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Bronze production in Southwestern Iberian Peninsula: the Late Bronze Age metallurgical workshop from Entre Águas 5 (Portugal)

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ABSTRACT

Archaeological works at Entre Águas 5 (Portugal) uncovered a seasonal LBA settlement with significant metallurgical remains (crucibles, moulds, prills and a tuyere) related to bronze production. Radiocarbon dating ascribes an occupation period (10th–9th century BC) previous to Phoenician establishment in Southwestern Iberia. In spite of the proliferation of metal artefacts during LBA, the production of bronze alloys is still poorly understood. An integrated analytical approach (EDXRF, optical microscopy, SEM–EDS, micro-EDXRF and Vickers microhardness) was used to characterise this metallurgy. Crucibles show immature slags with copious copper nodules, displaying variable tin content (*c.* 0–26 wt.%), low iron amount (<0.05 wt.%) and different cooling rates. Certain evidences point to direct reduction of oxide copper ores with cassiterite. Scorched moulds with residues of copper and tin indicate local casting of artefacts. Finished artefacts also recovered at the site have an analogous composition (bronze with ~10 wt.% Sn and low amounts of Pb, As and Fe) typical of coeval metallurgy in SW Iberia. Some artefacts reveal a relationship between typology and composition or manufacture: a higher tin content for a golden coloured ring or absence of the final hammering for a bracelet. An uncommon gilded nail (gold foil *c.* 140 μm thick; 11.6 wt.% Ag; ~1 wt.% Cu) attests the existence of evolved prestige typologies. This LBA settlement discloses a domestic metallurgy whose main features are typical in Iberian Peninsula. Finally, it should be emphasized that a collection as comprehensive and representative of a single workshop has rarely been studied, enabling a deeper understanding of the various operations involving the bronze production and manufacture of artefacts.

1. Introduction

During 2008, excavations to extract expansive clay for the core of an earthen fill dam have exposed some archaeological materials suggesting the existence of a habitat in the middle of an open valley located at Serpa County (Southern Portugal). Archaeological excavations have revealed a protohistoric settlement nearby a small stream (Enxoé River), a left bank tributary of the Guadiana River (Fig. 1). The location of this settlement – Entre Águas 5 (EA5) – suggests a seasonal occupation since the area would be partially flooded during winter. Archaeological work has covered only the areas with archaeological materials already exposed by mechanical work for clay extraction (sectors 1, 2 and 3) and revealed several negative structures together with a significant collection of ceramic, lithic and metallic artefacts (Rebelo et al., 2009). These negative structures are of two types: pits, found in sector 2, are smaller, deeper, have a cylindrical shape (pits III, IV, V, VI, VII and IX) and probably would be used to store agricultural products; and hut floors (sector 1: hut II; sector 3: huts VIII and X), larger structures composed by two circular and contiguous areas (resembling an 8), where combustion structures were recorded.

The hut X has become particularly important due to the metallic artefacts and, especially, the remains of metallurgical activities recovered in it, namely crucibles, moulds, one tuyere, and tens of small metallic prills. This structure was partially affected by mechanical work for clay extraction, while the undisturbed stratigraphic layers contained a homogeneous set of archaeological materials, namely ceramics identical to those found in the

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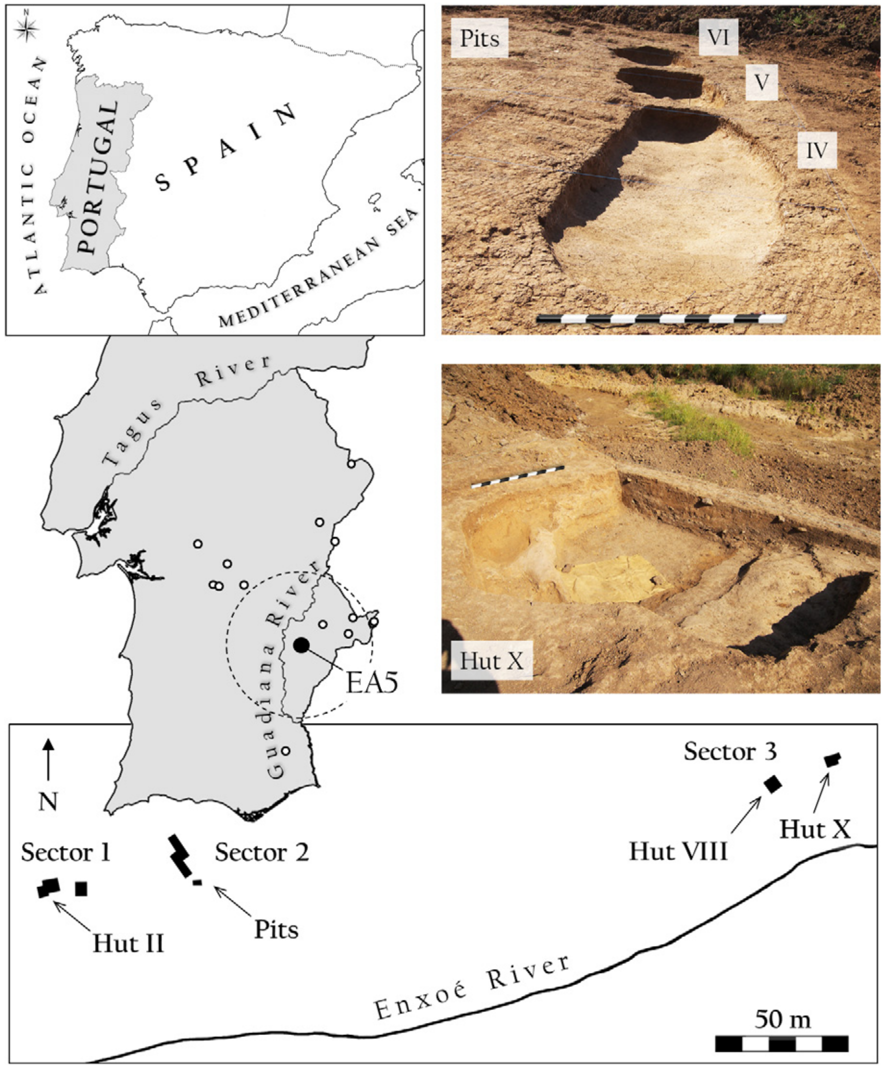

Fig. 1. Location of Entre Águas 5 (EA5) in Southern Portugal (circle equals 100 km), prehistoric copper mines given by Müller et al. (2007), photos of negative structures (pits and hut X; scale equals 1 m) and settlement plan with excavated sectors, huts and pits.

disturbed layers. All these artefacts belong to the same cultural period – the LBA of the SW Iberian Peninsula. The architecture of the hut floors is also typical of LBA housing structures from this region. Additionally, the typological features of the material culture recovered in the remaining negative structures are characteristic of this chronological period (Rebelo et al., 2009).

The research concerning the metallurgical production remains from hut X has become a unique opportunity to understand the LBA bronze production in this southwestern region of the Iberian Peninsula. The study also involves a discussion concerning the elemental and microstructural features of copper-based artefacts recovered from the settlement, including an exceptional example of the gilding technology, which is very uncommon in Western Europe before contacts with the Eastern Mediterranean region.

2. Radiocarbon chronology

Radiocarbon dates were obtained from charred wood and bone samples belonging to different contexts from EA5 (Table 1). Results indicate that huts (II, VIII and X) and dated pits (V and VI) share a coeval occupation that was already indicated by the recovered material culture. The date Sac-2404 (hut II/layer 203A) must be an outlier, perhaps due the "old wood effect", since a second date (Beta-313500) obtained with a short lived shrub sample, collected in the same layer, has a value statistically not different from the remaining dataset. Moreover, a small piece of charred wood of *Erica* entrapped among the slag from one of the crucibles gave a similar date (Beta-261318). Consequently, production remains from hut X can be ascribed to a single metallurgical workshop coeval with remaining huts and belonging to a moment comprised between the 10th and 9th centuries BC (Fig. 2). A metallurgical workshop with a reliable and precise chronology like the obtained here is unique among the LBA archaeological record from the SW Iberian Peninsula.

3. Production remains and metallic artefacts from EA5

All traces of metallurgical production recovered at EA5 come from the metallurgical workshop at hut X. Crucibles 1391A and 1374A have a socketed handle into which a clay covered rod or stick could be inserted to facilitate handling during operation (Fig. 3). The crucible 316 has a similar shape but the part that could contain the socket is missing. Socketed handle crucibles are commonly found among the archaeological record of the Eastern Mediterranean but are rather unusual in Iberian Peninsula (Urbina et al., 2007). The closest example from this region can be found in the

Table 1
Radiocarbon dates obtained from wood and bone samples from EA5 (* – crucible 1374; ** – *Calluna vulgaris*; *** – *Erica sp.*; Calendar ages using IntCal09, Reimer et al., 2009 and OxCal 4.1.7, Bronk Ramsey, 2009).

Lab. Ref.	Structure/layer	Sample type	$\delta^{13}C$ (‰)	^{14}C age (BP)	Calendar age (cal BC)	
					1σ	2σ
Sac-2404	Hut floor II/203A	Charred wood	−25.4	2900 ± 60	1210–1010	1290–920
Beta-313500	Hut floor II/203B	Charred wood**	−25.3	2780 ± 30	990–900	1010–840
Sac-2411	Pit V/502	Charred wood	−25.1	2660 ± 90	970–670	1040–540
Sac-2410	Pit VI/601	Charred wood	−25.7	2610 ± 70	890–590	920–520
Sac-2405	Hut floor VIII/809–1	Charred wood	−20.4	2740 ± 70	970–820	1110–790
Sac-2403	Hut floor X/1012	Bones	−21.6	2770 ± 50	980–840	1040–810
Sac-2409	Hut floor X/1012	Charred wood	−21.2	2650 ± 80	920–680	1010–540
Beta-261318	Hut floor X/1374*	Charred wood***	−23.2	2740 ± 40	920–830	980–810

socketed crucible from the LBA settlement of Martes, Southern Portugal (Calado and Mataloto, 2001) or in the socketed crucible of Cerro de San Cristobal (Diaz et al., 2001). The crucibles 1391A and 1374A from EA5, plus two other fragments, 1374A1 and 1374A2, have heavily slagged surfaces and evident metallic remains. Furthermore, these crucibles exhibit thick walls (up to 2 cm) suggesting that the heating would be done from above, as it seems to be common in pre and protohistoric metallurgical operations in the Iberian Peninsula (Waerenborgh, 1994; Rovira, 2004). The use of organic temper was encountered in some of the crucibles (1374A and 1391A) being an additional indication that the heating was done from above. The voids left from the burning of pieces of straw or chaff increase thermal insulation and help in producing the reducing conditions inside the crucible (Bayley and Rehren, 2007).

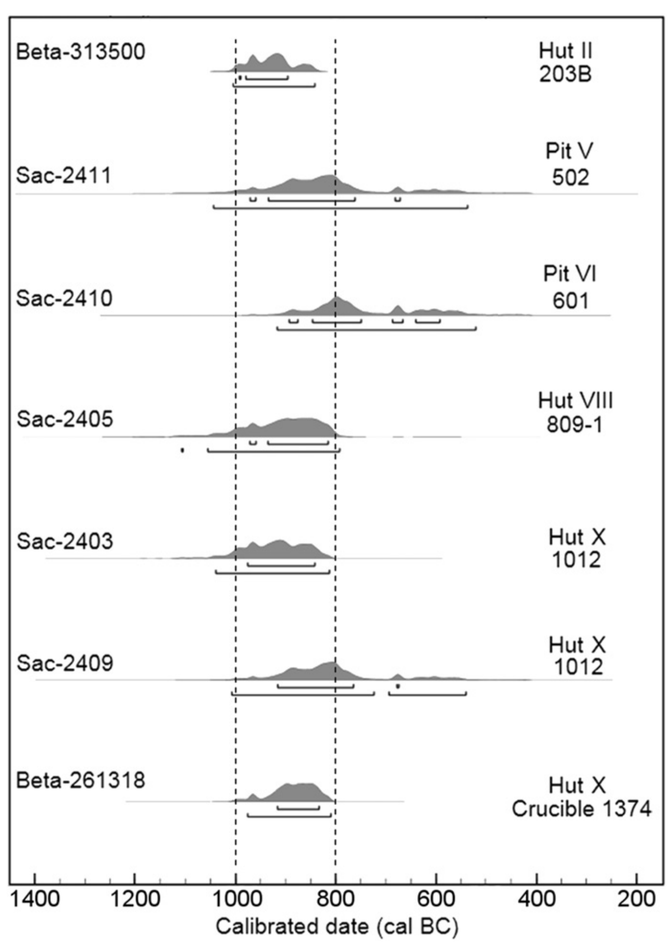

Fig. 2. Radiocarbon calibrated dataset generated by OxCal program (dashed lines are suggested limits for the metallurgical workshop at EA5).

Another interesting example from EA5 is a somewhat deeper crucible (1374) with a definite lip that would facilitate the pouring of molten metal into the mould (Fig. 3). This crucible exhibits a thinner layer of slag, as well as two other crucible fragments (1373 and 165). The study of slags in ceramic crucibles from the EBA/MBA metallurgical site of Peñalosa (Central Spain) suggests that shallow open examples were smelting crucibles, while deeper pots were used as melting crucibles. Furthermore, this type of lip is more common in the melting crucibles although being present in a few of the smelting vases (Onorato et al., 2010).

Many metallic prills with variable sizes and irregular or rounded shapes were also present in the metallurgical context from EA5. A set of 20 metallic prills with sizes ranging from 0.5 cm to 2 cm were selected for study. To avoid confusion, the smaller metallic inclusions entrapped among crucible slags will be designated as metallic nodules. The archaeological record from the Iberian Peninsula indicates that Chalcolithic and Bronze Age smelting operations did not produce true tapping slags (see, for example, Müller et al., 2004). Commonly, the slag must be crushed to remove the metal prills. This differs from Bronze Age metallurgy in other regions such as at the EBA site of Arisman (Iran) showing evidences that the slag and metal would be tapped together and worked in a semi-liquid state to improve separation (Rehren et al., 2012).

The cylinder-shaped tuyere from EA5 has a vitrified nozzle with traces of slag and metallic remains (Fig. 3). The study of the significant collection of tuyeres from the 8th–7th century BC Phoenician settlement of La Fonteta (SE Spain) did not identify a clear functional distinction between round and square types, although the last ones prevail among the iron metallurgy contexts (Renzi et al., 2009). A similar circumstance can be found among the coeval metallurgy of the Eastern Mediterranean, where it is unknown whether the square cross-section replaced round tuyeres in the bronze and iron production or if it was used only in the iron metallurgy (Eliyahu-Behar et al., 2012).

Metallurgical remains from EA5 also comprise 13 small clay fragments with thin walls (<1 cm), curved shapes and, in most cases, scorched surfaces (Fig. 3). These fragments were interpreted as moulds with inner surfaces scorched from contact with molten metal. Macroscopically, there are no other evidences of having been used, such as slag or metallic remains. The highly fragmented state of these moulds lead us to believe that they could have been used in lost-wax casting in spite of their thin walls (usually, the lost-wax casting uses a thick clay coverage). This technique was well known in the gold metallurgy of the Iberian Peninsula since the MBA, but rarely applied to bronze artefacts during the LBA (Armbruster, 2002).

Archaeological works at EA5 also uncovered several copper-based artefacts (Fig. 3), namely 1 awl, 2 beads, 1 bracelet, 2 fibula pins, 1 needle, 2 rings and 2 fragments of unknown type. All these objects come from the same archaeological context of the

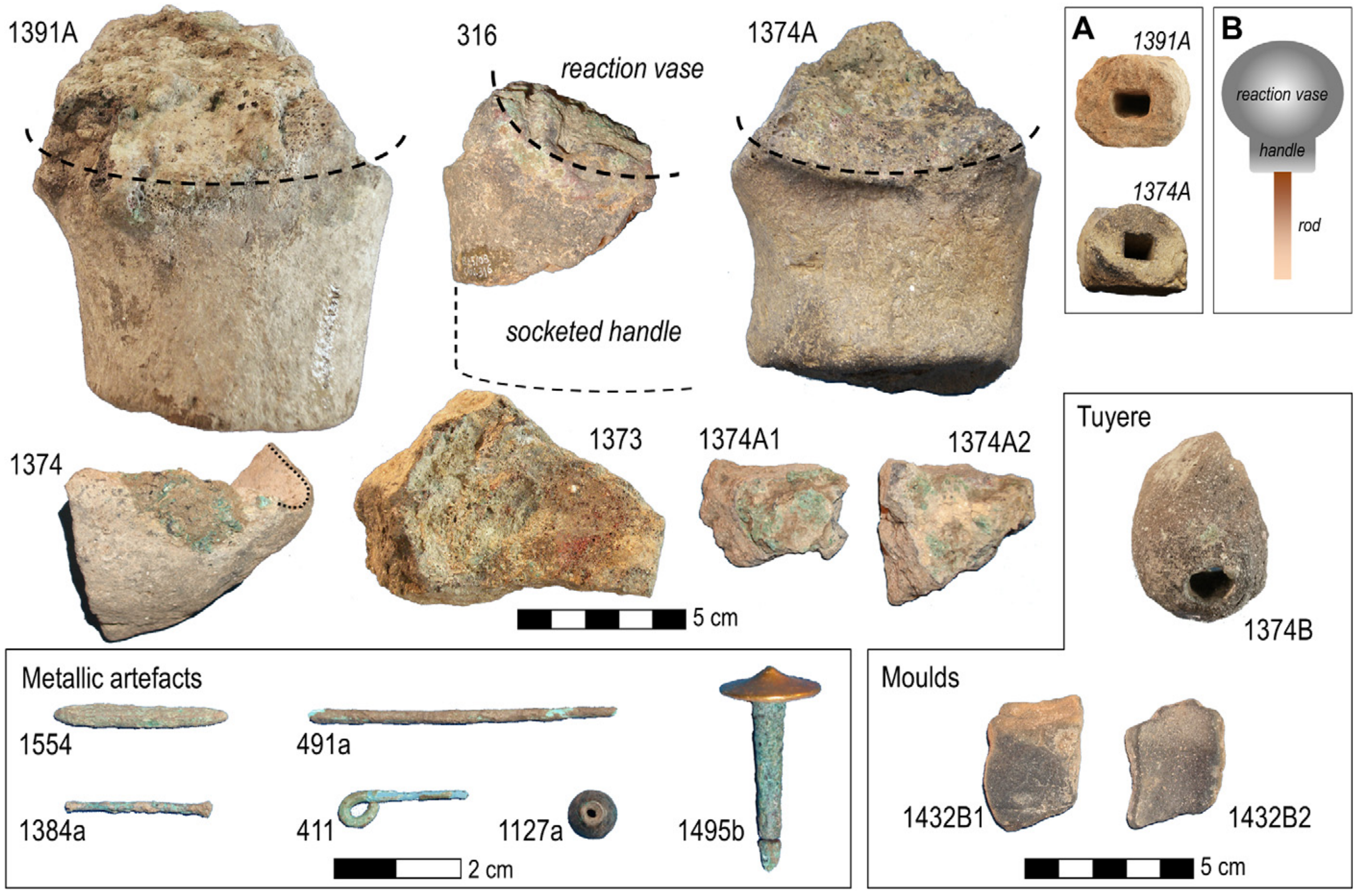

Fig. 3. Production remains and metallic artefacts recovered from the LBA settlement of EA5 (A: sockets from crucibles 1391A and 1374A; B: diagram of socketed crucible with rod).

metallurgical production remains (hut X), with the exception of the fibula pin 411 and the needle 491a, which belong to the hut II.

A prestige artefact was also recovered among those common tools and ornaments – a copper-based nail with the head covered by a gold foil (Fig. 3). Pre and protohistoric gilding is uncommon in the European region. Recently a copper nail with a gilded head was identified among the collection from the LBA settlement of Castro de São Romão, Central Portugal (Figueiredo et al., 2010a). This exceptional artefact underlines the importance of the metallic collection from EA5 and, together with the metallurgical production remains, establishes EA5 as a unique LBA site in SW Iberian Peninsula.

4. Materials and methods

Technical ceramics were analysed with a Kevex 771 EDXRF spectrometer equipped with a Rh X-ray tube, secondary excitation targets and a Si(Li) detector (FWHM 165 eV at 5.9 keV). Two excitation conditions (Ag and Gd secondary targets) were used to optimize the detection of the elements of interest. Other details about the equipment and analytical conditions were previously published (Araújo et al., 1993). Preparation for further analyses included cutting of a section and polishing with silicon carbide papers (400–4000 grit size). Microstructural characterisation was made with a Zeiss DSM 962 conventional tungsten filament scanning electron microscope with secondary electron (SE) and backscattered electron (BSE) imaging modes. Elemental semi-quantifications were made with the ZAF method using an Oxford Instruments INCAx-sight EDS spectrometer equipped with an ultra-thin window to detect elements with low atomic number ($Z < 5$). Experimental conditions consisted of 25 mm working distance, 20 kV accelerating voltage, approximately 3 A filament current and 70 μA emission current. Additionally, slagged samples were observed with a Leica DMI 5000 M optical microscope (50× to 1000×) under bright field illumination, dark field illumination and polarised light.

Prior to analysis, metallic artefacts were polished in a small area (∅ ~3–5 mm) using a manual drill with diamond pastes (15 μm–1 μm). It was assured that the polishing depth was enough to obtain a clean metal surface for analysis. Alternatively, a small section of incomplete artefacts was cut with a precision saw and mounted in epoxide resin, polished with silicon carbide papers (1000–4000 grit size) and finished with diamond pastes (1 and 1/4 μm). The elemental composition was determined with an ArtTAX Pro micro-EDXRF spectrometer equipped with Mo X-ray tube and silicon drift detector (FWHM 160 eV at 5.9 keV). Focussing polycapillary optics and accurate positioning system allow a minute area of primary radiation at the sample (∅ < 100 μm, Bronk et al., 2001). Each artefact was analysed in three independent spots with 40 kV of tube voltage, 0.5 mA of current intensity and 300 s of real time. Experimental calibration factors were calculated with Phosphor Bronze 551 and Leaded Bronze C50.01 standard reference materials. The accuracy is better than 2% for Cu and Sn, and better than 10% for Fe, As and Pb. Quantification limits are 0.5 wt.% Sn, 0.05 wt.% Fe and 0.10 wt.% for As and Pb. Additional experimental details were previously published (Valério et al., 2007). The microstructural characterisation comprised observation of unetched and etched samples (aqueous ferric chloride). The Vickers microhardness was measured using a Zwick-Roell Indentec apparatus by applying 0.20 kgf load during 10 s. The hardness value considered is the average of at least 3 indentation measures, having a relative standard deviation less than 5%.

5. Results and discussion

5.1. Bulk analyses

Elements enriched by metallurgical operations were identified by comparison of EDXRF analyses of inner/slagged and outer/clay surfaces of technical ceramics. The results have showed that slagged surfaces of crucibles are enriched in copper and tin, except in the crucible with a pouring lip that is only clearly enriched in copper (Fig. 4A and B). The presence of certain elements in these slagged surfaces result from various components always present in metallurgical operations – Ca, Mn and Fe from ceramics, gangue or wood ash (Etiégni and Campbell, 1991). Other elements usually present in copper-based alloys are more suggestive of metallurgical operations despite presenting different tendencies to become associated with the clay material. For example, the significant volatility and high free energy of oxidation of Zn, in addition to a high reactivity with clay silicates, results in a high Zn enrichment in the crucible even when it was only present at trace levels (Kearns et al., 2010). Thus, results established that most crucibles were used directly in the production of bronze, while the crucible with a pouring lip may have been used for the melting of copper nodules or copper scrap. Indeed, the lip on this crucible suggests a well liquefied charge, discordant with the high viscosity slag produced by these primitive smelting operations.

In the case of metallic prills, EDXRF analyses have established that the collection is entirely composed of bronzes. Similarly, the tuyere nozzle presents high amounts of copper and tin (Fig. 4C), while only some of the mould fragments were slightly enriched in these elements (Fig. 4D). Moulds often exhibit less evidence of have being used than crucibles because casting originates fewer residues than smelting or melting. Nevertheless, results obtained ascertain that moulds were used for casting of bronze alloys.

These analytical results readily establish distinct metallurgical operations in LBA workshop from EA5. The majority of production remains resulted from the production of bronze, while the crucible with a pouring lip was probably used in copper melting. Furthermore, the metallurgical operation involved the use of forced air through tuyeres, while bronze casting was also being performed in this workshop.

5.2. Smelting crucibles

The slag in socketed handle crucible 1374A is composed of a highly heterogeneous material with numerous metallic inclusions. Reactions between the metal and oxide melts with the crucible fabric and charcoal ash originated a vitreous matrix of aluminosilicates with Na, Mg, K, Ca, Mn and Fe (Fig. 5). The abundant presence of magnetite shows an iron-rich slag under local oxidising conditions. The poor reducing atmosphere attained inside the reaction vase is also evidenced by the numerous globules of cuprite and malachite, most likely formed by re-oxidising metallic copper during the operation (Hauptmann, 2007). Although, these copper compounds can also result from oxidation during long-term burial. The small globular Cu–S formations evidence the existence of matte (molten metal sulphide). Since smelting of oxide copper ores containing sulphide impurities resulted in slags with matte (Hanning et al., 2010), their presence in EA5 slag can also be understood as a natural occurrence in the copper ores. Other areas

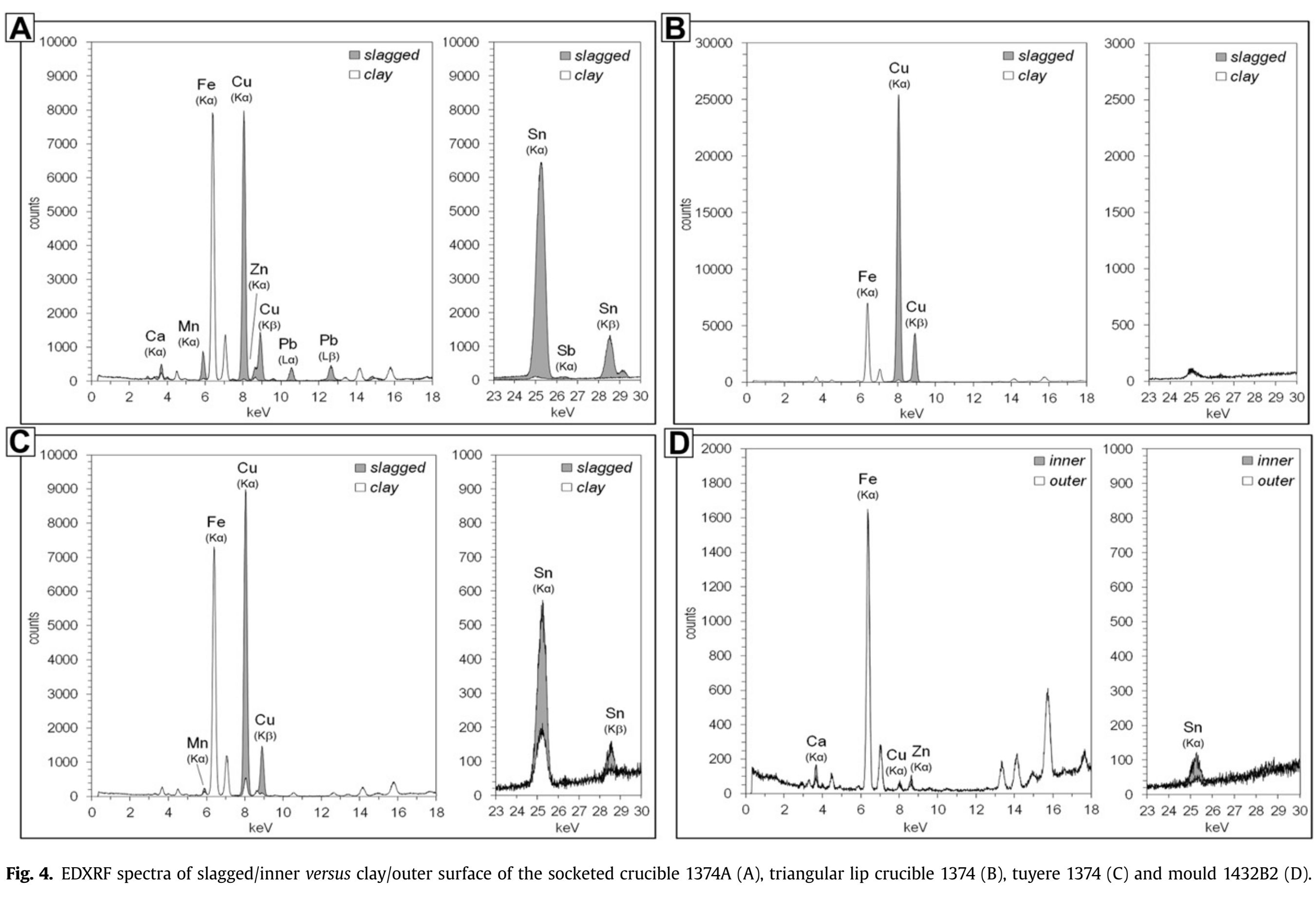

Fig. 4. EDXRF spectra of slagged/inner *versus* clay/outer surface of the socketed crucible 1374A (A), triangular lip crucible 1374 (B), tuyere 1374 (C) and mould 1432B2 (D).

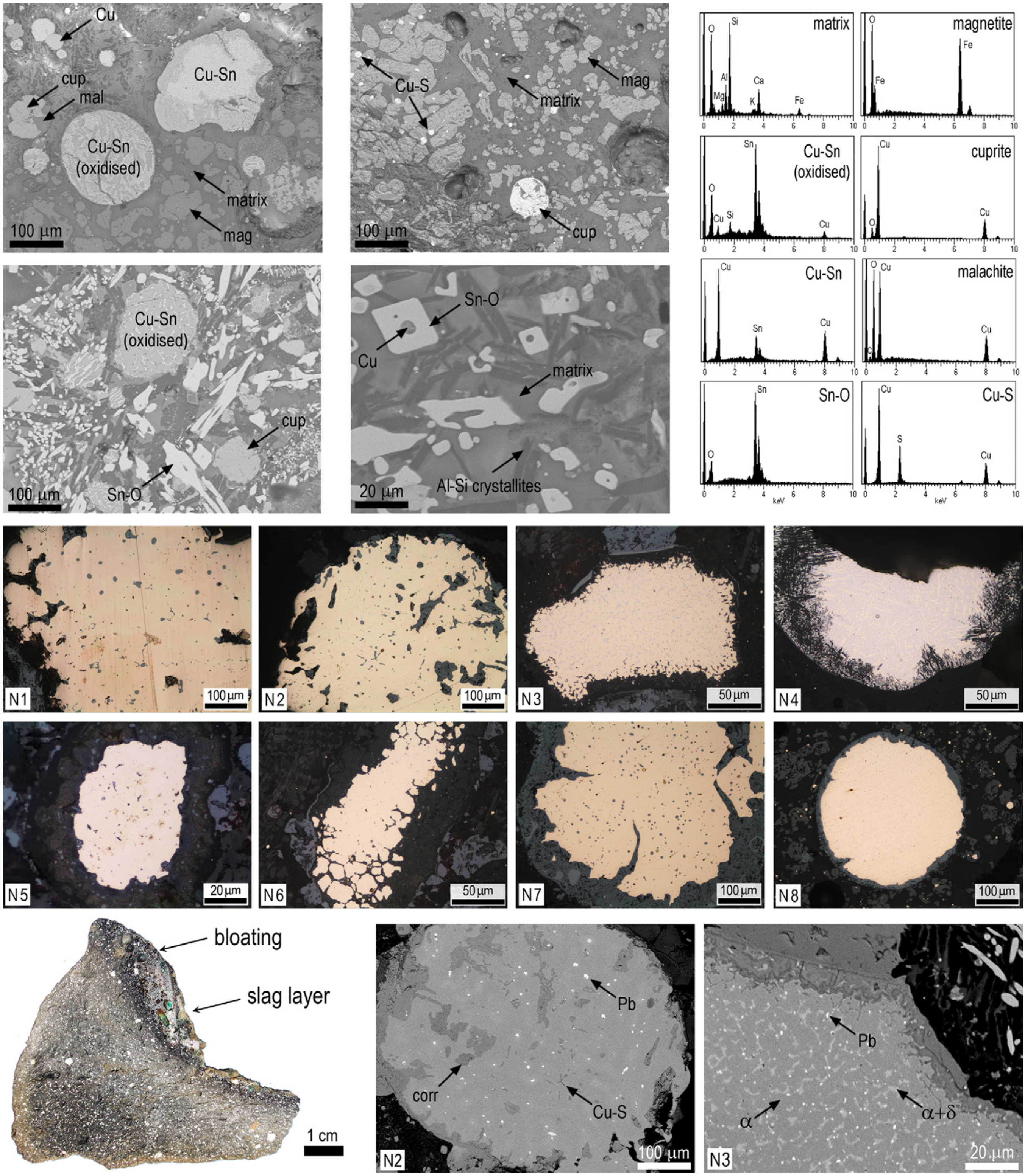

Fig. 5. SEM-BSE and OM-BF images of slag and metallic nodules in crucible 1374A (cross-section evidencing the slag layer and bloating of crucible ceramics).

of this slag present numerous tin oxide inclusions as globular or euhedral needles. The latter are a secondary product resulting from tin oxidation in molten phase. A copper nucleus inside some of them suggests that both metals were present in an oxidising environment, i.e. tin was oxidised leaving a metallic copper core (Dungworth, 2000). The considerable abundance of tin oxide inclusions, in addition to the absence of metallic tin, can be understood as an evidence of the use of cassiterite (Rovira, 2004). Results of microstructural analyses of slag in crucible 1374A are summarized in Table 2.

Table 2
SEM-EDS and optical microscopy results of crucible slags from the metallurgical workshop at EA5 (× – present; ××× – high amount; n.d. – not detected).

Crucible	Copper nodules	Bronze nodules	Cuprite	Malachite	Copper sulphide	Tin oxide	Magnetite	Other
1374A	×	×××	×	×	×	×××	×××	–
1391A	×	n.d.	×	×	n.d.	×××	×××	Cu–O–S relics
316	×	n.d.	×	×	n.d.	×××	×××	–
1374A2	×	n.d.	×	×	n.d.	×××	×××	–
1373	n.d.	×	×	×	n.d.	n.d.	n.d.	–
1374	n.d.	n.d.	×	×××	×××	n.d.	n.d.	Charcoal

Metallic nodules with different sizes (from few microns up to 1 mm) are quite abundant in slag from the crucible 1374A. A high loss of metal due to high viscosity of immature slags is a common characteristic of primitive smelting operations. Generally, metallic nodules show coarse granular microstructures (Fig. 5) that evidence the slow cooling rate of slag inside the crucible. Occasionally, the coarse microstructure enables recognition of coring due to a slightly faster cooling, e.g. nodule N1. SEM–EDS analyses identified Cu–S and Pb-rich inclusions in most metallic nodules as well as the $\alpha + \delta$ eutectoid in tin richer ones. In fact, the highly variable composition of these nodules is their more noteworthy characteristic (Table 3). This feature indicates the reasonably heterogeneous conditions (T and pO_2) inside the reaction vase, while low iron contents (<0.05 wt.%) evidence a poor reducing environment. All these characteristics exclude the possibility of bronze recycling, contrary suggesting the production of bronze with independent sources of copper and tin. For example, recent experiments involving the co-smelting of copper ores and cassiterite originated a slag with numerous metallic prills of copper and bronze (up to ~80 wt.% Sn) (Rovira et al., 2009).

The slag in the second socketed handle crucible (1391A) displays a comparable vitreous matrix with abundant copper nodules, copper oxide and tin oxide precipitates (Fig. 6). The numerous magnetite inclusions point to weak reducing conditions. Certainly, the most valuable information was given by relic mineral inclusions composed of copper sulphides and malachite. The morphology of these relics is very different from the more abundant globules of oxidised copper, eventually formed during the metallurgical operation or by long-term corrosion. Local unsuitable conditions (T↓ and pO_2↑) during operation seem to have prevented decomposition of these relics. Above all, their presence establishes the smelting of oxide copper ores rather than the use of metallic copper to produce bronze.

Samples from "socketed handle" crucible 316 and fragment 1374A2 show analogous features (Table 2), namely highly heterogeneous slags composed of an aluminosilicate matrix with euhedral tin oxide needles, magnetite precipitates, copper and bronze prills (Fig. 6). The similarity of these slags suggests that crucibles were used in analogous metallurgical operations, namely the smelting of copper ores with cassiterite to produce bronze.

Table 3
Composition of metallic nodules in crucible 1374A from the metallurgical workshop at EA5 (values in wt.%; n.d. – not detected).

Metallic nodule	SEM-EDS		Micro-EDXRF			
	Cu	Sn	Sn	Pb	As	Fe
N1	94.4	3.1	2.4	n.d.	<0.10	<0.05
N2	93.4	–	5.8	0.67	n.d.	<0.05
N4	75.4	24.6	–	–	–	–
N7	95.7	3.8	3.5	0.59	0.15	<0.05
N9	88.9	12.0	9.9	1.0	n.d.	0.05
N10	74.2	25.8	–	–	–	–

In the Iberian Peninsula, the archaeological record indicates that copper ores were reduced in open ceramic vessels, usually designated as smelting crucibles, until the Iron Age (Rovira, 2002). For instance, smelting crucibles with remains of copper or bronze slags were found in several SE Iberian sites, like Los Millares (Chalcolithic), Ronda (MBA) and Peña Negra (LBA) (Ramos, 1999). On the contrary, in Central European and Eastern Mediterranean regions the smelting of copper ores was often made in conventional and larger furnaces, such as the cylindrical clay furnaces from the LBA site of Politiko-Phorades, Cyprus (Hein et al., 2007) or the LBA copper smelting furnaces excavated near Mühlbach, Alpine Region, Austria (Herdits, 2003). However, it must be emphasized that crucible smelting was still utilised in the Eastern Mediterranean, as testified by the bronze slag inside a crucible from the 10th–9th century BC site of Tell es-Safi/Gath, Southern Levant (Eliyahu-Behar et al., 2012).

The adoption of efficient smelting furnaces must have resulted from the need to produce a higher amount of metal and/or to smelt complex ores, like the fahlore deposits of the Alpine regions in Central Europe (Orel and Drglin, 2005; Postma et al., 2011). These motivations seem to have been absent in the Iberian metallurgy until the Orientalizing period, since smelting crucibles were perfectly adapted to the processing of existing high-grade oxide copper ores (malachite and cuprite). Moreover, it seems that metallurgical activities were usually conducted on a domestic scale (Senna-Martinez and Pedro, 2000).

Similarly to EA5, other studies of LBA slags from the Iberian Peninsula suggest that the co-smelting of copper and tin ores was the preferred method to produce bronze (Rovira, 2007). Recent experimental tests confirmed that copper ore and cassiterite can be efficiently reduced with a simple crucible, using a couple of tuyeres and charcoal as fuel (Rovira et al., 2009). The metal prills produced in this way were melted in a flat-bottom crucible to obtain a bronze ingot. An alternative process involves the cementation of metallic copper with cassiterite, as suggested by the slag found in a LBA socketed handle crucible from Cerro de San Cristobal, also located in the Guadiana basin, in the southern Spanish Extremadura (Diaz et al., 2001). Bronze can also be obtained by melting metallic copper and tin, but the earliest evidence of this method comes from a slag belonging to an Orientalizing context of Carmona, SW Iberian Peninsula (Rovira, 2007). In the Portuguese territory the only available study in this matter comprises a slag from the habitat site of Baiões (Central Portugal) suggesting the use of a smelting crucible to reduce copper ores with cassiterite or metallic tin (Figueiredo et al., 2010b).

Recent studies indicate that the lead isotopic signature of copper artefacts, prills and slags from Chalcolithic settlements in the Portuguese Estremadura, such as Vila Nova de São Pedro (Müller and Soares, 2008), Leceia (Müller and Cardoso, 2008) and Zambujal (Müller et al., 2007) is consistent with that of copper ores from the Ossa Morena Zone (OMZ). In a preliminary survey Müller et al. (2007) have identified several copper mining sites in Southern Portugal. Some of them display evidences of having being worked during the Chalcolithic and/or Bronze Age (i.e. stone hammers and

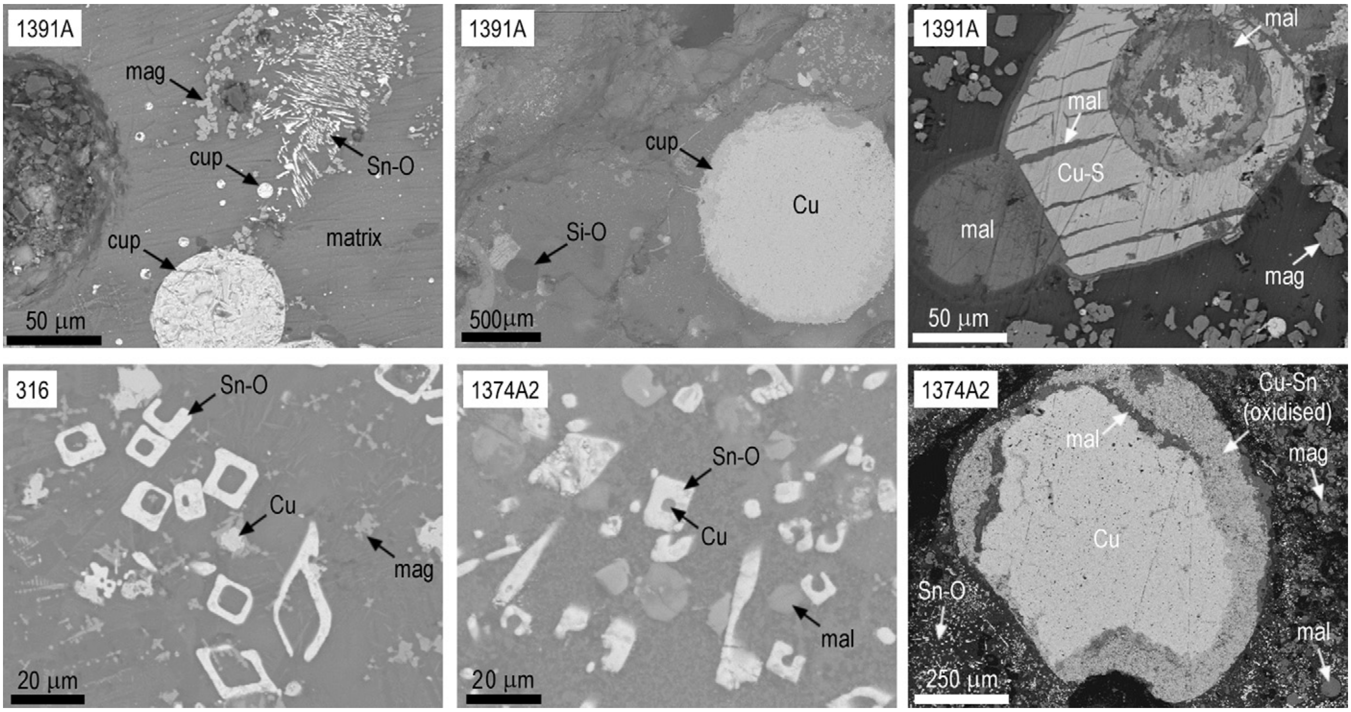

Fig. 6. SEM-BSE images of the slag in crucibles 1391A, 316 and 1374A2.

anvils) and are located not very far from EA5 (see Fig. 1). On the contrary, the nearest LBA sources of tin in the Portuguese territory are mostly located in the Central Portuguese region, probably alluvial deposits in local rivers (Figueiredo et al., 2010b). Tin could also be obtained from the more inland region of Caceres (Spain), as the LBA settlement of Cerro de Logrosan presents evidences from the exploitation of this resource (Rovira, 2002).

5.3. Melting crucibles

Slag in crucible 1373 comprises a thinner layer of a complex vitreous matrix (aluminosilicate with Na, Mg, K, Ca, Mn and Fe) with a few globular nodules of bronze presenting similar compositions (Fig. 7). This slag evidences a reduced interaction between metal/oxides and crucible ceramics, while copper and tin oxide precipitates, common in former slags, are absent (Table 2). These features seem to indicate that crucible 1373 was used in bronze melting rather than smelting.

The slag in the crucible with a pouring lip (1374) displays a different feature since it is composed of an oxide copper matrix with copper sulphide inclusions (Table 2 and Fig. 7). A charred wood inclusion entrapped among this slag was morphologically identified as *Erica* sp. (heather). This species is very common in southern Portuguese territory and has one of the highest calorific powers among the woods known to be used as fuel in ancient times (Martínez and Sala, 2010). Furthermore, charcoal inclusions are more commonly found amongst completely liquefied slags (Hauptmann, 2007). Considering these characteristics together with the typology of the crucible – somewhat deeper and with a pouring lip – it seems that it may have been used to melt copper. However, the high amount of matte suggests a primary copper source rich in sulphur rather than remelting of scrap copper.

5.4. Metallic prills

Some of metallic prills were analysed by micro-EDXRF to establish their compositions (Table 4). The bronze prills show a variable tin content (6.0–16.5 wt.%), comparable to the obtained in smaller bronze nodules entrapped in crucible slags. Moreover, the impurity pattern is very similar (Pb > As > Fe), which together with the very low amount of iron (<0.05 wt.%) points to the poorly reducing environment attained during smelting. Some

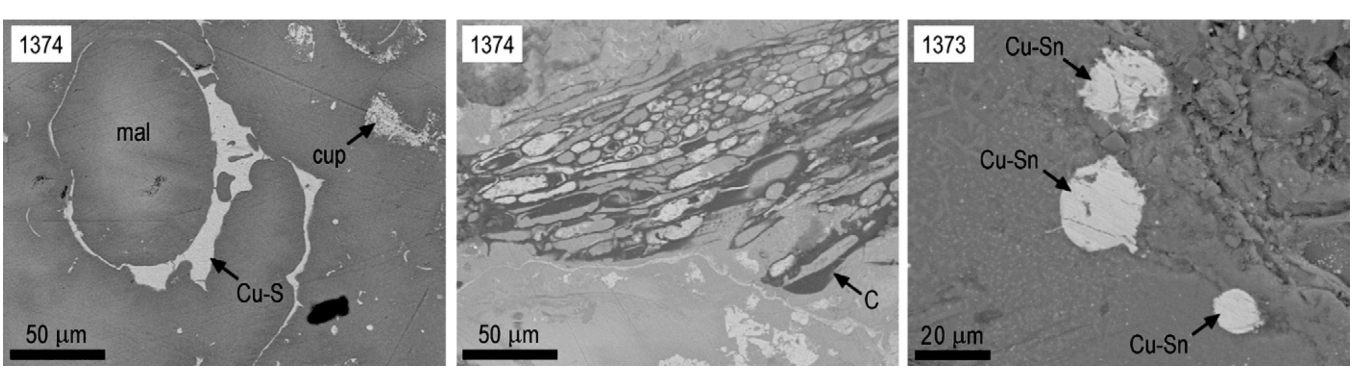

Fig. 7. SEM-BSE images of the slag in crucibles 1374 and 1373.

Table 4
Composition of metallic prills from the metallurgical workshop at EA5 (values in wt.%; n.d. – not detected; * – twin prills).

Prill	Reference	Shape and size	Cu	Sn	Pb	As	Fe
P1	1386a	Irregular (1.8 cm)	93.8	6.0	0.12	<0.10	<0.05
P2a*	1386f	Rounded (0.5 cm)	85.9	13.3	0.46	0.29	<0.05
P2b*	1386f	Rounded (0.5 cm)	84.1	14.9	0.68	0.27	<0.05
P3	1389a	Rounded (0.6 cm)	93.4	6.2	0.24	0.10	<0.05
P4	1390	Irregular (1.2 cm)	86.9	12.6	0.33	0.13	<0.05
P5	1426a	Irregular (0.9 cm)	83.2	16.5	0.30	n.d.	<0.05
P6	1699a	Rounded (0.7 cm)	83.2	15.6	0.82	0.38	<0.05

of the prills show coarse microstructures (P2a, P2b, P3 and P6, Fig. 8) that are compatible with the slow cooling rates inside a crucible. These prills tend to be rounded (see Table 4) due to liquid immiscibility, thus suggesting its formation inside a partially liquefied slag. Others have irregular shapes and cored dendritic structures (P1, P4 and P5, Fig. 8 and Table 4) showing relatively faster cooling rates.

5.5. Bronze artefacts

The results of micro-EDXRF analyses show that the collection of copper-based artefacts has a variable content of tin (1.6–15.5 wt.%) plus minor amounts of lead, arsenic and iron (Table 5). These copper-based artefacts can be considered rather pure since the sum of metallic impurities is below 1 wt.%. The iron content is very low and comparable to the metallic prills. Low amounts of iron are very common in Iberian bronzes before Orientalizing influences (Craddock and Meeks, 1987). LBA geographically closer examples can be found in habitat sites and hoards from Central Portugal, namely Baiões, Viseu (Figueiredo et al., 2010b), Canedotes, Viseu (Valério et al., 2007) and Freixianda, Ourém (Neira et al., 2011). In Southern Portugal, the 9th–8th century BC (Soares and Martins, 2010) fortified settlement of Castro dos Ratinhos (Moura) presents a bronze collection with low iron contents, suggesting that the smelting technology remained unchanged despite some Orientalizing influences, such as rectangular habitat structures, wheel-turned pottery, red slip ware, amphorae, iron and ivory artefacts (Valério et al., 2010).

The nearly exclusive usage of binary bronzes with suitable tin contents is another feature of this LBA metallurgical tradition. Actually, most artefacts from EA5 are composed of binary bronze alloys with an average tin content of 9.7 ± 3.2 wt.%, whereas only the bead 1127a has a tin content below 2 wt.%. The similarity with bronze alloys from Castro dos Ratinhos (10.1 ± 2.5 wt.% Sn) is remarkable evidencing that this LBA metallurgy lasted until later in this inland region of the Portuguese territory. However, a new metallurgical tradition was already present in this west end of the Iberian Peninsula, as established by the copper, leaded bronze and low-tin bronze (5.4 ± 2.0 wt.% Sn) artefacts from the 9th–7th century BC Phoenician seaboard settlement of Quinta do Almaraz (Valério et al., 2012).

Similarly to the Portuguese territory, LBA copper-based artefacts from the remaining regions of Iberia are commonly manufactured with binary bronze alloys. The exception can be found in the NW region, where leaded bronzes are common following the Atlantic tradition of the British Isles and of the Western France. Metallic artefacts from the SW Iberian region are well depicted by the hoard from Ria de Huelva (Huelva). Despite the controversy about its origin (ritual deposit, ship wreck or other), it is noteworthy to realize that this 11th–9th century BC collection of about 400 artefacts comprises bronze alloys with homogeneous content of tin (~8–14 wt.%) and low amount of impurities (Rovira, 1995).

The relatively standardized composition of LBA bronzes shows the expertise of ancient metallurgists even using primitive smelting crucibles. Furthermore, it provides some hints about the copper ores used, probably high-grade carbonate ores, as complex sources will certainly originate more variable compositions and higher amounts of impurities. A good example of this relation comes from the copper-based artefacts with 6–16 wt.% of Sb, As, Ag and Ni due to the smelting of complex Alpine fahlore deposits (Postma et al., 2011).

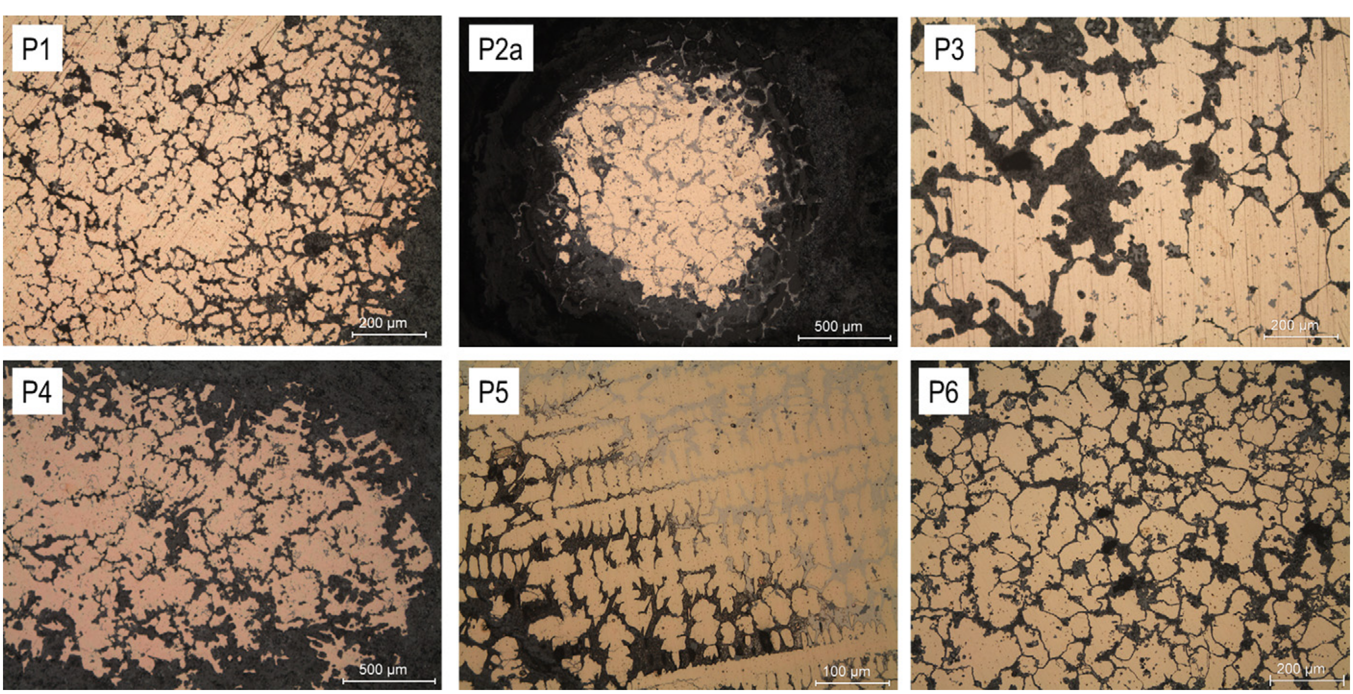

Fig. 8. OM-BF images of metallic prills recovered from the metallurgical workshop at EA5.

Table 5
Results of micro-EDXRF, optical microscopy, SEM-EDS and Vickers microhardness testing of copper-based artefacts from EA5 (composition in wt.%; n.d. – not detected; C: Casting; A: Annealing; F: Forging; FF: Final Forging; ↑: high amount; ↓: low amount; hardness in HV).

Artefact	Reference	Cu	Sn	Pb	As	Fe	Phases	Inclusions	Manufacture	Hardness
Awl	1554	88.3	11.6	n.d.	n.d.	<0.05	α	Cu–S↑	C + (F + A) + FF	–
Bead	1037	88.8	11.1	n.d.	<0.10	<0.05	α	Cu–S↑	C + (F + A) + FF	148 ± 8
Bead	1127a	97.6	1.6	0.49	0.33	<0.05	α	Cu–S↑	C + (F + A) + FF↓	–
Bracelet	314a	94.6	5.0	0.27	<0.10	<0.05	α	Cu–S↑	C + (F + A)	79 ± 1
Fibula (pin)	1384a	91.5	8.3	0.10	<0.10	<0.05	α	Cu–S	C + (F + A) + FF	146 ± 7
Fibula (pin)	411	89.6	10.3	n.d.	n.d.	<0.05	α	Cu–S↑	C + (F + A) + FF	166 ± 8
Fragment	314	90.1	9.5	0.20	<0.10	<0.05	α	Cu–S↑	C + (F + A) + FF	–
Fragment	1250	92.2	7.7	n.d.	<0.10	<0.05	α	Cu–S↑	C + (F + A) + FF	139 ± 4
Needle	491a	93.1	5.9	0.69	0.20	<0.05	α	Cu–S↑	C + (F + A) + FF↑	154 ± 3
Ring	1388	84.3	15.5	0.20	<0.10	<0.05	α, δ↑	Cu–S↑	C + (F + A) + FF↓	163 ± 6
Ring	1425	87.1	12.7	0.12	<0.10	<0.05	α	Cu–S↑	C + (F + A) + FF	126 ± 5

The microstructural characterisation of metallic artefacts from EA5 evidenced that the ring 1388 has a significant amount of $\alpha + \delta$ eutectoid (Fig. 9). This agrees with the high tin content of the ring (above the solubility limit in the α phase, i.e. ~14 wt.% Sn, Hanson and Pell-Walpole, 1951). The significant presence of the harder δ phase originates an alloy with a lower ductility, but this typology probably does not require a high toughness or a significant metalworking. These circumstances suggest that those ancient metallurgists were conscious that bronzes richer in tin were more difficult to work. Consequently, alloys with higher tin amounts could be retained for specific typologies. A recent study described the colour of copper alloys using the CIELAB colour space, establishing that the addition of up to 15 wt.% Sn reduces the redness of the alloy thus approaching of a golden hue (Fang and McDonnell, 2011). A golden colour allows recognizing the raw materials (prills or ingots) richer in tin and would certainly be appreciated in prestige artefacts.

The optical microscopy observations identify α-Cu deformed equiaxial structures with annealing twins and slip bands (Fig. 9). These characteristics evidence a common manufacturing process, which would be finished with hammering after cycles of forging and annealing (Table 5). The occurrence of small Cu–S inclusions is another common feature among these artefacts. For instance, the SEM–EDS analysis of ring 1388 shows a high amount of Cu–S inclusions, together with the $\alpha + \delta$ eutectoid displaying an interdendritic morphology. Cu–S inclusions are common in LBA artefacts from the Iberian Peninsula (e.g. Baiões, Figueiredo et al., 2010b; and Ria de Huelva, Rovira, 1995) indicating that the same type of ore was being processed. Similarly, metallurgical remains from EA5 point to the smelting of copper ores with significant amounts of sulphur.

The bracelet (314a) is the single artefact without the characteristic slip bands, originated by a final hammering (Fig. 9). The absence of this finishing operation in a well recrystallized microstructure resulted in a rather soft material (79 HV, Table 5), which, interestingly, is not detrimental to this specific typology. The final hammering was always applied to remaining artefacts regardless of their type, but the intensity of deformation differs. For instance, the needle 491a has a much higher density of slip bands than the ring 1388 (Fig. 9). Overall, the Vickers testing shows that final hammering actually produced a harder material, but other factors like the tin content, recrystallized α-Cu grain size and secondary

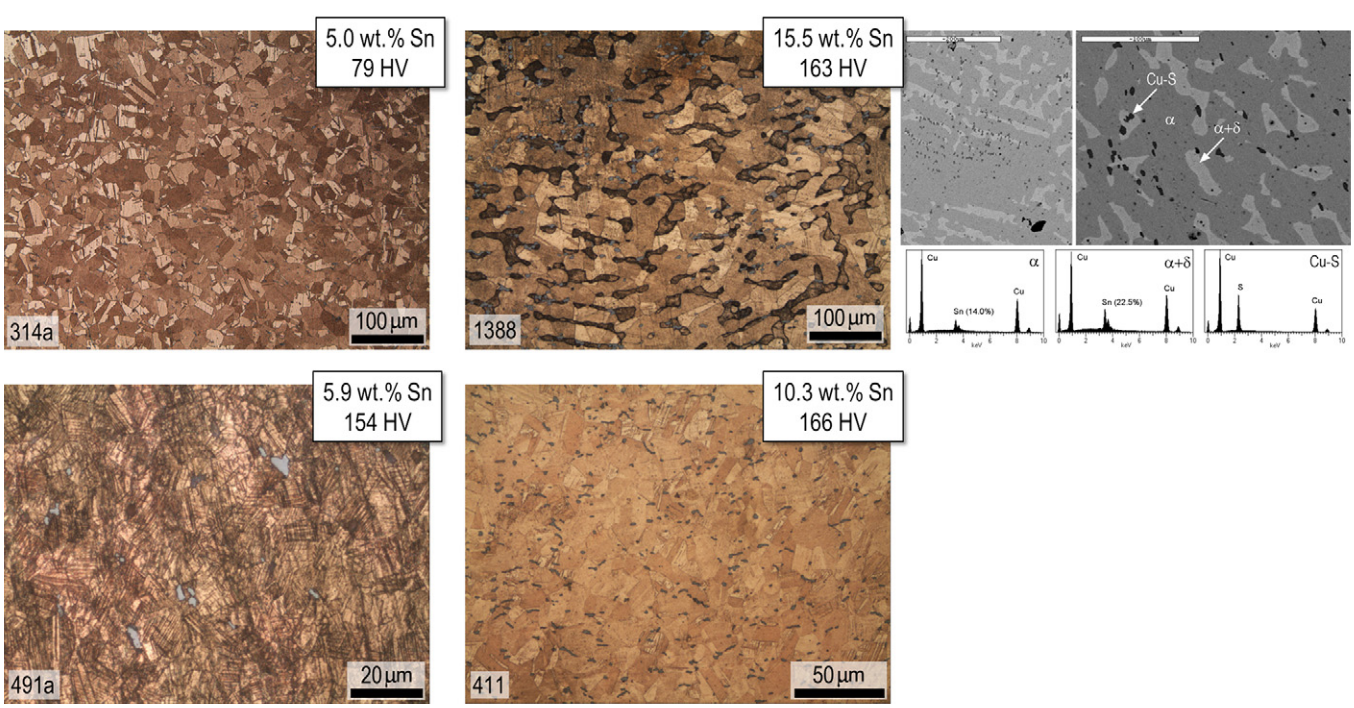

Fig. 9. OM-BF and SEM-BSE images of bronze artefacts recovered from the LBA settlement of EA5.

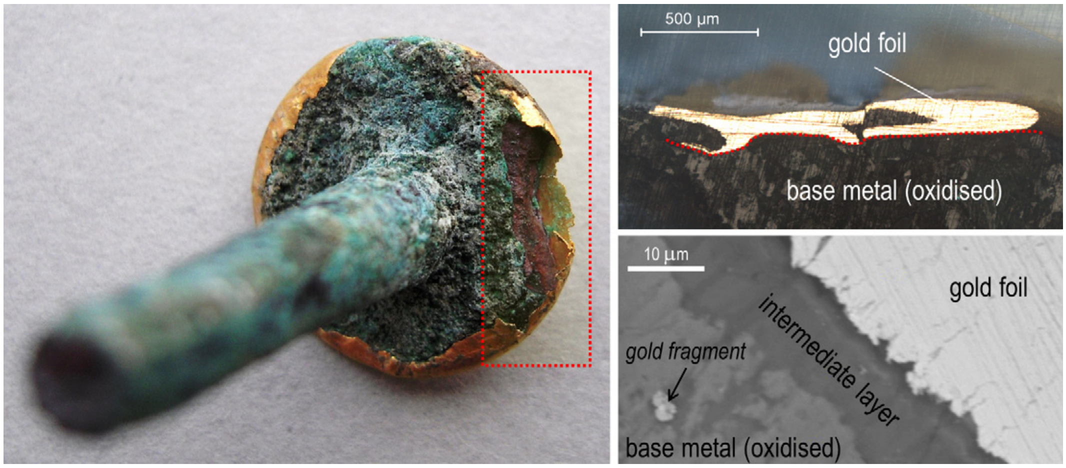

Fig. 10. Image of gilded nail 1495b showing the gold foil over a totally corroded bronze head (OM-BF and SEM-BSE images of contact area between foil and bronze substrate).

phases present also influence the final hardness. The high hardness of ring 1388 (163 HV) is a clear example of the effect of higher tin contents, in this case resulting from α-Cu phase super-saturation and precipitation of harder δ phase. Nevertheless, the equally high hardness of the needle 491a (154 HV) proofs that low-tin bronzes can be effectively strain hardened by a strong final hammering.

5.6. Gilded nail

Preliminary micro-EDXRF analyses made over corroded surface of the nail have established that the head and pin are made of bronze. The advanced state of corrosion of the artefact advised against any attempt to obtain a clean surface for analysis, but a small fragment previously detached was prepared for additional studies. This fragment is constituted by the base metal and gilding layer (Fig. 10). Optical microscopy and SEM–EDS analyses established that gold layer has a thickness of *c.* 140 µm and is composed of a gold alloy with 11.6 wt.% Ag and about 1 wt.% Cu. The method used can be classified as foil gilding, as opposed to leaf gilding that evidences an enhanced technique – the leaf can reach thicknesses of less than 1 µm – commonly applied to refined gold (Drayman-Weisser, 2000).

A systematic study (Soares et al., 1996), gathering about 100 analyses from the SAM project of prehistoric gold artefacts from the Portuguese territory (Hartmann, 1982), showed that the majority of Bronze Age artefacts has a silver content between 10 and 15 wt.%. Additionally, LBA gold artefacts show a high range of copper contents, whereas most artefacts from previous periods presents values bellow 0.5 wt.% Cu. Consequently, the gold alloy applied to this bronze nail is typical of the LBA metallurgy in Portuguese territory.

The next stage involved determining the process used to attach the foil in the base metal. A close observation indicates that the foil is bended over the edges of the bronze head (Fig. 10). Furthermore, the SEM–EDS analyses established that no gold was diffused to the base metal, which is completely corroded suggesting an initial weak cohesion between components. The expansion originated by bronze corrosion originated fissures in the foil and some gold fragments were detached to the oxidised layer of the base metal. These features indicate that the gilding involved mechanical work – the gold foil was burnished over the bronze head and the edges were bended to secure it – but no evidences were found of the application of heat to promote interdiffusion bonding between components. An intermediate layer, more friable and enriched in Si and Ca (in addition to Cu) should result from alteration processes. Alternatively, it might suggest the use of an adhesive to improve bonding. Although this technique is not usually associated with metalworking, it has been used occasionally for leaf gilding, such as in an Egyptian figurine gilded over a layer of finely ground dolomitic limestone (Oddy, 1981).

In Iberian Peninsula, earlier gildings involve thick gold foils over non-metallic hilts of swords and daggers from the Bronze Age (Perea et al., 2008). Gold foils were commonly applied with rivets or by bending the edges over the base material. Up to now, gilding over metal before the Orientalizing period was unknown since the earlier examples involve iron artefacts. Moreover, the gilded copper nail from the LBA settlement of Crasto de São Romão involved diffusion gilding, a method that suggests earlier contacts with Eastern Mediterranean societies (Figueiredo et al., 2010a). Consequently, considering that EA5 precedes the establishment of Phoenician settlements in the coastal region (i.e. during the late 9th and early 8th centuries BC) the gilded nail found in this settlement is probably the earlier evidence of gilding over metal in Iberia.

6. Conclusions

The elemental and microstructural study of material culture from EA5 opened a window into the LBA metallurgy in SW Iberian Peninsula. The remains of the metallurgical workshop found at EA5 are particularly important because of multiple evidences of different stages of the metallurgical process. The first operation consisted in smelting inside ceramic crucibles and some evidences point to co-smelting of oxide copper ores and cassiterite. The bronze prills formed in the high viscosity slag produced by this primitive smelting would be gathered to be melted later. This implies that crushing the slag to hand-pick metal prills was a common process among early metallurgists on the Iberian Peninsula, as well as in other European and Mediterranean regions in general. The slow cooling evidenced by many of metal prills is consistent with this hypothesis. A crucible with thinner slag layer and bronze nodules was probably used to melt these prills. The molten charge could have been poured directly into moulds to obtain artefacts, which would explain the almost absence of ingots in the archaeological record. Anyway, some of the fast cooling prills from EA5 could be casting spills. Apart from these metallurgical steps, there is another crucible at EA5 that suggests a second method of bronze production. The copper slag in this deeper crucible with a definite lip for pouring, suggests the production of metallic copper prior to alloying.

The impurity pattern of most finished artefacts recovered in this settlement is comparable to that of metallic prills locally produced (Pb > As > Fe) which suggests a possible local production of the artefacts. Additionally, the low iron content of bronzes indicates mild reduction conditions during smelting, which are common among primitive operations conducted in open crucibles. The set of copper-based artefacts from EA5 is mostly composed of binary bronzes with about 10 wt.% Sn. Some examples suggest that manufacture would be adjusted to the artefact functionality – a ring with a higher amount of tin has a more attractive golden colour, while a bracelet could exempt the hardening effect of final hammering.

The area excavated shows that the metallurgical activities (smelting, casting and, probably the manufacture of artefacts) were all done in the same area of the settlement suggesting a domestic metallurgy. Regional copper sources precluded the need for exchange networks, but perhaps a different matter was the probable importation of tin ores from more distant sources, such as the Central Portuguese region or the Caceres area in Spain. The exceptional gilded nail indicates circulation of quite evolved artefacts in addition to simple tools, ornaments and weapons, commonly found in LBA sites. Finally, the features evidenced by a comprehensive and significant set of archaeological remains from this metallurgical workshop (i.e. small scale production, crucible smelting, poor reducing atmosphere, co-smelting and absence of ingots), in addition to characteristics of the metal artefacts (bronze alloys with suitable tin contents), reveal similarities with the known LBA metallurgy from the SW Iberian Peninsula.

Acknowledgements

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