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Article

Tin and Bronze Production at the Outeiro de Baltar Hillfort (NW Iberia)

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Abstract: Findings of Iron Age metallurgical activities related to tin metal and mining are very rare. In the present work, we present a detailed study of the Outeiro de Baltar hillfort, dated to the Late Iron Age/Early Roman period, located in a place where 20th century tin mining work took place. Elemental and microstructural analysis by portable, micro and wavelength dispersive X-ray fluorescence spectrometry (pXRF, micro-XRF and WDXRF) and scanning electron microscopy with energy dispersion spectrometer (SEM-EDS) showed that metallurgical debris found at the archaeological site is related to tin smelting and binary and ternary bronze productions. Analysis of the artefacts of diverse typologies found at the site showed that a variety of metals and alloys were in circulation and use. Samples of tin ores (cassiterite) from the region were analyzed for comparison with an archaeological tin slag from the site. The analytical results point to the production of tin metal using local cassiterite and the production of bronze by directly adding cassiterite into a smelting process. Furthermore, data of remote sensing (airborne Light Detection and Ranging (LiDAR) and historical aerial imagery) and Geographical Information System (GIS) mapping were combined with archival mining documentation and maps to retrieve a landscape context for the site. The study showed that the place of the Outeiro de Baltar hillfort (NW Iberia) was mined periodically over time.

Keywords: cassiterite; mining; tin; bronze; Iron Age; Early Roman period; Iberian Peninsula; archaeometallurgy

1. Introduction

The Outeiro de Baltar hillfort (Baltar, Ourense, Galicia) is located on the northern slope of the Larouco mountain range in Spain, on granitic terrains, just some 5 km away from the Portuguese border (to the south). The hillfort is close to a small stream, Ferradal, which runs along its eastern side.

The area surrounding the Outeiro de Baltar hillfort shows a long-lasting human occupation since prehistory, with a particularly intense occupation during the Iron Age

and Roman times. From a distance up to 20 km around the hillfort, more than forty other hillforts are known (Figure 1), not always with a well-defined chronology. In addition to the abundant hillforts, unfortified settlements of the Roman period are also documented northwards and along the Rousiá stream, of which the Ferradal stream is a tributary [1].

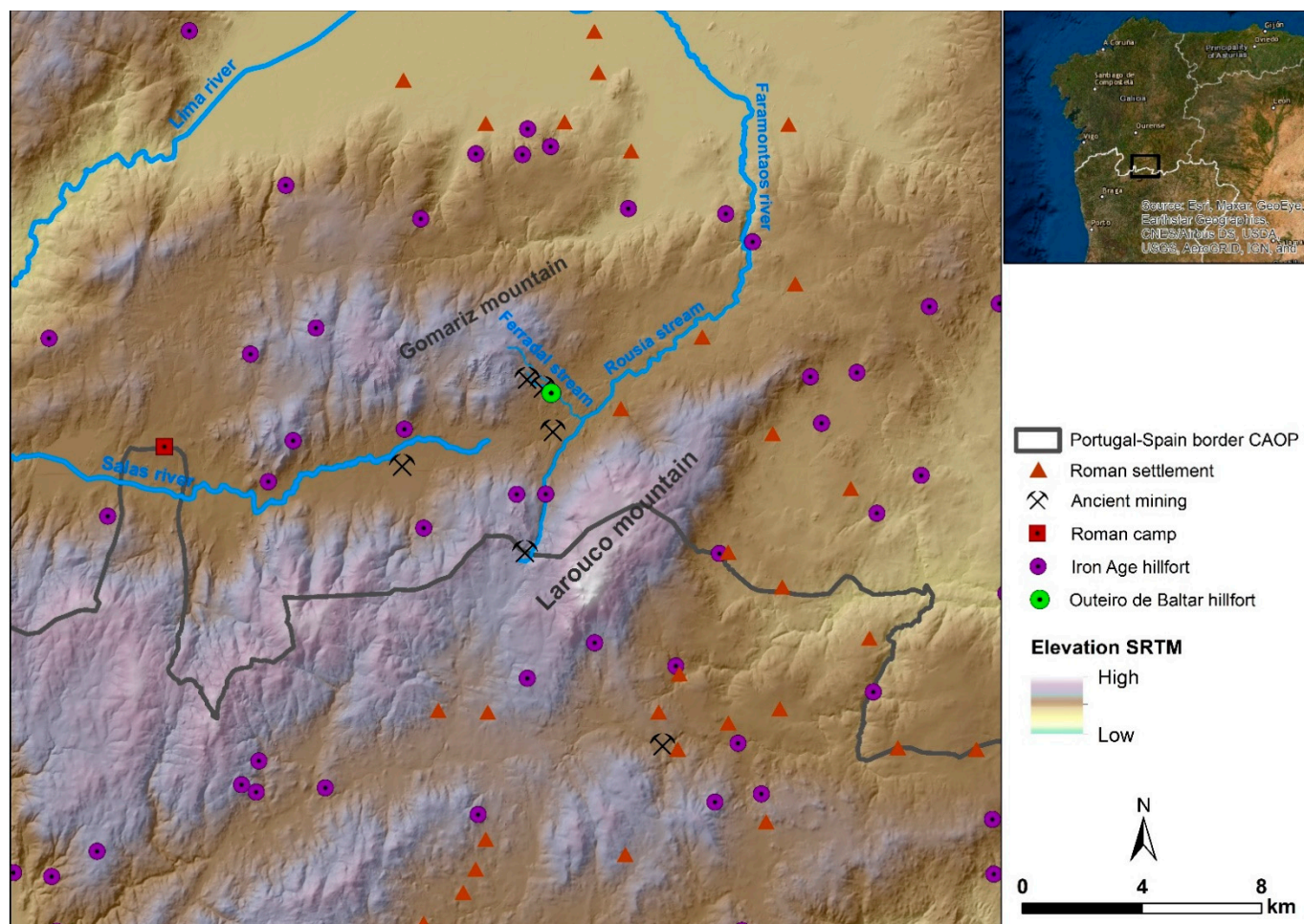


Figure 1. Archaeological landscape of the surroundings of the Outeiro de Baltar hillfort, with location of other Iron Age hillforts, ancient mining sites, Roman settlements and one military camp.

One of the particularities of the Outeiro de Baltar hillfort is that its eastern platform (near the Ferradal stream) was excavated/explored by a mining company named Somar (Somar S.A., Spain) during the 1940s. Due to the richness in tin and tungsten minerals in the area, the Somar company held a mining concession at the site [2]. As that exploitation progressed, several archaeological structures were uncovered, as well as material culture that was later delivered and deposited in a museum, the Museo Arqueológico Provincial de Ourense (Ourense, Spain). Based on the typology of the material culture recovered, a general chronology between the end of the second century BCE and the first half of the first century CE can be pointed out for the site's occupation [3–5]. Among the material recovered and deposited at the museum are lithics, ceramics, metal artefacts and a large number of metallurgical remains, namely slags and metal debris [6]. Since detailed studies on Iron Age metallurgical activities are very scarce for the region, and information on tin processing in protohistoric times is even rarer among the western European areas with cassiterite ores available [7], a detailed study on the metallurgical debris, on cassiterite samples from the region and a geomorphological context of the surrounding landscape of Outeiro de Baltar hillfort is of major pertinence.

Building on an integrated methodology, as developed elsewhere (e.g., Refs [7–9]), combining (i) remote-sensing (airborne LiDAR and historical aerial imagery) and GIS

mapping, (ii) archival mining documentation and maps, (iii) material culture studies with geological and metallurgical sampling and analysis, the current study presents new data for the Outeiro de Baltar hillfort. The results from the present study are relevant to acknowledge the importance of mining and metallurgical activities of the local protohistoric communities, with possible implications in the near and far exchange networks, especially related to tin and bronze products.

2. Materials and Techniques

2.1. Remote Sensing

Two airborne LiDAR coverages (2009 and 2016) provided by the Spanish National Geographic Institute (IGN) through the Plan Nacional de Ortofotografía Aérea (PNOA) project [10] are available for the area and were used in this study. The point clouds were already automatically classified with densities around 0.5 and 1 point/m², so in the present study, a 1-m digital terrain model (DTM) was extracted from the points classified as ground. From the DTM, different visualization techniques were applied to enhance the contrast of archaeological features, such as the local relief model [11], positive openness [12], visualization for archaeological topography (VAT) [13] and the sky-view factor [14].

In addition, in February 2022, during field work, a drone-derived airborne LiDAR survey was also conducted in the Outeiro de Baltar hillfort by the present team to obtain higher-resolution DTMs. The DJI Zenmuse L1 LiDAR sensor mounted on a DJI Matrice 300 RTK drone (SZ DJI Technology Co Ltd, Shenzhen, China) was used (flight height: 70 m, flight speed: 6 m/s, side overlap: 20%, generating a point cloud density of 225 points per square meter). Afterwards, DTMs with 0.25-, 0.50- and 1 m spatial resolution were generated and compared against the IGN-PNOA data.

For point cloud processing, DTM and visualization techniques generation, a combination of different software was used, namely LAStools [15], Relief Visualization Toolbox (RVT) [13,16] and planlauf/TERRAIN [17].

The airborne LiDAR data were compared against the historical aerial imagery made available through the IGN-PNOA project, in particular the American flight B series of 1956–1957 [18].

2.2. Archaeological Materials

Preliminary analyses by portable X-ray fluorescence spectroscopy (pXRF) were performed on 22 selected archaeological objects at the Museo Arqueológico Provincial de Ourense to gain information on the diversity of metals and alloys present in the collection. Posterior sampling was performed on 12 selected objects, including on metal debris, such as metallic nodules, to better understand the metallurgical processes practiced in Outeiro de Baltar hillfort. Samples included 1 crystal of cassiterite, 5 metallic nodules (metal debris produced during metallurgical operations, such as smelting or melting), 5 fragments of processed bars and 1 tin slag. Sample size ranged from 3 to 5 mm depending on the size of the original piece. A jeweler's saw was used for sampling the metal objects, and a precision set of plyers was used for sampling the mineral and slag objects. Samples were studied by optical microscopy, micro-energy dispersive X-ray fluorescence spectroscopy (micro-XRF) and scanning electron microscopy (SEM-EDS) depending on material nature and study aims. Additionally, two lithic objects—a possible broken mold and a hammerstone for crushing ore—were subjected to detailed photography record due to their probable relation with the local metallurgical and mining activities.

2.3. Set of Cassiterite Crystal Samples

A total of 13 tin-ore (cassiterite) samples from 10 mining sites of the region were studied. This set of ores was sampled from historic collections, namely 8 from the Geosciences Museums of the *Instituto Superior Técnico* (Portugal) and 5 from the Museum of Natural History of the Universidade de Santiago Compostela (Spain). These samples were selected based on the proximity to the Outeiro de Baltar hillfort, distancing up to ~50 km

in all directions. The set represented mainly primary (vein) sources. Together with the cassiterite sample from the archaeological collection of the Outeiro de Baltar hillfort (Museo Arqueológico Provincial de Ourense), the samples were analyzed by WDXRF and/or micro-XRF, depending on sample size and geometry.

Additionally, sediments from the Ferradal stream were collected and analyzed by WDXRF to evaluate its tin content to consider the possibility of a nearby alluvial source of cassiterite for the hillfort.

2.4. Digital Optical Microscopy

Cassiterite samples were observed and recorded with the use of a stereomicroscope Leica S9I (bright field mode) coupled with a digital camera, with acquisition of images involving the Leica Application Suite (LAS V4.12) software.

All archaeological samples were analyzed through optical microscopy (OM), using bright field, dark field and polarized light without chemical contrast. The observations were recorded with a Leica DMI5000M microscope coupled with a Leica DFC295 digital camera (Leica, Mannheim, Germany), with the use of the Leica Application Suite (LAS V4.9) software.

2.5. pXRF

At the museum, in situ analyses by portable X-ray fluorescence spectrometry (pXRF) were carried out with an Amptek spectrometer possessing an X-ray tube with a silver anode, a thermoelectrically cooled AMPTEK SDD detector (X-123SDD) with 7 mm² effective area, 7 mm diameter Be window, 180 eV power (FWHM) and an AMPTEK MCA Pocket 8000 A multi-channel system (Amptek, Inc., Bedford, USA). The analyzing conditions involved a voltage of 40 kV, a current of 10 µA and an acquisition time of 120 s. The Amptek ADMCA software (V1.0) was used to collect the spectra, and later, the ARTAX software (V7.4) was used for data evaluation.

2.6. WDXRF

Wavelength dispersive X-ray fluorescence spectrometry (WDXRF) analyses were performed on cassiterite samples and alluvial sediments for elemental composition evaluation, namely for the detection of minor and some trace elements (the detection of trace elements is strongly dependent on the equipment sensitivity and material sample size). The equipment used was a PANalytical XRF-WDS 4 kW AXIOS (PANalytical B.V., Almelo, The Netherlands) sequential spectrometer (Rh X-ray tube), and analyses were made under vacuum. Samples were analyzed without any preparation. Standardless semi-quantitative analysis was performed with the SuperQ software package (V.5.3A PANalytical B.V., Almelo, The Netherlands).

2.7. Micro-XRF

Micro-energy dispersive X-ray fluorescence analyses (micro-XRF) were performed on archaeological samples and cassiterite using an ArtTAX 800 spectrometer from Bruker equipped with a molybdenum X-ray tube, with focusing polycapillary lens (beam focus of 70 µm) and an electro-thermally cooled silicon XFlash 3001 with a resolution of 170 eV (Bruker, Billerica, USA). The analyzing conditions involved a voltage of 40 kV, current intensity of 600 µA and live time of 100 s. All samples were analyzed under air atmosphere, and at least 3 analyses were performed on each sample having been considered the average values.

The spectra were acquired using the software ARTAX, where the identification of the elements present in the samples was carried out. The quantification involved the use of Axil software (bAxil V1.8) and certified standards (BCS-CRM—Tin Ore 355; SMU—Blast-furnace slag 7-1-013; Bronzes (chill cast)—MBH 32X SN1, MBH 32X SN4, and MBH 32X SN7).

2.8. SEM-EDS

For detailed microstructure and elemental analysis of some selected archaeological samples, a Zeiss DSM 962 scanning electron microscopy (SEM) (Carl Zeiss AG, Oberkochen, Germany) with a secondary electron detector (SE), a back-scattered electron detector (BSE) and an energy dispersion spectrometer (EDS) from Oxford instruments INCAx-sight were used (Oxford Instruments, High Wycombe, UK). The EDS system was equipped with an SDD detector, with PentaFET precision and a resolution of 125 eV at Mn K α at 5,9 KeV, with the capacity to detect elements with atomic number superior to 5. The observations were performed using a working distance of 25 mm and an acceleration voltage of 20 kV. Quantitative analyses were performed based on the ZAF correction factors.

3. Results and Discussion

3.1. The Mining Landscape

From the geotectonic point of view, the Outeiro de Baltar hillfort and mining site are located in the northwest of the Hesperic Massif in a syn-tectonic two-mica granite from the Variscan Orogeny, outcropping in the “Galicia Trás-os-Montes Zone” (GTMZ) [19] (Figure 2). The granite is described as having coarse to medium grain size and dominant muscovite, emplaced during the last phase of the Variscan Orogeny. The first phases of the orogeny resulted in thickening the crust, making it behave ductilely and causing partial fusion of the country rock, later originating the granites. After the collision, a fragile period followed, allowing the ascent of granitic melts and the circulation of hydrothermal fluids in weak zones, leading to the concentration and mineralization of Sn, W, Mo, Li, Nb, Ta, Pb, Sb, Zn, Cu, Au and Ag [20,21] in quartz and pegmatitic veins. The main sources of Sn in the place of Outeiro de Baltar are the alluvial deposits resulting from the erosion of cassiterite-bearing veins [22].

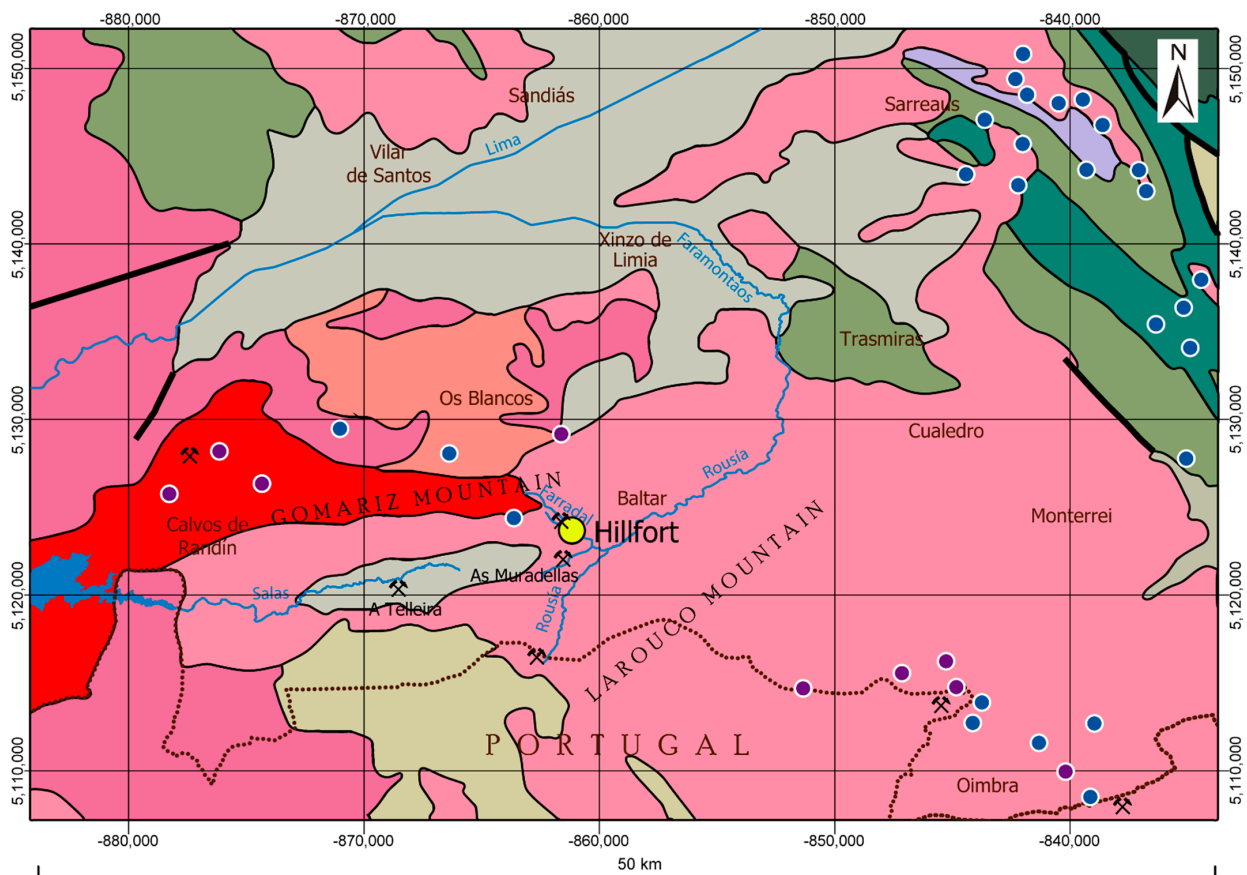


Figure 2. Cont.

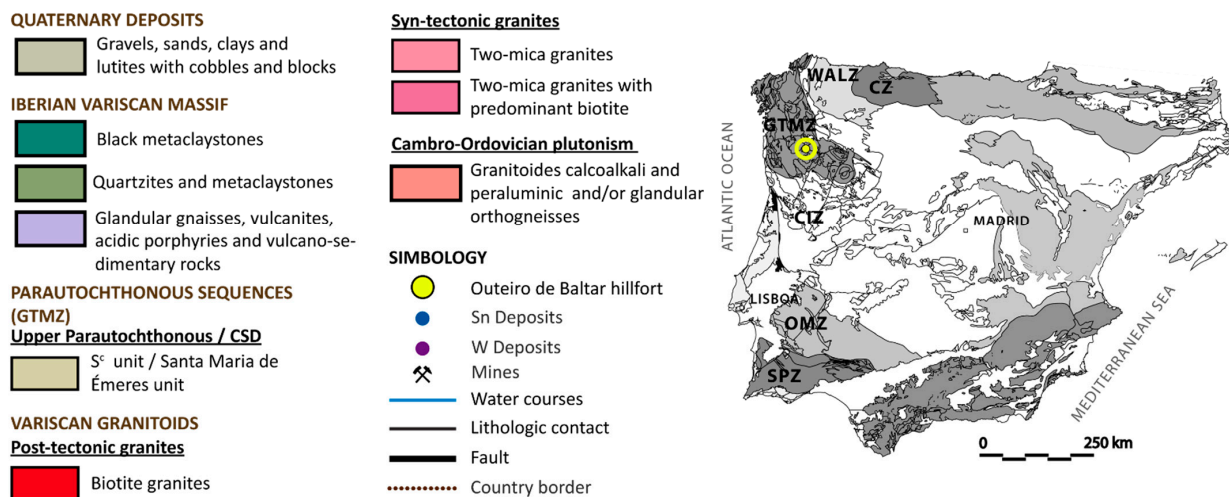


Figure 2. Geological setting of the Outeiro de Baltar hillfort and mining site (redrawn from Ref [23]) (CZ: Cantabrian Zone; WALZ: West Asturian-Leonese Zone; GTMZ: Galicia-Trás-os-Montes Zone; CIZ: Central Iberian Zone; OMZ: Ossa-Morena Zone; and SPZ: South Portuguese Zone). Location of water courses retrieved from Ref [24].

In the surrounding area of the Outeiro de Baltar hillfort, the important mineral presences are cassiterite and wolframite [25,26]. However, gold is also mentioned in locations to the northwest in association with tin ores, and during fieldwork, in some locations, the present team did identify some gold. The amount of gold metal is probably too low or localized to be relevant for today's geologists but could have been of interest for ancient miners.

Several mines are known in the area, of ancient and modern chronology. The most recent ones, of the 20th century, were registered for tin and tungsten mining but were of relatively small importance. In a report of the Geological and Mining Institute of Spain (IGME), only two places of interest are mentioned for this southern part of the Ourense Province: one in Calvos de Randín (alluvial cassiterite, two concessions) and the other in Baltar, in the center of our study area, where five concessions are registered in the name of the Somar company [27]. The Calvos de Randín place can be considered as a simple hint for cassiterite with no subsequent exploitation, since there are no recorded data on mining activity. On the other hand, the Baltar mines have documented activity for the period between 1942 and 1950, covering 276 hectares, where numerous small veins were sought in the kaolinized aplitic granite. Among these concessions, the Outeiro de Baltar hillfort is located within the concession "Nando" (Figure 3), and therefore, the hillfort can be placed nearby a mineralized area and close to several tin-bearing deposits. In addition to these places on the Spanish side of the border, concessions for tungsten (and possibly secondary tin) are registered on the Portuguese side, one active between 1943 and 1955 and the other between 1918 and 1972. Despite the documented information on the periods of activity of these modern mines, there are no data on the amount of ores retrieved or their precise extension within the concessions [25].

In addition to the 20th century modern mining activity, three ancient mines are known within a 10 km distance of the Outeiro de Baltar hillfort. Two are in alluvial deposits, and the third is located in the granitic substrate. They are considered to be of Roman times, but studies are needed to fully determine the chronologies of the mining. The first one, the Muradellas mine, is currently being studied by our team, and preliminary data allow us to consider this mine as a secondary alluvial deposit for tin. The second mine, As Telleiras, is another alluvial deposit, which could have produced tin and gold, based on samples collected by us. The third one is an opencast trench, recently identified [28] near the Portuguese border, presumed as exploited for gold. In addition to these three mines, during the drone-derived LiDAR survey carried out for the present work around the Outeiro de Baltar hillfort, we did also discover the presence of other alluvium mining works to the

north/northwest of the hillfort, along the margins of the Ferradal stream (Figure 4). These works, unknown to date, are only partially covered by our survey and would need further investigation, as the whole upper Ferradal stream could have been mined in antiquity. Based on our preliminary data, the topographical and morphological details derived from the LiDAR are similar to other mines known in the area and elsewhere [9], which were mined using water-powered (hydraulic) techniques in alluviums. Such mining techniques can date back to the Roman period (first to third centuries CE); however, previous mining activities, namely coetaneous with the hillfort, should not be excluded.

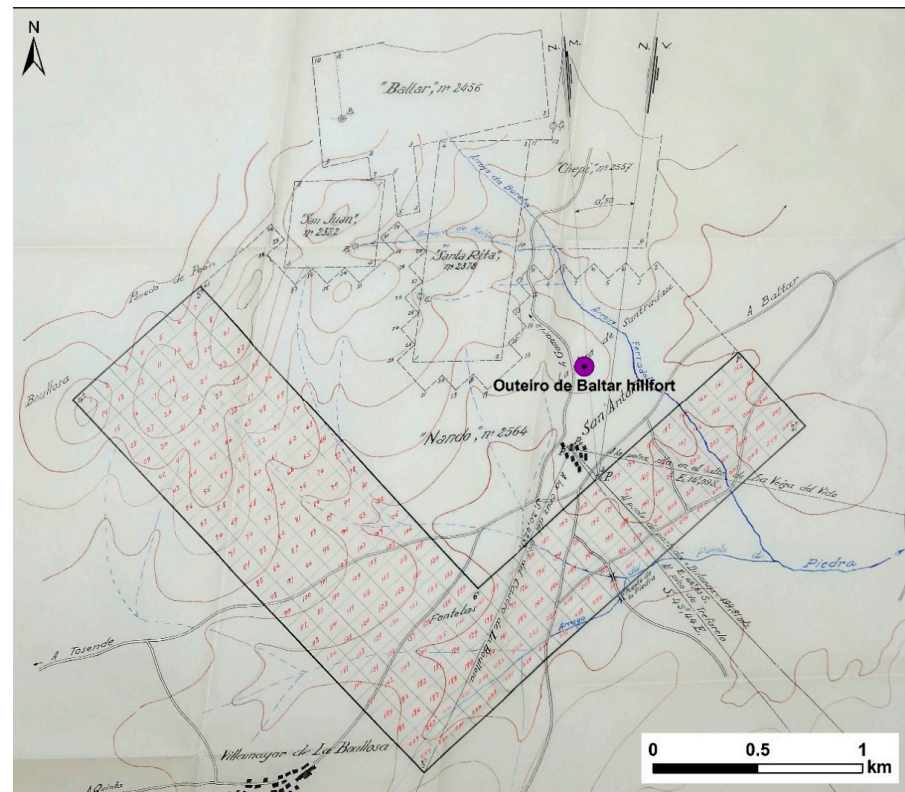


Figure 3. Map dating to 1947 of the mining concession of “Begoña” available at the Archivo Histórico Provincial de Ourense that includes the mining concession of “Nando” where the Outeiro de Baltar hillfort is located.

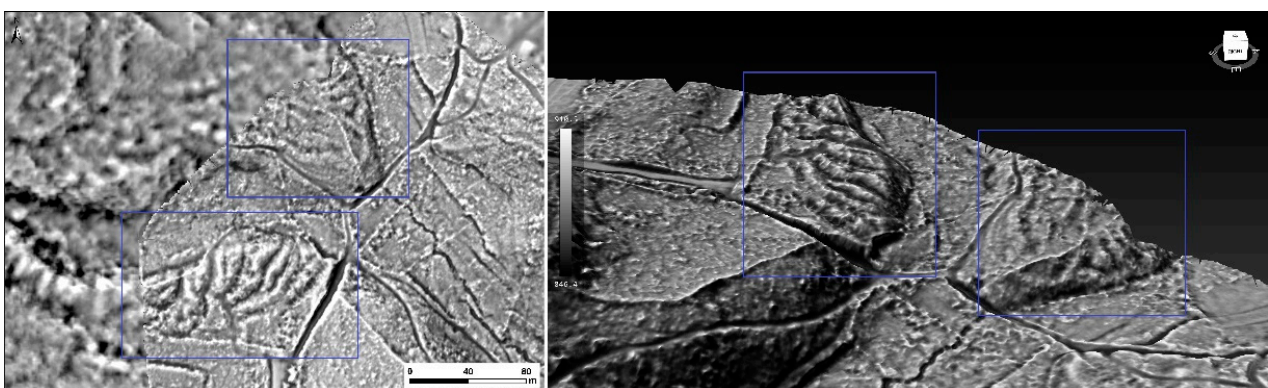


Figure 4. Detailed view of the identified ancient alluvial mining works (highlighted) in the margins of the Ferradal stream, north/northwest to the Outeiro de Baltar hillfort. Note the mining trenches excavated using a hydraulic system with tailings placed alongside. **Left:** 2D 0.50 m drone-derived local relief model overlapped with 1 m IGN-PNOA (2009) local relief model; **Right:** 3D 0.50 m drone-derived local relief model.

Although the modern geological databases only mention a few tin deposits close to the Outeiro de Baltar hillfort, the presence of ancient mines in the region and the recovery of materials related to ore processing in the Outeiro de Baltar hillfort by the Somar company give strong indications on the extent of resources available for mining at ancient times. From the exploitation conducted by the Somar company in the 1940s, several trenches still remain visible in the digital models on the eastern side of the hillfort [2] (Figure 5). This area most likely provides us the location from which the archaeological materials were uncovered. Additionally, we can attribute to this location the impressions and descriptions created by the miners, later documented by López Cuevillas and Taborda Chivite, i.e., that the miners of the Somar company recognized vestiges of the gangue of the ore between the houses of the hillfort, relating it to the mining activities performed by the ancient habitants, and even mentioned that the ores were processed very carefully [3]. The location of these findings does also show us that the occupation of the hillfort extended beyond the main visible rampart toward the Ferradal stream.

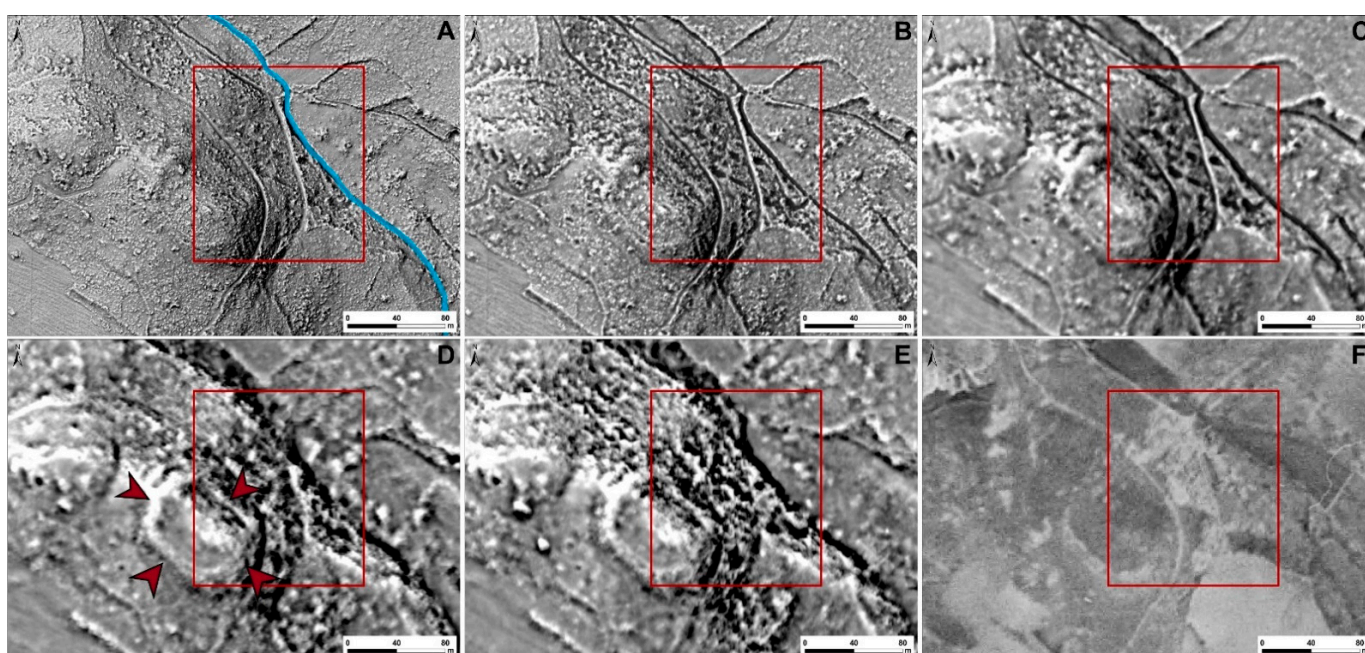


Figure 5. Outeiro de Baltar hillfort with the area explored by the Somar company highlighted (red square). Note the main visible rampart of the hillfort (of near-circular shape depicted in image (D) and the mining trenches near the Ferradal stream (the stream is depicted in blue in image (A), which affected part of the hillfort. (A) A 0.25 m drone-derived local relief model; (B) A 0.50 m drone-derived local relief model; (C) A 1 m drone-derived local relief model; (D) A 1 m IGN-PNOA (2009) local relief model; (E) A 1 m IGN-PNOA (2016) local relief model; (F) American flight B series of 1956–1957.

3.2. Archaeological Materials

3.2.1. Metal Artefacts and Lithic Tools

Among the artefacts from the Outeiro de Baltar hillfort that were analyzed by pXRF are five fibulae, four coins, one decorated pin and one terminal of conic shape, possibly from fibulae (some examples are shown in Figure 6).



Figure 6. Examples of some of the artefacts analyzed by pXRF from Outeiro de Baltar hillfort at the *Museo Arqueológico Provincial de Ourense* (Galicia, Spain), which include fibulae (732; 3.321; 3.354 (A); 3.354 (B)), a coin (3.327), a decorated pin (CE003363), a cassiterite crystal (3.316 (A)), pyrite crystals (3.316 (B)), a tin slag (CE 3.319 (C)) and metal scrap nodules (CE 3.319). Black scale applies to all artefacts' photographs, and gray scale (bottom right) only applies to the CE 3.319 photograph.

The diversity of the metal compositions of these artefacts is shown in Table 1, with major presence of artefacts of bronze with different amounts of lead (Cu-Sn(-Pb) alloys; material interpretation takes into account normal corrosion effects in bronzes [29]), namely one pin, one terminal, two bar fragments, one fibulae and two coins, three brass fibulae with some Sn and Pb (Cu-Zn alloy), one fragmented copper coin and one fragmented silver coin. These results show that a large diversity of metals and alloys, mostly copper-based, were at use and circulation by the Late Iron Age/Early Roman period in the region. Despite the lack of a real monetary economy in NW Iberia by the Late Iron Age, the presence of a few coins of diverse compositions in the collection shows that these exogenous items circulated among the local populations and could bear material value for exchanges as well as some aesthetical/symbolic value. It is known that silver, for example, was an appreciated metal that was circulating with a (proto-)monetary value during the Late Iron Age and the beginning of the Roman conquest (late second century BCE to early first century CE) [30,31]. In fact, several pure-silver ingots were identified in Iron Age hillforts nearby the Outeiro de Baltar. These include seventeen plano-convex ingots from the Calvos de Randín hoard (Outeiro da Cerca hillfort) and one from the Saceda hillfort [31], given that one of the silver ingots from the Calvos de Randín hoard was radiocarbon dated through a charcoal sample to 213–88 cal BCE [32]. Given the present work, it can be interesting to note that Calvos de Randín is one of the places with alluvial cassiterite where there were concessions during the 20th century in southern Ourense.

Table 1. Results from the pXRF elemental analyses (qualitative results) performed on selected artefacts from the Outeiro de Baltar hillfort collection at Museo Arqueológico Provincial de Ourense (Galicia, Spain). The material interpretation takes into account normal corrosion effects in bronzes, such as decuprification, which leads to enhancement in Sn and Pb contents on the corroded surfaces [29].

Item	Inv. Number	Elements Detected										Material Interpretation	
		Cu	Sn	Pb	Ag	As	Ni	Fe	Zn	Sb	Other		
Pin	3.363	+++	++	+	n.d.	n.d.	n.d.	-	n.d.	vest.		Cu-Sn-Pb	Bronze with lead
Terminal	3.363	+++	++	+	n.d.	n.d.	-	-	n.d.	n.d.		Cu-Sn-Pb	Bronze with lead
Bar	3.333	+++	++	+	n.d.	n.d.	n.d.	-	n.d.	n.d.		Cu-Sn-Pb	Bronze with some lead
Fibula	732	+++	-	-	n.d.	n.d.	n.d.	-	++	n.d.	Ca, Ti/Ba	Cu-Zn	Brass
Fibula	3.321	+++	+	+	n.d.	n.d.	n.d.	-	++	n.d.	Cl, Mn	Cu-Zn	Brass with Sn, Pb
Fibula	3.322	+++	-	-	n.d.	n.d.	n.d.	-	+	n.d.		Cu-Zn	Brass with some Sn, Pb
Fibula	3.354 (A)	+++	++	+	n.d.	n.d.	vest.	-	n.d.	vest.		Cu-Sn-Pb	Bronze with some lead
Fibula	3.354 (B)	+++	++	+	n.d.	n.d.	vest.	-	n.d.	vest.		Cu-Sn-Pb	Bronze with some lead
Coin	3.326 (A)	+	-	-	+++	n.d.	vest.	-	n.d.	n.d.	Au, Cl, Br, Bi	Ag	Silver
Coin	3.326 (B)	+++	++	++	n.d.	n.d.	n.d.	-	n.d.	vest.	Sr?, Mn	Cu-Sn-Pb	Leaded bronze
Coin	3.327	+++	++	++	n.d.	n.d.	n.d.	-	n.d.	n.d.		Cu-Sn-Pb	Leaded bronze
Coin	3.329	+++	-	-	n.d.	n.d.	n.d.	-	n.d.	n.d.	Zr?	Cu	Copper with some Sn, Pb
Bar frag.	CE00 3363	+++	++	+	n.d.	n.d.	n.d.	-	n.d.	n.d.		Cu-Sn-Pb	Bronze with some lead
Metal debris	CE 3.319 (A)	+++	++	++	n.d.	-	-	-	n.d.	n.d.		Cu-Sn-Pb	Bronze with lead
Metal debris	CE 3.319 (B)	+++	+	-	n.d.	n.d.	n.d.	-	n.d.	n.d.	Cl	Cu-Sn	Bronze
Metal debris	CE 3.319 (E)	+++	++	+	n.d.	n.d.	n.d.	-	n.d.	n.d.		Cu-Sn-Pb	Bronze with lead
Metal debris	CE 3.319 (F)	++	+	+++	n.d.	n.d.	n.d.	-	n.d.	n.d.		Cu-Sn-Pb	Leaded bronze
Metal debris	CE 3.319 (H)	+++	++	-	n.d.	n.d.	n.d.	-	n.d.	n.d.		Cu-Sn	Bronze
Metal debris	CE 3.319 (I)	+++	++	-	n.d.	n.d.	n.d.	-	n.d.	n.d.		Cu-Sn	Bronze
Debris/Slag	CE 3.319 (C)		+++	n.d.	n.d.	n.d.	n.d.	-	n.d.	n.d.	Ta, Nb, Ti, W, Zr, Mn		Tin slag
Ore/mineral	3.316 (A)	n.d.	+++	n.d.	n.d.	n.d.	n.d.	-	n.d.	n.d.	Ta?, Nb		Cassiterite (crystal)
Ore/mineral	3.316 (B)	-		n.d.	n.d.	n.d.	n.d.	+++	n.d.	n.d.	S++, Ca?		Pyrite (bearing some Cu)

Major elements (+++); minor elements (-); trace elements (vest.); not detected (n.d.). ?—These signs here have to exist, since it is not certain their identification.

Micro-XRF analysis performed over the cross-section (metal) surfaces of five sampled bar fragments (sampled from a package of dozens of small bars in the museum) shows Sn contents between 7 and 12% and Pb contents below 2.5%. This is in good agreement with what is considered as a good quality bronze alloy with respect to thermo-mechanical properties [33], and it holds attractive gold-like aesthetics.

In addition to these metal objects, two lithic artefacts in the museum collection were identified as probably related to metallurgical activities and ore processing. The first one is a broken block of granite with an elongated hollow, which could be part of an ingot mold. The second one is a rounded piece of granite with wear marks, which could have been used to crush ore (Figure 7). López Cuevillas and Taborda Chivite [3] also mentioned a pick with one sharp edge and the other flat, made of iron, which could have been used for mining. Additionally, their indication of a spherical granite stone with a hollow in the center, considered by them as a kind of hammer, is another element that we can sum up with the materials related to ore processing recovered from the archaeological site [3].



Figure 7. Lithic artefacts related to metallurgy and ore processing from Outeiro de Baltar hillfort: a broken mold (**left**) and a hammerstone to crush ore (**right**).

3.2.2. Slag, Metal Debris and Ores

The Outeiro de Baltar hillfort archaeological collection includes material assemblages, which could clearly be related to metallurgical debris, namely numerous metal pieces, mostly with nodular shapes, and two mineral crystals (Figure 6). The nodular-shaped metal pieces resemble other metallurgical assemblages recovered from the Late Bronze Age sites in Iberia, related to bronze production, such as smelting, melting and casting activities [34]. Seven pieces of this metallurgical debris and the two minerals were analyzed by pXRF (Table 1). The results showed that six pieces of debris are metal nodules of bronze (alloys with different amounts of Pb), and one piece is a tin slag, identified by its major amount of Sn, absence of Cu and presence of other elements, such as Ta, Nb, Ti, Mn, Fe, Zr and W. Previous archaeological and experimental studies [7,35] have shown that tin slags retain elements, which can be present in cassiterite and associated minerals, such as

Nb, Ta, Ti and W (among others), due to the fact that these elements preferentially remain in an oxidized state in relation to tin during smelting and are thus retained in the slag (are not dissolved or easily incorporated into the produced metallic tin). The analysis of the two minerals revealed that one is a cassiterite crystal with Fe, Ta and Nb (although in the museum, it was cataloged as wolframite), and the other is a pyrite with a small amount of Cu (copper-bearing pyrite). The analyses conducted on the samples of the debris (metal and slag) by micro-XRF (Table 2) showed that the metal nodules are made of bronze with more variable Sn and Pb contents (4–15% Sn and up to 12% Pb (one sample)) than those obtained for the bar artefact fragments. Microstructural observations of the metals by optical microscopy showed that the bars are composed of equiaxed alpha-phase grains, typical for worked and annealed objects, while the nodules showed coarse dendritic microstructures. The higher variations of Sn and Pb contents found among the nodules, together with their coarse microstructures, suggest that the nodules can be a result of the smelting processes (extractive operations to produce metal) rather than from recycling or melting processes (see discussion in Ref [34]). Another indication suggesting they are products of the smelting operations, and thus less refined, is the presence of a particle of Nb among the metallic alpha-phase (Cu-Sn) that was detected during a SEM-EDS analysis of the nodule CE 3.319 (F) (Figure 8). The presence of this trace element in bronze can be related to the direct use of cassiterite to produce bronze [35–37]. This would implicate a process of co-smelting or cementation (partial smelting process) involving the addition of cassiterite to copper ore or metallic copper. Although the Outeiro de Baltar metallurgists could have produced bronze by alloying metallic tin to metallic copper, the present results is evidence of the diversity in the metallurgical solutions in practice. In fact, evidence from other Iron Age sites showed that, on the Iberian Peninsula, co-smelting or cementation methods for bronze production were used alongside the alloying of metallic copper to metallic tin [38].

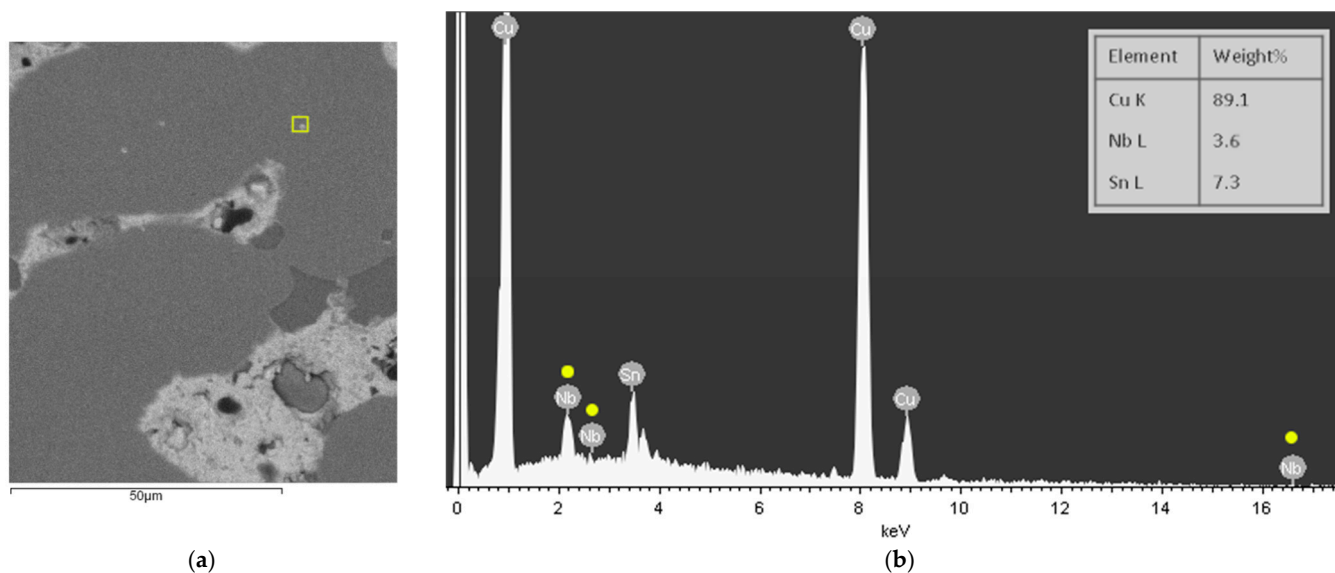


Figure 8. SEM-EDS analysis of the CE 3.319 (F) metallurgical debris (metallic nodule): (a) BSE image area with alpha-phase (Cu-Sn) (gray matrix), large lead-phase (white) and a highlighted small inclusion rich in Nb; (b) EDS spectra of analysis performed on the selected highlighted area in (a), where Nb is clearly visible among the Cu and Sn elements in the alpha phase.

Table 2. Results from micro-XRF analyses performed on a selection of sampled artefacts from the Outeiro de Baltar hillfort collection. Analyses performed over metal surfaces of the cross-sections from bar fragments and metal debris (nodules) are presented in the form of elements, and analysis performed on a sample of tin slag is presented in the form of oxides.

Item	Inv. Number	Elements (%)						Notes from OM Observations					
		Cu	Sn	Pb	As	Ni	Fe						
Bar frag.	CE00 3363(A)	87.1	11.7	1.16	n.d.	n.d.	0.05	Bronze alloy with a microstructure composed by equiaxed alpha-phase grains					
	CE00 3363(B)	86.0	11.3	2.31	0.09	0.14	0.08	Bronze alloy with a microstructure composed by equiaxed alpha-phase grains					
	CE00 3363(C)	86.4	11.8	1.52	0.05	0.13	0.09	Bronze alloy with a microstructure composed by equiaxed alpha-phase grains					
	CE00 3363(D)	90.8	6.76	2.04	0.14	0.13	0.12	Bronze alloy with a microstructure composed by equiaxed alpha-phase grains					
	CE00 3363(E)	85.1	13.4	1.33	0.03	n.d.	0.06	Bronze alloy with a microstructure composed by equiaxed alpha-phase grains and low amounts of (alpha + delta) eutectoid					
Metal debris	CE 3.319 (A)	89.4	7.98	2.33	0.13	0.15	<0.05	Bronze alloy with a coarse microstructure composed by alpha phase dendrites and (alpha + delta) eutectoid					
	CE 3.319 (B)	84.0	15.3	0.25	0.04	0.14	0.21	Bronze alloy with a coarse microstructure composed by alpha phase dendrites and (alpha + delta) eutectoid					
	CE 3.319 (E)	86.5	12.6	0.55	0.17	0.13	<0.05	Bronze alloy with a coarse microstructure composed by alpha phase dendrites and (alpha + delta) eutectoid					
	CE 3.319 (F)	78.4	8.50	12.3	0.44	0.29	0.16	Leaded bronze with a coarse microstructure					
	CE 3.319 (H)	95.3	4.19	0.20	n.d.	0.26	<0.05	Bronze with a coarse microstructure					
		Oxides (%)											
		SiO ₂	K ₂ O	TiO ₂	MnO	Fe ₂ O ₃	Rb ₂ O	SrO	ZrO	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃
Tin slag	CE 3.319 (C)	(n.q.)	3.5	32.7	2.1	10.2	0.06	0.04	0.5	1.4	41.7	3.4	4.3

For elements and oxides the composition is in wt.% normalized; n.q.—not quantified; n.d.—not detected.

The presence of lead in significant amounts in at least one of the nodules (CE 3.319 (F)) presumes the intentional additions of Pb. High lead contents are normally not desired in utilitarian artefacts, which have to be subjected to mechanical stress, since lead tends to aggregate in large globules in certain regions of the cast (due to the low solubility of lead in copper), resulting in objects that can be easily broken. Nevertheless, if added in small amounts, the mechanical resistance is not too much affected, and some improvements in castability can be achieved. Contrary to earlier periods, such as the Bronze Age, where binary bronzes were the norm in western Iberia [33,34], possibly at this later time, bronze artefacts were being produced with some Pb due to the large availability and circulation of Pb as a sub-product of silver metallurgy (namely from the cupellation process). Since the end of the Punic Wars (264 and 146 BCE), silver production on the southern peninsula increased significantly in Roman contexts with the subsequent amount of available lead [39]. The bronze metallurgy could have represented a way to use part of this excess lead in amounts that would not significantly modify the mechanical properties of bronze.

The micro-XRF analysis of the tin slag showed that it is composed of high quantities of Sn (42% SnO₂), Ti (32% TiO₂) and Fe (10% Fe₂O₃) but did also present Ta (3% Ta₂O₃), W (4% WO₃) and Nb (1.4% Nb₂O₅) in significant quantities (note that in this analysis, Si was not quantified). Compared to the only other Iron Age tin slags known in NW Iberia, those from the Carvalhelhos hillfort [7], the Baltar slag showed relatively higher Sn and Ti contents and lower Ta, Nb and Fe contents. The SEM-EDS analysis of the tin slag (Figure 9) shows an aluminosilicate vitreous matrix (~10% Al₂O₃ and ~50% SiO₂) with high amounts of Sn (~20% SnO₂), Ti (~9% TiO₂), Fe (~4% Fe₂O₃) and, in some areas, Nb (~4% Nb₂O₅). Dispersed among the vitreous matrix are numerous metallic tin globules up to ~50 µm in diameter, but normally < 10 µm, and occasional remnants of the gangue material (quartz inclusion) and charcoal used in the smelting process. The fact that Ta and W were not detected in the SEM-EDS analyses, despite having been detected in the pXRF and micro-XRF analyses, suggests that the slag is very heterogeneous at a macro scale. Compared to the microstructure of the Carvalhelhos slags, which are composed of a

vitreous matrix with thin Ta-Nb-Ti-oxide-rich dendrites and metallic tin globules, this slag differs by the absence of oxide-crystal phase formations.

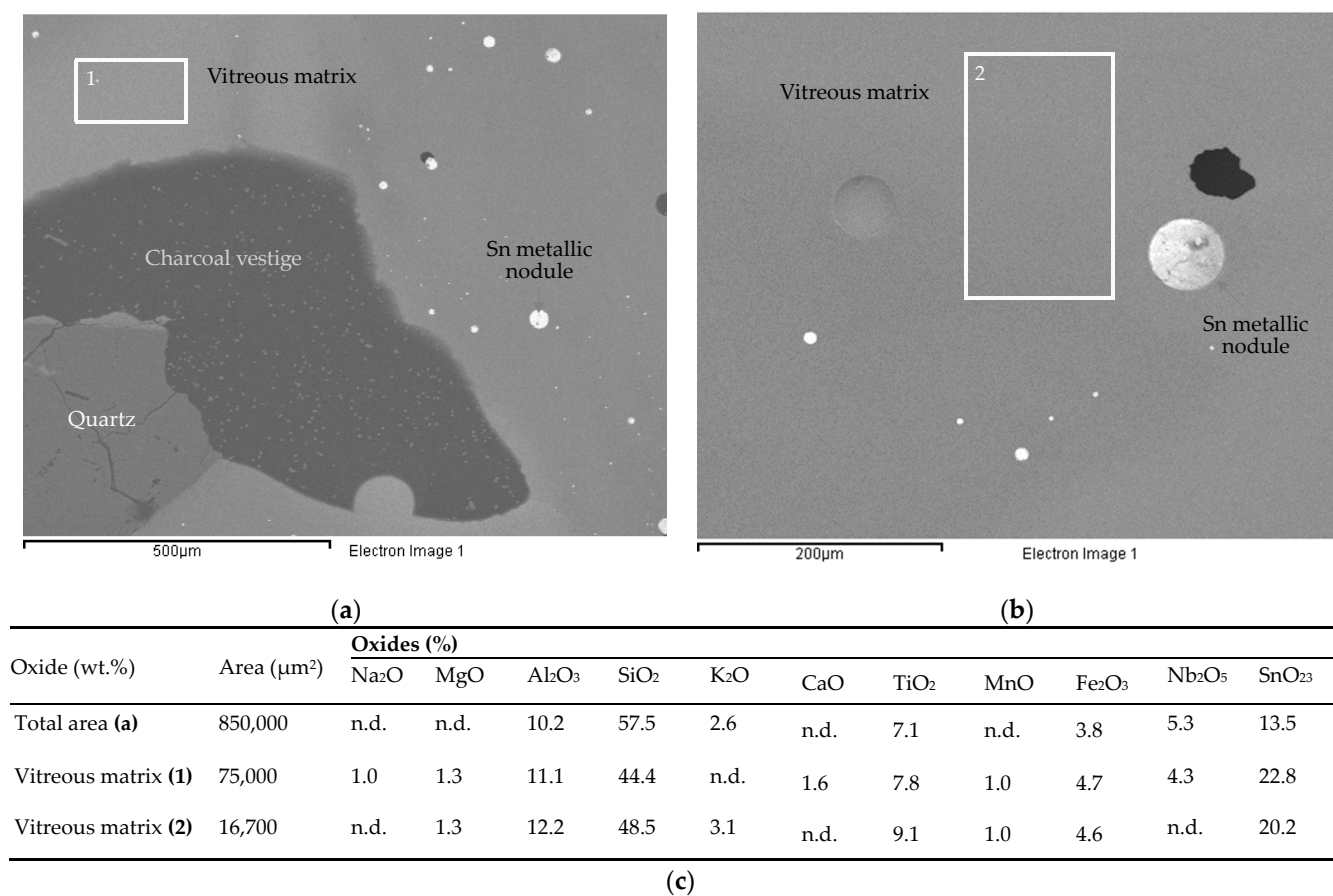


Figure 9. SEM-EDS analysis of the tin slag material: (a) BSE image of area showing gangue remains (such as quartz) from the cassiterite ores and charcoal from the smelting process among a vitreous matrix with numerous Sn (metallic) nodules; (b) BSE image of another area showing the vitreous matrix and Sn (metallic) nodules of various sizes and (c) EDS results of chemical composition of annotated areas.

The identification of a tin slag among the metallurgical remains of the Outeiro de Baltar hillfort testifies to the local production of metallic tin. So far, this is the second site with tin slags from the Iron Age identified in NW Iberia (the other is the Carvalhelhos hillfort, on the Portuguese border). Previous studies reporting on materials related to ancient metallic tin productions in Galicia, which include chemical analyses for a more secure attribution, refer to two tin ingots of a plano-convex shape found 1 m deep in two mining waste heaps (one in the Varilongo mines, Santa Comba, and the other in Rial de Cuns, Coristanco), probably from the Bronze Age, of 99.8 wt.% Sn [40]. On the other hand, reports on the vestiges of ancient tin mining are much more numerous, with at least 33 places in Galicia and north of Portugal retrieved from published archaeological and geological reports [41]. Most of these ancient mining sites lack, however, detailed studies to fully realize the extent, intensity and chronological sequences of tin mining.

The use of tin ore in different metallurgical operations, i.e., for bronze production in the co-smelting or cementation process and for metallic tin production, can be related to the practice of a diversity of metallurgical solutions, but it can also be interpreted as relating to different purposes. Provided that pure tin was rarely used to produce objects, being mainly used to be alloyed with copper for bronze production, one can suppose that the production of tin metal in the Baltar hillfort could be related to the production of tin ingots and trading purposes (this would be most valued in areas without tin resources).

The production of bronze by a more direct (and maybe efficient) operation, such as co-smelting or cementation, could serve the bronze artefact productions for local consumption as well as for trading, involving finished artefacts. The co-occurrence of several methods of bronze production has been reported since the Late Bronze Age [34,38,42–45], suggesting that the Iberian communities were able to adapt to various metal production processes depending on local resources, facility/efficiency of metallurgical operations, trade aims and consumption habits.

3.3. Set of Cassiterite Samples from the Region and Collected Sediments

In addition to cassiterite, which is part of the archaeological hillfort collection (previously discussed), a set of other cassiterite samples from 10 mining sites distancing up to ~50 km away from the hillfort were analyzed. This set of ores was from the historic museum collections and does not entirely cover the cassiterite outcrops available for mining in the region. Nevertheless, the present set was adequate for providing pertinent information on minor and some trace elements associated with the tin ores in the region, with direct implications for the elements that were later to be found in tin slags.

WDXRF and micro-XRF analysis of the tin ore samples showed that Si, Al, S, P, K, Ca, Fe, Ti, Nb and Rb were among the most common elements identified, which can be related to the associated minerals and gangues. Other common elements were Na, Mg, Mn, Zn, Ta, W, As, Sr and Cr. Additionally, traces of Cu were detected in the cassiterite samples from Vilameá, and traces of Pb were detected in the samples from Vilameá and Vilar de Cervos.

In the case of the micro-XRF analysis focusing on the micro-areas of the cassiterite grains, the main elements identified (apart from Sn) were traces of Fe, Nb, Ta, W, Ti and Mn (Figure 10). These elements (among others, such as Zr) are recognized to be common in Iberian cassiterites (substitution in cassiterite lattice or as inclusions and/or exclusions in different oxidation states and mineral types, e.g., columbo-tantalite) [46–48], and they can account for different colors exhibited by the cassiterite crystals. In the analyzed samples, differences in color can be clearly observed among the examples, such as a more reddish color of the Sarreaus sample, a more yellow-brown color of the Viveiro sample and a blackish color on the Minas da Borralha and Ribeira da Pena samples (Figure 10).

Taking into account the cassiterite set of the samples analyzed and the archaeological cassiterite found at the hillfort, some diversity based on the presence of Fe, Nb, Ta, W, Ti and Mn elements can be found among the different sites but also among the samples within a single site. However, a tendency can be found for the presence of Nb in the cassiterite samples closer to the Outeiro de Baltar hillfort and to the south, and for the presence of W in the cassiterite of the Outeiro de Baltar samples and in those to the north. Still, the recurrent presence of Nb, Ta, W and Ti in the regional cassiterites is very consistent with the appearance of those elements in the tin slag and the detection of Nb in the metal debris smelting nodule.

In addition to the cassiterite samples, alluvial sediments from the Ferradal stream that runs along the eastern side of the Outeiro de Baltar hillfort were collected and analyzed by WDXRF (Table 3). The results show relatively high amounts of Sn (5–7% SnO₂), suggesting that the alluvial deposits alongside the stream are very rich in cassiterite. This provides further support for the detection and interpretation of alluvium mining works on the margins of the Ferradal stream, as suggested by the high-resolution LiDAR images obtained to the north/northwest of the hillfort in this work. If those alluvium deposits were to have been mined during the Iron Age, one could expect tin slags with W, Ta, Nb, Fe, Ti and Zr elements present, just as detected in the archaeological tin slag, since all these elements were present in the sediment sample.

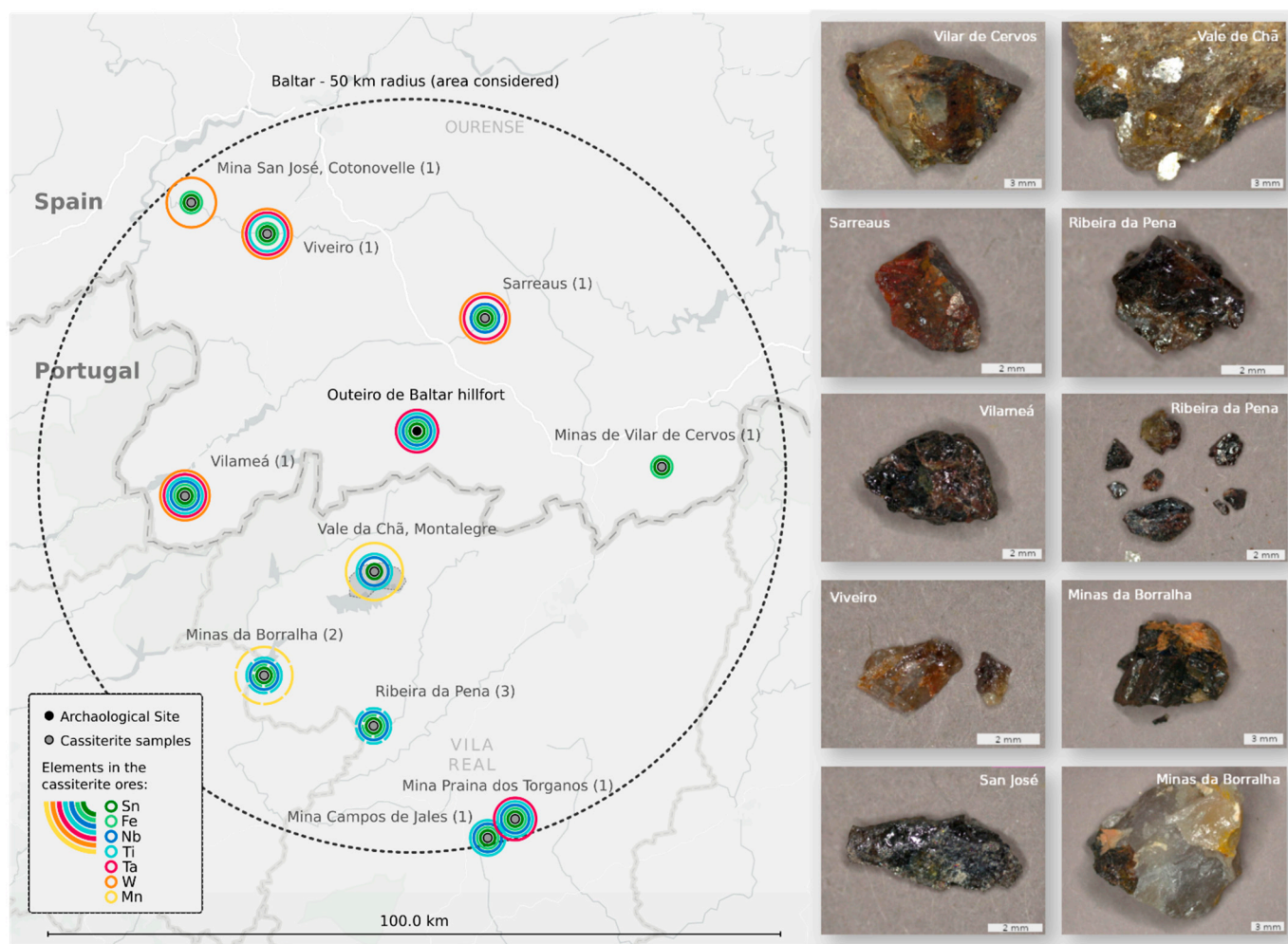


Figure 10. Location of the cassiterite samples analyzed in the present work (50 km radius considered around the Outeiro de Baltar hillfort) with annotation of different elements detected in the samples (based on WDXRF and micro-XRF analyses (left); dashed circle lines represent elements that were not always present in all the samples analyzed from one site) and photographs of some samples (on the right).

Table 3. Results from WDXRF analyses of the (alluvial) sediments collected in the Ferradal stream that runs along the eastern side of the Outeiro de Baltar hillfort. Three sub-parts (1, 2, 3) of the sediments were analyzed.

Part	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	Cr ₂ O ₃	MnO	Fe ₂ O ₃	ZnO	Rb ₂ O	SrO	ZrO ₂	Nb ₂ O ₅	SnO ₂	La ₂ O ₃	CeO ₂	Ta ₂ O ₅	WO ₃	ThO ₂
(1)	1.16	0.456	11.0	65.4	0.699	0.047	4.29	0.79	2.97	0.019	0.202	6.65	0.022	0.045	0.013	0.148	0.132	4.85	n.d.	0.066	0.143	0.83	0.009
(2)	1.36	0.441	10.3	61.0	0.813	0.047	3.98	0.97	3.97	n.d.	0.197	8.47	0.028	0.049	0.014	0.222	0.156	6.76	n.d.	0.085	0.190	1.32	0.016
(3)	n.d.	0.430	10.0	64.1	0.535	0.049	4.02	1.97	4.97	n.d.	0.168	8.30	0.026	0.052	0.012	0.209	0.151	6.43	0.057	0.097	0.131	0.82	0.018

Composition in oxides wt.% normalized; n.d.—not detected.

4. Conclusions

The present study showed that mining and metallurgical activities were performed by the local communities of the Outeiro de Baltar hillfort by the Late Iron Age/Early Roman period. These involved cassiterite mining and tin and bronze production. A tin slag was found and studied, making the Outeiro de Baltar hillfort the second Iron Age site with such evidence in NW Iberia and among the very few pre-medieval sites with tin slags in western Europe. The tin slag, in addition to Sn, also has Ta, Nb, W and Ti elements, which relates to elements that can be found in regional cassiterite ores, namely in cassiterite and the associated minerals from the alluvial sediments of the Ferradal stream. Additionally, it

was found that bronze alloys were being produced by adding cassiterite in a cementation or co-smelting process. The production of bronze by co-smelting or cementation instead of alloying tin and copper can be related to a faster, more direct or efficient operation, to the availability of local tin resources and to the long adoption of various metallurgical solutions since the Late Bronze Age, as recorded on other Iberian sites. Bronze was probably being produced to make finished products, such as artefacts, while metallic tin was being produced to make intermediary products, such as tin ingots. Both could have served local consumption, near and far-reaching trade, given that tin ingots would have easily integrated exchange networks with areas without tin resources. Based on the analyses of the metal nodules produced at the site, bronze with variable Sn (4–15%) and Pb (up to 15%) contents could have been produced. Analyses of five bar fragments, which could have been locally produced, showed that for these items, the tin and lead content would be around $11 \pm 2.5\%$ Sn and $< 2.5\%$ Pb, and thus considered to be of a good-quality bronze alloy. Additionally, analysis of various types of objects present on the hillfort, such as fibulae, bars and coins (the coins with an exogenous origin), showed that a large variety of metals and alloys were in circulation at the time: bronze, leaded bronze, brass, copper and silver metal.

In conclusion, the region of Baltar (and its surroundings) is very rich in cassiterite deposits and also in some gold. The 20th century tin and tungsten mining by the Somar company at the Outeiro de Baltar hillfort shows how areas with utilitarian minerals can be periodically worked over time, for various purposes and within different historical contexts. The native protohistoric societies certainly would have appreciated and benefited from their local tin resources, which would have provided them with valued materials that could integrate exchange networks within the Iberian Peninsula and elsewhere. The Roman conquest of this area, and of NW Iberia in general, certainly took into consideration the future control of ores and metals for market and profit purposes.

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