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Metallurgical production evidence in Castro de Vila Nova de São Pedro (Azambuja, Portugal)

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ABSTRACT

The Castro de Vila Nova de São Pedro (VNSP) is an emblematic settlement located at Azambuja (Portugal), occupied during the third and second millennia BC, predominantly during the Chalcolithic period.

The present study focuses on the chemical and microstructural characterization of selected metallurgical remains from the VNSP collection and aims to contribute to a better comprehension of the copper-based metallurgy on the Portuguese Estremadura. A set of metallurgical production remains (8 crucible and 6 slag fragments and 7 metallic prills) belonging to VNSP were characterized by using different analytical techniques: EDXRF spectrometry, micro-EDXRF spectrometry, optical microscopy and SEM-EDS.

Preliminary results on the elemental composition of the metallurgical production remains are consistent with copper and arsenical copper artefact production. These results are also in accordance with the artefact collection from VNSP previously studied and mainly composed of copper or arsenical copper (38% of the artefacts are copper alloyed with arsenic - As>2%) with low iron contents. Analyses of the metallic prills and slag residues have provided indications of melting and smelting operations.

KEYWORDS

Chalcolithic, melting, metallurgical remains, smelting.

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 *et al.* 1996; Soares *et al.* 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 evidence of metal production (Müller *et al.* 2008; Soares *et al.* 1993, 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 were recovered. The majority of the artefacts found in VNSP are currently deposited in the Carmo Archaeological Museum, Lisbon (Soares 2005).

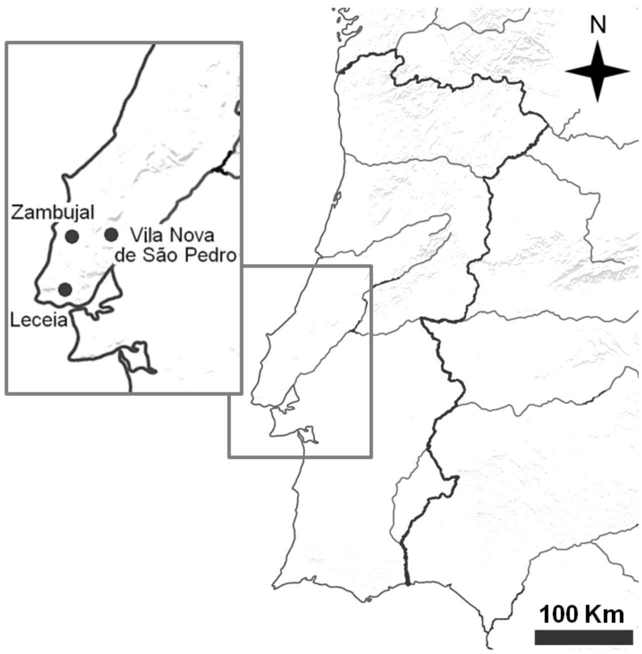

Fig. 1. Location of VNSP in Portuguese Estremadura.

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 metallurgical remains and copper and arsenical copper artefacts discovered at VNSP. A detailed overview of these studies was recently described in Pereira *et al.* (2013).

In the present work, results obtained during chemical and microstructural characterization of selected metallurgical debris (crucibles, slag, and prills) recovered at VNSP will be discussed, since they can be indicative of the type of metallurgy developed in this settlement. Also it is intended to assess and compare the arsenic content of the metallic remains (prills) with the copper-based artefacts from the same settlement.

An artefact collection from VNSP composed of 53 artefact fragments (Fig. 2) was previously studied (Pereira *et al.* 2013). Some of the fragments show intentional sectioning (like the cutting edges of axes) and might be scraps from the manufacturing process or parts of ingots put aside for later re-melting or shaping into smaller objects (Müller *et al.* 2008). The large quantity of artefact fragments recovered in this settlement (some with signs of sectioning) suggests the existence of remelting and recycling operations and could be a cause for the variable concentrations of arsenic found in the studied collection.

Another cause can be the metallurgical processes used to obtain arsenical copper alloys, which could also have an important role in the variability of the arsenic content. 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 (Lechtman *et al.* 1999, Hauptmann *et al.* 2003). Another possibility is alloying pure copper with a mineral with a high arsenic content (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 investigating the arsenic distribution in the metallurgical remains from VNSP.

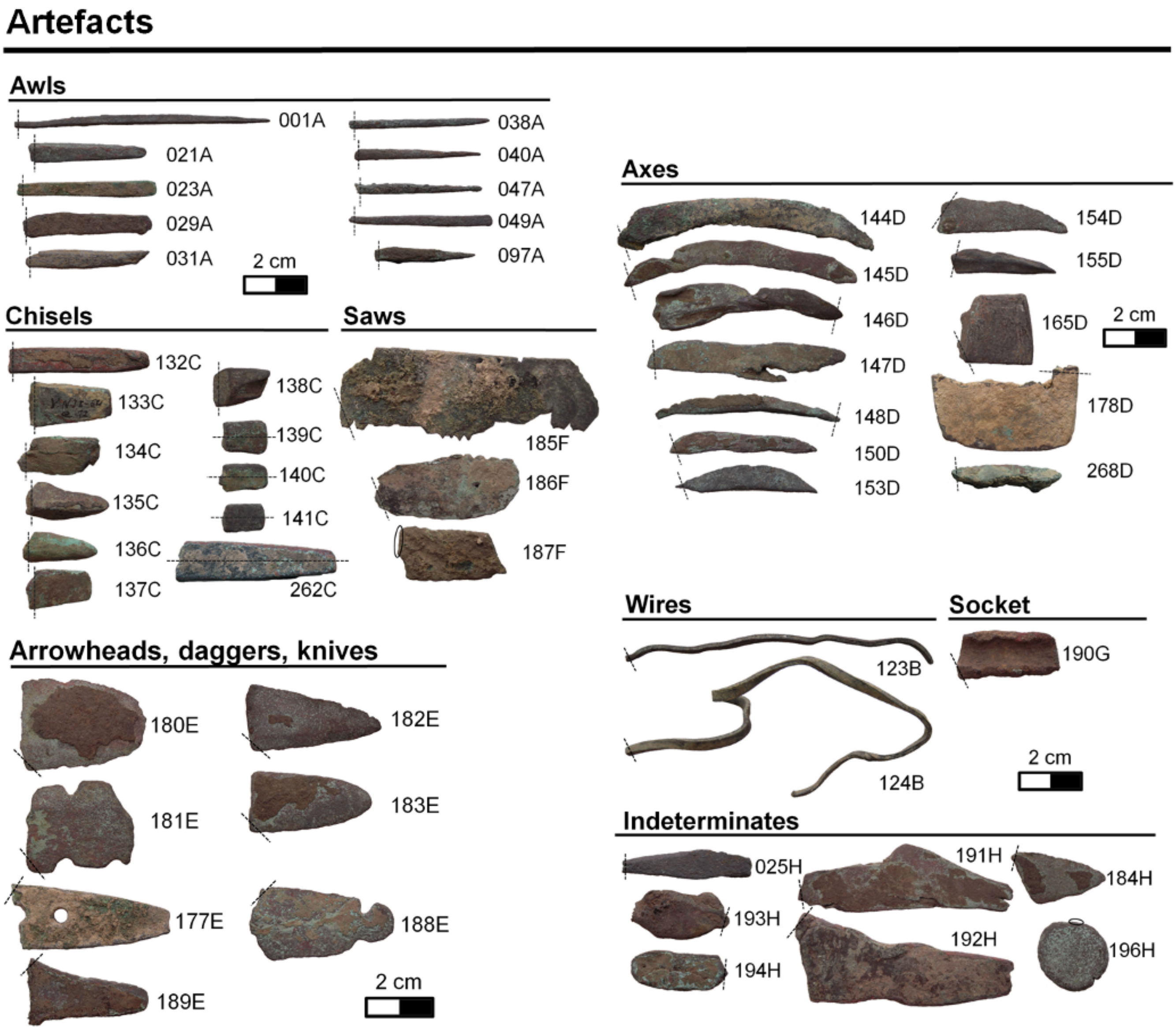

Fig. 2. Artefact collection from VNSP(in Pereira et al.2013).

Materials and Methods

The metallurgical remains selected for this study include 8 crucible fragments, 6 pieces of slag and 7 metallic prills (Fig. 3).

All the crucible fragments have rims with thick walls and curved shapes, with the exception of VNSP280, a flat fragment, possibly from the bottom of a crucible. In some cases metallurgical remains were macroscopically visible adhering to the ceramic body (see Table 1).

Micro-EDXRF analyses of the prills were performed with an ArtTAX Pro spectrometer in order to determine their elemental composition. This spectrometer is equipped with a low power 30 W Mo X-ray tube and an electro-thermally cooled silicon drift detector (FWHM 160 eV at 5.9 keV). Polycapillary lenses collimate the primary X-ray beam enabling a spatial resolution of approximately 100 μm. Quantitative determinations were done using WinAxil software with readings performed in 3 different spots on the cleaned areas for each artefact and using experimental calibration factors calculated through the analysis of the standard reference material Phosphor Bronze 551 from

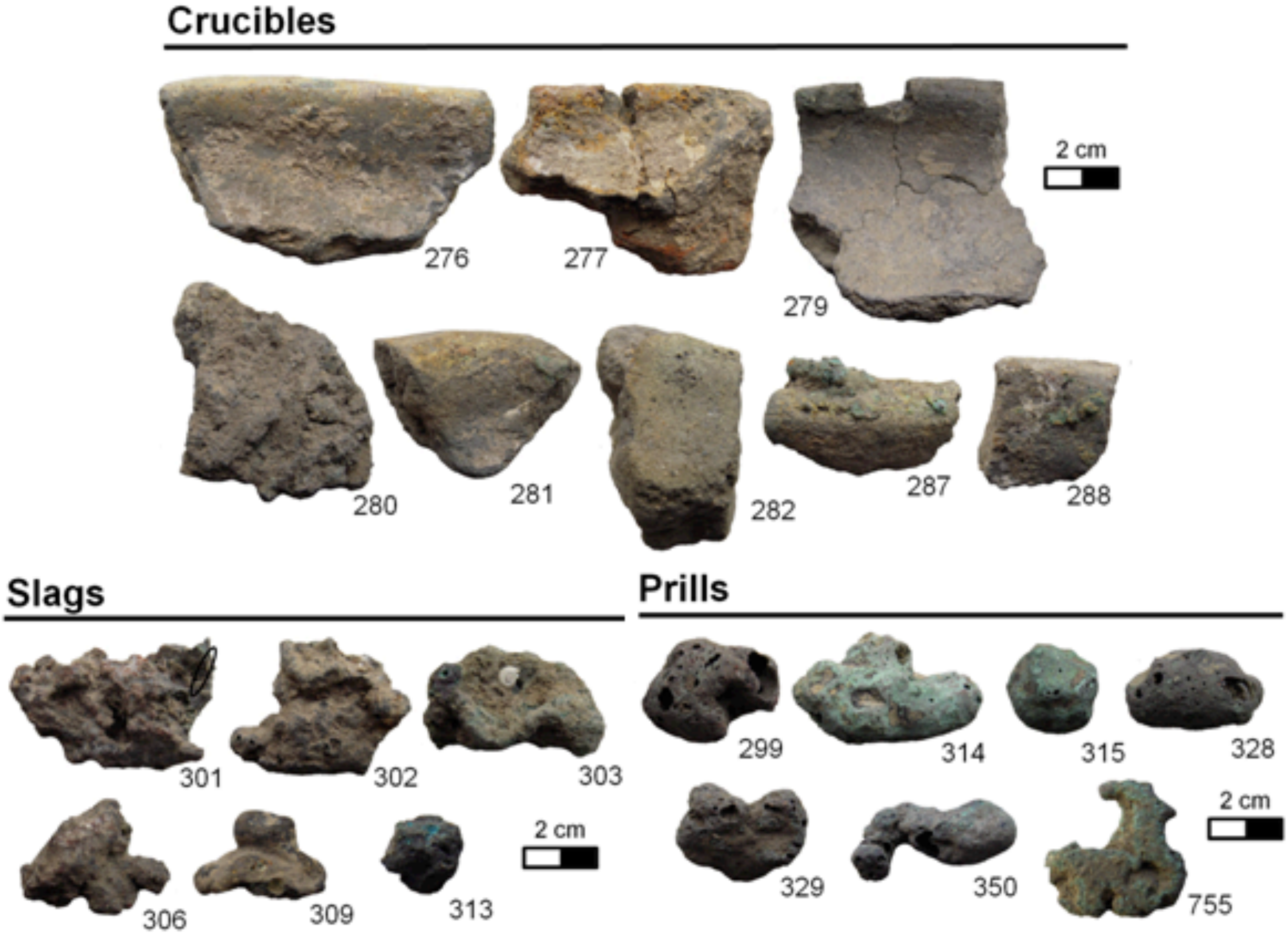

Fig. 3. Analysed crucibles, slag and prills from VNSP.

EDXRF analyses were performed on the inner and outer surfaces of the crucibles in order to establish the enriched elements in the areas that have more probability of being affected by the metallurgical operation (typically the rim and the inner surface). The equipment used was a Kevex 771 spectrometer 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).

The analysed slag and prills have variable sizes with irregular or more rounded shapes. The pieces of slag and the metallic prills were manually cleaned to remove corrosion products, in a small area (~4 mm^2).

British Chemical Standards (BCS). The quantification limits for elements usually present in archaeological copper and copper-arsenic alloys were 0.04 wt% Cu, 0.5 wt% Sb, 0.1 wt% Pb, 0.1 wt% As, 0.05 wt% Fe, 0.04 wt% Zn and 0.07 wt% Ni. Additional experimental details were previously published (Valério *et al.* 2007).

Metallographic observation of the small cleaned areas was carried out with an optical microscope Leica DMI 5000 M (50x to 1000x), under bright field (BF), dark field (DF) and polarized light (Pol) illumination.

Microstructural characterization of prills and slag was made in a scanning electron microscope Zeiss DSM 962 equipped with secondary electron (SE) and backscattered electron (BSE) detectors. Elemental semi-quantifications were made with the ZAF method with an Oxford Instruments INCA-sight EDS spectrometer equipped with an ultrathin window to detect elements with low atomic number (Z > 5). Working conditions consisted of 20 kV accelerating voltage, 1-2 μm spatial resolution, 70 μA of beam emission current, and 25 mm working distance. The EDS spectra were acquired for 60 s livetime with dead time adjusted to 30-40%.

Results and Discussion

Crucibles

The comparison of EDXRF spectra of inner and outer surfaces of the crucible fragments from VNSP shows enrichment in some elements on the inner surface (Table 1).

Table 1. Enriched elements in the surface areas of the crucibles affected by metallurgical operation: typically inner wall or rim. Macroscopically visible slag/metallic remains: × - p resent; n.d. – not detected.

Crucibles	Cu	As	Slag/metallic
VNSP276	+	+	×
VNSP277	+	+	n.d.
VNSP279	+	++	×
VNSP280	+	+++	×
VNSP281	+	++	×
VNSP282	+	+	n.d.
VNSP287	+	n.d.	×
VNSP288	+	+	×

An example of EDXRF spectra showing the enrichment in Cu and As elements in the inner wall surface of the crucible fragment VNSP280 is presented in Fig. 4.

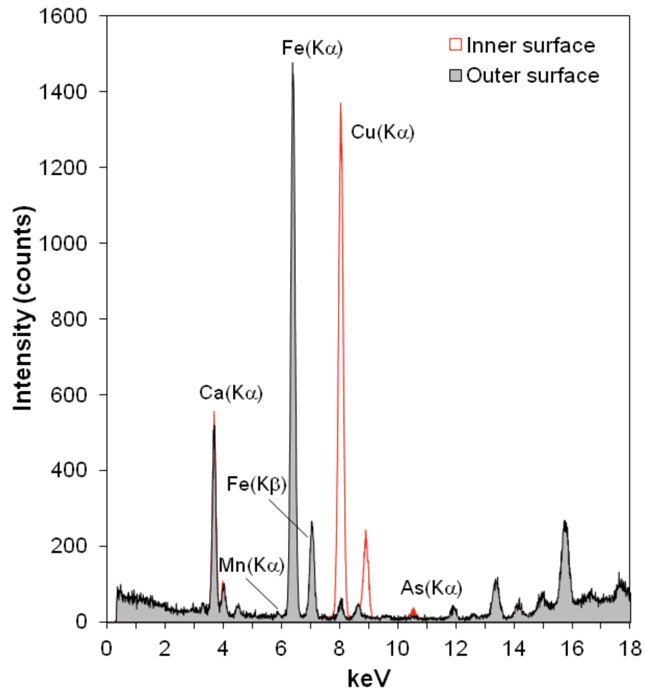

Fig. 4. EDXRF spectrum of the inner surface (red) with visible slag/metallic vestige compared with the outer surface (black spectrum) of VNSP280.

The enrichment in certain elements in the inner wall and/or rim surfaces of the crucibles is indicative of the metallurgical processes, concerning the metal or metals, performed on these ancient production remains. EDXRF results of the crucible fragments point to metallurgical activities in VNSP involving copper and copper with arsenic.

Slag

The identification of the slag main constituents is presented in Table 2.

Table 2. SEM-EDS analysis of slag from VNSP (Cup – cuprite, Ten – tenorite, Mag – magnetite, Del – delafossite; × – present; n.d. – not detected).[1] – Copper chloride; [2] – Vegetal structure remains (later identification indicates tree of the genus Quercus).

Slag	Cup	Ten	Mag	Del	Others
VNSP301	×	×	×	×	Cu-Cl-O[1]
VNSP302	×	n.d.	×	n.d.	Metallic Cu,
VNSP303	×	×	n.d.	n.d.	C+Cu+Si+Ca[2], Cu-Cl-O[1]
VNSP306	×	n.d.	×	×	-
VNSP309	×	n.d.	×	n.d.	Metallic Cu
VNSP313	×	n.d.	×	×	Cu-As

SEM-EDS characterisation identified a vitreous and heterogeneous matrix of aluminium silicates (Al, Si, K and Fe) with several copper oxides (cuprite and tenorite) and metallic inclusions in all pieces of slag. (Example: slag VNSP301 - Fig. 5).

Slag are mainly composed of complex silicates resulting from reactions between ore/metal with the crucible ceramics and the ash resulting from the wood/charcoal used for heating during smelting or melting operations (Tylecote 1992).

The low viscosity of heterogeneous slag commonly causes metallic globules to be trapped. In all the analysed pieces of slag, oxidised copper globules (cuprite and/or tenorite) were identified (Table 2). These globules may result from re-oxidising metallic copper, indicating a limited control over the redox conditions. They could also result from corrosion during burial of the metallurgical remains over an archaeological timescale (Hauptmann 2007).

In only two cases were small metallic copper globules (VNSP302 and VNSP309) present (Fig. 6A). In the case of slag VNSP313 copper globules with an arsenic rich phase (As-rich (γ) phase - Cu_3As) were also identified (Fig. 6B). The metallic globules analysed so far show coarse granular microstructures that evidence a slow cooling rate of the slag inside the crucible.

Magnetite (Fe_3O_4 - $FeO.Fe_2O_3$) was present in all slag with the exception of VNSP303. Delafossite ($CuFeO_2$) was identified in only 3 cases (VNSP301, VNSP306 and VNSP313). These observations suggest, with the exception of VNSP303, iron-rich slag formed under local oxidising conditions and provide evidence of a poorly reducing

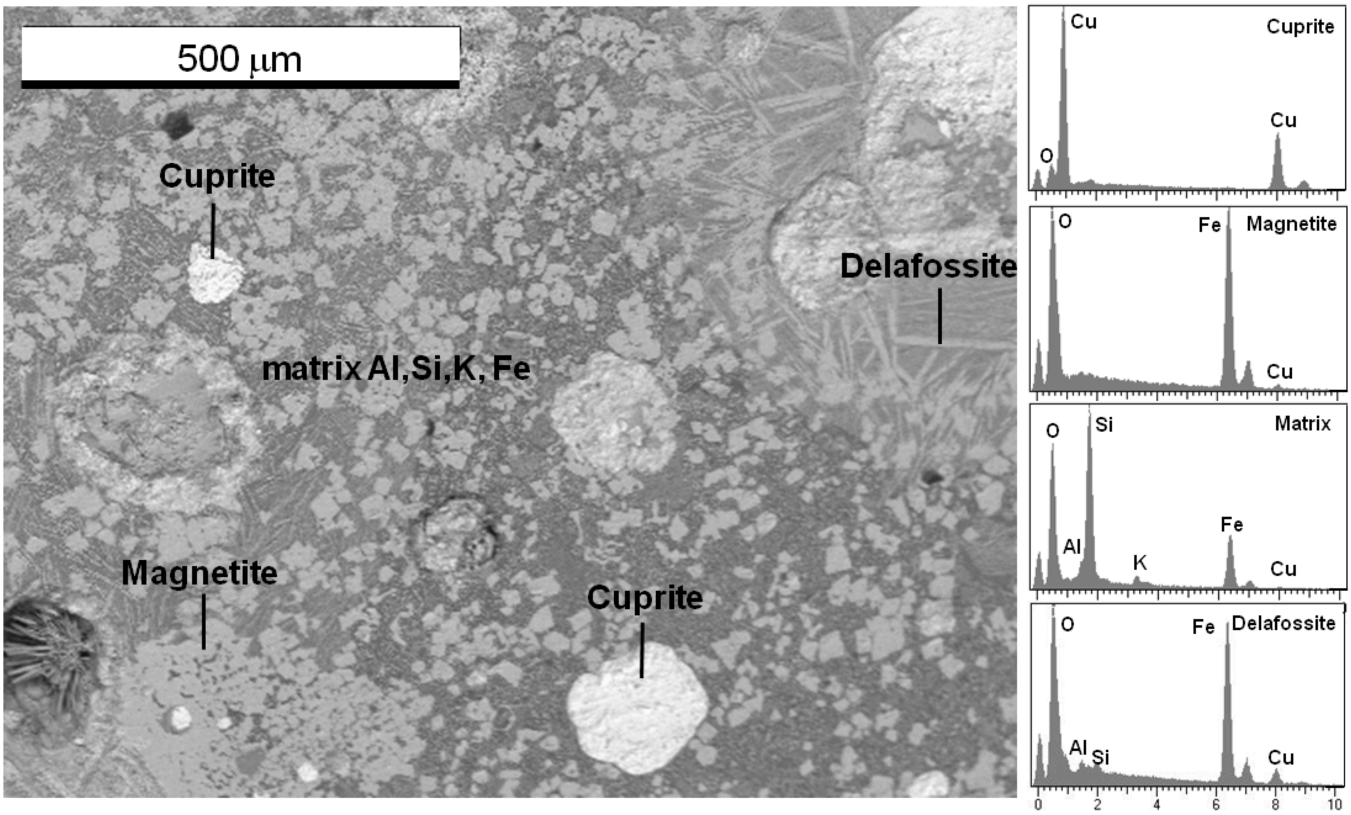

Fig. 5. SEM-BSE image of slag VNSP301, showing a highly heterogeneous matrix and the identification of cuprite globules, magnetite and delafossite.

atmosphere in the reaction vessel during the metallurgical operation.

In the majority of cases, these kind of metallurgical remains are difficult to attribute to melting or smelting operations. Smelting slag tend to be richer in iron silicates while the melting slag are richer in non-ferrous silicates and wood ash (Tylecote 1992). The highly heterogeneous matrices with several metallic inclusions are characteristic of more ancient slag produced in primitive smelting operations. Considering all these characteristics together, the slag analysed in this study provide evidence that could indicate smelting operations, with the exception of VNSP303. The identification of a vegetal structure and the absence of iron oxide compounds like magnetite and delafossite in VNSP303 could be indicative of a melting slag.

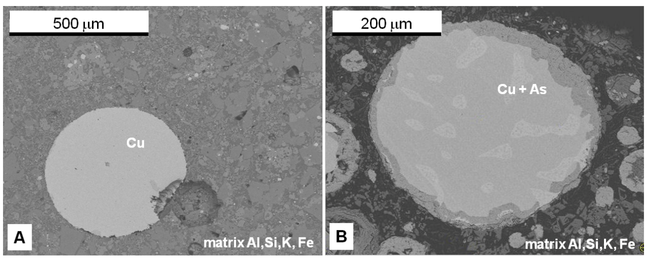

Fig. 6. SEM-BSE image showing the EDS identification of the metallic globule constituents: A:Cu (slag VNSP309) and B:Cu+As (slag VNSP313).

The later formation of corrosion products during burial of the metallurgical remains could explain the presence of copper chloride in VNSP301, possibly atacamite or paratacamite ($Cu_2Cl(OH)_3$).

The absence of impurities could also provide some indications about the ores used in the reduction process. The use of more complex copper ores than copper carbonates would possibly result in higher amounts of impurities and more variable compositions of the slag matrix.

Metallic Prills

Micro-EDXRF results are presented in Table 3 and indicate that the selected prills are composed of copper or copper with arsenic. Iron content is always below the quantification limit (<0.05%) with the exception of VNSP317 presenting 0.06% Fe, still a rather low amount.

These prills with low iron contents point to a poor reduction environment during the metallurgical operations involved in their production (smelting).

Other minor elements such as antimony, lead, zinc or nickel were not detected or were under the quantification limit.

Table 3. Elemental composition of the prills determined by micro-EDXRF (wt%).

Metallic prills	Cu (%)	As (%)	Fe (%)
VNSP316	99.9±0.1	<0.10	<0.05
VNSP317	97.8±0.2	2.12±0.26	0.06±0.10
VNSP318	98.9±0.1	1.10±0.15	<0.05
VNSP319	99.7±0.1	0.23±0.10	<0.05
VNSP320	98.8±0.1	1.18±0.10	<0.05
VNSP321	98.2±0.1	1.83±0.20	<0.05
VNSP327	99.6±0.1	0.38±0.10	<0.05

The copper and arsenical copper artefact composition from VNSP is consistent with the elemental distribution of the prills analysed up to now (Table 3) (Pereira *et al* 2013).

Conclusion

The analysed collection of metallurgical production remains from VNSP is consistent with the overall picture of copper and arsenical copper production in the Chalcolithic of Central Portugal. Results obtained on the elemental composition in crucible fragments, slag and prills indicate copper and arsenical copper artefact production. Slag analysed up to now give indications of melting and smelting operations. Also, the large quantity of scrap material recovered in this settlement suggests the existence of remelting and recycling operations (melting operations).

The heterogeneous composition and low viscosity of the slag are also characteristic of more ancient slag. The elemental composition of prills analysed so far is also indicative of copper and arsenical copper artefact production.

These results are in accordance with the earlier evidence of copper based metallurgical activities in the Iberian Peninsula where copper and arsenical copper were the only metals used in the manufacture of artefacts (Ruíz Taboada *et al.* 1999).

Further studies intend to continue the research concerning the slag and metallic lining of the crucibles found in VNSP. The studied fragments of slag are a small part of the larger collection from VNSP. It is important to explore further materials to have a more consistent view of the operations used, including the determination of elemental composition and microstructural characterization of a larger set of prills and metallic nodules. This will allow us to have more consistent information about the arsenic distribution in the metallurgical remains and a better comprehension of the artefact collection from VNSP.

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