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Ancient tin production: Slags from the Iron Age Carvalhelhos hillfort (NW Iberian Peninsula)

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ABSTRACT

Provenance and production of tin in the Ancient World has since long been a major topic of discussion among archaeologists. In Western Europe, where significant tin ore (cassiterite) deposits are known, only a few remains of ancient tin production, such as tin slags, have been detected. In the present work, elemental and microstructural analyses by WDXRF, SEM-EDS and XRD were performed on recently recognised tin slags from the Iron Age Carvalhelhos hillfort located in NW Iberia, a territory that represents the largest extension with tin mineralisation in Western Europe. Elemental and microstructural characterisation of cassiterite collected in a pilot field survey in the region of the hillfort are presented and discussed, as well as two ceramic fragments that could be part of a smelting structure and an iron slag from the settlement. Results show that the tin slags have variable but high contents in Sn, similarly to Pre-Medieval tin slags found in other Western European areas, but also high contents of Ta and Nb, which specifically distinguish them from other tin slags, such as those found in SW Britain. Tin ores from the hillfort region frequently have Ta and Nb in cassiterite solid solution or as inclusions of columbite group minerals, relating well with the Carvalhelhos tin slags. Up to present, the Carvalhelhos slags are amongst the very few ancient tin slags known in Western Europe, and their study can contribute to a better knowledge on ancient tin sources and trade routes.

1. Introduction

Tin (Sn) ores, such as cassiterite, are concentrated in a few geographical areas in Western Europe in contrast with copper (Cu) ores which are more widely spread. Among these regions are SW Britain, W France and NW Iberia, where tin deposits were available for ancient exploitation (Fig. 1a).

Tin was necessary for making bronze (Cu-Sn alloy), and access to it was important from Bronze Age onwards for the production of various types of artefacts. Nevertheless, despite much evidence for copper production and bronze artefact manufacturing, until now only scarce evidence for metallic tin production, such as tin slags or tin smelting furnaces has been found in archaeological Pre-Medieval contexts (Malham, 2010). The very few tin slags that have been identified (Table 1) originate from areas where cassiterite was available, and comprise: seven pieces of slag from Early Bronze Age (~1600 BCE) ritual enclosure at Caerloggas, Cornwall, SW England; a single tiny bead of slag discovered in one of the roundhouses of the Late Bronze Age settlement at Dean Moor, Devon, SW England (this particular slag is described with some detail but no analyses are available) (Tylecote et al., 1989; Malham, 2010); small size slags found in a geological borehole and dated to the Middle Bronze Age (~1400-1100 cal BCE) from St Renan in Bretagne, W France (Mahé-Le Carlier et al., 2001) and Roman tin slags from Centum Cellas, Belmonte, Portugal (Merideth, 1996).

Many of these slags underwent chemical and mineralogical analysis. These analyses showed that ancient tin slags are

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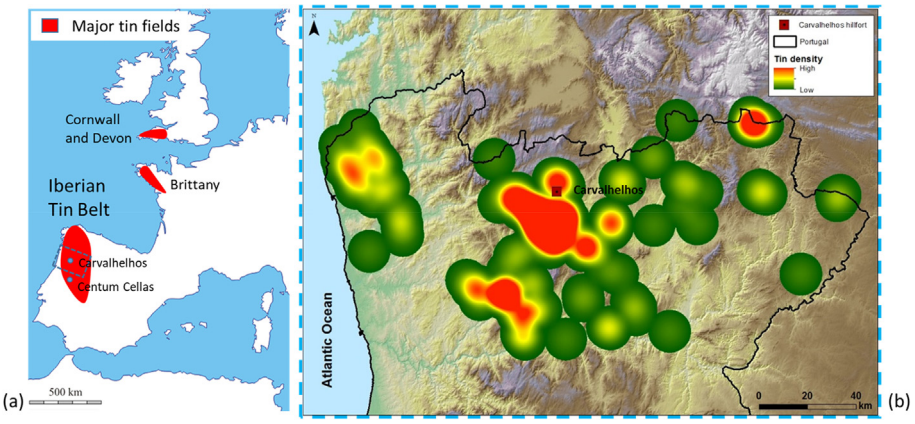

Fig. 1. Maps with: (a) major tin fields in Western Europe and location of Carvalhelhos hillfort and Centum Cellas Roman site (both with tin slags); (b) distribution of tin occurrences in Northern Portugal based on geological database (SIORMINP-LNEG). Note that the distribution and density of tin occurrences may have a strong relationship to 20th century tin extraction activities.

Table 1
List of ancient (Pre-Medieval) tin slags from Western Europe with some information about physical and chemical characteristics and notes on local/regional ores.

Tin slags	Chronological attribution	Size, colour and texture	Finding context	Elemental, microstructural or other characteristics	Notes on cassiterite ores from local or regional areas
Centum Cellas, Beira Baixa, Central Portugal (Merideth, 1996)	Roman, 1–3 century CE	Medium size (1–4 cm); Dark; Vitreous	Archaeological excavation of a Roman context	High Sn, Ta, Nb, Fe and Ti values; 5–17% SnO_2, 6–14% Nb_2O_5, 9–12% Ta_2O_5, 25–30% Fe_2O_3 and 8–16% TiO_2. Slags under furnace testing shows to begin to soften at 1200 °C and total fusion at ~1400 °C.	Cassiterite ores are present in both primary and secondary deposits. Associated with W or Ta-Nb. Cassiterite does frequently show banded regions rich in elements such as Nb, Ta, Ti and Fe.
St Renan, Bretagne, W France (Mahé-Le Carlier et al., 2001)	Middle Bronze Age	Small size, 1–2 mm	Geological borehole	Slags with different compositions and microstructures. Some still have unaltered cassiterite grains with associated minerals (quartz and feldspar) from the primary rock. Vitreous matrix can show absence of Sn or can be composed by Sn, Si, Al, Fe and Ti oxides. Some show dendrites of SnO_2 and others metallic Sn prills inside.	Regional minerals are very Sn rich and contain a low amount of impurities.
Caerloggas Downs, Cornwall, SW England (Malham, 2010; Tylecote et al., 1989)	Early Bronze Age (~1600 BCE)	Seven pieces of slag	Found at a ritual enclosure (burial)	Slag with ~41%Sn; begin to soften at 1050 °C. Glassy microstructure, iron silicate slag with pure metallic tin prills (some visible with the nacked eye). Single area scan ~40%SnO; ~31% SiO_2; ~13%Al_2O_3; 4%FeO; ~3%W; ~1.5%TiO_2; others <1%.	Rich cassiterite ores, frequent presence of W and Ti. Very low amounts of Ta and Nb (<0.1%).
Dean Moor, Devon, SW England (Malham, 2010)	Late Bronze Age	Single tiny bead of slag with reddish colour; ~3 mm size	Discovered in a hearth inside one roundhouse of a LBA settlement	(no analyses available)	Rich cassiterite ores, frequent presence of W and Ti (Ti possibly in higher amounts than in Cornish ores). Very low amounts of Ta and Nb (<0.1%).

heterogeneous at micro and macro levels, and that both composition and microstructure are strongly influenced by the geochemistry of the ores used (Malham, 2010). The type of gangue minerals in the ore specimens, the manner in which the ores were processed, as well as fluxes added and smelting technology, can also directly influence the characteristics of the slags.

The rich cassiterite resources of Iberia were exploited at least since classical times. Ancient authors such as Strabo (end of 1st century BCE to beginning of 1st century CE) and Pliny the Elder (1st century CE) commented on the richness in ores of the Iberian Peninsula and on the Cassiterides or Tin Islands, representing the first vague knowledge of the Greeks that tin was found overseas somewhere in or off Western Europe (Comendador Rey et al., 2008). Pliny the Elder in his work *Historia Naturalis* (Book XXIV) (Pliny, 1938) specified the origin of the tin traded to the Mediterranean by the Punic as "it is now known that it is a product of Lusitania and Gallecia". These two regions represent the modern northern and central Portugal, and the Spanish Galicia and Extremadura regions, which are also coincident with the Iberian tin belt.

The early presence, from Late Bronze Age, of artefacts with Mediterranean affiliations at inland tin-rich contexts have frequently been suggested to relate to trade routes involving mineral sources (Vilaça, 2006; Senna-Martínez, 2011). Also, Phoenician settlements in the Portuguese Atlantic coast from the early first millennium BCE are known, that provided navigable access to both the sea and the inland tin-rich areas through major rivers, and acted as trading-stations (Arruda, 2009; Wachsmann et al., 2009).

Indirect field evidence for early tin exploitations has been found during archaeological excavations or during the (re)opening of mining works for tungsten and tin exploitation during the first half of the 20th century. For the area to the north of the Douro River more than twenty tin mining sites were described to have "old" works in the mining engineers' reports (Meunier, 2011). These