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MICROANALYTICAL STUDY OF COPPER ORES FROM THE CHALCOLITHIC SETTLEMENT OF SÃO PEDRO (PORTUGAL): COPPER PRODUCTION IN THE SOUTH-WESTERN IBERIAN PENINSULA*

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Copper ores recovered at the third millennium BCE *settlement of São Pedro, Portugal, were characterized by micro-Raman spectroscopy, micro-energy dispersive X-ray spectrometry (micro-EDXRF) and micro-particle-induced X-ray emission spectrometry (micro-PIXE). The collection shows the common presence of secondary copper minerals (malachite, pseudomalachite and libethenite) combined with iron oxyhydroxides (hematite and goethite), while arsenic-rich minerals are absent and, therefore, can be excluded as the source of arsenical copper. Overall, these copper ores suggest a primitive technology involving the exploitation of the superficial zone of ore bodies and reliant on the fortuitous finding of arsenic-rich sources to produce the arsenical copper alloy frequently present among metallic collections of the Iberian Peninsula.*

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INTRODUCTION

The third millennium BCE witnessed the wide spread of copper metallurgy in the Iberian Peninsula, comprising ore smelting in ceramic crucibles to produce the raw metal, which was later used in tools and weapons of basic typology such as awls, flat axes, daggers and arrowheads (Rovira and Montero-Ruiz 2013). Early artefacts were composed of Cu with varying contents of arsenic, an alloying element that induces significant changes to the metal, such as a better castability, higher strain hardening and a silvery colour. However, it is still unclear whether the arsenical Cu alloy (Cu with more than 2 wt% arsenic) was intentionally produced and, if so, whether it would be used as a prestige symbol owing to its unique colour or be chosen for more practical reasons such as the higher hardness of hammered artefacts (Müller *et al.* 2007; Müller and Cardoso 2008; Müller and Soares 2008; Pereira *et al.* 2013; Valério *et al.* 2017).

The study of ore samples from ancient mines located in the south-western Iberian Peninsula suggests the common occurrence of secondary Cu ores occasionally associated with As-bearing minerals (Rothenberg and Blanco-Freijeiro 1981; Gauss 2015). However, the samples collected in modern times may not be representative of the ores exploited by prehistoric communities. On the contrary, ore samples recovered by archaeological excavations in Chalcolithic settlements are actual remnants of the raw materials collected in ancient times in the near-surface zone of ore bodies. Most likely, these raw materials would be high-grade Cu ores readily identifiable by their greenish colour and easily processed with the available smelting technology. A very small number of specimens belonging to settlements in south-western Iberian Peninsula have been studied, indicating them to be composed of a mixture of Cu carbonates and iron oxyhydroxides without As (Gaspar 1994; Sáez *et al.* 2003; Nocete *et al.* 2008).

Archaeological works at São Pedro, southern Portugal (Fig. 1), revealed a Chalcolithic settlement with a notable collection of metallurgical materials (Mataloto *et al.* 2017). Apart from many tools and weapons (Vidigal *et al.* 2016), the set included ore samples, ceramic crucibles and slags, all of which attest to the existence of metallurgical operations at the settlement. Moreover, the lead isotopic signature of metallic prills of local smelting operations is consistent with Cu sources in the Ossa Morena Zone (Gauss 2015). The metallurgical materials belong to different occupation phases (phases II–V), which radiocarbon dating of bone samples assigned to the second (Phase II) and third quarter (Phase IV) of the third millennium BCE (Valério *et al.* 2017). Between these phases, there was a short period (Phase III) involving the destruction of Phase II structures and the construction of Phase IV structures. The last occupation of the site (Phase V) could not be radiocarbon dated, but the existing stratigraphy and the existence of Bell Beaker ceramics ascribes it to the last quarter of the third millennium BCE.

The collection of ore samples from São Pedro settlement was then subjected to an elemental and mineralogical study to provide valuable answers about the metallurgy of this Chalcolithic community. A microanalytical methodology was chosen to preserve the physical integrity and archaeological significance of this irreplaceable evidence of prehistoric mining, although a few representative samples have required some processing for further study. Moreover, the eventual association of As with ores of distinct colour was investigated, as it would

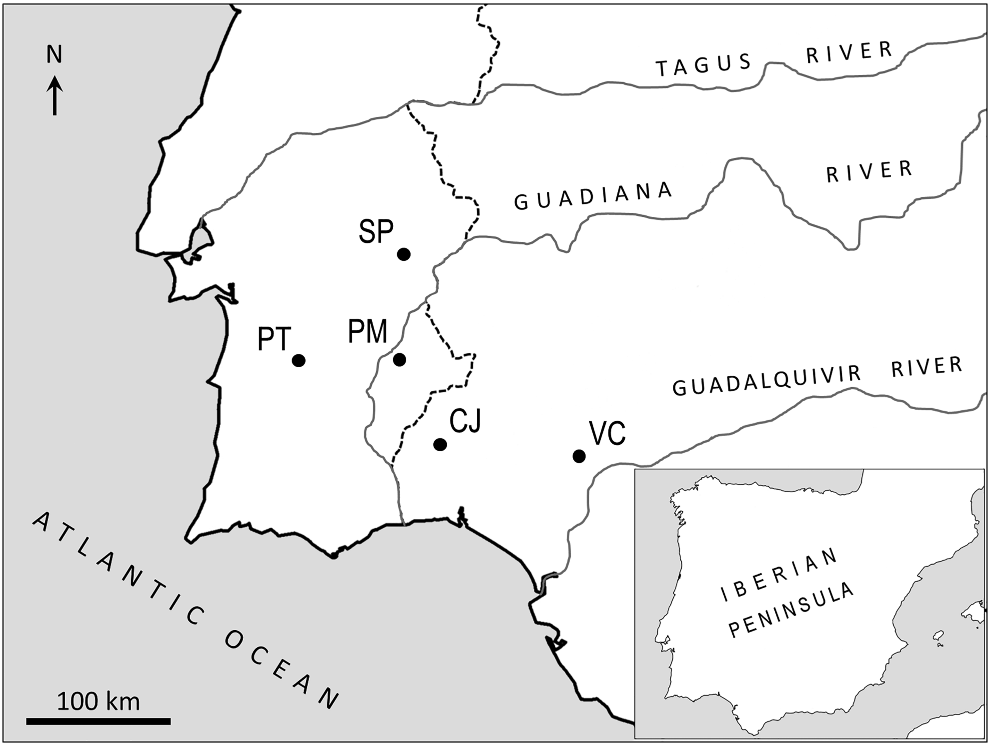

Figure 1 *South-western Iberian Peninsula with the location of São Pedro (SP) and other settlements with studied ore samples mentioned in the text: Porto Torrão (PT), Porto Mourão (PM), Cabezo Juré (CJ) and Valencina de la Concepción (VC) (Gaspar 1994; Sáez et al. 2003; Nocete et al. 2008).*

be a simple method to identify As-rich Cu ores, and thus to obtain the basis for the arsenical copper alloy often found in Chalcolithic artefacts.

MATERIALS AND METHODS

Ore samples

The set of ore samples recovered during archaeological excavations at São Pedro settlement comprises 22 small specimens from occupation phases II–IV and weighing between 0.1 and 14.8 g (Table 1). Considering that we are dealing with a primitive metallurgy, it is safe to assume that prehistoric miners would seek for the characteristic green colour of Cu ores, which are usually found in the supergene oxidized zone of certain type of ore bodies. In this region, we should emphasize the ore bodies comprising the Estremoz-Alandroal and Barrancos-S^{to} Aleixo regions (Mateus *et al.* 2003), which are 14–19 km from the settlement. Therefore, the relevance of each ore body to prehistoric miners would most likely be directly related to the amount of green constituents, and so the collection of ores from São Pedro was divided in four types according to the visual appearance of each sample: green (type I), seven samples; dark grey (type II), five samples; brown (type III), eight samples; and red (type IV), two samples. It should be emphasized that there is no clear relation between occupation phase and ore type (Table 1), thus

Table 1 *Distribution of ore samples between the different occupation phases of the Chalcolithic settlement of São Pedro*

Occupation phase	*Ore sample*	*Weight (g)*	*Type*
Phase II	SP0925	0.2	I
Phase II	SP2572	0.5	I
Phase II	SP2385	9.3	III
Phase II	SP2450	2.8	III
Phase II	SP2777	1.5	III
Phase II	SP2823	4.2	III
Phase III	SP1690	4.4	I
Phase III	SP1515	0.9	III
Phase III	SP1635	9.2	IV
Phase IV	SP0987	1.1	I
Phase IV	SP3030	0.1	I
Phase IV	SP0208	1.8	II
Phase IV	SP1465	7.1	II
Phase IV	SP1565	8.0	II
Phase IV	SP1586	14.7	II
Phase IV	SP2151	8.4	III
Phase IV	SP0743	3.1	IV
Phase V	SP0115	14.8	II
Unknown	SP000A	8.2	I
Unknown	SP000B	0.1	I
Unknown	SP000C	0.2	III
Unknown	SP000D	0.4	III

inhibiting a chronological valuation that could possibly point out to changes in sources of Cu exploited by this community. Other important factors in more recent times, such as the optimal metal recovery owing to the formation of a liquid slag with suitable Fe and silica contents, were not yet significant in those early stages due to the low quantity of metal entailed by Chalcolithic communities (Bourgarit 2007).

Initially, the samples were photographed with a QP colour reference card using a Nikon D200 digital camera. Closer observation with a Zeiss DiscoveryV20 stereomicroscope then enabled the selection of the areas suitable for micro-analysis. The mineralogical and elemental characterization was made by micro-Raman spectroscopy (micro-Raman) and micro-energy dispersive X-ray spectrometry (micro-EDXRF). Additionally, some representative samples were mounted in resin (Paralloid B72, 15% in acetone) and polished (up to 8000 grit size) for further characterization with elemental mapping analyses by micro-EDXRF and micro-particle-induced X-ray emission spectrometry (micro-PIXE), the latter being capable of a better spatial resolution, that is, typically $5 \times 5\,\mu m^2$ instead of $100 \times 100\,\mu m^2$.

Micro-Raman

Raman microscopy was carried out using a Labram 300 Jobin Yvon spectrometer equipped with a HeNe laser of 17 mW operating at 632.8 nm. Spectra were recorded as an extended scan. The laser beam was focused with 50× Olympus objective lens. The laser power at the surface of the samples was varied with the aid of a set of neutral density filters (optical densities of 0.3, 0.6 and 1.0). A minimum of 10-point analysis was made in each area of interest to obtain a reliable characterization of different constituents (Smith and Clark 2004).

Micro-EDXRF

Microanalyses were made with an ArtTAX Pro spectrometer equipped with a 30 W molybdenum X-ray tube, focusing polycapillary lenses and an electrothermally cooled silicon drift detector with a resolution of 160 eV at 5.9 keV. Polycapillary optics focus the primary X-ray beam enabling an optimal spatial resolution of around 70 µm, while a CCD camera and a motorized positioning system allow the precise selection of the analysis area on the sample surface (Bronk *et al.* 2001). Micro-EDXRF point analyses were carried out with 40 kV of tube voltage, 600 µA of current intensity and 100 s of live time spectrum acquisition, while the micro-EDXRF elemental mapping analyses were made with 40 kV, 600 µA and 20 s, in sample areas ranging from 0.6×0.6 to $1.6 \times 1.6\,\mathrm{mm}^2$ (100 or 200 µm step size, respectively).

Micro-PIXE

Elemental mapping analyses were carried out using an Oxford Microbeams scanning nuclear microprobe set-up using a 2.0 MeV proton beam generated by a 2.5 MV Van de Graaf accelerator, together with a $30\,\mathrm{mm}^2$ SDD X-ray detector with a resolution of 145 eV at 5.9 keV (Alves *et al.* 2000). With the beam focused down to $5 \times 5\,\mu\mathrm{m}^2$, elemental distribution maps were obtained from sample areas up to $2.64 \times 2.64\,\mathrm{mm}^2$.

RESULTS AND DISCUSSION

Elemental and mineralogical characterization

Micro-EDXRF analyses of type I samples ('green' ores) show pure Cu ores with minor amounts of Fe and As (Fig. 2). The Cu content of these ores depends mostly on the amount of gangue material and can hardly be estimated from such small samples. Micro-Raman analyses of type I samples identified the main ore component as malachite ($Cu_2CO_3(OH)_2$). Additionally, cuprite (Cu_2O) occurs as small inclusions in two samples (SP000A and SP000B). The gangue is mostly composed of hematite (α-Fe_2O_3) and goethite (α-FeO (OH)), in addition to some amount of quartz (SiO_2) and anatase (TiO_2). The smelting of such high-grade Cu ore would produce very little amount of slag, which is in accordance to what is usually found in prehistoric contexts with evidences of smelting operations in the Iberian Peninsula (Rovira and Montero-Ruiz 2013).

Micro-EDXRF analyses of type II samples ('dark grey' ores) evidence a composition quite different from the former group due to the presence of an Fe–Cu matrix with non-metallic impurities (Fig. 2). Moreover, none of these type II samples exhibits traces of As, which is a common impurity among type I Cu ores. Consequently, the type II ore samples proved to be a mixture of minerals with prevalence of Fe-bearing phases in dark grey areas versus the predominance of Cu-bearing phases in green areas. Micro-Raman analyses of type II ore samples identified a mixture of hematite and goethite with malachite, pseudomalachite ($Cu_5(PO_4)_2(OH)_4$) and libethenite (Cu_2PO_4OH). Additionally, one of these specimens (SP1586) showed some vestiges of tenorite (CuO).

Micro-EDXRF analyses of type III samples ('brown' ores) show an overall composition very similar to the one of type II ores, namely an Fe–Cu rich matrix with non-metallic impurities. A significant distinction consists in the presence of As in the majority of type III samples (SP1515, SP2151, SP2777 and SP2823), whereas this element is totally absent in type II ores. Moreover, micro-Raman analyses showed a higher ratio of goethite/hematite in type III samples, which can probably explain the different visual appearance of these two ore groups. There are

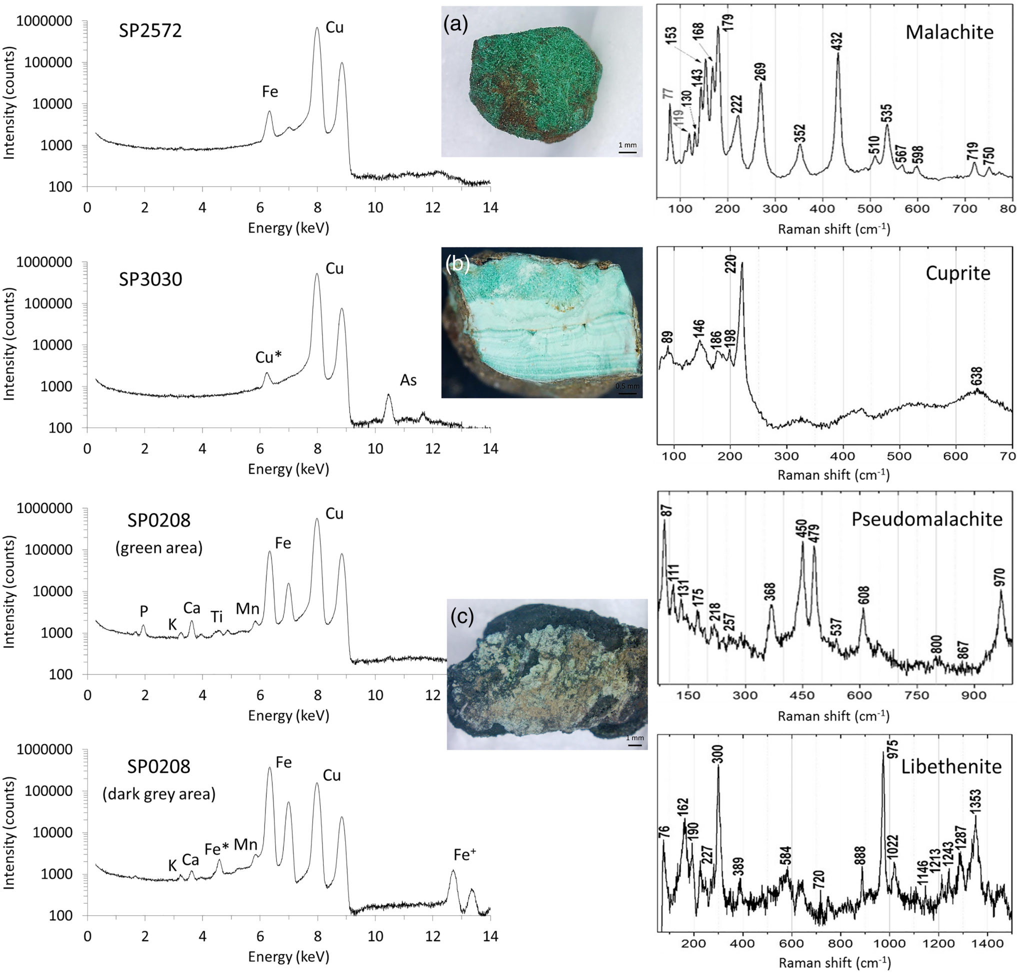

Figure 2 *Micro-EDXRF spectra of type I samples (A: SP2572 and B: SP3030) and a type II sample (C: SP0208—green and dark grey areas) (*escape peak; $^{+}$sum peak). Micro-Raman spectra of malachite, cuprite, pseudomalachite and libethenite identified in some type I and type II samples from the Chalcolithic settlement of São Pedro. [Colour figure can be viewed at wileyonlinelibrary.com]*

two samples, however, that have quite distinct compositions, despite showing the typical brown/green colour of type III samples: the micro-EDXRF analyses of SP000C and SP000D samples evidence a complex composition with low Cu content and the uncommon presence of chromium and lead (Fig. 3). Micro-Raman analyses identified hematite and quartz, in addition to celadonite ($(K,Al,Fe,Mg)AlSi_6O_{10}(OH)_2$) and crocoite ($PbCrO_4$). The latter component was only identified in sample SP000C, but the compositional resemblance established by micro-EDXRF analyses indicates that crocoite should be present in both samples.

Micro-EDXRF and micro-Raman analyses of type IV samples (‘red’ ores) evidence a mixture of Fe oxyhydroxides with Cu minerals (Fig. 3). The Cu species were identified as malachite, pseudomalachite and libethenite. Moreover, most of the Raman spectra of hematite and goethite show the MnO_2 characteristic bands (612 and 659 cm^{-1}; Montagner *et al*. 2013) indicating the

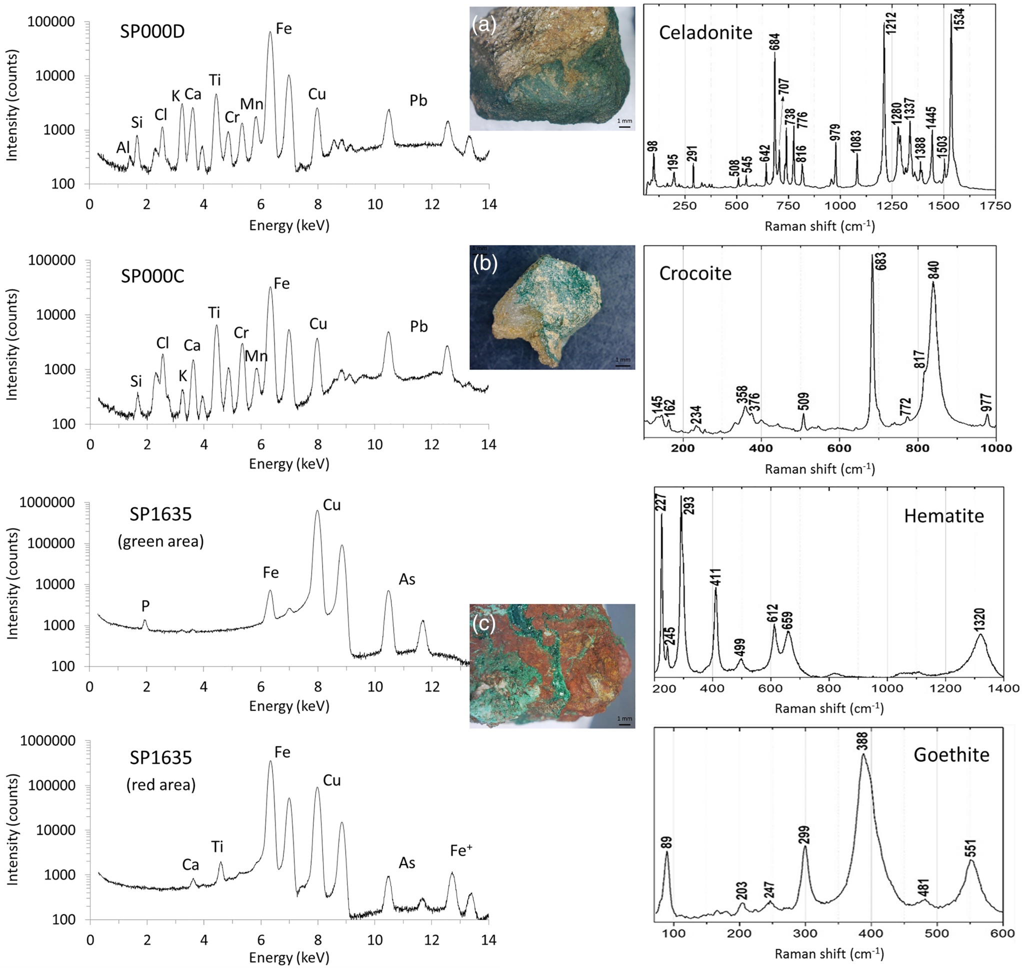

Figure 3 *Micro-EDXRF spectra of type III samples (A: SP000D and B: SP000C) and a type IV sample (C: SP1635—green and red areas) ($^+$ sum peak). Micro-Raman spectra of celadonite and crocoite detected in these type III samples and micro-Raman spectra of hematite and goethite identified in some type IV samples from São Pedro (the 612 and 659 cm^{-1} bands in the hematite spectrum are due to MnO_2 evidencing a manganese-rich hematite). [Colour figure can be viewed at wileyonlinelibrary.com]*

presence of Fe phases rich in manganese or mixture of Fe phases with manganese oxides (MnO_2), which is not uncommon in such circumstances. Another significant evidence concerns a poorly defined broad band (817–840 cm^{-1}) in the Raman spectra of hematite and goethite, which corresponds to the presence of adsorbed As in these Fe-rich phases (Das and Hendry 2011). The characteristic bands of MnO_2 and adsorbed As were identified in ore samples (types II–IV) showing a significant presence of those in Fe oxyhydroxides.

The mineral components identified in ore samples from São Pedro are summarized in Table 2. Apart from type I samples that proved to be very rich in malachite, the remaining ore types have variable amounts of other secondary Cu minerals such as pseudomalachite and libethenite, in addition to Fe-rich phases such as hematite and goethite. Despite the high content of Fe-bearing phases in type II–IV samples, Cu is also present in significant amounts in these ores (cf., for

Table 2 *Mineralogical composition identified by micro-Raman in ore samples from the Chalcolithic settlement of São Pedro*

Type	*Ore sample*	*Mineralogical composition*
I	SP000A	**Malachite**, cuprite, hematite, goethite, quartz, anatase
I	SP000B	**Malachite**, cuprite, anatase
I	SP0925	**Malachite**, hematite, goethite, quartz, anatase
I	SP0987	**Malachite**
I	SP1690	**Malachite**, hematite, goethite
I	SP2572	**Malachite**, goethite, anatase
I	SP3030	**Malachite**, hematite, goethite, anatase
II	SP0115	**Hematite**, **goethite**, **malachite**, quartz
II	SP0208	**Hematite**, **malachite**, **pseudomalachite**, quartz, anatase
II	SP1465	**Hematite**, **malachite**, quartz
II	SP1565	**Hematite**, **goethite**, **malachite**, libethenite, quartz
II	SP1586	**Hematite**, **malachite**, libethenite, tenorite, quartz
III	SP000C	**Hematite**, quartz, celadonite, crocoite
III	SP000D	**Hematite**, quartz, celadonite, crocoite (?)
III	SP1515	**Goethite, hematite**, **malachite**, **pseudomalachite**, quartz
III	SP2151	**Goethite, malachite**, **pseudomalachite**, anatase
III	SP2385	**Goethite, malachite**, quartz
III	SP2450	**Goethite, malachite**, tenorite, anatase
III	SP2777	**Hematite**, **malachite**
III	SP2823	**Goethite**, **hematite**, **malachite**, **pseudomalachite**, tenorite, anatase
IV	SP0743	**Hematite**, **goethite**, **libethenite**, quartz
IV	SP1635	**Hematite**, **goethite**, **malachite**, **pseudomalachite**, anatase, quartz

*Type I, 'green'; type II, 'dark grey'; type III, 'brown'; type IV, 'red'. Text shown in bold indicates a main mineralogical component.

instance, the micro-EDXRF spectra of type I, II and IV samples; Figs 2 and 3). Moreover, Cu is mostly present as an easily reducible phase (malachite), suggesting that type II–IV ores could also be used as a source of metal, in spite of being obviously less profitable than type I ores. Nevertheless, the smelting of ores with a high amount of Fe-rich phases would produce a certain amount of slag. In this case, the small volume of slags recovered in the archaeological record might be due to the small-scale metallurgical practice of this early chronological period and to the difficulty in finding those remains because of the crushing of the smelting charge to collect the Cu prills (Rovira 2002a; Hunt-Ortiz 2003). Alternatively, it should be considered whether the small amount of slag in the archaeological record implies the prevailing use of high-grade ores such as type I, while the other types (II–IV) would have only a minor role in this prehistoric metallurgy.

The ore concentration and Cu smelting at settlements such as São Pedro is another indication of the small-scale metallurgical practice of this period. The most logical action for large operations was to carry out these operations at the mining site, but there is evidence of the use of stone mortars and hammers in sites away from mining areas, for example, Amarguillo, Cerro do Castelo de Corte João Marques and Carmona (Hunt-Ortiz 2003). As pointed out by Rovira (2002a), this means that on many occasions the circulating commodity was the ore instead of the ingots or finished objects. The ore beneficiation at the settlement may also mean that some of the studied samples may have been discarded after being brought from the mine. For instance, the type IV samples (SP0743 and SP1635), rich in Fe oxides, could have been used as pigments for ritual practices, which are well documented in the south-western Iberian Peninsula at sites such as Pijotilla and Valencina de la Concepción (Hunt-Ortiz 2003). On the other hand, some of the studied samples are so small that they also may have been lost during the beneficiation process, thus being real vestiges of the smelting charge.

The As 'connection'

As constitutes the main metallic impurity of Cu ores recovered at the settlement of São Pedro. The pattern agrees with the collection of tools and weapons from this site, showing Cu with 2.3 ± 1.6 wt% As (average ± standard deviation, $n = 30$). More specifically, the set has 14 artefacts made of Cu and 16 artefacts composed of arsenical copper, including four high-arsenical Cu alloys (As $>$ 4 wt%) (Vidigal *et al.* 2016). The absence of significant amounts of other elements (e.g., Co, Ni, Zn, Sn, Sb, Pb or Bi) in artefacts of São Pedro is also in agreement with the majority of ore samples identified in this site. The exceptions are samples SP000C and SP000D due to the significant amount of Cr and Pb, in addition to samples SP1515, SP1635 and SP2823 due to the presence of Ni. The production of Cu with varying As content is a recurrent feature of the Chalcolithic metallurgy in the south-western Iberian Peninsula, as evidenced by a collection of about 200 artefacts from 26 archaeological sites spread throughout the region (Valério *et al.* 2019). The association of arsenical Cu alloys with certain articles, such as daggers and arrowheads, is another distinctive trait of this early metallurgy. The selection of As-rich raw materials could be made for aesthetic reasons rather than functional purposes due to the apparent inability of those metallurgists to exploit the hardening capability of As fully (e.g., Pereira *et al.* 2013; Valério *et al.* 2017). Other authors suggest that the differences in As content between different types of artefacts might be explained by the higher probability of recycling of metals collected in settlements when compared with objects chosen to be deposited in graves (Rovira and Delibes de Castro 2005; Rovira and Montero-Ruiz 2018).

There are some questions, however, regarding the production of Chalcolithic arsenical Cu alloys due to the low occurrence of As rich minerals in the supergene oxidized ores exploited during the third millennium BCE in the south-western Iberian Peninsula (Gaspar 1994; Sáez *et al.* 2003; Valério *et al.* 2007; Nocete *et al.* 2008; Gauss 2015). In the south-east region there is evidence of the use of Cu arsenates such as olivenite in the Chalcolithic settlements of Almizaraque (Rovira 2002b) and Agua Amarga (Artigas *et al.* 2016). However, a preliminary characterization by neutron activation analysis of six ore samples from São Pedro showed very low As contents, 0–0.30 wt% As (Gauss 2015, 264). A few smelting experiments with ores collected from five different ore deposits in Portugal suggested that ores with a low As content can produce Cu with a high As content (Hanning *et al.* 2010). The high partition coefficient of As between Cu and slag can be explained by the cementation of gaseous As_2O_3 into Cu (Hauptmann 2007, 205), hence this strong affinity of As to molten Cu (Sabatini 2015) will produce an enrichment in some smelting prills. Therefore, it has been argued that prills with a higher As content, which display a distinctive silvery colour, could be chosen to produce specific types of artefacts of high prestige value (Müller *et al.* 2007; Müller and Cardoso 2008; Müller and Soares 2008). However, it is arguable whether such a procedure based on the casual smelting of Cu ores with some As content would be enough to obtain the collection of artefacts from the settlement of São Pedro, which is predominantly (53%) composed of specimens made of arsenical Cu (Vidigal *et al.* 2016).

The assemblage of Cu ores from São Pedro opened a new possibility regarding the identification of As-rich sources. As the mineralogical characterization showed the absence of As minerals, an alternative method for the selection of As-rich Cu ores comprised the association of As with ores of distinct colour, which would be controlled by the chemistry of those ores. It should be stressed that among the unaltered and non-oxidized primary mineralogy of the Cu deposits surrounding the São Pedro settlement, apart from chalcopyrite ($CuFeS_2$), usually low but variable quantities of arsenopyrite (FeAsS) occur (Mateus *et al*. 2003). These deposits also develop variable deeply weathered profiles that result in the surface mineralogy with the secondary Cu ores. Some of those secondary Cu ores show quite significant amounts of Fe oxyhydroxides yielding a distinctive reddish colour. The micro-EDXRF mapping of one of those type IV ores (SP0743) confirmed the absence of As already identified by spot analyses, thus only exhibiting an association of Cu and phosphorous due to libethenite. The elemental mapping of the other type IV sample (SP1635) was much more informative, but the As seems to be associated either with Cu or with Fe depending on the analysed area (Fig. 4). Sample SP2823 was also characterized due to a significant presence of reddish areas, whose elemental mapping

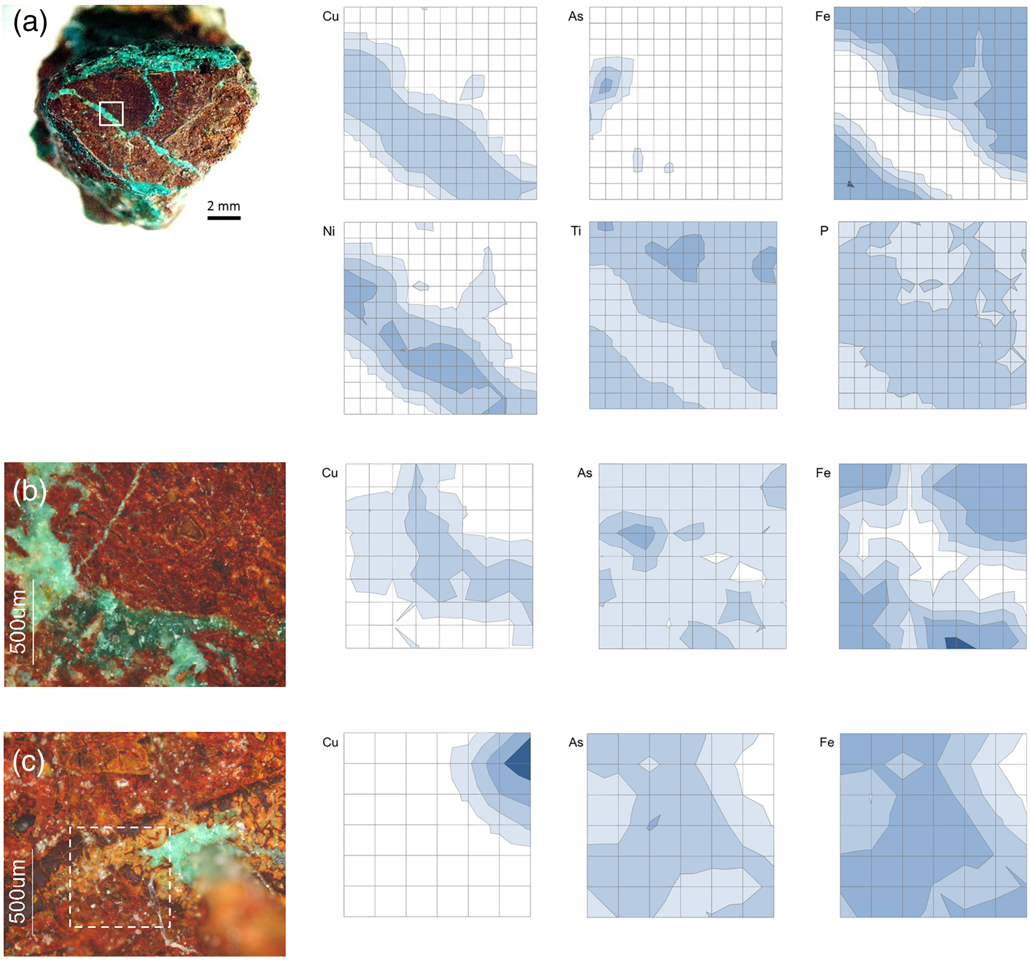

Figure 4 *Micro-EDXRF mapping of ore sample SP1635 from São Pedro (left: general image of the mapped area; area A: 1.2 × 1.2 mm^2 and 100 µm step size; area B: 1.6 × 1.6 mm^2 and 200 µm step size (the mapped area is larger than the optical image shown); area C: 0.6 × 0.6 mm^2 and 100 µm step size; the maps of Ni, Ti and P in areas B and C were not considered to simplify the figure). [Colour figure can be viewed at wileyonlinelibrary.com]*

evidenced a clear correlation between As and Fe (Fig. 5). The evident relationship of Fe and Mn in this sample was already identified by MnO$_2$ characteristic bands in the micro-Raman spectra of hematite and goethite resulting from the occurrence of Mn-rich Fe oxyhydroxides.

The elemental mapping of higher resolution using micro-PIXE was made on samples SP1635 and SP2823 to investigate better the apparent mixed behaviour of As (Fig. 6). The sample SP1635 has the As dispersed by Cu- and Fe-rich areas, but mostly associated with non-metallic elements (e.g., Si, P, K and Ca). Regarding the mapping of sample SP2823, the As is also distributed by Cu- and Fe-rich areas, although with some preponderance to these latter ones. These observations suggest a heterogeneous distribution of As in the ores, which seems to be controlled by its availability and current secondary mineralogy. First, it is likely that different ore types may have different sources (there are several known Cu deposits within a 20 km radius), since small differences in either primary or secondary mineralogy exist as has been reported by Mateus *et al*. (2003), and can result in the presence or absence of As in the collected ores. The different deposits of the Estremoz-Alandroal and S$^{\text{to}}$ Aleixo-Barrancos region have distinct As concentrations, mostly ranging from 0.1 to 0.7 wt%, but locally can go up to 8 wt

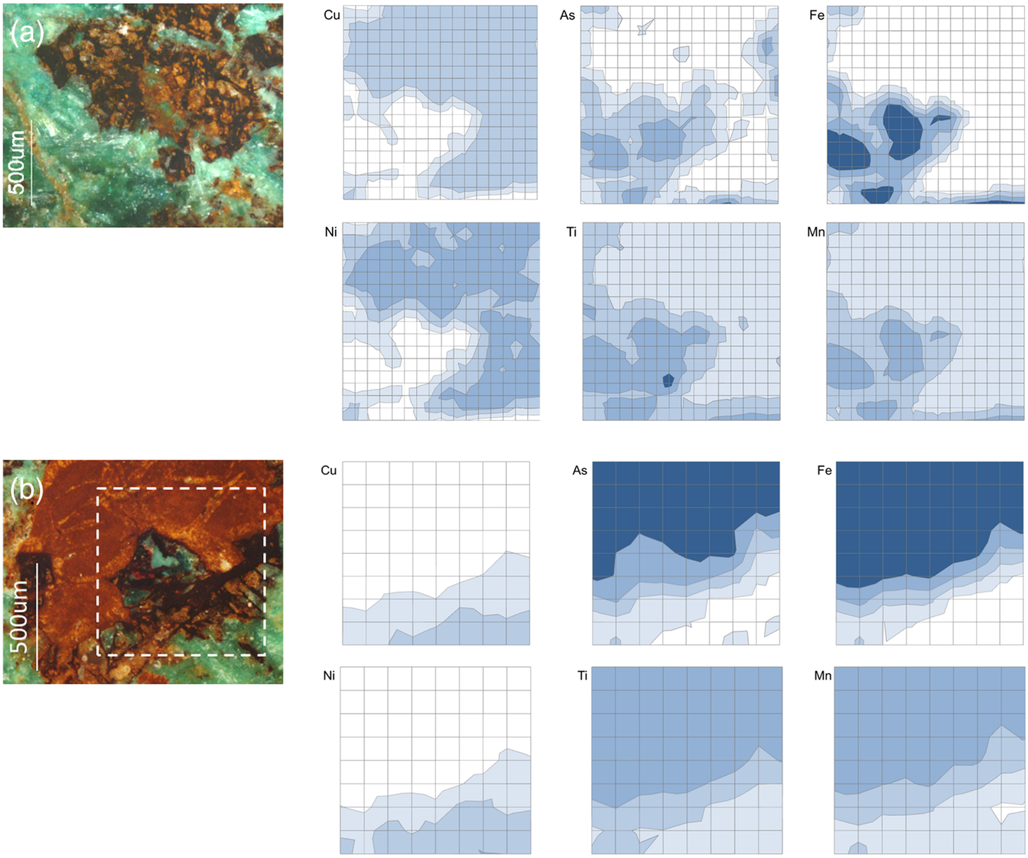

Figure 5 *Micro-EDXRF mapping of ore sample SP2823 from São Pedro (left: general image of the mapped area; area A: 1.6 × 1.6 mm^2 and 100 µm step size (the mapped area is larger than the optical image shown); area B: 0.8 × 0.8 mm^2 and 100 µm step size). [Colour figure can be viewed at wileyonlinelibrary.com]*

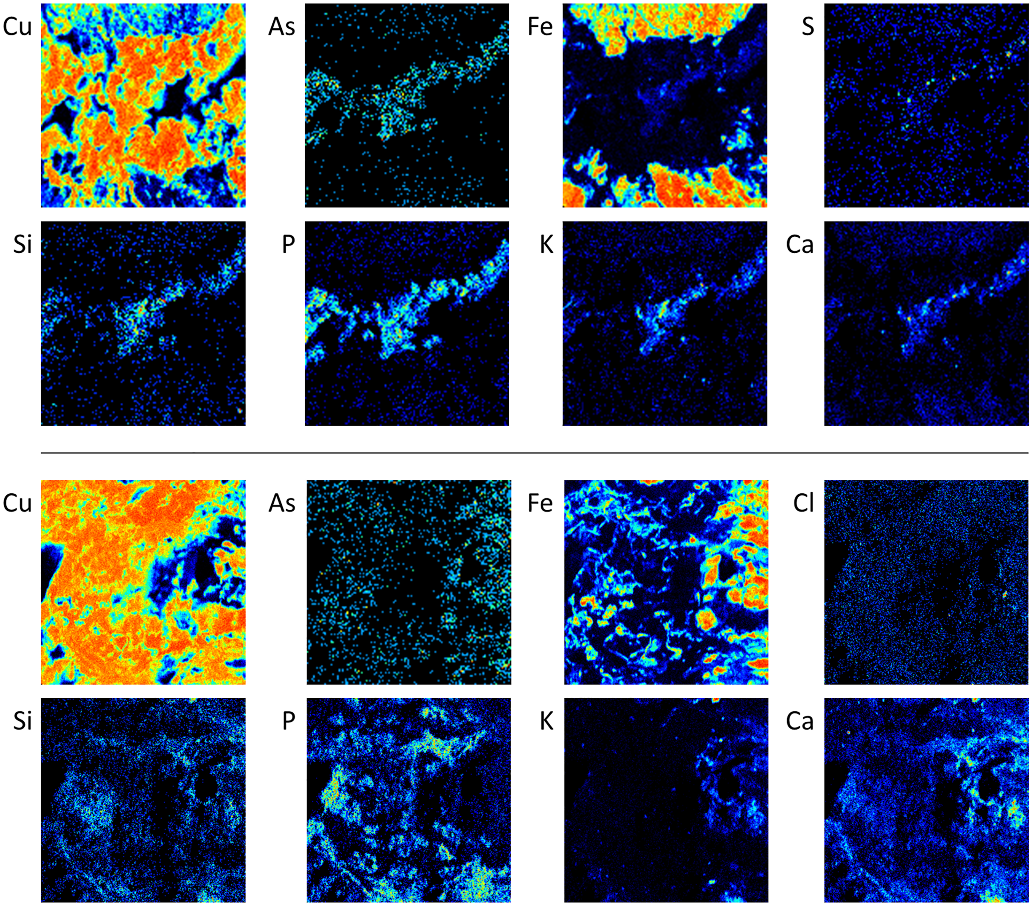

Figure 6 *Micro-PIXE mapping over a 2.64 × 2.64 mm*^{2} *area of ore samples SP1635 (top) and SP2823 (bottom) from the Chalcolithic settlement of São Pedro. [Colour figure can be viewed at wileyonlinelibrary.com]*

%. Second, As, as arsenate ion (AsO_4^{3-}), has the ability either to substitute for other anions or to sorb onto mineral phases. The affinity of As ions for Fe oxyhydroxide phases is well known (Campbell and Nordstrom 2014), and because arsenate is isostructural and isoelectric with phosphate (PO_4^{3-}), it can substitute this ion in the structure of phosphate minerals (Lee *et al.* 2009; Zhang *et al.* 2011). These aspects can explain part of the results obtained, especially the combined association of As with Cu and phosphorous, which would suggest its incorporation in the libethenite structure as observed in sample SP1635. Therefore, albeit As concentrations being relatively low, its distribution in the different ore samples depends on the relative chemical affinity for the coexisting phases and their timing of co-precipitation with As species. However, sorption onto other phases and the development of nanosized clusters within mineral mixtures is also a possibility. Consequently, it is not clear that Cu ores with significant amounts of Fe oxyhydroxides might have higher amounts of As and, therefore, the selection of 'reddish' Cu ores cannot be considered an alternative to produce the arsenical Cu alloy often associated with some prehistoric typologies.

CONCLUSIONS

The elemental and mineralogical characterization of ore samples recovered by archaeological excavations at the Chalcolithic settlement of São Pedro established that these ores were composed of a variable combination of secondary Cu minerals (malachite, pseudomalachite and libethenite) and Fe oxyhydroxides (hematite and goethite). These minerals are typical of the supergene oxidized zone of ore bodies, thus being easily exploited without the need of complex mining operations. However, it is conceivable that high-grade Cu ores mostly composed of malachite (type I) have played a major role in this prehistoric metallurgy due to the absence of significant amounts of slags in the archaeological record. Moreover, such secondary Cu minerals could be efficiently exploited, even with the primitive reducing conditions of the Chalcolithic metallurgy that result from smelting in open ceramic crucibles filled with crushed ore and covered by wood or charcoal.

The collection of ore samples from the São Pedro settlement did not show the As-rich minerals occasionally suggested as the source for arsenical Cu alloys in Chalcolithic assemblages. Moreover, there is no clear association of As with the distinct-looking ores exploited by those ancient communities, thus hindering the selection of As-rich Cu ores based on their colour, as was also proposed for the early metallurgy of the British Isles and the south-eastern Iberian Peninsula (Pollard *et al*. 1990; Montero-Ruiz 1994).

For the moment, the more likely method for the production of arsenical Cu alloys during the third millennium BCE in the south-western Iberian Peninsula seems to be the selection of As-rich Cu prills. It should be emphasized, however, that such a system is dependent on the fortuity of finding As-rich Cu ores and it could only thrive in a society with a low demand for metal. Therefore, the growing importance of arsenical Cu alloys, clearly visible among metallic collections of the following millennium (Valério *et al*. 2016), should have given rise to new production systems that require further research.

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REFERENCES

Alves, L. C., Breese, M. B. H., Alves, E., Paul, A., Silva, M. R., Silva, M. F., and Soares, J. C., 2000, Micron-scale analysis of SiC/SiC_f composites using the new Lisbon nuclear microprobe, *Nuclear Instruments and Methods in Physics Research Section B*, **161**, 334–8.

Artigas, N. E., Bourgarit, D., and Mille, B., 2016, Mezcla de minerales y cobre arsenical durante el Calcolítico. El exceptional Caso de Agua Amarga (La Fuensanta, Lorca), *Alberca*, **14**, 7–30.

Bourgarit, D., 2007, Chalcolithic copper smelting, in *Metals and mines: Studies in archaeometallurgy* (eds. S. La Niece, D. Hook, and P. T. Craddock), 3–14, Archetype Publications, Oxford.

Bronk, H., Rohrs, S., Bjeoumikhov, A., Langhoff, N., Schmalz, J., Wedell, R., Gorny, H. E., Herold, A., and Waldschlager, U., 2001, ArtTAX—a new mobile spectrometer for energy-dispersive micro X-ray fluorescence spectrometry on art and archaeological objects, *Fresenius Journal of Analytical Chemistry*, **371**, 307–16.

Campbell, K. M., and Nordstrom, D. K., 2014, Arsenic speciation and sorption in natural environments, in *Arsenic: Environmental geochemistry, mineralogy and microbiology* (eds. R. J. Bowell, C. N. Alpers, H. E. Jamieson, D. K. Nordstrom, and J. Majzlan), 185–216, Reviews in Mineralogy and Geochemistry, Vol. **79**, Mineralogical Society of America, Virginia.

Das, S., and Hendry, M. J., 2011, Application of Raman spectroscopy to identify iron minerals commonly found in mine wastes, *Chemical Geology*, **290**(3–4), 101–8.

Gaspar, O., 1994, Análise por microscopia óptica de reflexão de duas amostras de minerais, in *Arqueologia en el entorno del Bajo Guadiana: Actas del Encuentro Internacional de Arqueologia del Suroeste* (eds. J. M. Campos, J. A. Pérez, and F. Gómez), Vol. **192**, Universidad de Huelva, Huelva.

Gauss, R., 2015, *Zambujal und die anfänge der metallurgie in der Estremadura (Portugal)*, Wasmuth Verlag, Berlin.

Hanning, E., Gauss, R., and Goldenberg, G., 2010, Metal for Zambujal: Experimentally reconstructing a 5000-year-old technology, *Trabajos de Prehistoria*, **67**(2), 287–304.

Hauptmann, A., 2007, *The archaeometallurgy of copper. Evidence from Faynan*, Jordan, Springer Verlag, Berlin.

Hunt-Ortiz, M. A., 2003, *Prehistoric mining and metallurgy in south west Iberian Peninsula*, Archaeopress, Oxford.

Lee, Y. J., Stephens, P. W., Tang, Y., Li, W., Phillips, B. L., Parise, J. B., and Reeder, R. J., 2009, Arsenate substitution in hydroxylapatite: Structural characterisation of the $Ca_5(P_xAs_{1-x}O_4)_3OH$ solid solution, *American Mineralogist*, **94**(5–6), 666–75.

Mataloto, R., Costeira, C., and Nukushina, D., 2017, Local shop, for local people. Resource management during the 3rd millennium BCE at São Pedro (Redondo, Portugal), in *Key resources and sociocultural developments in the Iberian Chalcolithic* (eds. M. Bartelheim, P. B. Ramírez, and M. Kunst), 143–66, Tübingen Library Publishing, Tübingen.

Mateus, A., Matos, J. X., Rosa, C., and Oliveira, V., 2003, Cu-ores in quartz-carbonate veins at Estremoz-Alandroal and Barrancos-S^{to} Aleixo regions (Ossa Morena zone): A result of late-Variscan hydrothermal activity? *Ciências da Terra (UNL)*, **5**, F90–F93.

Montagner, C., Diogo, S., Joana, P., Melo, M. J., and Vilarigues, M., 2013, Ochres and earths: Matrix and chromophores characterisation of 19th and 20th century artist materials, *Spectrochimica Acta Part A*, **103**, 409–16.

Montero-Ruiz, I., 1994, *El origen de la metalurgia en el sudeste de la Península Ibérica*, Instituto de Estudios Almerienses, Almería.

Müller, R., and Cardoso, J. L., 2008, The origin and use of copper at the Chalcolithic fortification of Leceia (Oeiras, Portugal), *Madrider Mitteilungen*, **49**, 64–93.

Müller, R., and Soares, A. M. M., 2008, Traces of early copper production at the Chalcolithic fortification of Vila Nova de São Pedro (Azambuja, Portugal), *Madrider Mitteilungen*, **49**, 94–114.

Müller, R., Goldenberg, G., Bartelheim, M., Kunst, M., and Pernicka, E., 2007, Zambujal and the beginnings of metallurgy in southern Portugal, in *Metals and mines: Studies in archaeometallurgy* (eds. S. La Niece, D. Hook, and P. T. Craddock), 15–26, Archetype Publications, Oxford.

Nocete, F., Queipo, G., Sáez, R., Nieto, J. M., Inácio, M., Rodríguez-Bayona, M., Peramo, A., Vargas, J. M., Cruz-Auñón, R., Gil-Ibarguchi, J. I., and Santos, J. F., 2008, The smelting quartier of Valencina de la Concepción (Seville, Spain): The specialised copper industry in a political Centre of the Guadalquivir valley during the third millennium BCE (2750–2500 BCE), *Journal of Archaeological Science*, **35**, 717–32.

Pereira, F., Silva, R. J. C., Soares, A. M. M., and Araújo, M. F., 2013, The role of arsenic in Chalcolithic copper artefacts —Insights from Vila Nova de São Pedro (Portugal), *Journal of Archaeological Science*, **40**, 2045–56.

Pollard, A. M., Thomas, R. G., and Williams, P. A., 1990, Experimental smelting of arsenical copper ores: Implications for early bronze age copper production, in *Early mining in the British Isles* (eds. P. Crew and S. Crew), 72–4, Plas Tan y Bwlch, Gwynedd.

Rothenberg, B., and Blanco-Freijeiro, A., 1981, *Studies in ancient mining and metallurgy in south-west Spain. Explorations and excavations in the province of Huelva*, Institute for Archaeo-Metallurgical Studies, London.

Rovira, S., 2002a, Metallurgy and society in prehistoric Spain, in *Metals and society* (eds. B. S. Ottaway and E. C. Wager), 5–20, Archaeopress, Oxford.

Rovira, S., 2002b, Early slags and smelting by-products of copper metallurgy in Spain, in *The beginnings of metallurgy in the Old World* (eds. M. Bartelheim, E. Pernicka, and R. Krause), 83–98, Verlag Marie Leidorf, Rahden.

Rovira, S., and Delibes de Castro, G., 2005, Beaker metallurgical technology in the Iberian Peninsula: Pouring, moulding and post-smelting treatments, in *Bell beakers in the Iberian Peninsula and their European context* (eds. M. A. Rojo-Guerra, R. Garrido-Pena, and I. G.-M. de Lagrán), 513–21, Universidad de Valladolid, Valladolid.

Rovira, S., and Montero-Ruiz, I., 2013, Iberia: Technological development of prehistoric metallurgy, in *Metal matters. Innovative technologies and social change in prehistory and antiquity* (eds. S. Burmeister, S. Hansen, M. Kunst, and N. Müller-Scheessel), 231–9, Verlag Marie Leidorf, Rahden.

Rovira, S., and Montero-Ruiz, I., 2018, Proyecto ‘Arqueometalurgia de la Península Ibérica’ (1982–2017), *Trabajos de Prehistoria*, **75**(2), 223–47.

Sabatini, B. J., 2015, The As-Cu-Ni system: a chemical thermodynamic model for ancient recycling, *JOM*, **67**(12), 2984–92.

Sáez, R., Nocete, F., and Nieto, C., 2003, The extractive metallurgy of copper from Cabezo Juré, Huelva, Spain: Chemical and mineralogical study of slags dated to the Third Millenium B.C, *The Canadian Mineralogist*, **41**, 627–38.

Smith, G. D., and Clark, R. J. H., 2004, Raman microscopy in archaeological science, *Journal of Archaeological Science*, **31**, 1137–60.

Valério, P., Soares, A. M. M., Araújo, M. F., Silva, C. T., and Soares, J., 2007, Vestígios arqueometalúrgicos do povoado calcolítico fortificado do Porto das Carretas (Mourão), *O Arqueólogo Português*, **25**, 177–94.

Valério, P., Soares, A. M. M., Araújo, M. F., Silva, R. J. C., and Baptista, L., 2016, Middle Bronze Age arsenical copper alloys in Southern Portugal, *Archaeometry*, **58**(6), 1003–23.

Valério, P., Vidigal, R. O., Araújo, M. F., Soares, A. M. M., Silva, R. J. C., and Mataloto, R., 2017, Manufacture of copper weapons and tools from the Chalcolithic settlement of São Pedro (Portugal), *Materials and Manufacturing Processes*, **32**(7–8), 775–80.

Valério, P., Soares, J., Araújo, M. F., Alves, L. C., and Tavares da Silva, C., 2019, The composition of São Brás copper hoard in relation to the bell beaker metallurgy in southwestern Iberian Peninsula, *Archaeometry*, **61**(2), 392–405.

Vidigal, R. O., Valério, P., Araújo, M. F., Soares, A. M. M., and Mataloto, R., 2016, Micro-EDXRF study of Chalcolithic copper-based artefacts from southern Portugal, *X-Ray Spectrometry*, **45**, 63–8.

Zhang, X., Zhu, Y., Zeng, H., Wang, D., Liu, J., Qian, M., and Xu, L., 2011, Dissolution and solubility of the arsenate–phosphate hydroxylapatite solid solution [$Ca_5(P_xAs_{1-x}O_4)_3(OH)$] at 25°C, *Environmental Chemistry*, **8**, 133–45.