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Combining X-ray based methods to study the protohistoric bronze technology in Western Iberia

P. Valério [a,*], R.J.C. Silva [b], A.M.M. Soares [a], M.F. Araújo [a], A.P. Gonçalves [a], R.M. Soares [c]

[a] Centro de Ciências e Tecnologias Nucleares (C2TN), Instituto Superior Técnico, Universidade de Lisboa, Campus Tecnológico e Nuclear, Estrada Nacional 10 (km 139,7), 2695-066 Bobadela LRS, Portugal

[b] CENIMAT/I3N, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, FCT, Universidade Nova de Lisboa, 2829-516 Monte de Caparica, Portugal

[c] UNIARQ, Centro de Arqueologia da Universidade de Lisboa, Faculdade de Letras, Alameda da Universidade, 1600-214 Lisboa, Portugal

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ABSTRACT

The Phoenician arrival at Iberian coastal regions had an actual influence on indigenous technology. A collection of coeval metallurgical remains and artefacts was studied by EDXRF, micro-EDXRF, SEM–EDS and XRD, to identify certain features of the production and utilisation of metal in protohistoric Western Iberia. The composition of artefacts indicates a prevalence of Cu–Sn alloys with low content of impurities (Pb, As, Sb and Fe) during Late Bronze and Early Iron Ages, while the composition of slags points to a smaller loss of copper in Phoenician smelting operations. Moreover, the amount of iron impurities in metal proved to be a helpful discriminator between indigenous and Phoenician-based metallurgies, showing that later alloys have higher amounts of iron. Besides, the indigenous alloys have higher tin contents that can probably be explained by the easier access to metal sources of local communities.

1. Introduction

Analytical studies concerning the metallurgy in Western Iberia during the Late Bronze Age (LBA, 1200–800 BC) show that artefacts are composed of Cu–Sn alloys with low impurity patterns [5,10,12,28]. Local metallurgical remains indicate the production of such alloys by smelting metalliferous ores in ceramic crucibles [10,28]. Rovira and Montero-Ruiz [18] suggest that this primitive method endure through the Early Iron Age (EIA, 800–400 BC) despite the many innovations introduced by Eastern Mediterranean settlers and traders. In fact, Phoenician colonies have a more diversified metallurgy, including not only binary bronzes but also pure copper and leaded bronzes [11,24]. Coeval indigenous settlements, however, display a conservative metallurgy of binary bronzes revealing the difficulty or the slowness in the adoption of new technologies [9,25,27].

The study of metallurgical remains, such as crucibles, prills or slags can identify bronze production methods (co-smelting of ores, copper cementation or melting of pure metals). These methods influence the type and quality of produced alloys, while their use in distinct typologies due to technological, cultural or economic reasons (e.g. casting properties, colour, etc.) establishes the technological development of those ancient communities. Despite the already identified differences between indigenous and Phoenician/Orientalising metallurgies, there is a need for further knowledge concerning the ancient metals and alloys utilised in Western Iberia during protohistoric times.

This work characterises production remains and artefacts recovered from protohistoric archaeological sites in Southern Portugal and Portuguese Estremadura. Since the analysis of cultural materials raises important preservation issues, priority was given to non-invasive and microanalytical techniques. The combination of X-ray based methods and electron microscopy has been widely applied in this field [16,14]. Therefore, the collection followed an integrated study with EDXRF, micro-EDXRF, SEM–EDS and XRD. Analytical results were crossed with chronological data, identifying contrasts in the metal production and type of alloy used during the LBA and EIA. Finally, a technological discriminator was identified in a large collection of artefacts from Western Iberia, establishing differences between bronze alloys produced by indigenous and Phoenician-based metallurgies.

* Corresponding author. Tel.: +351 219946207.
E-mail addresses: pvalerio@ctn.ist.utl.pt (P. Valério), rjcs@fct.unl.pt (R.J.C. Silva), amsoares@ctn.ist.utl.pt (A.M.M. Soares), faraujo@ctn.ist.utl.pt (M.F. Araújo), apg@ctn.ist.utl.pt (A.P. Gonçalves), ruigusmao@hotmail.com (R.M. Soares).

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2. Materials and methods

Production remains and artefacts were recovered in protohistoric contexts in Southern Portugal and Portuguese Estremadura (Fig. 1). LBA locations are mostly settlements like Casarão da Mesquita 4, Monte do Guedelha, Salsa 3, Santa Margarida [1], Cerro da Mangancha [20], Outeiro do Circo [19] and Quinta do Marcelo [2]. EIA sites include the Phoenician colony of Quinta do Almaraz [24] and post-Orientalising contexts such as a burial at Nora Velha [22], the monumental building of Cabeço Redondo [23] and a not excavated context at Barrinhos 4 [21]. Castro dos Ratinhos has occupations from both periods [4], while the few artefacts without secure contexts have typologies that ascribe them to the period under discussion.

Production remains include crucibles, a tuyere, slag fragments, metallic prills and a casting cone, possibly from a spearhead. Crucibles have coarse ceramic fabrics including numerous quartz grains and many voids from burned out organic fibres, which increase the thermal insulation and reduction conditions [3]. Artefacts comprise tools, ornaments, weapons and other cases of uncertain functionality such as rings or a fragmented rod. Tranchets constitute one of the more interesting typologies since this tanged chisel usually ascribed to the cutting of hides is rare and perhaps reveals connections to the Atlantic cultural sphere [29]. A pivot of potter's wheel also analysed is culturally connected with the Mediterranean world, showing a new ceramic technology introduced by Orientalising influence. The metallic exemplar from Cabeço Redondo shows clear marks of centripetal rotation being an innovation upon older stone pivots.

Production remains were firstly submitted to non-invasive elemental analysis often involving the comparison of inner and outer surfaces. EDXRF analyses were made in a Kevex 771 spectrometer equipped with a Rh X-ray tube, secondary excitation targets and a Si(Li) detector (FWHM 165 eV at 5.9 keV). The area of excitation radiation on sample has approximately 2.5 cm diameter. Two excitation modes were used, namely a Ag secondary target (35 kV, 0.5 mA and 300 s of real time) and a Gd secondary target (57 kV, 1.0 mA and 300 s).

The preparation of metallurgical debris and some artefacts for micro-EDXRF and SEM–EDS analyses has involved the careful cut of a cross-section, which was polished with SiC papers progressively thinner (400–4000 grit size). Metallic cross-sections were mounted in epoxide resin and polished with diamond pastes (3 μm and 1 μm). However, most artefacts could not be sampled due to their archaeological significance. For them the corrosion layer was removed in a small area (3–5 mm diameter) by polishing with a cotton swab with diamond paste (6–1 μm: the procedure ended when optical microscopy observation confirmed a clean metal surface).

Micro-EDXRF analyses were made in an ArtTAX Pro spectrometer equipped with a Mo X-ray tube and a silicon drift detector (160 eV at 5.9 keV). Focusing polycapillary optics and laser positioning system enable a minimum area (<100 μm diameter) of primary radiation on sample [6]. Samples were analysed in 3 spots with a voltage of 40 kV, a current intensity of 0.5 mA and 300 s of real time. Quantification was made with WinAxil software including experimental calibration factors calculated with certified reference material Phosphor Bronze 551 (British Chemical Standards, BCS). Arsenic and antimony were calibrated with standard Bronze 5 (Des Industries de la Fonderie). The accuracy was assessed with certified reference material BCS Phosphor Bronze 552 being better than 10%, while quantification limits for minor elements detected are 0.50 wt.% Sn, 0.50 wt.% Sb, 0.20 wt.% Zn, 0.10 wt.% Pb, 0.10 wt.% As, 0.10 wt.% Ni and 0.05 wt.% Fe.

SEM–EDS analyses were performed in a Zeiss DSM 962 scanning electron microscope coupled with an Oxford Instruments

Fig. 1. Location of archaeological sites mentioned in the text and part of the studied collection, namely a pivot of potter's wheel (CRED-004), tranchets (SMAR-001 and QMAR-001), arrowhead (MGUE-001), belt lock (BAR4-001), spearhead (CRAT-001) and pendants (NVL2-001 and CRED-002).