



A novel approach to lead isotope provenance studies of tin and bronze: applications to South African, Botswanan and Romanian artifacts



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ABSTRACT

Lead isotopic ratios of cassiterite, the dominant ore of tin, evolve after crystallization through decay of uranium (U) and thorium (Th) to lead (Pb), due to the relatively elevated U/Pb ratios of this mineral. We show that the Pb isotopic ratios of smelted tin at Rooiberg, South Africa, form an isochron with a model age that matches the known geological age (~2 Ga) of the host granite for the Rooiberg cassiterite deposits. Since the Pb isotopic ratios of many prehistoric tin and bronze artifacts throughout southern Africa also fall on this isochron, we deduce that they were made with tin from either the Rooiberg deposits or similar age deposits that exist nearby. In addition, we show that bronze artifacts from Romania define an isochron corresponding to a Variscan age (~0.3 Ga), suggesting a central or western European tin deposit as its source, since no Variscan tin is known from the neighboring Carpathian Mountains. Implications of this approach for provenance studies of tin and bronzes around the world are examined given various major tin deposits and their age distribution.

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1. 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 intensely debated since J.D. Muhly's comprehensive survey of the geological, historical, and archaeological evidence for the origin of tin metal in antiquity (Muhly, 1973). The majority of tin must have been obtained through long-distance trade, but there is considerable disagreement over potential sources and trade routes (e.g., Franklin et al., 1979; Muhly, 1985; Yener et al., 1989; Pigott, 1999; Yener, 2000; Weeks, 2003; Nezafati et al., 2006).

When compared to the many published provenance studies of copper alloy artifacts, there has been remarkably little archaeological study of the provenance of ancient 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. However, to our knowledge, this approach has only been used in one other archaeological provenance study of the earliest known tin artifacts from Therme on Lesbos (Begemann et al., 1992). Other studies have attempted to use tin isotopes to characterize tin sources, although researchers commonly found that either the variations in tin isotopic ratios from different regions was quite small and/or barely larger than the analytical error (Gale, 1997; Begemann et al., 1999; Yi et al., 1999; Clayton et al., 2002; Nowell et al., 2002). Lastly, there are few published measurements of Pb isotopic ratios in cassiterite or in prehistoric tin metal. This runs in stark contrast to the thousands of published Pb isotopic ratios for copper ores and for prehistoric copper and copper alloys.

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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; Pernicka et al., 1997; Rohl and Needham, 1998; Weeks, 2003). Since these have without exception been compared to Pb isotopic data for copper sources (or to lead sources in the case of leaded bronzes), most researchers to date have implicitly assumed that the lead in bronze must derive primarily from the copper, or from added lead, rather than from the tin (Gale and Stos-Gale, 1982; Gale et al., 1985).

In this article, we call attention to the fact that the Pb isotopic signature of cassiterite can serve as a unique fingerprinting tool for the tin in both tin and bronze artifacts. Specifically, cassiterite is unique from many other metal ores (e.g., sulfides) because it commonly contains significantly larger concentrations of U relative to Pb. As a result, the Pb isotopic composition of cassiterite can be dominated by the Pb produced by the radioactive decay of U over time, rather than the Pb initially incorporated into the mineral. This makes cassiterite a potentially valuable mineral for direct U–Pb dating of ore deposits, although it has not been used for this purpose, partly because it is extremely difficult to fully dissolve cassiterite with acids (Gulson and Jones, 1992; Yuan et al., 2008). Here, we show that the tin metal smelted from old cassiterite deposits maintains the Pb isotopic signature of the cassiterite ore, and thus, that one can apply U–Pb isochron dating (Faure and Mensing, 2005) to “fingerprint” individual tin provinces. We suggest that under favorable instances, the contribution of relatively radiogenic Pb from tin can be used to tease out a “ghost” age of the tin metallogenetic province. Even if a specific ore deposit is not decipherable with this tool, the rarity and unusual provinciality of tin deposits around the globe may make identification of the tin metallogenetic province an important tool for understanding metal trades in bronze artifacts from antiquity.

1.1. Lead isotopic ratios of cassiterite – the geochemical basis

Lead has four stable isotopes – ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb – all of which were present at the time of earth's formation. The latter three are also the products of the radioactive decay of their parent isotopes – ^{238}U (half life 4.468 Gyr), ^{235}U (703.8 Myr), and ^{232}Th (14.01 Gyr) – respectively. The isotopic composition of lead in the Earth as a whole at any given time is the sum of the lead present at the time of its formation and lead that has been produced subsequently by radioactive decay. The Earth, however, is not isotopically homogeneous, but has separated into crust, mantle, and core, each with different initial U/Pb ratios. Each of these reservoirs subsequently evolved further by the additional decay of U and Th to Pb to acquire diverse, and unique, Pb isotopic compositions (Stacey and Kramers, 1975).

When a mineral crystallizes from a melt, and incorporates lead into its crystal structure, it acquires the Pb isotopic composition of its parent reservoir. This is called “common lead” (Faure and Mensing, 2005). If the mineral lattice cannot accommodate U and Th (and therefore cannot gain lead by radioactive decay over time) the “common lead” isotopic ratios will be preserved indefinitely, unless subsequent processes result in the addition or loss of Pb, or the addition of U and Th. Copper, lead, and silver sulfide minerals incorporate Pb, but generally cannot accommodate U and Th in their crystal lattices. Thus these minerals retain their “common lead” isotopic signatures from the time of their formation.

The use of Pb isotopic ratios in metal provenance studies is founded on the prerequisite that ore deposits can be clearly distinguished from each other (Lambert and Ruiz, 1999). 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. Ideally

isotope ratios for a given ore deposit on bivariate plots (e.g., $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$) will cluster tightly, providing a “fingerprint” for that deposit that is separated from equally tight clusters for other deposits. Archaeologists can then match the isotopic ratios of individual archaeological artifacts to the “fingerprints” of their parent ore sources (e.g., Gale and Stos-Gale, 1982; 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., 2000; Pernicka, 1995; Pollard, 2009), the lead fingerprinting approach has been successfully applied to many ancient copper, lead, and silver artifacts primarily to rule out certain metal sources and support various hypotheses of positive correlations between an ore deposit and a metal artifact.

This approach works well for minerals that have “common lead” isotopic signatures. However, some minerals do accommodate significant amounts of U and Th upon crystallization, and therefore have Pb isotopic ratios that evolve over time as a result of radioactive decay of U and Th to radiogenic ^{208}Pb , ^{207}Pb and ^{206}Pb . Cassiterite (SnO_2) is one such mineral. Cassiterite accepts very little lead upon crystallization because the charge and ionic radius for the common lead ion in aqueous solutions (Pb^{2+} , 119 pm) are substantially different from those of octahedrally-coordinated Sn^{4+} (83 pm). In contrast, U^{4+} (103 pm), Th^{4+} (108 pm), and U^{6+} (89 pm) are better able to substitute for Sn in the cassiterite lattice, and thus may be present in significantly higher concentrations (up to several hundred ppm) than the Pb^{2+} ion in cassiterite (Farthing, 2002).

As a result of the incorporation of U and Th, ratios of radiogenic Pb isotopes to ^{204}Pb in cassiterites from a single deposit exhibit a much larger range 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 15–22, but, as we show below, $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of tin smelted from a cassiterite deposit that crystallized two billion years ago can range from less than 20 to over 90. Thus the traditional isotopic “fingerprinting” method used for archaeological provenance studies of copper alloys, silver and lead artifacts cannot be used for provenance studies of tin artifacts smelted from old cassiterites – because ratios of any of the three radiogenic isotopes to ^{204}Pb do not produce the tight clusters typical of single-stage deposits of “common lead” minerals.

However, 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 (an isochron), with a uniform slope that equals the ratio of radiogenic ^{207}Pb to radiogenic ^{206}Pb . The slope of the isochron can then be used to calculate the age of the deposit:

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

Where:

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

λ_2 = decay constant for ^{235}U

λ_1 = decay constant for ^{238}U

t = time elapsed since crystallization of the ore deposit (Faure and Mensing, 2005)

Three calculated reference (i.e., synthetic) isochrons for hypothetical cassiterite deposits of ages 325 million years, 1.2 billion years, and 2 billion years are shown in Fig. 1. Each isochron is calculated from points representing crystals with different initial ratios of U to Pb, varying from 0 to 5. Crystals with the highest initial U to Pb ratios plot at the top right end of each isochron. Thus

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