Tin isotope fractionation during experimental cassiterite smelting and its implication for tracing the tin sources of prehistoric metal artefacts

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A B S T R A C T

Provenance studies of metal artefacts are well-established in the interdisciplinary field of science-based archaeology primarily using the chemical and isotopic composition. In the last decades, tin isotopes became gradually more important as a fingerprinting tool for the provenance of tin, but many questions especially regarding the behaviour of tin isotopes during pyrometallurgical processes are still not satisfactorily answered. This paper is a contribution to the understanding of tin isotope fractionation on tin ore smelting under prehistoric conditions and discusses the consequences for tin provenance studies. It presents the results of smelting experiments that were carried out with cassiterite in the laboratory and in the field, respectively. Besides chemical characterisation with XRF, SEM-EDX and Q-ICP-MS, tin isotope composition of tin ores and smelting products (tin metal, tin vapour, slag) were determined using solution MC-ICP-MS.

Although tin recovery on smelting in the field was low (20–30%) due to tin losses to fuming and slag formation, the results indicate that the tin isotope composition is less affected than anticipated from theoretical considerations (Rayleigh fractionation). If cassiterite is completely reduced during the smelting reaction the tin metal becomes enriched in heavy tin isotopes with a fractionation of $\Delta^{124}Sn = 0.09$–$0.18‰$ $(0.02$–$0.05‰$ $u^{-1})$ relative to the original cassiterite. An estimate of the provenance of the original cassiterite and the potential ore source would still be possible because the variability of tin isotope ratios in tin ore provinces is much larger. If the cassiterite becomes incompletely reduced, however, then fractionation increases significantly up to $\Delta^{124}Sn = 0.88‰$ $(0.22‰$ $u^{-1})$ and conclusions on tin sources are limited. Similarly, condensed tin vapours $(\Delta^{124}Sn = 1.13‰$ $(0.28‰$ $u^{-1}))$ and slags $(\Delta^{124}Sn = 0.42$–$1.32‰$ $(0.11$–$0.33‰$ $u^{-1}))$ that are by-products of the smelting process show large fractionation with respect to the original tin ore as well, which makes them unsuitable for provenance studies.

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1. Introduction

Reconstruction of ancient smelting techniques is an important subject of experimental archaeology. Experimental approaches often focused on the smelting of copper and iron ores due to their complex (pyro)metallurgical *chaîne opératoires* and their wide use since ancient times. Numerous smelting experiments were carried out in order to obtain a better perception of the processing of these metals under prehistorical conditions (*e.g.* Coghlan, 1939; Wynne and Tylecote, 1958; O'Kelly, 1961; Friede and Steel, 1975; Tylecote et al., 1977; Merkel, 1986; Crew, 1991; summary in Tylecote and Merkel, 1985). Experimental smelting of tin ores was also performed many times, not least to understand the feasibility of different bronze production techniques. Gowland (1912) was one of the first researchers who addressed the experimental reconstruction of prehistoric bronze production. In his experiments he showed that malachite and the chief tin ore mineral cassiterite (SnO_2) can straightforwardly be co-smelted in a bowl furnace to yield copper-tin alloys, as long as the furnace is fed with pure cassiterite (for difficulties with impure cassiterite charges see Johnson et al., 2017). His result has been confirmed by laboratory

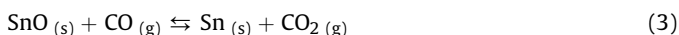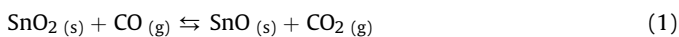experiments of Rostoker and Dvorak (1991) and more recently by the field experiments of Craddock et al. (2007) and Rovira et al. (2009). Rostoker and Dvorak (1991) demonstrated that co-smelting of cassiterite and copper sulphides is possible as well, though tin recovery within copper was much lower (20—30%) than during co-smelting of copper and tin oxides (70—85%). In general, tin contents in the resulting bronze alloys are difficult to control with all these methods.

This is also true for the so-called cementation technique. This method smelts cassiterite or stannite (Cu_2FeSnS_4) in the presence of molten or solid copper. During the process, tin metal is produced by reduction of the tin compounds, and it is readily absorbed by the copper (melt) yielding a copper-tin alloy. A variety of experimental approaches established the feasibility of the cementation technique (Maréchal, 1962; Charles, 1978; Herdits et al., 1995; Haustein and Pernicka, 2011; Lackinger, 2011), and some scholars consider it as an important process of prehistoric bronze production besides the co-smelting procedure (Charles, 1978; Rovira, 2007; Rovira et al., 2009; Valério et al., 2013; Erb-Satullo et al., 2015).

Alternatively, smelting of pure cassiterite produces tin metal, which could be added to metallic copper in a second step in order to produce a tin bronze with a desired composition in a more controlled manner. Numerous finds of tin ingots indicate that this process was extensively realised during the Bronze Age, at least in the later stages of the era (Begemann et al., 1999; Yalçın et al., 2005; Galili et al., 2013; Wang et al., 2016). Finds of metallic tin from the Early Bronze Age are scarce instead which does not exclude a priori a wide use of the direct alloying method already at this time.

Experimental smelting of cassiterite has been the subject of numerous investigations (Friede and Steel, 1976; Rapp, 1978; Earl, 1986; Tylecote et al., 1989; Timberlake, 1994; Earl and Yener, 1995; Yener et al., 2003; Craddock and Timberlake, 2005; Craddock et al., 2007; Krismer and Tropper, 2010; Figueiredo et al., 2017; Johnson et al., 2017). Large and small scale experiments demonstrated that cassiterite can be smelted without problems even under simple prehistoric conditions. However, tin recoveries were often poor due to significant tin losses to the atmosphere and to the slag. Highly volatile stannous oxide (SnO) is formed as an intermediate product during the reduction of cassiterite to tin metal

$$SnO_2 \text{ (s)} + CO \text{ (g)} \leftrightarrows SnO \text{ (s)} + CO_2 \text{ (g)} \qquad (1)$$

$$SnO \text{ (s)} \leftrightarrows SnO \text{ (g)} \qquad (2)$$

$$SnO \text{ (s)} + CO \text{ (g)} \leftrightarrows Sn \text{ (s)} + CO_2 \text{ (g)} \qquad (3)$$

that leads to considerable loss of tin (Tafel and Wagenmann, 1953; Wright, 1982; Zhang et al., 2015). Whereas Timberlake (1994) reported a tin recovery of 50% of the theoretically possible yield, recoveries during experimental smelts of Friede and Steel (1976), Earl (1986), Yener et al. (2003) and Krismer and Tropper (2010) were much lower with 12—42%.

For more than 20 years tin isotope analysis (TIA) has been used as a fingerprinting tool tracing the tin in archaeological artefacts to the ore bodies (Budd et al., 1995; Gale, 1997; Begemann et al., 1999; Yi et al., 1999; Clayton et al., 2002; Nowell et al., 2002; Gillis et al., 2003; Gillis and Clayton, 2008; Haustein et al., 2010; Balliana et al., 2013; Yamazaki et al., 2013, 2014; Nessel et al., 2015; Mason et al., 2016; Brügmann et al., 2017). However, little research has been done to examine and understand the behaviour of tin isotopes during pyrometallurgical processes, although theoretical considerations predicted considerable mass-dependent fractionation during melting of bronze metal (Budd et al., 1995). Only two experimental studies addressed the fractionation phenomenon

yielding contradictory results: Whereas Begemann et al. (1999) observed significant fractionation during bronze melting (0.07‰ u^{-1}), Yi et al. (1999) were not able to reproduce these observations in their experiments. The latter therefore concluded that pyrometallurgical operations have no major effect on tin isotopic composition. A third, more recent study carried out by Yamazaki et al. (2014) indicated that tin isotopes could fractionate during bronze casting. They observed an isotope fractionation of about 0.01—0.02‰ u^{-1}.

In contrast to bronze melting and casting, cassiterite smelting and its impact on the tin isotope systematics has never received attention, although it is the first and most invasive process in tin pyrometallurgy. Studies on copper, zinc and cadmium suggested that smelting can modify the isotopic composition of these metals (Cloquet et al., 2006; Mattielli et al., 2009; Shiel et al., 2010; Rose et al., 2016). For other metals, such as nickel and iron, the metal phase did not indicate any isotope fractionation relative to the starting material during smelting (Ratié et al., 2016; Milot et al., 2016). Given this evidence, it is difficult to predict the behaviour of tin during smelting properly, albeit it could behave in a similar manner like the volatile elements zinc and cadmium. In order to survey the systematics for tin, we initiated a series of field and laboratory experiments with tin ores. The primary aim of these experiments was to re-evaluate the different smelting and bronze production techniques possibly known in prehistory (cassiterite smelting, co-smelting, cementation) from the chemical, and for the first time also from the isotopic point of view. In this contribution we report on the impact of cassiterite smelting on the tin isotope systematics of tin and its by-products. The chemical and microstructural results will be briefly addressed; details were already described elsewhere (Figueiredo et al., 2017). The observations and results of our study will be discussed in terms of the relevance for tin provenancing.

2. Experimental setup, sample preparation and analytical methods

Hardly any trace of tin ore smelting and no tin smelting furnaces survived from the Bronze Age, a problem which already preoccupied earlier attempts in tin smelting. Archaeological evidence for smelting copper and iron ores suggests that simple bowl furnaces could have been common in early times (e.g. Tylecote and Merkel, 1985; Schoop, 2015; Dungworth, 2015), so it is not unreasonable to stress this kind of furnace also for the pyrometallurgical processing of tin in prehistory. In our experiments we followed the studies of Gowland (1912), Earl (1986) and Timberlake (1994) who used bowl furnaces as smelting structures for tin ores, but we are well aware the possibility of other furnace types for smelting tin in prehistory (e.g. shaft furnace; cf. Friede and Steel, 1976; Johnson et al., 2017).

Three smelting experiments in the field were performed in 2015 on the Campus de Ourense, University of Vigo, Spain, using primary cassiterite ores from Penouta, Galicia, Spain, and Gondiães, Trás-os-Montes, Portugal (Tables 1 and 2). Details of this campaign are described in Figueiredo et al. (2017), so information should be limited to the most relevant here. A simple bowl furnace was constructed by digging a semi-spherical cavity into the ground (diameter: 37 cm) and lining its walls with local clay (Fig. 1). Tuyères and bag bellows were installed along with a circle of stones in order to shield the operators and bellows against heat. Prior to smelting, the furnace structure was fired once to improve the heat resistance during the smelting procedure. Charcoal made from Spanish heather was used as fuel for all experiments, but no fluxes were added to the ore. For experiments 1 and 2 (F1 and F2) the crushed cassiterite concentrates (Table 2) were smelted using