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MIDDLE BRONZE AGE ARSENICAL COPPER ALLOYS IN SOUTHERN PORTUGAL*

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In the Iberian Peninsula, the copper metallurgy from the Chalcolithic to the Middle Bronze Age (MBA) was mostly characterized by low arsenic contents. A collection of 53 MBA artefacts from southern Portugal was analysed by micro-EDXRF, optical microscopy, SEM–EDS and Vickers to investigate the metal composition and manufacture. No technological distinction was found between artefacts from domestic and funerary contexts, which were radiocarbon-dated to 2000–1500 cal BC. *The arsenic contents of almost 100 MBA artefacts from this region, including the above-mentioned set, have a Gaussian distribution with a high average (3.9 wt% As). Possible explanations are discussed for this distinctive metallurgy at the south-western end of the Iberian Peninsula.*

KEYWORDS: WESTERN IBERIA, MIDDLE BRONZE AGE (MBA), CHALCOLITHIC, ARSENICAL COPPER ALLOY, MANUFACTURE

INTRODUCTION

Archaeological studies have long related the metals and alloys used by prehistoric communities with the technological evolution of humankind. The possibilities of attaining better castability, higher hardness and appealing colours were certainly among the first improvements recognized by ancient metallurgists. However, the production and use of arsenical copper alloys (>2 wt% As) has been a matter of discussion for a long time, while the archaeological record provides evidence of different developments in regions where those primitive alloys played an important role during prehistory.

The early metallurgy in Iberia was dominated by copper with variable amounts of arsenic for almost two millennia (~3000 – 1200 BC) (Harrison and Craddock 1981; Soares *et al.* 1996; Rovira 2004). Arsenical coppers were initially considered an evolution of copper metallurgy, which occurred sometime during the third millennium BC (Harrison and Craddock 1981; Craddock 1995). However, sites with early metallurgy have copper and arsenical copper

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artefacts, as well as copper ores with arsenic impurities. Some examples are found in the southern Iberian Peninsula, namely at Almizaraque (Delibes *et al.* 1991), Cerro Virtud (Ruíz-Taboada and Montero-Ruíz 1999), Los Millares (Rovira 2004), Carmona (Rovira and Gómez-Ramos 1998) and Cabezo Juré (Bayona *et al.* 2003). In Portuguese Estremadura, studied examples can also be found at Zambujal (Müller *et al.* 2007), Leceia (Müller and Cardoso 2008) and Vila Nova de São Pedro (Müller and Soares 2008; Pereira *et al.* 2013).

The comparison of the arsenic contents of ores and metals from Almizaraque has indicated that the metal production does not show any attempt to increase the amount of arsenic. Additionally, the arsenic content distribution of Chalcolithic artefacts from the south-eastern Iberian Peninsula suggests that the amount of arsenic should have resulted from the natural variability of the copper ores (Rovira 2004). Moreover, smelting experiments have showed that copper ores with low amounts of arsenic are capable of producing an arsenical copper alloy (Hauptmann 2007; Hanning *et al.* 2010).

Despite the apparently random scatter of the Chalcolithic metal composition, it seems that there is some relationship between typology and arsenic content. At Los Millares, the halberds, daggers and knives have higher amounts of arsenic than the remaining typologies (Rovira 2004). Palmela arrowheads, long awls, tanged daggers, saws and thin types of artefact are also more frequently made of metal with a high arsenic content than axes and smaller awls from Zambujal (Müller *et al.* 2007). At Leceia, there is also a tendency for thinly hammered artefacts (saws and blades) and elongated artefacts (awls and fish hooks) to have higher amounts of arsenic (Müller and Cardoso 2008). Similarly, the arsenical coppers from Vila Nova de São Pedro are mostly arrowheads, daggers and knives (Pereira *et al.* 2013).

If arsenical coppers seem to be associated with some of the Chalcolithic typologies, the reason for that is not obvious. Considering that most halberds and daggers were recovered from burials, it was assumed that grave goods might suffer less recycling than domestic artefacts (Rovira 2004). However, this does not explain the compositional differences among the artefacts exclusively recovered in settlements such as Leceia (Müller and Cardoso 2008) or Vila Nova de São Pedro (Pereira *et al.* 2013). In the British Isles, the difference has been attributed to the less oxidizing conditions of the two-piece moulds of halberds compared to the open moulds of axes and awls (Bray and Pollard 2012).

Lechtman (1996) studied the influence of arsenic in terms of the mechanical properties, showing that the strain-hardening behaviour of the copper–arsenic system would be ruled by the α phase properties; that is, increasing amounts of arsenic in solid solution confer a higher hardness upon cold work, while the γ phase (Cu_3As) has a negligible effect. However, recent works have found out that the arsenic content is not related to the hardness of artefacts, suggesting the inability of the prehistoric metallurgists to obtain tougher alloys (Pereira *et al.* 2013; Valério *et al.* 2014). On the other hand, the silvery colour of high-arsenic alloys would be appreciated for prestige artefacts (Rovira and Montero-Ruíz 2013). For instance, prestige goods from the Nahal Mishmar hoard (Israel) are made of arsenical copper, while common tools were manufactured using copper (Tadmor *et al.* 1995).

The metallurgy does not seem to have changed drastically in Iberia from the Chalcolithic to the Middle Bronze Age (MBA). Apart from the appearance of bronze and silver, the metallurgy continued to be dominated by copper, with variable arsenic contents (see, e.g., Hunt Ortiz 2003; Valério *et al.* 2014). The south-eastern region has been studied extensively—a comparison of about 300 artefacts from the Los Millares (Chalcolithic) and Argaric (EBA/MBA) cultures identified a slight increase in arsenic (from 2.0 to 2.4 wt% As, respectively) (Montero-Ruíz 1994). This was associated with the funerary origin of most Argaric examples and the exploitation of new ore sources (Rovira 2004). On the contrary, a similarly large collection from the south-western region (Spanish area) evidenced a small reduction in arsenic (Chalcolithic, 1.9 wt% As, $n = 120$; MBA, 1.1 wt% As, $n = 161$), despite a similar increase in MBA funerary contexts (Costa Caramé 2010). In southern Portugal, 40 artefacts recently recovered from MBA funerary structures and domestic contexts disclosed a metallurgy comprising more than 80% of arsenical coppers that exhibited an average of about 4 wt% As (Valério *et al.* 2014). This suggests a different trend of copper-based metals, especially considering that the Chalcolithic artefacts from this region point to lower arsenic contents (Orestes Vidigal *et al.* 2015).

An evolution of copper alloys has also been noted in other regions of the Old World. For instance, Bulgarian and Serbian artefacts show a noticeable increase in arsenic from the Chalcolithic to the Early Bronze Age (EBA), the arsenical coppers being attributed to the smelting of new ores that were richer in arsenic (Pernicka *et al.* 1993, 1997). On the other hand, the third millennium BC Iranian and Anatolian metallurgies indicate intentional alloying to produce an arsenical copper alloy (Thornton *et al.* 2009; Rehren *et al.* 2012; Pernicka 2014).

Therefore, it was considered imperative to continue the research concerning the apparently arsenic-rich metallurgy in southern Portugal during the MBA (~2000–1200 BC), to better understand the role of arsenical copper alloys in prehistoric metallurgy. This work establishes the composition, manufacture and hardness of tools, weapons and ornaments recovered from radiocarbon-dated archaeological contexts, allowing a reliable comparison with the Chalcolithic/EBA (~3000–2000 BC) metallurgies in southern Portugal and neighbouring regions.

METALS

The archaeological contexts

The artefacts belong to MBA contexts recently excavated in southern Portugal: Abelheira 1 (AB1), Horta da Morgadinha (HMG), Montinhos 6 (MT6), Pexem (PX), Torre Velha 12 (TV12), Vale Frio 2 (VF2) and Vinha das Caliças 5 (VC5) (Fig. 1). The archaeological excavations took place from 2009 to 2012, concerning structures and contexts identified during the implementation of several 'Irrigation Blocks' (Brinches–Enxoé, Ervidel and Pedrógão) related to the Alqueva Dam (Baptista 2013; Baptista *et al.* 2013a,2013b; Gomes *et al.* 2013). A dagger recovered at Carapetal (CR), a MBA cist accidentally discovered and excavated in the early 1970s (Soares 1977) was also analysed.

The metallic artefacts were recovered in different negative structures, namely pits/silos and funerary monuments comprising hypogea, cists and sub-rectangular pits (Table 1). Pits/silos are usually linked to the domestic sphere and display a multiple use, but sometimes have a funerary utilization. Hypogea, cists and sub-rectangular pits have only a funerary character. Moreover, all of these structures usually coexist in the neighbourhood of MBA habitats.

The hypogeum was a common MBA funerary structure in the southern Iberian Peninsula, initially considered characteristic of the Argaric culture (2250–1450 BC), where it was located underneath the houses (Lull 2000; Aranda Jiménez *et al.* 2009). The Belmeque hypogeum (Schubart 1974; Soares 1994; Soares *et al.* 2009) was long known in the south-western region, but only recent works have shown that hypogea are also widespread in this area. MBA contexts currently include hypogea at sites such as Torre Velha 3 (Alves *et al.* 2010), Torre Velha 12 (Gomes *et al.* 2013), Outeiro Alto 2 (Valera and Filipe 2010), Pexem (Baptista *et al.* 2013a), Montinhos 6 (Baptista *et al.* 2012) and Horta do Folgão (Nunes da Ponte *et al.* 2012). Hypogea are located in the vicinity of the domestic space, as denoted by many neighbouring pits sometimes filled up

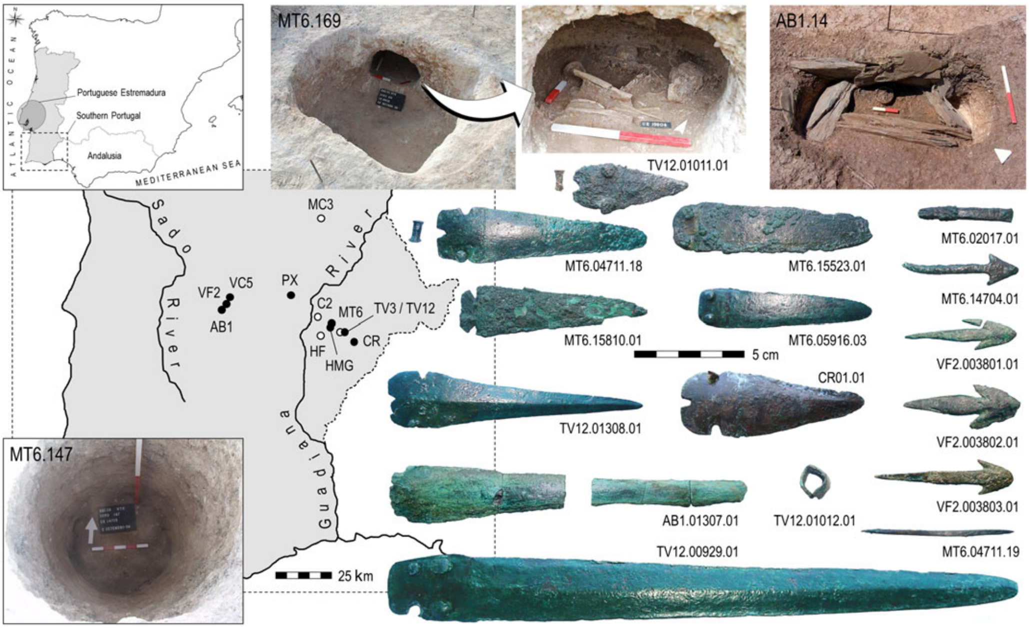

Figure 1 *A map of southern Portugal with the location of sites with metals characterized in this work (black circles: AB1, Abelheira 1; CR, Carapetal; HMG, Horta da Morgadinha; MT6, Montinhos 6; PX, Pexem; TV12, Torre Velha 12; VF2, Vale Frio 2; VC5, Vinha das Caliças 5) and other sites with coeval metals (white circles: C2, Tholos Centirã 2; HF, Horta do Folgão; MC3, Monte da Cabida 3; TV3, Torre Velha 3). Photographs of some of the artefacts studied and various funerary monuments (hypogeum MT6.169, cist AB1.14 and pit MT6.147).*

with domestic refuse. These western hypogea usually display a lesser wealth of funerary offerings than their south-eastern counterparts. The grave goods often include metals and ceramic containers. Meat offerings from commensality rituals are frequently present and the consumed meat (bovine or ovicaprid) might be linked to the social status of the buried person (Aranda Jiménez and Esquivel Guerrero 2007). The grave goods also seem to depict the social status, while some typologies are associated with gender (Castro-Martínez *et al.* 2006). For instance, awls are usually associated with female burials (Pavón Soldevila 2008; Lull *et al.* 2011). Actually, awls and daggers constitute the more common typologies in the studied hypogea, the latter showing a variable number of rivets, depending on the length of the blade (see Fig. 1). The use of rivets instead of notches to fix the handle was one of the innovations of the MBA (Hunt Ortiz 2003). The dagger and ring-shaped bead from hypogeum TV12.10 had relics of cloth, which in the latter case could be identified as linen fibres with a counterclockwise twist.

Until recently, the cist was the typical MBA burial structure in the south-western Iberian Peninsula. This rectangular structure is usually bounded by four slabs constituting the walls and is covered by a stone lid (see Fig. 1, cist AB1.14). Some regional examples are present at Atalaia (Schubart 1975), Monte da Cabida 3 (Antunes *et al.* 2012), Abelheira 1 (Baptista *et al.* 2013a) and Herdade do Montinho, Carapetal, Santa Justa, Barranco do Salto, Bugalhos, Talho do Chaparrinho and Carapinhais (Soares 1977, 1994; Soares *et al.* 2009). Sub-rectangular pits are shallow funerary structures similar to cists but not bounded by slabs. Some examples of sub-rectangular pits have been found at Atalaia (Schubart 1975), Pexem (Baptista *et al.* 2013a), Torre Velha 12 (Gomes *et al.* 2013) and Vale Frio 2 (Baptista *et al.* 2013b). The burial offerings from

Table 1 *Metals and radiocarbon dates of archaeological contexts from hypogea (H), cists (C), sub-rectangular pits (SP) and pits (P) at Abelheira 1 (AB1), Carapetal (CR), Horta da Morgadinha (HMG), Montinhos 6 (MT6), Pexem (PX), Torre Velha 12 (TV12), Vale Frio 2 (VF2) and Vinha das Caliças 5 (VC5). Calendar dates calculated using the calibration curve IntCal13 (Reimer et al.* 2013) and the calibration program CALIB 7.0 (Stuiver and Reimer 1993)

Context			*Radiocarbon dating*					
							Calendar date (cal BC)	
Type	*Structure*	*Metals*	*Sample*	*Laboratory reference*	$\delta^{13}C$ *(‰)*	^{14}C *age (BP)*	*1σ*	*2σ*
H	MT6.20	Chisel	Femur	Sac-2876	–19.6	3350 ± 80	1740–1530	1880–1450
H	MT6.47	Dagger and awl	–	–	–	–	–	–
H	MT6.49	Awl	–	–	–	–	–	–
H	MT6.59*	Dagger and awl	Femur	Sac-2867	–20.1	3380 ± 40	1740–1610	1770–1530
H	MT6.59*	Awl	Femur	Sac-2878	–20.2	3390 ± 40	1740–1640	1870–1560
H	MT6.59*	Awls	–	–	–	–	–	–
H	MT6.89	Awl	Femur	Sac-2845	–20.2	3250 ± 60	1610–1450	1660–1410
H	MT6.153	Awl	Femur	Sac-2877	–20.4	3360 ± 45	1730–1560	1750–1530
H	MT6.155[†]	Dagger and awl	Femur	Sac-2844	–20.4	3240 ± 40	1600–1450	1610–1440
H	MT6.155[†]	Awl	–	–	–	–	–	–
H	MT6.158[‡]	Dagger and awl	–	–	–	–	–	–
H	MT6.159	Awl	Femur	Sac-2879	–20.3	3360 ± 40	1740–1610	1740–1530
H	MT6.169	Chisel	–	–	–	–	–	–
H	PX.714	Awl	–	–	–	–	–	–
H	TV12.9.4	Dagger	Femur	Sac-2831	–20.2	3250 ± 70	1610–1450	1730–1400
H	TV12.10	Dagger and bead	Femur + tibia	Sac-2832	–20.3	3200 ± 60	1590–1410	1620–1310
C	AB1.12	Dagger	–	–	–	–	–	–
C	AB1.13	Awl	Femur	Sac-2918	–20.0	3460 ± 40	1880–1700	1900–1670
C	CR.01	Dagger	–	–	–	–	–	–
SP	PX.34	Awl	–	–	–	–	–	–
SP	TV12.13.3	Dagger	Femur	Sac-2833	–19.5	3450 ± 45	1870–1690	1890–1640
SP	VF2.38	Arrowheads	Humerus + radius	Sac-2917	–20.0	3360 ± 70	1740–1540	1880–1500
P	HMG.20	Awl	–	–	–	–	–	–

(*Continues*)

Table 1 *(Continued)*

Context			*Radiocarbon dating*					
							Calendar date (cal BC)	
Type	*Structure*	*Metals*	*Sample*	*Laboratory reference*	*$\delta^{13}C$ (‰)*	*^{14}C age (BP)*	*1σ*	*2σ*
P	MT6.22	Awl	–	–	–	–	–	–
P	MT6.147	Arrowhead	Charcoal	Sac-2843	–27.5	3450 ± 50	1880–1690	1890–1640
P	VC5.4	Awl	–	–	–	–	–	–
P	VF2.30	Bracelet	–	–	–	–	–	–

*Hypogeum with five inhumations;

†hypogeum with two burial chambers;

‡metals include metallic fragments.

cists and sub-rectangular pits are similar to those from hypogea, including ceramic ware sometimes associated with metals such as daggers or awls. The arrowhead set of sub-rectangular pit VF2.38 (see Fig. 1) is distinctive, suggesting a ceremonial deposition instead of a violent death (Baptista *et al.* 2013b). The archaeological record does not have a single site with both hypogea and cists or sub-rectangular pits, which seems to reflect distinct funerary traditions of neighbouring communities.

Pits/silos are rounded structures dug into the soil (see Fig. 1, pit MT6.147) for the storage of supplies and other materials. Sometimes they were also used as graves, but this seems to be a not very common secondary usage. For instance, from a total of 80 pits excavated at Torre Velha 3, only seven contained human skeletons (Alves *et al.* 2010). Moreover, inhumations in pits usually do not display grave goods, suggesting that those individuals had a low social status.

Radiocarbon chronology

The chronology of the archaeological contexts was obtained by radiocarbon dating of bone samples belonging to human inhumations at Abelheira 1, Montinhos 6, Torre Velha 12 and Vale Frio 2 (Table 1). An additional date was obtained from a charcoal sample closely associated with an arrowhead from pit 147 at Montinhos 6. The human bones from Carapetal and Pexem were unable to produce reliable samples for radiocarbon dating.

The set of radiocarbon dates establishes a period included in the MBA time interval, covering essentially the first half of the second millennium BC (Fig. 2). This chronology is very similar to the one obtained with a set of 17 bone samples of human inhumations, meat offerings and kitchen refuse from hypogea, cists and pits at Torre Velha 3 and Monte da Cabida 3; that is, ~1900–1300 cal BC (Valério *et al.* 2014). The new data confirm the contemporaneity of those different types of funerary monuments in southern Portugal.

In another issue, two inhumations from hypogeum MT6.59 (with five burials) show statistically indistinguishable results (1740–1630 cal BC and 1740–1640 cal BC, 1σ) indicating that they occurred over a short period of time and suggesting some kind of familial funerary structure, which was rather common among Argaric communities (Aranda and Molina 2006), but is still not yet investigated in the south-western region.

METHODOLOGY

The elemental and microstructural study of metallic artefacts has required the removal of corrosion products in a small area (∅ ~ 3–5 mm). The procedure involved polishing with diamond pastes of increasingly fine grit size (15 μm to 1 μm), followed by optical microscopy observations to verify a clean metallic surface. In fragmented artefacts, the cutting of a small section was allowed, which was then mounted in epoxide resin and polished with silicon carbide papers (1000 to 4000 grit size) and diamond pastes (3 μm and 1 μm). The latter originates a completely flat surface, allowing the measurement of the metal hardness.

Micro-EDXRF analyses were undertaken using an ArtTAX Pro spectrometer equipped with a 30 W Mo X-ray tube, a focusing polycapillary lens (an analysis area with a diameter less than 100 μm) and an electro-thermally cooled silicon drift detector (FWHM of 160 eV at 5.9 keV). Samples were analysed at three ‘spots’ using a tube voltage of 40 kV, a current intensity of 600 μA and 100 s of live time. Quantifications were made using the WinAxil software, and involving experimental calibration factors calculated by means of analyses of the following reference materials: Phosphor Bronze 551 (British Chemical Standards, BCS) and IDLF5 (Industries

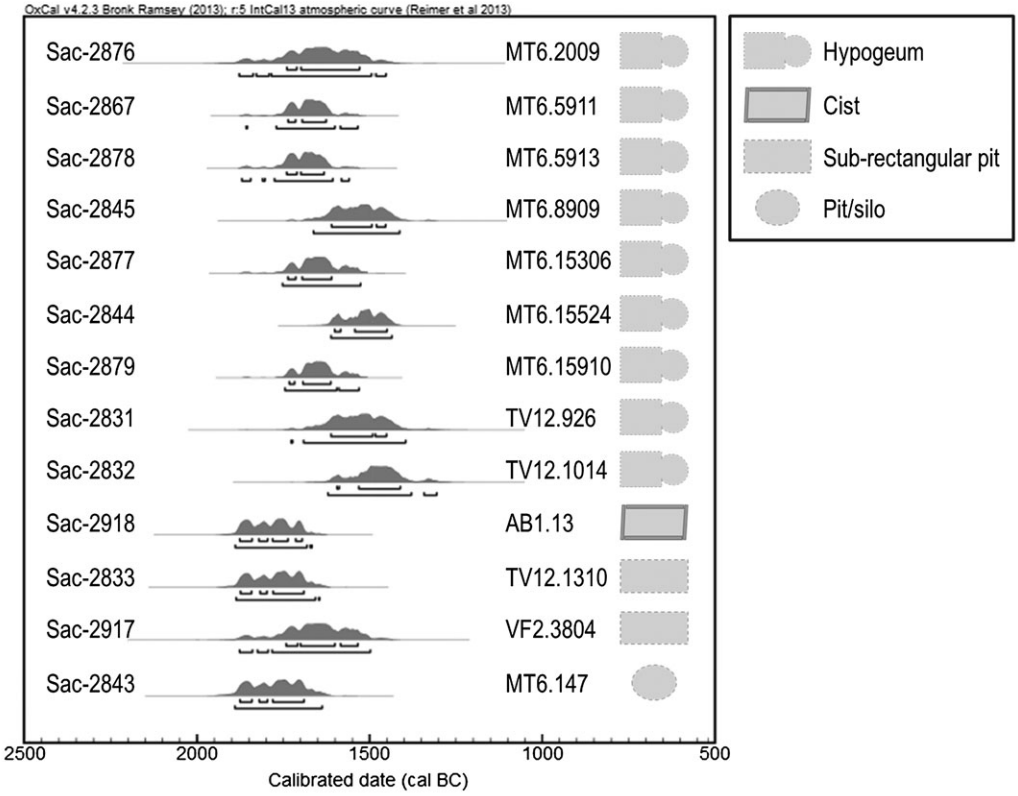

Figure 2 *Calibrated radiocarbon dates of archaeological structures at Montinhos 6, Torre Velha 12, Abelheira 1 and Vale Frio 2, using the IntCal13 calibration curve (Reimer et al.* 2013) and the OxCal program (V4.2.3) (Bronk Ramsey 2013).

de la Fonderie). The method's uncertainty is lower than 10% for the elements of interest. The quantification limits are 0.05 wt% Fe and 0.10 wt% As. The detection limits for elements usually present in copper-based artefacts are 0.02 wt% Ni, 0.06 wt% Zn, 0.15 wt% Sn, 0.15 wt% Sb and 0.03 wt% Pb.

Optical microscopy observations were undertaken using a Leica DMI 5000M microscope. Microstructural features were highlighted with aqueous ferric chloride etching. SEM–EDS analyses involved a Zeiss DSM 962, equipped with a conventional tungsten filament and working in secondary electron and backscattered electron imaging modes. The Oxford Instruments INCAx-sight EDS spectrometer has an ultra-thin window for the detection of low atomic number elements. The analysis area was partially coated with a carbon-conductive bridge to prevent charge accumulation. The analysing conditions involve 25 mm of working distance, 20 kV of accelerating voltage, 3 A of filament current and 70 μA of emission current.

Vickers microhardness testing was undertaken using Zwick–Roell Indentec equipment on samples mounted in epoxy resin. Vickers testing uses a 0.20 kgf load for a duration of 10 s. The hardness calculated comprises the average of at least three indentations having a relative standard deviation lower than 10%.

RESULTS

Awls

Copper-based awls from Abelheira 1, Horta da Morgadinha, Montinhos 6, Pexem and Vinha das Caliças 5 have relatively high arsenic contents and very low amounts of iron (Table 2). Moreover, no compositional differences were observed between examples from funerary monuments and domestic contexts. Overall, these tools have an average arsenic content of 4.7 ± 1.2 wt% ($n = 17$; samples with values within the three standard deviation interval; sample MT6.15810.02 was excluded due to its significantly higher value).

Although the majority of the awls are complete (having a variable length of between 3.7 and 9.2 cm, $n = 14$), no correlation could be found between length and arsenic content. The absence of such a correlation was also observed in awls from Torre Velha 3 and Monte da Cabida 3 (Valério *et al.* 2014). This contrasts with Chalcolithic awls from Zambujal, where smaller examples were made of copper and have been considered as tools for specific tasks such as leather working, while the longer ones were composed of arsenical copper and viewed as symbols of status (Müller *et al.* 2007). Therefore, the MBA long awl seems to maintain its prestige, despite having lost the distinction of a higher arsenic content that was characteristic during the Chalcolithic. From another perspective, the absence of such a correlation in the MBA artefacts could indicate that although the smaller artefacts may result from the continuous use and reconditioning of the longer ones, their recycling should include mostly mechanical work such as abrasion sharpening, since annealing would reduce the arsenic content.

Optical microscopy observations of awls have identified deformed equiaxial microstructures with annealing twins and slip bands with variable density (e.g., MT6.02200.02 and MT6.06920.01; Fig. 3). These features indicate post-casting operations including cycles of hammering and annealing followed by a final hammering of variable intensity (see Table 2).

Some of these microstructures have a distinct superficial layer (e.g., MT6.05920.01 and MT6.04910.05, Fig. 3). In the awl MT6.04910.05, this layer is particularly thick (~10–20 μm) and SEM–EDS quantification (27.4 wt% As) indicates that it is Cu_3As. Due to casting in non-equilibrium conditions, this intermetallic γ phase has also been identified in copper containing as low as 1–2 wt% arsenic (Northover 1989; Budd 1991). The arsenic-rich superficial layer is responsible for the silvery colour of arsenical copper alloys and usually is formed by inverse segregation of arsenic during casting.

Optical microscopy observations also identified a similar phase surrounding the grains of some microstructures. The awl with a higher arsenic content (MT6.15810.02) has an elevated amount of this phase (Fig. 3), which was also identified as Cu_3As (SEM–EDS: 26.9 wt% As). Budd (1991) reported that the solid solution could remain supersaturated in arsenic due to the fast cooling, while a subsequent low-temperature annealing would precipitate further Cu_3As, at a higher rate than the diffusion of As in solid solution. Arsenical copper recrystallizes at 300–400°C, but about 600–700°C would be necessary to remove the cast-in segregation in a reasonable time (Northover 1989). Therefore, the segregation bands in some of those prehistoric microstructures provide evidence of a low-temperature annealing (see Fig. 3) producing the observed intergranular Cu_3As. Another possible explanation for this As-rich phase comes from the arsenic segregation from solid solution during the long burial time (Budd and Ottaway 1995).

The morphology of the Cu_3As superficial layer and the orientation of the segregation bands in awl MT6.04910.05 indicate that this awl was rounded by hammering (see Fig. 3). If this example is representative of this type of awl—one side with a quadrangular section and the opposite side

Table 2 *The composition and manufacture of MBA artefacts from southern Portugal: F, forging; A, annealing; FF, final forging; ↓, low amount; ↑, high amount; ⊕, high amount on the edge of the blade; DR, deformation from riveting; n.a., not analysed*

Artefact	*Reference*	*Context*	*Cu (wt%)*	*As (wt%)*	*Fe (wt%)*	*Cu–As–O*	*Post-casting*
Awl	MT6.04711.19	Hypogeum	96.6 ± 0.1	3.35 ± 0.14	<0.05	↓	(F + A) + FF↑
Awl	MT6.04910.05	Hypogeum	95.6 ± 0.1	4.33 ± 0.09	<0.05	↓	(F + A) + FF
Awl	MT6.05914.01	Hypogeum	94.7 ± 0.1	5.22 ± 0.11	<0.05	↓	(F + A) + FF
Awl	MT6.05917.13	Hypogeum	93.8 ± 0.4	6.15 ± 0.44	<0.05	↓	(F + A) + FF
Awl	MT6.05920.01	Hypogeum	95.8 ± 0.3	4.17 ± 0.27	<0.05	↓	(F + A) + FF↓
Awl	MT6.05920.02	Hypogeum	95.3 ± 0.1	4.68 ± 0.09	<0.05	↓	(F + A) + FF↑
Awl	MT6.08910.02	Hypogeum	95.0 ± 0.1	4.97 ± 0.04	<0.05	↓	(F + A) + FF
Awl	MT6.15316.01	Hypogeum	95.5 ± 0.1	4.50 ± 0.04	<0.05	↓	(F + A) + FF
Awl	MT6.15515.01	Hypogeum	95.2 ± 0.5	4.72 ± 0.42	<0.05	↓	(F + A) + FF↑
Awl	MT6.15522.01	Hypogeum	94.3 ± 0.1	5.63 ± 0.11	<0.05	↑	(F + A) + FF↑
Awl	MT6.15810.02	Hypogeum	88.4 ± 0.5	11.6 ± 0.5	<0.05	↓	(F + A) + FF
Awl	MT6.15911.04	Hypogeum	94.2 ± 0.3	5.80 ± 0.28	<0.05	↓	(F + A) + FF
Awl	PX.00716.01	Hypogeum	94.4 ± 0.3	5.54 ± 0.29	<0.05	↓	(F + A) + FF
Awl	AB1.01307.01	Cist	93.6 ± 0.2	6.38 ± 0.20	<0.05	↓	(F + A) + FF
Awl	PX.03408.01	Sub-rectangular pit	95.2 ± 0.1	4.75 ± 0.01	<0.05	↓	(F + A) + FF
Awl	HMG.02004.07	Pit	98.6 ± 0.2	1.38 ± 0.23	<0.05	n.a.	n.a.
Awl	MT6.02200.02	Pit	95.1 ± 0.3	4.80 ± 0.20	<0.05	↓	(F + A) + FF↓
Awl	VC5.00404.01	Pit	96.6 ± 0.2	3.34 ± 0.24	<0.05	n.a.	n.a.
Dagger	MT6.04711.18	Hypogeum	95.0 ± 0.4	4.98 ± 0.35	<0.05	↓	(F + A) + FF⊕
Dagger	MT6.05916.03	Hypogeum	96.3 ± 0.2	3.68 ± 0.12	<0.05	↓	(F + A) + FF
Dagger	MT6.15523.01	Hypogeum	95.2 ± 0.1	4.77 ± 0.06	<0.05	↓	(F + A) + FF
Dagger	MT6.15810.01	Hypogeum	93.1 ± 0.1	6.89 ± 0.01	<0.05	↓	(F + A) + FF
Dagger	TV12.00929.01	Hypogeum	95.9 ± 0.1	4.04 ± 0.04	<0.05	↓	(F + A) + FF⊕
Dagger	TV12.01011.01	Hypogeum	94.8 ± 0.5	5.15 ± 0.46	<0.05	↓	(F + A) + FF
Dagger[a]	AB1.01207.01	Cist	81	19	<0.05	n.a.	n.a.
Dagger	CR.01.01	Cist	98.9 ± 0.3	1.07 ± 0.25	<0.05	↑	(F + A) + FF
Dagger	TV12.01308.01	Sub-rectangular pit	97.8 ± 0.4	2.14 ± 0.33	<0.05	↑	F⊕
Rivet	MT6.04711.18*	Hypogeum	95.1 ± 0.3	4.86 ± 0.32	<0.05	↑	DR
Rivet	MT6.04711.18[†]	Hypogeum	95.5 ± 0.5	4.45 ± 0.43	<0.05	↑	DR
Rivet	MT6.05916.03*	Hypogeum	96.3 ± 0.2	3.66 ± 0.15	<0.05	↓	DR

(*Continues*)

Table 2 *(Continued)*

Artefact	*Reference*	*Context*	*Cu (wt%)*	*As (wt%)*	*Fe (wt%)*	*Cu–As–O*	*Post-casting*
Rivet	MT6.05916.03[†]	Hypogeum	96.3 ± 0.1	3.63 ± 0.14	<0.05	↓	DR
Rivet	MT6.15523.01*	Hypogeum	95.8 ± 0.2	4.09 ± 0.21	0.06 ± 0.01	n.a.	n.a.
Rivet	MT6.15523.01[†]	Hypogeum	95.6 ± 0.3	4.36 ± 0.30	<0.05	n.a.	n.a.
Rivet	TV12.00929.01*	Hypogeum	97.1 ± 0.3	2.86 ± 0.29	<0.05	↑	DR
Rivet	TV12.00929.01[†]	Hypogeum	97.0 ± 0.3	2.99 ± 0.29	<0.05	↑	DR
Rivet	TV12.00929.01[‡]	Hypogeum	96.7 ± 0.2	3.29 ± 0.21	<0.05	↑	DR
Rivet	TV12.00929.01d	Hypogeum	97.2 ± 0.2	2.80 ± 0.15	<0.05	↑	DR
Rivet	TV12.01011.01*	Hypogeum	94.8 ± 0.5	5.18 ± 0.48	<0.05	n.a.	n.a.
Rivet	TV12.01011.01[†]	Hypogeum	95.3 ± 0.4	4.69 ± 0.34	<0.05	n.a.	n.a.
Rivet	TV12.01011.01[‡]	Hypogeum	98.5 ± 0.1	1.49 ± 0.08	<0.05	n.a.	n.a.
Rivet	CR.01.01*	Cist	89.5 ± 1.5	10.5 ± 1.5	<0.05	n.a.	n.a.
Rivet	TV12.01308.01*	Sub-rectangular pit	97.8 ± 0.4	2.17 ± 0.41	<0.05	↑	DR
Chisel	MT6.02017.01	Hypogeum	94.6 ± 0.4	5.31 ± 0.35	<0.05	↓	(F + A) + FF↓
Chisel	MT6.16907.01	Hypogeum	97.4 ± 0.2	2.59 ± 0.13	<0.05	↓	(F + A) + FF↓
Bead	TV12.01012.01	Hypogeum	95.4 ± 0.6	4.56 ± 0.65	<0.05	↓	(F + A) + FF
Fragment	MT6.15804.02*	Hypogeum	98.7 ± 0.1	1.29 ± 0.08	<0.05	↑	(F + A) + FF↑
Fragment	MT6.15804.02[†]	Hypogeum	98.5 ± 0.2	1.44 ± 0.21	<0.05	↑	(F + A) + FF↑
Fragment	MT6.15804.02[‡]	Hypogeum	96.0 ± 0.1	3.95 ± 0.07	<0.05	↓	(F + A) + FF↑
Arrowhead[†]	VF2.03801.01	Sub-rectangular pit	99.5 ± 0.1	0.46 ± 0.05	<0.05	↓	F↑
Arrowhead[†]	VF2.03802.01	Sub-rectangular pit	95.9 ± 0.2	4.03 ± 0.17	<0.05	↓	(F + A) + FF↑
Arrowhead[†]	VF2.03803.01	Sub-rectangular pit	97.6 ± 0.4	2.34 ± 0.32	<0.05	↓	F↑
Arrowhead[‡]	MT6.14704.01	Pit	96.2 ± 0.1	3.79 ± 0.10	<0.05	↓	A
Bracelet	VF2.03000.01	Pit	93.9 ± 0.6	6.00 ± 0.55	<0.05	↑	(F + A) + FF↓

*The metal has completely corroded;

[†] tang;

[‡] edge.

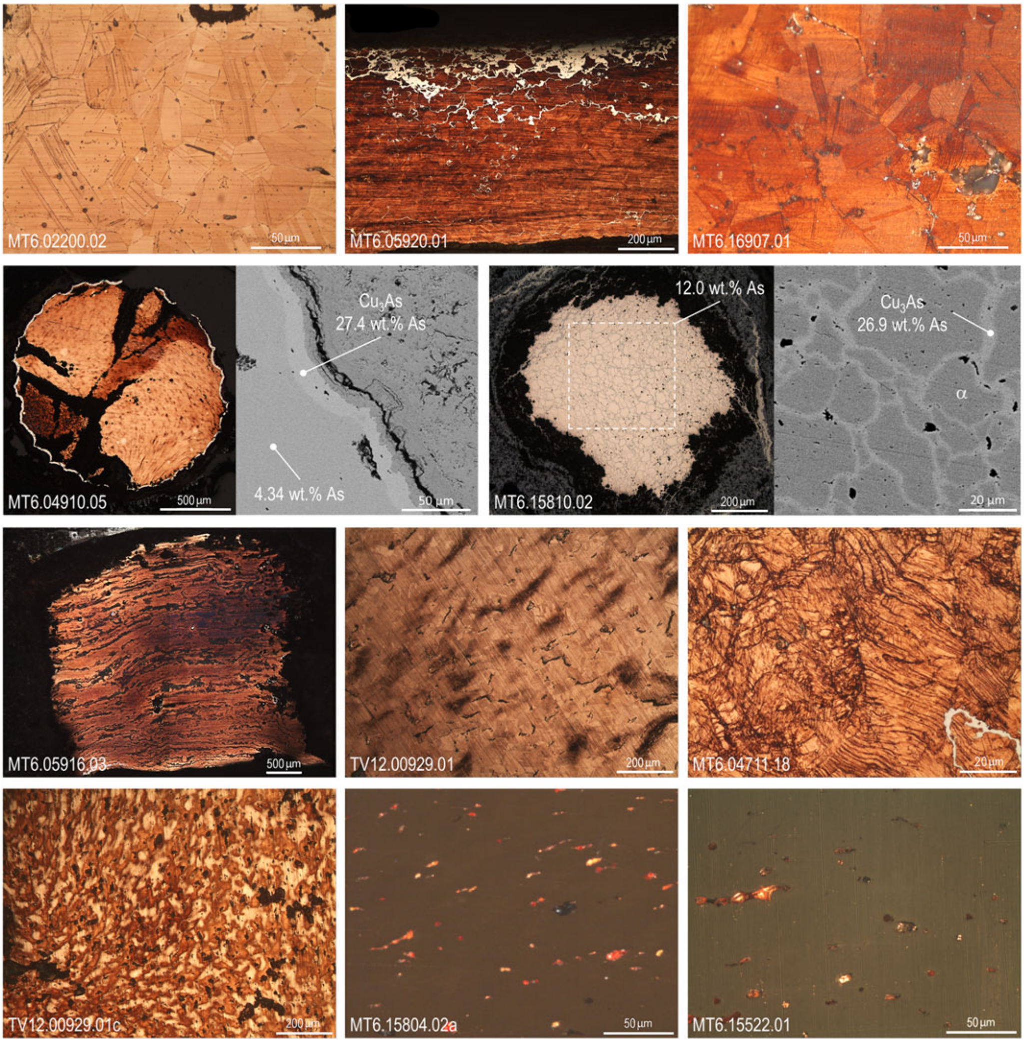

Figure 3 *Optical microscopy and SEM–EDS images of awls (MT6.02200.02, MT6.05920.01, MT6.04910.05 and MT6.15810.02), a chisel (MT6.16907.01), daggers (MT6.05916.03, TV12.00929.01 blade centre and MT6.04711.18 blade edge) and a rivet (TV12.00929.01c). Optical microscopy images of oxide inclusions in fragment MT6.15804.02a and awl MT6.15522.01.*

with a rounded one—then their manufacture involves the casting of a quadrangular rod that is rounded on one side. Otherwise, this might reveal a particular manufacture relying on an anomalous mechanical deformation. This issue has ethnographic parallels in other areas such as the Andean region, where the manufacture of awls relies mostly on cold work, being an adaptation of the production of gold ornaments (Lechtman 1996).

Vickers microhardness testing on selected awls identified different hardnesses, ranging from a value similar to that for non-hardened copper (MT6.02200.02: 61 ± 2 HV0.2) to a three-fold increase (MT6.15810.02: 200 ± 4 HV0.2). The higher hardness of awls MT6.04910.05 (129 ± 2 HV0.2), MT6.05914.01 (142 ± 4 HV0.2) and MT6.15810.02 is an outcome of the smaller grain size (efficient cycles of forging and annealing) and the higher density of slip bands (tougher final deformation). The differences among them can be attributed to increasing amounts of arsenic in solid solution (superior strain hardening), and even some differences in the amount of final cold work. Overall, these data show that awls could be extensively toughened, although they provide evidence of the irregular manufacture of prehistoric metallurgy.

These MBA awls have a higher hardness than Chalcolithic awls from Vila Nova de São Pedro (40–106 HV0.2; Pereira *et al.* 2013), mostly due to an increased usage of final forging. Moreover, the hardness of those MBA arsenical coppers is comparable to the hardness of early bronze awls from Torre Velha 3 (61–200 HV0.2; Valério *et al.* 2014), suggesting that the initial bronzes were mechanically equivalent to coeval arsenical coppers. A similar conclusion was obtained with regard to the hardness of arsenical coppers and coeval bronzes from the Argaric site of Cerro de San Cristóbal (Granada) (Aranda Jiménez *et al.* 2012).

Daggers and rivets

Micro-EDXRF analyses of daggers from Abelheira 1, Carapetal, Montinhos 6 and Torre Velha 12 show the presence of copper with relatively high amounts of arsenic and a very low iron content (Table 2). The dagger AB1.01207.01 is totally corroded (SEM–EDS identified a matrix of Cu–O and Cu–As–O compounds with a few silver inclusions). The remaining set has an average arsenic content of 4.1 ± 1.8 wt% ($n = 8$; samples with values within the three standard deviation interval). Daggers from hypogea seem to be richer in arsenic than the examples from a cist and a sub-rectangular pit, but the number of samples is not statistically significant.

The composition of the daggers is not distinguishable from that of the awls, but it must be noted that artefacts richer in arsenic in both sets belong to the same hypogeum; that is, awl MT6.15810.02 and dagger MT6.15810.01. These arsenic-rich artefacts show an increased amount of the Cu_3As phase, which is responsible for the silvery colour of such alloys. The presence of those artefacts in hypogeum MT6.158 evidences the particular interest of the group related to the grave in silvery-coloured offerings, probably to express the high status of the buried individual.

Most dagger microstructures have twinned grains and slip bands. The blades were mostly deformed alongside the central axis, as evidenced by segregation bands parallel to it (e.g., MT6.05916.03 and TV12.00929.01; Fig. 3). Moreover, the cutting edge was heavily hammered, thus showing a high density of deformation bands (e.g., MT6.04711.18; Fig. 3). Several experiments have proven that such extreme deformation becomes possible with a higher arsenic content (up to the solubility limit, ~7–8% As, in equilibrium) producing a stronger and more ductile alloy (Hanson and Marryat 1927; Lechtman 1996). Prehistoric tools with a harder cutting edge and a softer inner bulk were more efficient for cutting and had a greater toughness, thus reducing the probability of cracks and fractures (Shalev *et al.* 2014).

Similarly to the awls, the majority of the daggers have a low density of oxide inclusions (Cu–As–O, Table 2) which is facilitated by higher arsenic contents. McKerrell and Tylecote (1972) inferred that the oxygen in the metal reacts with arsenic to form arsenic trioxide that is then volatilized. In fact, this experimental work identified a significant loss of arsenic when working under oxidizing conditions: about 10% after melting and cooling twice, and 16% after melting and hot working twice. Experiments by Budd and Ottaway (1991) showed that the loss of arsenic could be avoided by melting and alloying under a layer of charcoal. Therefore, the low density of oxide inclusions of most awls and daggers provides evidence of some degree of control of the working conditions. Moreover, some exceptions are suggestive of the variable conditions of such primitive metallurgy; for example, the awl MT6.15522.01 displays a high arsenic content (5.63 wt%) and an elevated density of Cu–As–O inclusions, parallel to the value found in the low arsenic content (1.29 wt%) fragment MT6.15804.02a (Fig. 3).

A group of rivets from those daggers was also analysed by micro-EDXRF (Table 2). The results identified an average arsenic content of 3.6 ± 1.1 wt% (*n* = 14 samples; values within the three standard deviation interval; sample CR.01.01a was excluded due to its significantly higher value). The blade CR.01.01 has a very low arsenic amount (1.07 wt%) and displays a reddish colour that contrasts with the silvery rivet (10.5 wt% As) or rivets (probably three; see Fig. 1). Most daggers have a set of rivets with comparable arsenic contents, indicating that they were probably made from the same rod. However, the dagger TV12.01011.01 has one rivet with less arsenic than the remaining ones, which indicates that they were not obtained from the same casting. This agrees well with the unusually small and pointy blade of this dagger (see Fig. 1), also suggesting that this was a worn dagger that would have been recycled.

Optical microscopy observations of rivets show dendrites enhanced by the segregation of arsenic during the cooling of the molten alloy (Fig. 3). The blade was later riveted to the handle by hammering both sides of those small rods, leaving a deformed rivet structure. The higher density of Cu–As–O inclusions in most rivets may suggest a lower degree of control of the working conditions for these attachments, contrary to what is observed in most of the analysed tools and weapons.

Other types

Micro-EDXRF analyses of the remaining artefacts identified an average arsenic content of 3.3 ± 1.8 wt% (*n* = 11; samples with values within the three standard deviation interval) (Table 2). The group is mostly composed by arsenical coppers but also includes copper with a low arsenic content (one arrowhead and two fragments). The elements in each typology are too low to draw significant conclusions, but it can be stated that arrowheads show a quite variable arsenic content (0.46–4.03 wt%).

Besides a variable composition, arrowheads also exhibit different manufacturing sequences (Table 2). The tangs of arrowheads VF2.03801.01, VF2.03802.01 and VF2.03803.01 were heavily worked, but two of them had undergone only cold work, evidenced by elongated and thin segregation bands. The blade of arrowhead MT6.14704.01 has extremely large grains, but no traces of twins or slip bands. However, these features are most probably a consequence of fire in the structure where the artefact was found (the arrowhead was recovered among remains of charcoal and ashes of cork that once lined the pit wall).

The microstructure of chisel MT6.16907.01 shows intentional manufacturing features comprising forging and annealing (Fig. 3). Those chisels were not extensively toughened (low density of slip bands), thus having a low hardness (MT6.1690701: 62 ± 3 HV0.2). This agrees with the value of a MBA chisel from Torre Velha 3 (615: 73 ± 5 HV0.2; Valério *et al.* 2014) and the hardness values of Chalcolithic chisels from Vila Nova de São Pedro (36–97 HV0.2, Pereira *et al.* 2013). The tips of those Chalcolithic chisels was hardened (approximately +30%), but it was not possible to make similar tests on MBA examples. Finally, bracelet VF2.03000.01 was found to be slightly hardened (97 ± 7 HV0.2) due to a mild final hammering.

ARSENICAL COPPER ALLOYS AT THE SOUTH-WESTERN END OF IBERIA

The elemental compositions, microstructural features and hardness values of this set of MBA artefacts are very similar to those found in coeval metals in southern Portugal (Table 3). The latter belong to Torre Velha 3 and Monte da Cabida 3 (Valério *et al.* 2014), Horta do Folgão (Nunes da Ponte *et al*. 2012) and *Tholos* Centirã 2 (Henriques *et al.* 2013). The following discussion comprises all research on MBA metallurgy from southern Portugal, including almost 100 artefacts from nine archaeological sites (see Fig. 1).

The metallic artefacts belonging either to funerary monuments or to domestic contexts are mostly composed by arsenical copper alloys. Moreover, this MBA metallurgy exhibits a Gaussian distribution with a rather high arsenic content (3.9 ± 1.4 wt%; $n = 90$; four arsenic-rich alloys with values outside the three standard deviation interval were excluded) (Fig. 4 (a)). The post-casting manufacture of different types did not show significant differences since most involved thermomechanical work. Daggers seem to have a lengthier manufacturing process involving strong forging on the cutting edge, while rivets were typically as cast and arrowheads present variable manufacturing processes, with substantial cold work.

As mentioned in the previous section, the higher arsenic content of metals from a burial at Montinhos 6 (hypogeum MT6.158) suggests the high status of this individual. On the contrary, there are no meaningful distinctions among the arsenical coppers from burials and domestic contexts at Torre Velha 3, where the metallic symbols of status could eventually be associated with innovative materials such as silver and bronze (Valério *et al.* 2014). Moreover, the arsenical copper alloys from Montinhos 6 and Torre Velha 3 have similar average arsenic contents (4.4 ± 1.2 wt%, $n = 28$, and 4.1 ± 1.0 wt%, n = 27, respectively), which suggests the analogous hierarchical importance of these MBA communities.

Data for Chalcolithic metallurgy in southern Portugal are scarce, but artefacts analysed from several sites, namely from São Pedro, Três Moinhos, Atalaia do Peixoto, Castro dos Ratinhos and *Tholos* de Caladinho (Orestes Vidigal *et al.* 2015), have lower arsenic contents than their MBA counterparts (Fig. 4 (b)). Moreover, a study concerning the Chalcolithic metallurgy in the neighbouring region of western Andalusia, namely at La Junta, Cabezo Juré, Valencina de la Concepción, Amarguillo II and Cueva Antoniana (Bayona 2008), all perhaps based on the smelting of Iberian Pyrite Belt ores, does not change the picture with regard to metallurgy in the south-western Iberian Peninsula: half of the artefacts from these Chalcolithic sites have an arsenic content of less than 2 wt% (Fig. 4 (c)). A similar pattern can be found in Portuguese Estremadura, as evidenced by metals from Leceia (Müller and Cardoso 2008) and Vila Nova de São Pedro (Müller and Soares 2008; Pereira *et al.* 2013) (Fig. 4 (d)). Similar histograms of arsenic content suggest a common Chalcolithic metallurgy the low arsenic contents of which seem to arise from its natural distribution in copper ores. Lead isotopic studies have indicated that the Chalcolithic copper of Portuguese Estremadura came from the Ossa Morena Zone (Müller *et al.* 2007; Müller and Cardoso 2008; Müller and Soares 2008). In southern Portugal, there are no provenance studies, although the geographical setting is closer to the Iberian Pyrite Belt.

There is an obvious difference in the MBA metals of southern Portugal, which show an increased usage of arsenical copper alloys. It can be reasoned that Chalcolithic metals have a higher proportion of domestic contexts, thus including typologies that are not present among MBA artefacts. However, when comparing specific typologies such as awls, it is clear that MBA examples have higher amounts of arsenic than Chalcolithic ones (4.7 ± 0.9 wt% As, $n = 31$, and 2.5 ± 1.9 wt% As, $n = 14$, respectively). Post-casting operations also show an improvement, consisting of increased use of final cold work, since MBA tools and weapons are almost always

Table 3 *The composition of MBA artefacts from Torre Velha 3 (TV3), Monte da Cabida 3 (MC3), Horta do Folgão (HF) and Tholos Centirã 2 (C2): n.d., not detected*

Artefact	*Reference*	*Context*	*Cu (wt%)*	*As (wt.%)*	*Sn (wt%)*	*Ag (wt%)*	*Fe (wt%)*
Awl	TV3-395	Hypogeum	88.5 ± 0.6	<0.10	11.4 ± 0.6	n.d.	<0.05
Awl	TV3-401	Hypogeum	95.9 ± 0.1	4.03 ± 0.19	n.d.	n.d.	<0.05
Awl	TV3-403	Hypogeum	97.5 ± 0.2	2.49 ± 0.21	n.d.	n.d.	<0.05
Awl	TV3-405	Hypogeum	96.7 ± 0.7	3.24 ± 0.70	n.d.	n.d.	<0.05
Awl	TV3-408	Hypogeum	94.3 ± 0.5	5.70 ± 0.51	n.d.	n.d.	<0.05
Awl	TV3-410	Hypogeum	95.2 ± 0.2	4.74 ± 0.18	n.d.	n.d.	<0.05
Awl	TV3-411	Hypogeum	95.5 ± 0.2	4.45 ± 0.22	n.d.	n.d.	<0.05
Awl	TV3-412	Hypogeum	91.4 ± 0.5	4.09 ± 0.35	n.d.	4.65 ± 0.21	<0.05
Awl	TV3-416	Hypogeum	95.0 ± 0.1	4.91 ± 0.21	n.d.	n.d.	<0.05
Awl	TV3-418	Hypogeum	90.1 ± 0.6	0.64 ± 0.03	9.23 ± 0.51	n.d.	<0.05
Awl	TV3-419	Hypogeum	95.5 ± 0.2	4.46 ± 0.21	n.d.	n.d.	<0.05
Awl	TV3-421	Hypogeum	95.6 ± 0.1	4.38 ± 0.15	n.d.	n.d.	<0.05
Awl	TV3-422	Hypogeum	89.1 ± 0.1	2.17 ± 0.03	8.73 ± 0.06	n.d.	<0.05
Awl	HF-M1	Hypogeum	98.4 ± 0.2	1.64 ± 0.13	n.d.	n.d.	<0.05
Awl	MC3-M1	Cist	97.1 ± 0.5	2.81 ± 0.45	n.d.	n.d.	<0.05
Awl	MC3-M2	Cist	94.1 ± 0.4	5.88 ± 0.48	n.d.	n.d.	<0.05
Awl	MC3-M3	Cist	94.6 ± 0.4	5.37 ± 0.38	n.d.	n.d.	<0.05
Awl	TV3-390	Pit	95.6 ± 0.2	4.34 ± 0.21	n.d.	n.d.	<0.05
“Awl”	TV3-393	Pit	90.0 ± 0.2	n.d.	10.0 ± 0.2	n.d.	<0.05
Awl	TV3-407	Pit	95.3 ± 0.1	4.67 ± 0.16	n.d.	n.d.	<0.05
Dagger	TV3-406	Hypogeum	95.1 ± 0.4	4.82 ± 0.42	n.d.	n.d.	<0.05
Dagger	TV3-423	Hypogeum	96.3 ± 0.6	3.87 ± 0.21	n.d.	n.d.	<0.05
Dagger	TV3-428	Hypogeum	97.7 ± 0.1	2.33 ± 0.08	n.d.	n.d.	<0.05
Dagger	TV3-714	Hypogeum	90.8 ± 0.4	0.12 ± 0.01	9.03 ± 0.32	n.d.	<0.05
Dagger	MC3-M4	Cist	95.4 ± 0.6	4.59 ± 0.63	n.d.	n.d.	<0.05
Dagger	TV3-397	Pit	94.6 ± 0.1	5.31 ± 0.11	n.d.	n.d.	<0.05
Sword	HF-M2	Hypogeum	95.7 ± 0.5	4.27 ± 0.48	n.d.	n.d.	<0.05
Rivet	TV3-406a	Hypogeum	94.5 ± 0.3	5.45 ± 0.24	n.d.	n.d.	<0.05
Rivet	TV3-406b	Hypogeum	95.1 ± 0.2	4.81 ± 0.15	n.d.	n.d.	<0.05
Rivet	HF-M3	Hypogeum	97.0 ± 0.1	2.97 ± 0.06	n.d.	n.d.	<0.05
Rivet	MC3-M4a	Cist	73.5 ± 1.3	26.5 ± 1.3	n.d.	n.d.	<0.05
Rivet	TV3-391	Pit	94.6 ± 0.8	5.37 ± 0.74	n.d.	n.d.	<0.05
Bead	TV3-911	Hypogeum	97.3 ± 0.1	2.60 ± 0.11	n.d.	n.d.	<0.05
Bead	TV3-912	Hypogeum	97.4 ± 0.2	2.57 ± 0.16	n.d.	n.d.	<0.05
Ring	TV3-415	Hypogeum	86.7 ± 0.4	13.3 ± 0.4	n.d.	n.d.	<0.05
Arrowhead	TV3-392	Pit	95.7 ± 0.2	4.27 ± 0.18	n.d.	n.d.	<0.05
Arrowhead	TC3-M1	Other	96.5 ± 0.1	3.35 ± 0.12	n.d.	n.d.	0.07 ± 0.03
Chisel	TV3-398	Pit	95.8 ± 0.1	4.15 ± 0.09	n.d.	n.d.	<0.05
Chisel	TV3-615	Pit	95.3 ± 0.2	4.63 ± 0.24	n.d.	n.d.	<0.05
Fragment	TV3-400	Pit	98.5 ± 0.1	1.46 ± 0.04	n.d.	n.d.	<0.05
Fragment	TV3-429	Pit	97.4 ± 0.8	2.57 ± 0.76	n.d.	n.d.	<0.05
Fragment	MC3-M8	Pit	97.4 ± 0.3	2.58 ± 0.27	n.d.	n.d.	<0.05
Fragment	MC3-M9	Pit	99.0 ± 0.2	0.94 ± 0.21	n.d.	n.d.	<0.05
Saw	TV3-388	Pit	97.4 ± 0.3	2.58 ± 0.27	n.d.	n.d.	<0.05

in a strain-hardened state, contrary to Chalcolithic metals (see, e.g., the manufactures at Vila Nova de São Pedro; Pereira *et al.* 2013). A similar trend has been found among the *chaîne opératoire* of metals from the south-eastern Iberian Peninsula (Rovira 2004).

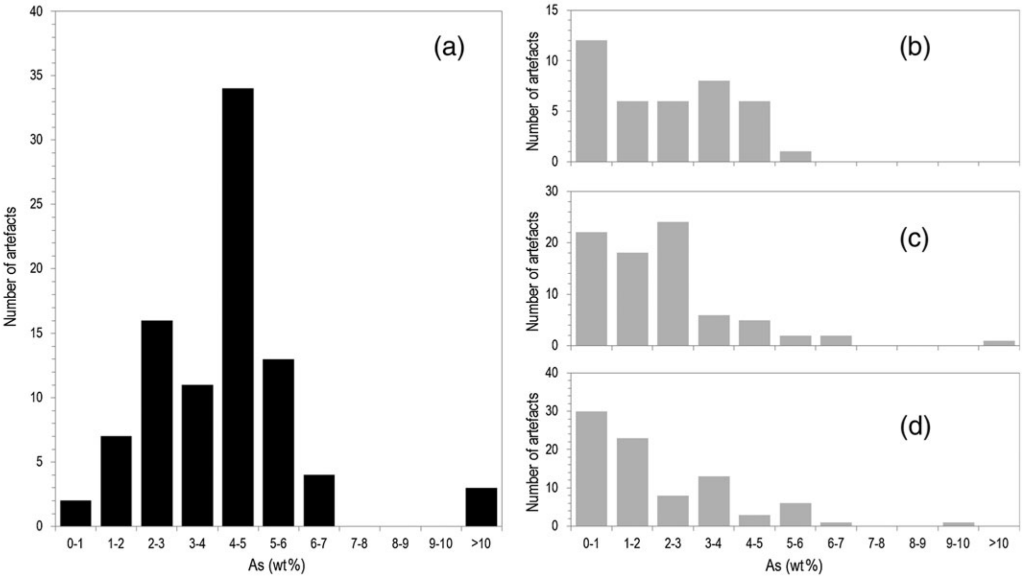

Figure 4 *Histograms of the arsenic content of MBA (left) and Chalcolithic (right) metals: (a) southern Portugal (this work; Nunes da Ponte et al. 2012; Henriques et al. 2013; Valério et al. 2014); (b) southern Portugal (Orestes Vidigal et al. 2015); (c) western Andalusia (Bayona 2008); (d) Portuguese Estremadura (Müller and Cardoso 2008; Pereira et al. 2013).*

The histogram of arsenic contents of MBA metals from southern Portugal resembles the distribution of tin in LBA bronzes; that is, a Gaussian curve centred on an intended content suggesting intentional alloying (see, e.g., Figueiredo *et al.* 2010; Valério *et al.* 2010). It is only in recent years that MBA domestic contexts have been recorded in southern Portugal, although without studied evidence of metal production. The absence of such evidence and the lack of experimental metallurgical studies hinder a comprehensive explanation for the emergence of those arsenic-rich copper alloys, but some hypotheses can be built up based on production methods identified in other regions of the Old World.

One possible explanation comes from recent research concerning the EBA metallurgy on the Iranian Plateau, showing the intentional production of speiss, a mixture of arsenical iron and iron arsenides (Thornton *et al.* 2009; Rehren *et al.* 2012). It has been suggested that the arsenical copper alloy could be produced by smelting the speiss and oxidized copper ore or by melting the speiss and copper. Also, in eastern Anatolia and Crete, a similar metallurgical process could have been used during the MBA (Thornton *et al.* 2009; Rehren *et al.* 2012). A recent experiment suggests that speiss can be added to molten copper to produce arsenical copper (Park and Gelegdorj 2014). Nevertheless, it should be emphasized that MBA slags bearing those characteristics have not yet been recorded in the Iberian Peninsula and, consequently, such an explanation is only a hypothesis, which needs to be demonstrated. An alternative reasoning, which is possibly more acceptable in the light of current knowledge, concerns the use of new ores that are richer in arsenic, as identified in the Balkan region (Pernicka *et al.* 1993, 1997). This transitional stage of alloying could also comprise the selection of arsenic-rich copper prills obtained from smelting. Again, any remains that could prove such operations have not been recorded to date in southern Portugal. Another explanation comprises the smelting of copper ores with higher temperatures and, especially, with more reducing conditions that minimize the arsenic losses. However, no significant advances are known regarding the MBA smelting technology and the iron content of artefacts remains low, reflecting the poor reducing conditions.

CONCLUSIONS

This research concerning MBA copper metallurgy at the south-western end of the Iberian Peninsula has significantly increased our knowledge about the diachrony of manufacture and use of arsenical copper alloys. A significant set of radiocarbon dates from archaeological contexts associated with metals has ascribed them mostly to the first half and the third quarter of the second millennium BC. Regarding the artefact composition, strong evidence was found for a regional preference for high arsenic contents (3.9 wt% average) for the manufacturing of tools and weapons, while no distinction was found between the composition and manufacture of metals from distinct funerary practices and domestic contexts. Moreover, the Gaussian distribution of MBA arsenic contents clearly indicates a change from what was in use in Chalcolithic metallurgies either in southern Portugal or in neighbouring regions. Regardless of the method used to obtain the arsenical copper alloy, there seems to have been a growing awareness amongst MBA metallurgists in southern Portugal of the aesthetic and practical value of this alloy, which indirectly reveals the growing importance of metal among prehistoric communities of the second millennium BC in this region.

However, the lack of studies related to the prehistoric production of arsenical copper makes the question of natural or intentional alloying an unsolvable issue at the present time. Provenance studies would be very important to ascertain possible changes in raw materials from the Chalcolithic to the MBA, while metallurgical experiments and the investigation of archaeological slags might suggest the evolution of metal production methods during this period. Further research into artefacts and production remains from the Beaker period (Late Chalcolithic/EBA) will be of particular importance, since this period is culturally an era of transition, and it will be interesting to ascertain the use of arsenical copper alloys and possible changes in the provenance of ores.

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REFERENCES

Alves, C., Costeira, C., Estrela, S., Porfírio, E., Serra, M., Soares, A. M. M., and Moreno-García, M., 2010, Middle Bronze Age funerary hypogea from Torre Velha 3 (Serpa, Portugal). The Southeast inside the Southwest?!, *Zephyrus*, **66**, 133–53.

Antunes, A. S., Deus, M., Soares, A. M. M., Santos, F., Arêz, L., Dewulf, J., Baptista, L., and Oliveira, L., 2012, Povoados abertos do Bronze Final no Médio Guadiana, in *Sidereum Ana II—el río Guadiana en el Bronce Final* (ed. J. Jiménez-Ávila), 277–308, Anejos de Aespa LXII, Instituto de Arqueología de Mérida, Mérida.

Aranda, G., and Molina, F., 2006, Wealth and power in the Bronze Age of the south-east of the Iberian Peninsula: the funerary record of Cerro de la Encina, *Oxford Journal of Archaeology*, **25**(1), 47–59.

Aranda Jiménez, G., and Esquivel Guerrero, J. A., 2007, Power and prestige in Argar culture societies: the commensal consumption of bovids and ovicaprids during funerary rituals, *Trabajos de Prehistoria*, **64**(2), 95–118.

Aranda Jiménez, G., Montón Subías, S., and Jiménez Brobeil, S., 2009, Conflicting evidence? Weapons and skeletons in the Bronze Age of south-east Iberia, *Antiquity*, **83**, 1038–51.

Aranda Jiménez, G., Alarcón García, E., Murillo-Barroso, M., Montero Ruiz, I., Jiménez-Brobeil, S., Sánchez Romero, M., and Rodríguez-Arisa, M. O., 2012, El yacimiento argárico del cerro de San Cristóbal (Ogíjares, Granada), *Menga*, **3**, 141–64.

Baptista, L., 2013, A Idade do Bronze no concelho de Serpa: um primeiro esboço de um conhecimento em construção, in *VI Encuentro de Arqueología del Suroeste Peninsular* (eds. J. J. Ávila, M. B. Alvarez and M. G. Cabezas), 669–708, Ayuntamiento de Villafranca de los Barros, Villafranca de los Barros.

Baptista, L., Rodrigues, Z., and Pinheiro, R., 2012, Espacialidades dos cadáveres em Montinhos 6: contributos para uma compreensão das práticas funerárias da Idade do Bronze no Sudoeste Peninsular, in *Actas do V Encontro de Arqueologia do Sudoeste Peninsular*, 149–70, Câmara Municipal de Almodôvar, Almodôvar.

Baptista, L., Gomes, S., Pinheiro, R., Rodrigues, Z., Vale, N., Grilo, J., Mendoça, R., Luís, L., Saraiva, A., and Mota, R., 2013a, Ponto de Situação dos trabalhos de minimização de impactes sobre o património cultural decorrentes da execução do Circuito Hidráulico de Pedrógão—Fase de Obra (1ª Fase) (Vidigueira e Beja, Portugal), in *VI Encuentro de Arqueología del Suroeste Peninsular* (eds. J. J. Ávila, M. B. Alvarez, and M. G. Cabezas), 2537–72, Ayuntamiento de Villafranca de los Barros, Villafranca de los Barros.

Baptista, L., Gomes, S., Pinheiro, R., Rodrigues, Z., Vale, N., Grilo, J., Mendoça, R., Luís, L., Saraiva, A., Mota, R., Fernandes, S., and Baptista, H., 2013b, Ponto de Situação dos trabalhos de minimização de impactes sobre o património cultural decorrentes da execução do Bloco de Rega de Ervidel—Fase de Obra (Aljustrel, Ferreira do Alentejo e Beja, Portugal), in *VI Encuentro de Arqueología del Suroeste Peninsular* (eds. J. J. Ávila, M. B. Alvarez, and M. G. Cabezas), 2489–536, Ayuntamiento de Villafranca de los Barros, Villafranca de los Barros.

Bayona, M. R., 2008, *La investigación de la actividad metalúrgica durante el III milenio A.N.E. en el Suroeste de la Península Ibérica*, British Archaeological Reports, International Series, Archaeopress, Oxford.

Bayona, M. R., Nocete, F., Sáez, R., Nieto, J. M., Alex, E., and Rovira, S., 2003, The prehistoric metallurgy of Cabezo Juré (Alosno, Huelva, Spain): the metal objects production, in *International Conference Archaeometallurgy in Europe*, Vol. **2**, 175–84, Associazione Italiana de Metallurgia, Milan.

Bray, P. J., and Pollard, A. M., 2012, A new interpretative approach to the chemistry of copper-alloy objects: source, recycling and technology, *Antiquity*, **86**, 853–67.

Bronk Ramsey, C., 2013, *Oxcal 4.2 Manual, Web interface build number: 80*. Last updated 24 May 2014; https://c14.arch.ox.ac.uk/oxcalhelp/hlp_contents.html

Budd, P., 1991, Eneolithic arsenical copper: heat treatment and the metallographic interpretation of manufacturing processes, in *Archaeometry '90: International Symposium on Archaeometry* (eds. E. Pernicka and G. A. Wagner), 35–44, Birkhäuser Verlag, Basel.

Budd, P., and Ottaway, B. S., 1991, The properties of arsenical copper alloys: implications for the development of Eneolithic metallurgy, in *Archaeological sciences 1989* (eds. P. Budd, B. Chapman, C. Jackson, R. Janaway, and B. Ottaway), 132–42, Oxbow Books, Oxford.

Budd, P., and Ottaway, B. S., 1995, Eneolithic arsenical copper: chance or choice?, in *Ancient mining and metallurgy in southeast Europe: international symposium* (ed. B. Jovanovic), 95–102, Archaeological Institute, Donji Milanovac.

Castro-Martínez, P. V., Escoriza-Mateu, T., and Oltra-Puigdomenech, J., 2006, Social hypotheses for the communities of the Iberian Mediterranean basin (from the VI to II millennia BC), in *Approaches to social inequality in Iberian recent prehistory* (eds. P. Díaz Del Río and L. García Sanjuán), 117–31, British Archaeological Reports, International Series, Archaeopress, Oxford.

Costa Caramé, M. E., 2010, *Las producciones metálicas del III y II milenio cal ANE en el Suroeste de la Península Ibérica*, British Archaeological Reports, International Series, Archaeopress, Oxford.

Craddock, P. T., 1995, *Early metal mining and production*, Cambridge University Press, Cambridge.

Delibes, G., Fernández-Miranda, M., Fernández-Posse, M. D., Martín, C., Montero, I., and Rovira, S., 1991, Almizaraque (Almería, Spain): archaeometallurgy during the Chalcolithic in the south-east of the Iberian Peninsula, in *Découverte du metal* (eds. C. Éluère and J.-P. Mohen), 303–15, Picard, Paris.

Figueiredo, E., Silva, R. J. C., Senna-Martinez, J. C., Araújo, M. F., Fernandes, F. M. B., and Vaz, J. L. I., 2010, Smelting and recycling evidences from the Late Bronze Age habitat site of Baiões (Viseu, Portugal), *Journal of Archaeological Science*, **37**, 1623–34.

Gomes, S., Baptista, L., and Rodrigues, Z., 2013, Tradições de inumação durante a Idade do Bronze em Torre Velha 12 (Salvador, Serpa), in *VI Encuentro de Arqueología del Suroeste Peninsular* (eds. J. J. Ávila, M. B. Alvarez, and M. G. Cabezas), 709–32, Ayuntamiento de Villafranca de los Barros, Villafranca de los Barros.

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

Hanson, D., and Marryat, C. B., 1927, Investigation of the effects of impurities on copper. Part III: the effect of arsenic on copper. Part IV: the effect of arsenic plus oxygen on copper, *Journal of the Institute of Metals*, **35**, 121–68.

Harrison, R. J., and Craddock, P. T., 1981, A study of the Bronze Age metalwork from the Iberian Peninsula in the British Museum, *Ampurias*, **43**, 113–79.

Hauptmann, A., 2007, *The archaeometallurgy of copper*, Springer-Verlag, Berlin.

Henriques, F. J. R., Soares, A. M. M., António, T. F. A., Curate, F., Valério, P., and Rosa, S. P., 2013, O *Tholos* Centirã 2 (Brinches, Serpa)—construtores e utilizadores; práticas funerárias e cronologias, in *VI Encuentro de Arqueología del Suroeste Peninsular* (eds. J. J. Ávila, M. B. Alvarez, and M. G. Cabezas), 319–35, Ayuntamiento de Villafranca de los Barros, Villafranca de los Barros.

Hunt Ortiz, M. A., 2003, *Prehistoric mining and metallurgy in south west Iberian Peninsula*, British Archaeological Reports, International Series, Archaeopress, Oxford.

Lechtman, H., 1996, Arsenic bronze: dirty copper or chosen alloy? A view from the Americas, *Journal of Field Archaeology*, **23**, 477–514.

Lull, V., 2000, Argaric society: death at home, *Antiquity*, **74**, 581–90.

Lull, V., Micó, R., Rihuete, C., and Risch, R., 2011, El Argar and the beginning of class society in the western Mediterranean, in *Sozialarchäologische perspektiven: gesellschaftlicher wandel 5000–1500 v. chr. zwischen Atlantik und Kaukasus* (eds. S. Hansen and J. Müller), 381–414, Deutsches Archäologisches Institut, Von Zabern.

McKerrell, H., and Tylecote, R. F., 1972, The working of copper–arsenic alloys in the Early Bronze Age and the effect on the determination of provenance, *Proceedings of the Prehistoric Society*, **38**, 209–18.

Montero-Ruíz, I., 1994, *El origen de la metalurgia en el Sureste Peninsular*, Instituto de Estudios Almerienses, Almería.

Müller, R., and Cardoso, J. L., 2008, The origins and the use of copper at the Chalcolithic fortification of Leceia, Portugal, *Madrider Mitteilungen*, **48**, 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. Niece, D. Hook, and P. T. Craddock), 15–26, Archetype, London.

Northover, J. P., 1989, Properties and use of arsenic–copper alloys, in *Old World archaeometallurgy* (eds. A. Hauptmann, E. Pernicka, and G. A. Wagner), 111–18, Deutsches Bergbau-Museums, Bochum.

Nunes da Ponte, T. R., Soares, A. M. M., Araújo, M. F., Frade, J. C., Ribeiro, I., Rodrigues, Z., Silva, R. J. C., and Valério, P., 2012, O Bronze Pleno do sudoeste da Horta do Folgão (Serpa, Portugal): os hipogeus funerários, *O Arqueólogo Português*, **2**, 265–95.

Orestes Vidigal, R., Valério, P., Araújo, M. F., Soares, A. M. M., and Mataloto, R., 2015, Micro-EDXRF study of Chalcolithic copper-based artefacts from southern Portugal, *X-Ray Spectrometry*, DOI: 10.1002/xrs.2658.

Park, J.-S., and Gelegdorj, E., 2014, A preliminary study on the loss of iron and arsenic in the re-melting of iron-bearing arsenical copper, *Archaeometry*, DOI: 10.1111/arcm.12128.

Pavón Soldevila, I., 2008, *El mundo funerario de la Edad del Bronce en la Tierra de Barros: una aproximación desde la bioarqueología de Las Minitas, Memorias de Arqueología Extremeña*, Junta de Extremadura, Mérida.

Pereira, F., Silva, R. J. C., Monge Soares, A. 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.

Pernicka, E., 2014, Provenance determination of archaeological metal objects, in *Archaeometallurgy in global perspective: methods and syntheses* (eds. B. W. Roberts and C. P. Thornton), 239–68, Springer, New York.

Pernicka, E., Begemann, F., Schmitt-Strecker, S., and Wagner, G. A., 1993, Eneolithic and Early Bronze Age copper artefacts from the Balkans and their relation to the Serbian copper ores, *Prähistorische Zeitschrift*, **66**, 1–57.

Pernicka, E., Begemann, F., Schmitt-Strecker, S., Todorova, H., and Kuleff, I., 1997, Prehistoric copper in Bulgaria, *Eurasia Antiqua*, **3**, 41–180.

Rehren, T., Boscher, L., and Pernicka, E., 2012, Large scale smelting of speiss and arsenical copper at Early Bronze Age Arisman, Iran, *Journal of Archaeological Science*, **39**, 1717–27.

Reimer, P. J., Bard, E., Bayliss, A., Beck, J. W., Blackwell, P. G., Bronk Ramsey, C., Buck, C. E., Cheng, H., Edwards, R. L., Friedrich, M., Grootes, P. M., Guilderson, T. P., Haflidason, H., Hajdas, I., Hatté, C., Heaton, T., Hoffmann, D. L., Hogg, A., Hughen, K. A., Kaiser, K., Kromer, B., Manning, S. W., Niu, M., Reimer, R., Richards, D. A., Scott, E. M., Southon, J. R., Staff, R. A., Turney, C., and van der Plicht, J., 2013, IntCal13 and Marine13 radiocarbon age calibration curves, 0–50,000 years cal BP, *Radiocarbon*, **55**(4), 1869–87.

Rovira, S., 2004, Tecnología metalúrgica y cambio cultural en la Prehistoria de la Península Ibérica, *Norba Revista de Historia*, **17**, 9–40.

Rovira, S., and Gómez-Ramos, P., 1998, Metalurgia Calcolítica en Carmona (Sevilla), *SPAL*, **7**, 69–79.

Rovira, S., and Montero-Ruíz, 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-Schessel), 231–9, Verlag Marie Leidorf GmbH, Rahden/Westf.

Ruíz-Taboada, A., and Montero-Ruíz, I., 1999, The oldest metallurgy in Western Europe, *Antiquity*, **73**, 897–902.

Schubart, H., 1974, Novos achados sepulcrais do Bronze do Sudoeste II, in *Actas das II Jornadas Arqueológicas*, 65–86, Associação dos Arqueólogos Portugueses, Lisboa.

Schubart, H., 1975, *Die Kultur der Bronzezeit im Südwesten der Iberischen Halbinsel*, Madrider Forschungen 9, Walter de Gruyter, Berlin.

Shalev, S., Caspi, E. N., Shilstein, S., Paradowska, A. M., Kockelmann, W., Kan-Cipor Meron, T., and Levy, Y., 2014, Middle Bronze Age II battle axes from Rishon Lezion, Israel: archaeology and metallurgy, *Archaeometry*, **56**, 279–95.

Soares, A. M. M., 1977, Uma cista do bronze do sudoeste em Aldeia Nova de São Bento (Serpa), *Setúbal Arqueológica*, **23**, 273–9.

Soares, A. M. M., 1994, O Bronze do Sudoeste na margem esquerda do Guadiana: as necrópoles do concelho de Serpa, in *Actas das V Jornadas Arqueológicas Associação dos Arqueólogos Portugueses*, 179–97, Associação dos Arqueólogos Portugueses, Lisboa.

Soares, A. M. M., Araújo, M. F., Alves, L., and Ferraz, M. T., 1996, Vestígios metalúrgicos em contextos calcolíticos e da Idade do Bronze no sul de Portugal, in *Miscellanea em homenagem ao professor Bairrão Oleiro* (ed. M. J. Maciel), 553–79, Edições Colibri, Lisboa.

Soares, A. M. M., Santos, F. J. C., Dewulf, J., Deus, M., and Antunes, A. S., 2009, Práticas rituais no Bronze do Sudoeste—alguns dados, *Estudos Arqueológicos de Oeiras*, **17**, 433–56.

Soares, A. M. M., Valério, P., Frade, J. C., Oliveira, M. J., Patoilo, D., Ribeiro, I., Arez, L., Santos, F. J. C., and Araújo, M. F., 2009, A Late Bronze Age stone mould for flat axes from Casarão da Mesquita 3 (São Manços, Évora, Portugal), in *Archaeometallurgy in Europe: 2nd international conference, Aquileia, Italy, 17–21 June 2007*, 145–57, Associazione Italiana di Metallurgia, Milan.

Stuiver, M., and Reimer, P. J., 1993, Extended ^{14}C data base and revised CALIB 3.0 ^{14}C age calibration, *Radiocarbon*, **35**(1), 215–30.

Tadmor, M., Kedem, D., Begemann, F., Hauptmann, A., Pernicka, E., and Schmitt-Strecker, S., 1995, The Nahal Mishmar Hoard from the Judean Desert: technology, composition, and provenance, *Atiqot*, **XXVII**, 95–148.

Thornton, C. P., Rehren, T., and Pigott, V. C., 2009, The production of speiss (iron arsenide) during the Early Bronze Age in Iran, *Journal of Archaeological Science*, **36**, 308–16.

Valera, A., and Filipe, V., 2010, *Outeiro Alto 2 (Brinches, Serpa): nota preliminar sobre um espaço funerário e de sociabilização, do Neolítico Final à Idade do Bronze*, *Apontamentos de Arqueologia e Património*, **5**, 49–56, Lisboa, NIA-ERA Arqueologia.

Valério, P., Soares, A. M. M., Araújo, M. F., Silva, R. J. C., Porfírio, E., and Serra, M., 2014, Arsenical copper and bronze in Middle Bronze Age burial sites of southern Portugal: the first bronzes in southwestern Iberia, *Journal of Archaeological Science*, **42**, 68–80.

Valério, P., Silva, R. J. C., Soares, A. M. M., Araújo, M. F., Fernandes, F. M. B., Silva, A. C., and Berrocal-Rangel, L., 2010, Technological continuity in Early Iron Age bronze metallurgy at the south-western Iberian Peninsula—a sight from Castro dos Ratinhos, *Journal of Archaeological Science*, **37**, 1811–19.