AN EXPERIMENTAL INVESTIGATION ON LEAD ISOTOPIC FRACTIONATION DURING METALLURGICAL PROCESSES*

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In this paper, experiments are designed to imitate the non-equilibrium evaporation metallurgical process of lead. The lead isotope ratios of the remaining lead liquid with different percentage losses were then determined using high-solution MC–ICP–MS. The results show that this process does alter lead isotopic ratios of the remaining liquid. However, the variations are so much smaller than the speculated values using the theoretical formula that in most ancient metallurgical processes, the lead isotopic fractionation can be neglected.

KEYWORDS: METALLURGICAL PROCESS, LEAD ISOTOPE, FRACTIONATION, MC–ICP–MS

INTRODUCTION

Lead has four isotopes, namely ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. Because the latter three isotopes are radiogenic and their abundances depend on geological age, lead has a large range of natural isotopic compositions. Thus lead isotope ratios are used in archaeological chemistry to trace the lead-containing artefacts back to their ore source (Gale and Stos-Gale 2000; Pollard *et al.* 2007). So far, lead isotope analysis is the most effective method for the provenance study of metal objects. Brill introduced this method into archaeology in the 1960s, to trace the source of the raw materials of ancient lead (Brill and Wampler 1967). Gale and Stos-Gale (1982) began to trace impure copper objects to their lead-bearing copper ores using this method. Since then, this method has been widely used to provenance lead-bearing artefacts (e.g., Gale and Stos-Gale 1989; Pernicka *et al.* 1990).

In China, the method was first applied to the study of the ore source of 12 Shang bronzes by Jin (1987). He concluded that part of the raw material for the Shang bronzes might originate from Yunnan Province, thousands of miles away from the centre of the Shang civilization. This argument came as a big surprise to Chinese archaeologists at that time, since the conventional idea is that Yunnan was not controlled by central China until after the Shang Dynasty. However, Jin's opinions were based only on the comparison with the geological data, and no archaeological background was involved. Thus his opinions have not been totally accepted by Chinese archaeologists. Recently, Cui and Wu (2008) compared the lead isotope ratios of the ancient Yunnan bronzes with Shang bronzes. The results show that the lead isotope characteristics of the bronzes found in these two regions are totally different from each other, which indicates that the source of the Shang bronzes may still be located in the area controlled by the Shang Dynasty, rather than in Yunnan.

As quoted in Gale and Stos-Gale (2000), Russell and Farquhar indicated that because of its large atomic weight, lead undergoes no isotopic fractionation during the processes employed in the various metal crafts, including smelting, melting, purifying and casting. Many experiments

have been conducted to simulate the metallurgical process, followed by measurements of the lead isotope ratios of ores and products. No isotopic fractionation has been observed during the process. Therefore, the view of Russell and Farquhar was accepted by other archaeochemists until 1995, when Budd and his colleagues raised questions about the possibility of fractionation (see, e.g., Budd *et al*. 1995, 1996; Pollard and Heron 1996; McGill *et al*. 1999). They considered that during the metallurgical process, the loss of lead may change the isotopic ratios of lead. Using a thermodynamic formula presented by Mulliken and Harkins (1922), they calculated the fractionation of an imaginary object that had the lead isotopic characteristics of the Laurion mine. The results suggested that the lead isotope ratios might extend the range of the Laurion isotopic field if the loss of lead achieved 40% by weight (Budd *et al*. 1995). Their paper caused much controversy among the Western academic community (see, e.g., Gale and Stos-Gale 1995; Muhly 1995; Pernicka 1995; Tite 1996; Macfarlane 1999). This famous controversy in the Western history of archaeometry settled down after Budd *et al*. announced that their simulation experiments did not show measurable isotopic alteration using Quadrupole ICP–MS (McGill *et al*. 1999). But few papers about the lead isotope method have been published since 2000. Despite the fact that the fractionation of lead could hardly be detected at that time, other heavy metals such as tin and zinc had been found to be isotopically fractionated during the non-equilibrium metallurgical process (Budd *et al*. 1999; Yi *et al*. 1999).

Chinese scholars began to focus on this issue much later than their counterparts in the West. Researchers from USTC (the University of Science and Technology of China) did some experiments to test the fractionation of lead isotopes; they claimed that fractionation was found during their experiments (Qin *et al*. 2004). The authors asserted that they had observed the lead vaporizing during the melting process. However, in most cases, the contents of lead in the alloys reported in that paper were greater than those in the liquids. Thus judging from their data, one can conclude that an increase in the lead—rather than a loss—was taking place during the evaporative process. Therefore, the validity of their conclusion was seen as deeply suspicious, because their data were at odds with each other and the analytical error was much larger than the difference (Jin 2005; Chen 2008).

The technique of high-precision multicollector – inductively coupled plasma – mass spectrometry (MC–ICP–MS) has been advanced rapidly. The latest generation of such instruments has an analytical sensitivity that is an order of magnitude better than that of TIMS (Pollard *et al*. 2007, 192–4). Thus it is possible to measure the change in the lead isotope ratios during the metallurgical process. This paper will discuss the relevant issues based on the data determined by MC–ICP–MS.

<div align="center">THE FRACTIONATION THEORY OF LEAD ISOTOPES</div>

Macfarlane (1999) pointed out that the state described by Budd *et al*. (1995) is consistent with the Rayleigh fractionation process in isotope geochemistry, which is an instantaneous equilibrium evaporation process. In this process, the equilibrium is achieved instantaneously and immediately broken because the vapour phase is moved away from the system. Since the light isotopes evaporate more easily than the heavy ones, the remaining liquid phase will be richer in heavy isotopes when the process comes to its end. The result can therefore be predicted using the Rayleigh fractionation formula:

$$R_l = R_{l0} f^{\frac{1}{\alpha}-1}$$

where f is the proportion of liquid remaining, α is the fractional factor, R_{l0} is the lead isotope ratio of the original liquid and R_l is the lead isotope ratio of the remaining liquid.

In the formula, α is an important parameter, which can affect the extent of the fractionation. But, as Macfarlane (1999) pointed out, α for lead could not be easily determined at that time. However, according to the experimental experience, the isotopic fractionation can be well described by the square root of the mass ratio between isotopes. The measured α is sometimes 'smaller than the square root of the ratio of the masses of the isotopes, but never greater' (Wang *et al*. 1994; see also Macfarlane 1999). Thus the best estimate of the maximum α can be represented by the square root of the ratio of the masses of the isotopes (Macfarlane 1999),

$$\alpha = \sqrt{\frac{M_h}{M_l}}$$

where M_h is the mass of the heavier isotope and M_l that of the lighter one. Therefore, the maximum values of α for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ are 1.00489, 1.00242 and 1.00484, respectively.

To summarize the two formulae, the loss of lead during a non-equilibrium evaporation metallurgical process (or an instantaneous equilibrium evaporation process) will alter the lead isotopic ratios of the remaining liquid. While the fractionation is not random, the direction of variation is to magnify the values of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ simultaneously. The fractional results can be predicted using the Rayleigh fractionation formula.

It is worth noting that the isotopic changes for the fractionation are totally different from the natural changes, since in the natural condition the abundance of ^{204}Pb never changes, because it is not radiogenic. However, the other three isotopes all increase over geological time. Thus we can see a negative correlation between $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{206}Pb$. In contrast, during a non-equilibrium evaporation metallurgical process, ^{204}Pb in the liquid phase is lost more rapidly than the other three isotopes, because it is the lightest. Therefore, in the plot of $^{206}Pb/^{204}Pb$ versus $^{207}Pb/^{206}Pb$, the data show some positive correlation, as we can see in the paper presented by Budd *et al*. (1995).

THE SIMULATION EXPERIMENT AND MEASUREMENTS

The fundamental idea of the experiment is to remove the lead vapour from liquid lead to achieve the non-equilibrium evaporation state. Our experimental procedure was as follows. First, a piece of lead, of 99.9% purity, was cut into nine parts and each part was weighed on a chemical balance with 0.1 mg accuracy. Then each part was put into a quartz vacuum tube, which was then put into a homemade muffle furnace, with one side open to the air. The end of the tube with the sample was put into the furnace and the other end was laid out of the furnace in order to make the temperature distribution of the whole tube uneven. The samples were heated to 650°C. Eight samples were melted by this method, leaving one as the original sample.

After the temperature reached the melting point of the lead, which is 327°C, the lead melted, and the liquid began to volatilize to the open side of the furnace because of the temperature difference. Since the temperatures of the different parts of the furnace were not even, the lead vapour condensed rapidly on the inner wall of the quartz tube, 2–3 cm from the sample. Thus the state of non-equilibrium evaporation was imitated effectively. The heating time was controlled in order to obtain samples with different lead losses.

After the melting experiments, the remaining lead was weighed to 0.1 mg accuracy, and the lead loss rate calculated for each sample. We dissolved all the samples, including the original one, in concentrated BV-III ultrapure nitric acid (63.02 wt%; all metal ion concentrations are less than 10^{-6}–10^{-7}%) , which then was diluted to about 2 mol l^{-1} with MilliQ ultra-pure water. Then the

solutions were sent to the MC–ICP–MS laboratory of the Geological Institute of China. The lead isotope ratios of the samples were then determined using a Nu Plasma high-resolution MC–ICP–MS. To guarantee the accuracy of the measurement and the repeatability of the data, the original sample was repeatedly measured before and after the measurement of each fractionated sample. The Nu Plasma is much more accurate than the traditional TIMS. The 2σ relative errors were less than 0.01%, 0.005% and 0.005% for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$, respectively.

RESULTS AND DISCUSSION

The fractionation of the lead isotopes

Table 1 shows the lead isotope results of the samples. Figure 1 shows the plots of three lead isotope ratio values ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{204}Pb$) versus loss of lead. The results indicate that the lead isotope ratios of the remaining liquid were altered in proportion to the loss of lead. The variations extended the 2σ relative errors of the instrument when the lead loss was more than 20%. When the loss of lead reached a value of 82.8%, the isotope ratio variations in the remaining liquid lead for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ were 0.04%, 0.03% and 0.06%, respectively, which is many times more than the instrumental 2σ relative errors.

As mentioned above, the Nu Plasma MC–ICP–MS has analytical sensitivities that are an order of magnitude better than conventional TIMS. Thus, using TIMS, only when the loss of lead exceeds 80% could the alteration of $^{208}Pb/^{206}Pb$ be determined. For $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{206}Pb$, their changes are still within the instrumental errors of TIMS. So, as pointed by Pollard *et al.* (2007), TIMS has no means of measuring the lead isotopic fractionation in the metallurgical process unless it is possible for the loss of lead to reach 80%.

It is considered that 'cupellation' is the most likely metallurgical process that could cause the lead isotopes to fractionate (Pollard and Heron 1996), because during such a process the loss of lead could exceed 90%. But according to our experiments, the variations for $^{206}Pb/^{204}Pb$ in such a process cannot reach 0.1%. For an isotopically homogeneous mine, the relative isotopic variations of such a field are often less than 1% (Gulson 1986). Therefore, a metallurgical process such as 'cupellation', which induces a large loss of lead, does change the lead isotope ratios, but the change in the isotopes cannot influence the use of lead isotope ratios to trace the metal back to its original mine.

In summary, the experimental results show that the lead isotope ratios can be altered during a non-equilibrium evaporation process, but the fractionation is very tiny. Using the high-resolution MC–ICP–MS, one can detect when the loss of lead exceeds 20%. However, for TIMS the variations of the lead isotope ratios can be observed only when the loss of lead exceeds 80%. Therefore, the method of provenancing the source of ancient metal using lead isotope ratios is not problematic.

The experimental value of the fractionation factor for lead

The fractionation factor is a parameter to test the fractional effect of an element. Up to now, no fractionation factor for lead has been reported. In our experiment, the high-resolution MC–ICP–MS makes it possible to obtain this factor. Based on the Rayleigh fractionation formula, the fractionation factor (α) depends on the proportion of liquid remaining, as well as the lead isotope ratios of the original and the residual liquid. It can be described as follows:

Table 1   *The experimental results of the lead isotope ratios determined with the different lead losses by the means of the Nu Plasma MC–ICP–MS*

Sample number*	Lead loss (%)	$^{208}Pb/^{204}Pb$	2σ	$^{207}Pb/^{204}Pb$	2σ	$^{206}Pb/^{204}Pb$	2σ	$^{207}Pb/^{206}Pb$	2σ	$^{208}Pb/^{206}Pb$	2σ
a-1	0	38.325	0.0028	15.633	0.001	18.071	0.001	0.86511	1.40E-05	2.1208	6.20E-05
a-2	18.5	38.331	0.0032	15.635	0.0011	18.072	0.0019	0.86520	4.50E-05	2.1211	1.20E-04
a-1	0	38.326	0.0031	15.634	0.0011	18.071	0.0011	0.86513	2.20E-05	2.1209	8.00E-05
1–2		38.301	0.0027	15.626	0.001	18.065	0.0011	0.86496	1.70E-05	2.1201	5.60E-05
a-1	0	38.317	0.0027	15.630	0.001	18.068	0.0011	0.86509	1.60E-05	2.1207	6.70E-05
a-3	26.1	38.331	0.0034	15.635	0.0012	18.070	0.002	0.86525	5.20E-05	2.1213	1.40E-04
a-1	0	38.328	0.0028	15.634	0.001	18.072	0.001	0.86513	1.70E-05	2.1209	6.20E-05
1–3		38.292	0.0031	15.624	0.0012	18.064	0.0011	0.86491	2.00E-05	2.1198	7.40E-05
a-1	0	38.324	0.0027	15.633	0.001	18.070	0.001	0.86513	1.70E-05	2.1209	5.50E-05
a-4	34.1	38.335	0.0036	15.636	0.0012	18.070	0.0021	0.86529	8.50E-05	2.1214	2.40E-04
a-1	0	38.325	0.0031	15.633	0.0012	18.071	0.0012	0.86512	2.00E-05	2.1208	6.30E-05
1–4		38.292	0.0031	15.623	0.0012	18.062	0.0012	0.86494	2.40E-05	2.1200	7.00E-05
a-1	0	38.322	0.0024	15.632	0.0009	18.068	0.0009	0.86516	1.80E-05	2.1210	5.40E-05
a-5	27.3	38.338	0.0029	15.637	0.0011	18.073	0.0017	0.86524	5.60E-05	2.1213	1.70E-04
a-1	0	38.322	0.0038	15.632	0.0012	18.069	0.0013	0.86512	2.20E-05	2.1208	1.00E-04
1–5		38.292	0.0025	15.623	0.001	18.063	0.0011	0.86491	1.70E-05	2.1199	5.20E-05
a-1	0	38.324	0.005	15.633	0.0018	18.070	0.0018	0.86514	2.80E-05	2.1209	1.00E-04
a-6	23.3	38.330	0.0031	15.634	0.0011	18.071	0.0011	0.86517	3.20E-05	2.1211	1.10E-04
a-1	0	38.322	0.0041	15.633	0.0015	18.070	0.0016	0.86512	2.10E-05	2.1208	8.10E-05
1–6		38.276	0.0041	15.618	0.0015	18.060	0.0018	0.86482	1.90E-05	2.1194	5.80E-05
a-1	0	38.333	0.0036	15.636	0.0013	18.073	0.0013	0.86519	2.50E-05	2.1211	8.30E-05
a-7	59.9	38.352	0.0027	15.641	0.001	18.077	0.001	0.86527	2.00E-05	2.1216	6.20E-05
a-1	0	38.320	0.004	15.631	0.0015	18.068	0.0015	0.86514	2.80E-05	2.1209	1.00E-04
1–7		38.303	0.0032	15.627	0.0012	18.065	0.0015	0.86503	2.60E-05	2.1203	8.00E-05
a-1	0	38.320	0.0041	15.632	0.0016	18.069	0.0018	0.86514	6.90E-05	2.1208	1.80E-04
a-8	82.8	38.359	0.0036	15.643	0.0014	18.076	0.0016	0.86537	1.80E-05	2.1220	5.80E-05
a-1	0	38.319	0.0026	15.631	0.0009	18.069	0.001	0.86511	2.30E-05	2.1207	9.30E-05
1–8		38.316	0.0041	15.630	0.0014	18.069	0.0015	0.86505	1.80E-05	2.1206	7.10E-05
a-1	0	38.317	0.0035	15.630	0.0012	18.067	0.0013	0.86514	2.90E-05	2.1208	9.00E-05
a-9	50	38.342	0.0034	15.638	0.0012	18.075	0.0012	0.86520	1.80E-05	2.1213	6.10E-05
a-1	0	38.329	0.003	15.635	0.0011	18.073	0.0011	0.86513	1.90E-05	2.1208	7.60E-05
1–9		38.309	0.0042	15.628	0.0015	18.067	0.0013	0.86501	2.40E-05	2.1203	8.80E-05
a-1		38.323	0.0037	15.633	0.0012	18.070	0.0012	0.86513	2.20E-05	2.1208	8.50E-05

*The a-sequence is liquid lead; that is, the remaining lead: a-1 is the original lead. The l-sequence is vaporized lead; that is, the lead condensing on the tube wall.
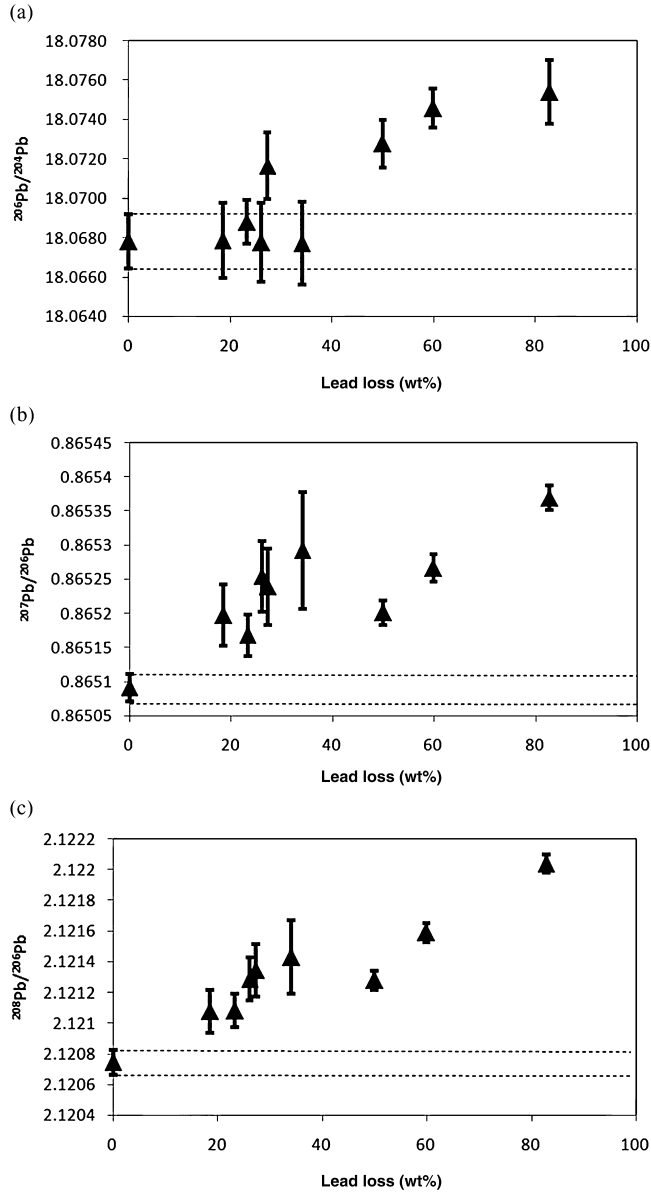
(a)

(b)

(c)

Figure 1   *The variation of lead isotope ratios with lead loss when heating the lead metal at 650°C in the experiment: (a) $^{206}Pb/^{204}Pb$; (b) $^{207}Pb/^{206}Pb$; (c) $^{208}Pb/^{206}Pb$.*

$$\alpha_{l-v} = \frac{\ln f}{\ln\left(f\dfrac{R_l}{R_{l0}}\right)}$$

where f is the proportion of liquid remaining, R_{l0} is the lead isotope ratio of the original liquid and R_l is the lead isotope ratio of the remaining liquid. Table 2 shows the α values for various losses

Table 2   *The fractionation factor calculated with the different lead losses*

| Sample number	Lead loss (%)	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
2	18.5	1.0008	1.0007	1.0002	1.0005	1.0007
3	23.3	1.0009	1.0005	1.0003	1.0002	1.0006
4	26.1	1.0012	1.0009	1.0002	1.0009	1.0012
5	27.3	1.0019	1.0014	1.0010	1.0005	1.0009
6	34.1	1.0011	1.0008	1.0003	1.0008	1.0011
7	50	1.0011	1.0008	1.0006	1.0002	1.0005
8	59.9	1.0012	1.0009	1.0007	1.0002	1.0005
9	82.8	1.0007	1.0005	1.0003	1.0002	1.0004
Average		1.0011	1.0008	1.0004	1.0004	1.0008
$(M_h/M_l)^{1/2}$		1.0098	1.0073	1.0049	1.0024	1.0048
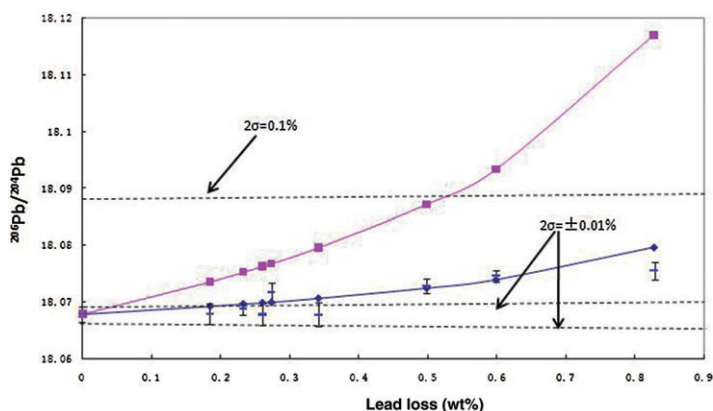
Figure 2   *The lead isotopic fractional curves drawn based on the maximum fractionation factor (the squares) and the average experimental fractionation factor (the diamonds): the experimental values are also plotted on the figure (the dashes).*

of lead. According to the Rayleigh fractionation theory, the maximum value of α is the square root of the ratio of the masses of the isotopes of interest. The theoretical maximum α values for the five lead isotope ratios are shown in the last row of Table 2.

We calculated the values of $^{206}Pb/^{204}Pb$ in the remaining liquid lead of this experiment based on the average experimental and the maximum fractionation factors. The fractionation curves are shown in Figure 2, together with the actual experimental values.

It can be concluded from Figure 2 that the experimental isotopic changes are much smaller than the maximum theoretical alteration represented by Budd *et al*. (1995) and Macfarlane (1999). The dash-dotted lines are 2σ relative error ranges for conventional TIMS and Nu Plasma, respectively. Hence if we were to use TIMS to detect the fractionation of the lead isotopes during the metallurgical process, we could not observe the change of $^{206}Pb/^{204}Pb$ over the 2σ relative error even if the lead loss was in excess of 80%. However, in ancient copper and lead metallurgical process, such a large loss of lead could not happen. The most likely process is cupellation in the lead–silver system, a process of lead loss in excess of 99%. According to the experimental fractionation factor, only the relative change of $^{208}Pb/^{206}Pb$ will exceed 0.05%, which could be

Table 3   *Lead isotope ratios of copper slags and ingots unearthed from the Nulasai copper-smelting site, Xinjiang*

Sample	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$
Slag	0.8595	2.1001	18.098
Slag	0.8596	2.1002	18.092
Slag	0.8597	2.1004	18.098
Slag	0.8596	2.1002	18.090
Slag	0.8597	2.1004	18.096
Average	0.8596	2.1002	18.095
Ingot	0.8607	2.1053	18.146
Ingot	0.8605	2.1049	18.096
Ingot	0.8606	2.1054	18.151
Ingot	0.8605	2.1049	18.148
Ingot	0.8603	2.1040	18.135
Average	0.8605	2.1049	18.135

determined by TIMS. But for an isotopically homogeneous lead mine, the isotopic variation is generally less than 1%; therefore, this situation will not influence the results of provenance studies using the lead isotope ratios method.

Possible lead isotopic fractionation in some archaeometallurgical cases

Admittedly, lead isotopic fractionation does occur in archaeometallurgical processes. However, the change is so insignificant that normally it does not exceed the instrument error. Thus researchers often consider that no fractionation will happen in such a process, and therefore that the fractionation cannot influence the results of the provenance study. However, because the experimental data themselves are a normal distribution, the data reflect the peak values of the distribution, namely the most probable data value. Thus if we do not take the instrument error into account, it might be observed that isotopic fractionation took place between the slag and ingot in some smelting or melting progress. When the values of $^{206}Pb/^{204}Pb$ are increasing with $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ all together, these are not random phenomena. Although the shifts might be smaller than the instrument errors, we can also form the judgement that the lead isotopes have fractionated.

Mei *et al*. (2002) report the lead isotope ratios of ores, slags and copper ingots found in Nulasai copper-smelting sites in the Xinjiang Uygur Autonomous Region. The data are listed in Table 3. From this table, we can see that the values of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ in the copper ingots are all higher than those in the slag. Thus isotopic fractionation may have happened during the copper-smelting process. Therefore, it can be concluded that the copper ingots are much richer in heavy isotopes than the slags during the smelting progress, due to their different densities.

Gale and Stos-Gale (2000) reported the lead isotope ratio results of cupelling experiments. Comparing with the analytical errors, the isotopic variations can be neglected. However, despite the very tiny differences, all reported lead isotope ratios of lead metal smelted from ore 61E are higher than the ore itself. If we leave the experimental error out of consideration, it can be concluded that the smelting process involves isotopic fractionation. The lead isotope ratios of

litharge from cupelling lead metal are slightly lower than the metal, except for ^{207}Pb/^{206}Pb, which is almost on a par with the lead metal. This means that the cupellation process still involves isotopic fractionation, but the litharge is rich in lighter isotopes. From the above, the archaeological evidence also proves that the smelting process could involve isotopic fractionation. However, the fractionation does not influence the result of provenance studies using lead isotope ratio methods.

CONCLUSIONS

In conclusion, the non-equilibrium or instantaneous equilibrium evaporation during metallurgical processing of lead will alter the lead isotopic ratios of the remaining liquid. However, the actual change is much smaller than predicted using the theoretical formula, and the isotopic variations can only be determined using high-resolution MC–ICP–MS when the losses of lead are in excess of 20%. But for TIMS, only when the lead loss exceeds 80% can the variation of ^{208}Pb/^{206}Pb be observed. In fact, such processes were not common in ancient metallurgy. Thus in the most ancient metallurgical processes, the lead isotopic fractionation should be neglected. Even in the cupellation process, in which the lead loss can reach 99%, it is not possible that the extent of isotopic alteration can exceed 0.1%.

Therefore, the results of the experiment suggest that fractionation in the ancient metallurgical process will not influence the result of provenance studies using lead isotope ratio methods. Consequently, lead isotope analysis is still the most useful method for determining the provenance of lead-bearing artefacts.

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