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Research paper

# Tin isotope characterization of bronze artifacts of the central Balkans

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ABSTRACT

Isotopic analysis has proved to be an effective approach to determine the provenance of copper ore sources for the production of bronze artifacts. More recently, methods for Sn isotopic analysis of bronze have been developed. However, the viability of tin isotopes as a means to define groupings that may be attributed to varying ore sources, production methods, or recycling is still in question. In part, this is due to the numerically and/or geographically limited nature of published datasets. This study reports on the Sn isotopic composition of 52 artifacts from the later Bronze Age (1500-1100 BCE) from Serbia and western Romania. The majority of samples cluster between 0.4 and 0.8 per mil for $\delta^{124}$Sn, and 0.2 and 0.4 per mil for $\delta^{120}$Sn (relative to NIST SRM 3161A), and this isotopic grouping of bronze artifacts occurs across Serbia. However, groupings of isotopically heavier and lighter artifacts are evident, and each corresponds to a more limited geographic range. Artifacts associated with higher δSn values are limited to the Vojvodina region of northern Serbia, whereas a cluster of bronzes with lower Sn-isotopic signatures are constrained to the Banat along the Serbia-Romania border, and Transylvania. One low-value outlier corresponds to an uncontextualized find near Kruševac at the southern extent of the study area. Geographic correlation of the low-value cluster with known tin mineralization in Transylvania, and the moderate-value cluster with placer tin deposits of western Serbia, suggests that these distinct bronze Sn-isotopic signatures might reflect exploitation of different tin ores. The small cluster of high Sn-isotopic values from bronzes from the Vojvodina region might reflect bronze recycling in this area that lies furthest from both known tin ore sources.



## 1. Introduction

Tin is a rare metal that is essential for bronze production, with the predominant ore mineral for tin being cassiterite ($SnO_2$). In contrast to those of western and Central Europe (e.g., Erzgebirge), tin sources in the Balkan region are poorly documented, but several small fluvial placer deposits have been described in western Serbia (Durman, 1997; Huska et al., 2014) (Fig. 1). In western Romania, cassiterite-bearing greisens have been noted in the Apuseni Mountains near Radna (Tatu, 1992) and Hondol (Glumac and Todd, 1991), and tin-bearing migmatitic gneisses occur at Gradistea de Munte (Hîrtopanu and Fairhurst, 2014) (Fig. 1). It is possible that one or more of these tin sources were exploited during the Late Bronze Age. Spatial correlation of Bronze Age habitation with tin-bearing streams near Mt. Cer, Serbia, suggests that these placer ores were potentially mined at that time (Huska et al., 2014). However, there is no direct evidence of prehistoric mining and smelting of any of these ore-bearing sands, and so the variability and provenance of tin in Bronze Age artifacts in the Balkan region remains an open question in archaeological research.

Isotopic analysis has grown in popularity as a means of providing “fingerprints” of bronze artifacts that can be matched to their parental ore sources. The traditional isotopic system used for determining copper provenance has been Pb due to its common occurrence as a trace or minor constituent of bronze artifacts.

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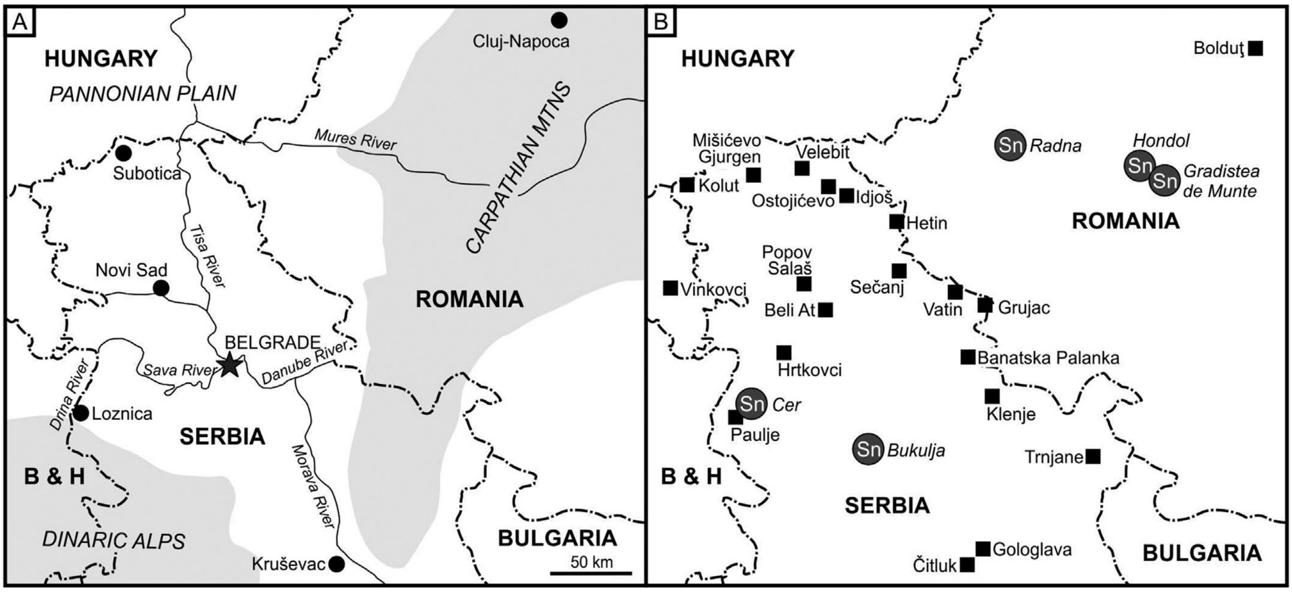


**Fig. 1.** Location of key geographic and geological sites. A) Geographic regions and features with mountainous regions shaded in grey; B) Sampled archaeological sites (black squares) and known tin occurrences (circles).

Furthermore, Pb has a wide natural variation in isotopic composition that is not affected during ore processing and/or the production of objects (Pernicka et al., 1993, 1997, and Pernicka, 2014; Gale and Stos-Gale, 2000; Cui and Wu, 2011; Balliana et al., 2013;). Several studies that have used Pb isotopes in bronzes have been successful in tracing copper, lead, and silver-bearing artifacts to their sources (e.g., Gale and Stos-Gale, 2000; Stos-Gale and Gale, 2009). This is primarily due to the fact that significant amounts of lead may be introduced to the alloy from copper ores. Attempts have been made to use Pb isotopic signatures to match tin artifacts to tin ore sources (Molofsky et al., 2014). However, given that any Pb that might have been associated with the tin ore would be overwhelmed by the contribution from the copper ore, Pb isotope analysis cannot be applied to tin provenancing in bronze artifacts (Begemann et al., 1999). Nevertheless, the success of Pb lead isotopes for copper provenancing has spurred investigations of the feasibility of "non-traditional" isotopic systems for provenance determination of ancient bronzes.

Budd et al. (1995) was the first to suggest the applicability of Sn isotopes in archaeological studies. They suggested that if melting of bronze results in fractionation of Sn isotope compositions then these isotopes might be used as tracers to detect recycling. Gale (1997) investigated these hypotheses using thermal ionization mass spectrometry (TIMS), but found no statistically significant isotopic fractionation in the ratio $^{122}Sn/^{116}Sn$, in part due to large error ranges. Even with a double spike and ionization enhancer to improve stabilization of ion beams and correction for mass fractionation, variations were indistinguishable from the analytical error when determined by TIMS (Clayton et al., 2002). The high ionization of Sn (7.3 eV) results in poor beam intensities and unstable ionization, thereby reducing analytical precision of Sn isotopic analysis using TIMS (De Laeter and Jeffrey, 1965, 1967; McNaughton and Loss, 1990; McNaughton and Rosman, 1991; Clayton et al., 2002). Additional complications included: (1) potential isobaric interference of the low abundance isotopes $^{112}Sn$, $^{114}Sn$, and $^{115}Sn$ by $^{112}Cd$, $^{114}Cd$, and $^{115}In$; (2) poor reproducibility of low-abundance isotopes; and (3) instrumental mass fractionation (Clayton et al., 2002).

Several studies have since investigated the use of Sn isotope values for solving archaeological problems using multicollector-inductively coupled plasma mass spectrometry (MC-ICP-MS). The very high ionization efficiency of MC-ICP-MS allows for the analysis of high ionization potential elements, such as tin. Several studies using MC-ICP-MS have yielded small but detectable variations in the isotopic composition of tin in bronze and cassiterite (Nowell et al., 2002; Haustein et al., 2010; Nickel et al., 2012; Balliana et al., 2013; and Yamazaki et al., 2013). So far, the datasets produced have been numerically and/or geographically limited, and have reached varying conclusions as to the viability of defining bronze groupings based on tin isotopes.

Using TIMS, Begemann et al. (1999) determined that bronzes from the Mediterranean region were isotopically distinguishable from those of Central Europe. Haustein et al. (2010) measured the Sn isotopic composition of the Sky Disc of Nebra by MC-ICP-MS and concluded that the tin in this object originated from the cassiterite ores of Cornwall, rather than the closer ores of the Erzgebirge. Yamazaki et al. (2014) analyzed six bronzes from two sites in China. The results of this study showed little variation in the Sn isotopic composition of the bronzes (0.4‰ in $\delta^{124}Sn/^{120}Sn$ with error ranges of approximately $\pm$ 0.1‰), and so concluded that the application of Sn isotope values to bronze provenance studies and differentiation of bronze groupings is of limited use.

The largest published data set of bronze isotope compositions consists of 32 artifacts from pre-Roman and Roman archaeological sites in northern Spain. This study found a considerably larger range in Sn isotopic composition (approximately 1.4‰ in $\delta^{124}Sn$ with error ranges of approximately 0.15‰). However, all samples in this study clustered without any evident subgroups. Balliana et al. (2013) noted that the lack of distinct compositions in their study could simply indicate a single tin source due to the limited geographic variation of the analyzed artifacts. They concluded that further testing of the feasibility of tin ore provenancing through isotope analysis was required. Larger sample sets that are more geographically diverse are necessary to test the feasibility of differentiating populations of bronze artifacts based on the isotopic composition of tin. This study addresses this need by reporting the Sn isotopic composition of a set of 52 later Bronze Age artifacts from a 9000 $km^2$ region of Serbia and western Romania.