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The supply of copper to the settlement of Leceia (Portugal) and the Estremadura region during the third millennium BC

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A R T I C L E I N F O

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A B S T R A C T

The Chalcolithic settlement of Leceia (Portugal) has one of the largest collections of copper artefacts and metallurgical debris in the Portuguese Estremadura. However, the absence of ores and smelting remains suggests that local metallurgical operations were related to the production of artefacts. In fact, the metal assemblage includes several fragments of flat axes, most of them with traces of sectioning, which may have been used as ingots. In order to validate this hypothesis and to identify the copper sources used, elemental, microstructural and Pb isotope characterisation of five axe-ingots was undertaken. The assemblage turned out to be composed of copper with varying amounts of arsenic (0.08–2.94 wt%) and oxide inclusions (Cu_2O and Cu-As-O). Some inclusions containing distinct contents of Bi, Sb and/or Sn were also identified, indicating the exploitation of different sources of copper ores. Pb isotope ratios displayed a cluster of four samples ($^{206}Pb/^{204}Pb$: 18.2378–18.3444) and one outlier with low radiogenic lead ($^{206}Pb/^{204}Pb$: 17.6625), signatures that compare well with those previously obtained for local artefacts and prills. Euclidean distances identified ore deposits in the Spanish provinces of Huelva and Cordoba as potential suppliers of copper, particularly the supergene copper ores from the mines of Rio Tinto, Cabezadas del Sandino, Preciosa and Quita Pellejo, all of which are located a considerable distance from the settlement of Leceia. Other probable copper sources are located in the mining districts of Linares-La Carolina and Los Pedroches, situated even further away from the Portuguese Estremadura. Consequently, the copper axe-ingots of Leceia, like the previously analysed local artefacts, provide evidence of long-distance trade relations with south-central Iberian Peninsula, which appear to be shared with coeval settlements in Estremadura, such as Vila Nova de São Pedro and Zambujal.

1. Introduction

The third millennium BC in the southwestern Iberian Peninsula is characterised by the inception of copper metallurgy. The earliest metal artefacts have very simple shapes and occur in archaeological contexts dated to the first half of this period, while the proliferation of those artefacts and new types of weapons (Palmela points and tanged daggers) only arise during the second half of the millennium (Hunt Ortiz, 2003; Soares, 2024; Rovira and Montero Ruiz, 2013; Soares and Valério, 2016; Soares et al., 2017). The limited metallurgical development observed in the Chalcolithic period, characterized by a small-scale and unspecialised technology with few significant changes over the course of the millennium, is likely the result of copper not yet having acquired the social and economic value necessary to stimulate production and consumption (Montero-Ruiz et al., 2021). Furthermore, there is a notable absence of Chalcolithic copper ornaments in the Iberian Peninsula, unlike what occurred in the early days of copper metallurgy in other regions across Eurasia. This absence suggests that copper did not possess an aesthetic or prestige value, being gold or non-metallic materials (e.g. ivory, variscite) the raw materials used in the ornaments worn by those Chalcolithic communities (Odriozola et al., 2013; Nocete et al., 2013; Valério et al., 2017). Additionally, the chaîne opératoire of those copper tools-

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weapons often included hammering and annealing cycles, being distinct from the one observed in the southeastern Iberian Peninsula where thermomechanical post-casting treatments appear to be rare. This discrepancy can be a good indication of how the inception of the copper metallurgy occurred among these ancient communities (Murillo-Barroso and Montero-Ruiz, 2012; Soares and Valério, in press).

The production of Chalcolithic copper in the Iberian Peninsula relied on the smelting of secondary copper ores in simple fireplaces using open ceramic bowls or crucibles (e.g. Müller et al., 2007; Murillo-Barroso et al., 2017; La Duc et al., 2022; Valério et al., 2020, 2023a). As the raw metal produced in smelting operations is much easier to transport than the equivalent larger mass of copper ore, the primary production activity was probably conducted close to the mines. This evidence has been recorded at Ganhoteira (Soares et al., 2020) and Mocissos mines (Goldenberg and Hanning, 2022). However, metallurgical activities also appear to have thrived in regions without significant copper ore deposits, as it happens in the Portuguese Estremadura. So, the copper, perhaps in the form of ingots, had to be delivered from sources that could be located at very long distances (Kunst, 2013). A series of fortified Chalcolithic settlements are known at the Portuguese Estremadura. Three of them, Vila Nova de São Pedro (VNSP, Azambuja), Zambujal (Torres Vedras) and Leceia (Oeiras), were subjected to extensive archaeological excavations. These settlements seem to have controlled certain areas, being part of a network of long distant trade (Müller and Cardoso, 2008; Müller and Soares, 2008; Kunst, 2013; Gauß, 2016). Due to the higher amount of copper artefacts and metallurgical debris, as well as exogenous materials (e.g. ivory and variscite), VNSP most likely played a significant role in this complex trade network, establishing itself as an important node for the import and distribution of raw materials and artefacts, both imported and locally manufactured (Arnaud et al., 2005; Jordão et al., 2026).

Early studies on copper from those Chalcolithic settlements suggested that the metal originated from the Ossa-Morena Zone (OMZ), from ore deposits located at least 150 km away from the studied settlements. An intense exchange of materials between the two regions also emerges when looking at other types of archaeological raw materials, such as the amphibolite most likely imported to the Portuguese Estremadura from Alentejo, *c.* 150-200 km away (Cardoso and Carvalhosa, 1995; Cardoso, 2004, 2020; Müller and Soares, 2008; Valera et al., 2008; Valera, 2013). More recently, a review in the light of new data on copper ore sources and theoretical developments in the application of Pb isotope signatures, included also the mining district of Los Pedroches

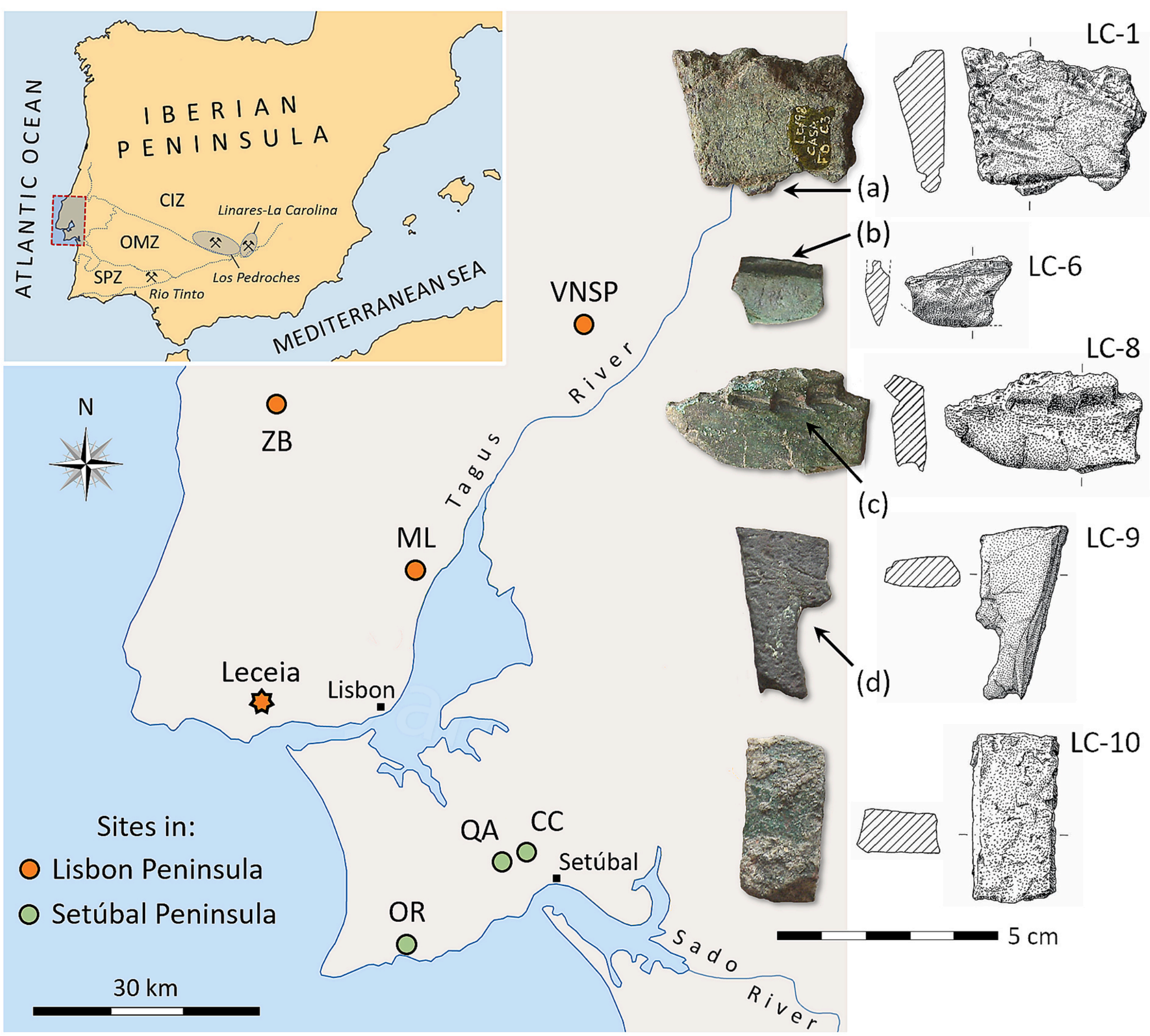

Fig. 1. Location of Leceia settlement, associated Chalcolithic sites and significant mining districs in the Western Iberian Peninsula (Sites: VNSP – Vila Nova de São Pedro; ZB – Zambujal; ML – Moita da Ladra; CC – Castro de Chibanes; QA – Quinta do Anjo; OR – Outeiro Redondo; Geological zones: CIZ – Central Iberian Zone; OMZ – Ossa-Morena Zone; SPZ – South Portuguese Zone). Photos and drawings of the fragments of axe-ingots from Leceia analised in this work (a to d – see the clear evidences of cutting to obtain lumps of metal on LC-1, LC6, LC-8 and LC-9, respectively).

(Central Iberian Zone, CIZ) as an important supplier of copper to the settlement of Leceia (Valério et al., 2023b).

The present work concerns the analytical characterisation of unstudied raw materials, namely five fragments of copper flat axes considered as ingots by Cardoso and Bottain, 2023 and recovered during archaeological excavations at Leceia. Flat axes have frequently been identified in Chalcolithic settlements in the Portuguese Estremadura and southern Portugal (Soares et al., 1994; Soares, 2005; Cardoso et al., 2020; Soares et al., 2020). However, their cutting edges generally show no signs of use, and it is also common to find fragments of these cutting edges detached from the body of the axe and without any trace of having been used. These pieces of evidence have led to the hypothesis that they may have been used as ingots (Soares et al., 1994; Soares, 2005; Cardoso et al., 2020; Soares et al., 2020). Moreover, the dendritic microstructures of many of these "axes", including the cutting edges like those observed in two examples from VNSP (Paço, 1955: Figs. 1, 2 and 3; Soares, 2024b), indicate that they were not subjected to strain hardening by hammering, thus reinforcing their interpretation as axe-ingots.

The Pb isotope signatures of a flat axe, or rather, an axe-ingot from the settlement of Três Moinhos (Baleizão) and another from Penedo (Torres Vedras) suggest long-distance trade of copper from northern Spain (La Profunda or El Milagro mines, Cantabrian Mountains) (Soares et al., 2020; Gauß, 2016). It is long clear that axe-ingots from Leceia contain information about Chalcolithic metallurgy (Cardoso and Fernandes, 1995) and the present study will provide valuable and new evidence about the supply of copper to the Portuguese Estremadura. Therefore, the composition, microstructure and Pb isotope signature of these artefacts were established with analyses by micro particle induced X-ray emission spectrometry (micro-PIXE), scanning electron microscopy with X-ray microanalysis (SEM-EDS), optical microscopy and multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS). The outcome of the analytical and archaeological interpretation will be then compared with Pb isotope data of coeval settlements in this region (VNSP and Zambujal), allowing an improved picture to be drawn about the copper supply to the Portuguese Estremadura during the third millennium BC.

2. The fortified settlement of Leceia

The archaeological site of Leceia (Oeiras) is located in the Portuguese Estremadura on a platform overlooking the Barcarena river valley, in close proximity to the Tagus estuary. The site was subjected to archaeological excavations carried out between 1983 and 2002, which uncovered Chalcolithic contexts dated to the third millennium BC (Cardoso and Soares, 1996). Archaeological excavations have revealed a complex fortified settlement with massive stone walls and towers, enclosing several round and ellipsoidal houses with stone foundations and, in some cases, possible adobe superstructures (Cardoso, 2022).

The first evidence of metallurgy in Leceia emerge during the Early Chalcolithic phase (*c.* 2800 – 2600/2500 BC), consisting of a few copper artefacts and a single ceramic crucible. The vast majority of the morphologically simple artefacts, in addition of prills and lumps (*c.* 150 items with a total mass of 1.4 kg) belong to the Middle/Late Chalcolithic phase (*c.* 2600/2500–2000 BC), showing the increasing importance of metallurgy in the course of the second half of the third millennium BC (Cardoso et al., 2020). However, considering the large time span of the settlement occupation (*c.* 800 years) we are clearly dealing with a small-scale metal production, most likely based on foundry and forging practices to manufacture morphologically basic objects.

As mentioned before, the artefact assemblage of Leceia consists of simple tools and weapons, such as awls, chisels, saws, fishhooks, knives and axe-ingots (flat axes). These types are characteristic of the Chalcolithic in the western Iberian Peninsula, with parallels in many coeval settlements of the Portuguese Estremadura, like VNSP (Pereira et al., 2013a), Zambujal (Gauß, 2016) and Moita da Ladra, in Vila Franca de Xira (Cardoso, 2014; Pereira et al., 2017), all located in the Lisbon Peninsula, in addition to Outeiro Redondo, in Sesimbra (Pereira et al., 2013b; Cardoso and Bottain, 2023) and Castro de Chibanes, in Palmela (Valério et al., 2023a), both situated in the Setubal Peninsula (Fig. 1).

Most of the prills and lumps at Leceia were found scattered in contexts located in the interior of the settlement, showing that metallurgical activities were conducted inside the walls and appear to have a domestic character. Moreover, the absence of ores and the presence of a single thick-walled crucible implies that these were secondary processes related to the production of artefacts. This scarce existence of metallurgical remains indicates that local metallurgical activities were not frequent at Leceia, suggesting that most of the artefacts used in local domestic activities came from other sites in the region, such as VNSP, which was certainly an important node in the network of trade, particularly for copper, that supplied the Chalcolithic settlements of the Lisbon Peninsula. However, the metallic set from Leceia also shows flat axes, most likely axe-ingots, since fragments thereof, particularly cutting edges not showing any traces of use (Cardoso et al., 2020, Fig. 7) and bodies presenting traces of chisel blows or cutting actions to obtain

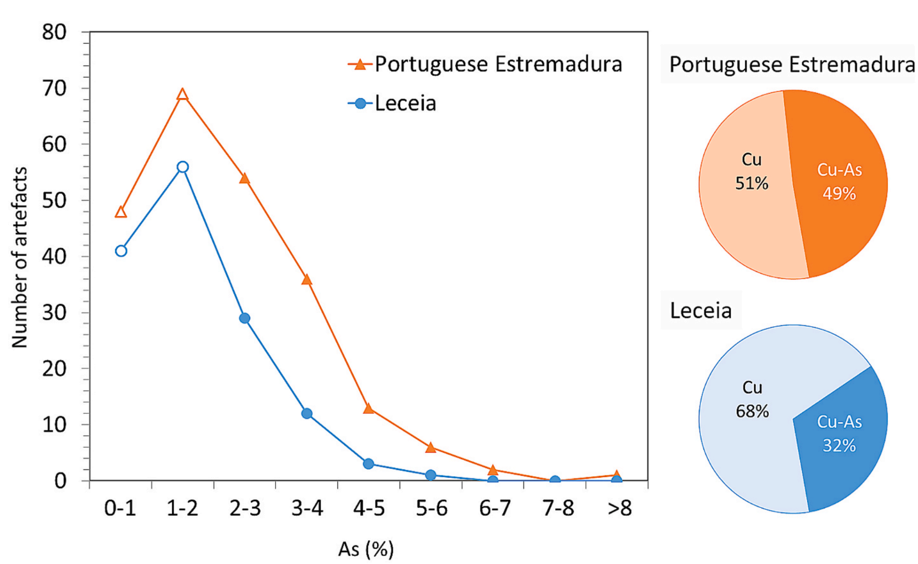

Fig. 2. Plot of arsenic contents of copper-based artefacts (left) and frequencies of copper versus arsenical copper artefacts (right) in the collections of Leceia and other Chalcolithic sites in the Portuguese Estremadura (total number of analysed artefacts equals 144 and 229, respectively).

lumps of metal for subsequent transformation into new tools or weapons. The axe-ingot fragments from Leceia that have been selected for study weigh between 12 g and 63 g, showing clear evidence of sectioning and one of them (LC-6) still retains part of the cutting edge (Fig. 1). Moreover, the specimen LC-8 has obvious chisel indentations and the exemplars LC-1, LC-6 and LC-9 exhibits cut marks, most likely made when obtaining fragments for foundry operations. The axe-ingot LC-1 belongs to the Early Chalcolithic phase (*c.* 2800 – 2600/2500 BC), while the remaining examples were recovered from contexts of the Middle/Late Chalcolithic phase (*c.* 2600/2500 – 2000 BC). Regional parallels for these axe-ingots have been recorded at the Chalcolithic settlements of VNSP (Soares, 2005), Zambujal (Sangmeister, 1995), Outeiro de São Mamede, in Bombarral (Cardoso, 2003) and Outeiro Redondo (Cardoso and Bottain, 2023).

3. Methodology

The process of sampling the five axe-ingots for micro-PIXE, SEM-EDS and optical microscopy involved cutting out a small fragment, which was mounted in epoxy resin and polished with SiC papers (P1000, P2500 and P4000 grit size) and diamond pastes (3 μm and 1 μm grit size). The efficiency of the polishing process was ascertained with optical microscopy observations made with a Zeiss Discovery V20 stereo-microscope (7.5-150× magnification). The area of the axe-ingots exposed by the cut was also drilled with a 1.5 mm diameter HSS drill bit to remove a small sample (*c.* 30 mg) for Pb isotope analysis by MC-ICP-MS. Finally, the exposed metal area on the artefact was protected with a corrosion inhibitor (benzotriazol, 3 % m/v in ethanol) and an acrylic polymer (paraloid B-72, 10 % m/v in ethanol), while the patina colouring was reproduced with a mixture of pigments dissolved in the same polymer solution.

3.1. Micro particle induced X-ray emission spectrometry

Elemental compositions of samples were determined by micro-PIXE in the external microbeam line of a 2.5 MV Van de Graaff accelerator at the Instituto Superior Técnico (Portugal). The external beam end-stage comprises OM150 triplet quadrupole lenses that enable the focusing of the 1.9 MeV external proton beam in a small sample area of about 60×70 μm^2 and allows beam scanning over an area physically limited by the aperture of the exit nozzle (100 nm thick silicon nitride membrane on a 1x1 mm^2 aperture Si frame). The characteristic X-rays were collected with a 30 mm^2 SDD detector (180 eV resolution at Mn-Kα) covered with a 50 μm thick mylar filter. GUPIXWIN v3.0 software was used for quantifications (Campbell et al., 2010). Detection limits were estimated as 0.01 wt% Fe, 0.03 wt% Ni, 0.04 wt% Zn, 0.02 wt% As, 0.04 wt% Sn and 0.02 wt% Pb (Valério et al., 2023a), while the accuracy of the quantification is listed in Supplementary Table 1.

3.2. Scanning electron microscopy with X-ray microanalysis and optical microscopy

Microstructural features of samples were identified by SEM-EDS using a Thermo Scientific Phenom ProX G6 electron microscope also at the Instituto Superior Técnico (Portugal) equipped with a CsB_6 electron source and SSD detector (25 mm^2 active area and 132 eV resolution at Mn-Kα). Optical microscopy images were obtained in an Olympus BX60M reflected light microscope (50-1000× magnification) equipped with a Canon EOS M100 digital camera. Experimental conditions of SEM-EDS analyses consisted of 15 kV of accelerating voltage and 7 mm of working distance. A conductive carbon bridge on the sample surface prevented charge accumulation. Images were obtained in the back-scattering mode (BSE) and the stoichiometry of constituents was determined with ZAF factors.

3.3. Multicollector inductively coupled plasma mass spectrometry

Pb isotope ratios of samples were determined by MC-ICP-MS at the Geochronology and Geochemistry SgIker Facility of the University of the Basque Country (UPV/EHU, Spain). Sample preparation was conducted in a PP Class-A (ISO-5) laminar flow bench within an ISO-7 clean lab. Samples were analysed in a Thermo Fisher Scientific Neptune MC-ICP-MS spectrometer using the NBS 997 thallium standard reference material for the internal mass correction ($^{205}Tl/^{203}Tl$ normalised ratio of 2.3889). The complete methodological details, in relation to the accuracy and reproducibility of the method were previously published (Rodríguez et al., 2020; Soares et al., 2020).

4. Results

4.1. Elemental composition

The elemental analysis of the axe-ingots from Leceia revealed a nearly pure copper matrix, with no other elements exhibiting significant contents apart from arsenic (Table 1). This element varies considerably in the small analysed assemblage, since two of the specimens (LC-8 and LC-10) contain 0.08-0.09 wt% As (values close to the determination limit of 0.06 wt% As), while the three remaining have distinct arsenic contents that range between 1.26 wt% and 2.94 wt%. The axe-ingot with a higher amount of arsenic (LC-1: 2.94 wt%) can already be considered an arsenical copper alloy (As > 2 wt%) and, curiously, this is the only exemplar from the Early Chalcolithic phase of Leceia.

4.2. Microstructural composition

SEM-EDS characterisation of axe-ingots from Leceia identified a copper matrix with many oxide inclusions (Cu_2O and Cu-As-O). Some of these oxide inclusions also contain other metal cations, such as Bi, Sb and/or Sn (Table 2). Moreover, the exemplar richer in arsenic (LC-1 with 2.94 wt%) also displayed an As-rich phase (32.6 wt% As), the composition of which is close to the stable intermetallic γ phase (Cu_3As: 28.2 wt % As), a common presence in ancient arsenical copper artefacts (Pereira et al., 2015).

4.3. Pb isotope signatures

Pb isotope ratios of axe-ingots from Leceia show a cluster with four samples (LC-1, LC-6, LC-8 and LC-10 with $^{206}Pb/^{204}Pb$: 18.2378-18.3444), while the exemplar LC-9 ($^{206}Pb/^{204}Pb$: 17.6625) has a quite different signature consisting of a significantly lower radiogenic lead content (Table 3).

5. Discussion

5.1. Chalcolithic metals in the Portuguese Estremadura

The large assemblage of 144 copper-based artefacts previously analysed from Leceia shows a wide variation of arsenic contents, namely from 0.10 wt% to 5.07 wt% (Cardoso et al., 2020). The plot of such arsenic contents clearly evidences that variability and low amounts are a common feature among artefacts from this settlement (Fig. 2). The collection has a low average arsenic content (1.7 ± 1.1 wt% As) and only a minority of items (32 %) can be considered to be composed by an arsenical copper alloy.

Other Chalcolithic collections from the Portuguese Estremadura can be taken into account, namely those from settlements in the Lisbon Peninsula, such as VNSP (Pereira et al., 2013a), Zambujal (Gauβ, 2016) and Moita da Ladra (Cardoso, 2014, Pereira et al., 2017), as well as those from sites in the Setúbal Peninsula, namely Outeiro Redondo (Pereira et al., 2013b; Cardoso and Bottain, 2023), Castro de Chibanes, Pedrão and Rotura (Valério et al., 2023a), in addition to the the necropolis of

Table 1
Micro-PIXE results of axe-ingots from Leceia (values in wt%; n.d. not detected; *additional details in Cardoso, 2022).

Sample	Weight (g)	Context*	Stratigraphy	Cu	As	Pb	Fe
LC-1	63	Hut FO (LC/98)	Layer 3	97.0	2.94	n.d.	<0.03
LC-6	12	Structure P (LC/88)	Layer 2	98.4	1.47	n.d.	<0.03
LC-8	43	Over structure FB (LC/93)	Layer 2	99.8	0.09	n.d.	<0.03
LC-9	27	Stronghold C (LC/86)	Layer 2	98.6	1.26	n.d.	<0.03
LC-10	44	Pavement EL (LC/90)	Layer 2	99.9	0.08	n.d.	<0.03

Table 2
SEM-EDS results of axe-ingots from Leceia (values in wt%; normalised; the numbers in brackets correspond to the point analyses identified in Fig. 3).

Sample	O	Cu	As	Sb	Sn	Bi
LC-1						
α-CuAs (1)	–	98.2	1.8	–	–	–
Inclusion (2)	24.7	4.7	55.0	2.2	–	13.4
Inclusion (3)	19.4	5.6	54.2	3.3	–	17.5
Inclusion (4)	21.5	13.6	62.0	1.9	–	1.0
α-CuAs (5)	–	92.4	7.6	–	–	–
As-rich phase (6)	-	67.4	32.6	–	–	–
Inclusion (7)	–	6.3	–	–	–	93.7
LC-6						
α-Cu (1)	–	99.5	0.5	–	–	–
Inclusion (2)	11.3	88.7	–	–	–	–
Inclusion (3)	13.5	55.3	31.2	–	–	–
Inclusion (4)	10.2	89.8	–	–	–	–
Inclusion (5)	14.6	46.3	36.8	–	–	–
α-Cu (6)	–	98.7	1.3	–	–	–
Inclusion (7)	11.4	88.6	–	–	–	–
Inclusion (8)	26.8	6.7	0.9	–	65.6	–
LC-8						
α-Cu (1)	–	100.0	–	–	–	–
Inclusion (2)	10.6	89.4	–	–	–	–
α-Cu (3)	–	100.0	–	–	–	–
Inclusion (4)	12.1	87.9	–	–	–	–
Inclusion (5)	12.1	87.9	–	–	–	–
Inclusion (6)	12.2	87.8	–	–	–	–
LC-9						
α-Cu (1)	–	98.7	1.3	–	–	–
α-Cu (2)	–	98.5	1.5	–	–	–
Inclusion (3)	18.5	38.9	41.6	–	–	1.0
Inclusion (4)	16.0	45.2	37.9	–	–	0.9
Inclusion (5)	18.3	37.6	41.9	0.6	–	1.6
Inclusion (6)	16.2	38.6	38.5	0.8	–	6.0
Inclusion (7)	17.5	34.4	39.9	0.8	–	7.4
α-Cu (8)	–	98.6	1.4	–	–	–
Inclusion (9)	11.4	88.6	–	–	–	–
Inclusion (10)	4.0	79.4	13.9	–	–	2.7
Inclusion (11)	18.8	31.5	40.8	–	0.6	8.3
LC-10						
α-Cu (1)	–	100.0	–	–	–	–
Inclusion (2)	11.8	88.2	–	–	–	–
Inclusion (3)	14.6	12.7	5.4	1.3	–	66.0
Inclusion (4)	16.0	15.6	5.4	4.6	–	56.0

Quinta do Anjo (Junghans et al., 1960, 1968, 1974). Furthermore, if there was indeed a network for the exchange of raw materials that encompassed the local settlements, of which VNSP was an important node, then at least the majority of the copper circulating in this region must have derived from the same ore deposits. The larger collection of 229 Chalcolithic artefacts from these last sites includes, like that one from Leceia, not only artefacts associated with pre-Bell Beaker contexts, but also those from contexts with elements of the Bell Beaker package. Generally, the distribution of arsenic contents in this collection is quite comparable to the pattern observed for Leceia (Fig. 2). The similarity suggests a common copper technology and the analogous utilisation of this metal among these sites of the Portuguese Estremadura. Moreover, this distribution of arsenic contents is significantly different from the Gaussian-type distribution of Middle Bronze Age artefacts in southern Portugal (MBA, *c.* 1800-1200 BC: 3.9 ± 1.4 wt% As; n = 90, Valério et al., 2016: fig. 4), which points to the deliberate production of arsenical copper alloys in the later period. Consequently, the arsenic pattern of Chalcolithic metals from Portuguese Estremadura suggests an unintentional production of such alloys, which owe their variable contents to the natural and irregular presence of this element in the smelted copper ores (Rovira and Montero Ruiz, 2013).

The lower incidence of arsenical copper alloys at Leceia compared with the other Chalcolithic settlements (32 % versus 49 %, Fig. 2) can probably be explained by the distinct presence of certain types. It should be noted that characteristic icons from contexts with Bell Beaker materials, such as Palmela points and tanged daggers, usually have higher arsenic contents compared to other types of artefacts (Valério et al., 2019). Moreover, the intensity of the presence of artefacts belonging to the Bell Beaker package varies from site to site. The presence of Bell Beaker artefacts at Leceia is concentrated in two contexts located outside the fortification (huts EN and FM), while their presence inside the fortified area is limited (Cardoso and Soares, 1990–1992). On the contrary, the Bell Beaker presence is widespread at Zambujal and Vila Nova de S. Pedro, exhibiting a high number of artefacts throughout almost the entire extent of the excavated area, which can eventually explain the higher incidence of arsenical coppers in these two settlements.

Regarding the microstructural composition of axe-ingots from Leceia, the single specimen from the Early Chalcolithic phase (LC-1) displays a α-phase with minimal inclusions (Fig. 3a). Furthermore, the variable arsenic content determined in the Cu-As matrix (1.8 wt% As and 7.6 wt% As, Table 2) implies a substantial degree of segregation, a characteristic that is prevalent in prehistoric arsenical copper alloys. The propensity of the Cu-As system for segregation under uncontrolled cooling conditions during casting is stipulated by the markedly negative slope of the solidus line (Subramanian and Laughlin, 1988). The arsenic-rich phase was recognised in a very small inclusion, probably resulting from long-term solid solution precipitation at ambient temperature (Pereira et al., 2015). Of greater significance is the observation that the few inclusions present within the LC-1 primary matrix associate the arsenic with bismuth and antimony (Fig. 3a and b). Consequently, these elements are expected to be significantly present in the copper ores that were smelted to produce this artefact.

The axe-ingot LC-6 belonging to the Middle/Late Chalcolithic phase of Leceia shows a α-Cu matrix with segregation (0.5 wt% As and 1.3 wt%

Table 3
MC-ICP-MS results with respective uncertainties of Pb isotope ratios of axe-ingots from Leceia.

Sample	$^{206}Pb/^{204}Pb$	2σ	$^{207}Pb/^{204}Pb$	2σ	$^{208}Pb/^{204}Pb$	2σ	$^{208}Pb/^{206}Pb$	2σ	$^{207}Pb/^{206}Pb$	2σ
LC-1	18.2639	0.0016	15.6421	0.0014	38.4278	0.0036	2.10402	0.00006	0.85645	0.00002
LC-6	18.3444	0.0010	15.6583	0.0009	38.3975	0.0025	2.09315	0.00006	0.85358	0.00001
LC-8	18.3152	0.0029	15.6498	0.0025	38.3750	0.0063	2.09525	0.00011	0.85447	0.00004
LC-9	17.6625	0.0009	15.5953	0.0009	37.5868	0.0023	2.12806	0.00005	0.88296	0.00001
LC-10	18.2378	0.0010	15.6509	0.0009	38.3331	0.0024	2.10185	0.00005	0.85816	0.00001

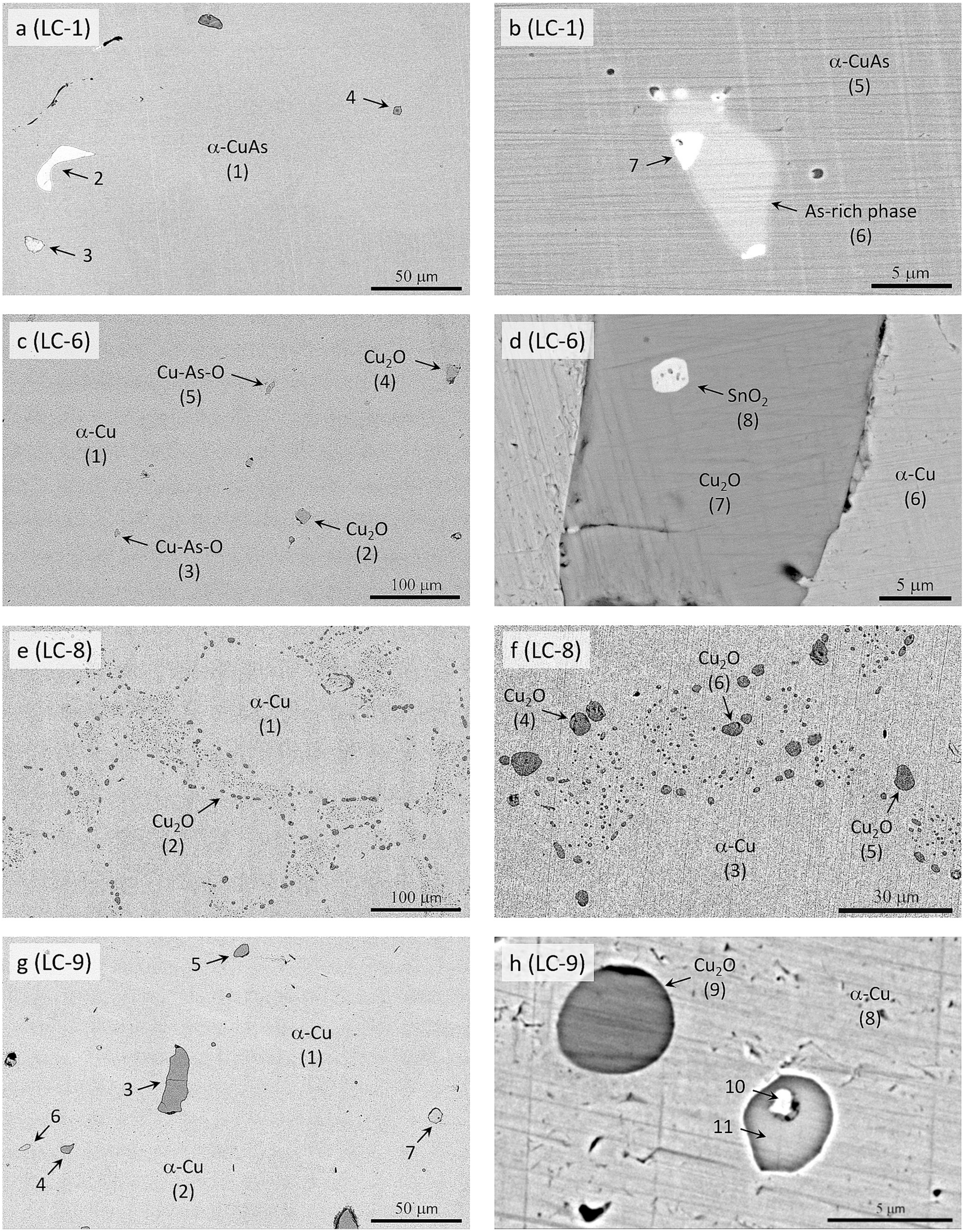

Fig. 3. SEM images (BSE mode) of the microstructures of axe-ingots belonging to the Early Chalcolithic phase (LC-1) and Middle/Late Chalcolithic phase (LC-6, LC-8 and LC-9) of Leceia (the numbers in brackets correspond to the SEM-EDS point analyses listed in Table 2).

As, Table 2) and few oxidic inclusions of variable composition (Fig. 3c). Some of these inclusions were identified as cuprous oxide (Cu_2O with a stoichiometric composition of 88.2 wt% Cu and 11.2 wt% O), while others exhibited variable arsenic contents. Cuprous oxide is formed by reaction of molten copper with oxygen. Budd (1991) hypothesised that these oxide inclusions are indicative of open mould casting, yet they in fact reflect a limited control over oxygen absorption during the various steps in the melting and casting processes of the prehistoric period (Kienlin et al., 2006). Moreover, it has been demonstrated that a significant presence of arsenic results in the reduction of the amount of cuprous oxide inclusions due to the deoxidising properties of arsenic (Hook et al., 1991). The influence of arsenic can be illustrated by the absence of cuprous oxide inclusions in the axe-ingot with the higher amount of this element (LC-1: 2.94 wt% As), contrasting with their existence in the axe-ingot LC-6 (1.47 wt% As), as well as in the examples LC-8 (0.09 wt% As) and LC-10 (0.08 wt% As). A further category of diagnostic compounds comprises minute tin oxide inclusions (presumably SnO_2, Fig. 3d), which may offer significant value in the identification of the provenance of copper.

The microstructure of the axe-ingot LC-8 is characterised by an intense interdendritic network of dark inclusions in the α-Cu matrix (Fig. 3e). The dark inclusions were identified through stoichiometric analysis as cuprous oxide (Cu_2O, Table 2), indicating an extremely high amount of oxygen absorption during the production of this artefact. The elevated presence of cuprous oxide inclusions increases the brittleness of the metal, thereby raising its susceptibility to fracture under conditions of more extreme utilisation. The absence of other types of diagnostic inclusions is also pertinent (Fig. 3f), as it indicates that the copper ores exploited were of a very high purity. Alternatively, the copper of axe-ingot LC-8 could have undergone substantial refinement, but this hypothesis is less probable when considering the early chronology of the artefact.

The axe-ingot LC-9 displays a α-Cu matrix with Cu-As-O inclusions of variable composition (Fig. 3g and Table 2). Some of these inclusions also exhibit bismuth and antimony, a feature that was already identified in the LC-1. However, these inclusions evidence higher amounts of bismuth in the latter example, which might indicate a higher content of this element in the smelted copper ore. A few cuprous oxide inclusions were also identified, in addition to a very small Cu-As-O inclusion combined with bismuth and tin (Fig. 3h), thus adding the latter element to the probable impurities of the exploited copper ores.

The axe-ingot LC-10 exhibits a microstructure analogous to that of the axe-ingot LC-8, distinguished by a substantial interdendritic network of cuprous oxide inclusions in the α-Cu phase (Fig. 4a). However, in the exemplar LC-10 it was possible to perceive that these oxidic inclusions are much more abundant in the area close to the outer surface of the axe-ingot (Fig. 4b and c). A good explanation for the observed discrepancy is the casting of the ingot in an open mould without the use of a deoxidant agent, such as a layer of charcoal. In such an oxidant environment, it is hypothesised that the surface layer of molten copper would absorb a greater amount of oxygen, thereby resulting in the observed microstructure. In addition to those cuprous oxides, some Cu-As-O inclusions with a high content of bismuth and antimony were also identified (Table 2). These inclusions are similar to the ones identified in the axe-ingots LC-1 and LC-9, suggesting the utilisation of copper ores with a similar pattern of metallic impurities.

Overall, the microstructures of these axe-ingots reveal a rudimentary metallurgy without concern about the oxygen uptake into the molten copper, which in extreme cases led to a more brittle metal unfit for heavy-duty tools and weapons. Evidently, this is irrelevant if the primary idea behind the manufacture of these items was to obtain ingots rather than common axes. On the other hand, the total absence of inclusions containing sulphur (e.g. Cu_2S) indicates the exploitation of copper oxide or copper carbonate ores, such as cuprite, malachite, azurite, pseudomalachite and libethenite (Valério et al., 2020). These secondary copper ores are often associated with arsenic (e.g. olivenite

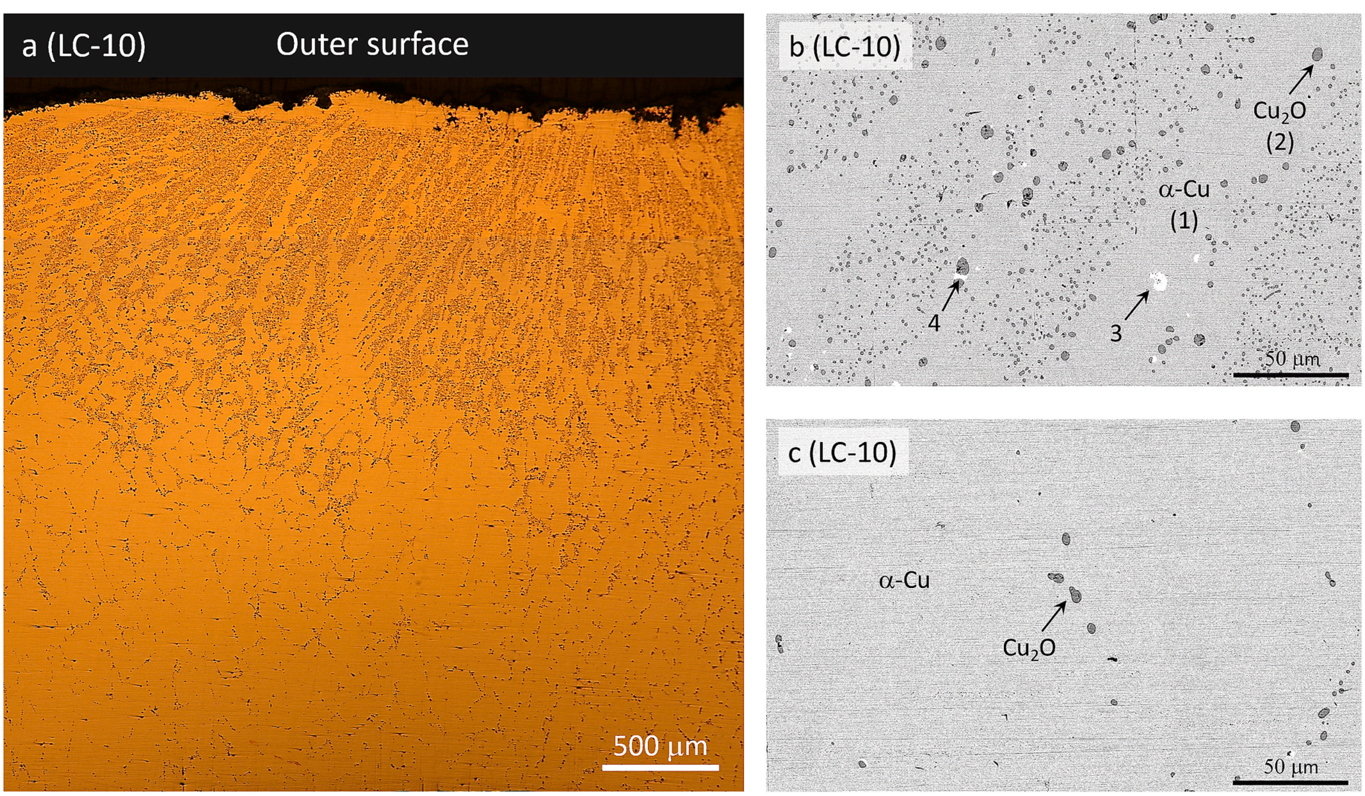

Fig. 4. Optical microscopy (bright field) and SEM images (BSE mode) of the microstructure of ingot LC-10 belonging to the Middle/Late Chalcolithic phase of Leceia (b: area closer to the outer surface; c: area in the inner region; the numbers in brackets of the SEM-EDS point analyses correspond to the quantifications listed in Table 2).

and conichalcite) and iron minerals (e.g. hematite and goethite) and could be efficiently smelted with the primitive reducing conditions of the Chalcolithic metallurgy in the Iberian Peninsula (Rovira and Montero Ruiz, 2013). Another interesting outcome is the presence of multiple so-called diagnostic inclusions containing a combination of various metallic cations (Bi, Sb, Sn, in addition to As), which indicate the exploitation of different copper ores sources.

5.2. The supply of copper to Leceia and Portuguese Estremadura

The Pb isotope ratios determined for the axe-ingots from Leceia were compared with values previously obtained for local artefacts and prills (Müller and Cardoso, 2008). The comparison of these Pb isotope ratios shows a good correspondence among some axe-ingots, artefacts and prills (Fig. 5). However, it should be noted that the $^{206}Pb/^{204}Pb$ ratios previously determined in five of these artefacts (see the figure) have a poor precision. Overall, considering the similarity of the Pb isotope signatures of axe-ingots, artefacts and prills it is conceivable that some of the finished objects from Leceia may have been locally made with metal sampled from these ingots, but the existence anomalous ratios (axe-ingot LC-9 and artefact LC-A11) indicates the use of additional sources with significantly lower radiogenic lead signature.

The identification of the copper sources likely exploited to obtain the axe-ingots recovered in Leceia relied in the comparison with the database of Pb isotope ratios published by Tomczyk (2022), which includes about 1000 copper ores from the Iberian Peninsula. A numerical approach based on the closest Euclidean neighbours was used to select the best candidates, since the overlay of the Pb signatures of the axe-ingots with the Pb signatures of so many copper mines make impossible to rely only on a graphical approach. Therefore, the best candidates will be copper ores with a low Euclidean distance ($d < 0.05$) to the sample under study, as well as being within the range of analytical uncertainty for each Pb isotope ratio (0.10 % for $^{206}Pb/^{204}Pb$, 0.14 % for $^{207}Pb/^{204}Pb$ and 0.20 % for $^{208}Pb/^{204}Pb$, according to Rodríguez et al., 2023). This improves the discrimination of sources since each Pb radiogenic isotope has a different formation sequence, i.e. ^{206}Pb, ^{207}Pb and ^{208}Pb are the final decay products of ^{238}U, ^{235}U and ^{232}Th, respectively.

The majority of the Euclidean neighbours of the axe-ingot LC-1 belongs to the Linares-La Carolina mining district located in the CIZ (Supplementary Table 2). The lower Euclidean distances correspond to the mines of La Buena-La Mala ($d = 0.008$), Las Riscas ($d = 0.010$), Valdeinfierno-San Arturo ($d = 0.023$) and Medianeria ($d = 0.027$) (Fig. 6). However, among the possible sources from Linares-La Carolina only the mine of Medianeria is dominated by secondary copper minerals (see Sáez et al., 2021), which excludes the other mines identified in this area. The exploitation of the Linares mining district is well documented during the El Argar period (Escanilla et al., 2025), but it should be noted that local mining works may have begun earlier during the Chalcolithic (Arboledas Martínez et al., 2015; Hunt Ortiz et al., 2011; Moreno Onorato et al., 2010). Other potential alternative sources for the copper of LC-1, based on Pb isotope signatures of secondary copper minerals, are Quita Pellejo (OMZ/Cordoba province) and Preciosa (SPZ, Gafo Formation, Huelva province), the latter mine being geographically much closer to Leceia.

In the case of the axe-ingot LC-6, no Euclidean neighbours were identified that satisfied both conditions, i.e. Euclidean distance lower than 0.05 and Pb ratios within the analytical uncertainty interval. However, when considering only the Euclidean distance criterium ($d < 0.05$) the Euclidean neighbours identified correspond to a copper ore of A. Tomilloso mine ($d = 0.031$) belonging to the Los Pedroches Batholith (CIZ), in addition to two copper mines located in the OMZ (La Sultana, Huelva province, $d = 0.036$; Cufenos II, Évora, $d = 0.48$) and two mines located in the SPZ (Cova dos Mouros, Alcoutim, $d = 0.038$; Corta Lago/Rio Tinto, Huelva, $d = 0.044$) (Supplementary Table 2 and Fig. 6). Among these sources, the one located closer to Leceia is the mine of Cufenos II (*c.* 100 km), but there are no secure evidences of ancient mining operations at this site. Similarly, Cova dos Mouros shows no traces of mining during prehistoric times (Matos et al., 2003). The hypothesis of the existence of ancient workings is based on the fact that the metallurgical debris recorded in the nearby Chalcolithic settlement of Cerro do Castelo de Santa Justa were attributed to copper from Cova dos Mouros (Gonçalves, 1989). However, there are no analyses of those metallurgical remains that could indicate a possible association between the two sites. Regarding the La Sultana mine, it must be noted that the sample analysed is a copper sulphide, therefore a type of ore not used in those earliest times of copper metallurgy in the Iberian Peninsula. On the contrary, the secondary copper ore from A. Tomilloso is also the closest Euclidean neighbour to the axe-ingot LC-8 (Supplementary Table 2 and Fig. 7). Therefore, on the basis of the available Pb isotope evidence, the copper ore from A. Tomilloso is a possible candidate for the provenance of copper in LC-6 and LC-8, not least because the Los Pedroches Batholith is located very close to the Linares-La Carolina mining district, which can be the source of copper of the LC-1. It is important to note that many of the copper deposits in Sierra Morena, such as the A. Tomilloso mine, have evidence of ancient exploitation,

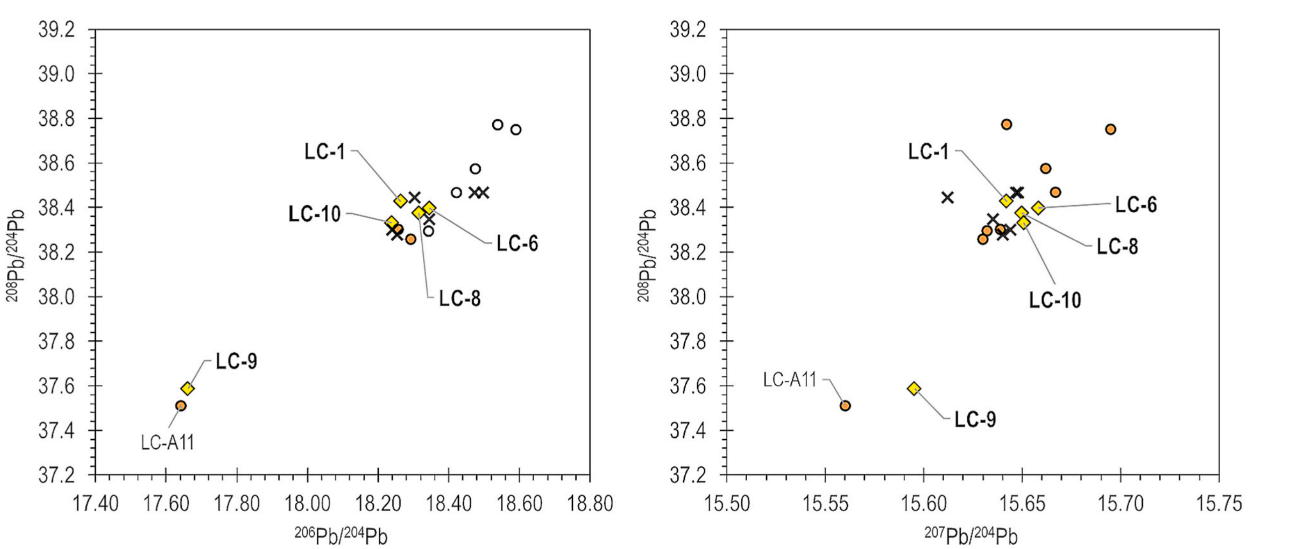

Fig. 5. Pb isotope ratios of axe-ingots from Leceia compared to values of local artefacts and prills previously analysed by Müller and Cardoso, 2008 (white circles correspond to $^{206}Pb/^{204}Pb$ values determined with a higher degree of uncertainty due to the low Pb content of the artefact).

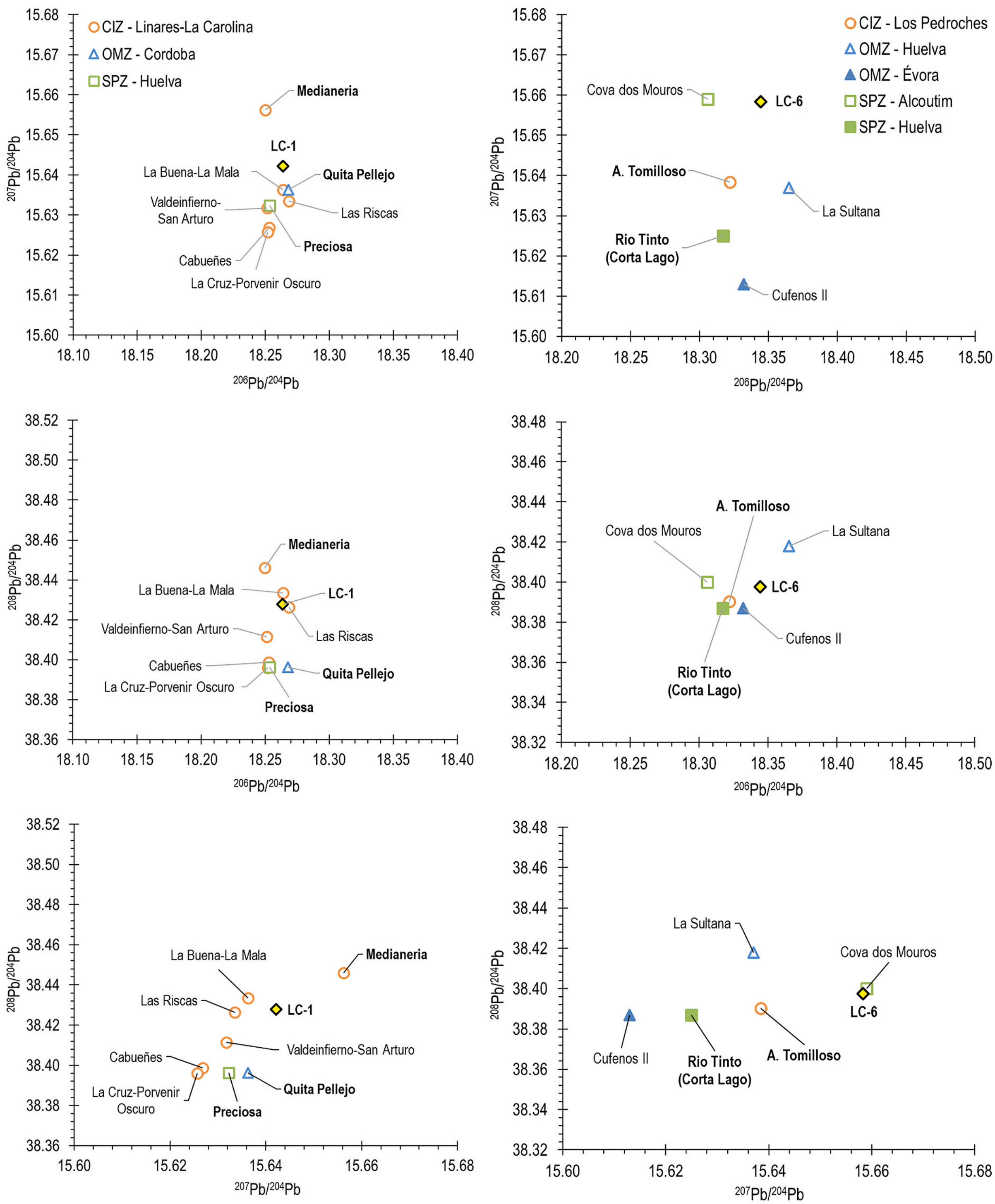

Fig. 6. Pb isotope ratios of axe-ingots LC-1 and LC-6 from Leceia compared to the respective Euclidean neighbours (the most likely sources are shown in bold – see explanation in text; CIZ – Central Iberian Zone; OMZ – Ossa-Morena Zone; SPZ – South Portuguese Zone; Pb isotope ratios of copper ores from database of Tomczyk, 2022).

although the precise chronology of mining operations is unknown (Klein et al., 2009).

All Euclidean neighbours of the axe-ingot LC-10 belong to deposits in the IPB (SPZ), namely those from the regions of Sevilla (Aznalcóllar mine) and Huelva (Rio Tinto, Monte Romero and Cabezadas del Sandino mines) (Supplementary Table 2 and Fig. 7). Apart from Cabezadas del Sandino, all these mines correspond to massive sulphide deposits of the Iberian Pyrite Belt (IPB), which were not exploited by prehistoric communities. Nevertheless, the analysed sample from Rio Tinto mine is a copper carbonate most likely coming from the gossan, whose supergene copper ore deposits may have been exploited by Chalcolithic miners. The same can be said about the copper carbonate from Corta Lago/Rio Tinto that has been identified as a possible source to the LC-6. In fact, the supergene ore deposits of the gossan of Tharsis mine (IPB), located not far from Rio Tinto, were exploited during the Chalcolithic as a source of copper for the settlement of Cabezo Juré (Nocete, 2004; Sáez Ramos et al., 1999). On the other hand, several stone hammers with a central grove were recovered at Monte Romero mine, which could be indicative

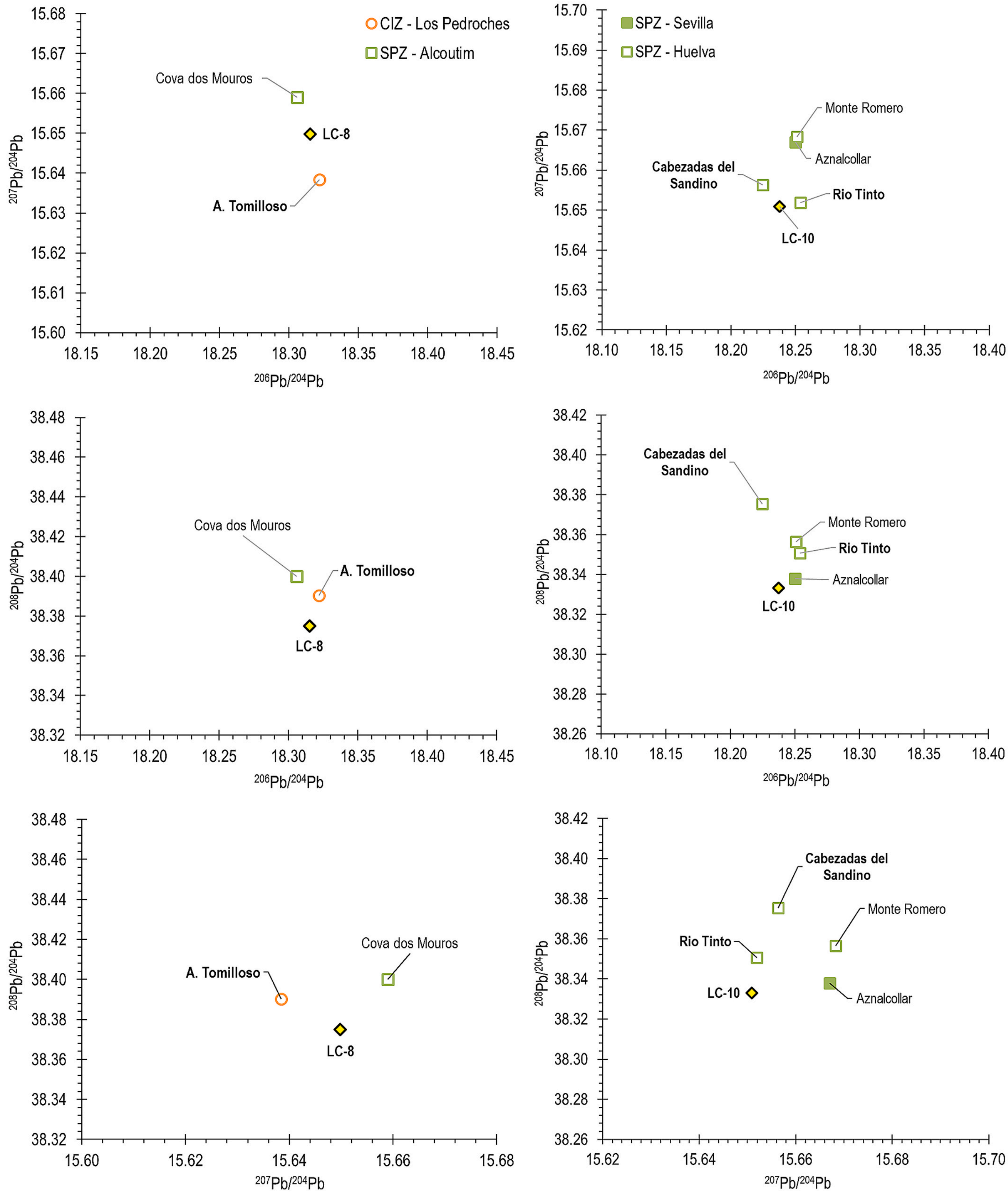

Fig. 7. Pb isotope ratios of axe-ingots LC-8 and LC-10 from Leceia compared to the respective Euclidean neighbours (the most likely sources are shown in bold – see explanation in text; CIZ – Central Iberian Zone; SPZ – South Portuguese Zone; Pb isotope ratios of copper ores from database of Tomczyk, 2022).

of prehistoric works, but local metallurgical activities appear instead to be related with an Iron Age exploitation of Ag-Cu complex ores (Hunt Ortiz, 2003, p. 113). Consequently, despite the limited data on IPB supergene copper deposits, the copper carbonates from Cabezadas del Sandino (Phyllite-Quartzite Group of the IPB, Sáez et al., 2021, table 2) and secondary copper ores from Rio Tinto are likely copper sources for the LC-10.

The axe-ingot LC-9 presents a Pb isotope signature ($^{206}Pb/^{204}Pb = 17.66$) indicative of a mineral deposit that was formed prior to the Variscan orogeny, usually attributable to a Cadomian chronology (Tornos and Chiaradia, 2004). The same can be said about a local artefact (LC-A11 with $^{206}Pb/^{204}Pb = 17.64$) previously analysed by Müller and Cardoso (2008). Mineral deposits exhibiting such low radiogenic composition are exceedingly rare in Western Europe, with the most notable example being the Precambrian massive sulphides of the Armorican massif in northwestern France (Chauris and Marcoux, 1994). Two clusters of low radiogenic populations are known in the Iberian Peninsula, both located in the OMZ, namely the volcanogenic massive sulphide deposits of the Badajoz-Cordoba shear zone (for instance, Puebla de la Reina, Nava-Paredón and Tinoca mines, the latter in the region of Campo Maior, Portalegre) and the mineral deposits of the Aracena Belt (Maria Luisa and Fuenteheridos). All these deposits show low and variable Pb isotope signatures ($17.49 < {}^{206}Pb/^{204}Pb < 17.92$, Tornos and Chiaradia, 2004, table 4; Marcoux et al., 2002, table 1). However, it should be noted that these Pb isotopic data corresponds to sulphide ores that have not been exploited in prehistoric times. During prehistoric times, only the supergene minerals found in these mines would have been exploited, but there are no isotopic data for these secondary deposits. This absence calls once more for the need to expand the Pb isotope database of sources possibly mined during the Prehistory, to maximise the reliability of the attributed provenance. Therefore, in this case it can only be proposed that the Pb isotopic signatures of these items (axe-ingot LC-9 and artefact LC-A11), belonging to contexts dating to the second half of the third millennium BC, point to copper deposits predating the Variscan orogeny in the OMZ, either located in the northeast area (Badajoz-Cordoba shear zone) or the southeast area (Aracena Belt).

Overall, the evaluation of the Pb isotope signatures of the copper axe-ingots from Leceia shows the import of metal from the southwestern and south-central regions of the Iberian Peninsula. The geographically closer mines of Huelva province (Rio Tinto, Cabezadas del Sandino and Preciosa) and the mine of Quita Pellejo (Cordoba province) seem to assume a special importance. Unfortunately, the lack of a chemical characterisation of the large majority of the copper ores analysed from those mines hinders a comparison with the diagnostic inclusions identified in the axe-ingots from Leceia. The evaluation would probably allow a more precise identification of the mining regions exploited to obtain that copper.

The mining districts of Linares-La Carolina and Los Pedroches Batholith cannot be readily discounted despite their considerable distance to the final destination of the ingots (*c.* 450 km). The existence of long-distance trade routes during the Chalcolithic has been previously documented in other Iberian regions. For instance, the copper of an axe-ingot recorded in the Chalcolithic settlement of Três Moinhos (Baleizão) has its provenance from El Milagro mine (Cantabrian Cornice), located approximately 600 km away (Soares et al., 2020). Another copper ingot from the Chalcolithic site of Folha do Ouro 1 (Serpa), with a tabular shape similar to those from Gamonedo (Onis, Asturias) and made of copper from the Encarnación mine (Linares-La Carolina mining district), also shows the existence of such long-distance dissemination of copper (Soares et al., 2022). Similarly, the Pb isotopes and trace elements from materials of the settlement of Laderas del Castillo (Alicante) evidence the exploitation of copper deposits located up to 300 km away (Escanilla et al., 2025). The exploitation pattern of this El Argar region points to the Linares-La Carolina and Los Pedroches mining districts. Moreover, these metal exchange networks seem to be rooted in earlier chronological phases and, thus, may also have supplied the settlement of Leceia. However, some of the copper of the Late Chalcolithic phase of Leceia seems to come from deposits older than the Variscan orogeny in the bordering belts of the OMZ or from the supergene deposits of oxides and carbonates existing in the gossans of the huge IPB massive sulphide deposits. The new data allows a deeper insight into the earlier inferences obtained from Pb isotope analyses performed on 14 samples from Leceia (Müller and Cardoso, 2008, Valério et al., 2023b), which had indicated distant copper deposits located in the Los Pedroches batholith, as well as in the Spanish areas of the OMZ and SPZ.

A comparison with the Pb isotopic fields of copper artefacts and metallurgical debris from other studied settlements in the Portuguesa Estremadura – VNSP and Zambujal – can certainly disclose the use of similar or different sources of metal, thus increasing the knowledge about the trade of copper to this region. VNSP has the largest collection of copper artefacts (*c.* 9 kg) in the Portuguese Estremadura, including several hundred large artefacts (e.g. about sixty flat axe-ingots, most of them fragmented and/or with cut marks). Similarly, metallurgical remains comprise hundreds of copper lumps and prills and also large amounts of technical ceramics, namely flat-bottomed crucibles and tuyeres (Müller and Soares, 2008; Pereira, 2017; Pereira et al., 2012, 2013a). This archaeometallurgical set is dominated by remains of secondary metallurgy, which lead some authors to believe that the few slags locally recovered could result from refining operations of raw copper to produce artefacts (Müller and Cardoso, 2008; Gauβ, 2016). On the other hand, the rich material recovered at VNSP would indicate that this settlement controlled an extensive area and has been, for sure, a node of a network of long-distance trade. Pb isotope ratios were carried out on 15 pieces of once molten copper (prills and scrap metal), as well on three slag fragments, two iron hydroxides and four limestone samples with traces of malachite (Müller and Soares, 2008, table 2). Despite the existence of a few values with a higher uncertainty, overall the Pb isotopic field of VNSP is very similar to the one of Leceia, although the latter show a slightly larger dispersion (Fig. 8). Moreover, the Leceia axe-ingots analysed in the present study fit the high-density area of the Pb isotopic field of VNSP, and there is a very good match between these Leceia exemplars and some VNSP items. For instance, LC-6 versus FM-VNSP24 and FM-VNSP26; LC-8 versus FM-VNSP24; and LC-10 versus FM-VNSP22 (see Supplementary Table 3). The signature of the LC-10 also matches that one of a Leceia prill (FM-L3). Consequently, it appears that these two Chalcolithic settlements may have shared several sources of copper, likely obtained the raw metal through the same trade routes, and may even have engaged in trade of some artefacts among themselves.

The settlement of Zambujal also showed a large and varied collection of copper artefacts and metallurgical debris (*c.* 900 artefacts totalling about 3-4 kg, Hanning et al., 2010, p. 287). The collection was also subjected to a sound research concerning, not only elemental compositions and microstructural features of artefacts and metallurgical remains, but also a provenance study using Pb isotopes and trace elements, which pointed to OMZ mineral deposits, namely in the Portuguese Alto Alentejo and bordering Spanish Extremadura (Gauβ, 2016). Though, these results will need to be revised considering the novel methodologies and new data on copper sources published in the meantime. The study also revealed two major types of technical ceramics associated to metallurgy: thick-walled flat-bottomed crucibles with varying shapes and some with small feet; and thin-walled crucibles with heavily vitrified rims and traces of copper. The first ones are more frequent and have been interpreted as remelting crucibles or moulds for casting a blank from which an artefact can be forged. The second ones are very rare and were only recorded in an early Bell Beaker context that preserved the highest concentration of metallurgical debris. Following Müller et al. (2007, p. 20), "it is difficult to directly associate the heavily vitrified crucibles with smelting practices since there are no clear slag remains adhering to them". Consequently, one can say that smelting operations were rare or non-existent in the Chalcolithic settlements of Portuguese

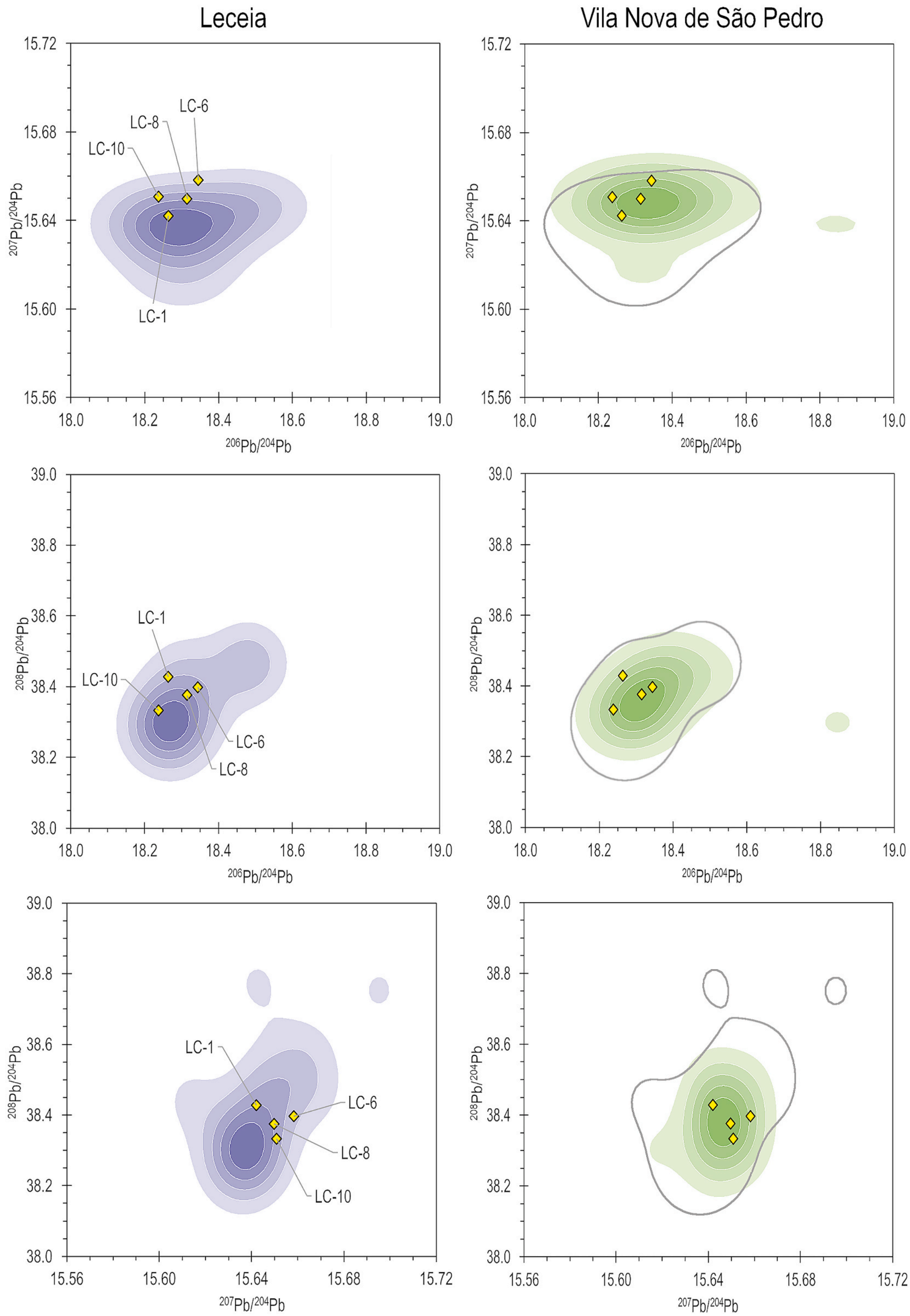

Fig. 8. Pb isotope ratios of axe-ingots from Leceia compared to the Pb isotopic field of the Chalcolithic settlement of Vila Nova de São Pedro in the Portuguese Estremadura (Pb isotopic fields of Leceia and Vila Nova de São Pedro correspond to the Kernel Density Estimation based on samples previously analysed by Müller and Cardoso (2008) and Müller and Soares (2008), respectively).

Estremadura, not least because the nearest copper ore sources were at least several dozen kilometres away. Regarding the Pb isotope ratios, Zambujal presents a larger Pb isotopic field than the other two settlements (Fig. 9). Despite the close correspondence with the signatures of Leceia axe-ingots, there are specimens at Zambujal that suggest the use of additional copper supply sources. The most obvious examples are some items with highly radiogenic Pb (prill Z204: $^{206}Pb/^{204}Pb = 20.26$; and Palmela point Z559: $^{206}Pb/^{204}Pb = 91.76$) implying the use of the aforementioned copper deposits from the Cantabrian Cordillera. However, it should be borne in mind that the number of isotopic analyses performed on artefacts from VNSP is much smaller than that performed on the metal artefacts from Zambujal. Regarding Leceia, the analyses

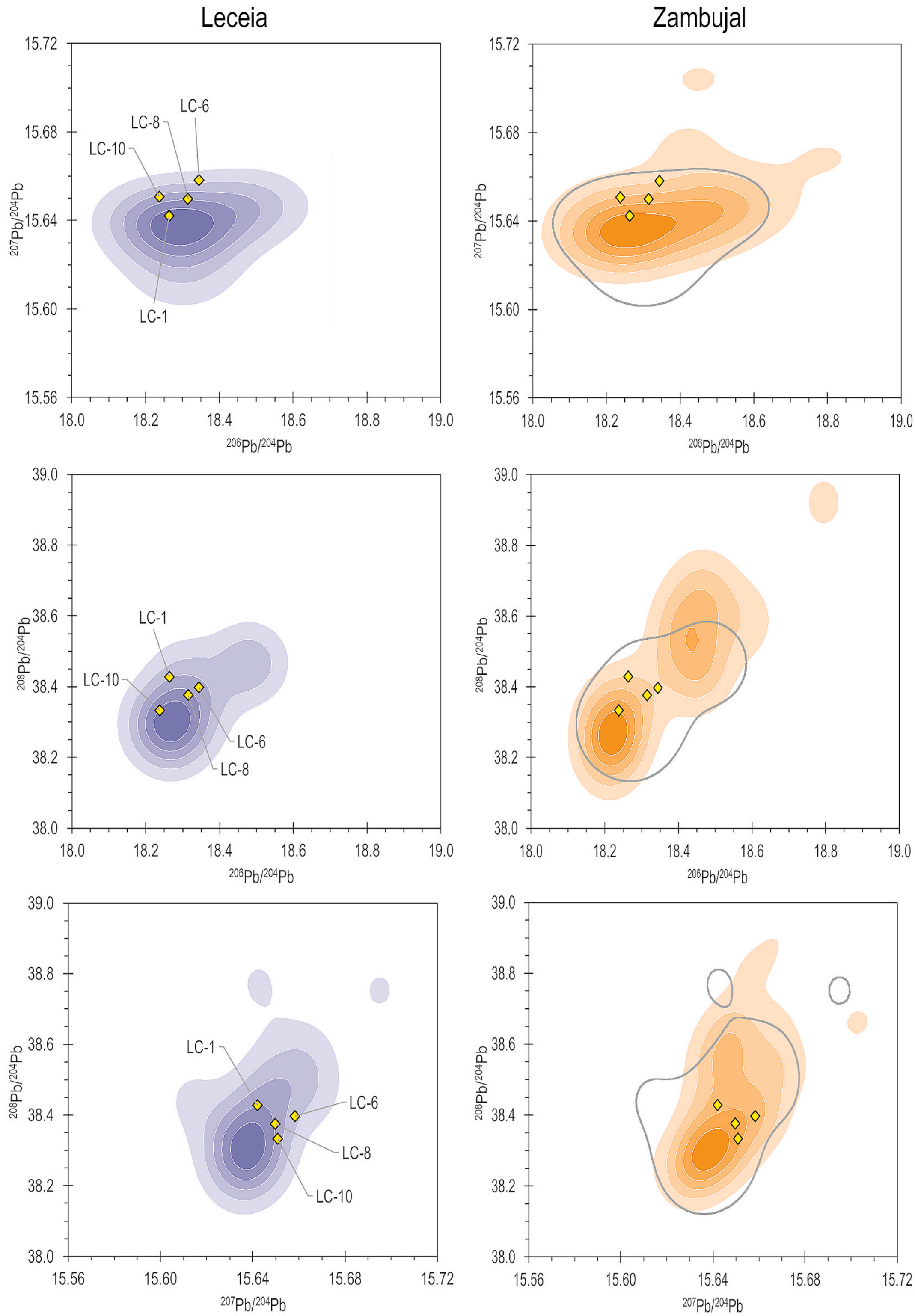

Fig. 9. Pb isotope ratios of axe-ingots from Leceia compared to the Pb isotopic field of the Chalcolithic settlement of Zambujal in the Portuguese Estremadura (Pb isotopic fields of Leceia and Zambujal correspond to the Kernel Density Estimation based on samples previously analysed by Müller and Cardoso (2008) and Gauβ (2016), respectively).

carried out so far are only a first approach to identifying the copper sources of the axe-ingots and other copper materials found at this archaeological site.

Finally, the AMALIA algorithm (Rodríguez et al., 2023) was used to determine possible matches between Pb isotope signatures of the axe-ingots from Leceia and those of Chalcolithic artefacts found in archaeological contexts of the Iberian Peninsula, in order to distinguish possible trade routes of copper. The exercise revealed that the signatures of Leceia axe-ingots match Pb isotope ratios of artefacts, not only from VNSP, but also from a few archaeological sites in Spain (Supplementary table 3). These are the cases of an awl from the Chalcolithic settlement of San Blás (Badajoz, Hunt Ortiz et al., 2012), a Palmela point and a rivet of a halberd from the Beaker tomb 1 of Humanejos (Madrid, Garrido-Pena et al., 2022), a Bronze Age awl from Castillejo del Bonete (Ciudad Real, Montero-Ruiz et al., 2014) and a flat axe recovered in a Bronze Age tomb at Cortijo del Tardón (Málaga, Rodríguez Vinceiro et al., 2018). However, little additional information can be gleaned from these matches, since the isotopic signatures of the artefacts from Humanejos and Cortijo de Tardón do not correspond to any of the isotopic signatures in the database of ores used by the AMALIA algorithm, while the copper from the San Blás awl may originate from mineralizations in the OMZ or Los Pedroches, without being possible to determine a more precise source. Only the Pb isotope signature of the Castillejo del Bonete awl has a precise match with an ore from the Polígono copper mine (Baños de la Encina, Linares district), but the awl context already belongs to the Bronze Age.

6. Conclusions

The analytical study of the axe-ingot fragments from Leceia identified the presence of copper with variable amounts of arsenic, a feature that is comparable, as expected, to the composition of prills, lumps and simple tools and weapons recovered in this fortified settlement. The microstructures of the axe-ingots suggest the utilisation of secondary copper ores with variable patterns of metallic inclusions, evidencing the exploitation of diverse ore deposits. Moreover, the conditions of the secondary metallurgical processes (melting and casting) exhibited considerable variability, which at times culminated in the formation of significant amounts of cuprous oxides. The Pb isotope signatures of axe-ingots are comparable with those of local prills and artefacts, suggesting that local secondary metallurgical activities included the manufacturing of artefacts with metal sampled from the examples under study.

The copper mines exploited to obtain the metal for the Leceia axe-ingots belong to the southwestern and south-central Iberian Peninsula. The only exemplar from the Early Chalcolithic phase (*c.* 2800 – 2600/2500 BC) has a possible source in secondary minerals from the Linares-La Carolina mining district. This area is located in the eastern Sierra Morena where, according some authors, the beginning of copper metallurgy by the first metallurgical communities seems to coincide with the strategic control of mineral resources and the increase in social complexity (Sáez et al., 2021). However, the Quinta Pellejo mine located in Cordoba province and the Preciosa mine situated in Huelva province are perhaps better candidates for the source of this copper, since they are closer to the Portuguese Estremadura, especially the ore deposits of the Preciosa mine. The copper of the axe-ingots from the Middle/Late Chalcolithic phase of Leceia seem to have a provenance from other deposits: LC-6 and LC-10 are probably originated in the supergene copper deposits of Rio Tinto district, but Cabezadas del Sandino mine could also be a good candidate for the copper of LC-10. It should be noted that all these mines are also located in the Huelva province. The copper in the LC-8 would have its origin in the copper ore deposit of A. Tomilloso mine, located in the Los Pedroches Batholith, further away from the Portuguese Estremadura. Finally, the provenance of LC-9 should be sought in a low-radiogenic ore deposit from the Badajoz-Cordoba shear zone or the Aracena Belt, but a more precise provenance cannot be determined at this time.

Overall, despite the limited data available so far regarding the southern Portuguese territory, there appears to be a low level of exploitation of copper mines in this territory during the Chalcolithic. This hypothesis is also supported by the highly radiogenic Pb content of many of the local ores (Gauß, 2016), which has no correspondence with the Pb isotopic signature of the large majority of Chalcolithic artefacts found in the Portuguese Estremadura or southern Portugal.

Other Chalcolithic settlements in the Portuguese Estremadura such as VNSP and Zambujal show Pb isotopic fields somewhat similar to the one of Leceia, suggesting that all these coeval settlements most likely shared the same trade network and exchanged metals with each other. Due the higher number of metallic artefacts and other goods recorded at VNSP compared with the other two fortified settlements (Leceia and Zambujal), the former would have been a node of this trade network. However, there must have been additional suppliers of copper, particularly for the settlement of Zambujal, but this fact needs to be better verified, not only by expanding the number of Pb isotope analyses, particularly of local ingots, but also considering the innovative methodological approaches and new data on Pb isotope ratios of copper sources. Finally, the long-distance trade of metals, that has now been attested once again, highlights the strong contacts between different areas of the south-central Iberian Peninsula and the Portuguese Estremadura during the third millennium BC.

CRediT authorship contribution statement

Pedro Valério: Writing – review & editing, Writing – original draft, Validation, Resources, Funding acquisition, Formal analysis. **João Luís Cardoso:** Writing – review & editing, Resources. **Luís C. Alves:** Writing – review & editing, Resources, Funding acquisition, Formal analysis. **António M. Monge Soares:** Writing – review & editing, Validation, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jasrep.2026.105960.

Data availability

Data will be made available on request.

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