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The role of arsenic in Chalcolithic copper artefacts – insights from Vila Nova de São Pedro (Portugal)

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ABSTRACT

The Castro of Vila Nova de São Pedro (VNSP) is an emblematic settlement located at Azambuja, Portuguese Estremadura. It was occupied during the third and second millennia BC, predominantly during the Chalcolithic period. A diversified collection of 53 copper-based artefacts (most part in a fragmentary condition), belonging to an extensive metallic collection recovered during excavations carried out in VNSP, was studied using micro-EDXRF spectrometry, optical microscopy and SEM-EDS. Additionally, Vickers microhardness measurements were performed to establish the effectiveness of the thermo-mechanical treatment in the hardness of the artefacts. Results show that the Largo do Carmo, artefact collection is mainly composed of copper or arsenical copper, being 37% of the artefacts made of copper alloyed with arsenic (As > 2%). A statistically significant association was found between copper alloyed with arsenic and artefacts classified as tools/weapons (arrowheads, daggers and knives). In several cases, the presence of arsenic rich phases in the microstructure, resulting from an inverse segregation phenomenon, shows no evidence of chemical homogeneity control during the artefact manufacture. Microstructural analyses also show that the majority of this group (73%) was shaped with forging plus annealing operation cycles and 23% of the artefacts received a final cold hammering after the forging and annealing. An association between the presence of a final forging treatment and artefacts presenting higher arsenic contents was also identified. Nevertheless, no direct correlation was found between the arsenic content of the alloy and its hardness. Also no direct correlation was found between the hardness and a final forging operation. However, it was observed that a harder forging was applied to the cutting edge of the artefacts and consequently a high hardness in this area was obtained despite the arsenic content of the alloy. Concerning arsenical copper alloys, all evidences point out that the potential for obtaining a harder material was not recognized by the ancient metallurgists and the selection of the alloy was possibly made based on colour.

1. Introduction

The earliest sites with evidence of metallurgy in the Portuguese territory belong to the transition of the fourth to the third millennium BC (Cardoso and Soares, 1996; Soares and Cabral, 1993). The Portuguese Estremadura is a key region in studies of the Chalcolithic metallurgy in the Iberian Peninsula due to the existence of impressive large settlements with evidences of metal production (Müller and Soares, 2008; Soares and Cabral, 1993; Soares et al., 1996). Within this region, three sites, Vila Nova de São Pedro (Azambuja), Zambujal (Torres Vedras) and Leceia (Oeiras) (Fig. 1), have been subject to extensive archaeological excavations. At the settlement of Vila Nova de São Pedro (VNSP) archaeological digging was carried out from 1937 to 1964 by archaeologist Afonso do Paço with the support of Reverend Eugene Jalhay. Alongside the practice of agriculture and grazing, some evidence of other practices such as hunting, fishing and gathering were found. Apart from the metallurgical collection (artefacts, crucibles and other remains of production), plenty of household utensils, namely pottery and loom weights, were collected in the settlement. Also an important lithic collection of arrowheads, gouges, axes, scrapers and worship idols

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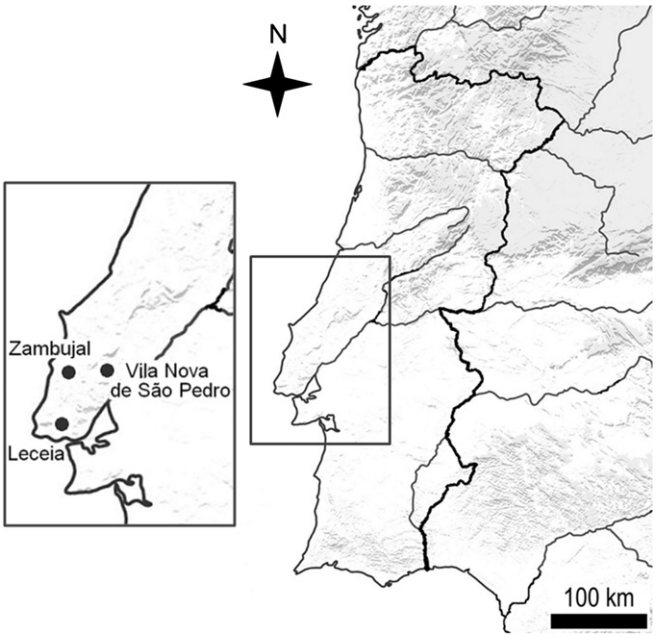

Fig. 1. Location of VNSP and other settlements in Portuguese Estremadura.

were recovered. The majority of the artefacts found in VNSP are currently deposited in the Carmo Archaeological Museum, Lisbon (Arnaud and Fernandes, 2005).

In spite of the extraordinary importance of the recovered metallurgical related materials, only a few studies have been carried out up to the present day regarding the several hundred copper and arsenical copper artefacts and metallurgical remains discovered at VNSP. An earlier study was published in 1952 presenting the elemental composition of few metallic objects found at VNSP (Paço and Arthur, 1952). Other studies carried out by the first author were mainly concerned with descriptions of artefacts or of the settlement (Paço, 1955, 1964).

Nevertheless, some important studies focused on the elemental characterization of artefacts and metallurgical remains led to important results and publications concerning the understanding of the early Iberian metallurgy. It is the case of the analysis carried out by the project "Studien zu den Anfängen der Metallurgie" (SAM; Junghans et al., 1960, 1968, 1974) which form the most comprehensive set of quantitative chemical data of prehistoric copper artefacts from Europe, including Portugal. The SAM programme quantitatively analysed more than 22,000 archaeological copper based artefacts using atomic emission spectroscopy in order to find similar compositionally groups. Of this large dataset, 1700 analysed artefacts were recovered at the Iberian Peninsula, including 87 from VNSP (Müller and Pernicka, 2009; Soares, 2005). A significant conclusion from this programme was that pure copper and arsenical copper were the dominant production during Copper Age to Early Bronze Age in the Iberian Peninsula (Junghans et al., 1968). Later, in order to group artefacts according to their chemical composition, a classification system was developed by Sangmeister using a combination of three two-dimensional element diagrams (showing the content of As–Ni, As–Bi and Sb–Ag) and defined regional groups (Müller and Pernicka, 2009; Sangmeister, 1995). Based on a typological chronology this author concluded that pure copper was primarily used during the Early Copper Age while arsenical copper with low concentrations of other elements was used throughout the Copper Age. Arsenical copper with high concentrations of antinomy, silver and/or nickel tended to occur in Late Copper Age (Müller and Pernicka, 2009; Sangmeister, 1995). Unfortunately, due to the lack of field notes of the early excavations performed in VNSP and the not detailed existing documentation is not possible to match the previous chronology to the materials excavated from VNSP.

In another study, "Bronze Age Metalwork from the Iberian Peninsula", based on the metallic collection belonging to the British Museum, about 100 metallic artefacts were characterized in terms of trace element patterns using atomic absorption spectrometry (Harrison and Craddock, 1981). An important finding from this study was the observation of a correlation between artefact typology and arsenic content in the alloy including artefacts recovered in Portugal (Müller and Pernicka, 2009). In the same decade, another analytical programme called "Proyecto de Arqueometalurgia" was initiated in Spain. Along this programme more than 10,000 analyses of Chalcolithic and Early Bronze Age copper artefacts were performed using X-ray fluorescence spectrometry in surface cleaned areas and complemented with metallographic analysis (Delibes and Montero, 1999; Rovira et al., 1997; Rovira and Gómez, 2003). This project has provided a comprehensive overview of Copper, Bronze and Iron Age metalwork of Spanish territory. According to their findings, the arsenical copper artefacts from the Chalcolithic period seem to be most likely manufactured from the direct use of the metal obtained during the processing of the ores (Müller and Pernicka, 2009).

More recently, in 2004, a research project was initiated by the German Archaeological Institute in cooperation with the Institute of Archaeometry (University of Mining and Metallurgy in Freiberg, Saxony) in order to characterize chemically and mineralogically the archaeometallurgical findings from Zambujal and other Chalcolithic sites of the Portuguese Estremadura, including VNSP. Several analytical techniques were used: X-ray fluorescence spectrometry and neutron activation analyses of ores, slags and copper objects, combined with lead isotope analyses and mineralogical analyses of ores, crucibles and slags (Müller and Cardoso, 2008; Müller and Soares, 2008; Müller et al., 2007). This project aimed to evaluate the impact of the metallurgical activities in Chalcolithic societies.

Some conclusions and findings from previous studies by several authors make clear that the subject regarding the intentional use of copper with higher arsenic contents to manufacture specific typologies is controversial and still under discussion (Cardoso and Guerra, 1997/1998; Ferreira, 1961; Müller and Cardoso, 2008; Müller and Pernicka, 2009; Müller and Soares, 2008; Müller et al., 2007; Northover, 1989; Rovira, 2004). It must be noted that the production of arsenical copper alloys can be accomplished through several metallurgical processes, namely the smelting of secondary copper ores, rich in arsenic, or co-smelting of these copper ores with oxides or sulphides, also rich in arsenic (Lechtmann and Klein, 1999; Hauptmann et al., 2003). Another possibility is alloying pure copper with a mineral with high content in arsenic (Müller et al., 2004, 2007). The provenance of the arsenic, the technological choices involved in the production of an arsenical copper alloy and how it was recognized and finally used (intentionally or not) are all important issues to be considered and to take into account when analysing the arsenic distribution in prehistoric alloys.

In the present study, a significant number of copper-based artefacts with different typologies, part of the VNSP collection that remained unpublished, were analysed. This study aims to contribute to the understanding of the early metallurgy in the Estremadura area. It was based in the assessment of the arsenic content of copper-based artefacts and its correlation with artefact typologies and functions. A further step concerning the methodologies used in the previous studies mentioned above was the