

**A NOVEL APPROACH TO LEAD ISOTOPE PROVENANCE  
STUDIES OF TIN AND BRONZE**

by

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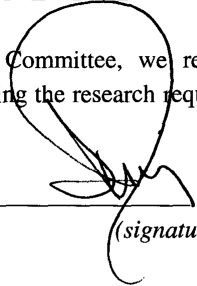
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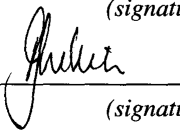
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# **A Novel Approach to Lead Isotope Provenance Studies of Tin and Bronze**

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## **Abstract**

Lead isotopic ratios of cassiterite, the dominant tin ore, evolve after crystallization through decay of uranium and thorium to lead. We show that the lead isotopic ratios of smelted tin at Rooiberg, South Africa, form an isochron that matches the known geological age of the Rooiberg cassiterite deposits. Since the lead isotopic ratios of several prehistoric tin and bronze artifacts throughout southern Africa also fall on this isochron, we deduce that they were made with tin from the Rooiberg deposits.

Implications of this approach for provenance studies of early tin and bronze in Eurasia are also examined.

**Keywords:** Provenance, tin, bronze, lead isotopes, isochron, Rooiberg, South Africa

## **Introduction**

One of the major unsolved questions in the later archaeology of the Old World is the source (or sources) of tin for the Bronze Age of the Near East and the eastern

Mediterranean – both of which lack major tin deposits. This has been a topic of debate since J.D. Muhly's comprehensive survey of the archaeological and geological evidence some thirty-six years ago (Muhly 1973). There is no question that most of the tin must have been obtained through long-distance trade, but there is considerable argument over potential sources and trade routes (Weeks 2003). However, in spite of much discovery and discussion, including the dating and distribution of early tin and bronze artifacts, the correlation of archaeological sequences from various areas, and the interpretation of ancient texts, this question is still far from resolution (e.g. Franklin *et al.* 1979; Muhly 1985; Yener *et al.* 1989; Pigott 1999; Yener 2000; Weeks 2003; Nezafati *et al.* 2006).

Archaeometry has contributed very little to this discussion. Lead isotopic ratios have been measured for many hundreds of bronze artifacts from the Mediterranean, Europe and western Asia. (e.g. Gale and Stos-Gale 1982; Budd *et al.* 1993; Weeks 2003).

However, since these have without exception been compared to lead isotopic data for copper sources (or lead sources in the case of leaded bronzes), it is clear that almost all researchers to date have implicitly assumed that the lead in bronze must derive from the copper, or from added lead, rather than from the tin. (This view is explicitly argued in Begemann *et al.* 1999).

When compared to the dozens of published studies of copper alloy artifacts and ore sources, there has been remarkably little archaeometric study of the provenance of tin. Rapp and colleagues (Rapp 1978; Rothe and Rapp 1995; Rapp *et al.* 1999) attempted to use trace elements to characterize deposits of cassiterite (the main tin ore) and tin metal

produced from cassiterite, but no archaeological applications followed. Tin has ten naturally-occurring isotopes (more than any other element), but an initial flurry of interest in the use of tin isotopes for provenance of archaeological tin (Gale 1997; Begemann *et al.* 1999; Yi *et al.* 1999; Clayton *et al.* 2002) subsided because, even with the highest precision attainable, the observed variations in the isotopic ratios of tin metal, cassiterite ore and archaeological bronzes in these studies were barely greater than the analytical errors. Begemann *et al.* (1999) measured lead isotopic ratios in 15 ancient tin ingots from Mediterranean shipwrecks, but these cannot be used to determine provenance because no attempt has ever been made to develop lead isotopic signatures for potential sources of tin ore.

In this article we demonstrate a method for characterizing tin sources through a case study of a tin source (Rooiberg) and prehistoric tin artifacts in Southern Africa. We show that cassiterite ore deposits, unlike copper, lead, and silver ore deposits, cannot be expected to show tight clusters of lead isotopic ratios. Instead we adapt the standard geochronological method of isochron dating (Faure and Mensing 2005) to characterize the Rooiberg tin source. Since cassiterite is difficult to dissolve, we measured isotopic ratios of smelted tin from excavated archaeological sites at the mine, and show that an isochron fitted to these data reproduces the known geological age of tin mineralization at Rooiberg. We then show that the isotopic ratios of prehistoric tin artifacts found throughout Southern Africa fall on this isochron, and thus confirm that the Rooiberg tin mines (or deposits of the same geological age) are the source of these prehistoric tin ingots. We also examine the isotopic ratios of prehistoric unleaded bronzes from

Bosutswe, Botswana (Denbow and Miller 2007) and show that these too provide an isochron matching the age of the Rooiberg tin deposit. This implies that in bronzes with low lead concentrations, we can sometimes identify the source of tin even after it has been alloyed with copper. Lastly, we consider whether our methodology might be applied to the question of sources of tin for the Bronze Age of Eurasia.

### **Lead isotope geochronology of cassiterite ore – the theoretical basis**

Lead has four isotopes -  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$  -, all of which were present at the time of earth's formation. However, the latter three are also the products of the radioactive decay of their parent isotopes -  $^{235}\text{U}$  (half life 703.8 Myr),  $^{238}\text{U}$  (4.468 Gyr), and  $^{232}\text{Th}$  (14.01 Gyr) - respectively. Consequently, the isotopic composition of Pb in the earth at any given time is the sum of the Pb present at the time of earth's formation and Pb that has been produced subsequently by radioactive decay. The two-stage Stacey-Kramers model (Stacey and Kramers 1975) infers the Pb isotopic ratios of the whole earth at any given time based on the known initial Pb isotopic ratios (from meteorites), and the assumption that the earth's mantle is a homogenous reservoir of Pb, U, and Th that evolves over time due to the predictable decay of U and Th to Pb.

In actuality, the earth is composed of different geologic reservoirs which separated from the "bulk" earth at various times, and contain varying amounts of Pb, U, and Th. As a result, individual reservoirs can have Pb isotopic ratios that differ substantially from those predicted by the Stacey-Kramers model. When a mineral incorporates Pb in its crystal structure, it acquires the lead isotopic composition of its parent reservoir. This is

called “common lead” (e.g., Faure and Mensing 2005). If the mineral lacks U and Th (and therefore cannot gain lead from radioactive decay over time) the “common lead” isotopic ratios will be preserved indefinitely, unless altered by subsequent metasomatism or metamorphism. Copper, lead and silver sulphide minerals incorporate Pb, but generally cannot accommodate U and Th in their crystal lattices. These minerals thus have “common lead” isotopic signatures, as do the secondary carbonate and hydroxide minerals derived from these sulfides. (Surficial chemical reactions do not cause fractionation of lead isotopes; nor does smelting to metal, or subsequent corrosion).

The use of lead isotopic ratios in archaeological provenance studies is founded on the assumption that ore deposits can be clearly distinguished from each other. In practice, this means that, within a given area, the variation in isotopic ratios within individual deposits of common lead minerals should be smaller than the variation in ratios between deposits (Wilson and Pollard 2001). Ideally the cluster of isotope ratios for a given deposit on bivariate plots (e.g.  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$ ) will provide a unique “fingerprint” for that deposit. Archaeologists can then match the isotopic ratios of individual archaeological artifacts to the “fingerprints” of their parent ore source (e.g., Gale and Stos-Gale 1982; Wilson and Pollard 2001; Weeks 2003; Thibodeau *et al.* 2007). Although there are often practical difficulties with this approach, including overlapping fingerprints of two or more sources, mixing of metal from different sources, and metal recycling (Budd *et al.* 1993; Pernicka 1995; Pollard 2009), the lead fingerprinting approach has been successfully applied to many ancient copper, lead, and silver artifacts.

However, this approach can only be applied to ore minerals that do not accept U and Th into their crystal lattices. But some ore minerals do accommodate substantial amounts of U and Th. These include cassiterite ( $\text{SnO}_2$ ), the dominant mineral in most tin deposits. This has a crystal structure similar to that of rutile ( $\text{TiO}_2$ ), which incorporates only small amounts of common lead upon crystallization, but readily accepts significant amounts of U and Th (Mezger *et al.* 1989). Cassiterite can contain several hundred parts per million (ppm) U and Th, so much that slag dumps from tin smelting have been investigated as potential radiation hazards (Farthing 2002). The lead isotopic ratios of cassiterite will therefore change after crystallization due to the radioactive decay of U and Th to Pb. Individual crystals within a single cassiterite deposit may contain different initial amounts of U and Th, and thus over time, gain significantly different amounts of radiogenic lead isotopes ( $^{208}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{206}\text{Pb}$ ). The amount of  $^{204}\text{Pb}$  does not increase, since it is not a product of radioactive decay. Thus the ratios of the three radiogenic lead isotopes to  $^{204}\text{Pb}$  will each increase after crystallization as functions of: (1) initial U, Th and Pb content; (2) the half-lives of the parent U and Th isotopes; and (3) time elapsed since crystallization.

Ratios of radiogenic lead isotopes to  $^{204}\text{Pb}$  in cassiterites can therefore be significantly more variable than those in “common lead” minerals like galena or chalcopyrite.

Published  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios for “common lead” minerals fall within the range of 15 to 22.

As we show below,  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios of tin smelted from a single cassiterite deposit that crystallized two billion years ago range from less than 20 to over 90. Thus the isotopic “fingerprinting” method used for archaeological provenance studies of copper alloys,

silver and lead artifacts can not necessarily be used for provenance of tin artifacts – at least not for those produced from old cassiterite – because ratios of any of the three radiogenic isotopes to  $^{204}\text{Pb}$  do not produce the tight clusters that define source fingerprints for “common lead” minerals. A new method, which does not rely on distinct isotopic clusters to characterize a single deposit, is needed to fingerprint cassiterite deposits.

Although cassiterite crystals from a single deposit may contain different amounts of U, the *ratio* of  $^{235}\text{U}$  to  $^{238}\text{U}$  within those crystals will be the same because both isotopes have identical chemical behavior, so they are incorporated in crystals in ratios identical to those in the parent ore-forming solution. Consequently, individual cassiterite crystals may accumulate different amounts of radiogenic  $^{207}\text{Pb}$  and  $^{206}\text{Pb}$ , but the ratio of  $^{207}\text{Pb}$  to  $^{206}\text{Pb}$  will be identical at any given time. Thus, on a plot of  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$ , all cassiterite crystals that crystallized at the same time from a single parent ore fluid will fall on a straight line, called an isochron. Since the slope of the isochron is simply the ratio of radiogenic  $^{207}\text{Pb}$  to  $^{206}\text{Pb}$ , its value can be used to calculate the age of the deposit:

$$\frac{^{207}\text{Pb}}{^{206}\text{Pb}}_{\text{radiogenic}} = \frac{^{235}\text{U} (e^{\lambda_2 t} - 1)}{^{238}\text{U} (e^{\lambda_1 t} - 1)} \quad (\text{Eq. 1})$$

Where:

$$\frac{^{235}\text{U}}{^{238}\text{U}} = \frac{1}{137.88} = \text{the present day ratio of } ^{235}\text{U} \text{ to } ^{238}\text{U}$$

$$\lambda_2 = \text{decay constant for } ^{235}\text{U}$$

$\lambda_1$ =decay constant for  $^{238}\text{U}$

t = time elapsed since crystallization of the ore deposit

(Faure and Mensing 2005)

Conversely, if the age and the initial “common lead” values of a deposit are known, a “reference” isochron can be constructed on which the  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  values of all cassiterite crystals from the deposit will plot. Three calculated reference isochrons for *hypothetical* cassiterite deposits of ages 2 billion years, 1.2 billion years, and 325 million years are shown in Figure 1. Each isochron is calculated from ten points representing crystals with different initial ratios of U to Pb, varying from 0 to 5. Cassiterite crystals which contained no U or Th will gain no radiogenic lead over time, and thus possess the same initial “common lead” isotopic signature that all cassiterite crystals (and all other minerals) in the deposit had at time of crystallization. These crystals anchor the isochrons in the bottom left corner, and in this illustration possess the common lead values predicted by the Stacey-Kramers model for deposits of those ages. Crystals which contain U and Th will plot further up the isochron according to the varying amounts they incorporated at time of crystallization, and thus the various amounts of radiogenic  $^{206}\text{Pb}$  and  $^{207}\text{Pb}$  they have accumulated *over time*. Crystals with the highest initial U to Pb ratios (5) plot at the top right end of each isochron.

Thus the isochron itself is the “fingerprint” of a given cassiterite deposit. Because lead isotopes do not fractionate during smelting, tin artifacts produced from a single cassiterite

deposit should in theory reproduce the same isochron as the cassiterite ore. (This assumes that the smelted tin has not picked up any lead from other materials (fuels and refractories) during smelting, and has not subsequently been mixed with tin from other ore deposits). Determining the geological provenance of a given tin artifact is then simply a matter of matching the  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios of the artifact to the isochrons of potential sources of cassiterite ore. If the ratios for tin objects fall on the isochron, then we may infer that they derived from that cassiterite deposit (or another with an identical isochron). Tin artifacts that plot off the isochrons (for example, the hypothetical points A and B in the enlarged portion of Figure 1) must originate from other sources, or be the product of mixing of materials from two or more sources.

It is important to note that although all three reference isochrons in Figure 1 contain crystals with the same ranges of U to Pb, the isochron for the 325 million year old deposit spans a much smaller range of radiogenic  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  values than that of the 1.25 or 2 billion year old deposits. This is because the accumulation of radiogenic lead is time-dependent, so that a 2 billion year old deposit will possess significantly more radiogenic lead than it did 1 billion years earlier. It follows that cassiterite deposits which are relatively young (<100 Ma) will not exhibit significantly radiogenic Pb isotopic signatures ( $^{206}\text{Pb}/^{204}\text{Pb} > 20$ ) unless they had high initial U to Pb ratios. As a result, most young cassiterite deposits should display Pb isotopic signatures that have not evolved appreciably from that of the initial common Pb they incorporated, making an isochron difficult to identify. We will return to this point later in this article, when we discuss the

potential application of our method to the problem of tin sources for the Bronze Age of Mesopotamia and the Mediterranean.

Finally, although cassiterite deposits of the same age will produce isochrons with the same slope, they may have had different initial isotopic ratios of common lead. In Figure 1, each reference isochron was anchored by the common lead values predicted by the Stacey-Kramers model for deposits of that age. But Stacey-Kramers is simply an idealized model for the lead isotopic composition of a “bulk” earth reservoir at any given time, and most real geologic reservoirs within the earths crust possess Pb isotopic compositions that depart from the Stacey-Kramers model. Figure 2 shows three calculated reference isochrons for deposits that all formed 1.2 billion years ago, but from isotopically distinct geologic reservoirs. As a result, each isochron is anchored at the lower end by a different initial “common lead” value (points A, B and C). Consequently, cassiterite deposits that formed at the same time may have distinctly different, but parallel isochrons – a fact that has positive implications for archaeological provenance studies of tin artifacts.

### **A test case: prehistoric tin production in South Africa**

Some two dozen cast tin ingots of distinctive shapes, and two shapeless lead-tin lumps, have been recovered over the last hundred years from surface contexts and archaeological excavations within a large area of northern South Africa, eastern Botswana and Zimbabwe (Fig. 3). The only prehistoric tin workings ever discovered in this region are in the Rooiberg valley, where hundreds of workings (up to 60 m deep) are estimated to have

produced some  $2 \times 10^6$  kg of tin before ca. 1850 AD (Recknagel 1908; Baumann 1919; Chirikure *et al.* 2007). The ores are composed of intergrown cassiterite and tourmaline, with minor discontinuous pockets of sulfides (pyrite, chalcopyrite, galena) (Leube and Stumpfl 1963; Rozendaal *et al.* 1995). The Rooiberg tin deposits were created by the emplacement of the Lebowa Granite Suite (LGS) of the Bushveld Igneous Complex, an event that is dated by U-Pb and Rb-Sr isotopic techniques to 2034-2088 Ma (Robb *et al.* 2000). All other tin deposits in Southern Africa are hosted in pegmatites, and none date within 300 Myr of the LGS (von Knorring and Condliffe 1987).

The questions that we seek to answer are the following:

- (1) Can an isochron be obtained on tin metal that is known to have been smelted from Rooiberg cassiterite?
- (2) Were all the tin, tin-lead, and bronze objects found within the area in Figure 3 produced from Rooiberg ores?

## **Methods**

Material was extracted from all samples using a hand-held electric drill and lead-free tungsten-carbide dental drill bits; a fresh bit was used for each sample. In order to avoid possible surface contamination, samples were immersed in a 1% HNO<sub>3</sub> solution for five to 20 minutes. Subsequently, either 1) corrosion on the samples was removed by drilling, after which the drill bit was replaced and the exposed metal was sampled or 2) in the case

of highly corroded samples, samples were used only after additional leaching. For several samples, both corroded and fresh material was sampled after leaching and subsequent lead isotopic analysis showed no significant difference between materials.

Samples were dissolved in 8M HNO<sub>3</sub> or aqua regia in clean Teflon containers at 125°C. Subsequently, all aqua regia solutions were dried down in a HEPA filtered environment, and each sample was re-dissolved in 8M HNO<sub>3</sub>. Lead was then separated using Sr-Spec™ resin in Teflon columns (as discussed in Chesley *et al.* 2002). Total process Pb blanks were run along with samples and were less than 100 pg. Lead isotopic analysis was conducted on a GV Instruments multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the University of Arizona, according to the methods discussed in Thibodeau *et al.* 2007. Data and errors were also calculated according to the methods in Thibodeau *et al.* 2007. External errors associated with each Pb isotopic ratio are reported as the 2σ percentage error in Tables 1 and 2. Lead concentrations from the initial solutions were measured on an Elan DRC-II ICP-MS instrument at the University of Arizona.

The <sup>207</sup>Pb-<sup>206</sup>Pb regression ages and MSWD (Mean Square of Weighted Deviates) were calculated (using the <sup>207</sup>Pb/<sup>204</sup>Pb and <sup>206</sup>Pb/<sup>204</sup>Pb values and the 2-sigma absolute errors) with Isoplot/Ex3 (Ludwig 2003).

## **Results**

### ***(A) Smelted tin***

High-precision Pb isotopic measurements were made on seven prehistoric tin ingots, two prehistoric lead-tin ingots, one sample of tin from the last run (1992) of the modern tin smelter at Rooiberg, five tin prills extracted from slags on prehistoric smelting sites in the Rooiberg valley, four of the glassy slags from which prills were extracted, and five samples of furnace ceramics (tuyeres). All results are reported in Table 1.

The first step in interpretation of these data is to establish that the smelted tin had not acquired lead from the slag during the smelting of the cassiterite ore. The technology of tin smelting in the Rooiberg valley has been intensively studied by Chirikure *et al.* (in review) who concluded that the cassiterite ores were concentrated to very high grade before smelting, so that only a minor amount of slag was produced relative to the amount of tin. The slags were formed by reaction between cassiterite, the residual gangue minerals intergrown with the cassiterite (tourmaline, Fe-Ca-Mg carbonates), and the ends of the tuyeres, which protruded into the furnaces and appear to have supplied most of the silica and alumina. The tuyeres are composed of clays naturally tempered with arkose rock fragments. Arkose and shales form the floor of the Rooiberg valley and are much older than the tin ore deposits within them (Rozendaal *et al.* 1995). As a result of their different ages and mineralogical compositions, we would expect that the clays derived from arkose and shales in the furnace lining and tuyeres would have different lead isotopic ratios than the tin ore.

The Pb isotopic ratios for tin prills, slags, and tuyeres from two smelting sites at the northern end of the Rooiberg valley are shown in Figure 4. The four slags are part of

matched pairs with four prills (i.e. the prills were drilled out of the slags). Note that: (1) the lead isotopic ratios of most of the tuyere and slag pieces are distinctly different from those of the tin prills; and (2) the isotopic ratios of the tin prills fall on a straight line. If we assume that this line is an isochron, we can calculate a model age for this set of samples. That age is  $2052 \pm 34$  Ma – a good match to the available radiometric ages of the Lebowa Granite Suite (2032-2088 Ma), the source of the ore-forming fluids for the Rooiberg tin deposits (Robb *et al.* 2000).

We therefore conclude that the tin prills did not pick up significant amounts of lead from either tuyeres or slags during smelting, and that the line is a valid fingerprint for the Rooiberg tin deposits, to which tin samples of unknown provenance may be compared. This line is not strictly an isochron in the sense of that term in geochronology, for the scatter of points around the line (as expressed by the Mean Square of Weighted Deviates (MSWD) is much too large. However, we are not trying to directly date the Rooiberg deposit, but rather utilize the isochron as a comparative tool for the purpose of archeological provenance analysis. The possible reasons for the large MSWD associated with our isochrons will be addressed later in the paper.

The next step in interpretation of the data is to see whether tin objects found at various distances from Rooiberg will plot on the same isochron. The  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios for all tin objects analyzed are shown in Figure 5. This includes the tin prills and ingots from Rooiberg smelting sites (from Fig. 4), tin from the modern Rooiberg smelter, both tin and lead-tin ingots from the archaeological sites shown in Figure 3, and several

undated surface finds of tin ingots. For contrast, we also analyzed a sample of tin from the modern smelter at Kamativi, Zimbabwe, which is a pegmatite tin deposit formed during the Kibaran orogeny (900-1100 Ma), and thus about 1000 Myr younger than the Rooiberg deposits (von Knorring and Condliffe 1987).

Once again, the Pb isotopic ratios of all of these objects (except for the Kamativi tin) define a straight line, which, if treated as an isochron, yields an age of  $2065 \pm 32$  Ma and a MSWD of 896. This age is almost identical to the isochron defined in Figure 4 for the tin prills and ingots recovered at Rooiberg. Thus we conclude that all the prehistoric tin objects that we have analyzed derived from the Rooiberg deposits, or from another tin deposit associated with the Lebowa Granite Suite. Since no evidence of prehistoric mining or smelting has been reported at other LGS tin deposits, the Rooiberg mines are the probable source of all these objects. It is also clear from Figure 5 that the modern tin sample from Kamativi falls significantly off the isochron, as would be expected of tin originating from a genetically unrelated and younger deposit (which would therefore produce an isochron with a different slope).

### ***(B) Isochrons versus mixing lines***

At this point we call attention to the open square symbol at the bottom left of the isochron (Fig. 5). This square actually represents two objects with essentially identical lead isotopic ratios and very similar chemical compositions (about 80% Pb, 20% Sn) (Miller 2002; Denbow and Miller 2007). These are the only two lead-tin alloys known from southern Africa prior to European colonization. Both were found in contexts dated by

radiocarbon techniques between 1450 and 1550 cal AD, but at sites (Great Zimbabwe and Bosutswe) that are 500 km apart (Fig. 3) (Miller 2002).

The lead isotopic ratios of these two objects are obviously those of the lead in the alloy, not the tin. As expected, they show “common lead” isotopic ratios, yet still plot right on the isochron defined by the tin ingots. The best explanation for this is that the lead in these objects possessed the same initial common lead isotopic signature as the cassiterite ore, and thus likely originated from the same deposit. This is not an unreasonable assumption because the Rooiberg tin ore deposits do contain minor amounts of galena (Leube and Stumpfl 1963). Because the galena and cassiterite in the Rooiberg deposit crystallized from the same hydrothermal fluids, it is expected that they would possess the same initial “common lead” isotopic signature.

In fact, many of our tin ingots contain Pb concentrations (Table 1) which are higher than would be expected in pure cassiterite from the Rooiberg tin deposits. This suggests to us that the “isochrons” in Figures 4 and 5 have a more complex explanation than we have provided so far. While the upper portions of these lines are radiogenic ( $^{206}\text{Pb}/^{204}\text{Pb} > 22$ ), the central and lower portions of the line ( $^{206}\text{Pb}/^{204}\text{Pb} < 22$ ) are probably better seen as mixing lines, in which the lead isotopic ratios reflect mixing of radiogenic lead from cassiterite with “common lead” from sulfide minerals. Once again, the fact that all samples fall on a single line that accurately reflects the known geological age of the Rooiberg deposits likely means that both the cassiterite and lead component had the same initial “common-lead” ratios.

Because galena (PbS) is ~85% Pb by weight, even a minute addition of this mineral to a low-lead cassiterite smelt will produce a metal dominated by the lead isotopic signature of the galena. To show this graphically, the  $^{206}\text{Pb}/^{204}\text{Pb}$  values of several of our tin samples have been plotted against their measured Pb concentrations (Fig. 6).

Superimposed on this plot are three calculated mixing lines between cassiterite (for which we assume a  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio of 90) and galena (for which we assume a  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio of 15). The lines represent mixtures of cassiterite containing 1, 10 and 100 ppm Pb with galena (850,000 ppm Pb). Almost all of our data points fall between the mixing lines which contain 1 and 10 ppm concentrations of Pb in the cassiterite, indicating that these are the most likely range of Pb concentrations in Rooiberg cassiterite. It is also evident from these mixing lines that the radiogenic Pb isotopic value ( $^{206}\text{Pb}/^{204}\text{Pb}=90$ ) of cassiterite is almost entirely overwhelmed by the common Pb isotopic value of galena ( $^{206}\text{Pb}/^{204}\text{Pb}=15$ ) when the latter constitutes only 0.05 wt% of the total. What this exercise shows very clearly is that it only takes only small additions of galena to cassiterite to bring even highly radiogenic isotopic ratios down to “common lead” values. These considerations do not invalidate the isochron approach, but do suggest that attributions of provenance are most secure for tin objects that have clearly radiogenic isotopic ratios.

***(C) Can the lead isotopic ratios of tin sources be recognized in bronzes?***

Having established an isochron/mixing line for the Rooiberg tin mines, we examine whether the isotopic ratios of Rooiberg tin can still be recognized after the tin has been alloyed with copper to make bronze. The earliest known bronzes in southern Africa are

tentatively dated (by association with materials dated by radiocarbon) to the interval 1220-1350 cal AD. These dates are earlier than any present evidence for tin mining in southern Africa, so these earliest bronzes have previously been assumed to be imported (Miller 2002; Denbow and Miller 2007). Our objective here is to examine whether these objects could instead have been made with Rooiberg tin.

The lead isotopic ratios of 33 bronzes and one copper object from the archaeological sites of Mapungubwe (13<sup>th</sup> century), Bosutswe (13<sup>th</sup>-16<sup>th</sup> centuries), Great Zimbabwe (a late component, 15<sup>th</sup>-16<sup>th</sup> centuries) and Thulamela (16<sup>th</sup>-17<sup>th</sup> centuries) are listed in Table 2. (For descriptions of the objects, see Miller (2002) and Denbow and Miller (2007)). The locations of these sites are shown in Figure 3.

A plot of  $^{207}\text{Pb}/^{204}\text{Pb}$  against  $^{206}\text{Pb}/^{204}\text{Pb}$  for the 33 bronze artifacts (Fig. 7) shows that about four-fifths of the samples display a strong linear trend, and that about one-fourth of the samples analyzed have radiogenic isotopic ratios ( $^{206}\text{Pb}/^{204}\text{Pb} > 22$ ). As copper ores generally possess “common lead” isotopic ratios, these radiogenic signatures are almost certainly contributed by the tin in the alloy.

Four bronzes (two from Thulamela and two from Great Zimbabwe) do not lie on the linear trend; nor does the single copper artifact (from Great Zimbabwe). We excluded these five samples in the calculation of an isochron (Fig. 6), which gave an age of  $2083 \pm 31$  Ma and a MSWD of 867. This isochron is identical within error to the isochron calculated for the tin artifacts from southern Africa (Fig. 4) This strongly suggests that

the tin utilized in these bronzes was obtained from the Rooiberg (or another LGS) tin deposit. In addition, the correlation of the highly radiogenic Mapungubwe bronze artifact (1220-1250 CE) with Rooiberg tin suggests that these deposits may have been exploited 200 years earlier than previously thought.

In light of the discussion of mixing lines above, it is quite surprising that the isotopic contribution of Rooiberg tin is so evident in this set of bronzes. At this point, we must consider the possibility that we are observing a mixing line between the common lead isotopic signature of the copper component, and the radiogenic lead isotopic signature of the tin component. The fact that this set of bronzes produces a calculated geological age that matches that of the Rooiberg tin deposits strongly suggests that both the copper and tin components derived from deposits related to emplacement of the Lebowa Granite Suite (2034-2088 Ma). There are several small copper deposits within the Rooiberg Valley that are genetically related to the emplacement of the LGS (Rozendaal *et al.* 1995), and thus would potentially exhibit the same initial “common lead” isotopic signature as the Rooiberg cassiterite deposits. If this hypothesis is correct (we have not yet undertaken lead isotopic analysis of these copper deposits), this would imply that the early bronzes like those at Bosutswe were alloyed near Rooiberg from copper and tin that are both related to the LGS.

Bronzes made by mixing Rooiberg tin with copper from distant deposits with very different “common lead” isotopic ratios would probably not fall on the line in Figure 7. This may explain the deviant isotopic ratios of some of the bronzes from later sites (Great

Zimbabwe, Thulamela). However this conclusion is speculative at this time – further isotopic characterization of southern African copper deposits needs to be done before we can confidently model the mixing of these coppers with Rooiberg tin.

As with the tin, the scatter (MSWD) of the data around the calculated isochron for the bronzes is much higher than is traditionally acceptable in geochronology, and is indicative of non-analytical scatter in the initial Pb isotopic ratios. In geochronology, isochrons are calculated from isotopic ratios obtained on unweathered minerals within a single rock or ore which is assumed to have crystallized at the same time from an isotopically homogenous fluid. The MSWD statistic is designed for this specific condition (Faure and Mensing 2005). The tin artifacts that we analyzed were likely smelted from cassiterite ore which included other minerals, and may have originated from any of the four separate clusters of known prehistoric tin mines in the Rooiberg valley (Baumann 1919). Because these mines may have contained slightly heterogeneous initial Pb isotopic ratios, resulting from crustal and fluid mixing at a local scale, there might have been slight systematic differences in the initial Pb isotopic ratios between them, as in tin granites from Cornwall (Chesley *et al.* 1993). The same can be said for the copper deposits.

Consequently, the high MSWDs are probably attributable to: (a) the low number of samples; (b) the high precision of the analyses (ironically, lower analytical error can result in a larger MSWD, since the smaller 2-sigma errors do not in many cases intersect the fitted line); (c) the possibility that the tin may derive from cassiterite from different

deposits within the LGS; and (d) the addition of “common lead” from copper sources and gangue minerals that have slightly different Pb isotopic ratios. But the scatter about these isochrons does not affect our interpretation, especially as far as the highly radiogenic lead isotopic ratios are concerned (which must be originating from an older tin deposit). We cannot be as sure about the provenance of bronzes that do not have radiogenic isotopic ratios; in these cases, trace element impurity patterns could provide useful additional information for distinguishing between potential sources.

## **Discussion**

Our application of isochron methodology is not meant to be a precise dating tool for geological deposits, but is presented as a new approach to provenance studies of tin and bronze. We have shown that under the right circumstances isochrons can be effective in determining the source of tin in bronzes. However, we wish to emphasize that in many archaeological contexts, bronzes will incorporate copper and/or lead that does NOT originate from a deposit genetically related to the tin, such that the potential isochron produced by the isotopic ratios of the tin may be obscured by mixture with the “common lead” isotopic ratios of the copper from a distant deposit. The number of possible copper sources is far too large to envision the calculation of mixing diagrams for all combinations of tin sources and copper sources. At the present time, the wider application of our approach is therefore probably restricted to bronzes that display radiogenic lead isotopic signatures ( $^{206}\text{Pb}/^{204}\text{Pb} > 22$ ). Up to this point, we have maintained that radiogenic lead isotopic signatures in bronzes are attributable solely to

the tin component. However, radiogenic copper deposits are known from some parts of world (e.g., Budd *et al.* 2000; Hauptman 1989), though they are rare.

Therefore, when radiogenic bronzes are encountered, the possibility that the Pb isotopic ratios point to a tin source should be seriously considered. As an example, we have replotted data originally published by Weeks (2003: Table 7.1) for copper and bronze artifacts from Oman, which are dated between 2400 and 1900 BC (Fig. 8). Note that two of these bronzes are radiogenic. An isochron calculated on these two points alone returns a model age of  $804 \pm 270$  Ma. Although a two point isochron is obviously not reliable (and there is a possibility that these two bronzes are not even utilizing the same tin ore source), this exercise does show that these bronzes were made with tin from an old ore deposit, which has had enough time to accumulate substantial amounts of radiogenic lead (see Figure 1). Consequently, it appears to exclude the possibility that the tin in these two bronzes derived from the major Afghan deposits, which were emplaced only around 80 Ma (Ludington and Peters 2007). More likely candidates would be the cassiterite deposits of India, which formed between 700 and 1500 Ma (Babu 1994).

The main group of bronzes at the lower left in Figure 8 plot with the copper samples, which exhibit significant scatter. Consequently, we can assume that we are not observing a single isochron produced by tin and copper components that are genetically related, as was the case with southern African bronzes. It is more likely that the “common lead” isotopic ratios of copper from several distinct deposits has overwhelmed the lead isotope ratios of any tin used to make the bronze (with exception of the two radiogenic bronzes).

If there is a mixing line present, it is obscured by the scatter of bronze and copper samples.

This brief excursion serves to draw attention to the fact that the age of formation of a tin deposit is a crucial variable. Afghan tin is too young to be positively identified by radiogenic lead isotopic ratios, but there are other sources of tin that are old enough to have developed radiogenic signatures. Those of India are between 700 and 1500 Ma (Babu 1994), while those of western peninsular Malaysia are 184-230 Ma (Schwartz *et al.* 1995), and tin deposits formed during the Variscan/Hercynian orogeny including those of Cornwall (Britain), the Erzgebirge (Germany), Iberian Massif (Portugal and Spain) formed in the interval 380-270 Ma (Guilbert and Park 1986). Isochrons for these sources should be developed.

## **Conclusions**

We present a new approach to determining the provenance of tin, whereby isochrons calculated from smelted tin can serve as the “fingerprints” of cassiterite deposits, and the provenance of tin artifacts can be inferred by matching their isotopic ratios to the isochrons of potential cassiterite deposits. Even though “fingerprints” have yet to be established for Eurasian tin ore deposits, we can already make some deductions, based simply upon whether the isotopic ratios of tin artifacts are, or are not, radiogenic. For example, only one of the fifteen tin ingots from Late Bronze Age shipwrecks that were analyzed by Begemann *et al.* (1999) has a radiogenic lead isotope signature (and then only barely), even though the lead content of most of the ingots is less than 20 ppm

(Table 4). From this we may infer that the ages of the tin deposits from which most of these ingots derived are probably too young to have developed radiogenic isotopic ratios. While tin from Afghanistan should not have radiogenic lead isotope signatures, it is too soon to leap to the conclusion that this was the source of these ingots; there may be other young tin deposits in Eurasia. A wide-ranging isotopic survey of potential Eurasian tin sources needs to be undertaken, using the approach demonstrated in this study.

Although there are relatively few finds of tin ingots from the Eurasian Bronze Age, there are many other samples of tin in another form. Between ca. 1400 and ca. 1150 BCE, certain high-status funerary vessels around the Aegean were completely covered with tin foil. Tin inlay is also known on pottery in Swiss lake dwellings from as early as the 13<sup>th</sup> century BCE (Gillis 1999). The sources of tin for these foils may be investigated by the techniques demonstrated here.

We have also drawn attention to the fact that the lead isotope ratios in bronze can sometimes be indicative of the source of tin in the alloy. Any bronze that has both a radiogenic lead isotope signature and a very low lead content would be worth further investigation by the methods discussed in this article. This approach will be particularly useful in regions that have very old (and thus highly radiogenic) tin sources, such as South Asia and Africa. Further research may also strengthen our understanding of the emergence of technology, trade, and cultural exchange during the Bronze Age of the Near East and the Mediterranean.

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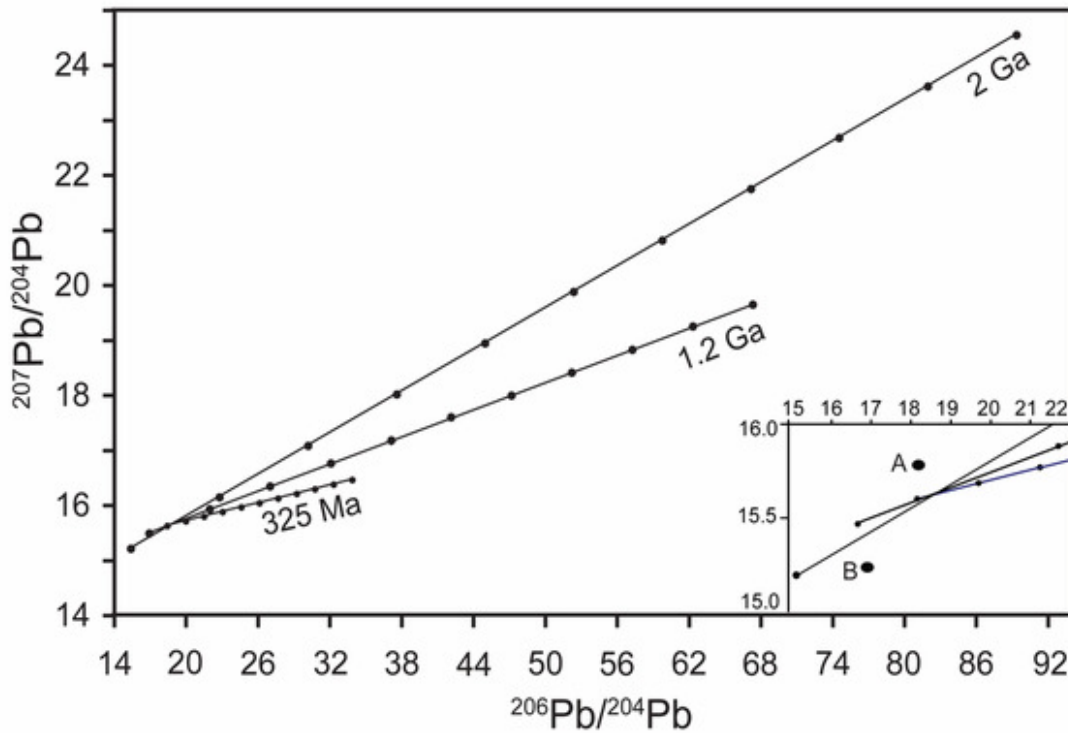
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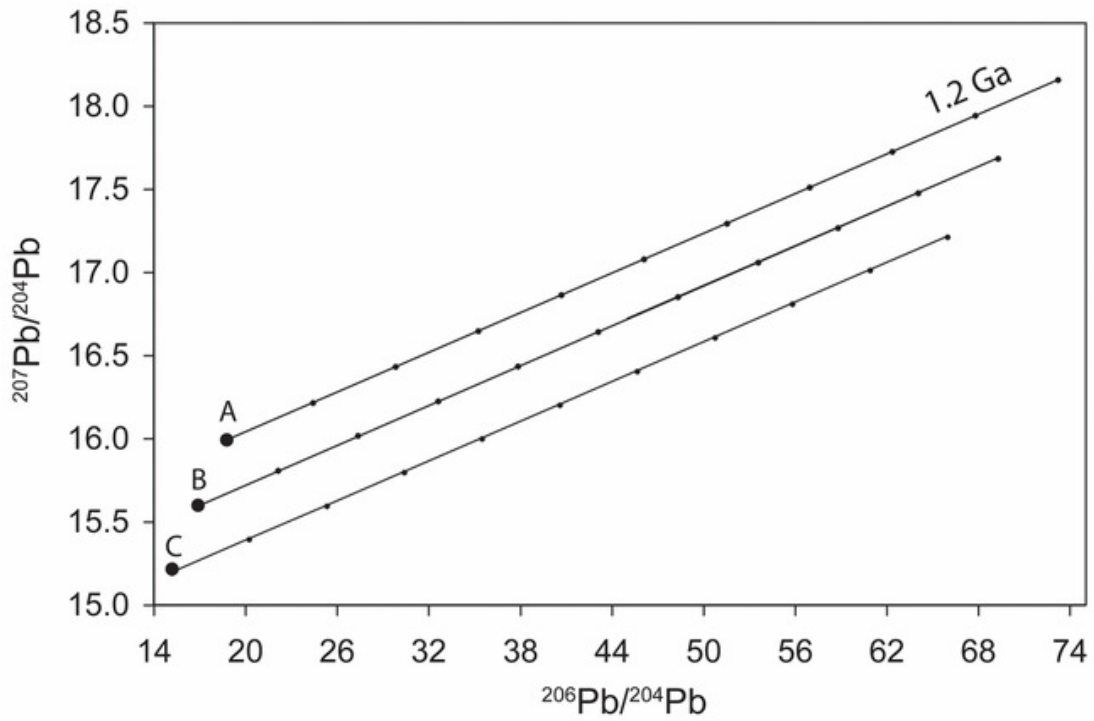
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## Figures



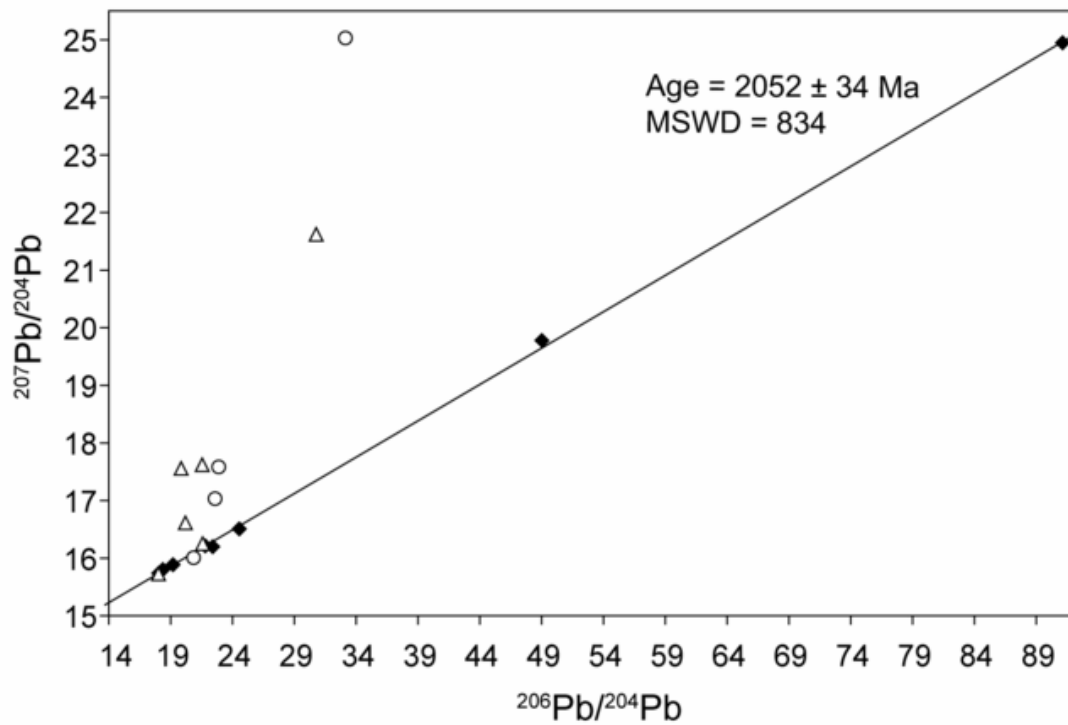
**Figure 1.** Three “reference” isochrons for hypothetical cassiterite deposits of ages 325 million, 1.2 billion, and 2 billion years. Slopes are calculated with equation 1, and isochrons are anchored by the common-lead isotopic ratios estimated by the Stacey Kramers model for ore deposits of their respective age. Each isochron contains ten points representing the radiogenic lead isotopic ratios produced by hypothetical cassiterite crystals with U-Pb ratios of 0 (bottom left-most point) to 5 (top right point). At bottom right is an enlarged section of the common-lead isotopic region. Points A and B clearly plot off the isochrons, and must therefore originate from a different tin source, or be the product of mixing of two or more sources. See discussion for further detail.



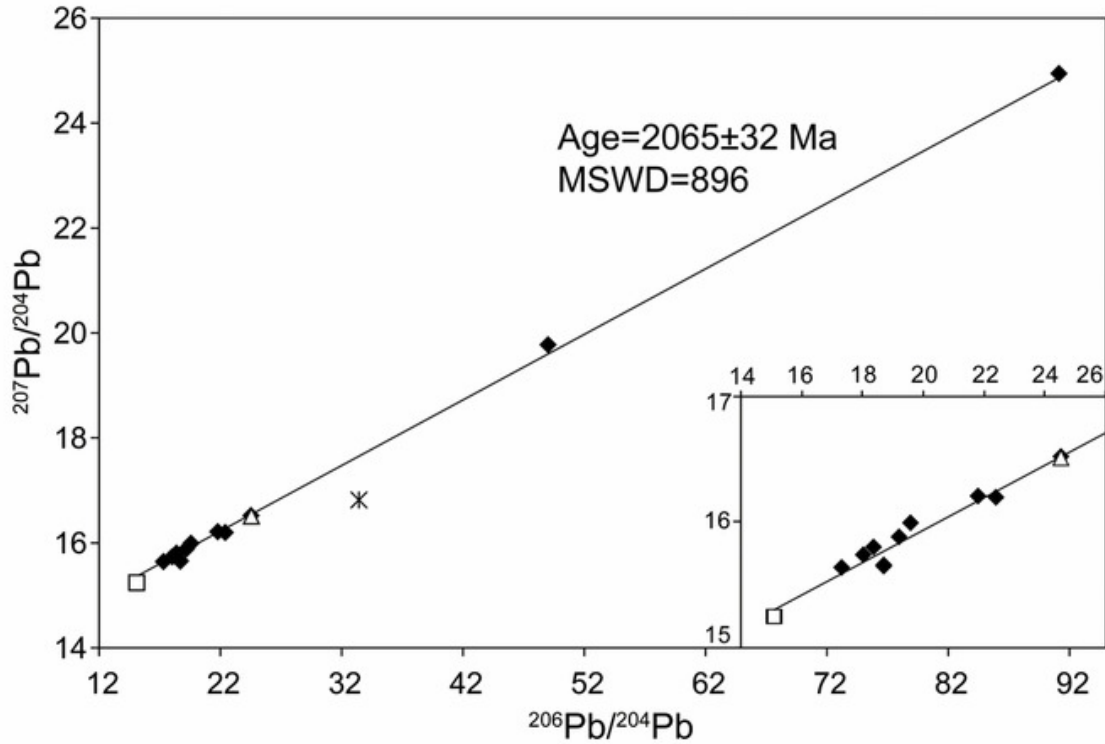
**Figure 2.** Three calculated “reference” isochrons for tin deposits which are all 1.2 billion years old, but formed in isotopically distinct geologic environments. Consequently, each deposit starts with a different common lead isotopic signature, indicated by points A, B, and C.



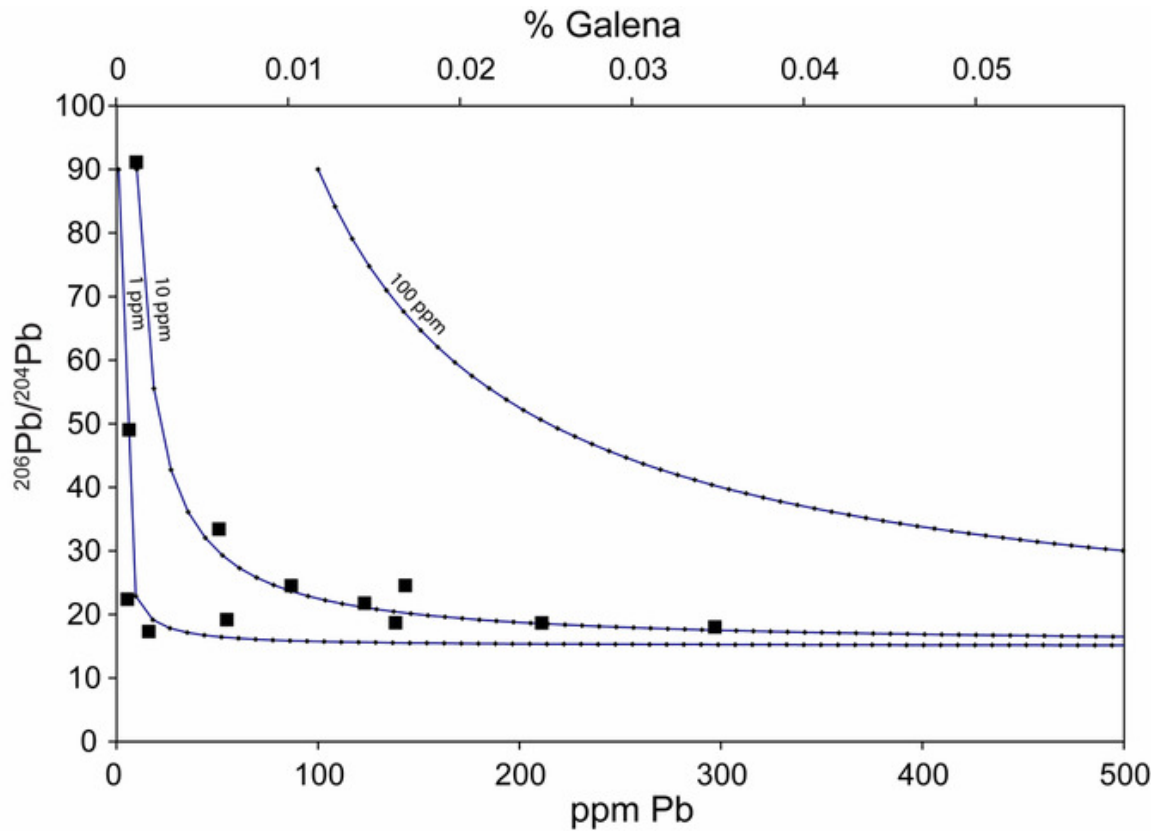
**Figure 3.** Map of southeast Africa displaying the location of modern towns (■) and archaeological sites where tin, lead-tin, and bronze artifacts were excavated (\*). Figure provided by Simon Hall.



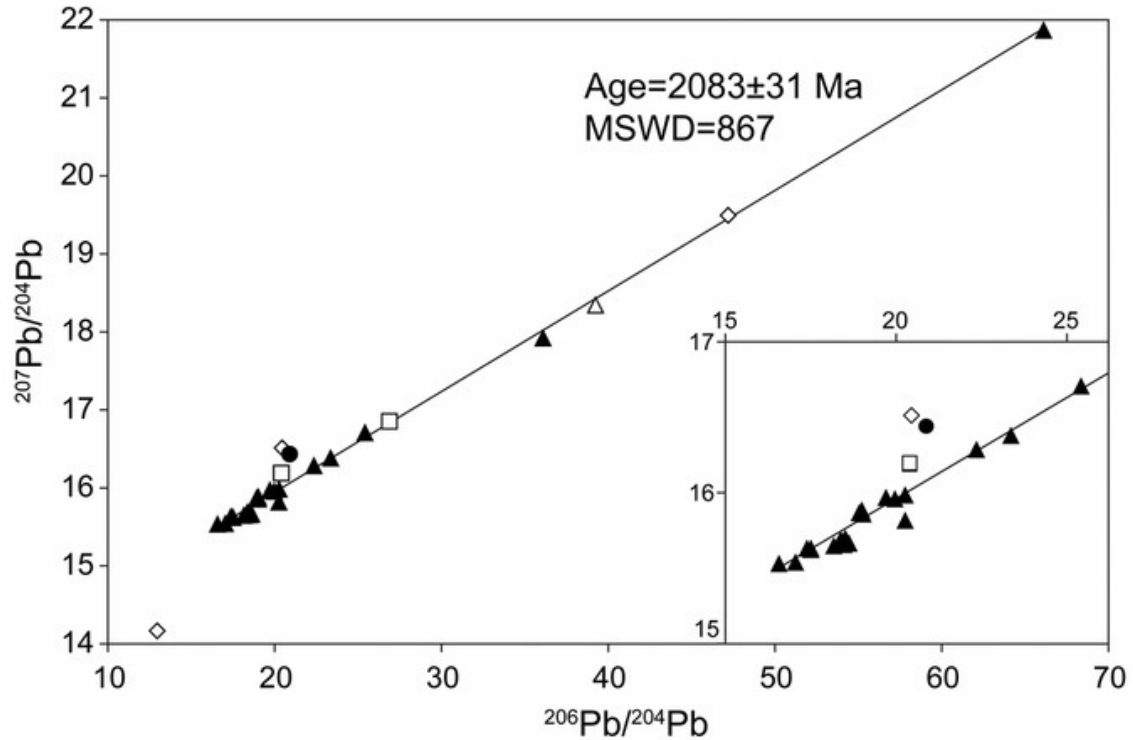
**Figure 4.** Lead isotopic ratios of tuyeres (o), slags ( $\Delta$ ), and tin prills and ingots ( $\blacklozenge$ ) from two prehistoric smelting sites adjacent to the Rooiberg tin deposits. The fitted isochron was calculated using only the isotopic values for the tin prills and ingots. Two-sigma analytical errors are in all cases smaller than the symbols used.



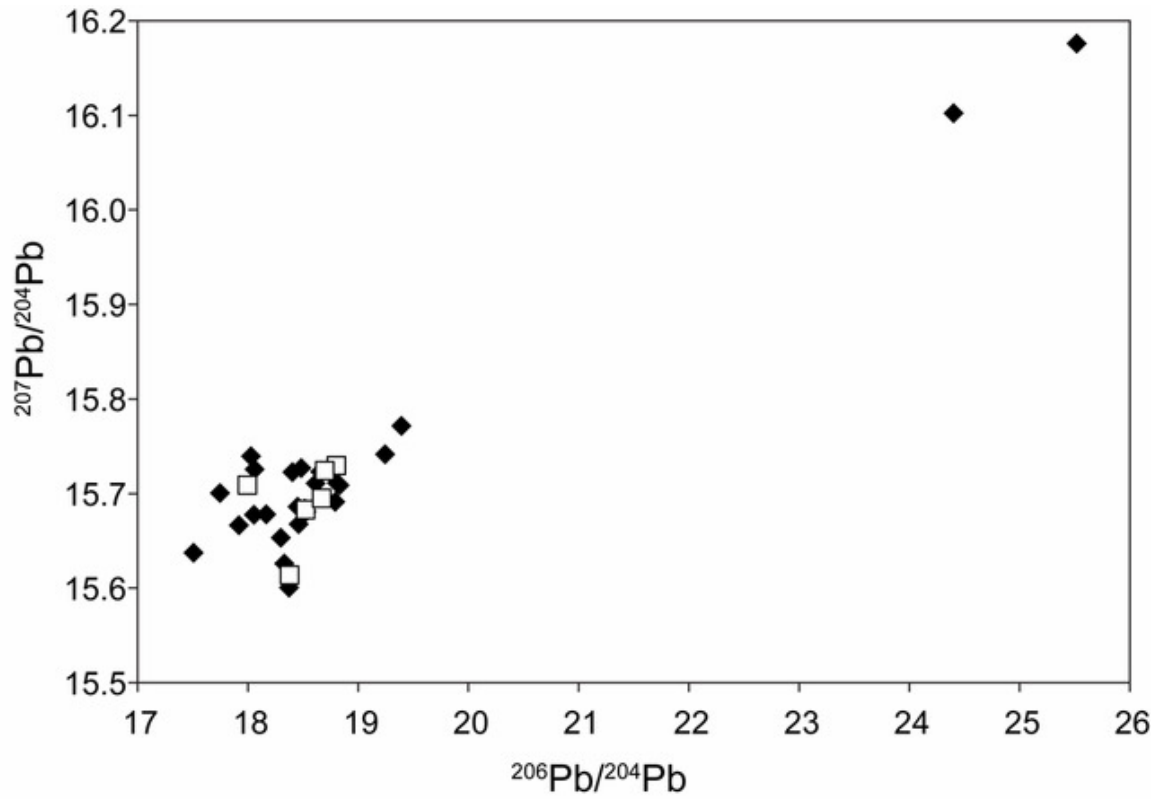
**Figure 5.** Lead isotopic ratios of prehistoric tin ingots & prills from southern Africa (◆), modern Rooiberg tin (Δ), and Bosutswe and Great Zimbabwe lead-tin ingots (□). The modern tin ingot from Kamativi, Zimbabwe (\*) was not included in the calculation of the fitted isochron. Two-sigma analytical errors are in all cases smaller than the symbols used.



**Figure 6.** The  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios and lead concentrations for southern African tin samples (■). Three calculated mixing lines between cassiterite (with 1, 10, and 100 ppm Pb) and galena (with 850,000 ppm Pb) are also plotted. The  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio of cassiterite is assumed to be 90 (based on our most radiogenic tin sample) while the  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio of galena is assumed to be 15.016 (based on the Stacey-Kramers model estimate for 2.06 Ga common-lead minerals). The top y-axis shows the weight percentage of galena in a tin smelt that would produce the associated  $^{206}\text{Pb}/^{204}\text{Pb}$  values and Pb concentrations associated with each mixing line.



**Figure 7.** Lead isotopic ratios for Bosutswe bronze objects (▲), Thulamela bronze objects (◇), the Mapungubwe bronze object (△), Great Zimbabwe bronze objects (□), and the Great Zimbabwe copper artifact (●). Two of the Thulamela bronzes diverge from the fitted isochron, as do two of the Great Zimbabwe bronzes (which plot directly on top of one another), and the Great Zimbabwe copper artifact. These were not included in the age calculation. Two-sigma analytical errors are in all cases smaller than the symbols used.



**Figure 8.** Lead isotopic ratios of bronzes (◆) and unalloyed copper (□) from Omani Early Bronze sites (from Table 3; after Weeks 2003). Two-sigma analytical errors are in all cases smaller than the symbols used.

## Tables

Group	Sample Name	Sample Type	Site Where Recovered	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	ppm Pb
1	14/47/3	Sn ingot	Polokwane area (surface)	24.5182	16.5232	40.4386	86.72
	21/39/1	Sn ingot	Rooiberg valley (surface)	21.7869	16.2130	40.2372	123.06
	14/47/2	Sn ingot	Polokwane area (surface)	18.6820	15.6557	38.4293	211.10
	14/47/1	Sn ingot	Polokwane area (surface)	18.7071	15.6543	38.4480	138.51
	21/39/3	Sn ingot	Rooiberg valley (surface)	91.1300	24.9451	42.0015	9.77
	Lerale	Sn ingot	Soutpansberg mountains (surface)	17.3056	15.6430	37.6398	16.01
	Z581	Sn ingot	Great Zimbabwe	19.5774	15.9949	40.0469	1199.58
	Z334	Sn-Pb lump	Great Zimbabwe	15.1111	15.2389	34.7595	N/A
	SKRT1	Sn prill	Smelterskop (Rooiberg Valley)	19.1970	15.8866	38.0019	54.73
	Sea 5K	Sn prill	Smelterskop (Rooiberg Valley)	18.0212	15.7371	37.7451	297.03
2	Sa-13A	Sn prill	Smelterskop (Rooiberg Valley)	18.3706	15.8045	38.7735	N/A
	Sa-14A	Sn prill	Elandsberg Ledge (Rooiberg Valley)	22.4040	16.1991	42.0485	5.37
	Sa-11A	Sn prill	Elandsberg Ledge (Rooiberg Valley)	49.0145	19.7772	49.5808	6.23
	Sa-1	Sn ingot	Rooiberg - modern smelter	24.5505	16.5100	40.6614	143.36
	Sa-2	Sn ingot	Kamativi - modern smelter	33.4215	16.8192	38.3840	50.85
	Sa-3	Tuyere	Smelterskop (Rooiberg Valley)	22.8902	17.5829	45.3804	N/A
	Sa-4	Tuyere	Smelterskop (Rooiberg Valley)	22.5955	17.0327	45.8834	N/A
	Sa-5R	Tuyere	Smelterskop (Rooiberg Valley)	20.8624	16.0070	41.6006	N/A
	Sa-10	Vitrified Tuyere	Smelterskop (Rooiberg Valley)	33.1413	25.0258	63.3200	N/A
	Sa-6	Slag	Smelterskop (Rooiberg Valley)	19.8507	17.5560	42.3753	N/A
	Sa-11B	Slag paired with Sa-11A	Elandsberg Ledge (Rooiberg Valley)	21.5751	16.2526	42.8486	N/A
	Sa-13B	Slag paired with Sa-13A	Smelterskop (Rooiberg Valley)	21.5412	17.6203	44.2727	N/A
	Sa-14B	Slag paired with Sa-14A	Elandsberg Ledge (Rooiberg Valley)	30.7701	21.6187	58.5696	N/A
	L11	Slag paired with Sea 5K	Smelterskop (Rooiberg Valley)	18.0141	15.7288	37.7226	N/A
	L15	Slag paired with SKRT1	Smelterskop (Rooiberg Valley)	20.1906	16.6137	39.8622	N/A
	3	BO1	Sn-Pb lump	Bosutswe	15.1138	15.2435	34.7792

Two sigma analytical errors (percent) for lead isotopic ratios

Group	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
1	0.0454	0.0512	0.0624
2	0.0295	0.0306	0.0376
3	0.0329	0.0293	0.0317

**Table 1.** The measured  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  values for southern African tin, slag, and tuyere samples. Samples run at the same time are grouped together and the corresponding percent two sigma errors for  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  values are listed at the bottom. The lead concentrations (ppm) measured by ICP-MS are also shown (N/A – no analyzed); all two sigma errors are less than 4% except that for the tin lerale, which has an error of 7.6%. The two lead-tin ingots are both roughly 80% Pb, 20% Sn, as determined with SEM-EDS by Miller (Miller 2002; Miller and Denbow 2007).

Group	Sample Name	Sample Type	Site Where Recovered	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
4	TM 101B	Sn-Cu Bronze	Thulamela	12.9506	14.1670	32.8226
	TM107	Sn-Cu Bronze	Thulamela	20.4519	16.5122	44.0058
	TM 101A	Sn-Cu Bronze	Thulamela	47.1849	19.4937	61.2450
	M366	Sn-Cu Bronze	Mapungubwe	39.2430	18.3434	52.5878
	B136	Sn-Cu Bronze	Bosutswe	66.1049	21.8655	82.2135
	B86	Sn-Cu Bronze	Bosutswe	20.2587	15.8164	39.1308
	B96	Sn-Cu Bronze	Bosutswe	18.6233	15.6615	38.6048
	B316	Sn-Cu Bronze	Bosutswe	19.9755	15.9555	39.3478
	B3	Sn-Cu Bronze	Bosutswe	19.7071	15.9684	40.0267
	B61	Sn-Cu Bronze	Bosutswe	17.0430	15.5402	36.3259
	B26	Sn-Cu Bronze	Bosutswe	18.6151	15.6633	38.6031
	B85	Sn-Cu Bronze	Bosutswe	18.3590	15.6807	38.3533
	B393	Sn-Cu Bronze	Bosutswe	19.0125	15.8834	39.2778
	B394	Sn-Cu Bronze	Bosutswe	19.0102	15.8811	39.2717
	B451	Sn-Cu Bronze	Bosutswe	18.5138	15.6964	38.8040
	B471	Sn-Cu Bronze	Bosutswe	18.1584	15.6469	37.7833
	B486	Sn-Cu Bronze	Bosutswe	36.0890	17.9204	49.2251
	B470	Sn-Cu Bronze	Bosutswe	18.4012	15.6842	38.6265
	B466	Sn-Cu Bronze	Bosutswe	23.3478	16.3811	39.8880
	B461	Sn-Cu Bronze	Bosutswe	18.3610	15.6824	38.3578
	BST4	Sn-Cu Bronze	Bosutswe	16.5718	15.5328	37.1136
	BST9	Sn-Cu Bronze	Bosutswe	17.3752	15.6280	36.8034
	BST6	Sn-Cu Bronze	Bosutswe	19.0205	15.8545	38.6197
	BST3	Sn-Cu Bronze	Bosutswe	25.4147	16.7073	45.8717
	B406	Sn-Cu Bronze	Bosutswe	22.3488	16.2826	40.1501
	B139	Sn-Cu Bronze	Bosutswe	18.4606	15.6535	38.6180
	B481	Sn-Cu Bronze	Bosutswe	18.9096	15.8657	39.9163
	BST1	Sn-Cu Bronze	Bosutswe	20.2650	15.9827	38.4642
	BST2	Sn-Cu Bronze	Bosutswe	17.4867	15.6268	36.8373
	BST8	Sn-Cu Bronze	Bosutswe	17.5027	15.6186	37.0283
5	Z428	Sn-Cu Bronze	Great Zimbabwe	26.8894	16.8527	40.2668
	Z158	Sn-Cu Bronze	Great Zimbabwe	20.4011	16.1872	39.9288
	Z144	Sn-Cu Bronze	Great Zimbabwe	20.4046	16.1891	39.9313
	Z10	Cu Artifact	Great Zimbabwe	20.9090	16.4335	41.7293

Two sigma analytical errors (percent)

Group	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
4	0.0307	0.0307	0.0406
5	0.0250	0.0226	0.0240

**Table 2.** The measured  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  values for southern African bronze and copper samples. Samples run at the same time are grouped together and the corresponding percent two sigma errors for  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  values are listed at the bottom.

Sample	Site	Major Elements	$^{207}\text{Pb}/^{206}\text{Pb}$	2 $\sigma$ abs. error	$^{206}\text{Pb}/^{204}\text{Pb}$	2 $\sigma$ abs. Error	$^{207}\text{Pb}/^{204}\text{Pb}$
M10-41	Al Sufouh	Cu	0.84658	0.00004	18.525	0.005	15.683
M10-38	Unar1	Cu	0.84959	0.00004	18.378	0.002	15.614
1019-3.59	Unar2	Cu	0.87285	0.00005	17.997	0.004	15.709
TA1227	Tell Abraq	Cu	0.84060	0.00002	18.671	0.001	15.695
TA1310	Tell Abraq	Cu	0.83650	0.00002	18.804	0.002	15.730
TA1461	Tell Abraq	Cu	0.84090	0.00001	18.699	0.001	15.724
AS1-2	Al Sufouh	Cu-As-Sn (low)	0.88469	0.00003	17.747	0.003	15.701
ASTombid	Al Sufouh	Cu-Sn(low)-As-Ni	0.85079	0.00003	18.485	0.003	15.727
M10-7	Unar1	Cu-Sn(low)	0.85014	0.00002	18.451	0.001	15.686
M10-13v	Unar1	Cu-Sn	0.84869	0.00004	18.461	0.004	15.668
M10-17 Avg.	Unar1	Cu-Sn(low)	0.81330	0.00003	19.392	0.005	15.772
M10-19	Unar1	Cu-Sn(low)	0.85542	0.00003	18.299	0.002	15.653
M10-22r	Unar1	Cu-Sn-Fe	0.85248	0.00005	18.330	0.003	15.626
M10-39	Unar1	Cu-Sn-Fe	0.84915	0.00005	18.372	0.002	15.601
1014.76	Unar2	Cu-Sn-As	0.86300	0.00003	18.167	0.004	15.678
1014.158	Unar2	Cu-Sn-As	0.86833	0.00001	18.055	0.002	15.678
1018-3.99	Unar2	Cu-Sn-As-(Ni)	0.84399	0.00002	18.615	0.002	15.711
1019-5.71	Unar2	Cu-Sn-As	0.84283	0.00003	18.655	0.003	15.723
1023-4.10	Unar2	Cu-Sn-(Fe)	0.85430	0.00002	18.404	0.004	15.723
1019-3.105	Unar2	Cu-Sn-As-Fe	0.87306	0.00004	18.028	0.004	15.740
1023-2.110	Unar2	Cu-Sn(low)-Fe	0.89320	0.00003	17.507	0.003	15.637
TA107 Avg.	Tell Abraq	Cu-Sn-As-Ni	0.81800	0.00001	19.244	0.001	15.742
TA699 Avg/	Tell Abraq	Cu-Sn	0.65990	0.00001	24.401	0.003	16.102
TA1217	Tell Abraq	Cu-Sn	0.83420	0.00002	18.831	0.003	15.709
TA1231	Tell Abraq	Cu-Sn(low)	0.87070	0.00001	18.061	0.001	15.726
TA1286	Tell Abraq	Cu-Sn	0.83500	0.00002	18.792	0.002	15.691
TA1306	Tell Abraq	Cu-Sn	0.83540	0.00002	18.807	0.001	15.711
TA1428	Tell Abraq	Cu-Sn(low)-Fe	0.84710	0.00002	18.515	0.001	15.684
TA1459	Tell Abraq	Cu-Sn	0.84620	0.00002	18.531	0.001	15.681
TA1614 Avg.	Tell Abraq	Cu-Sn-Fe	0.63390	0.00003	25.518	0.010	16.176
TA1648	Tell Abraq	Cu-Sn	0.87430	0.00002	17.919	0.001	15.667

**Table 3.** The  $^{206}\text{Pb}/^{204}\text{Pb}$ , and  $^{207}\text{Pb}/^{206}\text{Pb}$  values along with their corresponding absolute 2 sigma errors for pure copper and all Sn-bronze objects from Al Soufouh, Unar1, Unar2, and Tell Abraq in Oman, from Table 7.1 in Weeks, 2003. The  $^{207}\text{Pb}/^{204}\text{Pb}$  values are calculated by us from these data, and the corresponding absolute 2 sigma errors are assumed to be the same as those for  $^{206}\text{Pb}/^{204}\text{Pb}$  values.

Sample	Heidelberg no.	Pb (ppm)	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$
<b>Hishuley Carmel</b>					
Haifa 1111/1	3231	9	1.9621	0.7988	19.6657
Haifa 1111/2	3232	19	1.9776	0.8064	19.4401
Haifa 1111/3	3233	11	1.9429	0.7932	19.7824
Haifa 1111/4	3234	7	1.9361	0.7875	19.9521
Haifa 1111/5	3235	6	1.7213	0.7042	22.5327
<b>Kefar Shamir</b>					
Haifa 81-604	3240	220	2.0799	0.8372	18.7512
Haifa 81-605	3239	32	2.0325	0.8273	18.9502
Haifa 81-606	3241	8	1.9402	0.7897	19.9045
Haifa 81-607	3237	14	1.9372	0.7866	20.0000
Haifa 81-608	3238	12	1.9597	0.7969	19.7355
Haifa 81-609	3236	22	2.0206	0.8218	18.9574
<b>Uluburun</b>					
KW 197	3242	630	2.0561	0.8274	18.9574
KW 199	3243	8	2.0589	0.8286	18.9645
KW 203	3244	0.5	2.0083	0.8164	19.1865
KW 203A	3245	3	2.0379	0.8246	18.9934

**Table 4:** Lead isotopic ratios for 15 tin ingots from three Bronze Age shipwrecks in the Mediterranean, as reported by Begemann *et al.* 1999, Table A-2. (The  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios were calculated by us based on the original reported  $^{204}\text{Pb}/^{206}\text{Pb}$  ratios by Begemann *et al.*) Errors were not reported.