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Inclusions and metal composition of ancient copper-based artefacts: a diachronic view by micro-EDXRF and SEM-EDS

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A diachronic view of the metallurgy in the Portuguese territory during the first three millennia after its appearance in the Iberian Peninsula is presented based on the current state of the art. Results of micro-energy dispersive X-ray fluorescence (micro-EDXRF) analyses made on metal artefacts to determine their composition and scanning electron microscopy with energy dispersive analysis (SEM-EDS) analyses to study microstructural features as inclusions are shown to illustrate trends and specificities of each chronological period. Generally, in early periods, namely during the Copper Age and first stages of the Bronze Age, unalloyed copper and arsenical copper were at use, and only by the Late Bronze Age (LBA) did tin bronze substitute almost completely the previous role of copper. In the Early Iron Age, during the Orientalising period, a general decrease in the average tin content in bronzes seems to happen. Regarding the inclusions observed in the metal matrix, these seem to suffer a diversification with the appearance of tin bronzes. By the Copper Age, only Cu–O and Cu–As–O inclusions are observed, while by the LBA Cu–S inclusions become regular, besides others less frequent, as Sn–O, Cu–S–Fe and Pb globules. Overall, with the present analytical study, the complementary character of micro-EDXRF and SEM-EDS in the study of ancient metals is demonstrated, providing a first general overview of the ancient metallurgy at the Portuguese territory which is of key importance to specific investigations of the future.

Introduction

The study of ancient metallurgy, particularly concerning the pre- and proto-historic periods, has been an important and interesting field of work that has provided relevant information on the technological progress of ancient communities. Additionally, these studies have also provided relevant information on local innovations as well as on ancient trans-regional contacts.

Given the particular geographical location of the Portuguese territory – between the Atlantic and the Mediterranean waters – a diachronic view of the metallurgy in this region can be of major relevance to evaluate the Atlantic and Mediterranean influences along different periods and also to define local particularities.

In the last years, a multidisciplinary team has been working on the study of ancient metallurgy of the Portuguese territory as a result of several research projects and collaborations with national museums and archaeologists. Various studies have been performed on copper-based artefacts ranging a time span of ~3000 years, from Copper Age to Early Iron Age/Orientalising period. Overall, about 300 artefacts of various typologies and from various archaeological sites have been studied using a multiproxy approach that includes diverse analytical techniques. Some of the results have been published[1–8] and presented in scientific meetings.[9,10] Given the actual state of knowledge it becomes important to provide some important guidelines on the metallurgy of the Portuguese territory from the Copper Age to the Orientalising period, giving detailed compositional information of particularities such as inclusions besides the general elemental composition of the metals. This is of utmost importance because inclusions have been scarcely described although they can provide relevant archaeometallurgical information. Thus, in the present work, general trends and some specific examples are presented for each cultural period, based on the characterisation of the metal composition by micro-energy dispersive X-ray fluorescence (micro-EDXRF) and on the characterisation of inclusions in the metal matrix by scanning electron microscopy with energy dispersive analysis (SEM-EDS).

Among the wide variety of modern analytical techniques that are employed in the study of metals, EDXRF and SEM-EDS are well-established techniques. EDXRF, either in its conventional form or as micro-EDXRF, and SEM-EDS can be described as non-destructive (i.e. maintaining the physical integrity of the artefact) or micro-invasive (i.e. in the sense that sampling or cleaning of a very small surface is required, since ancient metal artefacts develop a superficial corrosion layer), multi-elemental, relatively fast and complementary, allowing not only average compositional information but also local information of very small areas.[11] Micro-EDXRF analysis is a valuable tool for metal investigations as it allows the evaluation of the composition of an alloy or metal including the main alloying elements and some impurities. The composition of an alloy can inform about the choices and/or technical skills of ancient metallurgists in creating alloys with specific properties

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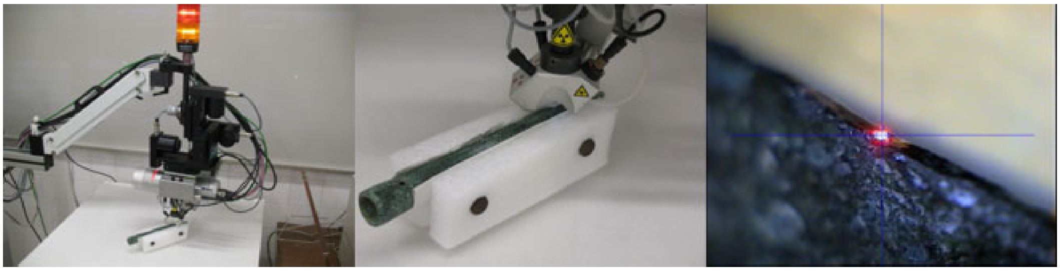

Figure 1. The ArtTAX Pro spectrometer during the analysis of a bronze spearhead from Penela (Central Portugal). On the right is an image obtained by the CCD camera during the selection of the measuring location. Here, in conjunction with a laser spot and crosshairs on the video display the reproducible settings of the measuring distance and location of the measured spot are assured (principle of optical triangulation, see also Ref. [13]).

Table 1. Micro-EDXRF analysis of Phosphor Bronze 553 from BCS (average ±1 SD for three spot analyses)

wt %	Cu	Sn	Pb	Zn	Fe	Ni
Certified	87.0	10.8	0.47	0.49	0.06	0.44
Obtained	87.7 ± 0.1	10.5 ± 0.1	0.56 ± 0.07	0.58 ± 0.01	0.05 ± 0.01	0.51 ± 0.01
Accuracy	0.8	2.5	19.1	18.4	10.2	15.9

Table 2. Quantification limits for micro-EDXRF analysis (calculated as $10 \times (\text{background})^{1/2}/\text{sensitivity}$)[14]

Cu	Sn	Pb	As	Fe	Ni
0.04%	0.05%	0.10%	0.10%	0.05%	0.07%

(e.g. mechanical, colour, casting). Minor elements can be relevant for the evaluation of similarities or differences among metals from different contexts and different chronological periods, helping in the track of ancient trade routes and providing complementary information concerning technological progresses.

The use of SEM-EDS in the study of ancient metals provides relevant microstructural information, namely the distribution of secondary phases and inclusions. Regarding the latest, it allows the identification of various types of inclusions whose presence is not always inferred by micro-EDXRF analysis, either because elements are present in low concentrations, randomly distributed within the matrix, or because they often contain light elements that are not detected by micro-EDXRF analysis. The identification of these inclusions can provide complementary information about smelting technologies, refining operations, ores used for metal manufacturing, and, in some cases, ore provenience, among others.

In the present work, key lines are presented for the most common metal and alloy compositions of artefacts from different chronological periods, ranging from the Copper Age to the Early Iron Age, and a detailed discussion of the variety of inclusions and their diverse origins and metallurgical implications will also be presented.

Experimental

Micro-EDXRF analyses were performed in the artefacts to study their metal composition. According to the characteristics of each artefact, analyses were performed in small sampled cross-sections (few cases) or in a small cleaned area free from the superficial corrosion layers (most cases). These prepared areas were later also studied by SEM-EDS.

The micro-EDXRF analyses were performed in an ArtTAX Pro spectrometer (Fig. 1), which comprises a low-power X-ray tube with a molybdenum anode; a set of polycapillary lens that generate a microspot of ~70 μm in diameter of primary radiation; an integrated CCD camera and three beam-crossing diodes that provide the control over the exact position on the sample to be analysed and a silicon drift electro-thermally cooled detector with a resolution of 160 eV at Mn-Kα.[12] Artefacts were analysed using 40 kV, 0.5 mA and 100 s of tube voltage, current intensity and live time, respectively, and three analyses were made on different spots of each area to account for possible heterogeneities, being considered the average value.

Quantitative analysis was made using the WinAxil software that uses fundamental parameters and experimental calibration factors that were calculated with the reference material Phosphor Bronze 551 from British Chemical Standards (BCS).

The accuracy of the analytical technique was determined with the analysis of another reference material – Phosphor Bronze 553 from BCS – and the results are shown in Table 1. Quantification limits were also calculated and are shown in Table 2. Due to the frequent presence of Pb and As in ancient metals and due to the interference between the lines of Pb (Lα) and As (Kα), the quantification limit of As was (under)estimated as being the quantification limit calculated for Pb.

SEM-EDS analyses were performed on some selected items to determine microstructural features as inclusions. The analyses were performed in a Zeiss model DSM 962 equipment allowing backscattered electrons (BSE) and secondary electrons (SE) imaging modes and an energy dispersive X-ray spectroscopy (EDS) analysis with an Oxford Instruments detector, model INCAx-sight, with an ultra thin window able to detect low atomic number elements as oxygen and carbon.

Analyses were made without a conductive coating over the examined surface (i.e. without a coating of gold or carbon) to prevent interference of external elements in the analysis. Generally, the items were placed in the SEM chamber with an electric contact of copper and/or carbon tape from one extreme of the examined

Figure 2. On the left is an image of the preparation of a bronze bracelet fragment from Medronhal cave (Central Portugal) for SEM-EDS analysis, with the enveloping of corroded surfaces with copper and carbon tape near the prepared and cleaned area, leaving the latest uncovered for analysis (the analysed area is the top right surface). The centre and right images show the placing of the artefact in the SEM-EDS chamber.

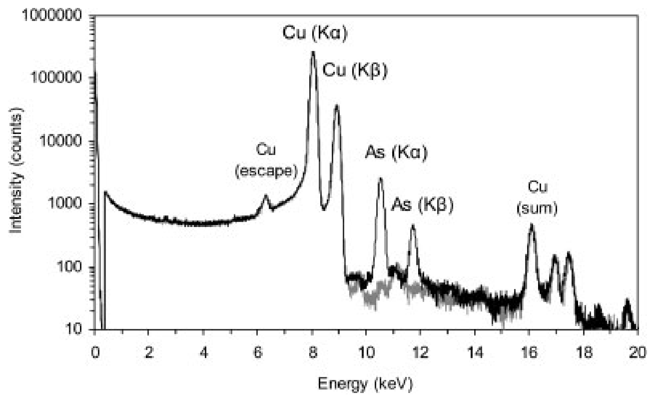

Figure 3. Micro-EDXRF spectra of a relatively pure copper fragment from Escoural archaeological site (South Portugal) (in grey), and a copper rivet with ~2 wt% As from Folgão (South Portugal) (in black).

surface to the ground, which also assisted the right positioning of the items and assured the cover of the less conductive corrosion layers (Fig. 2). Experimental conditions were regularly 20 kV of voltage, approximately 3 A of filament current and 70 μA of emission current.

Results and Discussion

The results are presented and discussed following the chronological order of the studied artefacts. Due to the lower number of studied cases belonging to the earlier periods and to a general continuity in the use of unalloyed copper from the Copper Age (~3000–2200 BC) to the first stages of Bronze Age (Early and Middle Bronze Ages ~2200–1200 BC), the artefacts from these two periods are discussed together in the first section.

Copper Age and first stages of Bronze Age

The Iberian Peninsula has been pointed out as a possible place for an independent development of early copper metallurgy.[15] Past studies[16] and more recent ones[17–20] on artefacts from the Portuguese territory have shown that the first metals used were normally relatively pure coppers occasionally containing some As. This element seems to be present mainly in the artefacts from the later stage of the Copper Age, the Bell Beaker period, when it can be present in relatively high values (>2 wt% As), making these materials be commonly described as arsenical coppers. In Fig. 3, micro-EDXRF spectrum of two artefacts, one with relatively pure copper and another with ~2 wt% As, are shown.

The relatively pure metal worked by these early metallurgical communities has been described as a result of (1) the exploration of local rich copper ores, as copper carbonates and oxides which can contain As impurities and (2) by the very simple smelting technologies that were used in early times (consisting in a small pit with a normal fire where a crucible was placed and filled with one or more layers of ore and charcoal from above), which did not reach reducing conditions enough to reduce other elements such as Fe, which would then not be incorporated in the metallic solution but instead discarded with the slag.[21]

SEM-EDS analysis of artefacts of relatively pure copper (without As) showed the regular presence of Cu–O inclusions in the metallic matrix of α-Cu phase (Fig. 4(a)). The presence of these inclusions can be understood as a result of the metallurgical process, as all molten metals are subjected to some degree of oxygen incorporation at high temperatures. During copper solidification, if the oxygen content in the melt is higher than 0.04 wt% (which is the general situation in normal melting and castings in the absence of a deoxidation agent), a eutectic reaction occurs producing cuprous oxide besides α-Cu. If eutectic cuprite is present in a considerable quantity the reaction of cuprous oxide with hydrogen results in steam that can give rise to high casting porosity and consequently to low mechanical strength. Thus, nowadays, deoxidation processes are employed (e.g. the addition of phosphorous) that besides reducing the cuprous oxide enhances fluidity and therefore castability.[22]

The SEM-EDS analysis of an artefact with ~2 wt% As (micro-EDXRF) has shown the presence of As-rich inclusions containing both Cu and O (Fig. 4(b)). As demonstrated by the work of Northover[23] for experimental microstructures of Cu–As alloys melted under reasonably reducing conditions, take-up of oxygen still happens, leading to the formation of cuprous and arsenous oxides (Cu_2O and As_2O_3). The presence of As in the melt will

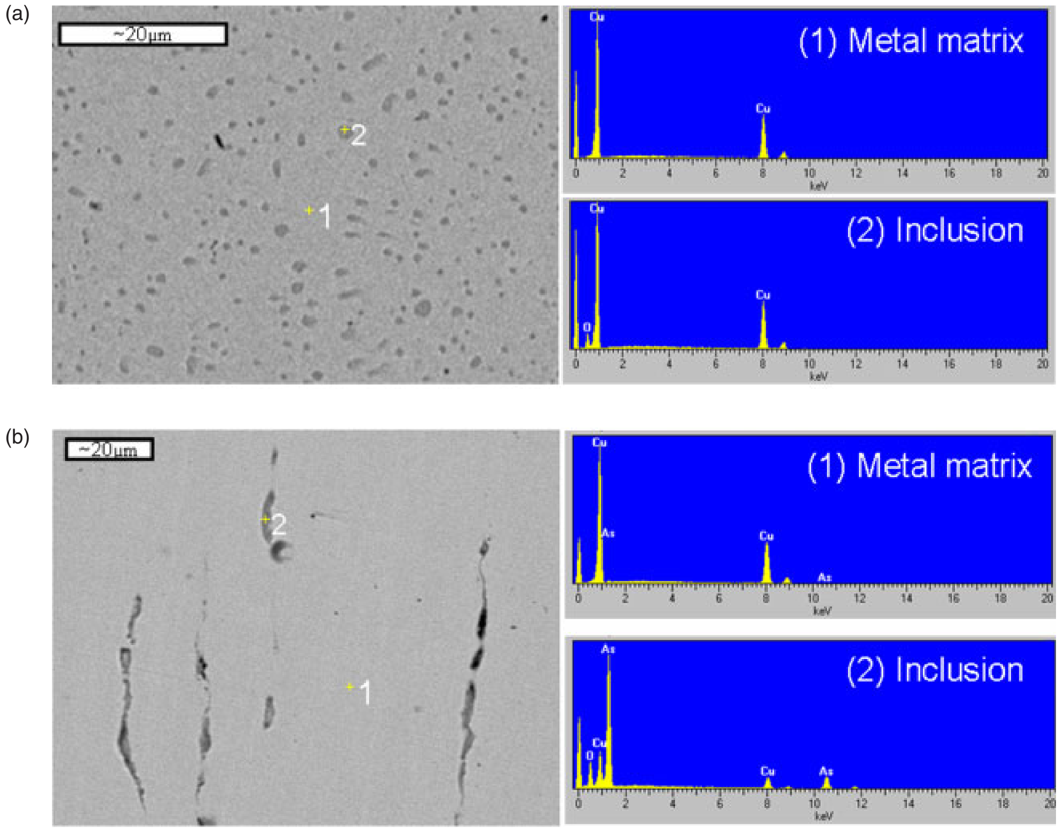

Figure 4. (a) SEM/BSE image of a relatively pure copper fragment from Escoural archaeological site (South Portugal) with inclusions (darker grey) and EDS analysis of (1) the metal matrix and (2) inclusion of Cu-O. (b) SEM/BSE image of a copper rivet with ∼2 wt% As (micro-EDXRF) from Folgão (South Portugal) with elongated (deformed) inclusions due to significant mechanical work on the artefact, and EDS analysis of (1) the metal matrix and (2) inclusion with Cu–As–O.

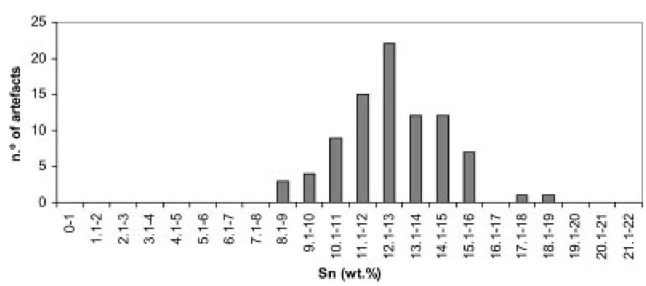

Figure 5. Histogram with Sn contents in bronzes from Late Bronze Age.

probably have some benefits to the cast, as the higher reactivity of As with oxygen will result in the decrease of casting defects promoted by cuprous oxide.

The advantages of arsenical coppers in relation to purer coppers have been frequently emphasised.[24–26] The presence of this element in the solid solution provides a strain hardening effect, which can have advantages in the production of some artefacts, as those with cutting edges. However, the actual contribution of As to the mechanical properties of the artefact (i.e. present in the solid solution) cannot just be evaluated by elemental analysis as micro-EDXRF, as this element might be present mainly among the inclusions, as demonstrated in the present SEM-EDS study. Thus, in the present case the hardening effect of As in the artefact would be less of a 2 wt% As in α-Cu solid solution. This example reveals the complementary character of both types of analyses, of major importance for the interpretation of artefacts composition.

Late Bronze Age

The latest studies on Late Bronze Age (LBA, ∼1200–800 BC) artefacts from the Portuguese territory have shown a general use of tin bronzes, occasionally with Pb and As as impurities.[3,4] The absence of leaded bronzes distinguishes this metallurgy from others in Atlantic territories, where tin bronzes with high concentrations of lead have been found.[27,28] In Fig. 5, a histogram with the Sn contents obtained by micro-EDXRF analysis in bronzes of various typologies and from various sites of the Portuguese territory is shown. The distribution of the Sn content is close to a normal distribution, of $\sim 12.7 \pm 1.9$ wt%. This composition suggests that the ancient metallurgists were aware of this alloy properties, since α-Cu phase can be substantially hardened by the solid solution of tin at concentrations above ∼10 wt%,[25] and the optimal thermomechanical properties can be achieved for alloys

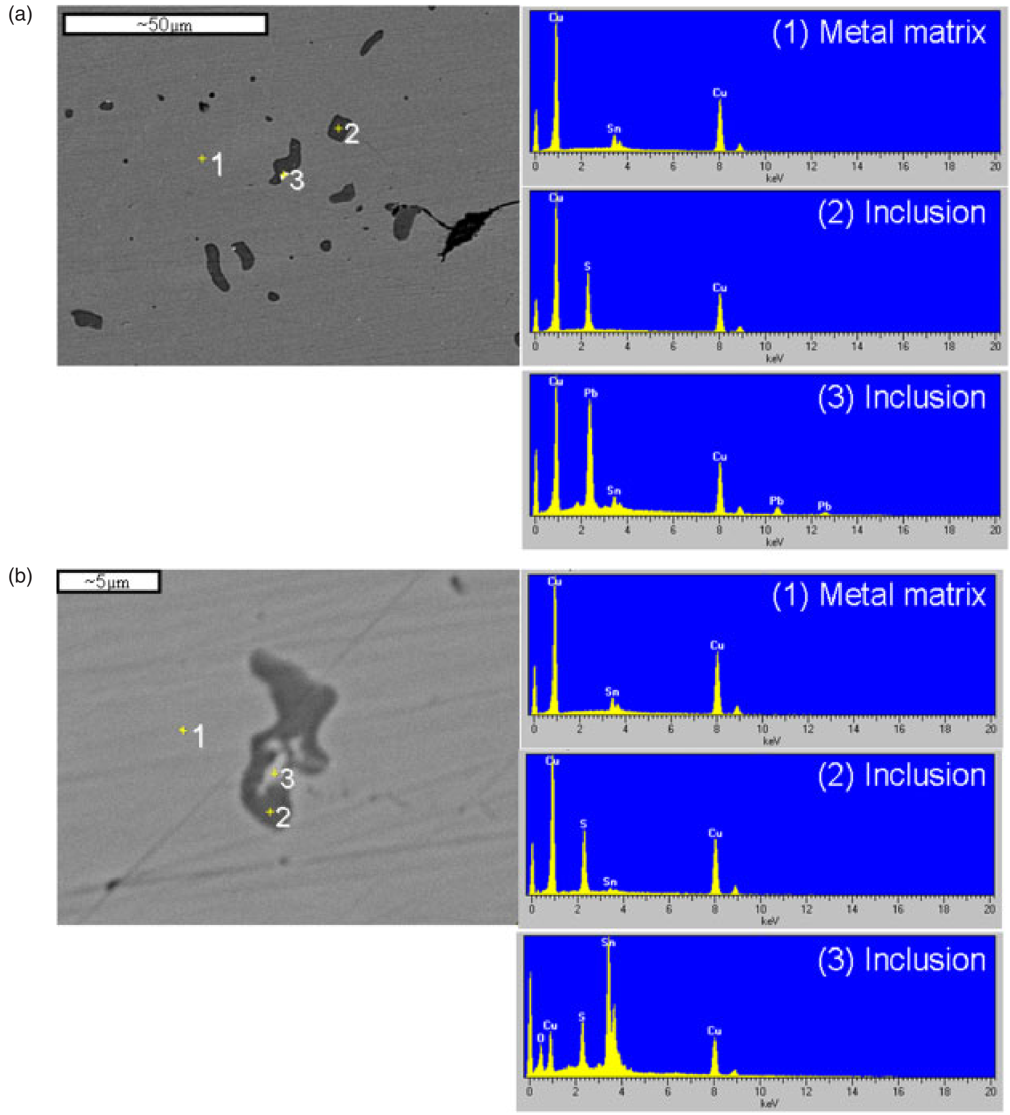

Figure 6. (A) SEM/BSE image of a bronze bracelet fragment from Medronhal cave (Central Portugal) with inclusions, and spot EDS analysis of (1) metal matrix, (2) inclusion of Cu–S and (3) inclusion of Pb. (B) SEM/BSE image of a bronze ring from the same site with an inclusion and spot EDS analysis of (1) metal matrix, (2) inclusion of Cu-S and (3) inclusion of Sn-O (due to the small size of some inclusions, the EDS spectrum also contains additional information from the surrounding area).

with <15 wt% Sn avoiding the formation of the brittle δ eutectoid (relatively Sn rich).

SEM-EDS analysis on selected LBA artefacts showed that the inclusions are different from those found among the items of the earlier period. The most regular impurities are Cu–S ones, which according to the Cu–S phase diagram are copper sulphides (Cu_2S). Also, other inclusions have been found in particular cases, as Sn–O, Cu–S–Fe, Pb, Au and Ag. In Fig. 6, BSE images and EDS spectra of some of these types of inclusions are shown. Because the inclusions are normally segregated to the last regions to solidify, the inclusions are normally found in the interdendritic regions and covering pore walls when these are present (Fig. 7).

The absence of Cu–O inclusions among the bronzes can be explained by the deoxidising action that tin has in the alloy, which is probably the reason for the presence of Sn-O inclusions in some artefacts.

The regular presence of Cu–S inclusions in these LBA bronzes and their absence in the earlier copper artefacts can suggest that further changes occurred between the two metallurgical periods, probably related with the ores used or with the smelting technologies (e.g. more reducing conditions in the later period), although evidences for the latest are scarce. Possibly, by LBA deeper mineralisations were worked, those more sulphur rich, contrasting with the more oxidised top mineralisation that were explored and probably exhausted in earlier periods, as suggested by Craddock[24]. The occasional presence of Cu–S–Fe impurities can also point out to this possibility, with the incorporation of minerals such as chalcopyrite and bornite in the smelt.

Additionally, the presence of very small Pb globules (regularly <0.5 wt% Pb by micro-EDXRF analysis) can point out to the explorations of different copper sources than those explored earlier, or to regular exchanges, as trans-regional trades, that would incorporate particularities of other copper sources. Regular recycling practices would in turn contribute to the dispersion of the various impurities in the alloys.

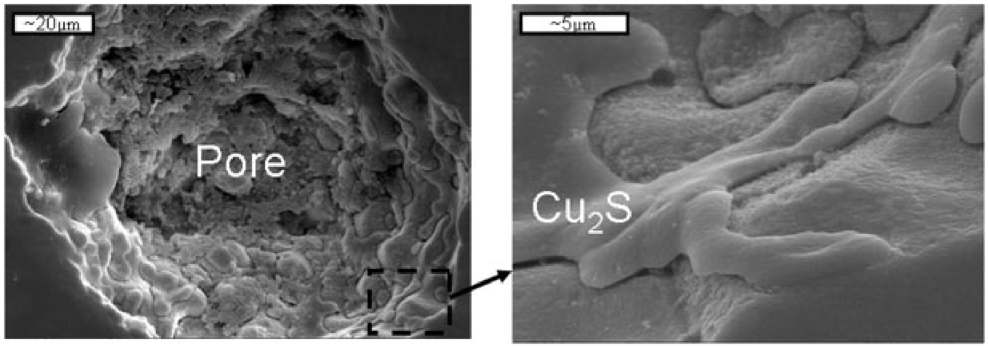

Figure 7. SEM/SE image of a pore in a bronze bar fragment from Santa Luzia archaeological site (Central Portugal) with the walls covered by copper sulphides as a result of microsegregation.

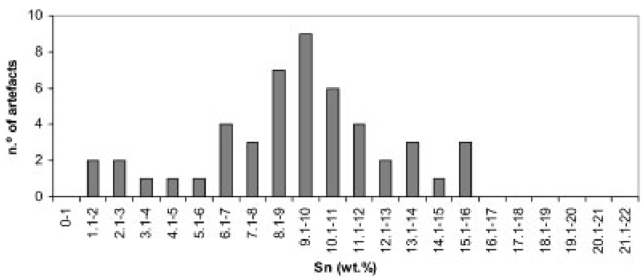

Figure 8. Histogram with Sn contents in bronzes from Early Iron Age.

Early Iron Age

Recent studies on artefacts from the Early Iron Age (~800–500 BC) in the Iberian Peninsula that include the Phoenician interactions with the indigenous populations (usually designated Orientalising period) have shown that tin bronzes were still the main alloy used for metal artefacts manufacture, although leaded tin bronzes and unalloyed coppers begin to be used more regularly.[1,6,29] Micro-EDXRF results from artefacts belonging to the Portuguese territory seem to indicate that tin bronzes from this cultural context show more dispersed Sn contents than the earlier ones, particularly due to the appearance of low tin bronzes that were absent in the LBA record (Fig. 8). The more dispersed and lower Sn contents found in the bronzes from this period can be related to an increase in the recycling of bronze scraps, as the preferential oxidation of tin during the melting operation leads to an impoverishment of the alloy.[30]

SEM-EDS analysis has shown that the inclusions found among the bronzes from this period are generally the same as those found in the earlier LBA period. However, two differences have been observed. Since Pb can now be present in higher contents, frequently up to ~2 wt.% Pb, the microstructure of these bronzes can be characterised by larger Pb globules, easily detected in the BSE images (Fig. 9(a)). Additionally, it has been observed that in some particular bronzes besides the Cu–S–Fe inclusions, Fe has also been detected in the metal matrix (Fig. 9(b)), a feature that has not been observed in the earlier LBA bronzes. Micro-EDXRF analysis made on these Orientalising bronzes have also shown Fe in higher contents than on the LBA bronzes, where the Fe contents are regularly below 0.05 wt%. Higher Fe contents in artefacts associated with the Mediterranean influences have previously been reported by Craddock[21] for the Iberian Peninsula and by other authors for the Mediterranean basin.[31] Differences in the Fe content among the two periods have been related to an improvement in the extraction technology of the smelting operations that would create more reducing conditions, allowing the incorporation of Fe in the molten bath, which in turn will be preserved in the metallic solid solution. This feature, however, can also be a result of other phenomena, as the uncontrolled recycling of bronzes with some iron artefacts that appear by this time, giving rise to this impurity in the metal matrix. The practice of uncontrolled recycling operations can also be supported by the irregular Sn contents, as demonstrated before, and in the appearance of bronzes with various Pb contents.

Conclusions

With the present work the value of the complementary information given by micro-EDXRF and SEM-EDS for the study of ancient metals was shown. Besides differences in the metal composition determined by micro-EDXRF, differences in the inclusions and metal matrix have also been found among the different chronological periods. During the early times – the Copper Age and first stages of the Bronze Age – artefacts were made with copper and arsenical copper. These metals were relatively pure, and the inclusions found are either a combination of copper with oxygen or also with As in the case of the presence of this element in the material. These early materials were replaced by binary bronzes with relatively constant tin contents during the LBA, with an average of ~13 wt% Sn, which can indicate that the superior properties of such an alloy were appreciated, and that the ancient metallurgists had developed skills which allowed control in the production of the alloy composition. By this period, the type of inclusions show a major change, being Cu–S the most common ones, and others, such as Sn–O, Cu–Fe–S and Pb globules also occasionally present. Finally, during the Early Iron Age with the Orientalising period an increase in the type of alloys used seem to happen, with the circulation of binary bronzes of various compositions, but also leaded bronzes and unalloyed coppers.

Generally, the specificities of the metallurgies during the different cultural periods seem to better reflect local developments at the first stages, with an increasing contribution of external influences by later periods, namely of Mediterranean character in the latest period. Possibly, besides more intense metal trade and exchanges, the development of increasingly higher reducing atmospheres during smelting and melting operations, the working of additional type of ores and the gradually more significant recycling of bronze scraps can account for the diversity in inclusions and alloy compositions, which is evidenced from the earlier to the later periods.

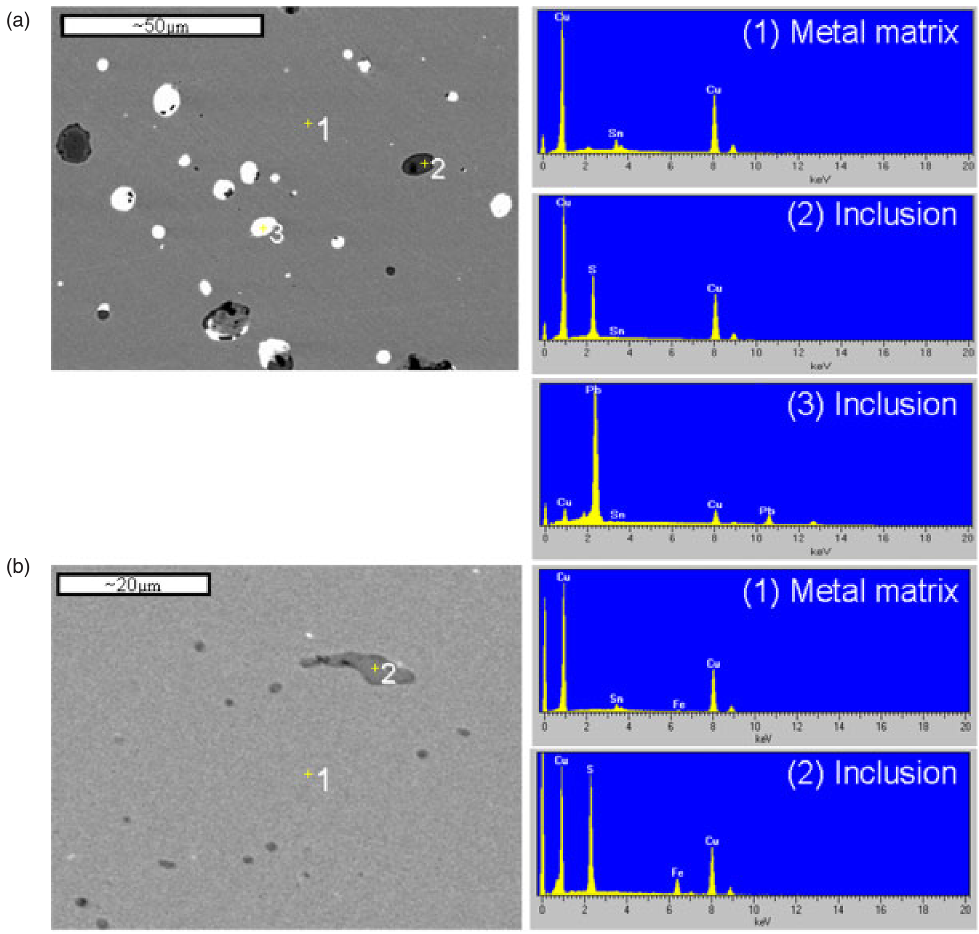

Figure 9. (a) SEM/BSE image of a bronze bar fragment from Fraga dos Corvos shelter (North Portugal) with inclusions that follow the dendritic solidification path, and spot EDS analysis of (1) metal matrix, (2) inclusion of Cu-S and (3) inclusion of Pb (bronze with ~2 wt% Pb by micro-EDXRF). (b) SEM/BSE image of a bronze rod from Palhais (South Portugal) with inclusions, and spot EDS analysis of (1) metal matrix, (2) inclusion of Cu-S-Fe.

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