



Diverse strategies for copper production in Chalcolithic Iberia

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ABSTRACT

Our understanding of early copper metallurgy in the Iberian Peninsula is mostly based on analysis from well-studied regions in the Southeast and Southwest. This paper focuses on two recently recovered Chalcolithic metallurgical assemblages outside these traditional research foci: two slagged crucibles from Lugar Viejo III (Zaragoza) and two large slag cakes from Cueva del Cañaveralejo (Córdoba). Analysis of the compositions and microstructures of the artifacts using optical microscopy and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) suggests they are related to primary copper production, namely smelting in crucible-furnaces under relatively oxidizing conditions, as is standard for this period. The slag layers on crucibles from Lugar Viejo indicate the production of copper with minor amounts of arsenic, also typical for this period. Of special note is the use of organic temper in the crucibles from Lugar Viejo, a practice found at the nearby site of Moncín but rare at other sites in Iberia. However, the slags from Cueva del Cañaveralejo are atypical in their large size (approx. 125 g each), fayalitic composition, unusual efficiency as demonstrated by a low copper content, and lack of arsenic; furthermore, the high sulfur content raises the possibility of the use of sulfidic ores. Results from both sites are compared against published data from well-known sites such as Los Millares, Las Pilas, Almizaraque, and Bauma del Serrat del Pont. The new data from Lugar Viejo and Cueva del Cañaveralejo reinforce the interpretation of metallurgy in the Iberian Peninsula as a low-skilled, conservative technology but also indicate the need for more research into regional variations. (See Supplementary Data 1 for a summary in Spanish).

1. Introduction and background

1.1. Objectives of work and previous research

The Chalcolithic Period, also known as the Copper Age or Eneolithic, c. 3200 – 2250 BCE (Chapman 2008), is of particular interest to scholars because it is the period when copper metallurgy spreads across the Iberian Peninsula, a region notable for its rich metalliferous deposits. Research on early metallurgy in Iberia began in the late 19th century, with the work of the Siret brothers (Las Primeras Edades del Metal 1890), and has continued throughout the 20th century and into the

present, including comprehensive initiatives such as CSIC's *Proyecto Arqueometalurgia de la Península Ibérica* (PAPI) (Rovira Llorens et al. 1997; Rovira Llorens and Montero Ruiz 2018). However, there has been a tendency for research into primary metallurgy (i.e. analysis of copper smelting, not analysis of the artifacts themselves) to focus primarily on two areas: the Southwest and the Southeast (Fig. 1). In the Southwest (i.e. Southern Portugal and Southwestern Spain), scholarship has centered on the western Iberian Pyrite Belt and adjacent regions, including sites such as Zambujal (Müller et al. 2007), Vila Nova de São Pedro (Müller and Soares 2008), Cabezo Jure (Sáez et al. 2003), Valencina de la Concepción (Nocete et al. 2008), and San Blas (Hunt Ortiz et al. 2009).

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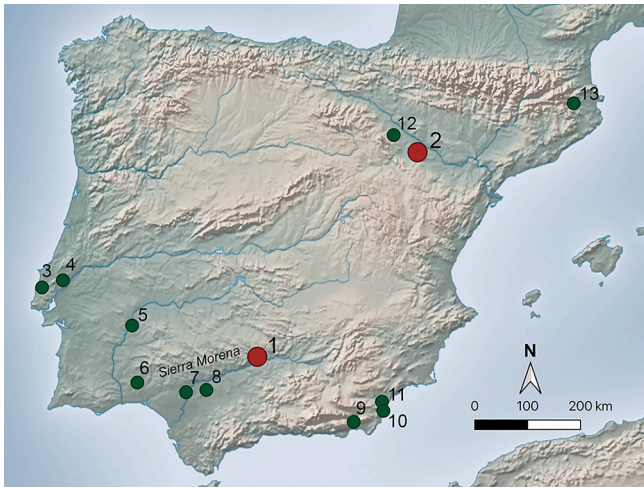


Fig. 1. Map of Chalcolithic/Early Bronze Age sites with metallurgical remains mentioned in the text. 1 = Cueva del Cañaveralejo, 2 = Lugar Viejo III, 3 = Zambujal, 4 = Vila Nova de São Pedro, 5 = San Blas, 6 = Cabezo Juré, 7 = Valencina de la Concepción, 8 = Dolores Quintanilla, 9 = Los Millares, 10 = Las Pilas, 11 = Almizaraque, 12 = Moncín, 13 = Bauma del Serrat del Pont. Base map: Made with Natural Earth.

In Southeastern Spain, extensively studied sites include Almizaraque (Müller et al. 2004; Murillo-Barroso et al. 2020), Los Millares (Hook et al. 1991), and Las Pilas (Murillo-Barroso et al. 2017), all in the province of Almería. Despite the ready abundance of ores across nearly all of the peninsula (Bartelheim and Montero-Ruiz 2009), relatively little attention has been given to Chalcolithic metallurgy in other regions [the few exceptions are around Madrid in central Spain (Rovira and Montero 2003; Rovira et al. 2011) and in Catalonia, including Bauma del Serrat del Pont (Alcalde et al. 1998; Soriano 2013; Montes-Landa et al. 2021)]. Perhaps the most notable exclusion is the central Sierra Morena, an area rich in metallic ores (IGME 1964; Domergue 1987; Hunt Ortiz 2003, 132–137) and an important source of metals in the Roman period (Domergue 1987, 86).

Together, this previous research has established an interpretation of Chalcolithic metallurgy in Iberia as a small-scale, low-skill technology, with little change over a millennium, with the conservatism of the technology resulting from an abundance of natural resources, a low level of social hierarchy, and the low social value of metals (Rovira 2002a, 5; Montero-Ruiz et al. 2021, 204). Unalloyed copper was produced from oxidic copper ores, such as malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) (Valério et al. 2020, 326); arsenical copper was produced where copper ores naturally contained arsenic (Rovira and Montero-Ruiz 2013, 234). Occasional finds of sulfides in slag are attributed to the contamination of oxidic ores with minor amounts of sulfidic ones (Müller et al. 2006, 44), not the intentional use of sulfidic ores as seen during the Chalcolithic in other parts of Eurasia, including neighboring France (Bourgarit 2007, 4). True furnaces were not used until the Iron Age; instead smelting was carried out in ceramic crucible-furnaces (*vasijas-horno*), which were wide, shallow, and round or oval in shape, with an average diameter of 15–30 cm (Rovira 2002b, 9; Rovira and Montero-Ruiz 2013, 233, Fig. 4; Rovira Llorens and Montero Ruiz 2018, 238). The limited quantity and small size of smelting slags found at many sites has been interpreted alternately as evidence that Chalcolithic copper smelting was a non-slugging process due to the use of high-quality oxidic ores (Rovira and Montero-Ruiz 2013, 232; Rovira and Renzi 2017, 756) and/or the consequence of the intentional crushing of immature slag in order to retrieve metal prills (Bourgarit 2007, 5).

However, because this interpretation has been mostly based on analysis from a few regions, it may have led to an overly homogeneous picture. Analysis of two recently recovered Chalcolithic metallurgical assemblages outside the traditional research foci identified how these

objects fit in the production sequence of copper and the production parameters employed. While the artifacts from Lugar Viejo III (Zaragoza) are standard for the period, those from Cueva del Cañaveralejo (Córdoba) are atypical.

1.2. Lugar Viejo III, Zaragoza, Aragón

Lugar Viejo III (Fig. 1) is one of a cluster of archaeological sites named Lugar Viejo (“old place”) located above the town of María de Huerva on the Huerva river, approximately 20 km away from the confluence with the Ebro at Zaragoza. The recent prehistory (i.e. from the Neolithic to the Bronze Age) of the middle Ebro basin is not yet well understood, with few sites known or investigated (Pérez Lambán et al. 2010, 287; Pérez-Lambán 2013; Aguilera Aragón 2017). The notable exception is Moncín (Zaragoza), a Chalcolithic to Bronze Age site, where numerous metal objects and metallurgical remains, albeit mostly dated to the Bronze Age, were found (Harrison et al. 1994). This area appears to be some distance from significant copper deposits, with mining activity at the few minor copper deposits nearby dated to the Roman period (IGME 1964; Domergue 1987).

The sites at Lugar Viejo were surveyed during a study of the Huerva river valley conducted by Fernando Pérez Lambán, Javier Fanlo Loras, and Jesús V. Picazo Millán from 2007 to 2009 (Pérez Lambán et al. 2010). Several crucible fragments with copper slag residues were dated to the Chalcolithic period on the basis of their association with Bell Beaker (*campaniforme*) ceramic sherds, and two fragments were analyzed for the present work. Also analyzed but not included in this article were a small green cupriferous rock and a fragment of a copper-lead “bar ingot,” both of uncertain date. There is no absolute dating for Lugar Viejo III, but the Bell Beaker phenomenon in Aragón is thought to date from approximately 2650 BCE – 2100 BCE (Harrison 1988).

1.3. Cueva del Cañaveralejo, Córdoba, Andalucía

Cueva del Cañaveralejo, in the vicinity of Adamuz, Córdoba (Fig. 1), is a karstic cave, located next to the Cañaveralejo arroyo, a tributary of the Guadalquivir river (Recio Espejo and López Vallejos 2007). The cave is located in the foothills of the central Sierra Morena, a mineral-rich area including the celebrated Cerro Muriano copper mine, the source of *aes marianum* mentioned by Pliny (Domergue 1987, 116). Nonetheless, only a few contemporary sites with metallurgical remains, such as El Llanete de los Moros (Martín de la Cruz, 1988; Rovira Llorens et al. 1997; Rovira and Montero 2000; Hunt Ortiz 2003), have been found in Córdoba province.

José C. Martín de la Cruz directed two excavation campaigns at Cueva del Cañaveralejo in 2006 and 2007 (Jabalquinto Expósito and Martín de la Cruz 2019). The cave showed evidence of use from the sixth millennium BCE to the second millennium BCE, with some gaps in occupation (Jabalquinto Expósito and Martín de la Cruz 2019, 55–57). Two slag cakes (*tortas de reducción*), identified as copper-related because of the green mineralization covering the surfaces, were found in Phase II of Corte A, dated to the third quarter of the third millennium BCE by accelerator mass spectroscopy (AMS) analysis of stratified bone (Table 1; Jabalquinto Expósito 2022).

A few ceramic sherds and stone fragments also had visible copper-bearing residues, but these were determined to be post-depositional accretions, caused by contact with the slag cakes. Other artifacts from

Table 1

Dating by AMS analysis of the relevant stratigraphic layer from Cueva del Cañaveralejo (Jabalquinto Expósito 2022, 153).

Code no.	BP	Cal 1 σ BC	Cal 2 σ BC
CNA. 3209.2.1	3938 \pm 35 BP	2487–2430 (52.6%)	2565–2531 (9.2%)
Cañaveralejo 4		2425–2401 (19.4%)	2528–2525 (0.3%)
		2381–2348 (27.8%)	2496–2334 (86.4%)

this phase included charcoal, lithics, and animal bones, some showing evidence of heating (Jabalquinto Expósito and Martín de la Cruz 2019). No other copper objects were found, with the exception of a small copper nodule dated to the earlier Phase III, the function of which remains unknown.

2. Methodology

Small samples of the slag cakes and crucible fragments were embedded in blocks using two-part epoxy resin (MetPrep Epo Set Resin); the blocks were ground and polished down to 1 μm using either diamond paste or alumina suspension. The samples were then examined with reflected light microscopy, under both plane- and cross-polarized light, using a Leica DM4500 P LED microscope, with features of interest recorded with an attached Leica DFC290 HD camera.

Carbon-coated cross-sections were examined using a Carl Zeiss EVO-25 scanning electron microscope with an Oxford Instruments X-Max 80 energy dispersive spectrometer (SEM-EDS). The instrument was operated with an accelerating voltage of 20 kV, a working distance of 8.5 mm, and an acquisition time required to achieve 750,000 X-ray counts.

Bulk compositions of the slag and ceramics are the average of analyses of five areas measured at 100x magnification (giving an effective area of 0.9 mm^2). Oxygen was calculated by stoichiometry, with iron assumed to be present as FeO. The measured areas were chosen to avoid large inclusions and corrosion but to include as many representative features as possible. Analysis of basalt and copper alloy certified reference materials (CRMs) are provided in Supplementary Data 4.

Two samples of slag CC4 and one sample of slag CC5 from Cueva del Cañaveralejo were removed by drilling and then sent to the SGIker facilities at the Universidad del País Vasco for lead isotope analysis. The samples were analyzed using a ThermoNEPTUNE multicollector ICP-MS. Sample preparation methods and measurement protocols are detailed in Rodríguez et al. 2020.

Thin sections of the crucibles from Lugar Viejo were prepared for ceramic petrography, using standard procedures as described in Quinn (2013), then examined under plane- and cross-polarized light using a Leica DM EP microscope, with photomicrographs taken using a Q-Imaging Go-3 camera.

3. Results and Discussion

3.1. Lugar Viejo: Results

The two crucible sherds from Lugar Viejo III are both body sherds, with unclear orientations (Fig. 2, Fig. S2.1a-b, Fig. S2.5a-c). Because of their small size, it is not possible to determine the overall shape or size of the vessel(s), if the sherds originally belonged to the same vessel, or if they come from purposely made crucibles or repurposed domestic vessels. The sherds are 1.2 – 1.8 cm thick, with the slag layers ranging in

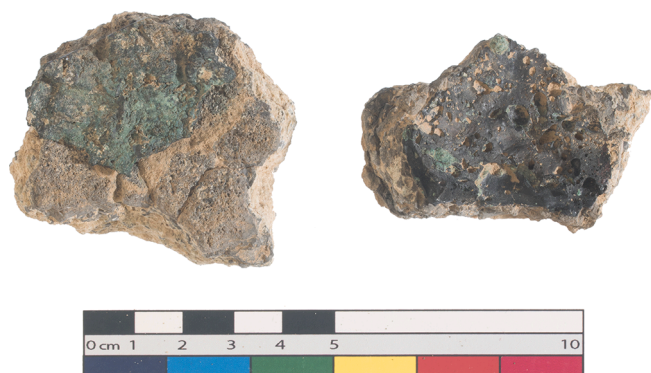


Fig. 2. Crucible sherds from Lugar Viejo III, LV1 (left) and LV2 (right).

thickness from 1.5 to 6.9 mm (Fig. 3). Visible green mineralization on the slag layers indicates the presence of copper.

The bulk composition of the slag layers consists, on average, of 35% silica, 25% iron oxide, 16% copper oxide, and 4% alumina, with 2% arsenic and lead oxides (Table 2). For both artifacts, the microstructures of the slag layers are heterogeneous, consisting of anhedral magnetite crystals sparsely and unevenly distributed through an iron silicate matrix (Fig. 4). Other features in the slag include magnetite dendrites and acicular crystals of delafossite (CuFeO_2) (Fig. S2.7a-b). The slag preserves traces of the original charge, including relict quartz, a fragment of a copper silicate mineral, and magnetite agglomerates (Fig. 5, Fig. S2.3a-b), the last commonly found in Chalcolithic slags resulting from the smelting of iron-rich copper ores (Müller and Soares 2008, 100). A lustrous white prill, identified as chalcocite (Cu_2S) is present in one of the samples, but otherwise, the slags have few sulfides and sulfates.

As might be expected from the greater than 10% copper oxide content in the bulk composition, metal prills are abundant in both crucibles. The prills, averaging 5 – 20 μm in diameter, but ranging up to 138 μm , were determined to be mostly copper with minor (less than 5%) iron and 1% arsenic (Table 3).

Both sherds show increasing amounts of bloating pores towards the interior slagged surface and a transition from dark gray in the interior to light gray or brown at the exterior edge, suggesting heating from within/above (Fig. 3). The crucibles appear to be made of the same fine-grained non-calcareous fabric, with alumina below 20% and unusually high magnesia (5 – 6%) (Table 4). Small amounts of sulfur most likely derive from post-depositional weathering.

Based on visual examination of the thin sections, the ceramic paste was estimated to contain 10 – 20 vol% inclusions, almost entirely small (less than 0.05 mm), sub-angular quartz. About 20 to 30 vol% of the fabric consists of elongate, branching voids, parallel to the ceramic body, deriving from the use of organic temper, which for the most part had burned out during firing (Fig. 6, Fig. S2.4a-b).

3.2. Lugar Viejo: Discussion

The crucibles appear to be the result of smelting copper, not other metallurgical operations such as refining or melting, because of the presence of relict ores and the elevated iron content (Farci et al. 2017, 343). Furthermore, although it is likely that some of the silica in the slag layer derives from the thermally altered ceramic, the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio is much higher in the slag than the ceramic (8.5 vs 3.0), indicating a siliceous component to the metallurgical charge – most likely, quartz gangue. The low sulfur content indicates the use of predominantly oxidic, not sulfidic ores; and the elevated copper content, averaging 16%



Fig. 3. Polished cross-section of crucible sherd (LV2) from Lugar Viejo III. Note the thin layer of slag on the interior surface, visible at top, and the transition of the ceramic body from dark gray to light gray/brown on the exterior edge.

Table 2

Average bulk composition of the slag layers on crucibles from Lugar Viejo and the slag cakes from Cueva del Cañaveralejo, obtained by SEM-EDS, in weight percent by oxide with results normalized to 100% and with oxygen calculated by stoichiometry. Original measured totals are also given. nd = not detected.

Site	Artifact	Feature	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	FeO	CuO	As ₂ O ₃	SnO ₂	PbO	Meas. Total
Lugar Viejo III	LV1 (n = 5)	bulk	2.8	4.0	35.8	1.4	0.8	0.3	1.2	11.8	25.0	13.3	2.5	nd	0.9	92.2
	LV2 (n = 5)	bulk	1.6	4.2	33.8	2.6	0.2	0.5	1.2	5.2	25.8	19.2	2.3	nd	3.3	85.8
	LV1 (n = 9)	matrix	1.1	4.7	44.6	1.6	nd	nd	1.8	20.3	12.2	6.0	5.1	nd	2.4	97.8
	LV2 (n = 5)	matrix	2.0	4.1	38.3	2.3	nd	nd	1.5	6.6	14.4	23.4	3.3	nd	4.1	89.6
Cueva del Caña.	CC4 (n = 15)	bulk	nd	0.9	23.7	1.7	0.2	0.2	0.2	0.5	66.6	5.8	nd	nd	nd	82.8
	CC5 (n = 10)	bulk	nd	0.6	24.3	1.6	0.1	0.1	0.2	0.6	69.0	3.4	nd	nd	nd	89.8
	CC4 (n = 8)	matrix	0.3	0.9	34.2	3.6	nd	nd	0.5	1.2	57.7	1.5	nd	nd	nd	84.7
	CC5 (n = 10)	matrix	0.4	0.3	32.6	1.5	nd	nd	0.3	0.3	63.9	0.7	nd	nd	nd	92.6

Extended results for these and the following analyses are provided in [Supplementary Data 3](#).

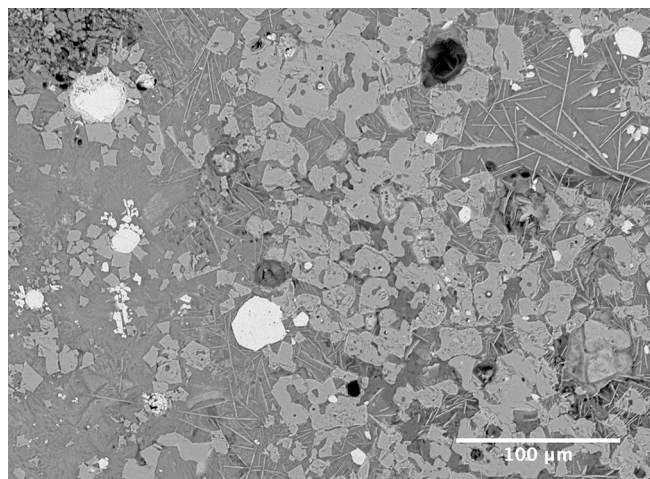


Fig. 4. SEM-BSE image of LV2, showing typical microstructure of slag from Lugar Viejo III, namely magnetite crystals (light gray) and pyroxene crystals (dark gray, here faintly visible) distributed throughout an iron silicate matrix (medium gray), with some delafossite crystals (acicular light gray) and some circular and irregularly shaped copper prills (white).

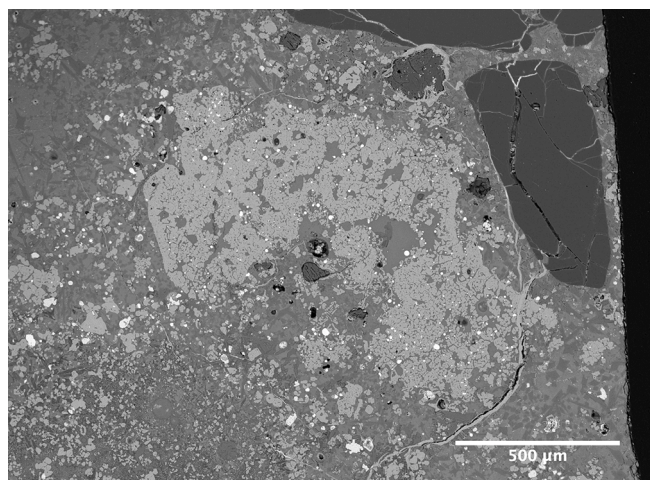


Fig. 5. SEM-BSE image of slag LV1, showing a magnetite agglomerate at center and a relict quartz grain at right.

CuO, indicates that copper metal was the intended product (as opposed to tin or gold). The copper content also highlights the inefficiency that is typical of early copper smelting in Iberia.

The slag composition is comparable to that found at some Chalcolithic sites in the Iberian Peninsula (Fig. 7). The slag microstructure, dominated by magnetite and delafossite but without fayalite, indicates smelting under only moderately reducing conditions and is in keeping with the “immature” slag typical of the period (cf. Almizaraque: Müller et al. 2004, 40; Vila Nova de São Pedro: Müller and Soares 2008, 100; Cabezo Juré: Sáez et al. 2003, 630; and Las Pilas: Murillo-Barroso et al. 2017, 1562).

The composition of the metal prills suggests that copper with minor arsenic content would have been produced, likely from the use of a polymetallic ore rather than the intentional addition of arsenic. Again, this putative end product fits into the model of Chalcolithic and Early Bronze Age copper metallurgy in Iberia, before the widespread adoption of tin bronzes (Rovira and Montero-Ruiz 2013, 234–5). At the moment, the ore sources used at Lugar Viejo III cannot be identified.

The crucibles themselves are also in keeping with Chalcolithic Iberian practices, appearing to be the typical *vasijas-horno*, which were heated from above, with minerals and charcoal held within (Murillo-Barroso et al. 2017, 1550). This method of heating was the common practice for Chalcolithic Iberia, found at multiple other Chalcolithic sites (Rovira and Ambert 2002, 97). Although the incompleteness of the sherds does not allow determination of the overall size or shape of the crucibles, the wall thickness of the sherds, at 1.2 – 1.8 cm, is similar to other sites, such as Los Millares (1.0 – 1.5 cm thick; Hook et al. 1991, 67) and Las Pilas (1 – 2 cm thick; Murillo-Barroso et al. 2017, 1549–50).

The bulk composition of the ceramics, specifically the relative proportions of silica, alumina, and alkalis plus iron oxide, would not meet modern standards of refractoriness (cf. Freestone 1989, 156) but was evidently sufficient. The alumina content of the crucibles from Lugar Viejo is around 19%; this parallels other sites, where the alumina content of the crucibles is below 25%, including Los Millares (Hook et al. 1991, 68), Las Pilas (Murillo-Barroso et al. 2017, 1550), and Bauma del Serrat del Pont (Montes-Landa et al. 2021, 14).

An interesting feature of the crucibles from Lugar Viejo is the use of plant temper. The nearby site of Moncín also had crucibles, albeit dated to the Bronze Age, tempered with organic matter, namely chopped straw or grass (Harrison et al. 1994, 279). Notably, domestic pottery from Moncín was not tempered with plant material, indicating a separation of production processes (Harrison et al. 1994, 284). This differs from other sites, for example, Las Pilas, where the same clay paste was used for both crucibles and regular pottery (del Pino Curbelo et al., 2019, 10), but parallels some sites, like Valencina de la Concepción, which show separate production streams (Inácio et al. 2017, 78).

Table 3

Average composition of copper prills in slag layers on crucibles from Lugar Viejo III and in slag cakes from Cueva del Cañaveralejo obtained by SEM-EDS, in weight percent by element with results normalized to 100%. Original measured totals are also given. nd = not detected.

Site	Artifact	O	Si	Ca	S	Fe	Cu	As	Sn	Meas. Total
Lugar Viejo III	LV1 (n = 13)	1.1	0.2	0.2	nd	3.3	94.1	1.1	nd	95.6
Lugar Viejo III	LV2 (n = 12)	0.7	0.2	nd	nd	1.6	96.4	1.1	nd	86.9
Cueva del Cañaveralejo	CC4 (n = 13)	0.9	0.3	nd	0.1	4.2	94.1	nd	0.3	98.7
Cueva del Cañaveralejo	CC5 (n = 15)	1.2	0.1	nd	0.2	5.1	92.6	nd	0.9	93.0

Table 4

Average composition of ceramic fabric of crucibles from Lugar Viejo III, obtained by SEM-EDS, in weight percent with results normalized to 100% and with oxygen calculated by stoichiometry. Original measured totals are also given.

Site	Artifact	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	Cl	K ₂ O	CaO	TiO ₂	FeO	Meas. Total
Lugar Viejo	LV1	0.7	5.4	18.9	57.7	1.1	nd	4.8	4.2	0.9	6.3	76.4
Lugar Viejo	LV2	1.0	5.7	19.0	57.0	1.6	0.1	4.7	3.6	0.9	6.4	67.5

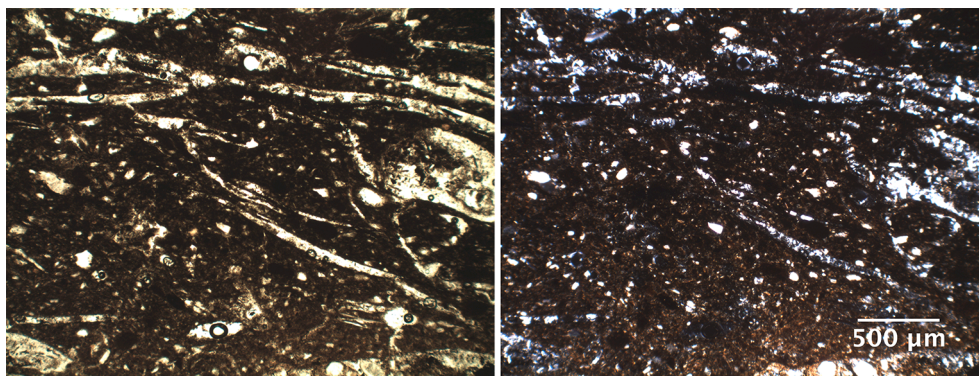


Fig. 6. Thin section of ceramic crucible LV2, under plane- and cross-polarized light. The thin horizontal voids derive from the use of organic temper.

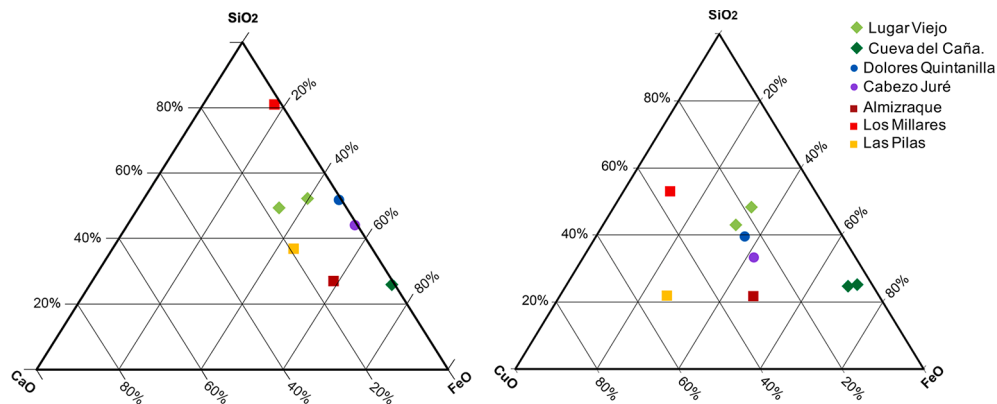


Fig. 7. Ternary diagrams of SiO₂-FeO-CaO and SiO₂-FeO-CuO in average slag compositions. For Las Pilas, the result is the average of the large slag fragments, not the slag layers on crucibles. (The data was taken from the following sources: Almizraque, Los Millares, and Dolores Quintanilla: [Rovira and Renzi 2017](#); Las Pilas: [Murillo-Barroso et al. 2017](#); Cabezo Juré: [Sáez et al. 2003](#).)

Organic inclusions have also been found in some of the Chalcolithic beakers repurposed as crucibles from Bauma del Serrat del Pont ([Montes-Landa et al. 2021](#), 13) and in some of the metallurgical ceramics from Cabezo Juré ([Inácio et al. 2017](#), 72). The elongated voids left by organic temper would improve the performance of the crucibles, making the fabric more insulating and arresting the propagation of cracks ([Martín-Torres and Rehren 2014](#), 123). In general, however, Iberian crucibles are much more frequently tempered with minerals than with organic materials, in contrast to their counterparts in Western Asia. The crucibles from Los Millares contain large mica-schist

inclusions ([Hook et al. 1991](#), 68), and those from Las Pilas contain large (up to 3 mm) quartz and potassium feldspar inclusions ([Murillo-Barroso et al. 2017](#), 1550). Crucibles and tuyeres from Valencina de la Concepción contain grog or organic temper ([Inácio et al. 2017](#), 74) and are made of a strikingly calcareous clay, around 35% CaO ([Inácio et al. 2017](#), 75).

3.3. Cueva del Cañaveralejo: Results

The two slag cakes (*tortas de reducción*) from Cueva del Cañaveralejo

are thick, dense, lumpy, and irregularly-shaped, without the smooth appearance of tap slag (Fig. 8, Figure S2.8, Figure S2.14). One of the artifacts (CC5) appears to have a slag meniscus, retaining the curved upper edge of a circular cake; it was extrapolated to represent 30% of a 10-cm diameter cake (Figure S2.14). The cakes weigh 127 and 124 g, and measure 6.3×7.8 cm and 5.6×6.5 cm, respectively.

The surfaces are covered in green secondary copper minerals, and pieces of charcoal are embedded on the outer surfaces and within the slag (Fig. 9). Because the slag cakes are large for Chalcolithic artifacts, three samples were taken from slag cake CC4 and two were taken from slag cake CC5 in order to evaluate the variation within the cakes.

The average bulk composition of the slag cakes consists of 68% iron oxide and 24% silica with aluminum, potassium, or calcium oxides each below one percent (Table 2, above). Copper oxide is present in varying concentrations up to 6%; arsenic, zinc, antimony, and lead are below the detection limit of c. 0.1%. Despite the heterogeneous macroscopic appearance of the slag (Fig. 9), the composition is fairly consistent within each slag cake.

As suggested by the bulk composition results, the slag has relatively few copper prills. Most prills were under $10 \mu\text{m}$ in diameter, with the largest around $100 \mu\text{m}$ in diameter; the prills contain notable (4.7%) concentrations of iron and minor (0.6%) tin but no detectable arsenic, silver, or lead (Table 3, above).

The microstructure of the slag cakes consists mostly of abundant, equant magnetite crystals, varying from 5 to $50 \mu\text{m}$ across, in an iron silicate “matrix” (Fig. 10). The matrix surrounding the magnetite comprises densely packed fayalite crystals, with a composition averaging 33% SiO_2 : 61% FeO (Table 2, above), with minor amounts of interstitial glass.

Lath-shaped delafossite (CuFeO_2) crystals are also present but limited to the edge of the slag cakes or around voids, probably reflecting localized oxidation (Figure S2.10). Relict quartz is also present within the slag cakes (Figure S2.13).

A notable feature of the slag is the presence of copper sulfides and sulfates. These include lustrous white prills of chalcocite (Cu_2S) (Fig. 11), lustrous yellow prills of a copper-iron sulfide, possibly bornite (Cu_5FeS_4) (Fig. 12), and copper sulfates, visible as blue crystals under plane-polarized light and possibly resulting from the weathering of the sulfides (Figures S2.12, S2.17).

Fragments of charcoal are found on the surface of and within the slag cakes (Fig. 9 and Fig. 13). Samples of the charcoal were removed and examined at high magnification with an optical microscope. One sample was tentatively identified as *Arbutus unedo* (strawberry tree/madroño) (O. Ortiz Morales, pers. comm., 2018); another less well-preserved sample from the other slag cake appeared to be *Pistacia* or *Arbutus* and conclusively not common fuel woods like *Pinus*, *Olea*, or *Quercus* (E. Allué, pers. comm., 2018).

Two samples from CC4 and one sample from CC5 were taken for lead isotope analysis (LIA); the results show differences between samples, even from within the same slag cake (Table 5). The use of LIA in order to



Fig. 8. Slag cakes from Cueva del Cañaveralejo, CC4 (left) and CC5 (right).

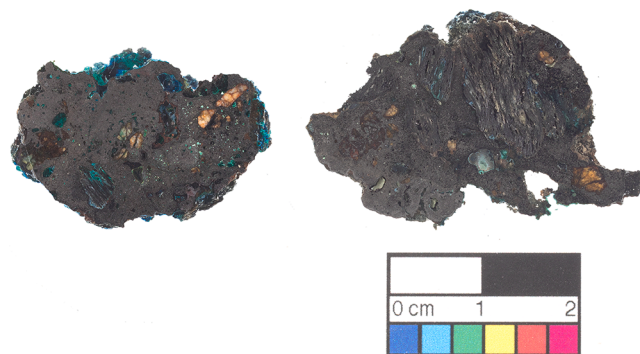


Fig. 9. Cross-sections of samples from the slag cakes from Cueva del Cañaveralejo, CC4 (left) and CC5 (right), with visible quartz grains (light yellow) and embedded charcoal.

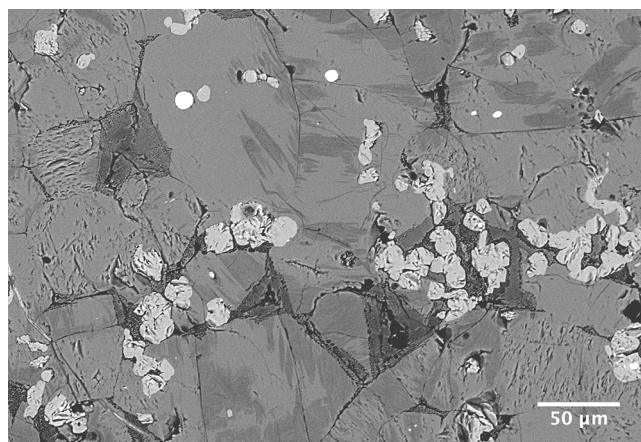


Fig. 10. SEM-BSE image of slag cake CC5, showing the typical microstructure of slag from Cueva del Cañaveralejo: abundant anedral magnetite crystals (light gray) surrounded by fayalite (medium gray), with scattered small copper prills (white).

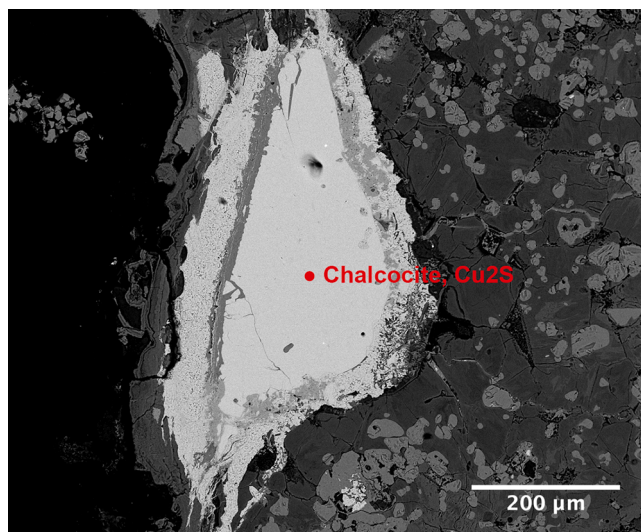


Fig. 11. SEM-BSE image of a lustrous white prill in slag CC5, identified as chalcocite, Cu_2S .

identify potential ore sources must take into account the very low lead content of the samples and the potential for contamination.

Preliminary XRF analysis (available in Supplementary Data 3)

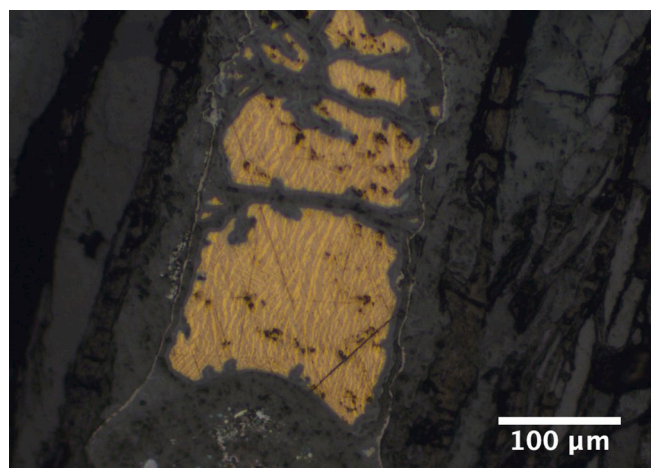


Fig. 12. Photomicrograph of lustrous yellow prills, identified as copper iron sulfide, possibly bornite (Cu_5FeS_4), in slag CC5, under plane-polarized light.

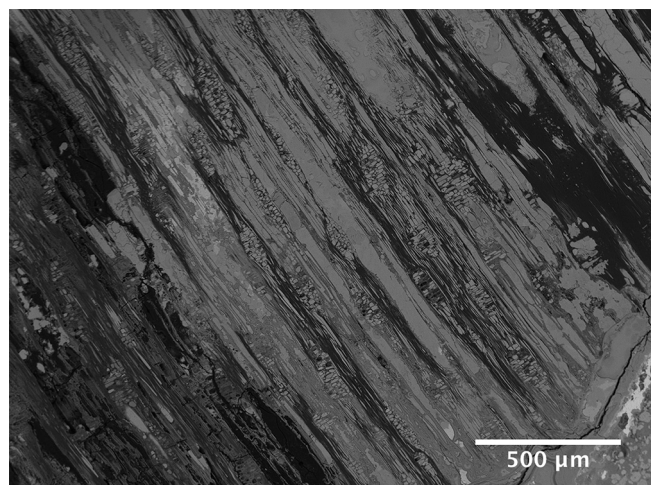


Fig. 13. SEM-BSE image of charcoal embedded within slag cake CC4.

confirmed lead levels higher in the surface compared to the interior. The Olympus Innov-X spectrometer employed tends to overestimate lead when present in low concentrations (Rovira Llorens and Montero Ruiz 2018), suggesting that the quantified concentration $\text{Pb} \cdot 100 / \text{Cu}$ of around 220 ppm in CC4 and around 400 ppm in CC5 is, in fact, lower. Results from the Innov-X spectrometer and from ICP-MS of copper ingots from Rochelongue (Aragón et al. 2022) and from Funtana Coberta (Montero-Ruiz et al., 2018) confirm that, at concentrations reported near the XRF detection limit (200 ppm), the actual amount of lead could be 50–80% lower. Although not quantitative, the LIA laboratory report also indicated higher lead content in the surface compared to the interior of CC4, and higher levels of lead in CC5 than in CC4.

LIA results can be affected by contamination from the gangue, the ceramic, the fuel, or the burial environment (Rademakers et al. 2017, 64–5), or when using ores inherently low in lead, as has been demonstrated by experimental copper smelting ((Rademakers et al. 2020, 16).

Table 5

Results of lead isotope analysis.

Artifact No.	Analysis No.	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$
CC4	PA25747C	18.3433	15.6793	38.5445	2.10129	0.85477
CC4	PA25747D	18.4339	15.6689	38.6051	2.09424	0.85000
CC5	PA25748	18.6011	15.6715	38.7319	2.08224	0.84251

This erratic contamination effect could explain the variation in the results of the two samples taken from different areas of slag CC4, as well as the difference of these samples from the sample from slag CC5.

The results were compared with previous analyses undertaken by CSIC and with published data, most now available in the IBERLID database (García de Madinabeitia et al., 2021). Euclidean distances, a mathematical method to calculate the distance between points in two or three dimensions, were used, following Birch et al. (2020, 90).

However, this approach, based on ratios with the isotope ^{204}Pb as the denominator, did not produce conclusive results (Table 6). Ores giving similar results to one of the samples (PA25747C) of CC4 slag are located in Sierra de Gador, where only lead ores are present, or the Venta del Molinillo copper mine in Huetor Santillan (Granada) in the Baetic range, south of the Guadalquivir and far from Cueva del Cañaveralejo. However, copper from the Venta del Molinillo mine contains arsenic, silver, and high levels of antimony (Murillo-Barroso and Aranda, forthcoming), unlike the pure copper processed at Cueva del Cañaveralejo. The other result (PA25747D) does not agree with a specific region but rather with samples from multiple locations (Almería, Tarragona, Castellón, Ibiza, and the Arditurri district in the Basque Country). The results for the CC5 slag are only compatible with the Zn-Pb ore deposits from Troya-Legorreta district (Velasco et al. 1996) in the Basque Country, therefore not reliable from an archaeological point of view.

A different approach is necessary to understand the results. If we use only the data from Los Pedroches and different subzones of the Ossa Morena, we find a more suitable model, accepting of some level of lead contamination. Samples from two copper mines (Los Cuatro Amigos and Cerro de la Colmena) in the municipality of Montoro, close to Cueva del Cañaveralejo, were recently published in Sáez et al. (2021). Using these mines as reference points, we clearly see in Fig. 14 that the results for Cueva del Cañaveralejo are moving away from the distribution line of Los Pedroches and Ossa Morena, with the results from Montoro following the same range of distribution. The main difference is detected in Fig. 14b, with the values for $^{207}\text{Pb} / ^{204}\text{Pb}$ higher than those from Montoro, but the values for $^{206}\text{Pb} / ^{204}\text{Pb}$ similar to Montoro. Therefore, and allowing for possible lead contamination in the slag isotopic signature, it seems probable that local ores from Ossa Morena or Los Pedroches were smelted in Cueva del Cañaveralejo. Copper and copper-iron sulfides are found in these areas, for example at the Los Cuatro Amigos mine, and copper ores containing tin were found at the Chalcolithic/Bronze Age archaeological site of Llanete de los Moros (Montoro) (Rovira Llorens et al. 1997, 166–170; Rovira and Montero 2003).

3.4. Cueva del Cañaveralejo: Discussion

The results of the analysis of the slag cakes from Cueva del Cañaveralejo show similarities but also significant differences to other Chalcolithic sites in Iberia. Like the crucibles from Lugar Viejo, the attribution of the slag cakes to copper smelting is confirmed by their iron-rich composition, relatively large size, the presence of residual quartz, and the absence of arsenic oxides or cassiterite (Hook et al. 1991, 69). The microstructure of the slag, with the dominance of magnetite, delafossite, copper prills, and cuprite, resembles other smelting slags from the period (see 3.2, Lugar Viejo: Discussion, above).

However, the slag cakes are exceptional in several ways. The most notable difference is their large size: the total weight of 250.7 g is high

Table 6

Geological samples which are closest matches to the slags from Cueva del Cañaveralejo slags, based on Euclidean distances of isotopic ratios.

Sample	Zone	Euclid. dist.	Sample	Zone	Euclid. dist.	Sample	Zone	Euclid. dist.
CC4 (PA25747C)		0	CC4 (PA25747D)		0	CC5 (PA25748)		0
Venta Molinillo	Betics-Granada	0.00539	Prevision	Betics-Granada	0.01130	Katabera	Central Vizcaya	0.0044
Fondon 1	Gador	0.01064	Galafura	CIZ-Portugal	0.01742	Troya	Troya-Legorreta	0.0170
Venta Molinillo	Betics-Granada	0.01088	Mina de Miravet	Castellón	0.01804	El Somo	Western Vizcaya	0.0214
Los Belgas	Gador	0.01425	Oportuna	Arditurri district	0.02161	Matienzo	Western Vizcaya	0.0217
Filon Violeta	Betics-Almería	0.01460	Binifabini	Menorca	0.02601	La Rasa Corta	Western Vizcaya	0.0232
Raimunda	Molar-Bellmunt-Falset	0.01558	Sa Mitja Lluna	Menorca	0.02602	Anselma	Western Vizcaya	0.0238
Raimunda	Molar-Bellmunt-Falset	0.01635	Vail de Ribes	Andorra	0.02655	Troya	Troya-Legorreta	0.0254
Neipin	Galicia	0.01682	Abundancia	Ossa Morena	0.02736	Lozoyuela	CIZ-Sierra Guadarrama	0.0298
Vallirana	Catalonian Central Ranges	0.01724	Barranc Fondo	Montserrat	0.02798	Peñoncillo 1	Betics-Almería	0.0346
Gava	Catalonian Central Ranges	0.01747	Torrubia	Ossa Morena	0.02959	Totanes	CIZ-Montes de Toledo	0.0349

compared to many other sites. For example, the total amount of slag found at Las Pilas was 377 g, with an average weight of 4 g, albeit up to a maximum of 109 g (Murillo-Barroso et al. 2017, 1541 and 1552–3), while only 30 g of slag were recovered from Zambujal (Gauss 2013, 213). The notable exceptions, both in Western Andalucía, are Cabezo Juré, where large cakes up to 1 kg were found (Sáez et al. 2003, 628), and Valencina de la Concepción, where over 16 kg of slag were recovered (Nocete et al. 2008, 725). The large size of the slag cakes supports the proposition that Chalcolithic copper smelting, was, at least in some cases, a slagging process and that the relatively small amount of slag preserved in the archaeological record is because of intentional crushing to retrieve the desired metal rather than the use of ultra-pure, non-slag-forming ores (pro Bourgarit 2007, 5; contra Rovira and Renzi 2017, 756). Of course, these options are not mutually exclusive, and, in fact, one of the main contentions of this paper is the variability of the archaeometallurgical record.

Another notable feature of the slag is its fayalitic composition: unusually high in iron oxide (66.6% and 69.0% FeO) and low in silica (23.7% and 24.3% SiO₂), with high smelting efficiency, as shown by the low copper oxide content (averaging 3.4 and 5.8% CuO). According to published results, slags from other Chalcolithic sites in Iberia never contain more than 60% FeO and often contain much less (Fig. 7). Copper loss is frequently high at other Chalcolithic sites, although variable even at the same site; for example, slags from Almizaraque have copper oxide contents ranging from 7.4 to 57.5 wt% (Rovira and Renzi 2017, 759).

In fact, the higher efficiency of copper smelting at Cueva del Cañaveralejo might be the result of its atypical composition. The average composition of the slag is located in a trough in the FeO-SiO₂ phase diagram: between 76% FeO: 24% SiO₂ and 62% FeO: 38% SiO₂, the liquidus point drops to between 1177 and 1205 °C (Verein Deutscher Eisenhüttenleute 1995, 79). Therefore slags with high iron content, such as those from Cueva del Cañaveralejo, would be liquid at a lower temperature than “typical” Chalcolithic Iberian slags, facilitating the separation of copper (Hauptmann 2014, 101). The charcoal inclusions might corroborate these findings, with charcoal more common in the liquified slag than in the semi-liquid slag at Faynan (Hauptmann 2007, 164.) It is not clear if the iron-rich composition, with its beneficial effects, was intentional or serendipitous.

In addition, the presence of sulfides in the slag is of interest. While sulfides have been found in small quantities in slag at other sites such as La Ceñuela (Rovira 2002b, 91), this is usually thought to be accidental (Müller et al. 2004, 51). While the results from Cueva del Cañaveralejo suggest that sulfidic ores were used in combination with oxidic ores, given the small sample size, it is not clear whether their use was intentional or merely the result of using mixed ores. Again, the occurrence of sulfides might explain the efficiency of the smelting: the co-

smelting of oxidic and sulfidic copper ores has been proposed, with chalcopyrite acting to reduce mixed ores into copper metal, with or without the assistance of carbon (Rostoker et al., 1989, 82; but for a criticism of this theory, see Bourgarit 2007, 10).

While no metal artifacts were recovered from the cave, the copper prills in the slag suggest the production of a fairly pure copper, with minor iron and tin but no arsenic, zinc, antimony, or lead. Ore fragments from El Llanete de los Moros, Montoro, Córdoba, dated to the Chalcolithic period, share a similar profile: copper with minor tin but little or no arsenic detected (Rovira Llorens et al., 1997, 168 – 169). LIA results, while not definitive, suggest that local ores from Ossa Morena or Los Pedroches were used.

Finally, while the identification of the fuel in the slag as *Pistacia* or *Arbutus* needs definite confirmation, it appears to differ from other sites with published anthracological results. The charcoal from the furnaces at Cabezo Juré was determined to be mostly *Quercus ilex* (holm oak) and *Olea europaea* (olive) (Rodríguez Ariza 2004, 250), with *Arbutus unedo* making up less than one percent of the fragments from the furnaces. At Valencina de la Concepción, *Quercus* of an unspecified species and *Elaeagnus angustifolia* (oleaster) were used for smelting (Nocete et al. 2008, 725). A charred fragment of *Erica* sp. (heather), a member of the *Ericaceae* family like *Arbutus*, was found in a Late Bronze Age crucible used for pouring molten copper at Entre Águas 5 in central Portugal (Valério et al. 2013, 446).

4. Conclusion

Analysis of the metallurgical artifacts from Lugar Viejo III and Cueva del Cañaveralejo confirmed that they are related to the smelting of (mostly) oxidic copper ores in crucible-furnaces, and as such, are consistent with the broader model of Chalcolithic metallurgy in Iberia. However, they also show peculiarities and demonstrate the danger of an “one size fits all” model.

At Lugar Viejo III, smelting conditions appear to have been similar to those documented across the Peninsula, but the use of organic temper in the crucible fabrics highlights the variability of metallurgical ceramics. Temper choice raises interesting questions about cross-craft production and about the transmission of technological knowledge. As metallurgy spread across Iberia, some elements of the *chaîne opératoire* may have been considered essential, while others were adapted to local resources and requirements. Future research on the complete copper production sequence, including technical ceramics and fuel choice, following methodologies like those suggested by Ottaway (2001, 88) and Roberts (2008, 356), would improve our understanding of the extent of the use of organic temper, the relationship between domestic and metallurgical ceramics, and more generally, the spread of metallurgy across Iberia and

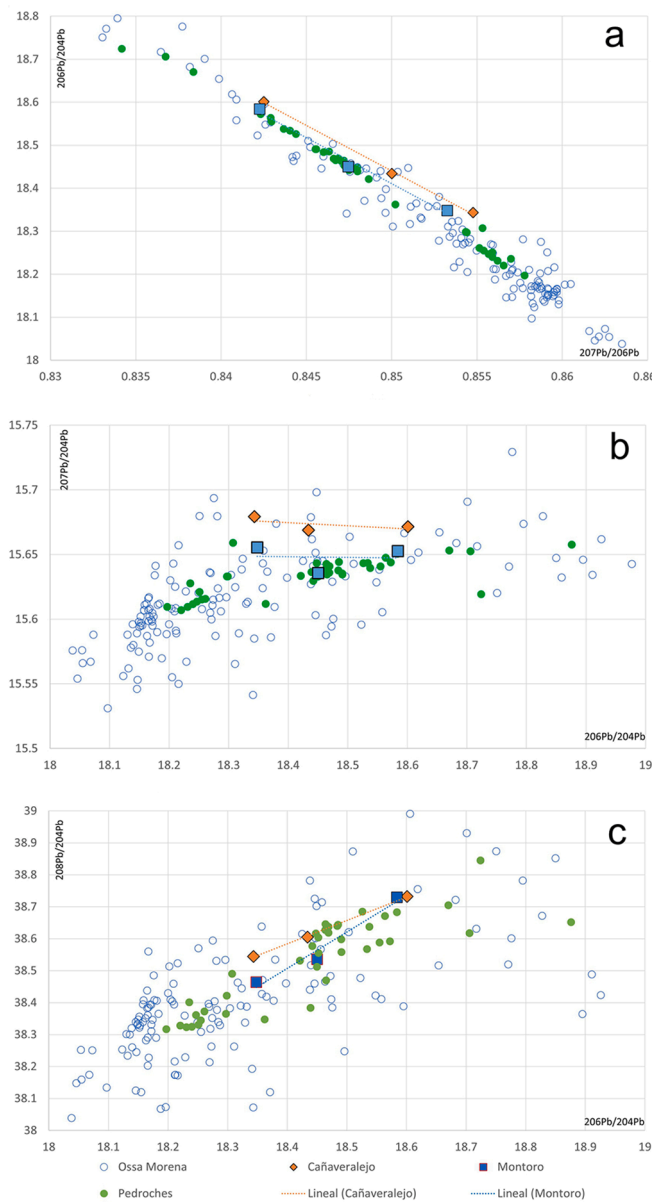


Fig. 14. a-c Lead isotope results for Cueva del Cañaveralejo, compared to previously published results for the Ossa Morena and Los Pedroches. Sources for data: [Hunt Ortiz 2003](#), [Gauss 2016](#), [Klein et al. 2009](#), [Marcoux et al. 2002](#), [Sáez et al. 2021](#), [Santos Zalduegui et al. 2004](#), [Tornos and Chiaradia 2004](#).

its social and cultural context.

The relatively large, fayalitic slag cakes from Cueva del Cañaveralejo provide some of the earliest evidence for fayalitic slag in Iberia, denoting optimum charge balance and redox conditions. This resulted in relatively low copper losses, preventing the need for slag crushing and beneficiation. The presence of sulfides is also noteworthy. These features differ from the established paradigm of Chalcolithic metallurgy in Iberia and more closely resemble smelting traditions documented in France and beyond ([Bourgarit 2007](#), 11). Research into possible connections with France, where matte smelting has been found ([Bourgarit et al. 2003](#)), would be desirable.

Finally, this study shows that while the general pattern of Chalcolithic metallurgy in Iberia still holds, it would be beneficial to expand research beyond traditionally studied areas. The regions around Lugar Viejo III and Cueva del Cañaveralejo would seem to be especially fruitful, both for examining regional differences as well as for investigating the diffusion of metallurgy across Iberia. Lugar Viejo III is

situated in the Ebro watershed, which has received little attention outside of its delta near Tarragona. The Ebro river valley could conceivably have been an important thoroughfare, possibly connecting Bell Beaker-era copper mines in the Cantabrian mountains, some of the earliest mines yet known ([de Blas Cortina 2014](#)), with the lower reaches of the river, in a network extending even to France. Likewise, the central Sierra Morena, the region around Cueva del Cañaveralejo, is rich in metalliferous deposits. The Guadalquivir river, on the southern border of the Sierra Morena, serves as a natural pathway, connecting the Sierra Morena to the rest of the Iberian Pyrite belt and sites such as Valencina de la Concepción; in the other direction, tributaries of the Guadalquivir extend almost to the cluster of sites in the Vera Basin in Almería.

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CRediT authorship contribution statement

Elizabeth La Duc: Conceptualization, Formal analysis, Investigation, Writing – original draft, Visualization, Writing – review & editing. **Ignacio Montero-Ruiz:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Writing – review & editing. **Ian C. Freestone:** Supervision, Writing – review & editing. **Javier Fanlo Loras:** Resources, Writing – review & editing. **Isabel María Jabalquinto Expósito:** Resources, Writing – review & editing. **José C. Martín de la Cruz:** Resources, Writing – review & editing. **Fernando Pérez-Lambán:** Resources, Writing – review & editing. **Jesús V. Picazo Millán:** Resources, Writing – review & editing. **Marcos Martín-Torres:** Conceptualization, Formal analysis, Funding acquisition, Supervision, Writing – original draft, Visualization, Writing – review & editing.

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.

Data availability

Extended results are provided in [Supplementary Data 2 and 3](#).

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Appendix A. Supplementary data

Supplementary data to this article, including an extended abstract translated into Spanish, can be found online at <https://doi.org/10.1016/j.jasrep.2022.103683>.

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