Beyond Provenance

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Isotopes are atoms which possess the same chemical characteristics (by having the same number of protons in their atomic nucleus) but have different atomic weights because of a variable number of neutrons in the nucleus. Most elements exist as more than one isotope: for example, carbon exists as $^{12}\text{C}$ (six protons plus six neutrons) and $^{13}\text{C}$ (six protons plus seven neutrons), with an average abundance ratio of 99:1. Apart from the light elements (those lighter than oxygen), which can be significantly fractionated by biological processes, most elements show relatively little variation in the abundances of their natural isotopes. For the heavier elements this variation arises largely from geological processes (such as different emplacement temperatures during mineralization). The exceptions tend to be elements which have one or more isotopes produced by the radioactive decay of other elements. Lead is one of the more unusual in that it has a very wide range of natural isotopic variation, due to the fact that three of its four stable isotopes ($^{206}\text{Pb}$, $^{207}\text{Pb}$, and $^{208}\text{Pb}$) lie at the end of major uranium and thorium radioactive decay chains. These chains with their respective half-lives are as follows:

$$
\begin{align*}
^{238}\text{U} & \rightarrow ^{206}\text{Pb} & T_{1/2} &= 4.468 \times 10^9 \text{ years} \\
^{235}\text{U} & \rightarrow ^{207}\text{Pb} & T_{1/2} &= 0.7038 \times 10^9 \text{ years} \\
^{232}\text{Th} & \rightarrow ^{208}\text{Pb} & T_{1/2} &= 14.01 \times 10^9 \text{ years}
\end{align*}
$$

Thus the abundance of these three isotopes of lead present in a deposit can increase dramatically depending on the amount of U and Th present. The fourth stable isotope, $^{204}\text{Pb}$, is not produced by radioactive decay but is residual from the formation of the universe, and is often therefore termed primeval. The accepted average natural abundances of the four stable isotopes of lead are $^{204}\text{Pb} = 1.4\%$, $^{206}\text{Pb} = 24.1\%$, $^{207}\text{Pb} = 22.1\%$, and $^{208}\text{Pb} = 52.4\%$, but the variation can be large. Russell and Farquhar (1960, 14) give examples of the ranges for each isotope abundance as follows: $^{204}\text{Pb} = 1.044 – 1.608\%$, $^{206}\text{Pb} = 21.53 – 28.39\%$, $^{207}\text{Pb} =$
19.22 – 23.46%, and $^{208}\text{Pb} = 51.2 – 53.40\%$. They even quote an extreme example of lead from a uranium mine with $^{204}\text{Pb} = 1.044\%$, $^{206}\text{Pb} = 41.87\%$, $^{207}\text{Pb} = 19.45\%$, and $^{208}\text{Pb} = 37.64\%$.

Although this range of natural isotopic variation is, relatively speaking, extremely large, it is usual to record and report lead isotopes as a set of three isotope ratios, since this allows greater precision in the measurements. Geologically, they are usually reported as $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$, but archaeologically the first results were published as $^{206}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ (Brill and Wampler 1967). Subsequent archaeological practice has tended to report $^{204}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$, originally because $^{204}\text{Pb}$ is the least abundant ($\sim 1.4\%$) and therefore ratios measured against $^{206}\text{Pb}$ ($\sim 24.1\%$ abundant) are capable of higher measurement precision. In the geochemical literature it is well known that modern magmatic and ore provinces tend to form very narrow alignments in plots of $^{207}\text{Pb}/^{206}\text{Pb}$ versus $^{208}\text{Pb}/^{206}\text{Pb}$, which overlap strongly (e.g., Albarède et al. 2012) and therefore have limited resolution between ore sources. For these reasons, we prefer to use the ratios as reported in the geological literature, i.e., as ratios to $^{204}\text{Pb}$. It is a simple procedure to mathematically convert between one set of ratios and another, but the quantities so produced are not necessarily equivalent. There are clearly seven possible ratios of the four isotopes, which are completely mathematically interchangeable. However, the practicalities are that in measurement by both TIMS (thermal ionization mass spectrometry—the original method) and ICPMS (inductively-coupled plasma mass spectrometry) (see Pollard et al. 2017b, 81–82) the data are actually recorded directly as three specific ratios rather than four independent abundances. Switching from the ratios as measured to another set therefore increases the error term associated with the calculated ratio, in a way which can be difficult to predict. Technically, therefore, the ratios should not be re-calculated from those which were originally measured (or, to put it another way, it does matter which ratios are quoted). However, the increase in the error term is only likely to affect the fourth or fifth decimal place of the reported ratio, and, as we show below, we are often only considering isotope ratios to the first or second decimal place. So, in our work, the conversion from measured ratio to a ratio against $^{204}\text{Pb}$, if necessary, should have very little effect.

Brill and Wampler (1967) showed that by using measurements of the lead isotope ratios, it was possible to differentiate lead ores (galena, PbS) coming from Laurion in Greece from those occurring in England and Spain. They did note that an ore sample from north-eastern Turkey fell into the same “isotope space” as that occupied by three ores from England, thus presaging some of the subsequent interpretational difficulties. Figure 1, using more than 6,700 isotope data for lead
ore deposits from Europe compiled by Hsu in the FLAME database, shows the variation in lead isotope ratios ($^{206}\text{Pb}/^{204}\text{Pb}$) across Europe. There is a general east-west trend, with lower values in the west ($^{206}\text{Pb}/^{204}\text{Pb} = 16.5 – 18.2$) and higher in the east ($18.6 – 21.4$), with the lowest values ($13.4 – 16.5$) in northwest Scotland and Fennoscandia, and a belt of much higher values (‘highly radiogenic’, $^{206}\text{Pb}/^{204}\text{Pb} > 21.4$) between Sweden and Norway. Even though this map for Europe is incomplete, it can be seen why it is not surprising that there is considerable overlap in the isotopic values of metalliferous ores from different sources, at least across mainland Europe and Anatolia.

The scope of the application of lead isotopes to archaeology was vastly increased when researchers realized that it could be applied not only to metallic lead artefacts (which are archaeologically rare) but also to the traces of lead left in silver objects extracted from argentiferous lead ores by cupellation (Barnes et al. 1974). Silver is quite common in Europe, and particularly so once metal coinage was introduced around the 8th century BCE in the eastern Mediterranean. However, the utility of the method was even further expanded when it was also applied to the traces of lead in copper objects (Gale and Stos-Gale 1982), present either as a result of smelting impure copper ores, or by some admixture of lead to the copper. The realization that the isotope ratios of lead in archaeological copper objects could be related to differences between specific metal deposits was universally hailed as a major breakthrough in the scientific study of ancient metallurgy. As noted in Chapter 1, traditional provenance studies using trace elements in copper had often only been seen to be partially successful, so the lead isotope method was widely applied to studies of the trade in metals, particularly in Bronze Age Anatolia and the Eastern Mediterranean. Early enthusiasm, however, soon became tempered by differences of opinion in data interpretation, with specific reservations focussing on issues such as the statistical definition of an “ore field” and, given that lead isotope ratio data are not normally distributed, the identification and treatment of “outliers” within the data (Pollard 2009). Modern techniques of data interpretation, such as kernel density modelling (Scaife et al. 1996: see below), can now easily overcome such objections, but nevertheless some issues remain. Little consideration has been given to the effect of mixing lead from different isotopic sources, as could happen when copper objects are recycled, or even when lead from different sources is mixed together. The system described here is designed to highlight such processes.
The evolution of lead isotope ratios: ‘ordinary’ and ‘highly-radiogenic’ leads

The conventional means of interpreting lead isotope data in archaeology derives directly from geological practice, which uses pairs of isotope plots (some combination of $^{206}\text{Pb} / ^{204}\text{Pb}$, $^{207}\text{Pb} / ^{204}\text{Pb}$ and $^{208}\text{Pb} / ^{204}\text{Pb}$) to calculate graphically the emplacement age of the lead deposit, based originally on the Holmes-Houtermans equations for the evolution of the isotopic composition of lead deposits (see Pollard et al. 2017b, 380–395). At its simplest level, the modern lead isotopic composition of an ore body is controlled by the original isotopic composition of the lead at the time of emplacement, the original amount of uranium and thorium in the deposit, and the geological age of the deposit. In the absence of unusually high concentrations of uranium and thorium, and in a closed geological environment, the isotope ratios of lead in a mineral deposit will evolve along predictable lines over geological time, and the geological age of such deposits can therefore be calculated from a measurement of these ratios (Dickin 2005;
Lead Isotope Data from Archaeological Copper Alloys

Faure 1986). Such deposits are termed \textit{conformable}, and they tend to have lead isotope ratios close to $^{206}\text{Pb}/^{204}\text{Pb} \approx 18.5$, $^{207}\text{Pb}/^{204}\text{Pb} \approx 13.3$, and $^{208}\text{Pb}/^{204}\text{Pb} \approx 38.3$, which is approximately the average lead isotopic composition in the Earth’s crust, as given above. Lead-containing minerals with such ratios are termed \textit{common} or \textit{ordinary} leads. The lead isotope ratios of minerals formed in the presence of excess uranium and/or thorium, however, evolve along different lines as a result of the production of additional quantities of $^{206}\text{Pb}$, $^{207}\text{Pb}$, and $^{208}\text{Pb}$, the exact enrichment depending on time and the amounts of uranium and thorium present. Such deposits are termed \textit{non-conformable}, and their ages cannot be calculated from measurements of the lead isotope ratios using simple evolutionary models—they can give predicted (model) ages which are in the future. They are generally referred to as \textit{anomalous} leads. It is worth pointing out that \textit{all} terrestrial lead deposits contain varying proportions of radiogenic lead, so the use of the term ‘radiogenic’ in many publications to describe anomalous lead is inappropriate. The term ‘highly radiogenic’ is more acceptable (e.g., for values of $^{206}\text{Pb}/^{204}\text{Pb} > 19.5$), and has been used in some of the archaeological literature, and also here.

Geologists were quick to exploit this new chronometric tool based on conformable lead deposits, firstly to obtain an estimate of the age of the Earth, and subsequently to estimate the geological age of the various metalliferous deposits. In practice, however, using lead isotopes to characterize metal deposits is not straightforward. Very few lead deposits are truly conformable, but, conversely, deposits with highly radiogenic lead isotope ratios are relatively rare. Moreover, deposits with highly radiogenic leads can be isotopically very heterogeneous (Liu R. \textit{et al}. 2018). In isotope geochemistry it has now been realised that simple equations such as those of Holmes-Houtermans and subsequent derivatives provide a poor description of the evolution of lead isotopes in terrestrial deposits. This is due to the complexity of the processes acting within the Earth’s crust. For example, when an ore fluid is forced through the crust, there can be mixing between the lead in the crustal rock and that in the ore fluid, which can be of quite different ages, resulting in a mineral deposit with isotopic values which do not match either that in the ore fluid nor in the surrounding rock.

**Lead isotopes in archaeological objects**

During all the archaeological discussion about the use of lead isotopes, little attention was paid to the question of data presentation, in terms of the archaeological utility of using a pair of isotope ratio plots. When we add to the geological complexity described above the possibility of anthropogenic mixing
of lead from different sources during smelting and metal production, we might argue that ‘conventional’ lead isotope bi-plots may not be the best way of looking at the data from archaeological objects. If we accept that, at least at certain times and places, the mixing of metal from different sources, or metal recycling, was a significant facet of human behaviour, then the uncritical use of lead isotope data on copper alloys is potentially misleading in terms of provenance (Pollard and Bray 2015). Within FLAME, we have therefore reconsidered the ways in which lead isotopes can be used archaeologically. As before, we focus primarily on assemblages of the objects themselves, and look for changes in the isotopic record over time and space. The objective is less to match the objects to specific ores, but more to identify changes in lead isotope values within the hypothesized metal flow, some of which may well be due to changes in ore source, but which also admits other possibilities, such as mixing and recycling. It is obvious that if metal from different sources is being mixed and recycled, then the measured lead isotope signature of the object may not correspond to any one specific source. This is in addition to the equally obvious statement that if lead is added to a low-lead copper base to form a leaded alloy, then the lead isotope signature of the object will be dominated by that of the added lead, not the copper, since the concentration of lead in most smelted copper is low.

In order to explore these ideas, we have proposed a different set of three diagrams which plot the inverse of the lead concentration (1/Pb) in the object against its lead isotope ratio (Pollard and Bray 2015). This parallels the method of presentation used by isotope geochemists for strontium isotope data (87Sr/86Sr), with the express purpose of being able to detect mixtures of two or more components. If two different sources of strontium are mixed (e.g., the merging of two rivers, each carrying sediment from different source rock), and each having different chemical abundances and isotopic ratios of strontium, then a plot of 1/Sr vs 87Sr/86Sr is used to calculate the strontium concentration and isotopic ratio of the mixture (Faure 1986, 144). Such mixing shows up as a hyperbolic mixing line if the isotope ratio is plotted directly against the strontium concentration, but it becomes linear if plotted as the isotope ratio against inverse concentration (Figure 2). The mathematics of the linear relationship between 206Pb/204Pb and 1/Pb are shown in the appendix to this chapter. Although for lead there are three such diagrams (1/Pb vs 206Pb/204Pb, 1/Pb vs 207Pb/204Pb and 1/Pb vs 208Pb/204Pb) rather than one for strontium, this method has proved extremely useful in a wide range of archaeological cases, especially when lead has been deliberately added to the copper alloy.
Figure 2:
Isotope mixing lines as seen in strontium isotopes (Faure 1986, 144).

Figure 3:
206Pb/204Pb plotted against 1/Pb for Chinese bronzes from a) the Anyang period of the Shang (c. 1200–1046 BCE) and b) the Western Zhou period (1046–771 BCE) (Liu 2016). The colour coding shows the allocation to Copper Group.

The most significant advantage of this form of presentation is that it provides a way of simultaneously displaying the concentration of lead in an object and its isotope ratio. To illustrate this method, Figure 3 shows a pair of 1/Pb vs. 206Pb/204Pb for Chinese Bronzes in the Sackler Collection, split into the Anyang phase of the late Shang (c. 1200–1046 BCE: Bagley 1987) and the Western Zhou (1046–771 BCE: Rawson 1990). Because the data contain objects with a wide range of lead concentrations (from roughly 0.01% up to 15%), we have presented the horizontal axis as a logarithmic scale, although it is labelled linearly. It is important to note, however, that although this is more convenient for display purposes, it does mean that the linearity of the mixing lines will be reduced.
Because the horizontal axis is inverse concentration, points to the left side of the plot have high lead concentrations, and points to the right are low in lead. Thus 0.1 on the x-axis corresponds to 10% Pb in the original object, and 10 is 0.1%. Although this may not always be true, crudely speaking, we can think of the right hand side of the diagram (with 1/Pb > 1, or the Pb concentration in the object <1%) as representing the lead isotope values in objects made of unalloyed copper, and the left hand side as being representative of the values in objects with deliberately added lead.

Objects on these diagrams lying on the same horizontal line have approximately the same value of $^{206}\text{Pb}/^{204}\text{Pb}$, and therefore have the potential to come from the same source, or at least from sources sharing similar isotopic values. Thus in these two diagrams we have drawn attention to two horizontal lines—one at approximately $^{206}\text{Pb}/^{204}\text{Pb} = 17.75$, often referred to in the Chinese lead isotope literature as ‘common lead’, and one at $^{206}\text{Pb}/^{204}\text{Pb} \approx 22$, referred to in the same literature as ‘highly radiogenic lead’. It is immediately obvious from this pair of diagrams that highly radiogenic lead is common in the Anyang period of the Shang Dynasty, but largely absent in the succeeding Western Zhou Dynasty. The overwhelming majority of data from the Western Zhou fall into a broad band between $17 < ^{206}\text{Pb}/^{204}\text{Pb} < 19$, irrespective of whether we look at the data above or below $1/Pb = 1$. This range of $^{206}\text{Pb}/^{204}\text{Pb}$ values could of course encompass several sources of common lead, but it does indicate that the unlead coppers ($1/Pb > 1$) have similar isotopic values to that in the added lead ($1/Pb < 1$). Since galenas (PbS) and chalcopyrites (CuFeS$_2$) forming in the same metalliferous veins are likely to have similar lead isotope ratios, this could imply a similar source location for both the lead and the copper. The situation is quite different in the earlier Anyang period data. Here the added lead is distributed between at least two distinct sets of lead isotope values, corresponding to the common and highly radiogenic leads, but the few unlead coppers represented suggest a definite mixing trend between copper containing ‘common’ lead ($^{206}\text{Pb}/^{204}\text{Pb}$ below 20) and the highly radiogenic added lead with a value of $^{206}\text{Pb}/^{204}\text{Pb}$ around 23. This seems to imply that the sources of copper used in both the Anyang period and the Western Zhou could have been the same, but that in the Anyang period it was mixed with highly radiogenic lead, which was largely not used during the Western Zhou.

Several further points can be made about this form of presentation. The first is that the pair of figures shown above are only one of a set of three possible representations, and that, for reasons of space, in Pollard et al. (2017a) only this figure was printed (although $1/Pb$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ and $1/Pb$ vs. $^{208}\text{Pb}/^{204}\text{Pb}$ were available in the online supplementary material). It is clearly possible that if another lead isotope ratio was used then the diagrams might look different, and a different
conclusion could be drawn. It is possible, for example, that significant differences could occur when $^{208}\text{Pb} / ^{204}\text{Pb}$ is plotted instead of $^{206}\text{Pb} / ^{204}\text{Pb}$, since $^{208}\text{Pb}$ is thorogenic (i.e., partially derived by radioactive decay from $^{232}\text{Th}$), whereas $^{206}\text{Pb}$ and $^{207}\text{Pb}$ are both uranogenic (from $^{238}\text{U}$ and $^{235}\text{U}$, respectively). Geochemically thorium is more insoluble than uranium, and is therefore less widely dispersed in the Earth’s crust than uranium. The plots of $1 / \text{Pb}$ vs. $^{207}\text{Pb} / ^{204}\text{Pb}$ and $1 / \text{Pb}$ vs. $^{208}\text{Pb} / ^{204}\text{Pb}$ for the same data as Figure 3a are shown here as **Figure 4** and in this case show no appreciable difference. In our experience this is usually the case, but it will not always be so, so all three representations should be studied before any conclusions are reached.

**Figure 4:**
a) $^{207}\text{Pb} / ^{204}\text{Pb}$ vs $1 / \text{Pb}$ and b) $^{208}\text{Pb} / ^{204}\text{Pb}$ vs $1 / \text{Pb}$ for same data as shown in Fig. 3a.
Another point to be made is that, as shown in these figures, we can also add the results of the trace element categorisation (Copper Groups) by colour coding the points, enabling us effectively to combine lead isotope, trace element and alloying information in a single diagram. In Figure 3a, for example (the Anyang Shang data), there appears to be a difference in the isotopic values of the lead associated with different copper groups. CG1 (Cu only, with no trace elements above 0.1%), for example, seems to be preferentially associated with Pb having a highly radiogenic signal, which may be useful in considering the sources of the copper and highly radiogenic lead. Conversely, CG12 (Cu with As, Sb and Ag) seems to be primarily alloyed with common lead—again, this is likely to have some significance in considering sources.

One significant observation is that, although modern lead isotope ratios are routinely measured to four or five decimal places, the lead isotope data as plotted in these figures are only discussed at the level of the first or second decimal place. This might indeed be wasteful in terms of information content, but when dealing with archaeological objects which may contain mixed or recycled lead, or even just considering the natural variation within ore sources, it is likely that in some cases only the first two decimal places are archaeologically significant. There may well be particular datasets where the full precision of the measurements might be needed, even when using this method of presentation, but just because we can measure an isotope ratio to five decimal places does not necessarily mean that it has archaeological significance to five decimal places.

We have also experimented with plotting the lead isotopes against elements other than lead. Although such plots lack the theoretical underpinning of a 1/Pb vs lead isotope ratio plot, they can nevertheless prove informative about mixing processes. Since nickel is resistant to oxidative loss, we can plot nickel as 1/Ni against the lead isotope ratio and use the absolute level of nickel as an indicator of dilution (since the most likely way of decreasing the nickel content of a copper alloy is to mix it with metal which contains no nickel; i.e., by dilution). If we see a change in the lead isotope value as a function of the nickel content, we can suggest that there has been a mixing process between two units of metal with different lead isotope values, but one containing higher nickel and one with little or no nickel. Figure 5 shows a comparison of 1/Ni vs. $^{206}\text{Pb}/^{204}\text{Pb}$ for Shang Anyang and Western Zhou bronzes from the Sackler collection, to be compared with Fig. 3 for lead. There is again a clear difference between the Shang and Western Zhou datasets. The Shang data shows samples with much lower nickel content (higher 1/Ni), and with clear mixing lines between the lower and higher values of nickel, but starting at the highly radiogenic value of $^{206}\text{Pb}/^{204}\text{Pb}$ and joining to both the common and highly radiogenic lead values. This is complicated to interpret since
the nickel is most likely to be associated with the copper, and the higher values of lead are likely to be separately added, but it could indicate a mixing between the common and highly radiogenic sources of lead. This utility of such approaches requires further investigation.

![Figure 5](image-url)

**Figure 5:** ${^{206}\text{Pb}}/{^{204}\text{Pb}}$ plotted against $1/\text{Ni}$ for Chinese bronzes from a) the Anyang period of the Shang (c. 1200–1046 BCE) and b) the Western Zhou period (1046–771 BCE).
Changes in lead isotopes in assemblages over time

Although for some regions there is now a relatively substantial number of lead isotope measurements on Bronze Age archaeological metal artefacts in the database, unfortunately, the majority of these are not associated with chemical data from the same object. This is because labs which are capable of measuring lead isotopes are often not equipped with instruments for chemical analysis, and vice versa. Without a measurement of the lead content in the object, we cannot produce 1/Pb vs isotope ratio plots for individual objects. We can, however, produce something almost as useful by simply plotting one of the measured isotope ratios in a chronological sequence of samples. This works well if we have a block of isotope data for each of several consecutive periods of time, and plot each period in the correct order. By grouping the data according to the chronological sequence we can reveal any patterns of change in the isotope values over time, which might be indicative of changing ore sources or reveal periods of intensive mixing. Within each group, however, the order of the samples along the horizontal axis is arbitrary. The method works equally well for comparing isotopic data from different contemporary sites. Objects with similar isotopic ratios will still show up as strong horizontal lines in these diagrams. If we make the assumption that horizontal lines with different isotopic values represent different sources (although single sources can of course show a range of values), then changes in the value of these lines may represent a switch in ore source. Essentially, these diagrams combine in a very simple way both isotopic and archaeological information.

Here we present the data in terms of 206Pb/204Pb, but, as with the 1/Pb vs isotopic ratio diagrams discussed above, similar figures can be produced for both 207Pb/204Pb and 208Pb/204Pb, which again show nothing different to the figure shown here. Figure 6 illustrates the method using lead isotope data in vessels from Bronze Age central China (Jin et al. 2017). In fact this figure shows the combination of a chronological sequence and a comparison of objects from contemporary sites. The chronological sequence consists of Erlitou (c. 1900–c. 1500 BCE), the Erligang (Zhengzhou) period of the Shang (c. 1500–c. 1400 BCE), the Anyang period of the Shang (c. 1400–1046 BCE) divided into the four Yinxu phases as discussed in Chapter 5, and the Western Zhou period (1046–771 BCE). The Erlitou period is represented only by samples from the Erlitou site itself, whereas the Erligang period has samples from Zhengzhou (the Erligang capital) and also from the Erligang period sites of Yuanqu and Panlongcheng. The samples representing the Anyang period all come from excavations at Anyang. The Western Zhou samples are from the Sackler collection (Bagley 1987), and are largely unprovenanced.
The most distinctive feature, as discussed above in relation to Figure 3, is the presence of so-called highly radiogenic lead from the Erligang period through to the late Anyang period. In the preceding Erlitou period there is no evidence for the use of this highly radiogenic lead (taken here to be $^{206}\text{Pb}/^{204}\text{Pb}$ above c. 19), but there seems to be at least two distinct common isotope values present at Erlitou ($^{206}\text{Pb}/^{204}\text{Pb} \sim 16.5–17$ and $^{206}\text{Pb}/^{204}\text{Pb} \sim 18–18.5$), with possibly some mixing between them. The lower of these two signatures ($^{206}\text{Pb}/^{204}\text{Pb} \sim 16.5$) appears to continue into the Erligang (Zhengzhou) period (c. 1500–1400 BCE), but the higher one is less well represented, if at all, in Erligang. This common lead is, however, supplemented during the Erligang period by lead containing a highly radiogenic component ($^{206}\text{Pb}/^{204}\text{Pb} \sim 19-23$), the significance of which is discussed further below. This Erligang pattern is broadly continued into the Anyang period of the later Shang (c. 1400–1046 BCE), but with some differences in detail. The earliest phase, Yinxu I, has a wide scatter of lead isotope values, ranging from $^{206}\text{Pb}/^{204}\text{Pb}$ below 16, up to highly radiogenic values of 23.5. In this respect it matches more closely the previous Erligang (Zhengzhou) and Panlongcheng patterns than it does the subsequent Yinxu phases. Yinxu Phase II is scattered across a similar but not identical range, consisting of a tight ‘low’ grouping at $^{206}\text{Pb}/^{204}\text{Pb} \sim 18-19$, which could correspond to the higher of the two earlier Erlitou groups, and going up to radiogenic values of $> 24$. Phase III shows a highly radiogenic group between 19 and 22, and predominantly (but not exclusively) the same common group at around 18 as seen in Phase II. However, Phase IV is strikingly different, in that, with the exception of two points, the highly radiogenic lead has disappeared and the values are mostly very consistent around a common value of 17.5, which is similar to the common lead values seen most notably at Panlongcheng. The Western Zhou data include a continuation of this ‘low’ source ($\sim 17.5$) which first appears in Yinxu Phase III and dominates Phase IV, but also contains a wider scatter of common lead with values between 18-19, which could include the common lead source identified in Yinxu Phase III. In the Western Zhou data, the highly radiogenic component has also virtually disappeared. The source of this highly radiogenic lead is one of the major questions in Chinese archaeometallurgy, and, although this method does not enlighten us as to where it comes from, it does show that it was accessed suddenly with the move of the Shang capital to Erligang (Zhengzhou), and ceased before the fall of Anyang, probably during the Yinxu III phase.
Lead isotope measurements have made a major impact on archaeological research over the last thirty years, but little thought has been given to presenting the data in such a way as to link it directly to archaeological questions. When presented, as here, in a different way, and when combined with chemical and other evidence, lead isotopes can provide an extremely powerful and independent tool for understanding the circulation of metal. As in the two previous chapters, however, in order to fully exploit this, this approach has to be linked with a shift in the emphasis of the question away from one of simple ‘provenance’ towards a more complex picture, of which ‘provenance’ is but one component.

The source(s) of Chinese highly radiogenic lead: geochemical parameters (Mu-Kappa-T)

More than thirty years have passed since the first report of the finding of highly radiogenic lead in Shang Dynasty Chinese bronzes (Jin 1987). Since then, the use of highly radiogenic lead in Bronze Age China has been frequently mentioned and discussed in many important publications. The most recent and high profile debate was triggered by Sun et al. (2016), who argued that the metal contained in the ritual bronze vessels unearthed at Anyang originated in Africa. Although extremely eye-catching, this paper has subsequently been heavily criticised, especially on archaeological grounds (Liu S.R. et al. 2018). Figure 6 above shows the widespread use of highly radiogenic lead in Chinese ritual bronzes from the Erligang (Zhengzhou) period (ca. 1500–1300 BC) until the Yinxu II Period of
Anyang (ca. 1200–1046 BC). Even more remarkably, isotopic measurements of bronzes from outside the Central Plains of China—that is, from Sanxingdui in Sichuan, from Panlongcheng and Xin’gan on the Middle Yangzi River—also show the use of highly radiogenic lead in their cast bronzes. Equally intriguing and mysterious, highly radiogenic lead appears to have disappeared in all areas by the subsequent Zhou dynasty. This provides one of the most enduring problems in Chinese archaeology, and a great challenge to lead isotope geochemists—where does the radiogenic lead come from, and why does its use appear to rise and fall synchronously over a large area in relatively short time period?

Another way of looking at this question is to ask ‘why hasn’t lead isotope geochemistry already solved this issue?’ One of the long-standing criticisms of the use of lead isotope data in archaeometallurgy has been the tendency to use lead isotope ratios as simple numbers which can potentially be used to characterise an ore source (e.g., Albarède et al. 2012). According to these commentaries, this ignores a crucial fact about lead isotopes—they evolve according to well-understood laws of radioactive decay and geochemistry. In other words, these numbers can tell us something about the geochemical and geochronological characteristics of the parent ores. An alternative approach has been described by Albarède et al. (2012), which uses the measured isotope ratios for each sample to calculate the parameters $\mu$ (the ratio of $^{238}\text{U}/^{204}\text{Pb}$ in the parent deposit), $\kappa$ (the ratio of $^{232}\text{Th}/^{238}\text{U}$ in the deposit), and $T$ (the ‘model age’ of the deposit). These have the advantage of being three independent geological parameters related to the characteristics of the ore source. The model age $T$ is an estimate of the geological age of the province in which the ores are found. Because of the assumptions invoked by the use of simple models for the emplacement of the ore deposit, the values of $T$ do not necessarily correspond to real geological ages (indeed, sometimes the model ages predict the formation of the deposit in the future), but they are usually good enough to identify geological provinces by their tectonic formation ages. Nevertheless, these three parameters describe the geochemical environment of the parent deposit, which should be similar within a particular deposit, but different between deposits of different ages and chemistry. Albarède et al. (2012) use the equations for the primary growth of radiogenic $^{206}\text{Pb}$, $^{207}\text{Pb}$ and $^{208}\text{Pb}$ from $^{238}\text{U}$, $^{235}\text{U}$ and $^{232}\text{Th}$ respectively (see Pollard et al. 2017b, 388–390) to generate a set of three simultaneous equations in terms of $T$, $\Delta\mu$ and $\Delta\kappa$, where $\Delta\mu = \mu - \mu^*$ and $\Delta\kappa = \kappa - \kappa^*$, and the asterisk signifies the value of each parameter in modern common lead ($\mu^* = 9.66$ and $\kappa^* = 3.90$). In this formulation, we can solve the three equations for three unknowns $T$, $\Delta\mu$ and $\Delta\kappa$ using a trust-region-dogleg algorithm to ensure rapid convergence, and then $\mu$ and $\kappa$ are easily obtained from the expressions for $\Delta\mu$ and $\Delta\kappa$. The model age can (usually) be used to assign the
origin of ores to a particular geological province, and variations in $\mu$ and $\kappa$ can help to discriminate segments within geological provinces.

We have used calculations of $T$, $\mu$, and $\kappa$ to further explore the variations within the highly radiogenic lead used in the Shang Dynasty of China. In most Shang and Zhou ritual bronzes, the lead levels are sufficiently high (~$5$-$20\%$) that the measured lead isotope ratio in a particular object must reflect that in the added lead, rather than the traces introduced by the copper or tin. During the 1980s, Jin Zhengyao and his colleagues argued that the lead contained in the ritual vessels found at Anyang might have originated in southwest China, specifically in northeast Yunnan (Jin 1987; Jin et al. 2004), since this appeared to be the only region in China capable of yielding such highly radiogenic lead. Furthermore, the predominance of objects containing highly radiogenic lead at the sites of Sanxingdui (Jin et al. 1995), Hanzhong (Wang et al. 2008) and Jinsha (Jin et al. 2004) in southwest China, and Panlongcheng and Xin’gan (Jin et al. 1994) in the south, seemed to reinforce the idea of a lead supply from somewhere south of the Yangzi river. This suggestion, however, raised some difficult questions for specialists in Chinese bronzes. Yunnan is very distant from Anyang, especially since there are many other sources of lead closer to the Central Plains, and there is as yet insufficient archaeological evidence to understand the nature of contact between the Central Plains and Yunnan in the Shang dynasty. There are also other, equally difficult, questions to consider. The phenomenon of the use of highly radiogenic lead in Chinese ritual bronzes of the Bronze Age is relatively short-lived, as discussed above. It ‘switches on’ at the beginning of the Erligang phase of the Shang (c. 1500 BCE), and is virtually gone by the end of the Anyang phase, around 1046 BCE, or even before (the end of Yinxu III). During these c. 400 years, the use of highly radiogenic lead is ubiquitous in the Shang world and beyond. Intuitively one feels that this must represent the widespread use of a single source of lead—otherwise how would smelters over a large area simultaneously switch to, and then switch away from, the use of highly radiogenic lead, assuming that they had no way of distinguishing between highly radiogenic and common lead? Conversely, if it is a single source, then how was the distribution system organised so that it simultaneously became ubiquitous at the Shang capital, but also at many other largely autonomous centres such as Sanxingdui in Sichuan Province?

In order to see if the available data on highly radiogenic lead in Bronze Age China suggests a single or multiple source, we have assembled all the available isotopic analyses used in Figure 6 from objects containing highly radiogenic lead (arbitrarily defined as those having values of $^{206}\text{Pb}/^{204}\text{Pb} > 19$), and converted the data to $T$, $\mu$, and $\kappa$. 
Figure 7 shows all the available lead isotope data for highly radiogenic lead (as defined above) for archaeological objects from the three Erligang period sites of Erligang, Yuanqu and Panlongcheng and the later Shang period at Anyang, plus the data from Bagley (1987) on the Western Zhou objects in the Sackler Collection, plotted as $\kappa$ ($^{232}$Th/$^{238}$U) vs. $\mu$ ($^{238}$U/$^{204}$Pb). A striking feature is that the vast majority of data all appear to overlap in one group elongated along the $\mu$ axis, which is indicative of highly variable initial concentrations of uranium. However, the total range of this group is surprisingly large, having values of $\mu$ between 9.77 and 11.16, and $\kappa$ between 3.67 and 4.09. Typical ranges for common sources of lead are much narrower, such as 9.64 – 9.70 for $\mu$ and 3.83 – 3.86 for $\kappa$ in Mexican ores (Cumming et al. 1979). One would of course expect a source of highly radiogenic lead to have a larger range of values than a common source. The key question is do these data represent a single source, or more than one source? Looking more closely at Figure 7, there is the possibility that the Anyang data are split into two groups, one as just described (heavily overlapped by the other sites) and another with $\mu$ between 11.66 and 12.18. This could simply be an artefact of the small sample numbers, but the fact that it is only data from Anyang which occupies this space suggests that there may have been more than one source of highly radiogenic lead used at Anyang.

In an attempt to match these radiogenic data to a specific area, we have created an admittedly incomplete set of data on modern highly radiogenic Chinese lead ores, which, after conversion to $\mu$, $\kappa$ and $T$, shows a total range for $\mu$ of approximately 10 – 20, and 2.5 – 6 for $\kappa$ (Figure 8). Plotting $\mu$ and $\kappa$ for highly radiogenic lead by
province, we find two substantial matches for the highly radiogenic leads found in Shang bronzes (the range of which, taken from Fig. 7, is shown by the blue box), one from Shandong and one from Yunnan province.

![Figure 8:](image)

Highly radiogenic lead ($^{206}$Pb/$^{204}$Pb > 19) in modern ore data from China, converted into T, μ, and κ.

This plotting of data from modern Chinese lead ores reveals some interesting but as yet far from conclusive suggestions as to where the radiogenic lead might have originated. Jin et al. (2017) observe that the Zhongtiao mountains (close to Erlitou and Zhengzhou) have some evidence for highly radiogenic lead (Xu et al. 2005), albeit only so far published as measured in chalcopyrite samples. Similarly, the Qinling mountains to the west of the central plains have some evidence for highly radiogenic lead (Zhu et al. 2006). As originally noted by Jin, northern Yunnan in the south-west of China remains a possible source of this metal (Jin et al. 1994; 2004).

Plotting the mu-kappa data for highly radiogenic leads found in Shang dynasty bronzes has shown that those from Erlitou, Zhengzhou, Panlongcheng and Yuanqu all occupy the same extended region of the graph, which could indicate that they come from a single source. There is some evidence that there may be a second source represented at Anyang, but not at the other sites. As yet the modern ore data are too limited to consider asking where these sources might be, but the original suggestion of Yunnan appears to be a possibility, alongside Shandong, although other, closer, sources such as Zhongtiao Mountain must also be considered.

All of this helps to shed more light on the phenomenon that is the use of highly radiogenic lead in Shang dynasty China, but does not specifically identify the number of sources, nor their locations. Two other pieces of the jigsaw have recently
been put together, both of which point (independently) to the use of multiple sources of highly radiogenic lead. One is the study of silver levels in the bronzes. As noted in Chapter 3, silver is unlike the other trace elements used to create Copper Groups because in leaded bronzes it is possible that it accompanies the lead and not the copper. In a recent study, Pollard et al. (submitted) concluded that there were at least two patterns of association between the silver and the lead, indicating two different geological provinces for the origin of the lead. Interestingly, there did not appear to be a clear difference between the Ag-Pb association in highly radiogenic and common leads where they co-occurred, suggesting that the two types of lead may have come from similar geological environments. Perhaps even more significantly, Liu R. et al. (2018) have extended the data shown in Figure 6 above to include lead isotope ratios from glasses, glazes and pigments into the Han and Tang dynasties. This shows clearly that highly radiogenic lead continued to be used for a wide range of materials and across a broad area of China well into the Tang dynasty. This suggests that sources containing highly radiogenic lead were probably widely available across China, thereby strongly supporting the likelihood that multiple sources of highly radiogenic lead could have been used by the Shang and their neighbours.

Kernel Density Estimates of lead isotope distributions

The practice that developed in the 1990s of drawing ‘90% confidence ellipses’ around archaeological data presented in an isotope ratio bi-plot to define an ore field has drawn much criticism. It either assumes a normal distribution of points in the space defined by the isotope ratios, which has been shown not to be true (Baxter and Gale 1998), or is an entirely arbitrary exercise, which often involves dropping data points as ‘outliers’ in order to achieve a regular ellipse. The use of kernel density estimates (KDEs) has been shown to be much more robust in defining the actual distribution of an ore field (Baxter et al. 1997; Scaife et al. 1999), but has not been widely adopted until recently because of the lack of simple algorithms to perform the calculation.

We now use the software developed by Christopher Bronk Ramsey for producing and comparing KDE distributions from the chemistry of volcanic tephra, and available within the open access database developed for the RESET project in Oxford (Response of Humans to Abrupt Environmental Transitions: c14. arch.ox.ac.uk) (Bronk Ramsey et al. 2015). As introduced in Chapter 5, kernel density estimates are a non-parametric way to convert continuous data into a smoothed probability density function, using a smoothing parameter $h$, called the
kernel. Using KDEs has three main advantages. Firstly, KDEs do not assume that
the data has to be normally distributed, which is particularly useful for lead isotope
ratios (although the way the kernel $h$ is usually derived is to use an approximation
which becomes more optimal the closer the distribution is to normality). Secondly,
KDEs can produce smoother distributions than conventional histograms whose
appearance is significantly affected by the choices of bin width and start/end points
of bins (see Chapter 4). Thirdly, the KDEs can easily generate a multi-dimensional
visualisation to compare different datasets in a way that histograms cannot. In
archaeology, KDEs have been found useful to interpret chemical compositions,
lead isotope ratios and spatial data (Baxter et al. 1997). Here we show that kernel
density distributions from different assemblages can also be compared to estimate
the likelihood of overlap—i.e., to answer the question ‘are these distributions the
same or different’.

The univariate kernel density estimator ($\hat{f}_h$) of the parent function ($f$) from
which the samples are derived is mathematically defined as follows:

$$
\hat{f}_h(x) = \frac{1}{n} \sum_{i=1}^{n} K_h (x - x_i) = \frac{1}{nh} \sum_{i=1}^{n} K \left( \frac{x - x_i}{h} \right)
$$

where $n$ is the sample size, $h$ is the kernel bandwidth and the kernel $K$ is a summed
probability density function over all the samples. The choice of kernel bandwidth
$h$ is crucial for the shape of the KDE and the subsequent interpretations. If $h$ is too
wide the distribution will be over-smoothed and may possibly hide important detail,
but if it is too narrow the distribution will be spikey and possibly discontinuous.
Many mathematical formulations have been put forward to select optimal kernel
widths in univariate cases, but there is no well-defined method to establish the
optimal kernel bandwidth in multidimensional data. According to Bronk Ramsey
et al. (2015), a commonly-used approximation for the optimal bandwidth of the
multidimensional kernel is:

$$
h = \left\{ \frac{4}{(d + 2)n} \right\}^{\frac{1}{(d + 4)}}
$$

where $d$ is the number of dimensions (parameters measured) and $n$ is the number
of samples in the dataset. This estimate approaches optimality as the data approach
multivariate normality. The details of the derivations are given in Bronk Ramsey
et al. (2015, 42).
Apart from producing smoothed quasi-continuous probability distributions for univariate or multivariate distributions, a key additional capability is to test the degree of overlap between two distributions. In the original application of this approach to tephrochronology, the purpose was to answer the question, based on a set of chemical measurements, does the volcanic glass found in place A match that of a particular source volcano? This methodology is, however, equally applicable to the chemical composition of metal assemblages, and also to lead isotope ratios. Again, Bronk Ramsey et al. (2015) provide the detailed mathematical calculations for comparing the chemical or isotopic compositions of two assemblages.

If we have two assemblages $X$ and $Y$ containing $n$ and $m$ samples respectively, then we can use the kernel density estimates derived above for $X$ and $Y$ to answer the question ‘how likely is it that each of the individual samples in assemblage $Y$ could belong to the distribution defined by $X$? Mathematically the average value for this probability is given by:

\[
q_x(x) = q_x(x_1, \ldots, x_d) = \frac{1}{n} \sum_{i=1}^{n} N_d(x_i, h^2 \sum x)
\]

\[
q_{x_j}(x) = \frac{1}{n-1} \sum_{i=1, i \neq j}^{n} N_d(x_i, h^2 \sum x)
\]

This absolute value of the average is not very useful because it depends on how the various parameters are standardized. It is better to normalise it against the average probability of the individual values of the $n$ samples in $X$ belonging to $X$. This gives a ratio of the two probabilities:

\[
B_{yx} = \frac{\frac{1}{m} \sum_{i=1}^{m} q_x(y_i)}{\frac{1}{n} \sum_{j=1}^{n} q_x(x_j)}
\]

\[
B_{xx} \equiv 1
\]

This ratio ($B_{yx}$) is a measure of the likelihood of assemblage $Y$ being a sub-set of assemblage $X$ (which is not the same as $B_{xy}$, the likelihood of $X$ being a sub-set of $Y$). This value should approach 1 if the distribution of the two datasets is similar,
but could exceed 1 if dataset $Y$ is located on top of the densest area of dataset $X$. Moreover, determining the threshold for the significance of matches is arbitrary. It is strictly not possible to demonstrate consistency between two datasets, only dissimilarity. Thus if the value of the ratio falls below 0.05 then it is probably safe to say at the equivalent of 95% confidence that the two distributions are different. It is more difficult to be certain about when we can accept the likelihood of similarity between two assemblages, but clearly values close to or greater than 1 would mean that we cannot disprove the possibility of them being from the same source.

Figure 9a shows two conventional sets of lead isotope diagrams ($^{207}$Pb/$^{204}$Pb vs. $^{206}$Pb/$^{204}$Pb and $^{208}$Pb/$^{204}$Pb vs. $^{206}$Pb/$^{204}$Pb) for data from north-west China (Hsu et al. 2018). The sites are the Wangdahu cemetery in Ningxia (WDH), modern galena ore data from the Dajing mine in Inner Mongolia (DAJ: Chu et al. 2002), plus data from metallurgical remains found at smelting sites associated with the Upper Xiajiadian culture (UX_ORE and UX_SLAG, for ore and slag samples respectively, from Dong 2012), and thought to derive at least in part from the Dajing mine (Yang 2015, 183). A striking feature of these diagrams is the linear array of isotope data for both uranium- and thorium-derived Pb for both Wangdahu and Dajing, but with different gradients. It is clear from the raw data that the lead in the objects recovered from the Wangdahu cemetery did not originate from the Dajing mine. However, some points of the Upper Xiajiadian ore and slag analyses seem to fall exactly on the straight line derived from the Dajing ore data, whereas other samples scatter to both sides of this line. Using KDE (Figure 9b), we can better visualise the data, and also statistically test the probability of association between the various assemblages represented.

The overlap between all pairs of probability distributions can be expressed as a matrix based on KDE estimates as described above (Table 1), using all three ratios (i.e., calculating the three dimensional overlap). It is clear that the Upper Xiajiadian ore and slags are substantially overlapping (UX_ORE and UX_SLAG = 1.137, UX_SLAG and UX_ORE = 0.907; see discussion above about the reason for this non-commutativity), and are both very likely to be a subset of the Dajing ore data given that the probabilities are very close to 1 (UX_ORE and DAJ, UX_SLAG and DAJ ≈ 0.95). There is no overlap between the Wangdahu data and any of the other data in the analysis. This makes sense since Dong (2012) has already argued that Xiajiadian people transferred Dajing ores to other places for further smelting whereas, as noted above, the WDH bronzes are highly unlikely to have been made from the Dajing ores or recycled Xiajiadian objects.
Figure 9:
a) Conventional isotope bi-plots of lead isotope data from north-west China, and b) a KDE rendition of the same data (Hsu et al. 2018).

Table 1:
Overlap of KDEs for the various groups shown in Fig. 9 (Hsu et al. 2018)
Although it is helpful to see these results expressed quantitatively, we should note that the numerical value of \( \approx 0.95 \) for the overlap between either UX-ORE and UX-SLAG and the Dajing data overlooks the fact that both sets of UX data extend far beyond the narrow line of the Dajing data. This asymmetric relationship is confirmed by the lower overlap between DAJ and UX-ORE (0.55) and DAJ and UX-SLAG (0.81), which are both lower than the reverse overlaps (0.95). In other words, some of the UX ore samples do not match exactly the Dajing ore data, suggesting that either the current Dajing data is not completely representative of the Dajing ores, or that ores from other areas were also smelted at these Upper Xiajiadian smelting sites.

KDEs provide the best rendition of the distribution of lead isotopes in an assemblage, and are clearly superior to distributions using ‘confidence elipses’, which are based on an assumption of normality in all three isotope ratios. As shown above, they can also be used to estimate the similarity (strictly, dissimilarity) between two assemblages by calculating the degree of overlap between the two probability distributions. This is an extremely useful quantitative method for assessing the similarity between the lead isotope data from different assemblages. It can also be used to calculate the similarity between groups defined by multivariate chemical data, as shown for tephra (Bronk Ramsey et al. 2015), and also for medieval glass (Bidegaray and Pollard 2018). The previous chapter showed that KDEs can also be used to represent the distribution of the alloying elements (or, indeed, trace elements) in an assemblage, and, by extension, can be used to compare distributions between assemblages. Potentially this could therefore provide an alternative to the use of cumulative frequency distributions (CFDs) and comparison using the Kolmogorov-Smirnov test.

The examples provided in this chapter have been chosen to illustrate a number of different ways in which lead isotope data can be used on archaeological material. Conventional lead isotope bi-plots, adopted from isotope geochemistry, have proved useful in some circumstances, but do not directly address archaeological situations where there is the potential for anthropogenic mixing of lead in archaeological objects. As with our consideration of trace elements and alloying elements, the methods presented here have been derived from a conviction that it is detecting change in the archaeological record which is significant, rather than a more limited focus on the ideas of provenance.
Appendix: Mixing model for lead isotopes

Assume that we create a mixture of two components A and B in differing proportions, specified by a mixing parameter $f_A$ defined as:

$$ f_A = \frac{A}{A+B} \quad (1) $$

where A and B are the weights of the two components in the mixture. If each component contains two elements (e.g., Cu and Pb), and Pb$_A$ and Pb$_B$ are the concentrations of Pb in components A and B, expressed in weight units, then the concentration of Pb in the resulting mixture is

$$ \text{Pb}_M = \text{Pb}_A \cdot f_A + \text{Pb}_B \cdot (1-f_A) \quad (2) $$

Rearranging this expression shows that Pb$_M$, the weight of Pb in the mixture, is a linear function of $f_A$:

$$ \text{Pb}_M = (\text{Pb}_A - \text{Pb}_B) \cdot f_A + \text{Pb}_B \quad (3) $$

Consider now that the two components A and B not only have different concentrations of lead but also different values of the set of three lead isotope ratios, having $^{204}\text{Pb}$ as denominator ($^{206}\text{Pb}/^{204}\text{Pb}^, ^{207}\text{Pb}/^{204}\text{Pb}^, ^{208}\text{Pb}/^{204}\text{Pb}$). If the ratio of $^{206}\text{Pb}/^{204}\text{Pb}$ in component A is $(^{206}\text{Pb}/^{204}\text{Pb})_A$, and that in B is $(^{206}\text{Pb}/^{204}\text{Pb})_B$, then the ratio in the mixture $(^{206}\text{Pb}/^{204}\text{Pb})_M$ is given by:

$$ (^{206}\text{Pb}/^{204}\text{Pb})_M = (^{206}\text{Pb}/^{204}\text{Pb})_A \cdot \frac{\text{Pb}_A}{\text{Pb}_M} \cdot f_A + (^{206}\text{Pb}/^{204}\text{Pb})_B \cdot \frac{\text{Pb}_B}{\text{Pb}_M} \cdot (1-f_A) \quad (4) $$

This equation contains two different weighting factors: $-f_A$ which relates to the abundances of the two components A and B, and $\text{Pb}_A/\text{Pb}_M$ and $\text{Pb}_B/\text{Pb}_M$, which relate to the fractions of Pb in the mixture contributed by A and B. We can eliminate $f_A$ from this equation by rearranging eqn. (3):

$$ f_A = \frac{\text{Pb}_M - \text{Pb}_B}{\text{Pb}_A - \text{Pb}_B} \quad (5) $$
Beyond Provenance

Giving:

\[
\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_M = \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_A \left(\frac{\text{Pb}_A}{\text{Pb}_M}\right) \frac{\text{Pb}_M - \text{Pb}_B}{(\text{Pb}_A - \text{Pb}_B)} + \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_B \left(\frac{\text{Pb}_B}{\text{Pb}_M}\right) \frac{1 - (\text{Pb}_M - \text{Pb}_B)/(\text{Pb}_A - \text{Pb}_B)}
\]

which rearranges to:

\[
\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_M = \text{Pb}_A \text{Pb}_B \left[\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_A - \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_B\right] / (\text{Pb}_M(\text{Pb}_A - \text{Pb}_B)) + \left[\text{Pb}_A \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_A - \text{Pb}_B \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_B\right] / (\text{Pb}_A - \text{Pb}_B)
\]

This is an equation of the form:

\[
\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_M = k \left(1/\text{Pb}_M\right) + c
\]

which is a linear equation between \(\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_M\) and \((1/\text{Pb}_M)\), where the gradient is given by:

\[
k = \text{Pb}_A \text{Pb}_B \left[\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_A - \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_B\right] / (\text{Pb}_A - \text{Pb}_B)
\]

and the intercept:

\[
c = \left[\text{Pb}_A \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_A - \text{Pb}_B \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_B\right] / (\text{Pb}_A - \text{Pb}_B)
\]

To summarize, the lead isotopic ratio of the mixture is a linear function of the reciprocal of lead concentration in the mixture. Thus, mixing lines in a two component mixture appear as straight lines when \(\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)\) is plotted against \((1/\text{Pb}_M)\). Similar equations apply for the equivalent relationships for \(^{207}\text{Pb}/^{204}\text{Pb}\) and \(^{208}\text{Pb}/^{204}\text{Pb}\).