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Iron-Age bronze statuettes in Southern Portugal: combining archaeological data with EDXRF and BSEM + EDS to assess provenance and production technology

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Abstract A simple, fast, and nondestructive analytical methodology combining X-ray Fluorescence (EDXRF) and Back-scattered Electron Microscopy coupled with Energy Dispersive Spectroscopy (BSEM+EDS) has been applied to characterize the alloy's composition of ex-votos metal statuettes of unknown provenance and age stored in the Museum of Évora in Southern Portugal, and to compare it with Iron-Age artefacts of similar typology recovered from the well-known Phoenician settlement (7th century BC) of Alcàcer do Sal located about 50 km W of Évora. The aim of the study was two-fold: (a) to confirm the age and provenance of the bronzes from the Alcàcer settlement; (b) to assess whether the combined archaeometric approach could shed light on the interaction between local (Iberian peninsula) and allochtonous (Phoenician) technological know-how and on how the "Orientalizing" Phoenician influence had been modulated locally in the making of metal artifacts. In this respect, for comparative purposes, selected bronze statuettes displaying "Orientalizing" features of inferred Phoenician origin from the Nuragic collection of the National Archaeological Museum in Cagliari and the G.A. Sanna Museum of Sassari, Sardinia, were also analyzed by EDXRF. Results indicate that all statuettes are made of an alloy of Cu/Sn or Cu/Sn/Pb with variable Sn and Pb content. The presence and content of Pb and of Fe (the latter always >0.05 %) in the alloy suggest a production technology involving the smelting of ferrous minerals and/or the use of reducing firing conditions with locally available Pb intentionally added as fluxing agent. The alloy's compositional data is consistent with a provenance of the Évora statuettes from the known Phoenician settlement of Alcàcer do Sal in Southern Portugal.

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1 Introduction

Phoenicians sailed around the Mediterranean and the Atlantic Ocean, acting as importers of technological skills during their numerous contacts with other cultures [1, 2]. During the Late Bronze Age (LBA) and Early Iron Age (EIA), they reached also the Southernmost and Westernmost seaboard regions of the Iberian Peninsula, where they started to establish important, settlements for commercial exchanges. In the last two decades, archaeological studies have, in fact, identified several Phoenician settlements (datable between the 9th and 6th centuries BC) in the South of what is now modern Portugal such as the ones in Santa Olaia, Alcàcer do Sal, Abul, Setubal, Castro Marim, and Quinta do Almaraz purposely established along important trade routes such as the valleys of the Mondego, Tagus, and Sado rivers [1]. Notwithstanding their continuous, general quest for new commercial markets and cultural exchanges in the Mediterranean and beyond, Phoenician interest in the

South-Western part of the Iberian peninsula was also linked to the presence of significant mineral resources in the area related, for instance, to the presence in S of the Iberian Pyrite Belt (IPB), an important geological ore characterized by massive sulfide deposits rich in Au, Ag, Cu, Pb that were known since ancient times [3–5]. As a matter of fact, it was from the East and from the Phoenician material culture that bronze metallurgical technology was spread throughout the ancient world.

Accordingly, bronze artefacts of Phoenician origin from sites both in the Mediterranean Basin as a whole and in the Iberian Peninsula in particular have been the topic of several archaeological/archaeometric studies combining typological characterization with a variety of advanced chemical and physical analytical techniques [6–23]. Some of these studies [6–11, 18, 20–22] suggest that, while late Bronze Age Iberian metallurgy (between the end of the 2nd millennium to the early 1st millennium BC) was characterized by binary Cu/Sn alloys with Pb <2 % and with Sn content between 8–14 %, higher variability in Sn and higher Pb contents (together with Fe content >0.05 %) became common at the beginning of the Iron Age (about 800–400 BC) following the establishment of the first Phoenician settlement in the South-Western coastal regions of the Peninsula. It is well known that the Phoenicians used to introduce new technological know-how in their most important colonies. In the metallurgical field, one of these innovations consisted in the use of Pb as a fluxing agent in the bronze manufacturing process. Lead in fact enhances the fluidity of the molten bronze alloy and increases the temperature solidification range, thus facilitating the casting of decorative objects of intricate design [7–11, 20–22]. In fact, autochthonous Iberian technologies and imported Phoenician know-how frequently merged giving rise to a new, "hybrid" typology of production, the so-called Orientalizing art that could be characterized archaeometrically by distinct alloy's compositions and, archaeologically, by distinct typological features [6, 20–22]. In the case of the southwestermost regions of the Iberian Peninsula, including what is now Southern Portugal, archaeometallurgical studies on Early Iron-Age and Late Bronze-Age artefacts, although forthcoming in recent years [20–22], are still relatively scarce; in these regions, there are still important examples where the presence of leaded bronze is not detected even a century after the first Phoenician colonization, such as is the case of the settlement of Castro dos Ratinhos, where only binary Cu/Sn bronzes can be found [23].

To contribute to this open scientific debate on Phoenician influence on the Iberian Peninsula archaeometallurgical technology, a simple, fast, and nondestructive analytical methodology, combining Energy-Dispersive X-ray Fluorescence (EDXRF) and Variable Pressure Electron Microscopy coupled with Energy Dispersive Spectroscopy (VP-SEM+EDS), has been used to characterize the alloy's composition of eight small metal artefacts belonging to the Évora Museum Collection in Évora, Southern Portugal (Fig. 1). The combined use of ND microscopical and chemical techniques has proved useful in unraveling technological processes and perform provenance analysis not only on bronzes [12–16] but also on a variety of historical materials of complex, heterogeneous composition such as mortars [24, 25], glass [26], bricks [27], and stone [28–35]. The Évora bronze figurines were particularly interesting from an archaeological point of view for two reasons: (a) as no analytical data was to date available on their alloy

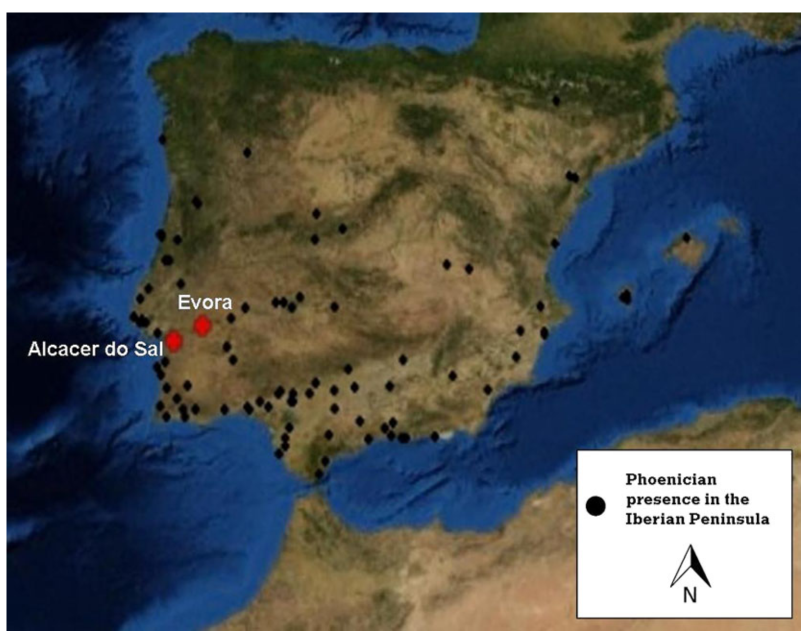

Fig. 1 Location map (Évora, Alcàcer do Sal)

Fig. 2 Iron-Age artifacts from the Évora's Museum collection

composition, their dating and provenance were effectively unknown despite typological studies tentatively assigning them to the well-known Phoenician settlement of Alcácer do Sal (VII century BC), around 50 km E of Évora (Fig. 1, [1]); (b) despite their age assignment still remaining a subject of debate amongst archaeologists, typologically, they had been interpreted either as ex votos consecrated to the local Lusitanian cult of the goddess Adaegina and/or as votive offering to the Phoenician cult of Baal and Astarte. The aim of the study was therefore two-fold: (a) to provide for the first time analytical data on the Évora statuettes in order to confirm/discard their provenance from the Alcàcer settlement and hence their Phoenician connection; (b) to assess whether the combined, nondestructive and relatively simple methodological approach adopted in this study could shed light on the interaction between local (Iberian peninsula) and allochtonous ("Orientalizing"-Phoenician) bronze making technology and, in turn, be useful to understand if/how the "orientalizing" influence had been locally modulated.

As the elemental composition of Iberian "Orientalizing" bronze sets is comparable to collections from related Mediterranean areas, such as Sardinia and Sicily [36] (with respect, for instance, to the alloy's Sn and Pb content), to further test the nature of the Évora's bronzes, EDXRF analyses were also performed on selected bronze statuettes of known "Orientalizing" origin belonging to the Nuragic collection of the National Archaeological Museum of Cagliari and of the G.A. Sanna Archaeological Museum of Sassari in Sardinia, an important Phoenician area of influence within the Mediterranean Basin.

2 Materials and methods

2.1 Bronze statuettes

The studied collection of bronze statuettes belonging to the Museum of Évora, Southern Portugal, consisted of eight figurines (Fig. 2): four human (three male, 3296, 3298, and 3299, and one female, 3300, in the act of praying), three zoomorphic (representing goat-like figures, 3294, 3295, and 3297), and an anthropomorphic tripod (5062). From an archaeological perspective, the origin of these statuettes was controversial. They had been interpreted either as: (a) vestiges of an ancient religion of unknown age introduced in the Iberian Peninsula; in this respect, the statuettes had been linked to the Phoenicians cult of the gods Baal and Astarte, which resulted in the large-scale production of male and female praying statuettes as votive offerings; (b) insofar as the zoomorphic statuettes are concerned, ex-votos consecrated to cult of Adaegina, a local goddess venerated in the Southern Portugal and in the adjacent Spanish province of Extremadura [44]; in this respect, it is worth noting that the same small statuary typology has also been found in bronze artefacts from the Nuristan region of Iran, thus confirming a link with oriental bronze metallurgy.

Six Iron-Age bronze statuettes dated from the end of the 5th century–begining of the 4th BC and belonging to the Alcàcer do Sal Phoenician settlement and typologically similar to the Évora's ones were selected for analysis (Fig. 3): three anthropomorphic (one male, 1319, and two fragments representing a left foot and a leg, 2062 and 1437), three zoomorphic (a bull entire figure, 1328, and a fragment of a bull's head, 1074), and a fragment of a bull's horn (2063).

Fig. 3 Iron-Age artifacts from the Alcàcer do Sal settlement

Four anthropomorphic bronze statuettes from the Nuragic collection of the Cagliari National Archaeological Museum (three male figurines in the act of praying and one archer) and one zoomorphic figurine (representing a moufflon exceedingly similar typologically to the goat statuettes from Évora) from the Sassari Archaeological Museum were also analyzed by EDXRF (Figs. 4 and 5). The Sardinian bronze artefacts come from a wide selection of Nuragic settlements with attested "Orientalizing" (Phoenician and Punic) influence in the islands Bonorva, Flumenelongu, Anthas, Sardara, and Laerru.

To avoid contamination from surficial corrosion patinas, the surface area to be analyzed of all the artefacts under study were cleaned by grinding with abrasive paper of different grit sizes and diamond paste and etched in a Fe-chloride solution to obtain a cleaned area of about 3–5 mm^2. The cleaned areas were then analyzed by EDXRF performing at least three measurements per each statuette; care was applied to analyze only the middle/top areas of each statuette in order to obtain meaningful elemental alloy compositional data least affected by compositional heterogeneity, caused, for instance, by the migration of Pb in peripheral areas. As it has been the case in the study of other archaeomaterials from Southwestern Iberia [26], the spatial resolution and phase contrast of BSEM imaging proved useful in the investigation of the micro-texture of the bronzes, while the EDS system provided 2D major elements maps highlighting compositional heterogeneities.

2.2 EDXRF

Due to logistical constraints related to the nonmovable nature of the samples, two EDXRF spectrometers were used in this study taking care to apply the same analytical conditions: one for the Portuguese samples (Évora and Alcàcer do Sal) and the other for the Sardinian ones. The first spectrometer was an Eclipse IV Oxford Instruments X-Ray tube (45 kV, 50 μA, 2.25 W) with an Rh anode. The outcoming radiation was collimated by a tantalum collimator resulting in a 5-mm-diameter beam at the sample surface, placed at 55 mm distance from the tube and 10 mm from the detector. The Super silicon drift detector (SDD) was an Amptek XR-100SDD with a 25-mm^2 detection area and 500-μm thickness, and with a 12.5-μm Be window. Energy resolution was 140 eV at Mn$K\alpha$ FWHM 5.9 keV, and the acquisition system was an Amptek DppPMCA. The angle between the incident and emitted beam was 90°. This geometry allows for a high background reduction due to Compton scattering. The sample was positioned at the focal point of two laser beams. The X-ray generator was operated at 40 kV and 20 μA, with an acquisition time of 150 s. All measurements undertaken were carried out in ambient air. Data were processed and quantified using the WinAxil 4.5.2 software comprising fundamental parameters and experimental calibration factors. The accuracy of the quantitative results was validated by analysis of bronze standards.

The second spectrometer was an Amptek MiniX X-ray tube equipped with Ag anode (50 kV, 80 μA). The X-ray detector was an X-123SDD by Amptek with again a resolution of 140 eV at Mn$K\alpha$ FWHM 5.9 keV. This system is very similar to the previous one. Due to the morphology of the samples, the detector was placed orthogonally to the sample surface while the X-ray tube was at 30°. Setup of both measurements has been calibrated by using certificated bronze sample. All measurements were carried out under ambient air. An innovative reverse Monte Carlo simulation [37, 38] quantification approach has been used. This approach allows one to significantly improve the sensitivity of the spectrometers taking in account also the nonplanar nature of the surface. Other Monte Carlo codes are capable to cope with rough surfaces by using regular structures such as hemispheres or stripes. In our case, the rough surface could be modeled using any irregular shape. Our Monte Carlo code makes use of a constantly updated X-ray library for any X-ray data (X-relic) [38–40]. The Monte Carlo code has been tested on a variety of cultural heritage items [41–47]. The LOD of the system is about 10 ppm. This approach

Fig. 4 Anthropomorphic nuragic bronzes artifacts from Sardinia: (*1*) Archer from Sardara, (*2*) Male statuette from Bonorva, (*3*) Male statuette from Flumenelongu, (*4*) Prayer from Antas

gives another calibration because the Monte Carlo has been tested on certified samples.

2.3 BSEM + EDS

A HITACHI S3700N Variable Pressure-SEM, interfaced with a Quanta EDS microanalysis system has been used. The Quanta system was equipped with a Broker AXS X-Flash® Silicon Drift Detector (129 EVE Spectral Resolution at FWHM/MN Kα). Standardless PB/ZAF quantitative elemental analysis was performed using the Bruker ESPRIT software. The operating conditions for EDS analysis were as follows: backscattered electron mode (BSEM), 20 kV accelerating voltage, 10 mm working distance, 120 mA emission current. The detection limits with this configuration for major elements (>Na) were in the order of 0.1 wt%. The large chamber of the HITACHI S3700N allowed the direct analysis of the small statuettes without the need of subsampling, therefore permitting one to perform a totally Non-Destructive (ND) type of investigation.

Fig. 5 Nuragic bronze artefact representing a mufflon from Laerru (Sardinia)

3 Results and discussion

Qualitative EDXRF data interpretation performed by comparing superimposed spectra from the two sites confirms that the eight statuettes belonging to the Évora museum's collection and the six selected ones from Alcàcer do Sal are mostly made of the same type of alloy, i.e., a leaded bronze (Cu–Sn–Pb) alloy with variable Sn content. Normalized quantitative data (Table 1) confirm the compositional similarities between the two sites. In particular, notwithstanding the fairly high variability in the range of Pb contents observed across the dataset (Table 1), all bronzes from Évora and four out of six artefacts from Alcàcer collections show significantly high Pb contents with an average Pb value of 15.7 wt% in Évora and of 8.8 wt% in Alcàcer do Sal. Textural analysis by BSEM + EDS analysis of cleaned areas of the bronze samples shows that the Pb, due to its low miscibility with Cu, occurs as segregated, scattered inclusions with globular and interdendritic morphology (Figs. 6 and 7): the large size and very sharp and distinguishable edges of the lead globules observed, for instance, in sample 3297 (Fig. 8) demonstrate that the bronze production process involved a particularly slow cooling phase.

On the other hand, BSEM + EDS analysis of the two samples from Alcàcer do Sal (1319–1328) with low Pb content confirms the absence of Pb enrichment areas in the

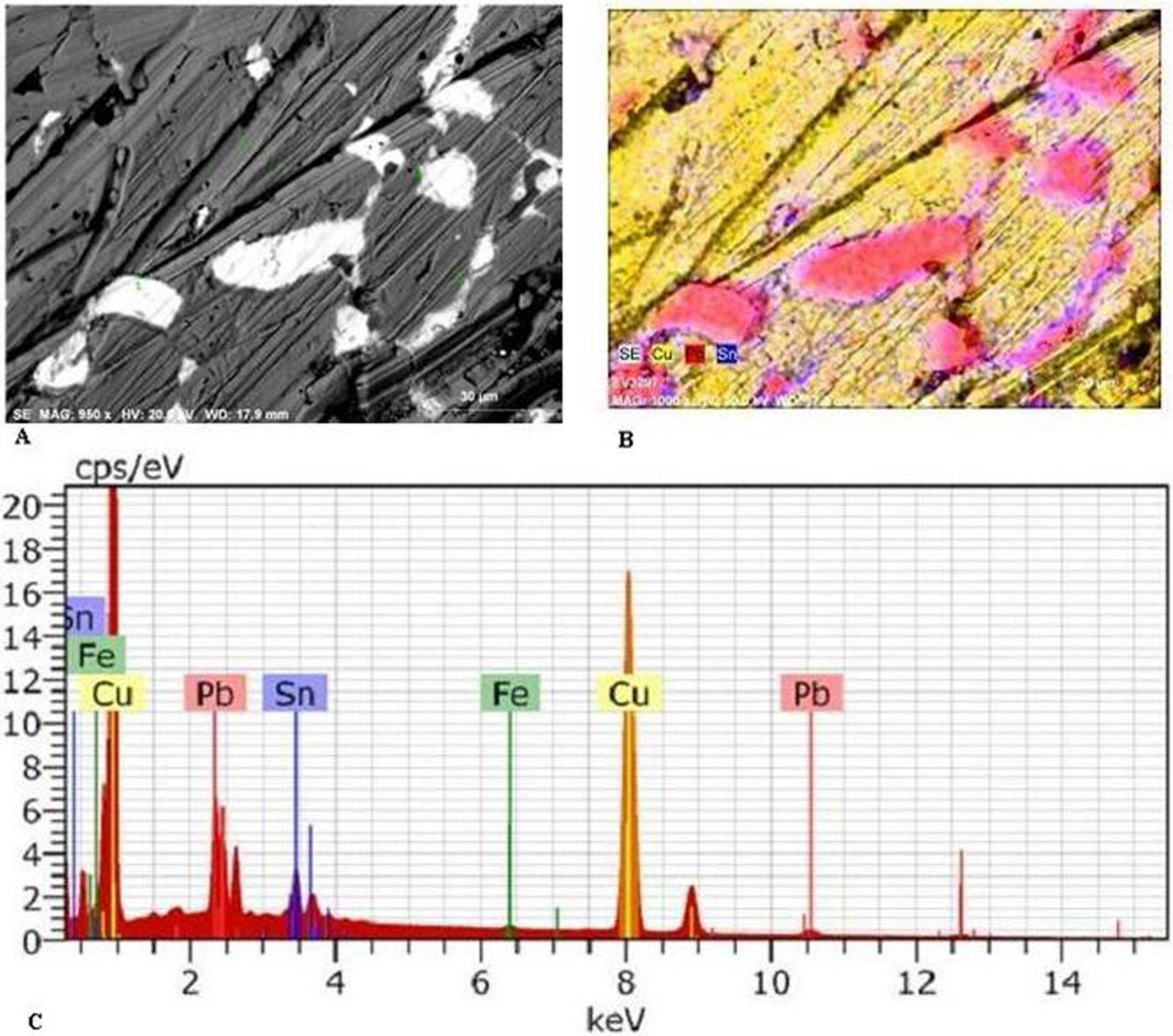

Fig. 6 (**a**) Backscattered image; (**b**) elemental EDS map; (**c**) spectrum of the whole area from the SEM–EDS analysis of 3297 artefact (Évora)

alloy. The significant presence of leaded bronze (i.e., Pb >2 wt%) in the objects under study is not unexpected as bronze artefacts from other Iron Age Orientalizing settlements in the Southwestern regions of the Iberian Peninsula revealed a significant usage of leaded bronzes, and indeed an increased use of leaded bronze was identified (and linked to a "Orientalizing" production) also in the South-Eastern regions of the Peninsula [19]. Nevertheless, the lead values in the Évora and Alcàcer bronzes appear much higher than the ones reported for leaded bronze objects from other Phoenician settlements in the South of Portugal [21]. Pb contents in small bronze artefacts recovered from the Early Iron-Age Phoenician Quinta do Almaraz settlement (9th–7th centuries BC), for instance, show values ranging between 4.6 and 5.9 wt% [33]. The reason behind the unusually high Pb content detected in this study could be manifold: (a) archaeological evidence assigns the Alcàcer do Sal statuettes to the late 5th–early 4th century BC, therefore placing them two to four centuries after those of the Quinta da Almaraz settlement (9th–7th centuries BC). It may therefore be assumed that the propensity by the local material culture to adopt the "new" imported leaded bronze technique, somewhat low at the start [21], increased with time with the result that, not only an increasing number of artefacts were being produced with leaded bronze but also that the mastery of the technique allowed the use of higher amounts of lead during bronze production. In fact, whereas only a few bronzes from the Quinta da Almaraz site contained Pb (the rest be-

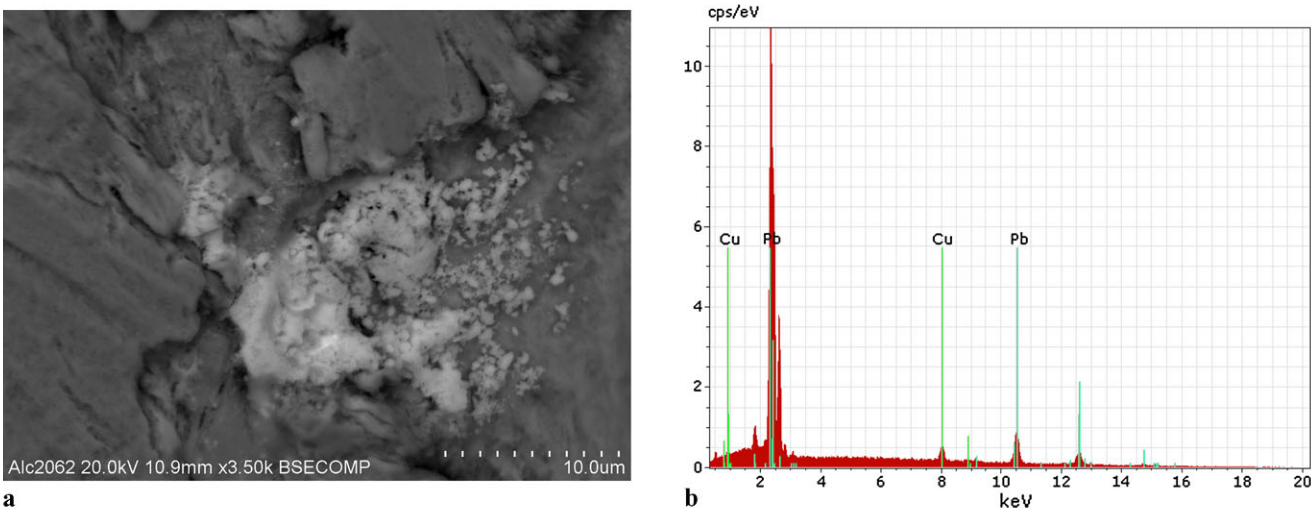

Fig. 7 (**a**) Backscattered image; (**b**) spectrum of Pb globule from 2062 artefact (Alcàcer do Sal)

ing binary Cu–Sn alloys), in the cases investigated here all (but two) samples were made of a Cu/Sn/Pb ternary alloys; (b) another factor that could explain the unusually high Pb content of the bronzes hereby investigated may be related to the post-Phoenician increasing rate of extraction of Pb from the abundant galena-bearing deposits present within the local Iberian Pyrite Belt ore [4, 5]; (c) a third explanation may be more related to the specific functionality of the objects: it is well known that abundant low melting point Pb inclusions in bronzes such as the ones encountered in this study are responsible not only for a higher degree of castability during the bronze making process but also for a flow hardness final metal product. The intentional addition of Pb, therefore, is often associated with the need to produce objects with complex decorative features, i.e., not requiring high strength and a somewhat standardized alloy composition such as it is the case in the production of object destined to be used as weapons (daggers, spears, etc., [21]). This is the case of the statuettes examined in this study, which, although in a somewhat simplified fashion, do show attention to figurative details (Figs. 2 and 3); moreover, their archaeological interpretation as ex-votos (dedicated either to local or to Phoenician "gods") suggests that these were objects of "decorative or worshipping" production, again not requiring high resistance to mechanical stress or material strength: in this respect, the addition of lead could have facilitated the production process allowing faster (i.e., low temperature) casting, which is typical of "as cast" technology in small statuary bronze production in the Iberian Peninsula [18].

Except in one case (ref. 3295, goat in Évora), significant impurities of Fe are present in the bronzes from both sites investigated: content ranges from 0.1 up to 1.5 wt% averaging in Évora 0.34 wt% and in Alcàcer 0.37 wt%. These values are higher when compared with those of pre-Phoenician Late Bronze-Age artefacts in the Iberian Peninsula, which

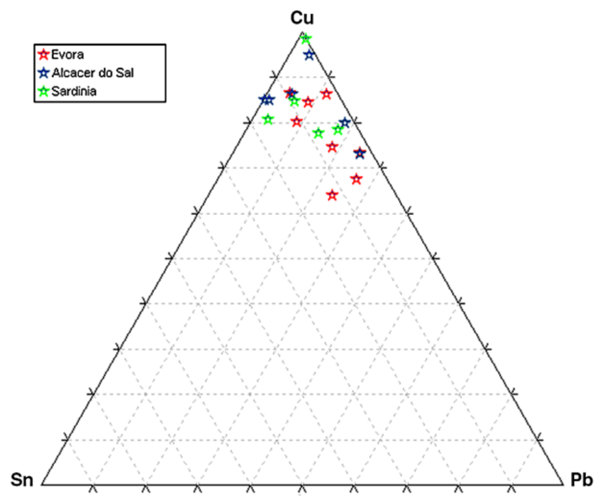

Fig. 8 Ternary Cu–Sn–Pb plot from EDXRF analytical dataset (Évora, Alcàcer do Sal, and Sardinia)

have been found not to exceed 0.05 wt% [20] whereas appear fully consistent with increased Fe contents as reported in Early Iron-Age bronzes across Portugal [22], Spain [18, 48–50], and indeed the whole of the Mediterranean [36]. The widespread Fe increase from LBA to EIA has been explained, with the introduction by the Phoenicians of a more efficient copper smelting technology associated with higher reducing conditions attainable only in high-technology furnaces [10, 13, 14, 36, 48]. Additionally, it has to be noted that the bronze makers could have extracted copper from local mineral deposits containing high impurities of Fe; such it is the case with the sulfide deposits in the IPB, where the mineral chalcopyrite is known to be present in significant amounts [4].

The Sn content of the bronze statuettes investigated show in both sites a high degree of variability ranging from

Table 1 EDXRF quantitative data (WinAxil and Monte Carlo methods) from the Évora, Alcàcer do Sal, and Sardinia's samples investigated)

Artifact	Description	Fe	Cu	Sn	Pb
Évora 3296	Prayer (male)	1.50 ± 0.02	66.6 ± 0.1	5.8 ± 0.2	26.1 ± 0.2
Évora 3297	Goat	930 ppm ± 40 ppm	74.5 ± 0.1	7.0 ± 0.2	18.5 ± 0.1
Évora 3299	Prayer (male)	800 ppm ± 40 ppm	86.3 ± 0.1	2.20 ± 0.08	11.5 ± 0.1
Évora 5062	Tripod	0.30 ± 0.07	86.2 ± 0.1	9.2 ± 0.2	4.3 ± 0.1
Évora 3300	Prayer (female)	0.46 ± 0.01	63.6 ± 0.1	12.3 ± 0.3	23.6 ± 0.2
Évora 3295	Goat	370 ppm ± 40 ppm	80.3 ± 0.1	11.0 ± 0.2	8.7 ± 0.1
Évora 3294	Goat	430 ppm ± 30 ppm	84.4 ± 0.1	6.8 ± 0.2	8.8 ± 0.1
Évora 3298	Prayer (male)	0.21 ± 0.01	73.2 ± 0.1	2.29 ± 0.1	24.3 ± 0.2
Alcàcer do Sal 1074	Bull's head	0.42 ± 0.01	79.5 ± 0.1	1.88 ± 0.1	18.2 ± 0.1
Alcàcer do Sal 1437	Human leg	650 ppm ± 40 ppm	73.0 ± 0.1	2.50 ± 0.1	24.5 ± 0.2
Alcàcer do Sal 2063	Bovine horn	0.40 ± 0.01	94.5 ± 0.2	1.15 ± 0.1	4.00 ± 0.07
Alcàcer do Sal 2062	Human foot	0.24 ± 0.01	86.0 ± 0.1	8.8 ± 0.2	5.00 ± 0.05
Alcàcer do Sal 1328	Bull (entire figure)	0.46 ± 0.01	84.7 ± 0.1	14.7 ± 0.3	0.14 ± 0.01
Alcàcer do Sal 1319	Prayer (male)	740 ppm ± 40 ppm	85.1 ± 0.1	13.8 ± 0.3	1.10 ± 0.02
Laerru	Moufflon	1.51 ± 0.01	83.4 ± 0.1	9.0 ± 0.1	6.0 ± 0.1
Bonorva	Prayer	2.00 ± 0.01	79.0 ± 0.1	16.0 ± 0.1	3.0 ± 0.1
Sardara	Archer	1.00 ± 0.01	77.5 ± 0.1	8.1 ± 0.1	14.1 ± 0.1
Flumenelongu	Prayer	0.40 ± 0.01	78.1 ± 0.1	4.0 ± 0.1	17.5 ± 0.1
Antas	Prayer	0.84 ± 0.01	97.7 ± 0.1	0.04 ± 0.01	1.4 ± 0.1

Results from EDXRF analyses of artefacts from Évora and Alcàcer do Sal (Axil X-Ray analysis software) and the five archaeological area in Sardinia (Monte Carlo Simulation Method). Values in wt% and ppm.

2.20 wt% to 12.3 wt% in Évora and from 1.15 wt% to 14.7 wt% in Alcàcer do Sal. Two compositionally groups may be identified: a low Sn one (Évora, 3298 and 3299, and Alcàcer 1074, 1437, and 2063) and a high Sn one (Évora. 3294, 3295, 3296, 3297, 3300, and 5062; Alcàcer, 1319, 1328, and 2062). The low-tin bronzes group is consistent with reported alloy compositional data from Late Bronze-Age and Iron-Age bronzes in the South-Western end of the Iberian Peninsula [21]. The low Sn content in these artefacts has been interpreted as due to an increasing usage of recycled bronze scrap by the ancient metal makers: in this case, the low tin content can be explained by preferential oxidation of this element during repeated melting cycles, a process that has been reproduced experimentally in melting tests in the laboratory, where significant Sn depletion in the final alloy product was found [51]. The practice of using scrap bronze was indeed common in Late Bronze–Early Iron Age metallurgy workshops throughout sites located in the western end of the Iberian Peninsula either in Portugal (Castro dos Ratinhos, Quinta da Almaraz) or Spain (Cancho Roano, Talavera La Vieira) and has been commonly associated with "Orientalizing" production technologies [21]. It has to be said that low tin in bronzes could also be associated with historical periods of shortages in tin supply, as it occurred in Northern Italy [52] and in central Iberian Peninsula during the LBA [53]. It is, however, unlikely that such a shortage occurred in the examples examined here as abundant Sn-rich mineral resources (from cassiterite-bearing granitic rocks) were readily available from nearby regions in the North of Portugal [4, 5, 54].

The observed high variability in Sn content in the studied bronze artefacts with the identification of low-Sn bronze artifacts associated with high-Sn ones have been related with the introduction during the Iberian Iron Age of a different mode of bronze production involving the direct cosmelting of copper and tin ores [10]. In fact, in the Iberian Peninsula as a whole, mixed Cu–Sn ores are not as scarce as initially thought, having been recently identified in several mining areas exploited since ancient times (e.g., Toledo, Murcia, and Sierra Morena). In Portugal, though, while Cu mineral resources are mainly concentrated in the South, being associated with the IPB ore deposits, tin ores (mainly from cassiterite, a Cu–Sn mineral) are mainly located in the North [54]. It is therefore unlikely that Cu–Sn cosmelting could be advocated as playing a major role in explaining the high Sn variability observed in this study. A diversified network of local raw materials supply centers from the North and from the South of Portugal coupled with the varying rate of use of scrap bronze may provide, instead, a better way to explain the analytical data. In fact, the increasing use by the populations inhabiting the South-Western regions of the Iberian Peninsula of local raw materials for the production of everyday ornaments such as the "ex-votos" bronze figurines in this study has been reported since LBA times [21].

As already mentioned, Iron-Age "Orientalizing" bronze objects Phoenician settlements in the Iberian Peninsula are quite comparable from both typological and compositional points of view to artifacts from related Mediterranean areas, such as Sardinia, Italy, and Sicily [36]. The presence of Phoenician traders in Sardinia, for example, is documented as early as the IX century BC, but the influence of Phoenician culture on the local Nuragic civilization became stable and recorded in the material culture of the island only by the second half of the VIII century BC. As in the Iberian Peninsula case, the Phoenician interest in Sardinia was related to the island wealth of local mineral resources (Cu, Pb, Ag [55, 56]). Compositional data related to Nuragic bronze artifacts from Italian and foreign collections are readily available in the literature [55, 57–59]. In most cases, the analytical data shows the metals to be a binary bronze alloy with a few exceptions in which the alloy is ternary. EDXRF analyses of selected bronze statuettes from the Sardinian Museum collections in Cagliari and Sassari showing typical "Orientalizing" features (including the zoomorphic statuette representing a moufflon from the Laerru site displaying typological features almost identical to the goat bronzes of the Évora Museum) are presented in Table 1 and in the ternary diagram (Cu–Sn–Pb) of Fig. 8. As compared with the data in the literature, the Sardinian statuettes selected for the present study show higher lead content. Furthermore, the EDXRF analyses confirm in all but one case (the Anthas bronzes, see below) the compositional similarities with the Portuguese samples here investigated inasmuch as they reveal the use of a ternary Cu–Sn–Pb alloy characterized by high Pb contents with an average of 8.4 wt% and highly variable Sn contents with an average 7.4 wt%. As it is the case with the Évora and Alcàcer objects, also in the Sardinian artifacts both Sn and Pb show a high compositional variability ranging respectively from 0.04 to 16 wt% and from 1.4 to 17.5 wt%. As it occurred in other Mediterranean regions [6], also in Sardinia the introduction of leaded bronze started as a subsequent phase of metalworking [55]; it is not therefore unusual to find, from Early Iron Age onwards, high lead contents accompanied by variable amounts of tin in bronze making. As seen previously in the case of the Iberian small statuary, the use of leaded bronze is coincident with the first Phoenician settlements in Sardinia, especially when decorative or votive objects were the intended final products. On the other hand, the figurine from the Antas settlement (Table 1) appears to be composed by almost pure Cu (97.7 wt%) with almost no Sn (0.04 wt%) and quite low Pb (1.4 wt%). It has to be noted that also in the Iberian Peninsula, the EIA saw a sudden increase in the production of copper artefacts [60]. This could be due either to the EIA smelting of almost pure Cu ores or to the reuse of older Cu-based scrap material.

4 Conclusions

The EDXRF analytical results suggest that the bronze artifacts from Évora and Alcàcer not only share common typological and functional features but also a common alloy's composition, i.e., they are made of a ternary leaded bronze alloy with variable Pb and Sn contents. The provenance of the Évora's bronze statuettes collection from the Phoenician Alcàcer do Sal settlement and their dating (late 5th–early 4th century BC), already hypothesized on the basis of archaeological evidence alone, can then be confirmed. Their alloy composition is in line with the compositional ranges for bronzes introduced in the Iberian Peninsula during Late Bronze to Early Iron Age by the Phoenicians and is also compatible with the alloy's composition of selected "Orientalizing" statuettes from Iron-Age collection in a museum of Sardinia. The micromorphology analysis by BSEM-EDS of the Portuguese samples shows that the Pb was added deliberately during the bronze making production to lower the melting temperature and to increase the fluidity of the melt. The bronze production technology was characterized by a slow cooling phase allowing the segregation of lead into well-defined globular and interdendritic areas. The relatively high iron content of the artifacts founds correspondence on Iron-Age bronzes in the Phoenician-influenced Mediterranean Basin and could be interpreted, besides the use of iron bearing minerals, as a result from an initial smelting of the raw materials under a strong reducing atmosphere. The high variability both in Sn and in Pb contents reflects in most cases the combined influence of local availability of geological raw materials for metal production and of indigenous versus Phoenician technology of production. In fact, results do not indicate a unique mode of production but rather the use of mixed technologies, which is the hallmark of the "Orientalizing" mode of bronze manufacturing.

Notwithstanding the need for expanding the dataset both in terms of number of geographical distribution of samples to get a wider perspective of bronze metallurgy during Phoenician presence in the Mediterranean, the simple, fast, and nondestructive analytical approach used in this study proved useful in providing new analytical data to complement archaeological evidence. It has to be stressed that an ND methodological approach such as the one adopted in this investigation becomes an essential prerequisite of archaeometric research, especially when dealing with important archaeological objects stored in Museum collections around the world.

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