X-RAY SPECTROMETRY

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Micro-EDXRF study of Chalcolithic copper-based artefacts from Southern Portugal

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A collection of 39 metallic artefacts recovered in archaeological sites of Southern Portugal was studied by micro-EDXRF to identify their compositions and the use of metal among ancient communities. Artefacts presented different typologies such as tools (e.g. awls, chisels and a saw) and weapons (e.g. daggers and arrowheads) mostly belonging to 2500–2000 BC. The results show copper with variable amounts of As and very low content of other impurities, such as Fe, Pb or Sb. Moreover, nearly half of the collection is composed by arsenical copper alloys, and an association was found between arsenic content and typology because the weapons group (mostly daggers) present higher values than tools (mostly awls). These results suggest some criteria in the selection of arsenic-rich copper ores or smelting products. Finally, the compositions were compared to those of other collections from neighbouring regions and different chronology to determine metallurgical parallels. Copyright © 2015 John Wiley & Sons, Ltd.

Introduction

The study of the ancient metallurgy can provide important information about the technological progress of prehistoric societies. It is known that copper with variable amounts of arsenic and low concentrations of other impurities was the dominant metallurgical production in Iberian Peninsula during Chalcolithic till Middle Bronze Age. [1,2] Nevertheless, the true significance of arsenical copper as an alloy, intentional or not, is still uncertain and subject of many discussions. It is recognized that the addition of arsenic to copper leads to colour changes and, in certain conditions, to an increase of hardness and toughness, but another matter is if prehistoric man was aware of these advantages of arsenical copper alloys.

In relation to the Portuguese territory, only a few studies have been carried out and, for the most part, concerning Chalcolithic metallurgical evidences from the Portuguese Estremadura. [3–7] The research reveals that the artefacts are made of copper with low and variable arsenic contents, suggesting that even though no significant association between the arsenic amount and mechanical properties was found, there is some correlation between some artefact typologies and the arsenical copper alloy (considered as copper with more than 2 wt.% As). However, it should be emphasized that there are no modern analytical studies regarding the understanding of Chalcolithic metallurgy in the southern region of the Portuguese territory.

In the present research a group of about 40 artefacts from Southern Portugal was analysed with micro energy dispersive X-ray spectrometry in order to identify their major and trace elements composition. EDXRF is one of the firsts analytical techniques used in cultural objects studies providing quantitative analysis of elements with relatively fast, multi-elemental and non-destructive analysis. [8–10] In the last decades, micro-EDXRF systems have been developed to have minimum lateral resolutions (typically, the spot size is $<300\,\mu$m)[11–13] thus allowing the analysis of minute areas and becoming essential to study different types of cultural materials. Concerning the superficial corrosion commonly found in archaeological metals and the relatively low penetration of the X-rays, the removal of the upper surface layer is necessary to effectively analyse the underlying metal. The use of micro-EDXRF requires only the cleaning of a very small sized area thus causing a minimum impact to the object.

Besides the identification of the composition of metals used in Southern Portugal during the Chalcolithic, a comparison with neighbouring regions and different chronological periods was made in order to better understand that ancient metallurgy in the Southwestern end of the Iberian Peninsula.

Materials and methods

Artefact collection

The set of artefacts selected for study was recovered in archaeological excavations and surveys carried out in five different archaeological sites from Southern Portugal: Atalaia do Peixoto (AP), Castro dos Ratinhos (CR), São Pedro (SP), Três Moínhos (TM) and Tholos de Caladinho (TC). The collection is mostly composed by artefacts from São Pedro, mainly belonging to 2500–2000 BC [14]. The remaining artefacts have a similar broad chronology, being culturally ascribed to the Beaker Period, with the exception of that of Atalaia do Peixoto, which is from an earlier Chalcolithic phase.

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Artefacts include different typologies such as weapons and tools. An absence or low incidence of ornaments is common in Chalcolithic collections, perhaps suggesting that copper ornaments had not reached an aesthetic and prestige value like those made of gold. [15] Weapon types comprise arrowheads and daggers, which could serve many general purposes. Some consider them as tools related with everyday life tasks or ceremonial practices, as for instance the case of daggers. [16] Tools include different types (awls, an axe, chisels, spatulas, a needle and a saw) that were used by Chalcolithic communities to work with different materials, such as wood, leather or ceramics. One of the spatulas from São Pedro settlement (SP58) presents a peculiar shape resembling a large spoon. Finally, other artefacts have an indeterminate function since at the time of recovery they were too fragmented and shapeless to enable a correct identification.

Sample analysis

The elemental composition of metallic artefacts was determined by micro-EDXRF spectrometry. Because of the cultural and archaeological significance of these materials, the preparation involved only the cleaning of a very small area (about 3–5 mm diameter) at the surface, which was latter polished with a manual drill and diamond pastes of increasingly smaller grit size (6 μm to 1 μm). In the few artefacts that were already broken it was easier, and has a lower impact on the artefact, to cut a small section (~1–3 mm long). These analyses were done in the small sampled cross section previously mounted in epoxy resin, polished with abrasive papers (1000, 2500 and 4000 grit sizes) and finished with 3 μm and 1 μm diamond pastes.

Micro-EDXRF analyses were performed using an ArtTAX Pro spectrometer from Bruker (Germany), operating with a low power molybdenum X-ray tube, focusing polycapillary lens and a silicon drift electro-thermally cooled detector with a resolution of 160 eV at 5.9 keV (Mn-Kα). The accurate positioning system and polycapillary optics enable a small area of primary radiation at the sample, ~70 μm diameter [11]. Artefacts were analysed with a tube voltage of 40 kV, a current intensity of 600 μA and a live time of 100 s. Three analyses were made in different places, to take into account possible sample heterogeneity, being considered the average value.

Quantitative determinations were made with WinAxil software involving secondary fluorescence corrections and experimental calibration factors calculated with the analysis of the certified standard reference material British Chemical Standards (BSC) Phosphor Bronze 551. In order to calculate the uncertainty associated to the analytical technique another certified standard reference material was used: Phosphor Bronze BCS 552 (Table 1). Overall, the method presents relative errors below 10%. The higher error for zinc results from the spectral interference between the characteristic lines of zinc and copper (Zn-Kα with Cu-Kβ). In the case of iron, the lower accuracy is because of the proximity to the detection limit, in addition to the overlapping of Fe-Kα and Cu-Kα escape peak.

Quantification limits for the elements usually detected in this type of artefacts were determined with the analysis of reference standards BCS Phosphor Bronze 551 and Industries de la Fonderie 5: 0.33 wt.% Sb, 0.10 wt.% Pb, 0.05 wt.% Fe, 0.04 wt.% Cu and 0.10 wt.% As (calculated as 10/3×detection limit). The remaining elements that sometimes are found in this type of archaeological materials were below the detection limit, namely 0.15 wt.% Sn, 0.01 wt.% Ni and 0.01 wt.% Zn (calculated as 3×background$^{0.5}$/sensitivity). Sn and Sb exhibit higher values when compared to other elements because of the lower fluorescence yield of the Sn-L and Sb-L lines.

Results and discussion

Micro-EDXRF analyses of Chalcolithic artefacts allowed a preliminary identification of two main compositional groups comprising pure copper and copper with variable arsenic contents (Fig. 1).

Table 1. Micro-EDXRF analysis of certified standard reference material BCS 552 (average ± standard deviation)

	Cu (wt.%)	Sn (wt.%)	Pb (wt.%)	Ni (wt.%)	Zn (wt.%)	Fe (wt.%)
Certified	87.7	9.78	0.63	0.56	0.35	0.12
Obtained	88.1 ± 0.1	10.0 ± 0.06	0.64 ± 0.04	0.60 ± 0.02	0.46 ± 0.03	0.10 ± 0.01
Uncertainty	0.4%	2.2%	1.6%	7.1%	31%	20%

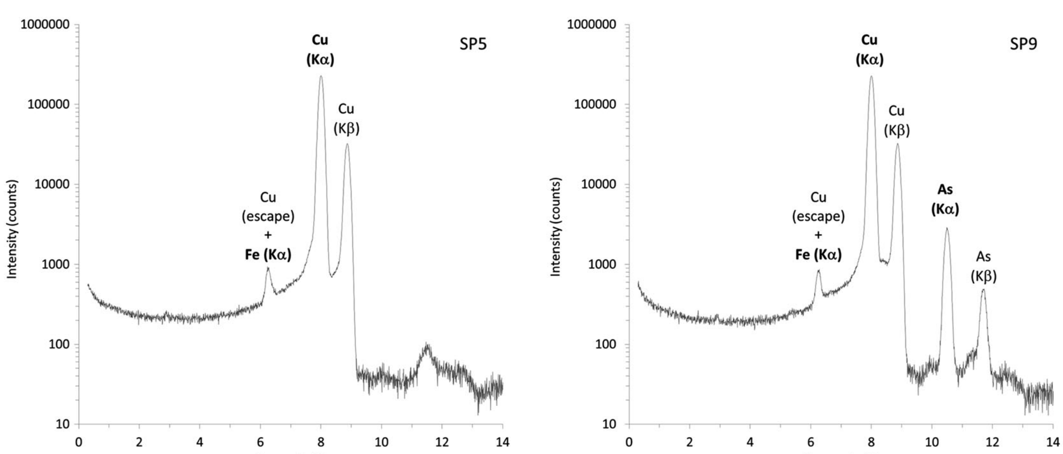

Figure 1. Micro-EDXRF spectra of Chalcolithic daggers from São Pedro: (SP5) pure copper and (SP9) arsenical copper (note the logarithmic scale on y-axis; figures in bold correspond to X-ray lines used for quantification).

Analytical results show that the arsenic content is variable reaching values up to 5.08 wt.%, the iron content is always very low (<0.05 wt.%) and only two examples have measurable amounts of other elements, namely 0.78 wt.% Sb (axe TM01) and 0.14 wt.% Pb (plaque SP14) (Table 2). These differences on arsenic contents confer different properties to the alloy, including the decreasing of melting temperature and casting defects, in addition to hardening effects and colour modifications.

Moreover, a slight difference was verified in the arsenic content distribution between the group of weapons (average of 3.0 ± 1.5 wt.% As, n = 13) and tools (average of 2.2 ± 1.6 wt.% As, n = 19) (Fig. 2). The higher frequency of arsenical copper alloys from weapons may indicate some criteria in the selection of arsenic-rich copper ores or smelting products (arsenic-rich nodules). The rational for this may be related to increase the object hardness, as the addition of arsenic leads to an improvement of mechanical properties, especially upon cold work. However, the addition of As to copper also allows to turn reddish-copper into silvery-copper. The colour change of Chalcolithic weapons was already referred as a way to revert the object functionality to a more prestige or aesthetic role. [3] In another example, at Tepe Yahya (Iran) the tools are made from low-As copper (1–2 wt.% As) while a number of decorative items is made of high-As copper (3–7 wt.% As), possibly because the value of an object was determined by its colour, and thus the more arsenic-rich material with its silvery sheen would be desirable for decorative items. [17] However, the relation between type and function is often complex, e.g. the use-wear analysis of Chalcolithic artefacts from the Italian peninsula shows that most classes embody both utilitarian and non-utilitarian values: axes were primarily used for practical tasks, but were mostly withdrawn from circulation when still usable, while daggers were employed in a range of symbolical practices that left little wear on cutting edges. [18]

The low-arsenic content of some artefacts may be related with a possible metal recycling, if we consider that these items could result

Table 2. Elemental composition of artefacts from Chalcolithic sites in Southern Portugal (Atalaia do Peixoto, Castro dos Ratinhos, São Pedro, Tholos de Caladinho and Três Moínhos; n.d.—not detected)

Type	Artefact	Code	Cu (wt.%)	As (wt.%)	Pb (wt.%)	Sb (wt.%)	Fe (wt.%)
Weapons	Arrowhead	SP61	96.3 ± 0.5	3.65 ± 0.46	n.d.	n.d.	<0.05
	Arrowhead	SP68	94.8 ± 0.5	4.92 ± 0.08	n.d.	n.d.	<0.05
	Arrowhead	TC06	99.0 ± 0.1	0.98 ± 0.10	n.d.	n.d.	<0.05
	Dagger	CR04	95.8 ± 0.1	4.17 ± 0.10	n.d.	n.d.	<0.05
	Dagger	SP05	99.9 ± 0.1	0.10 ± 0.01	n.d.	n.d.	<0.05
	Dagger	SP09	97.0 ± 0.1	2.89 ± 0.20	n.d.	n.d.	<0.05
	Dagger (?)	SP15	98.7 ± 0.3	1.22 ± 0.35	n.d.	n.d.	<0.05
	Dagger	SP55	96.8 ± 0.4	3.15 ± 0.35	n.d.	n.d.	<0.05
	Dagger	SP56	96.1 ± 0.2	3.86 ± 0.25	n.d.	n.d.	<0.05
	Dagger	SP67	96.5 ± 0.1	3.45 ± 0.83	n.d.	n.d.	<0.05
	Dagger	TM02	95.5 ± 1.2	4.52 ± 1.20	n.d.	n.d.	<0.05
	Dagger	TM03	97.7 ± 0.9	2.33 ± 0.90	n.d.	n.d.	<0.05
	Dagger	TM04	95.6 ± 0.1	4.38 ± 0.10	n.d.	n.d.	<0.05
Tools	Awl	SP17	96.4 ± 0.5	3.54 ± 0.44	n.d.	n.d.	<0.05
	Awl	SP22	99.9 ± 0.1	0.10 ± 0.01	n.d.	n.d.	<0.05
	Awl	SP23	95.5 ± 0.6	4.41 ± 0.57	n.d.	n.d.	<0.05
	Awl	SP57	97.5 ± 0.2	2.46 ± 0.16	n.d.	n.d.	<0.05
	Awl	SP62	96.3 ± 0.1	3.62 ± 0.21	n.d.	n.d.	<0.05
	Awl	SP64	98.7 ± 0.1	1.27 ± 0.05	n.d.	n.d.	<0.05
	Awl	SP66	98.6 ± 0.1	1.40 ± 0.12	n.d.	n.d.	<0.05
	Awl	SP69	97.7 ± 0.1	2.23 ± 0.01	n.d.	n.d.	<0.05
	Awl	SP71	99.3 ± 0.1	0.62 ± 0.01	n.d.	n.d.	<0.05
	Awl	SP72	94.9 ± 0.5	5.08 ± 0.50	n.d.	n.d.	<0.05
	Axe	TM01	98.8 ± 0.4	0.44 ± 0.12	n.d.	0.78	<0.05
	Chisel	SP06	98.5 ± 0.2	1.48 ± 0.21	n.d.	n.d.	<0.05
	Chisel	SP20	96.1 ± 0.1	3.84 ± 0.12	n.d.	n.d.	<0.05
	Chisel	SP60	99.9 ± 0.1	0.10 ± 0.01	n.d.	n.d.	<0.05
	Chisel	SP70	99.1 ± 0.1	0.84 ± 0.01	n.d.	n.d.	<0.05
	Needle	SP07	99.0 ± 0.1	0.96 ± 0.12	n.d.	n.d.	<0.05
	Saw	SP59	97.1 ± 0.1	2.89 ± 1.00	n.d.	n.d.	<0.05
	Spatula	SP58	95.3 ± 0.1	4.38 ± 0.01	n.d.	n.d.	<0.05
	Spatula	SP63	97.6 ± 0.4	2.37 ± 0.37	n.d.	n.d.	<0.05
Others	Plaque	SP14	99.4 ± 0.2	0.10 ± 0.01	0.45	n.d.	<0.05
	Fragment	AP01	99.9 ± 0.1	0.10 ± 0.01	n.d.	n.d.	<0.05
	Fragment	SP02	98.1 ± 0.3	1.87 ± 0.29	n.d.	n.d.	<0.05
	Fragment	SP13	98.4 ± 0.1	1.54 ± 0.14	n.d.	n.d.	<0.05
	Fragment	SP65	99.7 ± 0.1	0.29 ± 0.04	n.d.	n.d.	<0.05
	Fragment	TM05	96.2 ± 0.1	3.84 ± 0.10	n.d.	n.d.	<0.05
	Rod	SP74	99.9 ± 0.2	0.10 ± 0.01	n.d.	n.d.	<0.05

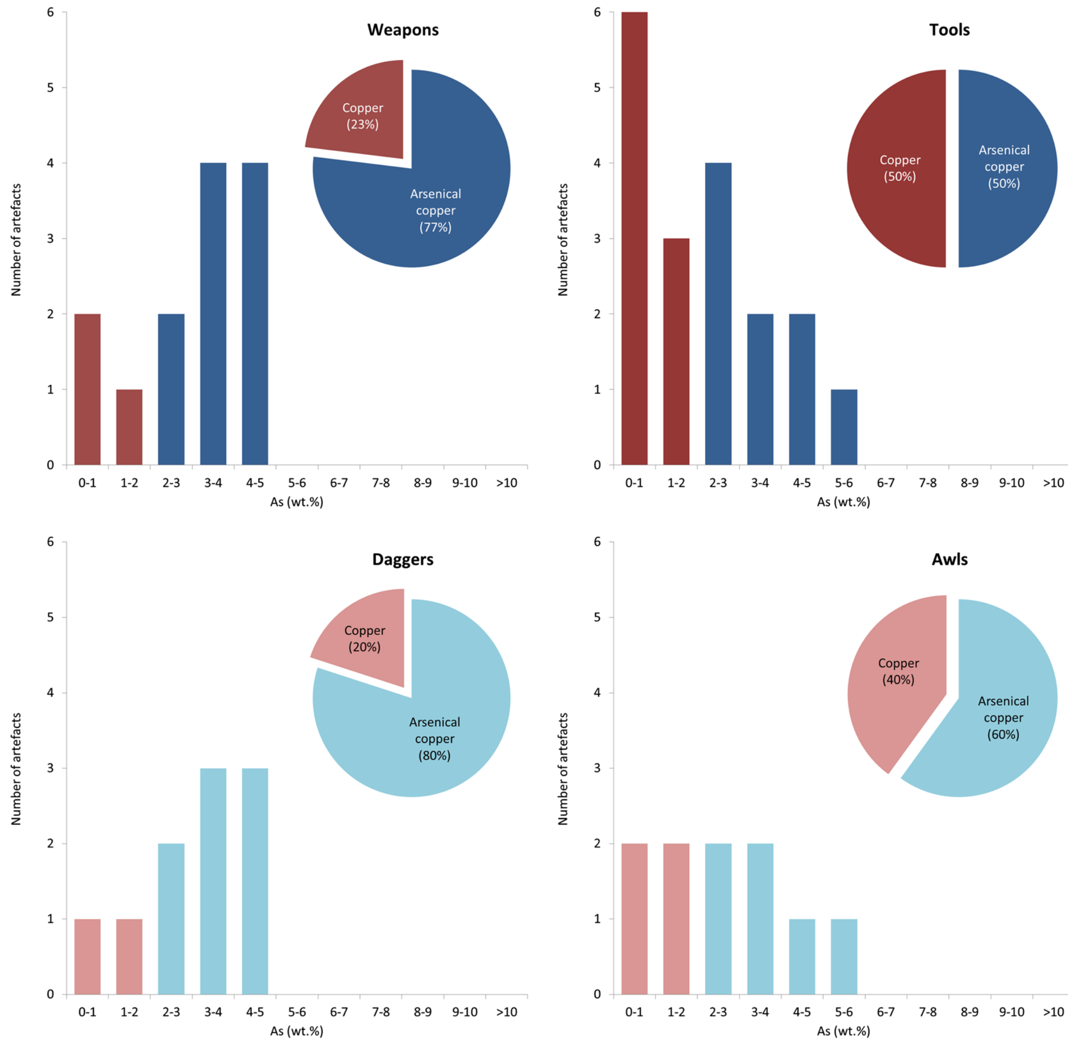

Figure 2. Histograms of arsenic contents and distributions of Chalcolithic copper and arsenical copper weapons, tools, daggers and awls in Southern Portugal.

from a reutilization of broken artefacts reconditioned by thermomechanical operations. The use of scrap made of arsenical copper under prehistoric conditions (oxidising atmosphere) leads to arsenic losses by evaporation of As_2O_3 fumes. Experiments made by McKerrell and Tylecote [19] on arsenical copper ingots showed an arsenic reduction from 4.2 wt.% to 0.8 wt.% after a single melting and several hot workings under oxidising conditions.

The comparison between daggers and awls (the only types with a significant number of examples, 10 each) also identified a tendency to higher amounts of arsenic on daggers (Fig. 2). The relation of arsenical copper alloy with some typologies such as Palmela points, saws, long awls and tanged daggers was already identified at the Chalcolithic settlement of Zambujal. [4] Authors suggested that arsenic copper alloys could be obtained by the selection by colour of arsenic-rich metal droplets obtained through the smelting of arsenic bearing copper ores.

Studies on Chalcolithic artefacts from Vila Nova de São Pedro [3] and Leceia, [5] located in the neighbouring region of Southern Portugal to the North (Portuguese Estremadura), reveal a somewhat lower frequency of arsenical copper alloys (Fig. 3). Moreover, the arsenic contents distribution has been interpreted as resulting from the natural variability of arsenic impurities in the smelted copper ores. In the nearby region to the East (Western Andalusia), the study of Chalcolithic artefacts [20] has identified a similar situation although with a percentage of arsenical copper alloys that is closer to the obtained for Southern Portugal (Fig. 3). The arsenic variability in several sites of Western Andalusia was associated to the thermomechanical treatments because the lower arsenic amounts were often detected in worked artefacts.

In the Southeastern Iberian Peninsula the high arsenic content was associated, not only with the ores utilized, but also as an indirect indicator of the low use of scrap metal because of the arsenic losses during thermal recycling processes. [21] Contrary, in other regions like the Levant such regional differences were attributed to the existence of maritime and overland trade routes that facilitate the access to raw materials. [22] Overall, the differences in the frequency of Chalcolithic arsenical coppers are often attributed to the different copper mines. However, in the Portuguese Estremadura the Pb isotopic compositions strongly suggest the use of copper from the Ossa Morena Zone [4,23] covering part of Western Andalusia and Southern Portugal.

Chronologically speaking, the circumstances become even more interesting because Middle Bronze Age artefacts from Southern Portugal have a higher proportion of arsenical copper alloys [24,25] (Fig. 3). In the Eastern Mediterranean, an estimated 20 tons of slag from the Early Bronze Age site of Arisman provided evidence of

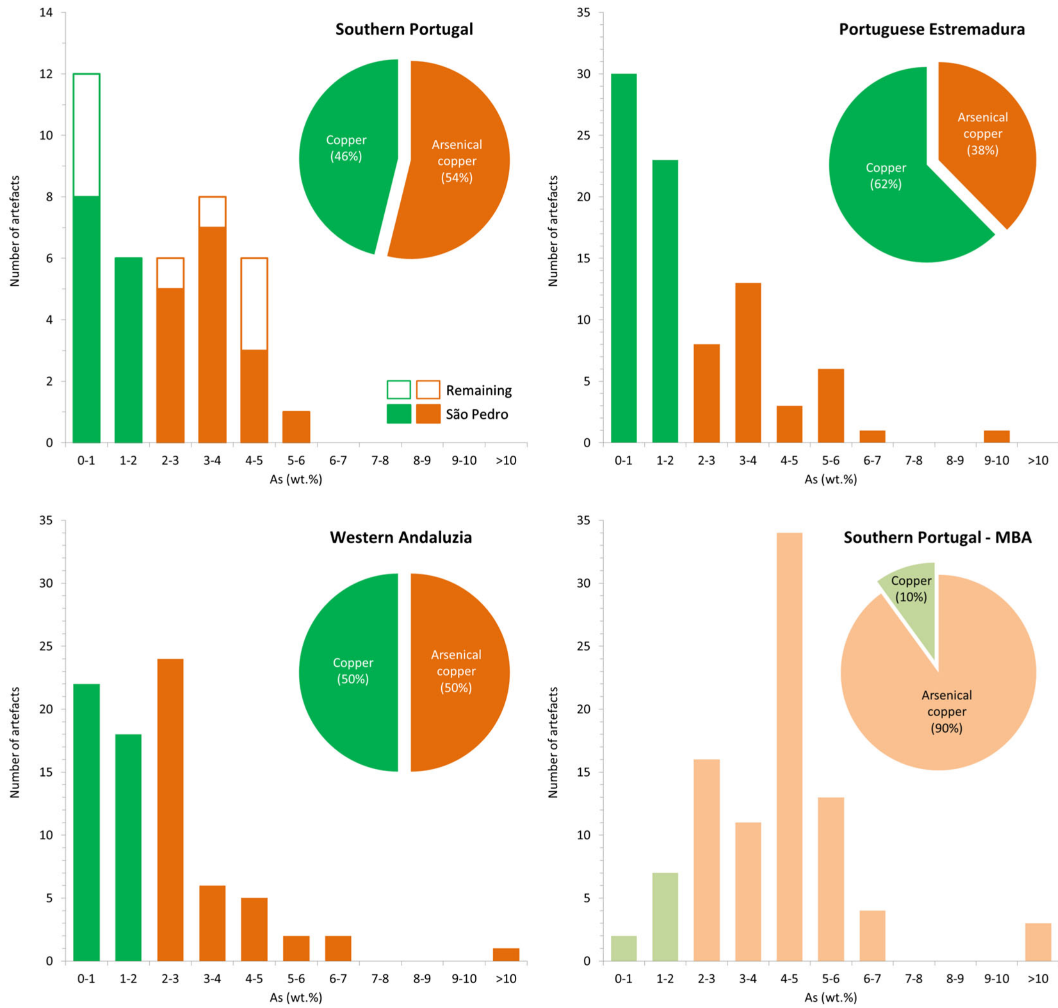

Figure 3. Histograms of arsenic contents and distributions of Chalcolithic copper and arsenical copper artefacts in Southern Portugal, Portuguese Estremadura [3,5] and Western Andaluzia, [20] in addition to Middle Bronze Age copper and arsenical copper artefacts from Southern Portugal. [24,25]

large-scale production of metal including arsenical coppers that could have been produced by smelting a mixture of speiss with copper ore or metallic copper. [26] Nevertheless, such archaeological evidences do not exist in the Iberian Peninsula and the arsenic-rich alloys from this incipient stage of metallurgical technology could be obtained by picking arsenic-rich smelting prills, as suggested for other Chalcolithic sites located in near (Zambujal [4]) or distant regions (Shiqmim, Israel [27])

Conclusions

The micro-EDXRF as a non-destructive analytical technique has proven to be an important tool to study archaeological artefacts allowing sample preservation for further studies, museological exhibition and cultural preservation.

The present study revealed a collection of 2500–2000 BC artefacts from Southern Portugal comprising from pure copper to arsenical copper alloys with up to 5 wt.% As. Although the true significance of arsenical copper alloys is still a matter of debate, the data collected indicate the preference for higher arsenic-copper alloys for weapons such as daggers that can be considered prestige objects among those communities. This primitive technology is comparable to the Chalcolithic metallurgies found in other regions of the Iberian Peninsula, but has a lower amount of arsenical copper alloys than Middle Bronze Age archaeological contexts in Southern Portugal.

Finally, additional studies concerning Chalcolithic and Middle Bronze Age artefacts with different functions and typologies are essential to better establish the evolution and use of copper and arsenical copper alloys in this southwestern end of the Iberian Peninsula.

Acknowledgements

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