensers, pockets and lids (Fig. 2 right), where distillation by ascending would take place within a single container separated in two chambers. During the 2010 field survey, only fragments of different parts of retorts were discovered, including the bottom parts of the pots (usually with metallurgical residues remaining inside), the walls and top parts of the pots, the condensers and an iron lid. Although no pockets were found, horizontal ceramic partitions with a hole on one side must have been added to separate two zones (for distillation and condensation) and collect zinc (Fig. 2 right). The analyses of the pots and the condensers from Dafengmen are presented below.

4.1.1. Pots

The pots are relatively long and narrow. Their flat circular bases are 4–5 cm in diameter; the bodies widen gradually to maximum diameters at the rims of around 10 cm. The sizes of the pots cannot be accurately determined due to the lack of complete examples, but they can be as tall as 40 cm as the relatively intact pot found in 2004 shows (Fig. 2 left). The wall thickness increases from the rims (~0.8 cm) to the bases (~1.5 cm). They were made by wheel throwing as seen from the shallow spiral markings on the surfaces. All the fragments studied were used, displaying rusty colours on the surfaces. The colours of cross sections of the pot fragments are mostly bluish grey – the result of the reducing conditions during use.

The pot fabrics show high levels of ZnO contamination, varying from 5% to 17%. To estimate the original compositions of unused pots, the ZnO contents were omitted, and the data renormalised to 100%. The renormalised compositions of the ceramic matrices show 44–52% SiO_2, 29–37% Al_2O_3, 5–12% FeO, 3–6% TiO_2, 3–5% K_2O and low levels of other oxides (Table 2). Their bulk compositions, obtained from relatively large area analyses by SEM-EDS, are generally indistinguishable from the matrix compositions, only with higher levels of ZnO and slightly lower levels of K_2O.

The fabrics contain abundant ill-sorted inclusions up to 2 mm large (Fig. 3). Most of the inclusions are rock fragments, with edges dissolving into the matrices; some of them have developed bloating pores within as a result of exposure to high temperatures. These rock fragments contain high levels of SiO_2 (46–49%) and Al_2O_3 (36–41%), and a few percent of K_2O (4–6%), TiO_2 (2–4%) and FeO (1–6%). Their high Al_2O_3 concentrations indicate they are probably fragments of aluminous rocks, i.e. shales or mudstones composed of kaolinite, $Al_2Si_2O_5(OH)_4$, and other minerals containing K_2O, TiO_2, FeO, CaO and MgO. They show similar compositions to the kaolinitic clay matrices, which have elevated levels of FeO but lower levels of Al_2O_3 due to more ferruginous impurities present in the

Table 2
Average matrix (top half) and bulk (bottom half) compositions of six pot samples from Dafengmen (wt%), normalised to 100%. Analyses on polished sections at areas of ~150 by ~200 μm and ~2 by ~2.5 mm respectively by SEM-EDS. For both sets of compositions, the bottom half rows show the same results after omitting ZnO and renormalising to 100%. '–' means 'not detected'.

Sample	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	Cr_2O_3	MnO	FeO	ZnO
SDB11	0.6	34.9	44.9	1.0	–	–	4.0	0.4	3.4	0.1	0.1	5.3	5.3
SDT13	0.4	25.3	42.7	0.3	0.1	–	3.7	0.8	2.7	0.1	0.8	5.9	17.2
SDT14	0.5	29.1	40.7	0.4	0.1	–	2.9	1.7	3.9	0.1	0.4	4.0	16.2
SDT15	0.6	25.6	44.3	0.2	–	0.1	4.0	0.6	2.9	0.1	0.2	10.9	10.5
SDT17	0.5	30.2	43.2	0.2	0.1	–	4.3	0.9	4.1	0.2	0.1	7.4	8.8
SDT18	0.5	30.8	41.1	0.2	0.2	0.1	4.6	1.2	5.7	0.3	0.4	9.2	5.7
SDB11	0.6	37.0	47.4	1.0	–	–	4.2	0.4	3.6	0.1	0.1	5.6	
SDT13	0.5	30.5	51.8	0.4	0.1	–	4.4	0.9	3.2	0.2	0.9	7.1	
SDT14	0.6	34.8	48.5	0.5	0.1	–	3.5	2.0	4.7	0.2	0.4	4.7	
SDT15	0.6	28.6	49.5	0.2	–	0.1	4.5	0.7	3.2	0.2	0.2	12.2	
SDT17	0.5	33.2	47.3	0.2	0.1	–	4.8	1.0	4.5	0.2	0.1	8.1	
SDT18	0.5	32.6	43.9	0.2	0.2	0.1	4.9	1.2	6.0	0.3	0.4	9.7	
SDB11	0.6	31.6	44.8	0.6	0.1	0.1	2.3	0.5	3.1	0.2	0.2	8.6	7.3
SDT13	0.3	22.9	35.7	0.3	0.5	–	1.9	0.5	2.5	0.1	0.5	9.4	25.4
SDT14	0.5	25.8	31.2	0.4	0.3	0.1	1.6	0.5	2.9	0.2	0.4	6.7	29.4
SDT15	0.4	26.5	41.3	0.2	0.1	0.1	2.9	0.4	3.1	0.1	0.2	8.2	16.5
SDT17	0.3	25.5	35.7	0.3	0.2	0.1	2.5	0.5	3.5	0.1	0.1	9.6	21.6
SDT18	0.4	29.3	36.8	0.2	0.2	0.1	2.9	0.5	3.1	0.3	0.3	7.9	18.0
SDB11	0.6	34.2	48.4	0.6	0.1	0.1	2.5	0.5	3.3	0.2	0.2	9.3	
SDT13	0.5	30.7	47.7	0.4	0.6	0.1	2.5	0.7	3.3	0.2	0.7	12.6	
SDT14	0.6	36.5	44.4	0.5	0.5	0.1	2.2	0.7	4.1	0.2	0.6	9.6	
SDT15	0.5	31.7	49.4	0.3	0.1	0.1	3.4	0.5	3.7	0.2	0.2	9.9	
SDT17	0.4	32.5	45.6	0.4	0.3	0.1	3.1	0.7	4.5	0.1	0.1	12.2	
SDT18	0.5	35.7	44.8	0.3	0.3	0.1	3.5	0.7	3.8	0.3	0.3	9.7	

clay. Thus the clay is probably the weathering product of the parent aluminous rocks; the rock fragments were likely procured together with the clay, and served as temper. Aluminous rocks and associated clay are generally found in coal-bearing strata of the Permo-Carboniferous eras in north China and also in southwest China, often directly underlying coal seams. According to geological survey reports of coal deposits within the Fengdu and Shizhu regions, bauxite, an aluminous rock, is often found underlying the coal seams. The bauxite ore in the Fangdou Mountain Coalfield (Fig. 1) contains ~37% SiO_2, ~32% Al_2O_3 and ~11% FeO (Sichuan Geology Bureau, 1961), highly comparable to the raw materials used for making the pots found at Dafengmen.

In addition to the inclusions of rock fragments, there is a significant amount of ferruginous concretions (up to 2 mm, Fig. 3), within some of which metallic iron prills formed. Iron prills can also be seen in the matrices, indicating highly reducing conditions maintained during firing. Similar features have been identified in the ceramic fabrics of 19th-century Indian steel-making crucibles (Freestone and Tite, 1986, 18). In some areas, quartz grains have melted and subsequently recrystallised as silica crystals intergrown with tiny crystals rich in iron, zinc and titanium.

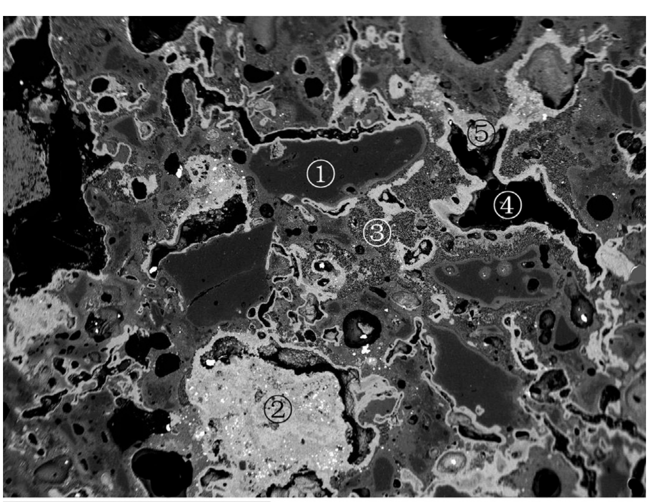

Fig. 3. BSE image of the pot fabric of SDT13, including rock fragments (1), ferruginous concretions (2), silica (3), pores (4) and the zinc-rich layers (5) lining the pores.

It is worth noting that the pot fabrics are very porous (Fig. 3). Most of the pores are elongated and surround large inclusions. The large open porosity made the fabrics prone to be heavily permeated by zinc vapour: both the clay and the inclusions were chemically altered by zinc oxide, and zinc oxide reacted with the ceramic fabrics, forming zinc-rich layers within cracks and pores. The intense zinc contamination is also noticeable in the elevated ZnO levels recorded in the ceramic matrix analyses.

4.1.2. Condensers

The condenser fragments found at Dafengmen usually appear detached from the pots. One relatively well preserved fragment is about 6 cm in height and has an estimated diameter of over 10 cm (Fig. 4 left), which would fit the rim dimensions of the better preserved pots. Whitish zinc oxide crusts adhere to the yellowish and brownish fragments internally and externally. There are large mineral inclusions visible in the fractures of two samples, SDT3 and SDT5 (not analysed). The condensers show various shades of yellow, brown and grey, while the cross sections of the three samples studied are yellow or brown on the inside and grey on the outside, denoting oxidising and reducing conditions respectively.

The condenser fabrics are contaminated by extraordinarily high levels of ZnO (53–55%). After omitting the ZnO contents and renormalising the data, the estimated condenser compositions show 63–68% SiO_2, 14–16% Al_2O_3, 8–12% FeO, 2–6% MgO, 1–3% K_2O, ~1% CaO and 0.5–1.4% SO_3 (Table 3). As such, they appear to have been made with a different clay from the pots, with lower levels of Al_2O_3, K_2O and TiO_2, but higher SiO_2 and MgO.

The makeup of the condenser fabrics is hard to establish due to the heavy zinc contamination. A few large grains of quartz and

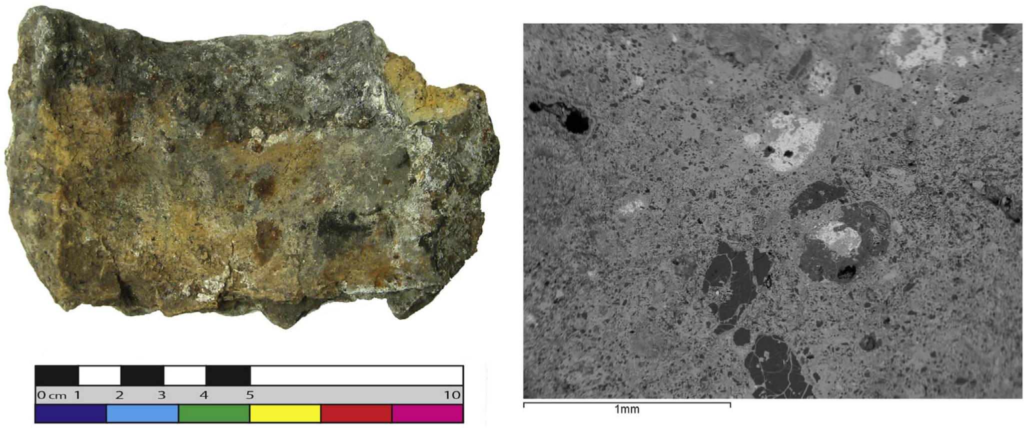

Fig. 4. Left: the internal surface of condenser SDT1; right: BSE image of the condenser fabric of SDT1, showing the heavily contaminated fabric and a few grains of inclusions.

feldspar are scattered in the fabrics (Fig. 4 right). Coal fragments were only detected in SDT1, while rock fragments composed mainly of silt-sized quartz and feldspar grains were found in SDT2 and SDT3.

4.2. Slag

Most of the slag samples are rusty lumps inside the bottom parts of retorts. Occasionally white inclusions are seen trapped within the slag (Fig. 5).

The five slag samples from Dafengmen contain variable concentrations of SiO_2 (18–35%), FeO (17–26%), ZnO (9–32%), BaO (5–19%), SO_3 (3–12%), Al_2O_3 (5–8%), CaO (2–6%), MgO (1–4%), and below 1% K_2O and TiO_2. It should be noted that their BaO and SO_3 contents are rather high; in addition, they contain around 1% PbO (except SDB9) and minor amounts of CuO, As_2O_3 and Sb_2O_3 (Table 4).

The slag samples are composed mainly of newly-formed crystals rather than glassy phases. The assemblages of crystals in one small area differ significantly from other areas even in a small sample about 2 cm across. The most common newly-formed crystals include feldspar (mostly barium feldspar, $BaAl_2Si_2O_8$), olivine [$(Zn, Fe, Mg)_2SiO_4$] and pyroxene [$(Ca, Fe, Mg, Zn)_2Si_2O_6$] (Fig. 6 a). These crystals are larger than those in the slag samples from the Fengdu sites (Zhou et al., 2012), denoting a slower cooling after firing.

Together with these crystals, there is also a considerable quantity of zinc sulphides; some of the large crystals are most likely residual sulphidic zinc ores (SDB7 and SDB9) (Fig. 6 b), while the small ones probably formed during the distillation process. There are other residual ore minerals identified, such as barite ($BaSO_4$) in SDB7 and SDB10 and zinc silicates in SDB6. The zinc silicates appear as internally recrystallised iron-bearing zinc silicates, similar to those found in slag samples from Muxiexi, one of the Fengdu sites (Zhou et al., 2012). Therefore, it can be inferred that the macroscopically visible white inclusions within the slag of SDB7 could be the residual grains of zinc silicates from the ores.

In most of the samples only a few metallic iron prills were found, mostly in the glassy phases, where they appear together with zinc sulphides. Only in SDB12 there is a large lump consisting of a cluster of globules of metallic iron and iron-bearing zinc oxide (~12% FeO) together with a few zinc- and iron-rich olivines and zinc-rich pyroxenes (Fig. 6 c), resembling those in slag sample CMB1 from Muxiexi (Zhou et al., 2012). The presence of this residual, partly reacted lump in the slag is either due to an insufficient amount of reducing gases, or the relatively large size and low porosity of the original zinc ore fragment. The coexistence of metallic iron and zinc oxide confirms that iron oxides were reduced more easily than zinc oxide, as can be inferred from the Ellingham diagram. Further secondary iron oxides are found deposited in the holes left by the corrosion of metallic iron, pores, cracks or surfaces.

A few inclusions of metallic lead, lead oxide and lead carbonate are embedded in SDB6, SDB7 and SDB9. The lead particles in SDB6 contain up to 6% silver. Of these samples, SDB9 contains the highest level of PbO: there is a significant amount of lead oxide surrounded by lead carbonates; in some cases metallic lead appears embedded within the lead oxide (Fig. 6 d). Some small metallic copper prills were identified within the lead oxide; they contain 1.5–2.5% zinc, 1.8–1.9% antimony and 0.6–0.8% iron. These lead and copper phases may have derived from lead and copper minerals in zinc ores, probably cerussite ($PbCO_3$) and malachite [$Cu_2CO_3(OH)_2$]. As shown in the Ellingham diagram, copper and lead oxides are more easily reduced to metal than zinc oxide, which would explain the presence of these metals in zinc distillation retorts. Metallic lead is known to have formed in more recent, traditional zinc distillation retorts, e.g. in Xiaoshuijing, Hezhang, Guizhou, where this metal was recovered from the distillation residues by panning crushed slag in water (Xu, 1998).

In contrast with the slag samples from the Fengdu sites (Zhou et al. 2012), only one (SDB10) among five samples examined was found to contain some residues of coal and charcoal. This suggests that coal and charcoal were added as reducing agents, but probably in a relatively lower proportion, so typically no excess was left in the slag.

Table 3
Average bulk compositions of three condenser fabrics from Dafengmen (wt%), normalised to 100%. Analyses on polished sections at areas of ~2 by ~2.5 mm by SEM-EDS. The bottom half rows show the same results after omitting ZnO and renormalising to 100%.

Sample	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	FeO	ZnO
SDT1	1.0	7.1	29.8	0.3	0.5	0.1	1.1	0.4	0.4	0.1	4.3	54.9
SDT2	1.3	7.1	30.0	0.3	0.7	0.1	1.2	0.5	0.4	0.1	5.8	52.5
SDT3	2.6	6.4	30.1	0.2	0.2	0.1	0.5	0.3	0.4	0.1	3.6	55.5
SDT1	2.3	15.8	66.2	0.6	1.1	0.1	2.4	0.9	0.9	0.2	9.5	
SDT2	2.7	14.9	63.2	0.7	1.4	0.2	2.5	1.1	0.9	0.2	12.2	
SDT3	5.8	14.3	67.6	0.5	0.5	0.3	1.1	0.8	0.9	0.1	8.1	

Fig. 5. Rusty slag with white inclusions within the ceramic pot in SDB7.

5. Discussion

5.1. Retort design

The pots forming the main parts of the retorts from Dafengmen are not jar-shaped like those from the Fengdu sites, which were probably directly adapted from domestic jars with few, if any, modifications in shape. They are still flat bottomed, but taller and slimmer without an expanded central section. While retaining a volume similar to that of the jar-shaped pots (about 2 L), the shape of the Dafengmen ones can be argued to be technically more advantageous for zinc distillation. Firstly, it would be easier to adjust temperature gradients between the pots and the condensers when using taller pots, or rather, pots with a larger ratio of height to rim diameter. Furthermore, such pots have a higher ratio of surface area to volume, which could facilitate heat absorption and even heat distribution within the charge (Rehren, 2003). The tall pots are thicker in the bottom parts than in the top parts, which would increase structural stability and strength to hold the charge.

Turning to the material properties of the ceramic fabrics, the pots were made of kaolinitic clay and rock fragments. Compared to the pot fabrics from the Fengdu sites, they appear much more refractory, with higher levels of Al_2O_3 (over 30%), while the moderate concentrations of fluxing oxides, K_2O and FeO in particular, would decrease their refractoriness to a certain extent (Fig. 7). However, the partial reduction of the iron oxide to metal would decrease the fluxing action of iron oxide. The high TiO_2 levels would further increase the refractoriness. Although the degree to which their refractoriness was decreased by the fluxing oxides is difficult to estimate, the Dafengmen fabrics can be deemed quite refractory. The presence of elongated cracks around the inclusions and open voids could help arrest crack propagation, thus increasing the toughness and thermal shock resistance.

At the same time, the high levels of zinc oxide documented in the Dafengmen pots suggest that these were less resistant to the penetration of zinc vapour, in stark contrast with the zinc-resistant pots from the Fengdu sites. The main reason behind this disparity is that the Dafengmen pot fabrics are dominated by open porosity; while the Fengdu pots have predominantly small closed voids. Employing such porous retorts for zinc distillation would not only lead to the zinc losses into the pot fabrics (and the subsequent deterioration of the ceramic), but also to more losses into the air, thus decreasing the yield.

Kaolinitic clays were commonly employed for making fine-grained high-fired ceramics in ancient China, including white stonewares of the Neolithic period and the Shang Dynasty (the 16th–11th centuries BC) and white porcelains of the Xing and Ding Kilns during the Tang and Song Dynasties (AD 618–1279) (Kerr and Wood, 2004). They are also known to have been used to make metallurgical crucibles in medieval and later times: for example, the famous Hessian crucibles (made in the German region of Hesse) and the crucibles made in Stamford, Lincolnshire (Martinón-Torres and Rehren, 2009; Freestone and Tite, 1986); as well as steel-making crucibles in Central Asia (Rehren and Papachristou, 2003) (Fig. 8). There is, however, a key aspect that maximises the performance characteristics of pyrotechnical ceramics made from kaolinitic clays: a high-temperature prefiring in pottery kilns. For example, Hessian crucibles made of kaolinitic clay and relatively coarse temper similar to the Dafengmen pots were prefired at temperatures over 1100 °C before they were used for any metallurgical process. The fabrics of Hessian crucibles thus developed mullite-rich vitrified matrices and closed porosity; hence they were less prone to contamination or other chemical distortion during use (Martinón-Torres et al. 2008; Martinón-Torres and Rehren, 2009). Thus, the good thermal refractoriness of the Dafengmen pots, contrasting with a seemingly poor chemical refractoriness, may also be due to the fact that they were not prefired at temperatures high enough to develop vitrified matrices in order to be resistant to zinc vapour. Unfortunately, the prefiring temperatures cannot be estimated as no unused pots have been found at Dafengmen, and thus this explanation remains as an untested hypothesis.

Overall, it can be argued that the pots were highly specialised ceramics produced for zinc smelting in terms of formal and material characteristics. The tall, narrow pots made of kaolinitic clay and rock fragments rich in fluxing oxides were specifically chosen to make retorts for zinc distillation. They were probably manufactured in specialised ceramic workshops and fired in kilns, which is

Table 4
Bulk compositions (top half) and crystalline phases (bottom half) of five slag samples from Dafengmen (wt%), normalised to 100%. Analyses on polished sections at areas of ~2 by ~2.5 mm and ~400 by ~600 μm respectively by SEM-EDS. '–' means 'not detected'.

Sample	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	FeO	CuO	ZnO	As_2O_3	Sb_2O_3	BaO	PbO
SDB6	1.7	4.6	18.3	0.1	11.6	0.1	0.1	2.9	0.6	0.1	17.2	0.2	21.8	0.5	0.2	18.9	1.1
SDB7	1.9	8.0	30.8	0.1	6.8	0.1	0.9	3.3	0.6	–	22.3	0.4	9.2	1.5	0.3	13.1	0.7
SDB9	1.9	5.4	24.5	0.2	6.5	0.1	0.3	2.0	0.5	0.1	26.3	0.9	13.5	0.4	0.2	12.4	4.8
SDB10	1.3	6.6	35.3	0.2	2.6	0.1	1.0	2.1	0.4	0.1	24.6	0.1	16.8	0.3	–	7.2	1.3
SDB12	3.7	4.5	21.0	0.2	5.1	0.1	0.2	6.0	0.2	0.1	19.6	0.2	32.4	0.3	0.2	5.4	0.8
SDB6	1.7	6.5	20.5	0.2	12.8	–	0.2	2.4	0.4	–	8.6	0.3	19.4	0.2	0.1	26.3	0.4
SDB7	2.5	9.0	36.8	0.2	3.0	–	1.4	3.6	0.9	0.1	21.0	0.3	7.6	0.9	0.2	12.2	0.3
SDB9	2.1	6.6	27.5	0.3	9.5	0.1	0.3	2.5	0.5	0.0	13.7	1.3	11.9	0.3	0.2	21.6	1.6
SDB10	1.6	9.6	42.8	0.2	2.0	0.1	1.5	3.7	0.4	0.1	13.8	–	17.4	0.2	0.2	5.9	0.5
SDB12	1.8	3.7	22.2	0.1	8.2	–	0.2	2.6	0.2	0.1	14.0	–	41.7	0.2	0.2	4.7	0.1

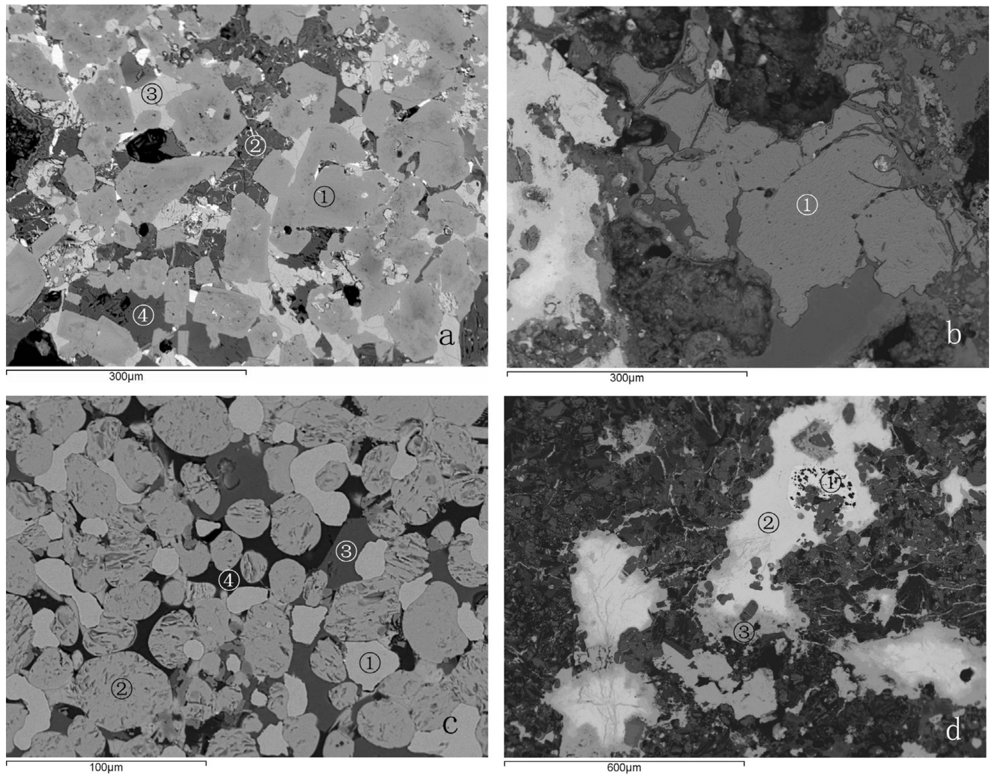

Fig. 6. BSE images of the slag samples from Dafengmen. a. barium feldspar (1), olivines (2)(3) and pyroxene (4) in SDB6; b. residual grains of zinc sulphides (1) in SDB9; c. metallic iron prills (1), zinc oxide (2), olivine (3) and pyroxene (4) in a large lump in SDB12; d. lead (1), lead oxide (2) and lead carbonates (3) in SDB9. The metallic lead particles are studded with silicon carbide grains (black) from the grinding papers used during sample preparation, due to the softness of lead metal.

supported by the fact that there was an 'earthen jar factory' at Dafengmen as recorded in a local history document (Ran and Ran, 1991). However, the pots were made without much care, as is indicated by the larger size of the inclusions and the likely lower firing temperatures compared with those from Fengdu. On the whole, they seem technically less developed than these earlier ones.

Turning to the condensers, these are composed of common clay and are similar in form and material to those from the Fengdu sites, though they contain slightly higher concentrations of fluxing oxides and lower amounts of SiO_2 (Fig. 7). Their raw materials were not well prepared, as seen from the very large inclusions that were most likely not deliberately added but naturally present in the clay. The condensers were probably not prefired, and during use they were exposed to temperatures lower than 800 °C. The absence of pockets in the material collected during field surveys suggests that either the pockets were too fragile to survive or they were reused to

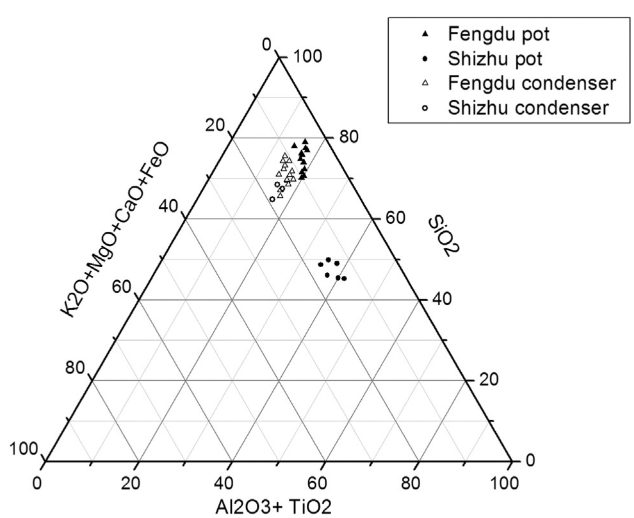

Fig. 7. Ternary diagram of SiO_2–(Al_2O_3 + TiO_2)–(K_2O + MgO + CaO + FeO) showing the bulk compositions of the pot and condenser fabrics from Fengdu (three sites) and Shizhu (Dafengmen).

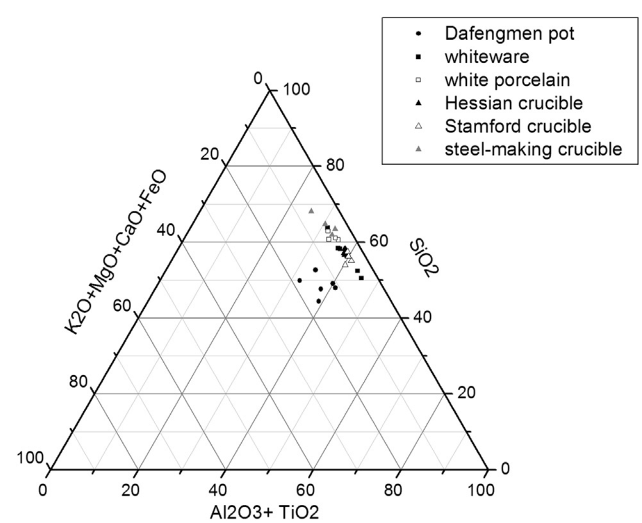

Fig. 8. Ternary diagram of SiO_2–(Al_2O_3 + TiO_2)–(K_2O + MgO + CaO + FeO) showing the matrix compositions of the Dafengmen pots and some kaolinitic ceramics: Neolithic and Shang whitewares (Kerr and Wood, 2004), Ding white porcelains (Kerr and Wood, 2004), Hessian crucibles (Martinón-Torres and Rehren, 2009), Stamford crucibles (Freestone and Tite, 1986) and Central Asian steel-making crucibles (Rehren and Papachristou, 2003).

charge the retorts to recover some zinc. The condensers and pockets were likely made at the zinc workshops rather than in specialised ceramic workshops, as they had to be fitted to the pots after these had been charged.

Although no pockets have been found at Dafengmen, ceramic dishes with a vent up one side must have been placed within the condensers to provide a place for the metallic zinc to collect (Fig. 2 right). The pockets might have been made of non-refractory clay, heavily contaminated with zinc oxide and recycled as part of charge to recover zinc (see discussion in next section).

The iron lid fragment discovered at Dafengmen is approximately 2 mm thick and 12 cm in diameter, quite a good fit for the opening of the condensers. The iron lid shows ferrite grains with a large number of wüstite-silicates slag inclusions, mostly elongated and oriented parallel to the surfaces. Although the quality of the iron was not exceptional due to the abundant slag inclusions, it was sufficient for its use as a lid for a zinc distillation retort. As iron has good thermal conductivity, such a thin iron lid could transfer heat fast into the air and keep the condensation zone at low enough temperatures for condensation. As in traditional zinc production processes (Xu, 1998; Craddock and Zhou, 2003), a small hole should have been present in the lid, opposite the hole in the pocket, so that the gases generated by the process could escape (Fig. 2 right).

5.2. The charge

On the basis of the analytical results, we suggest that oxidic zinc ores, possibly coal/charcoal and recycled zinc-impregnated ceramics made up the charge of the Dafengmen retorts.

Compared to those from Fengdu, the slag samples from Dafengmen contain lower levels of SiO_2, Al_2O_3, K_2O, MgO and CaO, higher levels of BaO, ZnO, SO_3 and PbO, and similar levels of FeO and other oxides (Fig. 9). The enrichment of FeO, ZnO, SO_3, PbO and minor amounts of CuO and As_2O_3 clearly derived from the ores, which were dominated by iron-rich oxidic zinc ores but also contained sulphidic zinc minerals (sphalerite, ZnS) and oxidic lead/copper minerals (probably cerussite and malachite). In addition, the ores contained gangue minerals, such as barite ($BaSO_4$), calcite, ($CaCO_3$), and dolomite [$CaMg(CO_3)_2$], leading to the significant levels of BaO, CaO and MgO. It should be noted that the abundance of sphalerite and barite minerals would generate a lot of sulphur, which would readily recombine with metallic zinc to form zinc sulphide. In addition, as with iron impurities, the lead/copper minerals would be reduced to metals before the zinc, which would consume a few more reducing agents. In general, therefore, the zinc ores used at Dafengmen appear of worse quality than the ores used at the Fengdu sites. Most of the impurities would have stayed in the slag, while the reduced lead would have partly volatilised and condensed with the zinc. Although no metallic zinc lumps have been found at Dafengmen, the zinc products are expected to have been richer in lead than those from the Fengdu sites.

The ratios of SiO_2 to Al_2O_3 in the slag samples are very different from those in the pot fabrics, but similar to those in the condenser fabrics (Fig. 10). This is consistent with the possibility that most of the SiO_2 and Al_2O_3 could have come from used condensers and pockets, which would have been crushed to retrieve some of the zinc lost in them. Although no pockets were collected for analysis, it can be assumed that their composition would be similar to that of the condensers, as both parts are likely to have been made and fitted to the retorts at the site (cf. Zhou et al., 2012); in this sense, perhaps the very scarcity of pockets at the site provides indirect evidence to support the idea that they were recycled. Part of the SiO_2 and Al_2O_3 in the slag could also have derived from zinc ores and coal. Ores with zinc silicate minerals would have introduced more SiO_2, but it appears that this source of SiO_2 did not contribute too much to the slag.

The reducing agents might have been coal and charcoal, but there are very limited amounts of these remaining in the slag. It may be inferred that all the carbon was consumed during the process, and perhaps an insufficient quantity of reducing agents was present in the charge – which would partly explain the considerable amount of unreduced zinc left in the slag. The ash of coal and charcoal would have contributed further CaO, MgO, K_2O and FeO to the slag, while some sulphur could also have come from the coal.

The internal heterogeneity and abundant residual grains in the slag suggest that the charge was never fully molten during the process, so it is difficult to estimate the operating temperatures from the slag itself. As an alternative, it is possible to estimate it from the degree of vitrification of the pots. Refiring experiments were carried out, and indicated that the Fengdu pots had been exposed to temperatures around 1200 °C. Conversely, the Dafengmen pot (SDT11) bloated until failure when refired at 1200 °C, indicating that operating temperatures at Dafengmen must have been lower. After heating, the charge probably cooled slowly, explaining the large crystal size of the slag phases.

5.3. Technical efficiency

The technology of zinc distillation at Dafengmen was generally similar to that documented at the Fengdu sites: the overall design of retorts with pots, condensers, pockets and lids forming two chambers; the use of iron-rich oxidic zinc ores; a combination of coal and charcoal as reducing agents inside the retorts; and the rectangular furnaces fuelled by coal. These can all be seen as elements of the same technological tradition of Chinese zinc distillation. However, the high-resolution reconstruction allowed by the

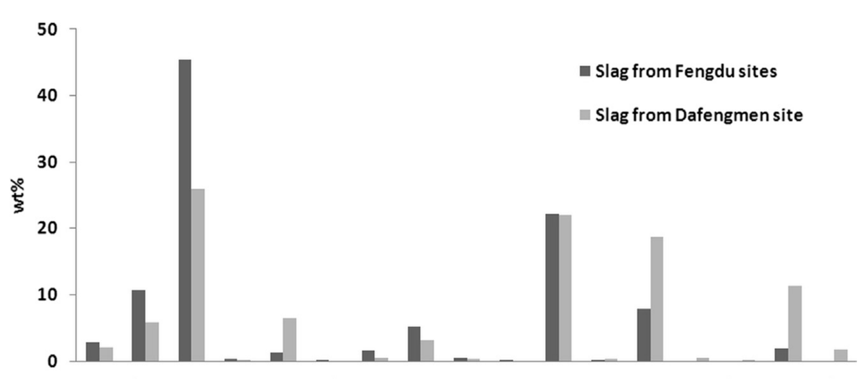

Fig. 9. Bar chart comparing average bulk compositions of the slag samples from the Fengdu sites and Dafengmen.

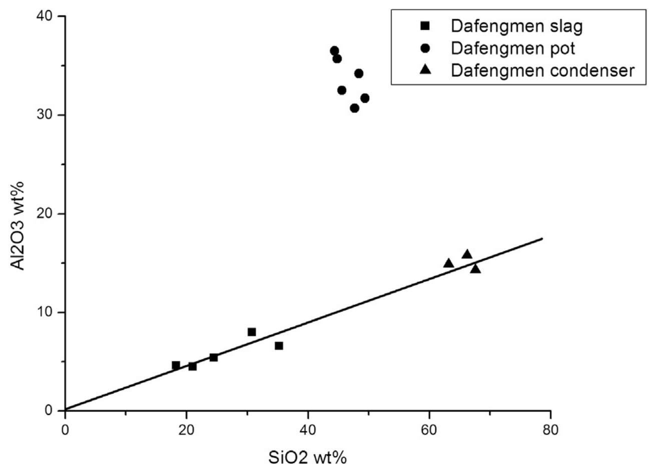

Fig. 10. The SiO_2 and Al_2O_3 contents in the slag, pot and condenser samples from Dafengmen. Note the linear correlation of the SiO_2 and Al_2O_3 contents of the slag and condenser samples.

analytical study also highlights the different technical efficiency of these two groups of sites.

Ideally, one might assess technical efficiency by calculating the proportions of zinc metal produced relative to the amount of zinc contained in the ores. However, we do not know the typical zinc content in the ores, the quantity of ores that went into each retort load, or how much zinc was produced per retort. As an alternative proxy, one can look at how much zinc was lost, i.e. zinc that was contained in the ores but did not make it to the final ingot. This is an approach that, while not without its problems, has been used in other archaeometallurgical studies, assessing copper or iron losses in the slag (e.g. Rehren et al., 2007; Pryce et al., 2010).

For zinc distillation, there are three kinds of zinc losses. One is the loss of zinc into the slag which was caused by the incomplete reduction of zinc minerals in the ores. An estimate of the amount of zinc lost in this way may be obtained by measuring the zinc contents of the slag, and the quantity of slag produced per smelt. The loss of zinc to the slag is affected by several parameters, such as: the purity of ores; an excess of sulphur (either from the ores or the coal) combining with the zinc; ore grain sizes being too large or too small; an insufficient amount of reducing gases in the retort; or perhaps the process temperatures or duration not being appropriate. Our study indicates that the zinc ores used at Dafengmen contained more types of impurities that those at the Fengdu sites. They contained more sulphur-bearing minerals (zinc sulphide and barite), which generated more sulphur to trap zinc in the slag. They also contained relatively higher amounts of iron oxides and other impurities (lead/copper minerals), which would consume reducing agents. The charge may also have had larger ore grain sizes, as indicated by the large lump in SDB12. Furthermore, there was a smaller proportion of reducing agents inside the Dafengmen retorts, which would make the reduction less efficient. In addition, the process temperature at Dafengmen may have been lower than that at the Fengdu sites.

Secondly, zinc vapour would be lost as it penetrated into the ceramic fabrics of the retorts, such as pots, condensers and pockets. Although the taller and slimmer Dafengmen pots were made of highly refractory clay, they were made very porous and probably prefired in a relatively low temperature, so they were not resistant to the zinc attack. If such pots were reused, the cumulative fluxing effect of zinc contamination would lead to collapse. It thus appears that the Dafengmen pots could not be reused, otherwise they would have collapsed. As such, the higher levels of zinc in the Dafengmen pot fabrics could also indicate more zinc loss into pots per smelt. Since condensers are also not likely to have been reused, their zinc levels can also be informative. As no pockets were found at Dafengmen, zinc losses into these retort parts cannot be quantified.

Thirdly, an excessive temperature or an insufficiently reducing atmosphere in the consenser could result in the oxidation of zinc and the escape of metal as a vapour into the air; however, this zinc loss cannot be easily evaluated from the production remains.

Obviously, any comparison of the zinc losses between sites using the above parameters can only be indicative. We do not know how much slag was left inside each retort per smelt and how many times a given retort was used. More importantly, we should not forget that efficiency is a relative parameter that should be assessed in each particular context – for example, by considering the costs of raw materials, fuel and labour, the value of products, etc. In addition, the sample analysed so far is relatively small and quite variable. However, even if only superficially compared, the remarkably higher zinc levels in the slag, pots and condensers from Dafengmen stand out next to those at the Fengdu sites (Fig. 11), and indicate higher zinc losses at the Qing site. This is even more significant if one bears in mind the extremely large numbers of such artefacts left behind by the zinc makers. It thus seems compelling that, on a technical basis, the later, Qing technology was less efficient than that documented at the Ming sites.

5.4. Broader contextualisation

The scale of production must have been very large from the estimated 250,000 tonnes of retort fragments and slag left in the Dafengmen valley. As the site was dated to the Qing period, it may have been one of the zinc factories documented in *Local Gazetteer of Shizhu* (RGALHS, 2009). If this is correct, the zinc factory at Dafengmen should have been set up in order to supply zinc to the Sichuan provincial mint, which was located in Chengdu, 350 km west of Chongqing; it could have been capitalised and run by private merchants, while supervised and taxed by the government, who set up two local offices nearby to administer mining and smelting affairs. The factory was either composed of a number of production units centred around the furnaces, just like the Fengdu sites; or spatially divided into different working areas. Without further historical evidence and archaeological information, the workshop layout and labour division within the factory remain unclear.

The Dafengmen site was near the zinc deposits of the Laochangping region, and it was situated within the Qiyao Mountain Coalfield (Fig. 1), which ran from the southwest to northeast of the Qiyao Mountain, and produced mainly bituminous coal and anthracite. The coal seam at Xiaofengmen, near Dafengmen, was in the weathering zone, about 0.5 m thick, and therefore suitable for opencast mining (Sichuan Geology Bureau, 1961). In addition, the coalfield might also have provided kaolinitic clay for making the pots of the retorts. Therefore, in terms of the procurement and transport of raw materials, the location of Dafengmen site was more suitable than the Fengdu sites, which were much further away from both the zinc and coal sources (Zhou et al., 2012).

Although the location of Dafengmen seems ideal, the technology of zinc distillation was less technically efficient than those practiced at the Fengdu sites. Craftspeople at Dafengmen smelted zinc ores with more impurities, and mixed the ores with a lower proportion of reducing agents in less-than-ideal retorts, leading to greater losses of zinc. It seems that they were trying to save on materials and labour costs. This would be consistent with the recorded decline of zinc production at Baishaling, one zinc factory in Laochangping, due to the growing availability of cheap zinc from Guizhou in the market, as documented in *Local Gazetteer of Shizhu*

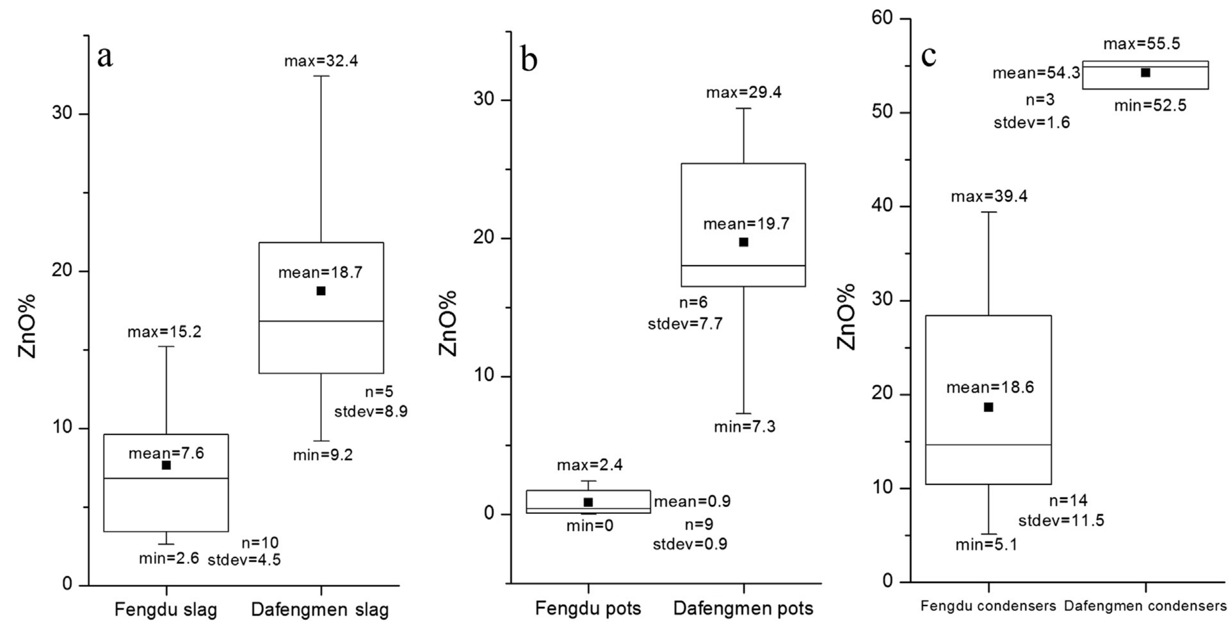

Fig. 11. Box and whisker charts of zinc oxide levels (wt%) of the slag (a), pot (b) and condenser (c) samples from the Fengdu sites and the Dafengmen site. All the zinc oxide values were bulk compositions of the slag, pots and condensers (max = maximum value; min = minimum value; mean = average value; *n* = number of samples; stdev = standard deviation).

(RGALHS, 2009). Guizhou was the largest zinc production area in Qing China and Guizhou zinc was supplied to the central mint and also provincial mints (Ma, 2010a, 2010b, 2011). If zinc produced locally could not compete with the cheap Guizhou zinc, then the production could not bring in profits or even cause serious losses. Under such circumstances, it appears that the smelters would have tried to manage the production by keeping down the costs. The result was a distillation process that, even if taking place in a theoretically ideal location, was not technically efficient, with great metal losses. Therefore, the zinc yield at Dafengmen would have been lower than that of the sites in Fengdu.

6. Conclusion

The analyses of production remains from the Dafengmen site have allowed a detailed reconstruction of zinc distillation technology employed in Shizhu during the Qing Dynasty. The zinc smelting site used elongated, tapering, flat-bottomed retorts composed of ceramic pots, condensers, pockets and iron lids. The pots were made of kaolinitic clay mixed with rock fragments. Although the raw materials were very refractory, they were not prefired to temperatures high enough to maximise the performance characteristics of the fabrics. The retorts were charged with oxidic zinc ores containing some impurities and a low proportion of reducing agents. The zinc ores were reduced at high temperatures and under strongly reducing conditions; the zinc vapour formed and entered the upper, cooler condensation area.

In comparison with the earlier Fengdu sites, the Dafengmen site shows a technology that had access to potentially better resources (kaolinitic clay for long pots, ores from nearby lead-zinc deposits and coal from nearby coal deposits), but which did not exploit their full potential by making more refined, higher fired pots and exploiting ores of better grades from the same deposits. This suggests that the technical knowledge existed (where to find good design and clays for retorts, and good ores), but the smelters probably operated at a time of stringent constraints on resources, labour and capital in the Qing Dynasty.

Overall, the case studies presented in this paper and the previous paper (Zhou et al., 2012) provide high-resolution reconstructions of the technology and organisation of zinc production in the Ming and Qing Dynasties and allow comparisons based on varying regional and temporal contexts. Production remains from more zinc smelting sites in Chongqing and other parts of China could be analysed and interpreted following the theoretical framework and methodology established. Analysing production remains from archaeological sites coupled with historical research will hopefully contribute to a comprehensive picture of zinc distillation technology in China – one that appreciates a diversity of technical solutions but also the sociocultural contexts in which they were embedded.

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