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Non-destructive characterization of archeological Cu-based artifacts from the early metallurgy of southern Portugal

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Abstract In this study, Monte Carlo (MC) simulations combined with energy dispersive X-ray fluorescence (EDXRF) spectroscopy have been used to characterize non-destructively a collection of Cu-based artifacts recovered from two archeological sites in southern Portugal: (a) the Chalcolithic E.T.A.R. site of Vila Nova de Mil Fontes and (b) the Middle Bronze Age site of Quinta do Estácio 6. The metal artifacts show a multilayered structure made up of three distinct layers: (a) brownish carbonate soil-derived crust, (b) green oxidized corrosion patina, and (c) bulk metal. In order to assess the reliability of the EDXRF-based Monte Carlo simulations to reproduce the composition of the alloy substrate in archeological bronze artifacts without the need to previously remove the superficial corrosion and soil derived patinas, EDXRF analysis together with scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) was also performed on cleaned and patina-/crust-coated areas of the artifacts. Characterization of the mineralogical composition of the corrosion products in the surface patinas was further determined by means of X-ray diffraction (XRD). Results suggest that the adopted EDXRF/Monte Carlo protocol may represent a safe and fast analytical approach in the quantitative characterization of the bulk chemical composition of Cu-based metal artifacts even in the presence of fairly thick corrosion patinas and/or soil-derived encrustations at the surface of the archeological objects.

Keywords Monte Carlo simulation · EDXRF · Early metallurgy · Cu-based artifacts · Southern Portugal

Introduction

One of the most distinctive elements to take into consideration when analyzing an archeological object is its uniqueness. Since artifacts are often the only witnesses of the past, the removal of fragments cannot always be regarded as an acceptable systematic practice.

Indeed, the growing concern towards these issues has led to a decrease in invasive analytical approaches. Within this context, X-ray fluorescence spectroscopy (XRF) has become a routine and relatively low-cost technique for a non-destructive analytical approach to compositional studies of archeological objects, including metals, also due to the increased accessibility of easy to use and miniaturized X-ray detectors and tubes with built-in calibration software (Figueiredo et al. 2011; Bottaini et al. 2012; Schiavon et al. 2013; Bottaini et al. 2016).

Although XRF qualitative analysis easily allows the identification of the chemical elements present in the alloy, quantification of the same data is often essential to clarify more relevant issues about ancient metal production technologies. The determination of the chemical composition of an archeological alloy object is, however, a particularly challenging task as Cu-based artifacts that have remained buried for thousands of years usually exhibit thick, rough corrosion layers whose chemical composition differs from that of the original metal alloy, both in

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terms of the abundance of the major elements present, such as Cu, Sn, Fe, and Pb, and in terms of the addition of new elements (Fe, Ca, Cl, P, S) from the surrounding soil environment. This enrichment led to the formation of different chemical compounds on the metal surface such as carbonates, oxides, sulfates, or sulfides, originated by electrochemical reactions between the metal and the burial environment (Robbiola and Portier 2006). This is why mechanical and/or chemical cleaning of archeological metals prior to chemical analysis to expose the "pristine" metal surface has become a routine procedure in archaeometric research. On the other hand, one must consider that the patina itself belongs to the artifacts as it is part of its history and should not be removed but preserved, whenever possible, in place.

In order to overcome this problem, in recent years, a Monte Carlo (MC) simulation/energy dispersive X-ray fluorescence (EDXRF) spectroscopy combined analytical setup has been developed as a quantification tool able to obtain quantitative, reliable data on the original metal substrate, taking into account not only surface patinas often present on metal alloys but also the inherent surface roughness typical of almost every archeological artifact (Brunetti and Golosio 2014). This methodology has been successfully tested on a number of archeological binary (Cu/Sn) bronze artifacts (Bottaini et al. 2015; Manso et al. 2015; Brunetti et al. 2016; Schiavon et al. 2016). It is, however, the first time that the same combined analytical approach is tested on Cu and As-Cu alloys (with variable concentrations of impurities such as Sn and Pb), artifacts that are commonly found within the early metallurgy production in prehistoric times. In particular, the Cu-based objects investigated in this study were discovered during excavation campaigns carried out in two archeological sites in southern Portugal from the Chalcolithic and Middle Bronze Age, respectively, the E.T.A.R. of Vila Nova de Mil Fontes (VNMF) and the Quinta do Estácio 6 site (EST) (Fig. 1). Every artifact displays a multilayered structure characterized by the presence of three layers: (a) soil-derived crust, (b) corrosion patina, and (c) metal substrate.

Materials

The E.T.A.R. of Vila Nova de Mil Fontes site is located in a cliff not far from the mouth of the Mira River, over a consolidated dune covering a large area of about 1 km in length along the cliff face. Following a first prospection campaign, carried out about 20 years ago, an area of 525 m^2 of the site has been recently excavated showing signs of intermittent occupation documented by different structures such as post holes, fire places, pits, and a large circular hut (10 m in diameter) with a large entrance in alignment with the winter solstice (Fig. 2a). The group of metals analyzed in this paper comes from an archeological context that has been dated at the

second quarter of the III millennium BC (ICEN-726: 4500 ± 60BP–2850-2622 cal BC) (Silva and Soares 1997) and includes one awl (VNMF-10), one knife (VNMF-5), two saws (VNMF-6 e VNMF-61), and one fragment of undefined shape (VNMF-55) (Fig. 2b) (Valera and Parreira 2014).

The Quinta do Estácio 6 (EST) is a large site located on a smooth hill, not far from the city of Beja (Fig. 3a). The archeological excavation carried out in this site allowed recovery of materials with different chronologies, ranging from the Late Neolithic to the Late Roman period. Metals from EST come from a more recent archeological context than those from VNMF, having been recovered inside structures attributed to the Middle Bronze Age ("Bronze Pleno," ca. 2000–1500 BC). The group of artifacts consists of one flat axe (EST-771), three awls (EST-62, EST-124, EST-1275A), one bracelet (EST-383), and one spearhead (EST-1275B) (Fig. 3b).

Thus, the group of metals analyzed in this paper has been found at two different sites from southern Portugal and has been recovered in archeological contexts dated to the second quarter of the III millennium BC as for E.T.A.R. de Vila Nova de Mil Fontes and the first half of the II millennium BC regarding the objects from EST. Anyway, despite their wide age range, all the metal objects investigated in the current study can be considered as belonging to the early metallurgy of southwest Iberia that was characterized by the production of metal artifacts with simple morphologies (flat axes, arrowheads, spearheads, saws, awls, knifes, etc.) made either in pure Cu and/or in Cu/As alloys, generally with low concentration of other elements as impurities (Soares et al. 1996; Ruíz Taboada and Montero-Ruiz 1999; Hunt-Ortiz 2003; Rovira 2004). During this stage, ranging from the end of IV/ beginning of the III millennium BC (Soares et al. 1996) up to the half of the II millennium BC, the production of Cu-based objects in the region appears to be a small-scale activity, not experiencing significant changes from a typological, compositional, or technological point of view, until the first appearance of objects made with a Sn-containing alloy (Valério et al. 2014).

Experimental

EDXRF/Monte Carlo simulation

The elemental analyses have been performed with a Bruker TRACER III-SD handheld spectrometer equipped with a rhodium tube and silicon drift detector. The operating conditions were 40 kV and 12.5 μA current with an Al/Ti filter (304.8 μm aluminum/25.4 μm titanium) and 60 s acquisition time. Bruker S1PXRF v.3.8.30 software has been used for the acquisition of the spectra. In order to obtain compositional data on the original bronze alloy without removing the surface patinas, the EDXRF analyses were combined with MC simulations.

Fig. 1 Map localization of E.T.A.R. de Vila Nova de Mil Fontes (VNMF) and Quinta do Estácio 6 (EST)

The MC simulation codes used in this work have already been described in literature (Brunetti et al. 2015). The MC techniques are probabilistic techniques capable of reproducing the real phenomenon to be simulated. In the case of X-ray interaction with matter, a set of photons is probabilistically generated, according to the real X-ray source used in the experiment, and their interaction with the sample is determined also on a probabilistic basis biased by the so-called cross sections of the X-ray photons with the specific materials making up the sample. In order to obtain a realistic MC simulation of a XRF experiment, it is important to give the following: (a) an accurate description of sample structure and composition, (b) the geometry of the experimental setup, and (c) a detailed characterization of the X-ray source emission, especially if an unfiltered or quasi-unfiltered excitation mode is being used. Accurate X-ray source characterization is, probably, the most critical part of the simulation as this information is not always

available nor easily obtainable from the manufacturer. For this reason, a direct measurement of the X-ray emission is often mandatory. In our case, the quality of the simulation is assessed by comparing, at first visually and then by performing a Chi-square test, simulated and measured spectra: when the simulated spectrum matches exactly the experimental one, the sample can be considered determined both in its composition and structure. The error in the determination is around 2.0–5.0 wt.% of the value of the concentration, with the lowest error related to higher concentrations.

SEM-EDS

SEM-EDS was carried out using a HITACHI S3700N interfaced with a Quanta EDS microanalysis system equipped with a Bruker AXS XFlash silicon drift detector (129 eV spectral resolution at FWHM/Mn Kα). Standardless PB/ZAF

Fig. 2 a Circular hut from E.T.A.R de Vila Nova de Mil Fontes. **b** Studied artifacts from VNMF as analyzed, i.e., recovered by the brownish carbonate soil-derived crust and green oxidized corrosion patinas: *1* awl (VNMF-10); *2* saw (VNMF-61); *3* knife (VNMF-65); *4* saw (VNMF-6); *5* metal fragment (VNMF-55)
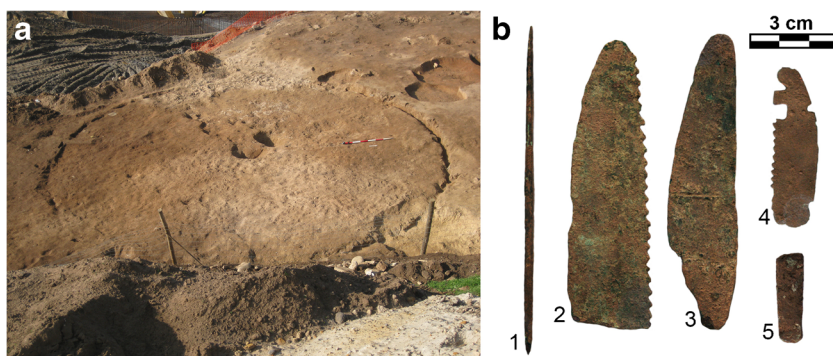
Fig. 3 a Portion of the excavated area at Quinta do Estácio 6 showing a group of negative structures. b Analyzed artifacts as analyzed displaying the multilayered structure composed by the soil-derived crust and the corrosion patina: *6* flat axe (EST-771); *7* awl (EST-1275A); *8* awl (EST-62); *9* awl (EST-124); *10* spearhead (EST-1275B); *11* bracelet (EST-383)

quantitative elemental analysis was performed using the Bruker ESPRIT 1.9 software.

μXRD

μXRD analyses were carried out using a Bruker AXS D8 Discovery XRD with the Da Vinci design using a Cu Kα source operating at 40 kV and 40 mA and a lynxeye one-dimensional detector. Scans were run from 3° to 75° at a step size of 0.05° with a counting time of 1 s/step. Evaluation of X-ray diffractograms was made by using the DIFFRAC.EVA software package (BRUKER/AXS GmbH, Germany) and the attached specific PDF database files (ICDD, Denver, CO, USA).

Results and discussion

All artifacts were covered by a brownish carbonate soil-derived crust and a green oxidized corrosion patina that has been firstly characterized by μXRD. The results revealed that crystalline phases of the patina are mainly composed of cuprite (Cu_2O), malachite ($Cu_2CO_3(OH)_2$), tenorite (CuO), brochantite ($Cu_4SO_4(OH)_6$), and atacamite ($Cu_2Cl(OH)_3$) (Fig. 4). The occurrence of quartz (SiO_2) and calcite ($CaCO_3$) can result from the contamination from the soil (Fig. 3). SEM-EDS investigation also allowed to characterize the superficial layers consisting of both corrosion patina and

soil-derived products, highlighting the difference with the bulk metal composition (Fig. 5).

XRF spectra obtained from the surface of the artifacts are depicted in Fig. 6. In Fig. 6a, the experimental spectrum of the saw VNMF-6 is shown superimposed to the simulated spectrum. The model used for the simulation is formed by a two-layered structure, where the surface is composed of a light matrix, essentially containing iron oxides. Small amounts of Ca, Ti, As, Br, Rb, and Sr are also present in this layer, according to the peaks observed in the measured EDXRF spectrum. The unfitted peaks are due to the X-ray tube, which are the two K-line peaks of the Rh anode, each of them producing also a scattering peak. From the simulation, this patina/incrustation layer is 80 μm thick.

In Fig. 6b, the experimental and the simulation spectra from the spearhead EST-1275B are reported. The model and composition are quite similar to those of the previous sample, but in this case, also Cu oxides are present in the patina layer together with a small amount of Ca that can be ascribed to soil contamination. In this case, the patina is 45 μm thick.

In Fig. 6c, the experimental and the MC simulations of the bracelet EST-383 are displayed. The composition of this sample is very similar to the previous one even in the patina thickness (42 μm).

The quantitative results, as determined by the combined EDXRF and MC simulation protocol, indicate that the artifacts are pure copper and copper with variable As content, also containing Pb and Sn in minor concentrations (Table 1). Values reported in Table 1 are normalized to 100.0 wt.%.
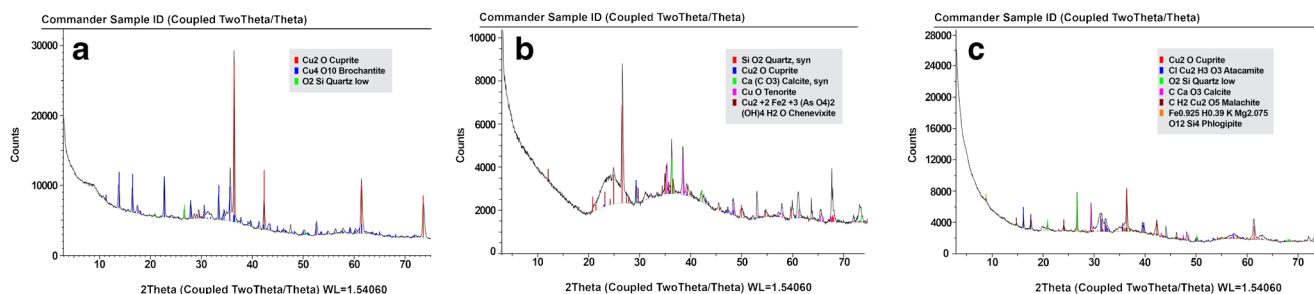

Fig. 4 XRD diffractogram of soil-derived products and corrosion layer from the a knife VNMF-65, b flat axe EST-771, and c saw VNMF-61
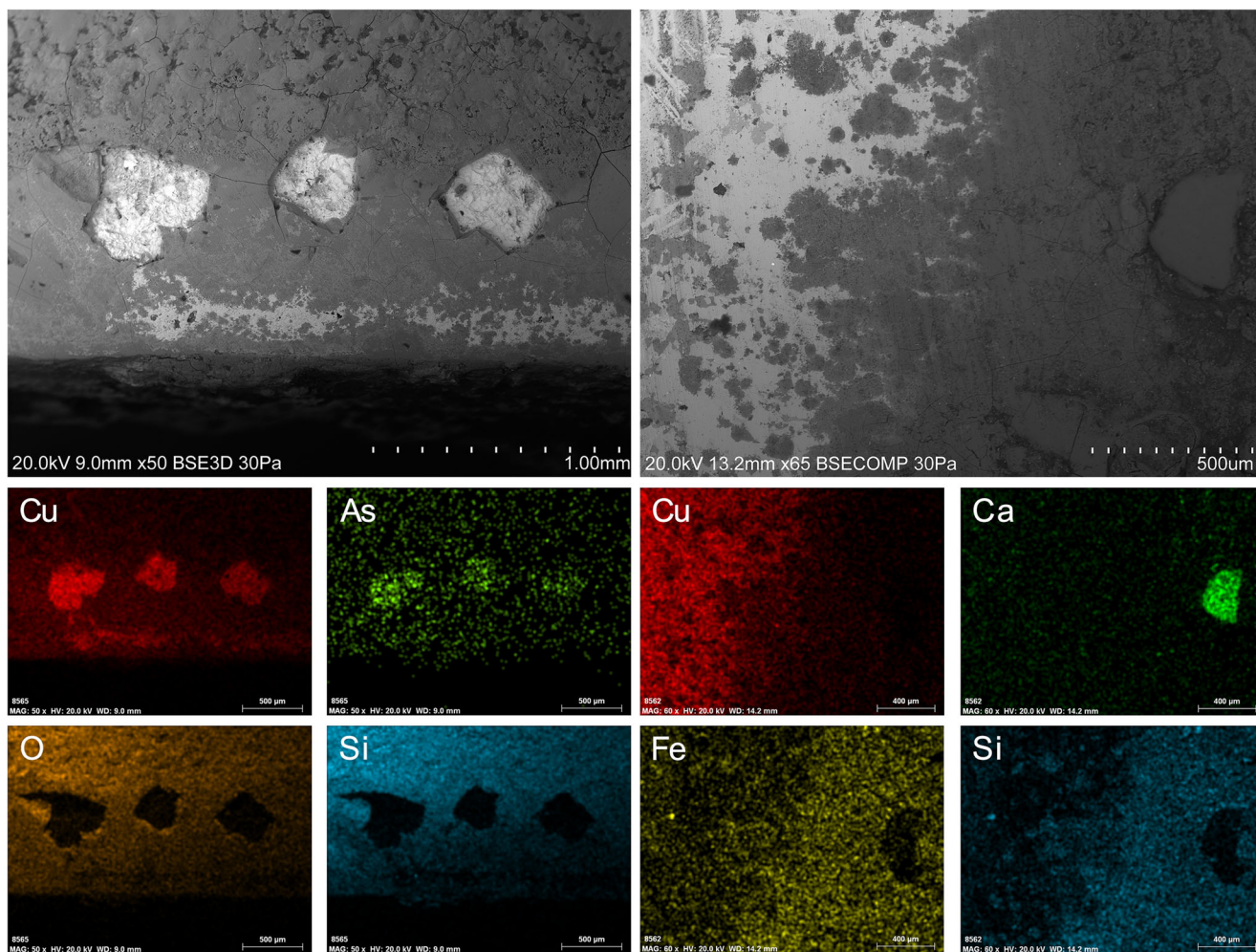
Fig. 5 Backscattered electron image with EDS elemental distribution maps of **a** the flat axe EST-771, showing the different concentrations of the elements in the bulk metal (As and Cu) and in the superficial layer (O and Si); **b** the knife VNMF-65 displaying the distribution of Cu (alloy) and Ca, Fe and Si in the outer stratum

Thus, for example, a value of 99.95 wt.% for copper in the VNMF-61 sample should take into account an error of about 2.0 wt.% in this concentration estimation, and so, the concentration value should be rounded to 100.0 wt.% for a correct error representation. However, in doing such an operation, one could generate confusion when considering the presence of low concentrations of minor elements such as Pb for example. It has to be said, however, that, from an archaeometric point of view, to distinguish between 99.9 vs 100.0 wt.% concentration value, it does not appear significant.

A first aspect to be highlighted within the metals analyzed is the non-uniform distribution and the high variability of As content, ranging from 0.1 wt.% in EST-62 to 8.0 wt.% in EST-1275, with n.d. values in three artifacts (VNMF-6, VNMF-55, and EST-124). Notwithstanding the limitation imposed by the somewhat limited number of samples investigated, at a first glance, the results seem to point to the absence of any clear relationship between the amount of As and the typological and morphological characteristics of the metal objects under consideration. This circumstance appears to be in contrast with what has been documented in various sites from southern and central Portugal using copper and arsenical copper technology, such as Atalaia do Peixoto, Castro dos Ratinhos, São Pedro, Três Moínhos, Tholos de Caladinho (Orestes Vidigal et al. 2015), Zambujal (Müller et al. 2007), Leceia (Müller and Cardoso 2008a), and Vila Nova de São Pedro (Müller and Soares 2008b; Pereira et al. 2013), and where correlations between As concentration and certain artifact types have been identified and interpreted as the evidence of an intended selection made by the ancient metallurgists of the alloys produced. On the other hand, similarly to what has been detected at VNMF and EST, chemical analyses on metal artifacts found in the neighboring region of Andalusia, such as at Cabeço Juré and La Junta e Valencina de la Concepción, did not allow detection of any link between As contents and specific metal typologies and functionalities (Bayona 2008), thus attesting a controversial reality, whose interpretation appears to not be unanimous among researchers.
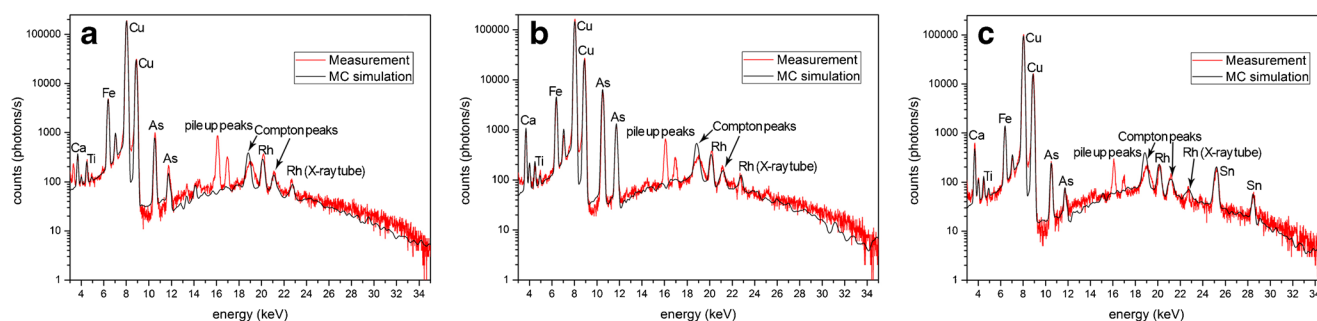
Fig. 6 Experimental (*red*) and simulated (*black*) spectra of the **a** saw VNMF-6, **b** spearhead EST-1275B, and **c** bracelet EST-383

Within the analyzed artifacts, the As average value reaches 1.86 wt.% in VNMF and 1.8 wt.% in EST, without any significant difference in the As distribution between Chalcolithic (VNMF) and Middle Bronze Age (EST) metals (Fig. 7a). It is important to highlight that, although the introduction of arsenic starts to produce a beneficial effect in the final alloy product at concentrations of about 0.5 wt.% (Lechtman 1996), a marked improvement in the mechanical properties of the alloy mainly occurs only at As values of around 3.0–4.0 wt.% (Rovira 2004; Subramanian and Laughlin 1998). Accordingly, within the metals analyzed in this study, only three objects, i.e., the saw ETAR-61 (4.0 wt.% As), the knife ETAR-65 (5.0 wt.% As), and the spearhead EST-1275B (8.0 wt.% As), appear to contain As in sufficient amounts to benefit from an appreciable increase in hardness by mechanical treatment, while most artifacts show an As content lower than 1.0 wt.% (Fig. 7b).

The prolonged debate over the significance of the presence and the variability of As in early copper artifacts has led several researchers to attempt to define a specific compositional pattern based on the As content in the alloy that could allow to distinguish between the following: the (a) deliberate action taken by the ancient metallurgist within the productive process and (b) accidental As impurities already present in the original ore metal raw material. This topic is still a matter of dispute and different arsenic thresholds have been adopted by a number of researchers to distinguish between alloys in which As could be considered as

a deliberate addition or an accidental occurrence (Cardoso and Guerra 1997/1998; Craddock 1995; Hunt-Ortiz 2003; Lechtman 1996; Northover 1989; Rovira 2004). Thus, as it is evident, to interpret the low and erratic arsenic content is not an easy task, even because several plausible causes can explain this variability.

The practice of recycling metals, for example, may have had a determining role for the composition of the analyzed artifacts, particularly with regard to the reduced amount of As: in fact, the remelting of scrap metals made of arsenical copper may cause a loss by oxidation and evaporation of this element during the production process. In this way, also as a consequence of the little control that ancient metalworkers had over the smelting and/or the reducing atmosphere during melting and annealing treatments, the use of arsenical copper scraps as raw material could easily have led to a considerable variability of As in the final alloy (Bray and Pollard 2015; Budd 1990; Hauptmann 2007; Jung 2003; Lechtman and Klein 1999; McKerrell and Tylecote 1972; Sabatini 2015; Tylecote et al. 1977).

Moreover, there has been recently a certain consensus among researchers regarding the presence of irregular arsenic amount as an indicator for the use of polymetallic Cu/As ores (arsenates) that could lead to the production of natural Cu/As alloys with variable As contents, up to 8.0 wt.% (Craddock 1995; Rovira and Montero-Ruiz 2003). In fact, copper ores are almost never pure, but typically contain impurities of Fe, Sn, and As, sometimes in very high concentrations (Hunt-

Table 1 EDXRF/MC simulation analyses on metals from and E.T.A.R. de Vila Nova de Mil Fontes (VNMF) and Quinta do Estácio 6 (EST)

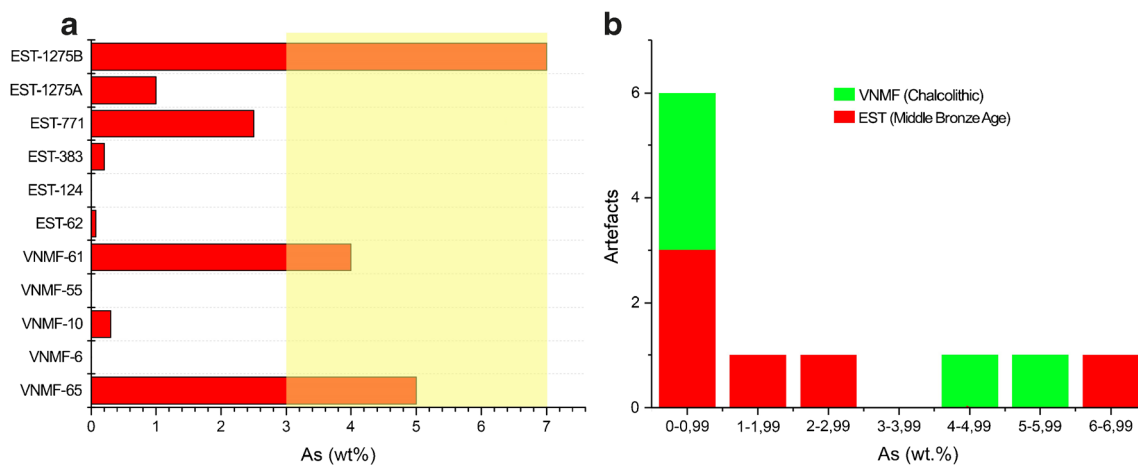|	Type	N. inv.	Cu (wt.%)	As (wt.%)	Sn (wt.%)	Pb (wt.%)
VNMF	Knife	VNMF-65	95.0	5.0	n.d.	n.d.
VNMF	Saw	VNMF-6	100.0	n.d.	n.d.	n.d.
VNMF	Awl	VNMF-10	99.7	0.3	n.d.	n.d.
VNMF	Fragment	VNMF-55	100.0	n.d.	n.d.	n.d.
VNMF	Saw	VNMF-61	95.95	4.0	n.d.	0.05
EST	Awl	EST-62	99.93	0.07	n.d.	n.d.
EST	Awl	EST-124	100.0	n.d.	n.d.	n.d.
EST	Bracelet	EST-383	98.1	0.2	1.7	n.d.
EST	Flat axe	EST-771	97.5	2.5	n.d.	n.d.
EST	Awl	EST-1275A	99.0	1.0	n.d.	n.d.
EST	Spearhead	EST-1275B	92.0	8.0	n.d.	n.d.

Fig. 7 Histograms of **a** As distribution and **b** As contents within the analyzed metals

Ortiz 2003). According to experimental studies, Cu ores containing minor As can be enough to produce arsenical copper alloys. In fact, due to its volatility during the smelting process, As boils and sublimes at 613 °C, and arsenic gaseous can be incorporated within the final Cu metal objects. This process leads to an enrichment of As in the copper, resulting in the arsenic amounts in the metal to be higher than the ones originally present in the ore (Pollard et al. 1991; Hanning et al. 2010). Therefore, the use of polymetallic Cu ores with unpredictable As impurities could lead to the production of final alloys whose As content could hardly be controlled by the ancient metalworkers, thus explaining the high variability and the erratic nature of this element in the finished artifacts.

In this way, also considering that copper ores associated with arsenic-bearing minerals are effectively known in Southwestern Iberia (Ferreira 1961, 1970; Hunt-Ortiz 2003; Müller et al. 2007), the As contents occurring in most of the artifacts from VNMF and EST could hardly be interpreted as the result of an intentional addition of As to Cu alloys, being much more likely that the As in the final alloy may arise from the use of a mineral rich in arsenic as raw material.

Beside Cu and As, EDXRF analyses identified the presence of Pb and Sn, respectively, in only one sample. Although lead appears as an impurity only in the saw VNMF-61, BSEM analyses identified the occurrence of small Pb-rich globular inclusions in most of the objects from VNMF and EST, together with Sb and Bi ones (Fig. 8). The occurrence of these inclusions, not detected by EDXRF due to their low concentration and random dispersion in the alloy, could also be related with the use of ores containing impurities of such elements.

As for tin, it was identified in the EST-383 bracelet (1.7 wt.%), also containing low amount of As (0.2 wt.%). Notwithstanding the closeness from a chronological point view with the most ancient tin bronzes currently known from the Portuguese territory, dating back to the second quarter of the II millennium BC (Valério et al. 2014), the low tin content of the bracelet EST-383 makes this alloy comparable from a

chemical point of view with a group of copper-based artifacts belonging to the III and early II millennium BC. Even if this kind of composition is quite rare in Portuguese territory, metals with low content of both Sn and As have been detected, for example, in copper-based metals from Chalcolithic and Early Bronze Age within the SAM project (Junghans et al. 1968; see, for instance, analysis with numbers 1438, 1474, 1539, 1699, 1776, etc.). Cu-based objects with low tin amount and absence or low As content are known from the Chalcolithic sites of Cerro do Castelo de Santa Justa and Cerro do Castelo de Corte João Marques, both in southern Portugal (Gonçalves et al. 1989). Also, in Spanish territory, three awls with low tin percentages (<3.0 wt.%) and As content not exceeding 0.5 wt.% were recovered from contexts attributed to the III/II millennium BC at the site of Cueva Sagrada (Murcia) (Montero-Ruiz 1991).

It is worth highlighting that the effects induced by tin in a copper-based alloy are similar to the ones produced by the presence of As, also becoming noticeable only at concentrations >3.0–4.0 wt.% (Rovira 2004). Thus, lower amounts, such as the 1.7 wt.% contained in the bracelet EST-383, appear to have had little influence on the properties of the final alloy product. As well as for the arsenic content, the low occurrence of tin (<2.0 wt.%) could depend on the remelting of copper-tin alloys without the addition of fresh tin or on the use of polymetallic copper ores with tin impurities as well (Tylecote 1976; Rovira and Montero-Ruiz 2003). An alternative interpretation has been proposed by Giumlia-Mair et al. that states that poor tin metals from the site of al-Midamman (Yemen), dating back to the half of the III millennium BC, could also be interpreted as evidence for tests performed by ancient metallurgists in their quest to experiment adding Sn as a new alloying compound (Giumlia-Mair et al. 2002).

Taking into account the absence of Sn ores in southern Portugal and given the poor technological development of the regional metallurgy from the Chalcolithic up to the Middle Bronze Age, the Sn amount found in the bracelet from

Fig. 8 Backscattered electron image with EDS elemental distribution maps and EDS spectra of the metal fragment VNMF-55, showing the presence of inclusions rich in Pb, Sb, and Bi
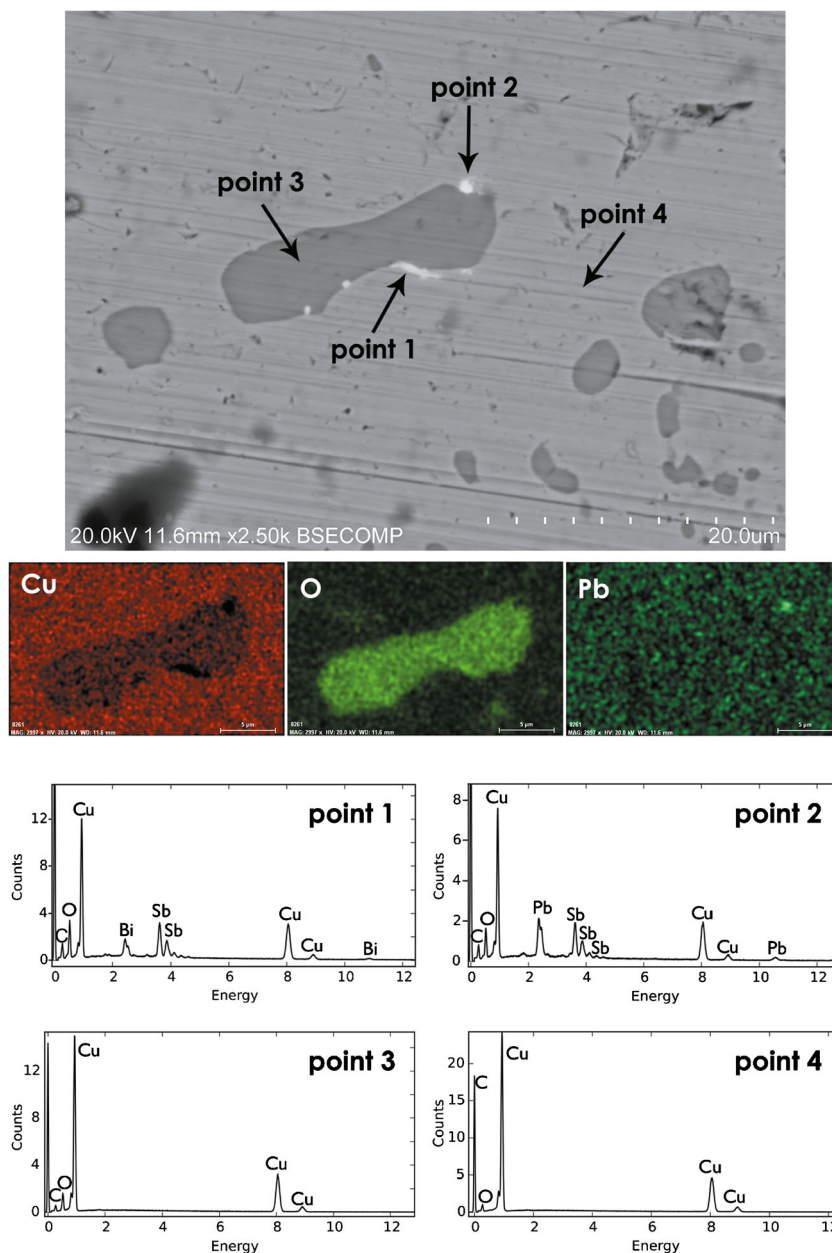
Quinta do Estácio 6 does not seem to be the result of a technological option, i.e., intentional addition of Sn to the alloy. It rather seems to depend on the use of polymetallic Cu ores with tin compounds. Further evidences confirming this hypothesis may come from two sites of southwestern Iberia, namely Llanete de los Moros (Hunt-Ortiz 2003) and Porto das Carretas (Valério et al. 2007), where copper ore fragments with tin impurities have also been found. Also, the local presence of Cu/Sn ores (Rovira and Montero-Ruiz 2003), such as stannoidite ($Cu_8(Fe,Zn)_3Sn_2S_{12}$) and stannite (Cu_2FeSnS_4), both identified in the Iberian Pyrite Belt ore in southern Portugal, in samples respectively from the Neves Corvo (Benzaazoua et al. 2003) and from the Lagoa Salgada deposits

(Oliveira et al. 2009) would strengthen, finally, this assumption.

Conclusions

In the current research, the application of the combined EDXRF/MC simulation protocol has been applied to the study of two collections of metals recovered during the archeological excavations at the Chalcolithic E.T.A.R. de Vila Nova de Mil Fontes site and at the Middle Bronze Age site of Quinta do Estácio 6 site, both in southern Portugal. Unlike the majority of the analytical methodologies used to

obtain quantitative data on archeological metals, the applied spectroscopic analytical protocol implemented in this paper does not require any preliminary removal of corrosion and/or soil-derived superficial patinas, thus allowing to preserve the esthetic integrity of the analyzed objects.

The results showed that the artifacts are composed of either pure Cu and by a Cu/As alloy, also being sporadically present minor elements such as Pb (VNMF-61) and Sn (EST-383). Although the two groups of metals analyzed in this paper have been found in archeological contexts with a distinct chronology, no appreciable differences can be identified in terms of both chemical composition and As variability between the artifacts from the Chalcolithic VNMF and those from the Middle Bronze Age EST. At the same time, and unlike other regional cases, there is no apparent evidence of correlation between the typology and the function of the artifacts and their own As content, not being evident the use of a specific alloy for the production of a certain type of objects or of objects with specific functionalities. Thus, and according with the data, it seems plausible that ancient metalworkers made use of recycled scrap metals with variable amount of As or of Cu ores containing different amounts of As (and in the case of the bracelet from EST, of Sn), being the intentional addition of As during the metal production process admissible only for those artifacts showing higher As content.

Although very few archaeometric analyses have characterized properly the metals produced in southern Portugal in the period ranging from the Chalcolithic to the Middle Bronze Age, the elemental composition of the alloys used for making the objects studied in the present paper is in line with the early metallurgy known both in southern Portugal and in the neighboring regions, namely in Andalusia and Central Portugal. This circumstance highlights a framework already noted in previous studies, in which the production of metal artifacts from these regions appears to be characterized by a prolonged conservative character, without archeological clues able to exhibit any form of technological innovations within the metallurgical process for nearly 2000 years.

In summary, the results obtained on the metals from E.T.A.R. de Vila Nova de Mil Fontes and Quinta do Estácio 6 confirm that EDXRF/MC protocol is a reliable and accurate XRF quantification methodology, proving to work also when applied for the first time to patina-covered pure Cu metal objects thus extending its range of applications as a nondestructive potential analytical tool in the study of metallic archaeomaterials, being particularly suitable for those metals for which, due to their uniqueness and valuable nature, sampling is not an admissible alternative.

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