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Distilling zinc with zinc sulfide ores: The technology of Qing Dynasty zinc production in Guiyang, Central South China

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ABSTRACT

It is difficult to distill metal zinc partly due to the reduction temperature of zinc oxide ores close to the boiling point of metallic zinc. The treatment of zinc sulfide ores is more complicated since they have to be roasted before smelting. Previous archaeometallurgical studies on zinc smelting technology in China mainly focus on the distillation of zinc oxide ores. This paper, for the first time, presents analytical results of archaeological evidence about the distillation of zinc sulfide ores in Guiyang in southern China dated back to the Qing Dynasty (CE 1636–1912). The smelting remains including ores, distillation retorts and slags, especially the roasting hearths and zinc calcine firstly discovered and confirmed in zinc smelting sites were characterized comprehensively by p-XRF, OM, SEM-EDS and XRD. It was revealed that the zinc smelting technology in the Tongmuling site and the Doulingxia site was mainly based on the distillation of zinc sulfide ores, which should be oxidized by a lengthy roasting processing at the lower temperature before the distilling. In order to enhance the condensation efficiency, the height of the condensers in the distillation retorts has been significantly increased. Most of the zinc products were ordered by the Minting sub-Bureau of Baonan in Changsha.

1. Introduction

The development and evolution of metallurgy technology play a crucial role in studying political and economic development in ancient China. Although zinc has been known for some three thousand years in the form of brass, the preparation of zinc metal itself is of comparatively recent origin (Craddock, 1987). It is believed that the most important reason is that the reduction temperature of zinc oxide is quite close to the boiling point of metallic zinc. Therefore, if the metallic zinc cannot be condensed and recovered in time, it will quickly volatilize again and be re-oxidized once it is in contact with air (Hu and Han, 1984). In order to successfully produce the metallic zinc, advanced zinc reduction and distillation techniques rather than conventional smelting furnaces could be a big challenge (Craddock and Zhou, 2003). Before the establishment of an industrial scale of zinc smelting in Europe in the 18th century, only India and China can produce metallic zinc on a large scale (Craddock, 2009; Boni, 2003).

As known, zinc ores used in pyrometallurgical smelting are mainly divided into two categories. One is nonsulfide, mainly referring to zinc oxide ores, which include smithsonite (calamine, $ZnCO_3$) and hemimorphite [$Zn_4Si_2O_7(OH)_2$ (H_2O)]. The other is sulfide, mainly referring to sphalerite (ZnS). Zinc oxide ores can be directly reduced and distilled by mixing with reducing agents in the retorts. In contrast, the treatment of sulfide zinc ores is more complicated since they have to be roasted before smelting. From the perspective of distribution, the oxidized zinc zone is often located on the surface of the deposit (Boni, 2003; Hitzman et al., 2003). It should be emphasized that in China, and even in the world, the reserve of zinc sulfide minerals is much larger than that of zinc oxide (Liu et al., 2017). Therefore, the mastery of smelting technology of zinc sulfide ores is undoubtedly significant.

We would like to mention that ancient Chinese zinc pyrometallurgical technology is mainly based on the smelting of oxidized zinc ores. According to the literature, the earliest recording in the *Tian Gong Kai Wu* printed in 1637 indicates that zinc is extracted from calamine (Song and Zou, 2013). Based on the investigations of traditional Chinese zinc smelting workshops, until the late 20th century, zinc ores used to extract zinc include mainly smithsonite and hydrated zinc carbonate, which was found in the karst limestone hills of Western Central China, including the provinces of Yunnan (Zhou, 1997), Guizhou (Xu, 1986) and Sichuan (Craddock and Zhou, 2003; Mei,

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1990). In recent years, several large-scale zinc smelting ruins of the Ming (CE 1368–1644) and Qing (CE 1636–1912) Dynasties were discovered in Chongqing, southwest China (Liu et al., 2007; Li et al., 2013a,b). The archaeological evidence and scientific analysis indicated that the ores used in these sites were nonsulfide, including smithsonite and hemimorphite (Zhou, et al., 2012; Zhou, et al., 2014). Combined with the literature, the investigations of traditional zinc-smelting technology and the archaeological evidence, at present, the distillation technology of zinc oxide ores has been reconstructed in detail, and the principle of smelting has been elaborated (Zhou, et al., 2012; Zhou, et al., 2014; Luo, et al., 2016). However, the research on the smelting technology of zinc sulfide ores is distinctly absent.

The existing literature shows that ancient India is considered as the earliest country in which metallic zinc was produced. Archeological evidence shows that the distillation of zinc originated ~1000 years ago on the Aravalli Hills of Rajasthan in Zawar in the north-west of India (Craddock et al., 1983; Craddock, 1997). In Zawar, zinc ores consist mainly of sulfide minerals, including sphalerite (ZnS), galena (PbS) and pyrite (FeS_2) (Willies et al., 1984). The scientific analysis showed that sulfur content detected in the residue was as low as 0.5 wt%, indicating that the ores should have been fully roasted before smelting (Freestone et al., 1990). However, archaeologists have as yet found no remains of any kilns or ovens suitable for the roasting (Craddock, 1987).

Since September 2015, a comprehensive field archaeological survey was carried out on a large scale of ancient zinc-smelting sites in Guiyang County, Hunan Province. The Tongmuling site, as one of the well-preserved sites, was excavated proactively (see Fig. 1). Due to its large scale, proper preservation and complete structure, the evacuation of the Tongmuling site was awarded as one of the Top Ten Archaeological Discoveries in China in 2016, which is the highest government award in archaeology in China. During this excavation, a plenty of important remains such as zinc smelting furnaces, house foundations, roasting hearths and refining stoves were discovered. Additionally, a series of remains, including smelting retorts, ceramics, slags, and several copper-based coins were unearthed. Based on the unearthed ceramics, the "*Qianlong Tongbao*" coins and the typology of the retorts, it was deduced that this site should be established in the Qing Dynasty (CE 1636–1912) (Mo et al., 2018). Additionally, during the field survey of the Doulingxia site (Fig. 1), which is another site near the Tongmuling site, a basket of reddish-brown powders was found. As confirmed by the laboratory work, these powders were zinc calcine, a by-product of the roasted zinc sulfide ores. Compared with the zinc-smelting sites found in Chongqing (Zhou et al., 2012; Zhou et al., 2014), the sites in Guiyang County showed their uniqueness with a large number of cylindrical roasting hearths and zinc calcine, although there were similarities in terms of the rectangular smelting furnaces and the distillation retorts.

The smelting remains from the Tongmuling site were initially studied by Zhou et al. (2018). Based on the analytical results of the distillation retorts and the residual slag inside the pots, they confirmed that the ores used for smelting in the Tongmuling site included mainly zinc sulfide contained ores, which were calcined before their smelting (Zhou et al., 2018). However, it is still necessary to conduct a more systematic analysis of the valuable remains, especially the ores, slag tipped out from the pots, roasting hearths, and zinc calcine. Based on archaeological evidence, combining with recordings on the traditional zinc smelting and materials characterization results, the goal of the present investigation is to clarify and reconstruct the technologically important distillation and metallurgy technology of zinc sulfide ores of the Qing Dynasty in Guiyang, Central South China.

2. Material and methods

2.1. Material

Except for the zinc calcine samples from the Doulingxia site, the other samples were collected from the Tongmuling site, including ores, pots, condensers, lids, pockets, crude zinc, and slag. The specific information of the samples is shown in Table 1.

2.2. Methods

In the present investigation, the portable X-ray fluorescence spectrometer (p-XRF), optical microscope (OM), scanning electron microscope spectrometer coupled with energy dispersive spectroscopy (SEM-EDS), and X-ray diffractometer (XRD) were used to analyze the remains. The p-XRF (Oxford X-met 7500) was used for on-site qualitative analysis during the excavation. The results provided a scientific basis for judging the components and structure of the remains. The analysis mode was Minning_LE_FP. The data were chosen as the average value of twice testing results for 60 s.

In contrast, the quantitative analysis was carried out in the laboratory. The ores, pockets, and the bulk crude zinc, which are relatively rarely unearthed in the sites, were analyzed by non-destructive

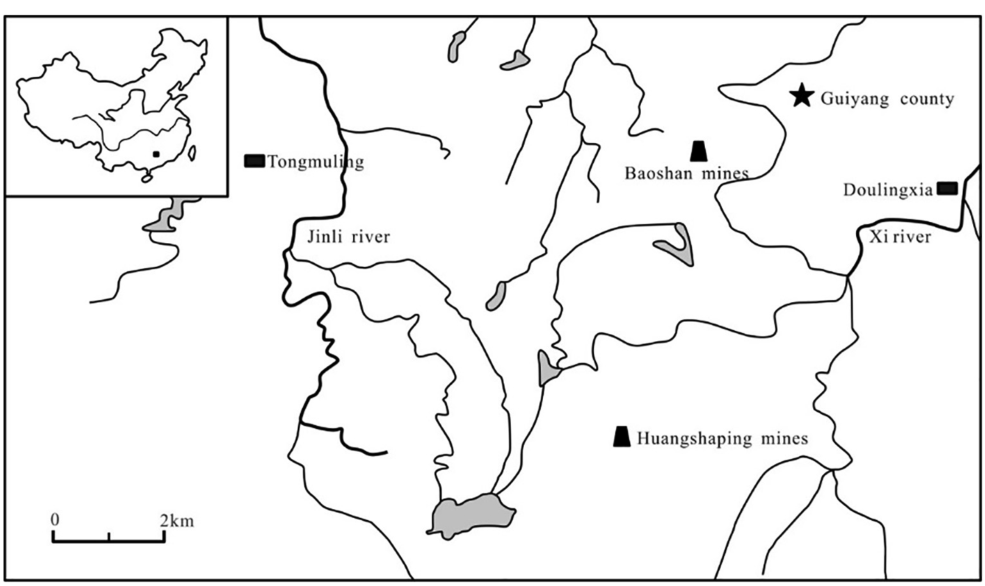

Fig. 1. Map showing the location of the zinc smelting sites of Tongmuling and Doulingxia, near the Baoshan and Huangshaping mines.

Table 1
Sampling information on the important remains unearthed in Guiyang.

Sample type	Quantity	Comments
Ores (TO)	5	Mostly excavated near the roasting hearths with different size and shape.
Distilling pots (TP)	11	Three unused pots and eight used pots.
Condensers (TC)	6	Badly damaged, leaving only a few parts of the rims.
Condensation lid (TL)	1	Iron texture with severe corrosion.
Pockets (Tp)	3	Two of them are relatively intact, and the other is remaining on the surface of the unearthed coarse zinc.
Crude zinc(TCZ)	1	The colour is light blue-grey, and the texture is loose and brittle, with some condensation pockets remaining on the lower end.
Granular slag (TS)	6	The reddish-brown slag particles collected in the ruins
Vitrified slag (TSP)	7	The slags attached inside the used pots.
Zinc calcine (DZC)	1	Reddish-brown powder with small particles.

and micro-destructive techniques. In contrast, for pots, condensers, slag and zinc calcine, which can be extensively collected in the sites, multiple samples were characterized in order to obtain more comprehensive information.

SEM-EDS was used to analyze the pots, condensers, crude zinc block, pockets, slag and zinc calcine. For the only two well-preserved pockets (Tp1 and Tp2), the full pockets were directly bonded to the sample stage for analysis to avoid their destruction. For the fine powdery samples, including the granular slag and zinc calcine, the samples were dried and directly pasted on the conductive adhesive. Before testing, the unstuck particles were blown out by a powerful air gun. For the other bulk samples, they were cold-inlaid with epoxy resin and polished after solidification. The granular slags were also cold-inlaid with epoxy resin to observe the cross-section of the samples. The surfaces of the samples were sprayed with gold after cleaning and drying. The instrument used for the analysis was a Zeiss EVO MA 10 tungsten filament scanning electron microscope equipped with a Brooke Xflash 6130 energy spectrum probe. The testing was conducted with an accelerating voltage of 20 kV and a working distance of 10.5 mm. Sodium was neglected in all analyses, as both Na K_α and Na K_β peaks overlap with the Zn L_α peak. The nominal detection limit of EDS is about 0.1%, but results below this limit are presented for indicative purposes.

The mineralogical components were determined by XRD. The instrument was an Ultima IV equipped with Cu K_α radiation and secondary graphite monochromator. The tube voltage and tube current were 40 kV and 40 mA, respectively. The scanning angle range (2θ) was in a range from 3° to 75° with a scanning speed of 8°/min.

3. Results

3.1. Ores

A few ores with different size and shape were unearthed from the Tongmuling site (Fig. 2). Most of the ores were excavated from nearby the roasting hearths. According to the analytical results (Tables 2 and 3), the five ores can be divided into two categories. One is mainly composed of oxidized minerals, such as hematite, with a quite low amount of ZnO. The other is mainly sulfide minerals, such as sphalerite (ZnS), pyrite (FeS_2), and galena (PbS).

In addition to low content of sphalerite, the main component in the sulfide ore TM02 is galena. However, zinc content in the ore TM02 is very low, only 3.8 wt%. In contrast, the sulfide ores TM03 and TM04 are of similar chemical composition (Table 2). Both are rich in Fe_2O_3, Zn, and S. It is noticeable that a large amount of sphalerite and pyrite can be found in the ores TM03 and TM04. The zinc content in TM03 and TM04 is 12.34 wt% and 15.28 wt%, respectively. Besides, the content of Fe_2O_3 is very high as well, 45.69–56.78 wt%. In contrast, the content of galena is much lower, only 1.81–2.86 wt% of Pb contained in the ores. It is believed that the ores TM03 and TM04 represent the main ore types that are used to extract the zinc in the Tongmuling site.

As shown in Fig. 3(a), the content in volume percentage of sphalerite, pyrite, and galena in the ore TM04 is ~17 vol%, ~12 vol%, and

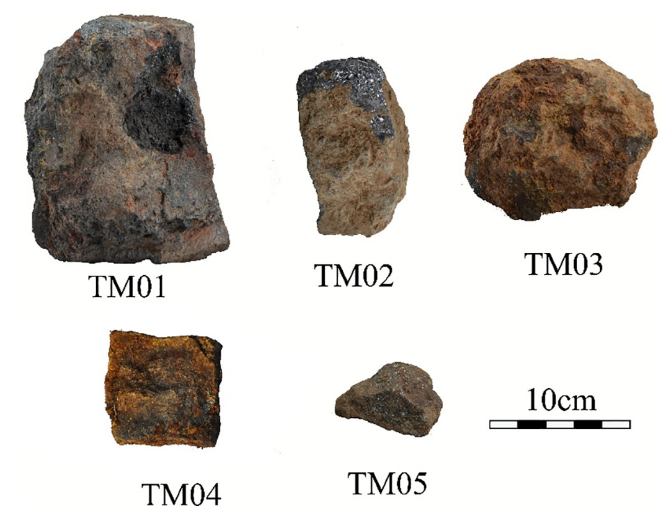

Fig. 2. The ores unearthed in the Tongmuling site.

~8 vol%, respectively. They were disseminated in an impregnated substrate composed of non-metallic minerals. The intergrowth of galena and sphalerite are usually distributed on the edge of pyrite, and some of them are surrounded by pyrite (Fig. 3(b)). The composition and the symbiotic relationship of the metallic minerals are highly consistent with the characteristics of the deposit in the Baoshan-Huangshaping mining areas (Zhang, 2007; Wei et al., 2006), indicating that the ores should be mined from the local mining belt (Luo et al., 2018).

3.2. Retorts

Among the debris in the Tongmuling site, the most common remains are jar-shaped pots. In addition, a small number of relatively complete condensers, lids, two pockets and a block of bulk crude zinc were discovered in the site, as shown in Fig. 4. These remains could be helpful for the reconstruction of the retorts for zinc distillation as archeological evidence. Analytical results of the samples related to the retorts from the Tongmuling site are presented as below.

As shown in Fig. 4, the pots are of mostly flat-bottom and bulging cylindrical pottery jars. The height is about 32 cm. The diameter of the rim, maximum diameter, and bottom is about 6.0 cm, 8.5 cm, and 7.0 cm, respectively. The pots keep the trace of the wheel-throwing with no glaze on the surface. As indicated in the microstructural SEM image (Fig. 5(a)), the unused pots are highly sintered with a large number of fine quartz particles and pores in the matrix. The unused pots are composed of 53–60 wt% SiO_2, 20–23 wt% Al_2O_3, 12–16 wt% FeO, and low levels of alkali and earth alkali oxides (Table 4). As summarized in Table 5, the phase composition results suggest the appearance of cristobalite (SiO_2) and mullite ($Al_6Si_2O_{13}$). This implies that the firing temperature of the pots should be above 1200 °C (Arahori and Suzuki, 1987).

Comparing with the unused pots, the microstructure and

Table 2
p-XRF analysis results of ores from the Tongmuling site, normalized to 100 wt%. “n.d.” means the concentration is below the detection limit.

Sample No.	Content (wt.%)												
	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CuO	As_2O_3	S	Zn	Pb
TM01	1.56	2.70	8.92	0.50	0.39	0.53	n.d.	82.00	0.03	0.19	2.44	0.29	0.45
TM02	1.20	10.75	17.06	0.97	0.48	0.70	0.40	4.87	0.41	4.93	17.51	3.8	36.92
TM03	n.d.	3.98	9.25	0.81	1.10	0.22	0.20	56.78	0.24	0.44	11.77	12.34	2.86
TM04	1.74	5.99	11.29	2.71	0.29	0.4	0.86	45.69	0.09	1.59	13.85	15.28	1.81
TM05	1.49	7.77	7.83	0.24	0.09	0.29	0.03	78.92	0.12	0.21	1.62	0.44	0.94

Table 3
XRD analysis results of the ore samples from the Tongmuling site.

No.	Main phases	Mineral types
TM01	Hematite (Fe_2O_3), Quartz	Oxidized
TM02	Galena (PbS), Sphalerite (ZnS), Anglesite ($PbSO_4$), Pyrite (FeS_2)	Sulfide
TM03	Sphalerite, Pyrite, Galena, Anglesite, Siderite ($FeCO_3$)	Sulfide
TM04	Sphalerite, Pyrite, Phlogopite ($KMg_3(Si_3Al)O_{10}(OH)_2$), Goethite (FeO(OH))	Sulfide
TM05	Hematite, Quartz	Oxidized

composition of the used pots have not been changed significantly. Only a small amount of zinc, lead and sulfur intrusion in the matrix of some pots, which leads to a specific increase in the content of ZnO, PbO, and SO_3 (Table 4). The used pots were externally covered by clay wraps, which appear as a dense and bloated layer, made of fine clay with scarce inclusions and now heavily vitrified (Fig. 5(b)). It should be pointed out that there are more willemite (Zn_2SiO_4) and gahnite ($ZnAl_2O_4$) in the wraps than in the matrix of the pots, so that the ZnO content in the wraps significantly increases, up to 36 wt% (Table 4).

Most of the condensers were incompletely attached to the rims of the used pots, indicating that they had been destroyed before abandonment. Only two relatively well-preserved trumpet-shaped condensers were found with an upper rim diameter and a height of ~12 cm and ~15 cm, respectively. The condensers were jointed to the rims of pots by clay (Mo et al., 2018). The interfaces between condensers and pots were well combined with no division surface (Fig. 5(c)), indicating that the condensers were made and connected to the rims of the pots in the smelting workshop. A large amount of gahnite and willemite can be found in the matrix of the condensers as well (Fig. 5(c)). As shown in Table 4, the content of ZnO is in a range of from 20 wt% to 29 wt%.

A relatively complete block of crude zinc with residual condensation pocket was found inside one of the well-preserved condensers. The main phases of the crude zinc block included zinc oxide and a large amount of hydrozincite ($Zn_5(OH)_6(CO_3)_2$) (Table 5), indicating that the crude zinc has been severely oxidized. This oxidation was most likely formed by the reaction of zinc vapor with the water vapor and carbon dioxide during distilling. However, it is possible that the missing crude zinc could have been oxidized after burial.

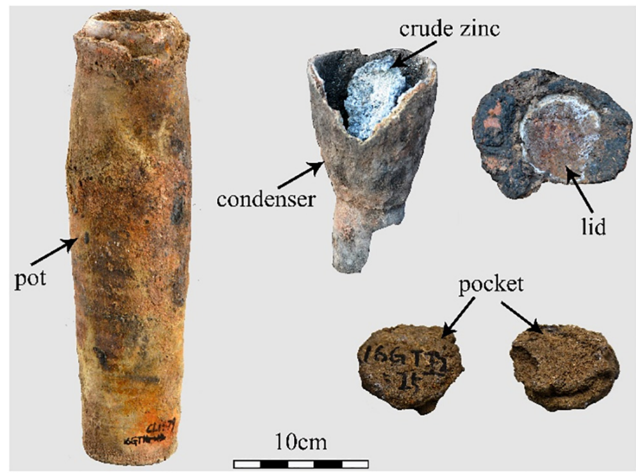

Fig. 4. The remains related to the retorts unearthed in the Tongmuling site.

Only two pockets with relatively complete preservation were discovered (Tp1 and Tp2) at the Tongmuling site. One of the pockets is of subcircular form, and the traces showing it contacted with the rim of a pot can be observed (Fig. 4). The other pocket is a circular sheet with a slightly convex side. The microstructure of the pocket (Tp3) is shown to be similar to that of the condensers. Both are porous with a large amount of willemite and gahnite in the matrix (Fig. 5(d)). However, the pocket is denser with smaller holes than those of the condensers. The EDS results show that no noticeable zinc residue remained on either side and the ZnO content is significantly lower than that of the condensers and the residue pocket. It indicates clearly that neither of the two pockets has been used. Besides, the composition of the pockets is

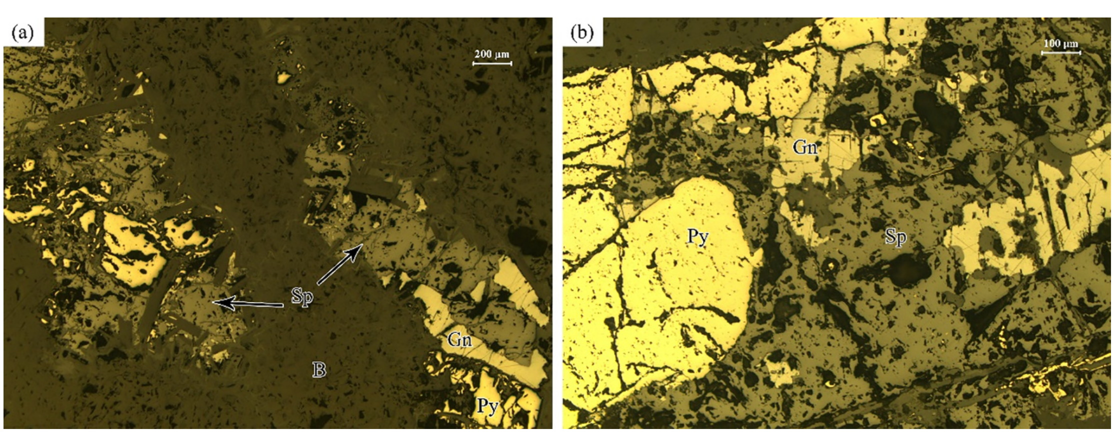

Fig. 3. The single polarized images of the ore TM04: (a) Sphalerite (Sp), galena (Gn), and pyrite (Py) are disseminated in an embedded substrate composed of non-metallic minerals (B); (b) Sphalerite and galena are intergrowth and distributed along the edge of pyrite.

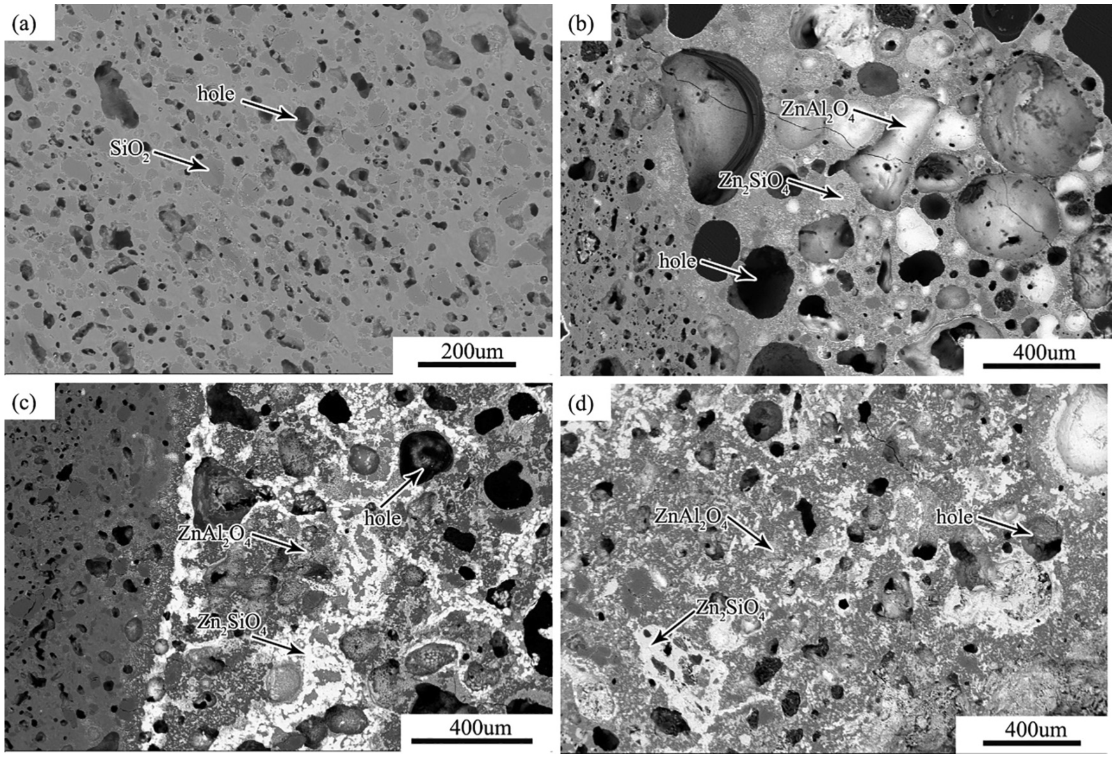

Fig. 5. Backscattered electron images of (a) unused pot TP02; (b) clay wrap on the outside of the used pot TP4; (c) interface between the rim of pot (left) and condenser (right); (d) residual pocket at the lower end of the crude zinc block.

significantly different from that of the condensers. The content of FeO and PbO in the pockets is notably higher than that of the condensers, but the ZnO content is much lower. The detected ZnO, PbO and FeO could stem from the raw materials of the condensation pockets.

Five iron condensation lids were discovered in the Tongmuling site as well. All of the lids were severely corroded. The iron lids are of subcircular shape with a diameter of about 12 cm, which is similar to the size of the upper rims of condensers. The clay and white zinc oxide particles appear on the surface of the lid, and the traces of contact with the rims of the condensers can be observed (Fig. 4). It should be noted that there is a structural gap at the edge of the lid as reported (Mo et al., 2018).

Table 4
EDS results of the samples related to the distilling retorts, in weight percent, normalized to 100 wt%. "n.d." means "not detected".

Description	No.	Oxide contents (wt%)											
		MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	TiO_2	MnO	FeO	CuO	ZnO	PbO
Unused pots	TP01	n.d.	22.5	55.9	1.5	3.5	0.2	2.8	0.0	12.4	0.4	0.0	0.9
	TP02	0.4	23.0	53.8	1.0	2.2	n.d.	2.3	0.3	16.1	0.2	0.3	0.3
	TP03	0.3	20.1	59.6	n.d.	2.2	n.d.	3.2	0.5	13.8	n.d.	n.d.	0.3
Used pots	TP1	0.2	19.3	54.3	2.4	3.1	1.3	2.8	1.2	12.4	n.d.	2.8	0.3
	TP2	0.4	20.2	54.3	1.2	3.2	0.2	3.2	0.2	12.9	0.1	2.9	1.2
	TP4	0.5	20.0	59.2	0.3	3.5	0.2	2.4	0.1	10.0	0.5	0.5	2.8
	TP5	0.1	9.3	63.7	0.5	1.8	0.1	2.1	0.6	14.7	1.3	5.2	0.7
	TP6	0.6	21.3	56.5	3.5	2.6	n.d.	3.2	0.4	10.0	0.4	0.4	1.3
	TP7	n.d.	19.0	55.8	3.0	3.3	0.3	2.7	0.1	14.7	0.5	0.1	0.7
	TP8	0.2	18.7	58.9	n.d.	3.0	n.d.	3.6	n.d.	11.2	n.d.	4.3	n.d.
Clay wraps	TP1-3	n.d.	18.7	45.1	n.d.	1.9	0.2	2.2	0.5	7.1	0.4	22.6	1.3
	TP2-3	0.2	18.4	57.9	0.2	2.2	0.4	1.8	0.2	6.1	0.2	11.7	0.8
	TP4-3	0.2	17.1	44.4	1.2	2.7	0.4	1.4	0.2	22.2	0.3	9.2	0.6
	TP7-3	0.1	14.0	39.2	0.1	1.4	0.3	1.6	0.5	5.8	0.1	36.8	n.d.
Condensers	TC1	n.d.	13.5	43.3	0.3	1.3	0.6	1.8	1.6	10.7	0.1	26.3	0.5
	TC2	n.d.	14.8	44.8	0.3	1.1	0.7	2.0	0.4	10.8	0.2	24.4	0.5
	TC3	0.1	13.7	44.6	0.5	1.6	0.5	1.7	0.3	10.8	0.2	25.3	0.7
	TC4	n.d.	14.8	47.4	0.2	1.5	0.5	2.2	0.5	11.2	0.2	20.8	0.7
	TC5	n.d.	13.1	45.9	0.2	0.7	0.3	1.6	0.4	10.4	0.2	27.0	0.2
	TC6	n.d.	12.9	43.7	0.5	1.2	0.4	1.9	0.4	9.6	0.1	28.7	0.6
Crude zinc	TCZ1	3.6	2.2	11.9	3.3	n.d.	0.2	n.d.	n.d.	0.4	n.d.	78.3	0.2
Pockets	Tp1-1	n.d.	23.0	34.8	n.d.	1.8	0.7	2.2	1.4	19.3	1.0	9.5	6.2
	Tp1-2	n.d.	16.6	36.1	0.1	2.7	2.6	1.7	0.9	20.9	1.0	8.1	9.3
	Tp2-1	n.d.	18.0	44.5	0.4	2.2	0.7	2.2	0.2	19.5	0.2	5.7	6.4
	Tp2-2	n.d.	21.0	40.4	0.2	2.4	1.1	2.3	0.4	17.5	0.3	8.9	5.5
	Tp3	n.d.	11.0	38.8	0.3	2.6	1.3	1.0	1.4	6.2	0.1	35.5	1.9

Table 5
XRD phase identification results of the samples related to the distilling retorts.

Sample No.	Sample type	Main Phases
TP01	Unused pot	Quartz (SiO_2), Cristobalite (SiO_2), Mullite ($Al_6Si_2O_{13}$)
TP1	Used pot	Quartz, Cristobalite, Mullite, Willemite (Zn_2SiO_4), Gahnite ($ZnAl_2O_4$)
TC1	Condenser	Gahnite, Willemite, Quartz, Tridymite (SiO_2)
TCZ1	Coarse zinc	Zinc oxide (ZnO), Hydrozincite ($Zn_5(OH)_6(CO_3)_2$), Quartz, Willemite (Zn_2SiO_4), Hemimorphite ($Zn_4Si_2O_7(OH)_2H_2O$), Gahnite

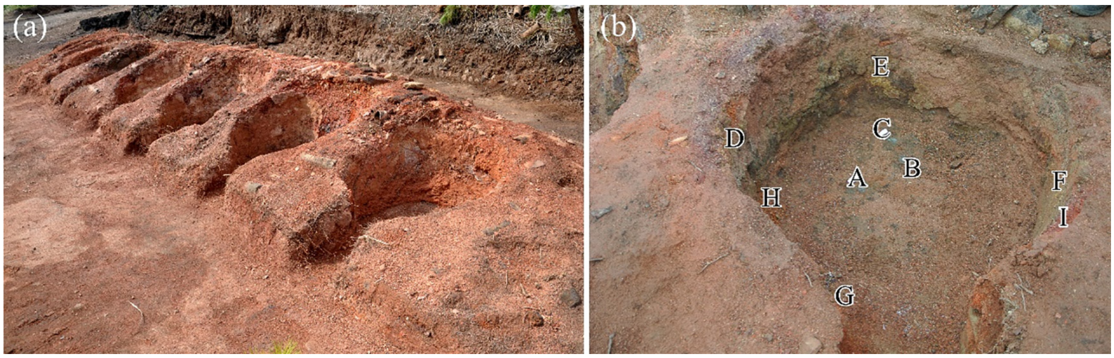

Fig. 6. The Cylindrical roasting hearths excavated in the Tongmuling site: (a) one of roasting platforms; (b) testing points of p-XRF analyses.

3.3. Roasting hearths and zinc calcine

Six groups of roasting hearths were discovered in the Tongmuling site. Each group consists of 4 or 8 cylindrical hearths arranged in one line. The diameters of the roasting hearths are ~0.8 to 1.0 m, and the heights are ~0.6–0.9 m (Fig. 6). As shown in the p-XRF analytical results (Table 6), the on-site measured content of Fe_2O_3, ZnO and PbO in the roasting hearth is significantly higher than that in the typical soil. However, a small amount of SO_3, MnO, CuO, and As_2O_3 can be found in several on-site testing points. These oxides are mainly introduced from the calcined ores, indicating that the ore calcined in the furnace should contain a considerable content of S, Fe, Zn and Pb, accompanied by a small amount of Mn, As and Cu containing minerals.

In addition, during the excavation of the Doulingxia site, two similar groups of the roasting hearths and a basket of well-preserved reddish-brown powders were found. The XRD patterns in Fig. 7 show that the powders are mainly composed of franklinite ($ZnFe_2O_4$), cerussite ($PbCO_3$), willemite (Zn_2SiO_4), hemimorphite [$Zn_4Si_2O_7(OH)_2H_2O$], and a small amount of anglesite ($PbSO_4$), quartz (SiO_2), hematite (Fe_2O_3) and fluorite (CaF_2). Among them, franklinite known as zinc calcine is a product of roasted iron-rich sphalerite (Dou, 2003; Li, 2013). This indicates that the powders should have been calcined. These results are consistent with those of the discovered ores mainly composing of sphalerite, pyrite, and galena.

Moreover, the calcine contains 4.69 wt% of PbO, 3.6 wt% of MnO, and 2.15 wt% of As_2O_3, respectively (Table 7). However, the content of sulfur is too low to be detected in the case of area-scanning analysis. The sulfur only can be detected by the micro-analysis technique in several particles. The structure of sulfur contained particles is denser than that of the other particles (Fig. 8). It is possible that they are the incompletely calcined minerals of sphalerite or zinc sulfate. Except for a

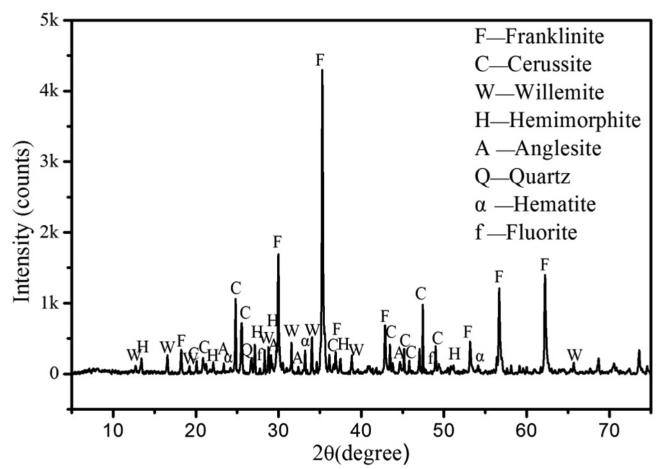

Fig. 7. XRD patterns of the zinc calcine (DZC-1) showing that the main phases include franklinite, cerussite, willemite, hemimorphite, and a small amount of anglesite, quartz, hematite and fluorite.

Table 6
p-XRF analysis results of one of the roasting hearths from Tongmuling site, normalized to 100 wt%. “n.d.” means “not detected”.

Point	Oxide contents (wt%)												
	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CuO	ZnO	As_2O_3	PbO
A	8.34	9.69	0.55	n.d.	n.d.	0.15	0.14	2.05	6.47	2.49	48.89	1.07	20.16
B	10.39	10.53	0.43	1.70	n.d.	0.11	n.d.	1.34	4.83	0.84	66.34	0.83	2.65
C	2.85	11.45	0.21	n.d.	n.d.	0.11	n.d.	2.50	9.14	1.01	66.60	n.d.	6.13
D	11.85	19.94	0.53	n.d.	0.78	0.27	1.20	0.30	11.13	0.24	19.10	1.33	33.32
E	28.65	20.89	0.58	6.08	1.24	0.15	1.23	0.14	10.50	0.29	21.96	0.93	7.37
F	20.36	26.88	0.46	2.17	1.56	0.17	0.95	0.47	8.01	0.40	32.16	0.53	5.88
G	12.59	27.48	0.86	1.18	1.35	0.26	2.10	0.09	38.11	0.20	3.84	n.d.	11.94
H	22.80	29.59	0.78	4.46	1.30	0.21	1.56	0.09	30.67	0.19	3.78	n.d.	4.58
I	19.41	32.72	0.58	3.75	1.24	0.20	2.44	0.12	25.46	0.14	6.40	0.41	7.15

Table 7
SEM-EDS results of zinc calcine from the Doulingxia site, in weight percent and normalized to 100 wt%. Analyses of areas 1–5 are shown in Fig. 8. "n.d." means "not detected".

Descriptions	Oxide contents (wt%)												
	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CuO	ZnO	As_2O_3	PbO
Mean (area-scanning)	n.d.	4.5	10.0	n.d.	2.4	0.5	0.3	3.6	47.9	0.7	23.3	2.2	4.7
1	n.d.	4.6	10.7	n.d.	0.2	1.0	0.2	5.9	47.2	0.6	27.6	n.d.	2.1
2	n.d.	1.4	2.2	n.d.	n.d.	0.2	0.4	3.0	34.4	0.1	18.8	2.3	37.1
3	n.d.	4.0	17.9	0.2	0.4	41.3	0.4	1.8	11.9	0.2	20.2	0.1	1.6
4	0.2	3.5	8.5	n.d.	0.1	1.8	0.4	4.8	51.2	0.8	24.9	0.2	3.9
5	n.d.	3.0	4.3	7.2	n.d.	n.d.	n.d.	2.9	36.2	1.8	44.7	n.d.	n.d.

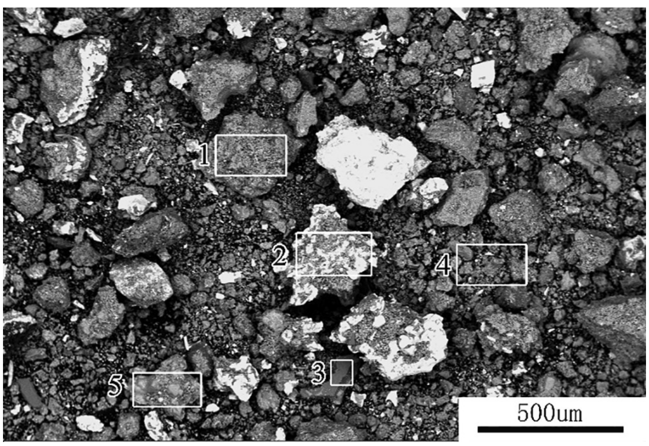

Fig. 8. Backscattered electron image of zinc calcine (DZC-1). The white particles are cerussite and anglesite, and some cerussite and anglesite particles are embedded in the franklinite.

small amount of $PbSO_4$, the sulfur content in the calcine is quite low as seen in Table 7 and no distinct phases of $ZnSO_4$ and ZnS can be observed. This clearly indicated that the ores had been almost fully roasted.

Furthermore, the zinc calcine particle size is quite small, generally less than 0.5 mm, indicating that it had been ground and sifted. However, most of the lead-containing mineral particles within this particle size cannot be separated effectively from the zinc-containing minerals as indicated in Fig. 8.

3.4. Slag

In the Tongmuling site, a large amount of scattered granular slag was found as well. The slag can be tipped out from the pots easily and does not affect the recycling of the pots. However, some slag could be converted into vitrified slag, which often adheres to the bottom of the abandoned pots (Fig. 9). The vitrified slags can aggravate the corrosion of pots and even affect the recycling of pots, so they should be avoided during distilling.

As seen in Table 8 and Fig. 10, the EDS results show that the oxide content in the different slags is significantly different. Especially, the content of FeO and PbO in the granular slag is much higher than that in the vitrified slags. In contrast, the content of MgO, SO_3, CaO, TiO_2 and ZnO is significantly higher in the vitrified slags.

The particles of granular slag are of irregular shape with a diameter of about 1–2 mm (Fig. 11(a)). The cross-section shows that the chemical composition and microstructure of the granular slags are quite heterogeneous (Fig. 11(b)). These particles are composed mainly of primary crystals rather than amorphous glassy phases. Additionally, quartz or cristobalite with cracks is present in the slag particles. A few inclusions of lead oxide, mostly anglesite, are embedded in the particles.

Fig. 9. The granular slag tipped out from the pots (left) and the slags attached inside the pot TP4 (right).

The primary oxide in the granular slag is FeO, with an average of 50.5 wt%. A notable amount of iron oxides are observed to be distributed in the holes and cracks as well as on the particle surface. Only a trace amount of metallic iron prills can be found in the glassy phases of some vitrified slag particles (Fig. 11(c)). Lead oxide phases and amorphous lead-manganese oxide can be found on the surface of the slag particles (Fig. 11(a)). As clearly demonstrated in the equilibrium curve (Hua, 2007), the reduction of the zinc smelting usually needs a more reducing atmosphere than that of the iron and lead smelting. It implies that the franklinite and lead oxide phases in the zinc calcine would be reduced during the distillation process. Therefore, when the distilling processing is finished, a large amount of metallic iron and lead should be present in the granular slag. However, given their burial in a humid environment in southern China, the metallic iron and lead in the slag can be easily oxidized.

It should be noted that the MnO content in the both slags is rather high, especially in the granular slag (Table 8). The manganese is present mainly in the lead oxide as solid solution. In contrast, its content (~2 wt%) in the metallic iron prills is very low. Additionally, manganese was detected in some unreacted sulfide mineral grains (Fig. 11(c)), containing ~34.9 wt% Zn, ~40.5 wt% Fe, ~16.2 wt% Mn, and ~3.7 wt% S. Combined with the result of the MnO content in the zinc calcine (Table 7), it is likely that the manganese in the slag originates from the manganese minerals in the zinc sulfide ores.

The microstructure and composition of the vitrified slag are much different from that of the granular slag. It is noticeable that the oxide content in the vitrified slags can change in a wide range, especially for

Table 8
SEM-EDS results of the slags unearthed in the Tongmuling site, in weight percent, normalized to 100 wt%. "n.d." means "not detected".

Sample No.	Oxide contents (wt%)											
	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	TiO_2	MnO	FeO	CuO	ZnO	PbO
TS01	n.d.	8.7	15.9	n.d.	2.3	n.d.	n.d.	8.0	51.7	n.d.	3.7	9.7
TS02	0.1	10.5	18.7	n.d.	2.2	n.d.	n.d.	5.2	48.6	0.6	3.8	10.3
TS03	0.4	7.9	14.7	n.d.	3.3	n.d.	n.d.	11.1	40.3	1.2	4.1	17.1
TS04	0.1	9.1	13.6	n.d.	1.6	1.2	0.4	5.9	54.0	0.6	2.2	11.3
TS05	n.d.	9.0	14.6	n.d.	1.8	1.7	0.3	4.3	58.1	0.8	3.6	6.0
TS06	n.d.	9.8	13.8	n.d.	2.3	4.1	0.5	7.7	50.5	0.7	3.4	7.3
Mean	0.1	9.2	15.2	n.d.	2.2	1.2	0.2	7.0	50.5	0.7	3.5	10.3
TSP1-3	0.5	14.7	34.6	3.4	2.4	9.8	3.8	5.0	11.4	0.7	13.5	0.2
TSP2-3	0.2	12.4	9.7	0.3	0.2	0.4	0.1	1.8	72.8	0.2	0.3	1.6
TSP4-2	1.0	24.1	48.6	4.4	3.5	3.4	3.3	1.0	6.9	n.d.	3.0	0.9
TSP5-3	0.8	14.4	52.4	6.8	3.8	3.8	2.7	6.0	6.9	0.1	1.0	1.2
TSP6-3	n.d.	17.2	39.0	2.0	6.2	3.3	2.3	4.4	8.1	0.4	12.4	4.8
TSP7-3	8.3	14.2	30.3	4.6	0.0	3.8	1.8	4.2	21.0	4.4	5.3	2.1
TSP8-3	2.7	9.9	26.2	2.1	1.4	7.7	0.8	2.0	31.2	1.1	13.0	2.2
Mean	1.9	15.3	34.4	3.4	2.5	4.6	2.1	3.5	22.6	1.0	6.9	1.9

ZnO, PbO, and FeO as shown in Table 8. The attached slags are heterogeneous with the ZnO and PbO rich phases encapsulated in the vitrified matrix that contains notable content of CaO and MgO (Fig. 11(d)). The appearance of the vitrified slags could hinder the contact of zinc oxide with the reducing agents and trap the zinc vapor, resulting in an increased content of ZnO in the slags and a decrease in the zinc yield. It should be mentioned that it is necessary to limit the content of alkaline oxide in the reaction ingredients to avoid the formation of vitrified slags. It should have been achieved by selecting proper ores and reducing coals (Xu, 1958).

Until now, it is clear that the presence of franklinite in the calcine will not result in the decrease in the zinc yield. Although the slags contain a notable content of FeO, metallic iron is rarely found in the vitrified slags (Fig. 11 (d)). It is likely that sufficient reducing coal had been added in the pots to prevent the formation of molten slag during the distillation processing. Since the melting point of iron is higher than the distillation temperature, the metallic iron could remain as solid-state particles (Fig. 11 (a)). Therefore, the slags in the pots can be of a good gas permeability that is helpful for the escape of zinc vapor.

4. Discussion

As mentioned above, the metallurgy of the zinc sulfide ores presents a big challenge since they have to be roasted before smelting. Combining with the modern physico-chemistry metallurgical theory and the results above, the distillation technology of zinc sulfide ores in the Tongmuling site that is the core goal in the present investigation can be revealed and reconstructed. Besides, the archaeological background of the large-scale zinc smelting activities in Guiyang County is discussed.

4.1. Reconstruction of the distilling retorts

As clearly revealed above, the retorts of the Tongmuling site are mainly composed of pots, condensers, condensation pockets, and lids. Combining with the archaeological evidence and related recordings

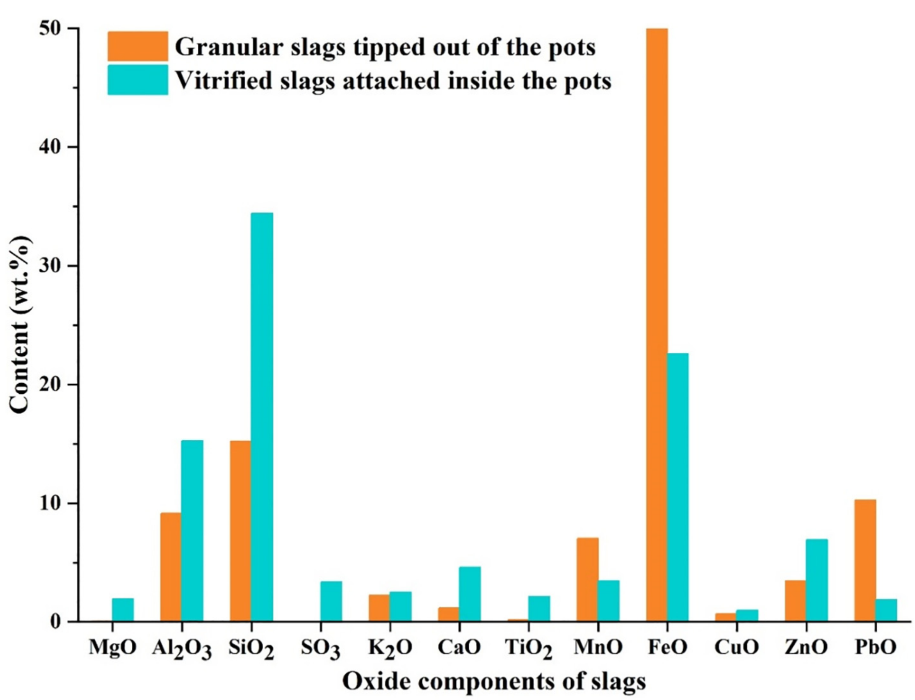

Fig. 10. Comparison of the mean oxide contents in the granular slags tipped out from the pots and the vitrified slags attached inside the pots.

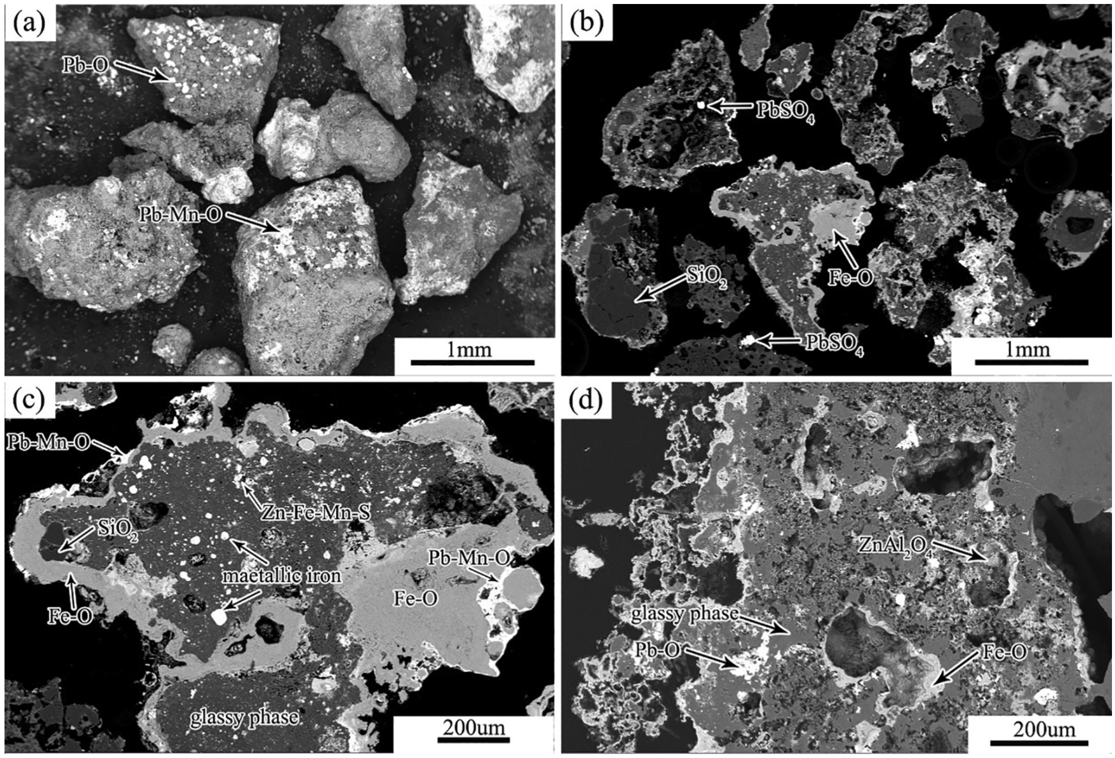

Fig. 11. Backscattered electron images of the zinc smelting slags: (a) granular slags tipped out from the pots with the lead-rich phases on the particle surface; (b) cross-section of the granular slags; (c) a trace amount of metallic iron prills and Zn-Fe-Mn-S mineral grains found in a vitrified particle; (d) slags attached in the bottom of the pot with a vitrified substrate.

(Guo and Bai, 1993; Zhou, 1997; Zhou, 1930), the reconstruction of a distillation retort structure is shown in Fig. 12.

As containers for the reaction materials and core component for the zinc metallurgy, the pots would have been required to have excellent heat resistance and chemical attack resistance. It should be mentioned that no pot production remains were found in the Tongmuling site and other zinc smelting sites. However, during the field investigation, a kiln site in which the same smelting pots were fired was discovered in a small village called Tang Luo Hu, in Guiyang County. The pots used in the Tongmuling site were produced at this pottery workshop and transported to the zinc smelting workshops. With 20–23 wt% of Al_2O_3, the clay used for the pots is quite refractory. A certain amount of Al_2O_3 can promote the formation of mullite, which is an ideal refractory material with high refractoriness, excellent thermal shock resistance, and creep resistance. The analysis of the unused and used pots show that the pots present excellent slag resistance and zinc erosion resistance during the distilling processing. In addition, the performance of the pots is further improved by wrapping a thin layer of clay on the pot surface. The clay wraps are likely intended to provide a viscous wrapping to counteract the effect of any cracks in the main pots and make the heat from the furnaces more evenly distributed in the pots to prevent the formation of a steep thermal gradient and subsequent cracking (Martinon-Torres and Rehren, 2002). The pots would be recycled, usually more than five times, after tipped out of slags (Zhou, 1997).

As an essential part of the retort, the condenser is jointed to the rim of the pots with the clay. Unlike the pots that were fired in specific workshops, the condensers were fired in the smelting workshop. Except that the efficiency of on-site production was significantly lower than that of pre-firing, there are several factors that need to be considered to produce these condensers on-site. Firstly, the condensers must match the rims of the pots with various diameters to avoid leakage of zinc vapor. Secondly, the fire resistance of the condensers is lower than that of the pots, and high-temperature sintering is not necessary. The last and most important factor is that the porous structure may facilitate the absorption of escaping zinc oxide vapor, which could be recycled by resmelting the fragments of the used condensers. In the Tongmuling site, a crushing working area and a pile of fragments of condensers and pockets were discovered. It should be pointed out that the fragments of condensers not only have a considerable content of zinc but also can improve the gas permeability of the reaction ingredients.

After the zinc vapor evaporates into the condenser through the airway, it is condensed to the liquid zinc and dropped into the pocket. Therefore, the pockets are required to have a functional zinc storage capacity. Only two relatively complete pockets were found in the Tongmuling site because most of the pockets were recycled due to their high content of ZnO (Table 2). The size of the two pockets matched well with the rims of pots. However, there were several drawbacks in the structural design of the two pocket remains. Obviously, the storage capacity of the two pockets was too small. Besides, the airway should be on the highest side of the pocket to prevent zinc liquid backflow and blocking the airway (Guo and Bai, 1993). It is believed that the two pockets were unusable and abandoned pockets. Therefore, when reconstructing the zinc distilling retorts at the Tongmuling site, completely conforming to the shape and structure of the unearthed pockets is not advisable. It is necessary to consider the purpose of the condensation pockets and reference to the relevant literature records. According to the literature, the raw materials for the pockets are mainly sifted slag ash and clay. Impurities are not allowed in the pockets to avoid immersion accidents (Cao, 1917; Guo and Bai, 1993). This description is consistent with the composition and microstructure of the pockets. Combining with the EDS analysis results of the granular slags (Table 6), the high content of FeO and PbO in the pockets is likely to come from the slag ash. Therefore, the selection of the material for the pockets is relatively strict as evidenced by the microstructure in Fig. 5 (d) in which no visible inclusions could be observed.

It is well known that when the temperature is too high, the iron lids could be cooled by sprinkling water to enhance the condensation and reduce the volatilization loss of zinc vapor (Mei, 1990). With better

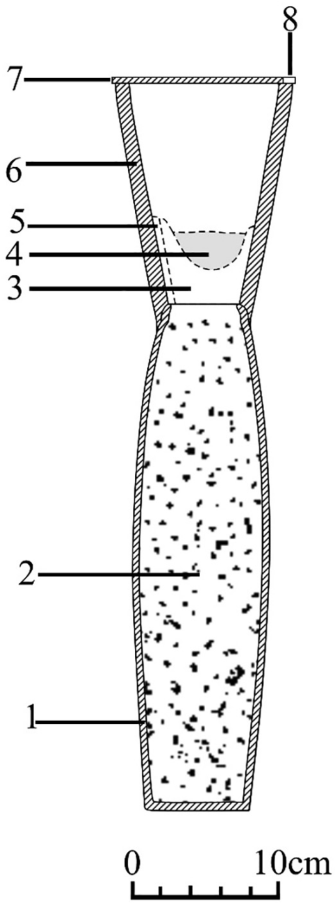

Fig. 12. Reconstruction of a retort (1-pot, 2-reaction ingredients, 3-pocket, 4-liquid zinc, 5-airway, 6-condenser, 7-lid, 8-exhaust hole).

thermal shock resistance and thermal conductivity, the iron lids present a better performance than clay lids (Craddock, 1997). We would like to stress that there was a small exhaust hole located on the opposite side of the airway. The exhaust hole, which is critical to the success of the distillation, is used to adjust the air pressure in the pots to avoid bursting inside the container. Furthermore, the hole could exhaust the water vapor and other volatile waste gases in the pots during the pre-heating stage (Zhou, 1997).

The most crucial development in the traditional zinc smelting technology in China since the era of *Tian Gong Kai Wu* (CE 1637) has been the application and improvement of condensation units (Mei, 1990). Compared with the zinc smelting technology in other areas in China based on the literature and the archaeological discoveries, the most noticeable difference in the zinc distillation retorts in the Tongmuling site is the relatively higher condensers. According to the investigations of the traditional zinc smelting technology in Guizhou (Hu and Han, 1984; Xu, 1986) and Yunnan (Craddock, 1997; Zhou, 1997) in southwest China, there are no separate condensers attached on the rims of the pots. Instead, some "bucket-shaped separators" are added into the inside of the pots as the condensation chambers (Mei, 1990). The condensers discovered from the zinc smelting sites in Chongqing are similar to that of the Tongmuling site. Both are jointed externally to the pots by the clay. However, the height of condensers in Chongqing is only 5 cm (Zhou et al., 2012). With a much larger height, the condensation efficiency in the condensers found in the Tongmuling site could be higher. This was realized by separating the cooling zone far away from the reduction zone (Mei, 1990).

4.2. Reconstruction of the technological smelting process

It is well known that the zinc oxide ores can be directly mixed with reducing agents and placed in the pots for distillation smelting (Zhou et al., 2012). By comparison, the smelting of zinc sulfide ores is more complicated because of the extra roasting processing. Now the whole process of the zinc sulfide smelting in the Tongmuling site can be divided into three phases, including the roasting, distillation, and refining, as shown in Fig. 13.

The first step that is also the most critical is the roasting of zinc sulfide ores. The ores for the zinc smelting in the Tongmuling site are sulfide ores, which mainly contain sphalerite in addition to a certain amount of pyrite and galena. It has been recognized that sphalerite and zinc sulfate cannot be reduced during the distillation process. The high content of sulphur residue in the calcine results in a high waste of zinc. Therefore, the main purpose of the roasting processing is to remove the sulfur and reduce the sulfide containing ores into oxidized ones. Besides, the roasting could remove the moisture and harmful arsenic compounds (Xu, 1958). Furthermore, the roasting could increase the porosity of the ores and facilitate ore crushing. Therefore, some of the zinc oxide ores were also roasted before distillation in traditional zinc smelting in southwest China (Xu, 1958; Mei, 1990).

The shape and arrangement of the roasting hearths found in the Tongmuling site is similar to that in the Songbai Traditional Zinc Smelting Plant in Hunan province. It was reported that the Songbai Zinc smelting plant started to carry out zinc smelting in 1905 by technicians recruited from Guiyang (Zhou, 1930). It was recorded that the roasting hearths in the Songbai plant in the 1930s (Fig. 14) were round hearths built with clay bricks, 3 *chi* (1 m) in diameter, and 5 *chi* (1.67 m) in height. In each plant, 12 to 16 roasting hearths were arranged in a line. The roasting hearth was filled with firewood, coal, and ore sand in turn. It was noted that in order to control the roasting temperature to avoid

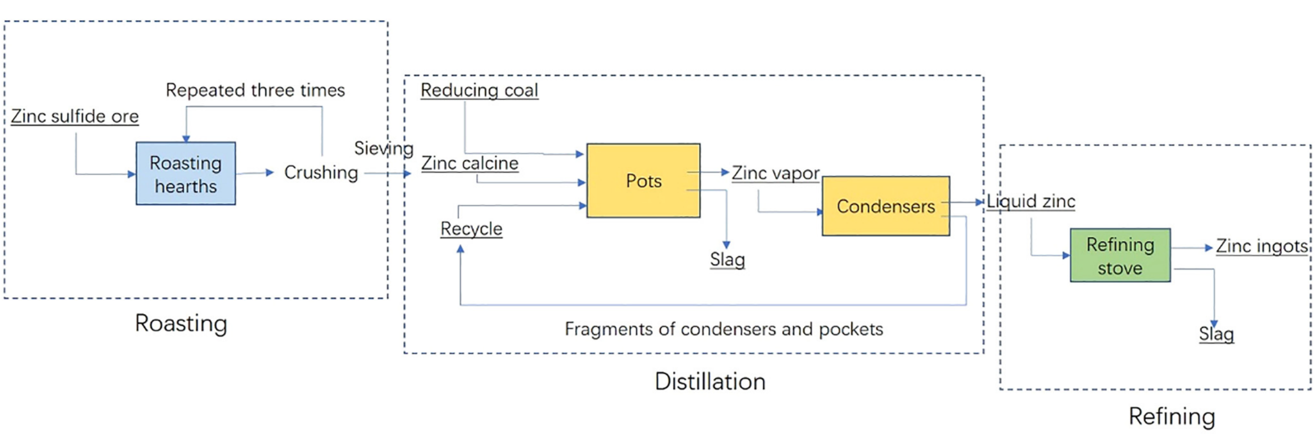

Fig. 13. Reconstruction of the distillation process of zinc sulfide ores in the Tongmuling site.

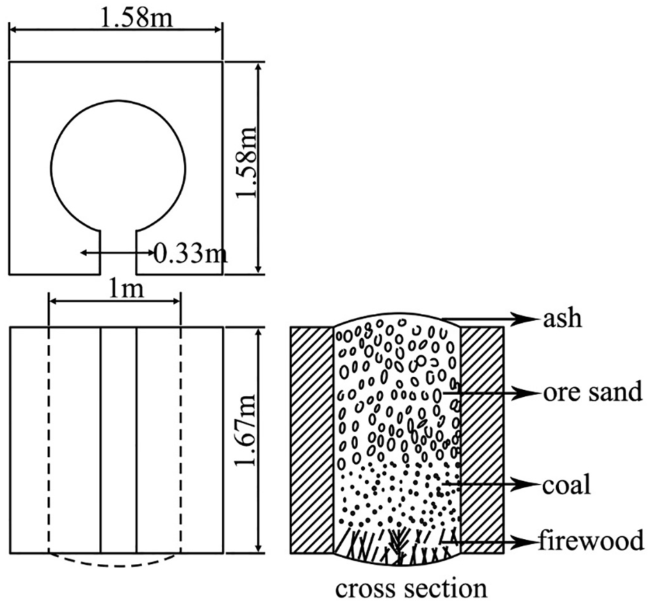

Fig. 14. Schematic diagram of the roasting hearth in the Songbai Traditional Zinc Smelting Plant in the 1930s (Zhou, 1930).

zinc loss caused by excessive heating, a layer of ash covered the top of the hearth. Moreover, the door of the hearth was sealed by clay bricks before ignition. On the seventh day, the ores could be taken out and crushed into smaller pieces. The entire roasting process usually took 21 days, which required repeated calcination and crushing three times (Lian, 1936). According to the description of the whole process, the roasting of zinc sulfide ores in the Songbai plant was a lengthy process at a lower temperature.

It is believed that the roasting method at the Tongmuling site could be consistent with that in the Songbai zinc smelting plant. This possibility can be further indicated from the phase composition of the zinc calcine found in the Doulingxia site as well. For example, a considerable amount of lead was detected in the calcine as lead oxide and lead sulfate. In contrast, Pb-Zn silicates, which can be obtained by heating at 950 °C for 6 h in the fluid-bed roaster of modern industry (Chen and Dutrizac, 2004), were not detected in the calcine. It indicated that the roasting temperature should be much lower than 950°C. However, zinc sulfate is easily formed at a lower temperature (Hua, 2007). Therefore, only a lengthy oxidative process can result in the full decomposition of zinc sulfate (Xu, 1979). During such a lengthy heating process, the hematite was converted to franklinite by continuous inward diffusion of zinc (Graydon and Kirk, 1988). The analytical results of the zinc calcine showed that roasting at a lower temperature and a lengthy time could successfully remove the sulfur from the ore, even it is less efficiently.

The second step is the distilling of zinc calcine. The distillation was carried out in the rectangular furnaces, which were also known as trough furnaces. A total of eight rectangular furnaces were excavated in the Tongmuling site. Among them, the most well-preserved furnace is 15.2 m long and 1.7 m wide, with a refining stove in the end. Forty rows of furnace bars are arranged in parallel on the hearth, and each bar could accommodate three retorts. The reaction ingredients are mainly composed of crushed and sieved zinc calcine, reducing coal, and the recycled materials, including the fragments of condensers and pockets. Before the ingredients are charged into the pots, they needed to be thoroughly mixed and moistened with an appropriate amount of water (Cao, 1917). The distilled zinc vapor enters into the condensers through the airway and cools into liquid zinc, which could be stored in the pockets. For a successful condensation, the temperature in the pots and the condensers must be strictly controlled. Especially, it is necessary to maintain a sufficient reducing atmosphere in the retort to avoid the oxidation of zinc vapor.

The third step is the refining of crude zinc. The refining was generally carried out with an iron wok by the end of the furnaces (Zhou, 1997). The pure liquid zinc could be obtained by heating and stirring constantly, and removing the residue floatings on the surface. The final zinc ingots are cast by pouring the refined zinc liquid into a mould (Craddock, 1997). Three refining stoves were excavated in the Tongmuling site. All are located at the end of the rectangular furnaces. It is reasonably deduced that the final products in the Tongmuling site should be refined zinc ingots.

4.3. Zinc for minting

We would like to stress that archaeological field investigations show that there are at least twenty large-scale zinc smelting sites besides the Tongmuling and the Doulingxia sites in Guiyang County. All of these sites have several common characteristics. For example, a large amount of zinc smelting debris was found to be accumulated including the pots and slags. Unfortunately, most of the sites have not been investigated in detail until now. Especially, it is still a big challenge to estimate the relative age of these sites and the duration of smelting. Although the yield of zinc cannot be figured out accurately based on the area and the accumulative thickness of the debris, it can still be seen that the zinc smelting in Guiyang plays a crucial role in the political and economic developments of Hunan Province in the Qing Dynasty.

Metallic copper, lead, zinc and tin are important coin production materials in ancient China. Therefore, it is highly likely that the large-scale production of zinc in Guiyang met the official minting demand. In the early stage of the Qing Dynasty (CE 1644–1775), in addition to a Central Minting Bureau in Beijing, the minting sub-bureau in most local provinces was set up to cast a large number of brass coins as well. The Minting sub-Bureau in Changsha, the capital of Hunan Province, was named as the Minting sub-Bureau of Baonan in the 6th year of Emperor Kangxi (CE 1667). Due to plenty of polymetallic mines, Guiyang County lay in the center of the area of production of raw materials for coin production in Hunan (Lin, 2004). Zinc content in the coins minted by the Minting sub-Bureau of Baonan is about 40–50 wt%. It was estimated that during the most prosperous period of the Minting sub-Bureau of Baonan in the Qing Dynasty, the annual consumption of zinc was about 325 tons (Lin, 2007). In addition to partial purchase from Guangxi and Guizhou provinces, most zinc for coin production could be provided for the Minting sub-Bureau of Baonan using the zinc metallurgy technology described above.

It is clear that the main driving force for the zinc production in Guiyang stemmed from the demand for coin production. However, it was mandatory to develop efficient novel smelting and refining techniques for the large-scale production from sulfur-containing ores to meet the consumption of the Minting sub-Bureau of Baonan. It is stressed that during the reigns of emperors Kangxi and Yongzheng (CE 1662–1735), coin production actually was stopped due to the lack of sufficient raw materials or high-quality zinc in the Minting Sub-Bureau of Baonan. However, the minting in Hunan kept developing from the 8th Year of Emperor Qianlong (CE 1743) to the 25th year of Emperor Jiaqing (CE 1821). Especially, the production peak of the zinc smelting was between the 21st year (CE 1756) and 43rd year (CE 1778) of Emperor Qianlong. It was estimated that there were over 20 melting furnaces for casting coins in the Minting sub-Bureau of Baonan during this period (Lin, 2010). To meet the demand of coin production, the annual output of zinc in Hunan could reach up to 250 tons. In contrast, the annual zinc production in Hunan in the other periods was estimated to be only in a range of 6.5–10 tons (Lin, 2007).

5. Conclusion and outlook

The distillation and metallurgy technology of zinc sulfide ores in Guiyang County has been reconstructed. The zinc distillation technology in Guiyang (Qing Dynasty) is quite similar to the traditional zinc smelting technology in southwest China, for example, the typology of the retorts and the zinc smelting furnaces. However, several distinct local characteristics have been identified. Due to the zinc sulfide ores rather than the zinc oxide ores in Guiyang, a lengthy roasting process was developed to fully oxidise the zinc sulfide ores at lower temperature before distillation. High-quality zinc ingots could be produced by reducing calcine using a sufficient amount of reduced coal, combining with the improved design of the distillation retorts by increasing the height of the condensers.

Recent field archaeological survey revealed that the remains from different zinc smelting sites in Guiyang were highly diverse. Pots found at these sites present several different characteristics in terms of shape, raw materials and slags attached inside the bottom as well. It is believed that the zinc smelting technology in Guiyang should have experienced a long period of development and evolution. How zinc smelting technology evolved in Guiyang can reflect the history of zinc smelting technology in ancient China. More relevant analytical work is under way.

In summary, it is clear that the main driving force for the zinc production in Guiyang stemmed from the demand for coin production. Most of the zinc ingots were ordered by the Minting sub-Bureau of Baonan. Further zinc was mainly supplied by Guangxi and Guizhou. As can be seen, the shape of the roasting hearths in Guiyang was similar to the "bowl-type furnaces" found in Guangxi (Huang, 2014; Huang and Liang, 2012; Huang et al., 2012). Given the adjacency of Guiyang to Guangxi province, it is believed that the zinc smelting and metallurgy technology in Guiyang could have a specific relationship with that in Guangxi. Clearly, further archaeological excavation work and detailed materials characterization of the remains are necessary to reconstruct the zinc smelting technology in Guangxi so that the development and evolution of the technologically important zinc metallurgy from sulfur-containing ores in ancient southern China can be clarified.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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