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A first appraisal on copper sources for Chalcolithic settlements in southern Portugal using Pb isotope analysis

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ABSTRACT

This work presents the first provenance study on copper in use by 3rd millennium BC communities in southern Portugal. Copper ores from small mines and copper artefacts from Chalcolithic settlements were subjected to Pb isotope analysis. Some of Pb isotope ratios obtained in ores from the Ossa-Morena Zone, but also from the South Portuguese Zone, evince the existence of deposits with highly radiogenic Pb, which was previously considered rare in the Iberian Peninsula. Pb isotope ratios of artefacts were compared with Pb isotope fields of closer geological/tectonostratigraphic zones, namely the South Portuguese Zone, Ossa-Morena Zone and Central Iberian Zone. The assessment suggests that most artefacts were produced with copper from the Ossa-Morena Zone. Nevertheless, a flat axe of the Três Moinhos settlement is a remarkable exception due to its highly radiogenic Pb signature, which only has parallels in the Iberian Peninsula on copper ores of the Chalcolithic mines of La Profunda and El Milagro (northern Spain). Consequently, this flat axe constitutes the first indication of a possible long-distance trade of copper between the Cantabrian region and southwestern Iberian Peninsula during the 3rd millennium BC.

1. Introduction

The archaeometallurgical research regarding the southwestern end of Iberian Peninsula has been identifying the use of copper with varying content of arsenic to produce metallic artefacts during the 3rd millennium BC, i.e. during the Chalcolithic period when the first metallurgical manifestations made their appearance in this region (Valério et al., 2016, 2019). The study of artefacts and metallurgical remains suggests the smelting of copper ores naturally containing arsenic (Rovira and Montero Ruiz, 2013), although copper sources exploited by local settlements are still unknown. The pioneer work of Gauß (2016) identified a supply of copper from mines in Ossa-Morena Zone to Chalcolithic settlements in central Portugal, but the provenance of copper used in Chalcolithic sites of southern Portugal, with the exception of an insight concerning the settlement of São Pedro (Redondo, Alentejo), were not investigated. Therefore, the present work depicts a first appraisal on copper sources to Chalcolithic settlements of this southwestern region of the Iberian Peninsula using new lead isotope analysis (LIA) of copper ores and artefacts, in addition to LIA databases of copper ores from close tectonostratigraphic zones, namely the South Portuguese Zone (SPZ), Ossa-Morena Zone (OMZ) and Central Iberian Zone (CIZ).

2. Lead isotope ratios in provenance studies

LIA of ores and metallic artefacts have been the most widely used and reliable tool to identify the geological origin of prehistoric metal. The LIA reliability arises from the absence of Pb isotopic fractionation in metallurgical operations conducted to convert the ore into a metal and from the metal on the finished artefact. Provenance studies employ four stable Pb isotopes, namely ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. The ^{204}Pb is a stable primeval isotope and, consequently, it shows a constant content in mineral deposits (*c.* 1.4%), while ^{206}Pb, ^{207}Pb and ^{208}Pb are final decay products of ^{238}U, ^{235}U and ^{232}Th, respectively. These three stable isotopes, whose content in the ore depends on the age of the mineral deposit, are called radiogenic isotopes.

The isotope ratios ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb are

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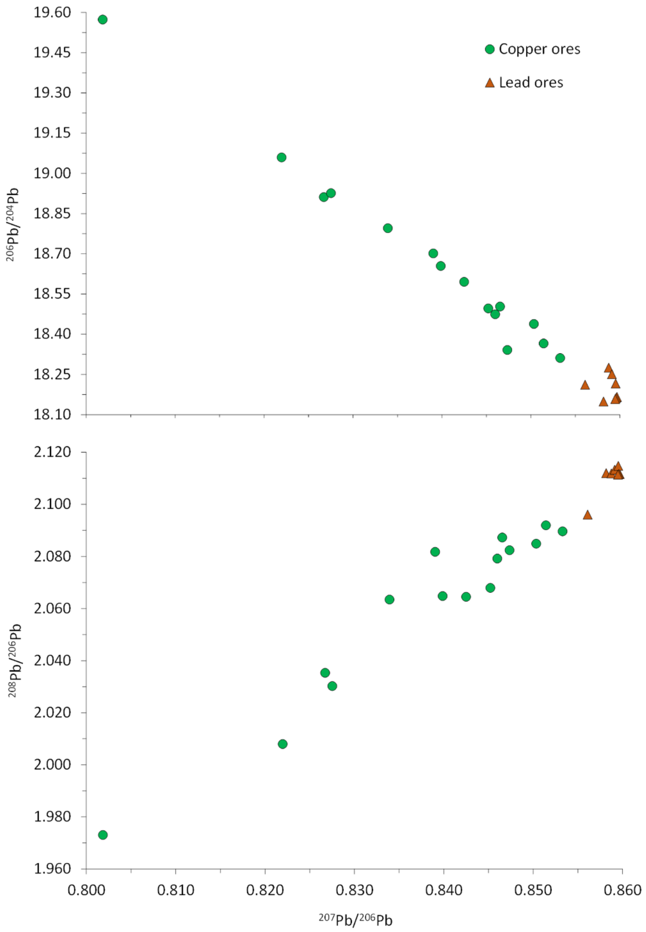

Fig. 1. Pb isotope ratios of malachite, chalcopyrite and galena samples from mines located in the OMZ (Hunt Ortiz, 2003).

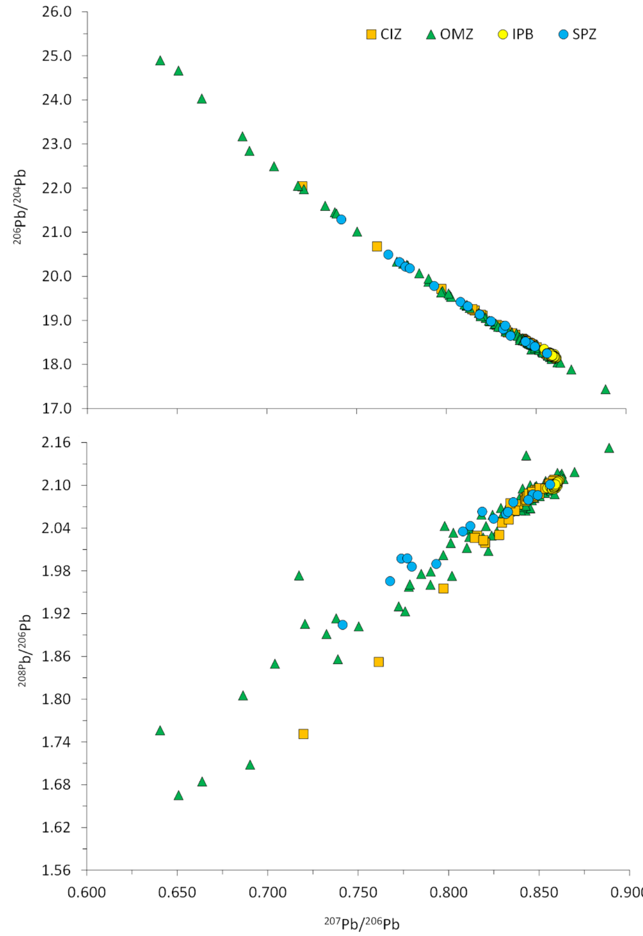

Fig. 2. Pb isotope ratios of copper ores from mines located in distinct tectonostratigraphic zones of southwestern Iberian Peninsula (see references in text).

commonly used to establish the geological age of mineral processes, while ^{206}Pb/^{204}Pb, ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratios are generally used in provenance studies (the last two ratios also depend on the ^{238}U, ^{235}U and ^{232}Th contents in the deposit). Geological deposits may show overlapping isotopic fields, so archaeological considerations and trace element content of ores and artefacts may help to surpass such difficulty. However, trace element contents should be used with caution, given the variable conditions of primitive metallurgical operations and distinct behaviour of such elements in metallurgical operations, not only to convert the ore into metal, but also on the manufacture of the artefact (Stos-Gale and Gale, 2009).

Mineral deposits that behave as closed systems show approximated values of 18.5 for ^{206}Pb/^{204}Pb, 15.6 for ^{207}Pb/^{204}Pb and 38.3 for ^{208}Pb/^{204}Pb (Hofmann, 2001. Fig. 1; Pollard et al., 2018, p. 149). For example, the volcanic-hosted polymetallic massive sulphide deposits of the Iberian Pyrite Belt (IPB), which is part of the SPZ, have an extremely homogeneous isotopic field with average values of 18.183 (^{206}Pb/^{204}Pb), 15.622 (^{207}Pb/^{204}Pb) and 38.183 (^{208}Pb/^{204}Pb). Following Marcoux (1998), the IPB signature is characteristic of the isotopic composition of the south Iberian crust from the Devonian to the Early Carboniferous (Dinantian) and "*their constancy implies a homogenization of the mineralizing fluids before the deposition of the massive sulphides from hydrothermal fluids circulating through interconnected regional fracture systems*" (p. 45).

Mineral deposits formed during several geologic episodes, in addition to those deposits showing high content of uranium and/or thorium, have a distinct behaviour. The latter are said to contain highly radiogenic Pb since the content of radiogenic isotopes will be higher than usual, i.e. ^{206}Pb/^{204}Pb $>$ 19, while, commonly ^{207}Pb/^{206}Pb $>$ 0.8 and ^{208}Pb/^{206}Pb $<$ 2.0. It should be noted that the lower limit of highly radiogenic Pb varies from author to author. Marcoux (1998) uses the ^{206}Pb/^{204}Pb ratio of 18.40, Pollard et al. (2018) considers 19.5 (p. 149) or 19 (p. 160), while Liu et al. (2018) and Chen et al. (2019) employ a value of 20. There are few known mineral deposits with highly radiogenic Pb in Europe, some exceptions being the occurrences in Scandinavian Peninsula (Pollard et al., 2018) and a copper deposit in Wales, the Great Orme mine (Budd et al., 2000; Williams and Le Carlier de Veslud, 2019). Moreover, this type of ore deposits has only been recently identified in some mines of the Iberian Peninsula, some of them with prehistoric works, namely at El Milagro, Asturias (Huelga-Suarez et al., 2014a) and La Profunda, León (Huelga-Suarez et al., 2014b), in addition to small-scale mines in Ossa-Morena Zone and South Portuguese Zone, like Safira, Mocissos and Barrigão, among others (Gauß, 2016, Tabs. 10.13 and 10.14), and also at the La Turquesa mine, Cornudella de Montsant (Alt Priorat) (Montero Ruiz, 2018). As mentioned before, mineral deposits formed during different geologic episodes or even during a long geologic period may also show a considerable variability of Pb isotope ratios. Therefore, the ideal characterisation of a mineralisation should include a significant number of samples, at least 10 according to Baron et al. (2014), > 20 (Stos-Gale, 1992) or even 40 or more, following Baxter et al. (2000). Moreover, in archaeological research, sampling should focus on the mining sector that archaeological evidence indicates as having been exploited during the concerned time period. On the other hand, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios should also be added to the ones (^{206}Pb/^{204}Pb, ^{207}Pb/^{206}Pb, ^{208}Pb/^{206}Pb) commonly used in provenance studies to help differentiating between overlapping isotopic fields (Baron et al., 2014).

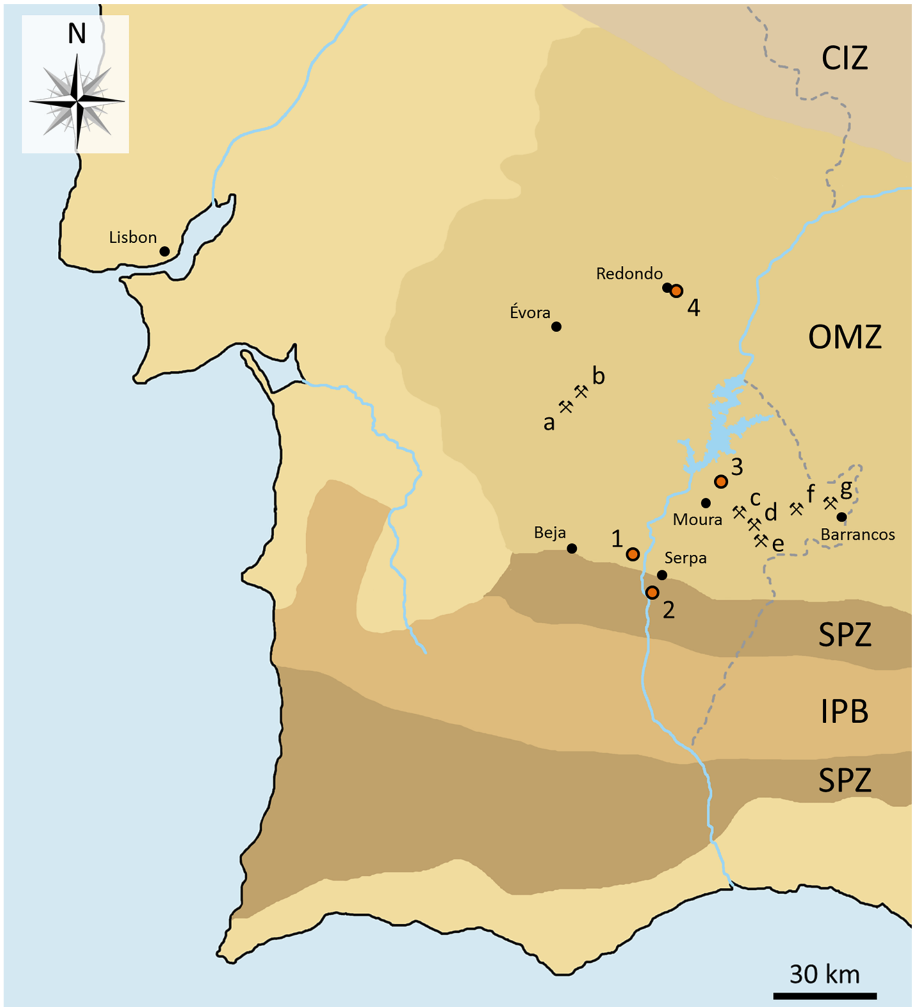

Fig. 3. Map of southern Portugal with location of surveyed mines (a: Ganhoteira: b: Fajoas; c: Rui Gomes; d: Corujeira; e: Serra da Preguiça; f: Aparis; and g: Minancos) and Chalcolithic settlements with analised metals (1: Três Moinhos; 2: São Brás 3; 3: Porto Mourão and 4: São Pedro).

3. Available data on Pb isotope signature of ores from southern Iberian Peninsula

Copper ores most likely to be exploited by prehistoric communities of southwestern Iberian Peninsula belong to three distinct tectonostratigraphic zones (SPZ, OMZ and CIZ), whose available database of Pb isotope ratios of copper ores will now be discussed.

3.1. Ossa-Morena Zone

OMZ ore deposits can be grouped into several types due to the complex evolution of this geological zone, which has given rise to a wide variety of geological formations with different ages (Tornos et al., 2004). Up until recently, the OMZ Pb isotope database mostly refers to ore samples collected from relatively large Spanish mines active during the last century, being most samples of lead and zinc ores, namely galena and sphalerite. Tornos and Chiaradia (2004) published results of 56 ore samples, to which can be added 23 samples analysed by Hunt Ortiz (2003) and six samples published by Klein et al. (2009). This data set contains only 27 copper ores, which show a distinct Pb isotope signature when compared to lead and zinc ores, as can be easily seen in the graphical representation (Fig. 1) based on the results obtained by Hunt Ortiz. As we are essentially interested in the origin of the copper, the database we assembled refers only to isotopic compositions determined in copper ores, as recommended by several authors in order to identify the provenance of prehistoric copper (Stos-Gale and Gale, 2009; Baron et al., 2014). Moreover, as seen above, isotopic signatures of copper ores may differ from those of lead ores in the same geological zone. In addition, lead metal was only produced in the Iberian Peninsula since the Iron Age and not during Prehistory, the chronological period that interests us here.

Roland Gauß recently published the LIA of 51 copper ores from OMZ mineral deposits, for the first time including only occurrences from the Portuguese area (Gauß, 2016). The sampled ore bodies correspond mostly to small mines, some of them with traces of prehistoric exploitation, such as Tinoca, Vieiros, Mocissos, Safira, Entre Águas, Souséis, Vale de Nogueira, Entre-as-Matas, Volta Ferreira, Arradinha and Rui Gomes (see Gauß, 2016: Abb. 6.7). Additionally, the study also includes the LIA of six copper ore samples collected during archaeological excavations at the Chalcolithic settlement of São Pedro, Redondo (Gauß, 2016).

Then, the OMZ Pb isotope field of copper ore samples has the following boundaries: $^{206}Pb/^{204}Pb$ = 17.44 to 24.90; $^{207}Pb/^{206}Pb$ = 0.64 to 0.89; and $^{208}Pb/^{206}Pb$ = 1.67 to 2.15. Consequently, some copper ore bodies in the Portuguese region have Pb isotope ratios indicating the existence of highly radiogenic Pb. Note that these examples mostly belong to the Barrancos region and the nearby mines of Rui Gomes and Corujeira, several of them showing traces of prehistoric works. Additionally, highly radiogenic Pb is also present in the more distant Mocissos mine, where archaeological excavations attest the prehistoric

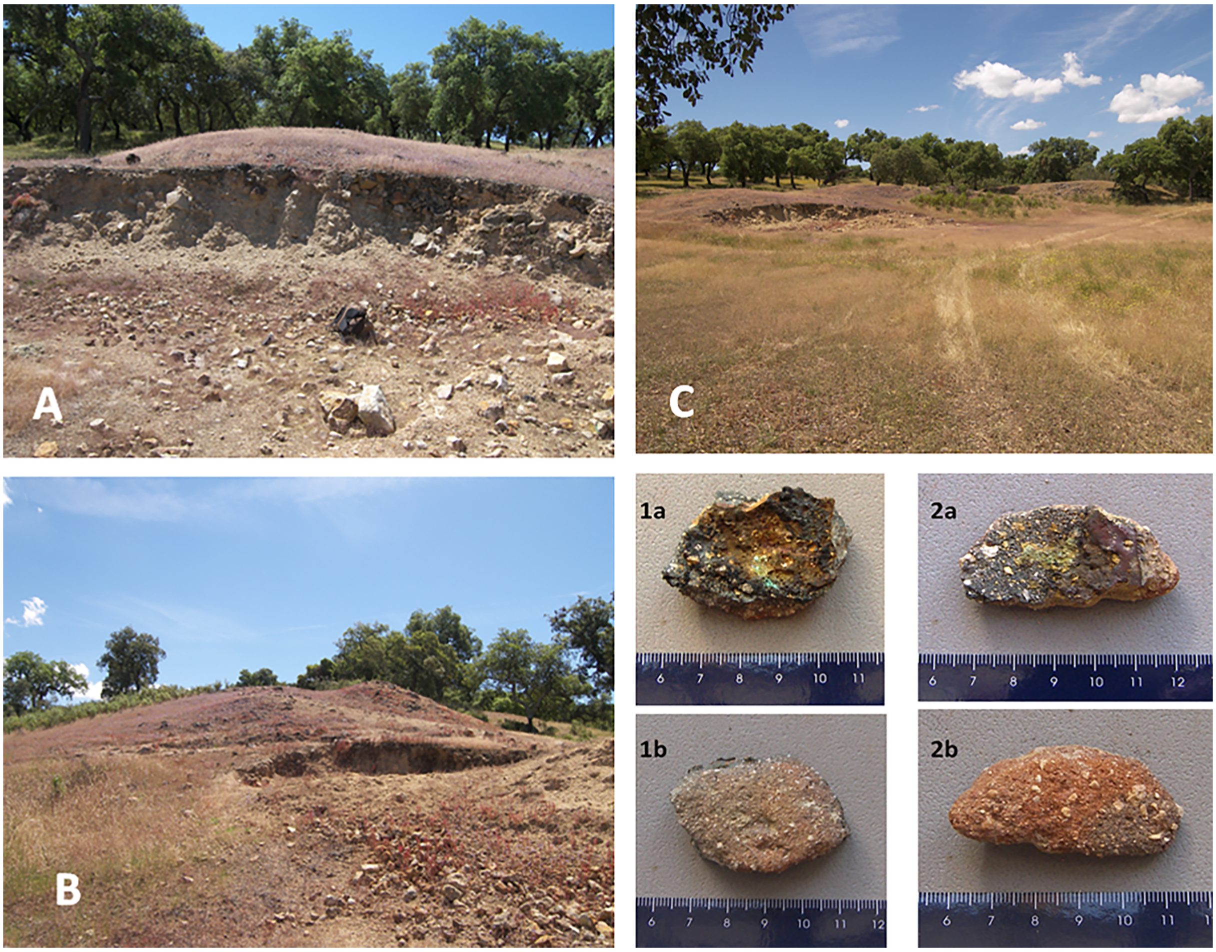

Fig. 4. Ganhoteira copper mine with waste mineral heaps (A to C). Ceramic (crucible) fragments with traces of metallurgical use (1a, 1b; 2a, 2b) were found in the exposed profile of a waste minerals heap (A).

exploitation together with smelting operations concerning copper ores (Hanning et al., 2010). Moreover, it should be noted that some samples from the Aracena region analysed by Hunt Ortiz (2003), namely two copper ores from Cala and Teuler mines, already pointed to a highly radiogenic Pb ($^{206}Pb/^{204}Pb > 19$). Finally, half of the copper ore samples from São Pedro settlement also show values of highly radiogenic Pb (Gauß, 2016).

3.2. South Portuguese Zone and Iberian Pyrite Belt

IPB massive polymetallic sulphide deposits have an extremely homogeneous Pb isotope field, as mentioned by Marcoux (1998) and later confirmed by the LIA of numerous ores (Hunt Ortiz, 2003; Klein et al., 2009; Gauß, 2016). The collection consists of results from about 130 ore samples from different deposits of polymetallic sulphides, supergene and gossan mineralisations. The Pb isotope field of this dataset has the following narrow boundaries: $^{206}Pb/^{204}Pb$ = 18.135 to 18.276; $^{207}Pb/^{206}Pb$ = 0.855 to 0.861; and $^{208}Pb/^{206}Pb$ = 2.094 to 2.106. On the contrary, the LIA of secondary copper minerals (17 samples) from small ore bodies not belonging to the IPB, but located in the SPZ, reveals a much more heterogeneous field, namely of $^{206}Pb/^{204}Pb$ = 18.248 to 21.241; $^{207}Pb/^{206}Pb$ = 0.742 to 0.856; and $^{208}Pb/^{206}Pb$ = 1.904 to 2.101 (Gauß, 2016). Some of these small-scale mines also have the signature of highly radiogenic Pb (Brancanes, Barrigão, Cerro da Mina, Santiago do Cacém and Mina do Penedo), but only the Alcaria Queimada II mine (Algarve region) shows evidences of ancient exploitation. To sum up, the IPB Pb isotope field is very well defined (130 samples), but the limits of the SPZ field (excluding the IPB ores) still seem somewhat unclear, thus requiring further research.

3.3. Central Iberian Zone

The first and most extensive Pb isotope database of CIZ consisted in 125 galena samples from the Alcudia Valley, Linares-La Carolina region and the Los Pedroches batholith (Santos Zalduegui et al., 2004). Klein et al. (2009) published LIA of 41 secondary copper ore samples, mostly belonging to Los Pedroches. The CIZ is located immediately north to the OMZ and only three copper ore samples from Portuguese mines in this tectonostratigraphic zone (Vila Velha de Rodão I and Vila Velha de Rodão II, district of Castelo Branco, and Pires, district of Guarda) were analysed (Gauß, 2016). The CIZ Pb isotope field of copper ores has the following limits: $^{206}Pb/^{204}Pb$ = 18.166 to 22.038; $^{207}Pb/^{206}Pb$ = 0.7198 to 0.8591; and $^{208}Pb/^{206}Pb$ = 1.7509 to 2.1079. It should be emphasized that the CIZ also has a very heterogeneous set of Pb isotope ratios, including several occurrences with highly radiogenic lead.

3.4. Lead isotope fields of tectonostratigraphic zones in southwestern Iberian Peninsula

The comparison of LIA of copper ores from OMZ, SPZ and CIZ evidences a considerable overlap of Pb isotope fields (Fig. 2). However, the absence of SPZ and CIZ data in the end sections of OMZ Pb isotope field may result from the lower number of analysed samples of those two regions. Finally, it is very interesting to find out that all tectonostratigraphic zones in southwestern Iberian Peninsula show occurrences

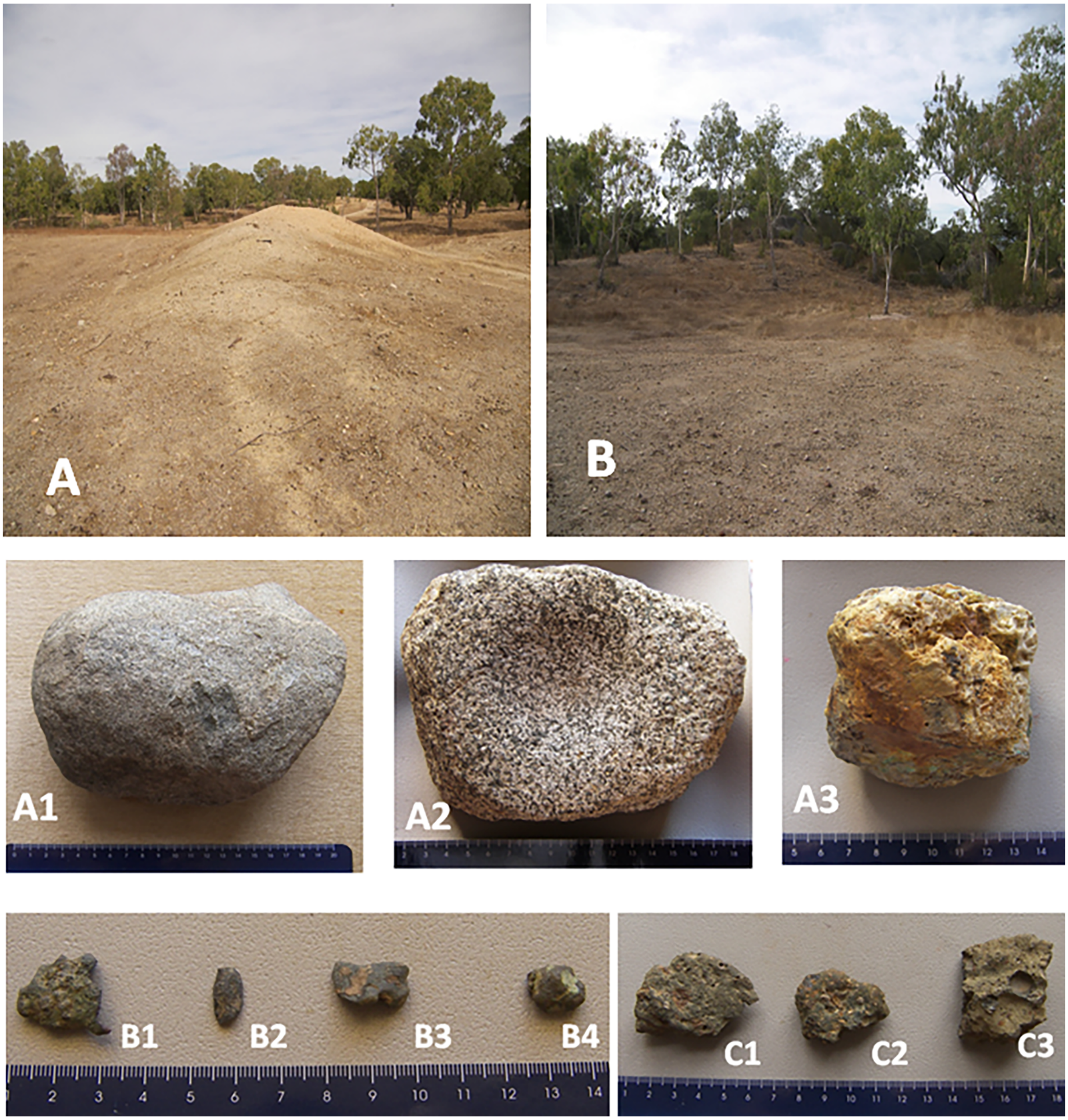

Fig. 5. Fajoas copper mine with waste mineral heap (A) and possible mining camp (B) showing some evidence of ancient exploitation (A1: hammerstone; A2: anvil (granite); A3: stone striker (quartz); B1 to B4: copper nodules; and C1 to C3: slag).

of highly radiogenic Pb.

4. New LIA data concerning copper ores from OMZ and Chalcolithic artefacts from Alentejo (southern Portugal) – methodology

The study comprises c. 30 samples recovered at ore bodies and archaeological sites located in southern Portugal (Fig. 3). LIA focused on nine copper ore samples from deposits located in the OMZ, namely from the mines of Aparis and Minancos (Barrancos), Rui Gomes, Corujeira and Serra da Preguiça (Moura), Ganhoteira and Fajoas (Portel), in addition to four copper artefacts recovered in Chalcolithic settlements located in the Guadiana basin, i.e. Três Moinhos (Beja), São Brás 3 (Serpa) and Porto Mourão (Moura). Two metallic copper nodules from Fajoas were analysed too. Besides these samples, other metallurgical remains (metallic nodules, three fragments of ceramic crucibles and slag fragments), most likely resulting from smelting operations carried out near the copper mines of Ganhoteira and Fajoas, were also object of elemental analysis.

4.1. Samples

4.1.1. Copper ores and metallurgical remains

Malachite and chalcopyrite samples were collected in waste mineral heaps at mines of Aparis, Minancos, Rui Gomes, Corujeira, Serra da Preguiça, Ganhoteira and Fajoas. A few grooved mining hammerstones recovered at Minancos and Rui Gomes attest the prehistoric exploitation of these mines, although a more precise chronological assignment (Chalcolithic or Bronze Age) is not possible.

The survey carried out at Ganhoteira and Fajoas mines arose from the probable presence of highly radiogenic Pb, as suggested by known evidence about the local association of copper ores with uranium ores

Fig. 6. Copper artefacts of Chalcolithic settlements in southern Portugal (from left to right: flat axe (TM-1) and chisel (TM-8) from Três Moinhos, axe blade (SB3-1) from São Brás 3 and flat axe (PM-2) from Porto Mourão).

Table 1
Pb isotope ratios of NIST SRM 981 (average ratios of n determinations during a single analytical session).

n	$^{206}Pb/^{204}Pb$	2σ	$^{207}Pb/^{204}Pb$	2σ	$^{208}Pb/^{204}Pb$	2σ	$^{208}Pb/^{206}Pb$	2σ	$^{207}Pb/^{206}Pb$	2σ
5	16.9433	0.0010	15.5019	0.0016	36.7318	0.0047	2.1679	0.0003	0.91493	0.00009
3	16.9436	0.0012	15.5008	0.0004	36.7284	0.0016	2.1677	0.0001	0.9148	0.0001
3	16.9435	0.0012	15.5013	0.0017	36.7299	0.0049	2.1678	0.0001	0.91488	0.00004

(SIORMINP1547U, SIORMINP0920U). The survey exceeded initial expectations due to several traces of prehistoric exploitation identified in both sites, where several waste mineral heaps can be observed (Figs. 4 and 5). A metallic nodule and three fragments of ceramic crucibles showing a slagged inner surface with green spots were recovered in a waste mineral heap, probably of Chalcolithic chronology, at Ganhoteira. Two of the crucible fragments were found in the profile of a trench made in the heap possibly by technicians of the Portuguese Nuclear Energy Commission, in 1959, while the other crucible fragment was recovered at the base of that trench and the metallic nodule in a very close area. No habitat remains were found. At Fajoas, several waste mineral heaps were also identified and traces of a possible mining camp were found very close in the immediate vicinity of the larger heap. Most of the surface-collected pottery in this site belongs to the Roman-Republican period, but some sherds seem to correspond to a Bronze Age occupation. In addition of copper ores, the survey of this larger heap identified metallic nodules, slag, vitrified ceramics and a hammerstone, while the area of the probable mining camp also revealed a granite anvil and a lot of metallic nodules, certainly resulting from metallurgical operations, maybe the smelting of copper ores, carried out in the immediate vicinity of the mine. It should also be borne in mind that other small copper mines with traces of old works exist close to the Fajoas mine. In addition to the Ganhoteira mine located about 5 km from Fajoas, there are the mines of Sobral das Minas (1 km from Ganhoteira and 6 km from Fajoas), and Angerinha (4 km from Ganhoteira and 9 km from Fajoas). At Sobral das Minas and Angerinha there is no association of their copper ores with uranium ores, contrary to what happens at Ganhoteira and Fajoas. Angerinha have been object of archaeological digging by the Roland Gauß team (Gauß, 2016). So it cannot be ruled out that some ore processed in Fajoas also came from these mines and that the human occupations summarily identified at the very small site of Fajoas, which we called the mining camp, are not seasonal but permanent. Only future archaeological excavations can clarify this issue: mining camp or small village.

4.1.2. Copper artefacts

Copper artefacts included in this study were identified by archaeological surveys at 3rd millennium BC settlements of Três Moinhos (Soares, 1992), São Brás 3 (Parreira, 1983; Soares et al., 1994) and Porto Mourão (Soares et al., 1996). These artefacts, namely three flat axes and a chisel, all very fragmented (Fig. 6), are common tools of the Chalcolithic period.

4.2. Elemental analysis of copper samples

p-EDXRF analyses of copper ores were made with a portable Bruker S1 Titan equipped with a Rh X-ray tube, a SSD detector and a 5 mm collimator for the analysis of small size samples. This equipment was mainly used for the analysis of copper ores. Micro-EDXRF analyses involved an ArtTAX Pro spectrometer equipped with a 30 W Mo X-ray tube, focusing polycapillary lens and an electro-thermally cooled Si drift detector with a FWHM of 160 eV at 5.9 keV (Bronk et al., 2001). The quantification of metallic nodules was made with WinAxil software comprising experimental calibration factors calculated with reference standards (British Chemical Standards Phosphor Bronze 551 and BNF Metals Technology Centre Leaded Bronze C50.01). The relative uncertainty is lower than 2% for major elements and lower than 10% for minor elements, while the detection limits for elements usually present in prehistoric copper are 0.01% Ni, 0.01% Zn, 0.03% As, 0.18% Ag, 0.15% Sn, 0.10% Sb and 0.03% Pb. Additional details concerning the experimental procedure have been previously published (Valério et al., 2019).

4.3. Microstructural analysis of copper artefacts

Optical microscopy observations were made in a Leica DMI 5000 M reflected light microscope (50–1000× magnification) equipped with bright field, dark field and polarised light illumination modes. Mounted samples were observed unetched and after etching with an aqueous ferric chloride solution. Further experimental details have been previously described (Valério et al., 2010).

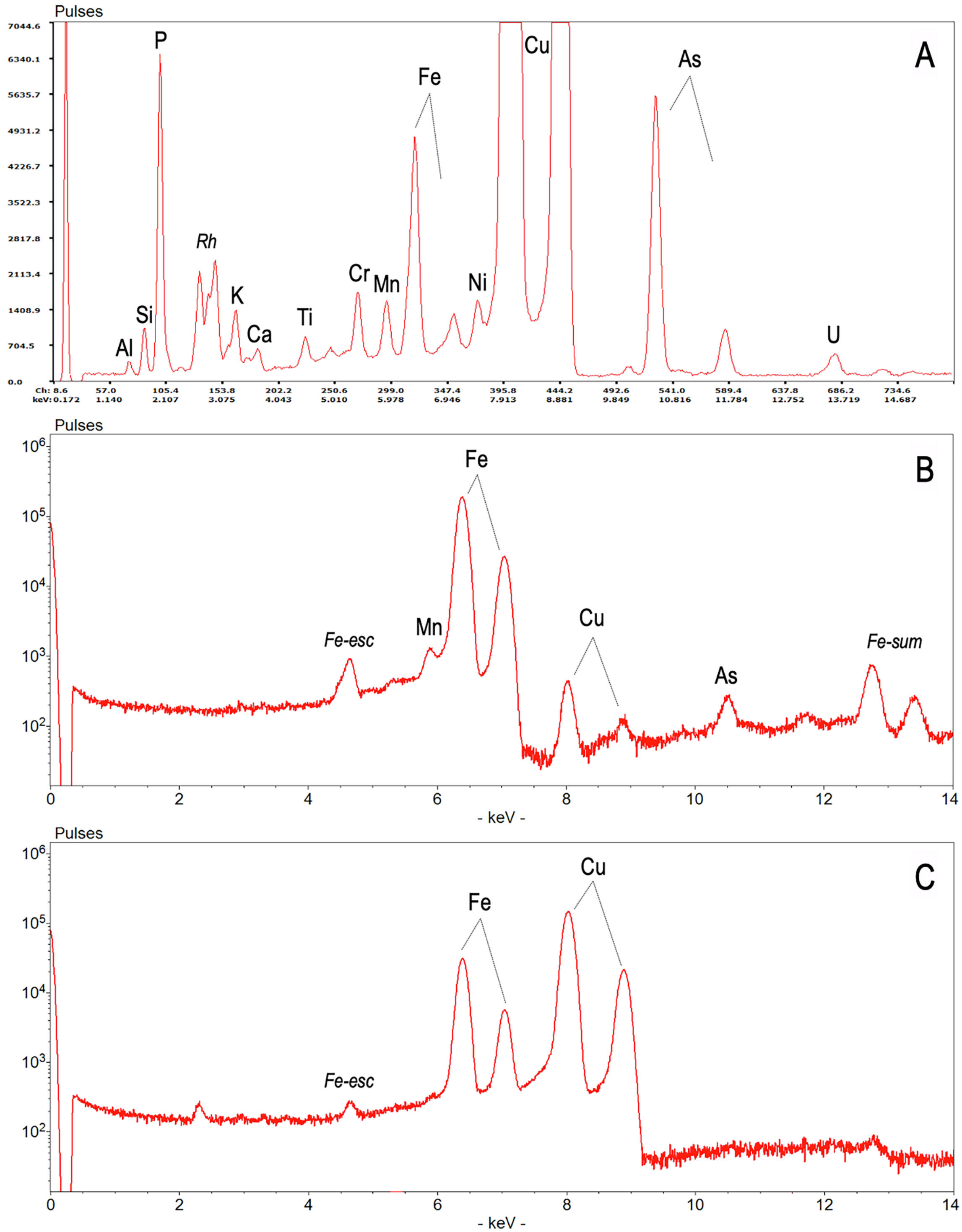

Fig. 7. EDXRF spectra of ore sample and metallurgical remains from surveyed copper mines, namely (A) copper ore FA-1-A of Fajoas; (B) slagged ceramic (crucible) GA-1-A3 of Ganhoteira; (C) slag fragment FA-1-A1 of Fajoas (Rh X-ray peaks belong to the X-ray source; Fe-esc and Fe-sum correspond to escape and sum peaks of iron).

4.4. Lead isotope analysis

All samples were analysed at the Geochronology and Geochemistry SgIker Facility of the University of the Basque Country UPV/EHU (Spain). Sample preparation was done in PP Class-A (ISO-5) laminar flow benches within an ISO-7 clean lab. Sample aliquots of about 10–50 mg were weighted in PFA vials and digested overnight with 0.5 ml of HNO_3 7 N at 70 °C. The solutions were evaporated to dryness and dissolved in 1 ml of HCl 1 N for chromatography. Pb was isolated from each sample by extraction chromatography, using a method adapted from Gale (1996). The final 0.4 ml solution of Pb in HCl 6 N was evaporated to dryness and stored for mass spectrometry.

Purified Pb samples were dissolved in 1.5 ml of HNO_3 0.32 N and conveniently diluted to obtain a concentration of about 200 ng Pb/g solution. The samples were introduced as wet aerosols into a Thermo Neptune MC-ICP-MS using an ESI 100 Âµl min^{-1} PFA nebulizer and a dual cyclonic-Scott double pass spray chamber. Malachite samples with Pb content lower than 100 ng Pb/g solution were diluted to a 20 ng Pb/

Table 2
Elemental composition of nodules from waste mineral heaps and artefacts from Chalcolithic sites in southern Portugal.

Site	Artefact	Ref.	Cu (%)	As (%)	Ni (%)	Sb (%)	Fe (%)	References
Ganhoteira	Nodule	GA1-B1	99.8	n.d.	n.d.	n.d.	< 0.05	this work
Fajoas	Nodule	FA1-B1	99.9	n.d.	n.d.	n.d.	< 0.05	this work
Fajoas	Nodule	FA1-B2	99.7	< 0.10	0.20	n.d.	< 0.05	this work
Fajoas	Nodule	FA1-B3	99.7	< 0.10	0.21	n.d.	< 0.05	this work
Fajoas	Nodule	FA1-B4	99.9	< 0.10	n.d.	n.d.	< 0.05	this work
Três Moinhos	Axe	TM-1	98.8	0.44	n.d.	0.78	< 0.05	Orestes Vidigal et al. (2016)
Três Moinhos	Chisel	TM-8	96.3	3.67	n.d.	n.d.	< 0.05	Valério et al. (2016)
São Brás 3	Axe	SB3-1	99.9	n.d.	n.d.	n.d.	< 0.05	Valério et al. (2016)
Porto Mourão	Axe	PM-2	99.5	0.40	n.d.	n.d.	< 0.05	This work

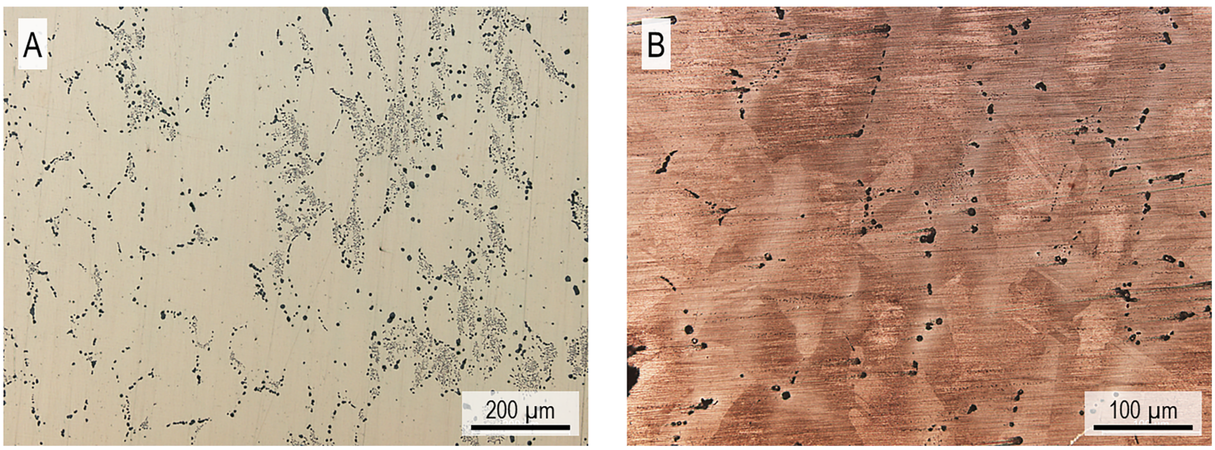

Fig. 8. Microstructure of PM-2 axe from Porto Mourão (A: Cu_2O inclusions resulting from the Cu–O eutectic system solidification; B: large grains with annealing twins).

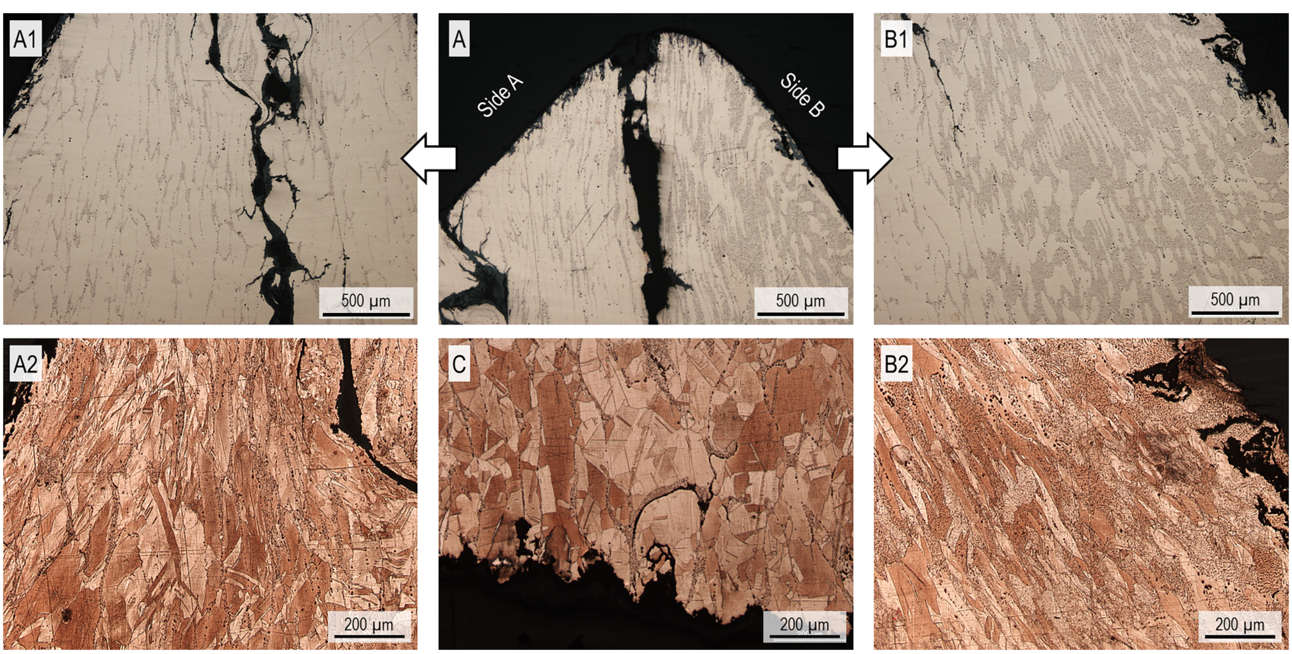

Fig. 9. Microstructure of SB3-1 axe cutting edge from São Brás 3 (A: tip of the cutting edge; A1-B1: sides A and B showing different density of oxide inclusions; A2-B2: sides A and B showing deformed grains with annealing twins; C: ancient fracture without cutting marks).

g solution and introduced as dry aerosols with an ESI 50 Âµl min^{-1} PFA nebulizer and an ESI Apex-IR desolvating unit.

Spectrometric (chemical + electronic) blanks have been subtracted with the On-Peak-Zeroes routine, measuring a blank 0.32 N HNO_3 solution before each sample for 60 s. The spectrometric method comprised a static multi-collection routine of 105 cycles with an integration time of 8 s per cycle. Instrumental mass bias was corrected online after the addition of a proportional amount of a solution of the thallium certified reference material NBS-997, and using $^{205}Tl/^{203}Tl$ = 2.3889 (Thirlwall, 2002). The accuracy and reproducibility of the method was verified by periodic determinations under the same conditions of the lead certified reference material NIST SRM 981 Common Lead Isotopic

Table 3
Pb isotope ratios of copper ores from mines in southern Portugal (chalcopyrite samples of Aparis, Rui Gomes, Corujeira and Serra da Preguiça mines; malachite samples of remaining mines).

Mine	Refs.	$^{206}Pb/^{204}Pb$	2σ	$^{207}Pb/^{204}Pb$	2σ	$^{208}Pb/^{204}Pb$	2σ	$^{208}Pb/^{206}Pb$	2σ	$^{207}Pb/^{206}Pb$	2σ
Aparis	AP-1	18.6823	0.0007	15.6589	0.0007	38.7216	0.0020	2.07264	0.00005	0.83817	0.00001
Minancos	MN-1	19.7170	0.0008	15.7429	0.0007	38.2722	0.0020	1.99180	0.00004	0.79844	0.00001
Rui Gomes	RG-1	21.2904	0.0019	15.7880	0.0019	41.1989	0.0059	1.93510	0.00015	0.74156	0.00003
Corujeira	CR-1	18.3570	0.0009	15.6240	0.0008	38.6380	0.0021	2.10481	0.00004	0.85112	0.00001
Serra da Preguiça	SP-1	18.6187	0.0007	15.6516	0.0007	38.7552	0.0019	2.08152	0.00004	0.84064	0.00001
Ganhoteira	GA-1	22.8755	0.0014	15.9185	0.0011	47.4821	0.0034	2.07568	0.00005	0.69588	0.00001
Fajoas	FA-1	18.7761	0.0008	15.7293	0.0007	38.6014	0.0018	2.05588	0.00003	0.83773	0.00001
Fajoas	FA-2	18.8277	0.0010	15.6796	0.0009	38.6719	0.0024	2.05399	0.00005	0.83280	0.00001
Fajoas	FA-2–3	20.2596	0.0009	15.7424	0.0007	38.2852	0.0022	1.92296	0.00004	0.77703	0.00001

Table 4
Pb isotope ratios of copper nodules from Fajoas waste mineral heap and artefacts from Chalcolithic sites in southern Portugal.

Site	Artefact	Ref.	$^{206}Pb/^{204}Pb$	2σ	$^{207}Pb/^{204}Pb$	2σ	$^{208}Pb/^{204}Pb$	2σ	$^{208}Pb/^{206}Pb$	2σ	$^{207}Pb/^{206}Pb$	2σ
Fajoas	Nodule	FA1-B1	17.4620	0.0007	15.5081	0.0007	37.5937	0.0019	2.15288	0.00005	0.88810	0.00001
Fajoas	Nodule	FA1-B3	18.8031	0.0008	15.6673	0.0007	38.7068	0.0022	2.05853	0.00005	0.83323	0.00001
Três Moinhos	Axe	TM-1	31.2250	0.0012	16.3298	0.0007	38.8069	0.0019	1.24281	0.00002	0.52297	0.00001
Três Moinhos	Chisel	TM-8	18.7051	0.0008	15.6893	0.0008	38.8069	0.0024	2.07591	0.00006	0.83877	0.00001
São Brás 3	Axe	SB3-1	18.5695	0.0009	15.6688	0.0008	38.6777	0.0021	2.08286	0.00005	0.84379	0.00001
Porto Mourão	Axe	PM-2	18.5909	0.0006	15.6838	0.0006	38.7776	0.0019	2.08584	0.00005	0.84362	0.00001

Table 5
Pb isotope ratios of copper nodules from the Chalcolithic settlement of São Pedro (Gauß, 2016).

Artefact	Ref.	$^{208}Pb/^{206}Pb$	2σ	$^{207}Pb/^{206}Pb$	2σ	$^{206}Pb/^{204}Pb$	2σ
Nodule	SP1	2.1075	0.02	0.8547	0.01	18.295	0.04
Nodule	SP2	1.9728	0.05	0.7891	0.14	20.029	0.67
Nodule	SP3	2.0705	0.39	0.8371	0.10	18.858	0.06
Nodule	SP4	2.0950	0.07	0.8494	0.01	18.397	0.34

Standard (Table 1).

5. Results

5.1. Elemental and microstructural characterisation

The elemental analysis of metallurgical remains of Ganhoteira and Fajoas mines clearly relates these materials with the copper metallurgy, i.e. the inner surface of the ceramic crucibles from Ganhoteira (GA-1-A3) has significant levels of copper and arsenic, while a slag sample from Fajoas (FA-1-A1) is highly enriched in copper (Fig. 7). The elemental analysis of copper ore samples from Fajoas shows the distinctive presence of uranium, in addition to arsenic and nickel (Fig. 7). Similarly, the copper nodules recovered in the larger waste heap of Fajoas proved to be composed of very pure copper (FA1-B1) or with traces of arsenic (FA1-B4) or even with traces of arsenic and a small percentage of nickel (FA1-B2 and FA1-B3) (Table 2). So, these copper nodules likely originated from smelting operations conducted in the vicinity of the mines, being the slightly different level of trace elements a predictable result of the variable conditions prevailing in prehistoric smelting operations. However, LIA results of these samples may or may not confirm this inference.

The elemental characterisation of the flat axe from Porto Mourão (Moura) indicates pure copper with some arsenic and very low content of iron (Table 2). The axes from Três Moinhos (Baleizão) and São Brás 3 (Serpa), in addition to a chisel from Três Moinhos were previously analysed, evidencing a composition of copper with variable arsenic contents (Orestes Vidigal et al., 2016; Valério et al., 2016). It should be noted that flat axes composed of pure copper and showing a typical as-cast microstructure have sometimes been considered to be ingots (Soares et al., 1994, 1996; Ruiz-Taboada et al., 2019). To shed some

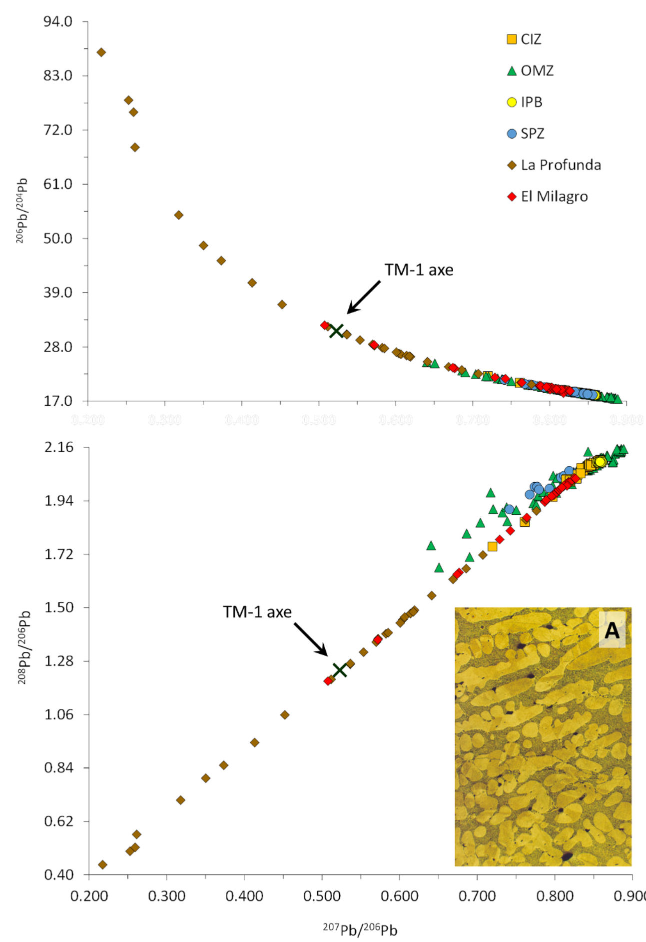

Fig. 10. Pb isotope ratios of TM-1 axe from Três Moinhos compared with Pb isotope ratios of copper ores from La Profunda, El Milagro and other mines located in the tectonostratigraphic zones of southwestern Iberian Peninsula (A: the dendritic microstructure of TM-1 axe, original magnification: 40×, Soares et al. (1994); see other references in text).

Table 6
Pb isotope ratios of artefacts from Chalcolithic settlements of Três Moinhos (this work), Penedo and Zambujal (Gauß, 2016).

Site	Artefact	Ref.	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$
Três Moinhos	Axe	TM-1	1.24281	0.52297	31.2250
Penedo	Axe	P1	1.2715	0.5387	30.000
Zambujal	Palmela point	Z559	0.4204	0.2119	91.762

light on this matter, the axe of Porto Mourão (PM-2: main body) and the axe of São Brás 3 (SB3: cutting edge fragment) were subjected to microstructural characterisation. The PM-2 axe has a very high density of Cu_2O inclusions resulting from the Cu–O eutectic system solidification, due to primitive conditions of the casting operation (Fig. 8). Moreover, it shows large grains with a few annealing twins evidencing some thermomechanical post-casting processing. The SB3-1 blade has a large fracture on the tip and a very high amount of oxides with an uneven distribution (Fig. 9). The side showing a significantly lower amount of oxide inclusions may correspond to the upper side of the flat axe casted in an open mould due to easier degassing of the upper side during cooling. Additionally, the elongated morphology of oxide inclusions and grains indicates shaping by hammering, while the existence of annealing twins shows that hammering was followed by annealing. The thermomechanical processing of these axes seems to confirm that they were indeed produced to be tools, but the high oxide density makes the metal brittle, causing fractures such as the one observed at the cutting edge of the SB3 axe. It must be noted that this axe fragment seems to have been broken since it does not show any cutting marks in the region of the ancient fracture (see Fig. 9C). Finally, the TM-1 axe, whose microstructure has been previously characterized (Soares et al., 1996), shows large grains with annealing twins coexisting with an as-cast microstructure with several pores and cracks. The elemental composition consists of copper with arsenic and antimony as impurities, although the content of the latter is relatively high. It must be taken into account that the higher antimony content together with the isotopic signature can give strong clues about the provenance of the copper metal used in the manufacture of this axe.

5.2. Lead isotope analysis

Chalcopyrite and malachite samples collected in OMZ mines and referred to above were subjected to Pb isotope analysis (Table 3). Additionally, Pb isotope ratios was determined in two copper nodules recovered in the larger waste mineral heap at Fajoas mine, as well as in four copper artefacts from Chalcolithic settlements located in the Guadiana basin (Table 4). In a first approach, copper nodules recovered

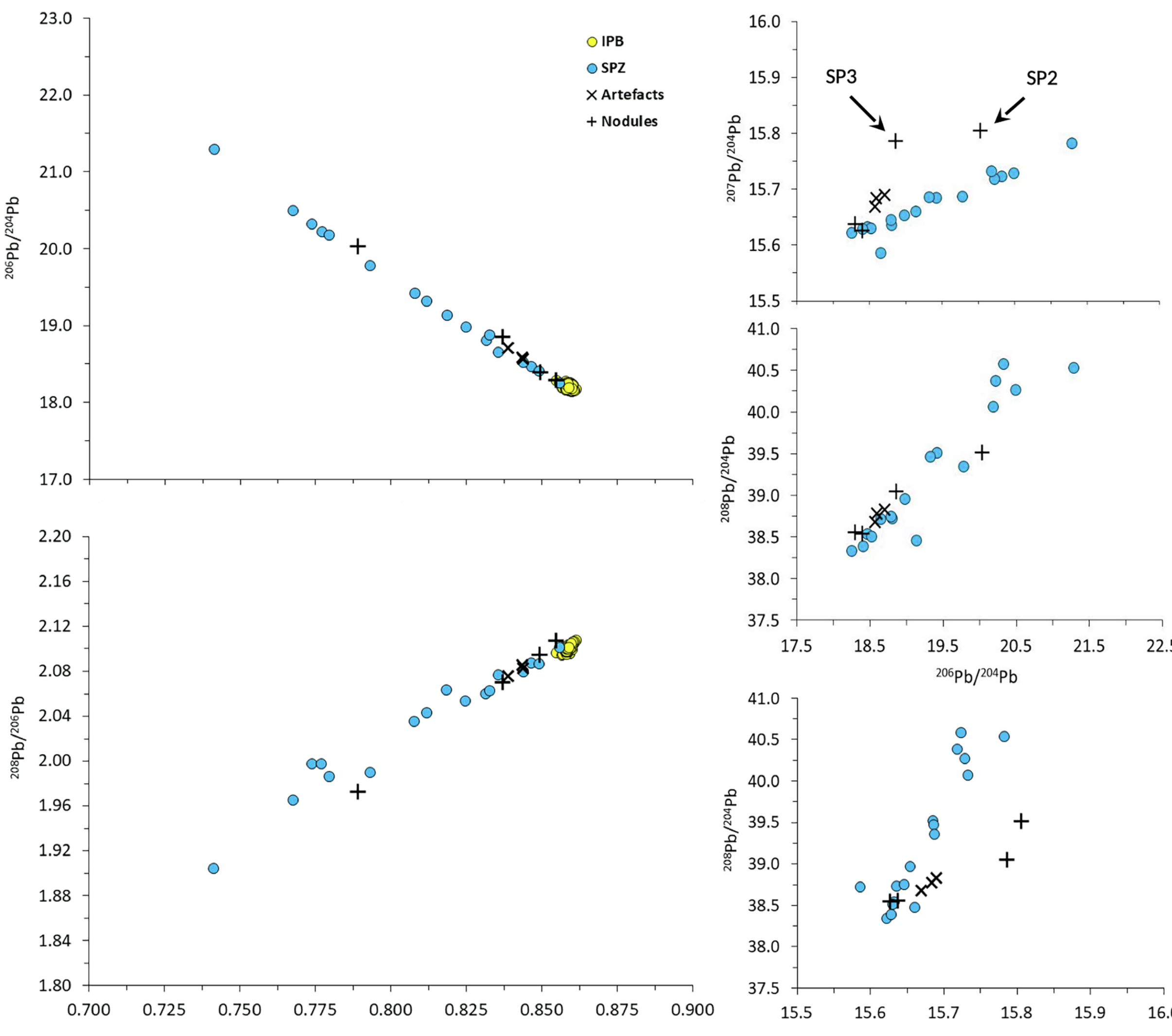

Fig. 11. Pb isotope ratios of artefacts (TM-8, SB3-1 and PM-2) and nodules (SP1, SP2, SP3 and SP4) from Chalcolithic settlements in southern Portugal compared with SPZ Pb isotope field (see references in text).

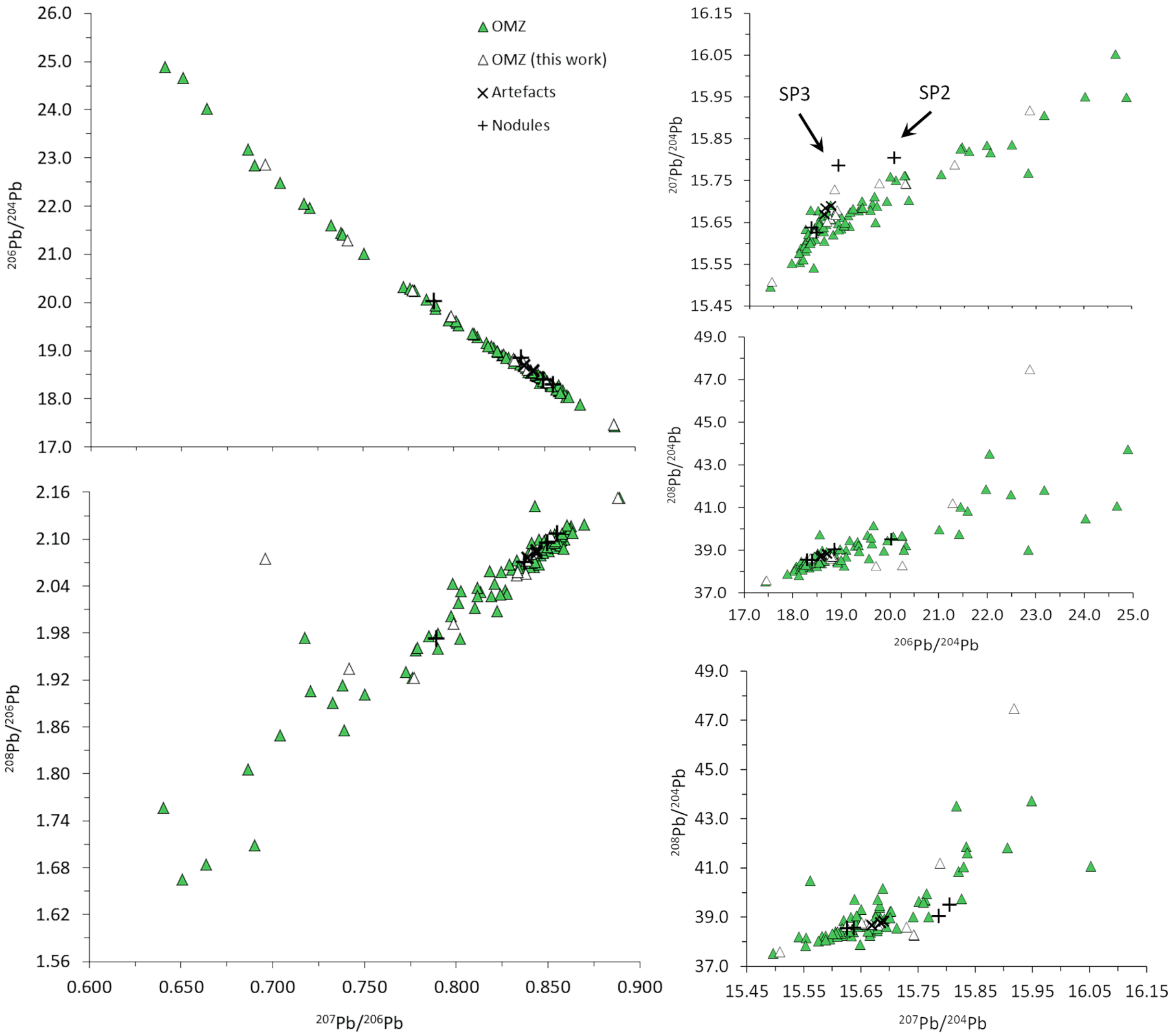

Fig. 12. Pb isotope ratios of artefacts (TM-8, SB3-1 and PM-2) and nodules (SP1, SP2, SP3 and SP4) from Chalcolithic settlements in southern Portugal compared with OMZ Pb isotope field (see references in text).

at the Fajoas larger heap most likely resulted from the smelting of local copper ores. Nevertheless, the Pb isotope ratios of these two nodules are somewhat distinct: $^{206}Pb/^{204}Pb$ of FA1-B1 has a value of 17.4620, while FA1-B3 nodule has a value of 18.8031 (Table 4), being integrable in the set of values determined for copper ore samples from Fajoas. In addition, FA1-B1 and FA1-B3 differ in their elementary composition (Table 2), which may also indicate a different provenance. While FA1-B3 may result from the smelting of copper ores from Fajoas, FA1-B1 (without nickel) may result from copper of any of the small copper ore bodies in the vicinity of Fajoas. Nevertheless, ores and nodules from Fajoas, together with the isotopic data in Table 3, will be used for the establishment of the OMZ isotopic field.

6. Discussion. Copper sources in southern Portugal during the Chalcolithic

Apart from four copper artefacts analysed in this work, only other four samples from southern Portugal were subjected until now to Pb isotope analysis, namely four copper nodules collected during archaeological excavations at the Chalcolithic settlement of São Pedro, Redondo (Table 5), all of which were assigned to the OMZ (Gauß, 2016). The LIA of six copper ore samples from this settlement were also published by Gauß (2016, Tabs. 10.13 and 10.14). Half of these ore samples show values of highly radiogenic Pb, while two samples have $^{206}Pb/^{204}Pb$ values of 18.996 and 18.124, and the last one a $^{206}Pb/^{204}Pb$ value of 17.885. These figures indicate that, similarly to that what occurs at Fajoas, probably more than one source should be attributed to the copper ores found at São Pedro.

The following considerations will seek to determine the copper sources of these eight artefacts using the LIA database of copper ores from mines located in geological zones of southwestern Iberian Peninsula.

Considering the OMZ, SPZ and CIZ copper ore databases, it is clear that the copper axe of Três Moinhos (TM-1) does not match any of these three isotopic fields, i.e. the 31.2250 $^{206}Pb/^{204}Pb$ ratio of TM-1 axe is much higher than the uppermost value of these zones, namely the value of 24.897 of the $^{206}Pb/^{204}Pb$ ratio of a malachite sample collected from OMZ Safira mine (Gauß, 2016). However, two mines, in the Iberian Peninsula, with traces of prehistoric works are known to have copper ores with very high radiogenic Pb, namely La Profunda ($^{206}Pb/^{204}Pb$ maximum of 87.7622, Huelga-Suarez et al., 2014b) and El Milagro ($^{206}Pb/^{204}Pb$ maximum of 32.3759, Huelga-Suarez et al., 2014a). The Pb isotope signature of TM-1 axe clearly matches the signatures of La Profunda and El Milagro (Fig. 10). Furthermore, a Sb content of 0.78% was determined in this flat axe (Table 2) and the presence of this element is recurrent in ores and prehistoric artefacts attributed to these

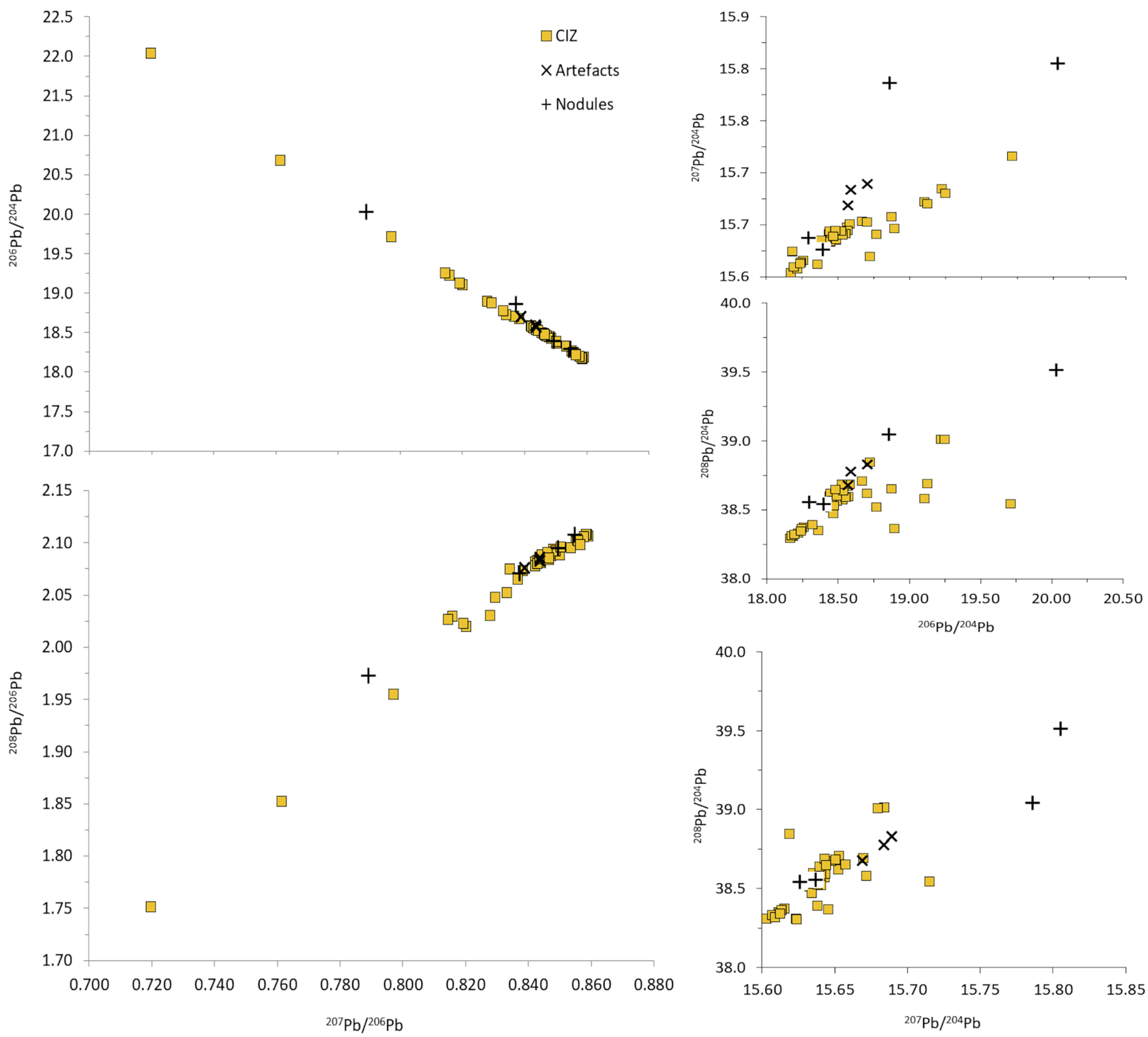

Fig. 13. Pb isotope ratios of artefacts (TM-8, SB3-1 and PM-2) and nodules (SP1 to SP4) from Chalcolithic settlements in southern Portugal compared with CIZ Pb isotope field (see references in text).

mines (De Blas Cortina, 1983; Reguera-Galan et al., 2019). In addition, the copper from several ingots from a hoard found not far from El Milagro mine, at Gamonedo, would also have its origin in these mines, although the hoard was tentatively attributed to the Early Bronze Age (De Blas Cortina, 1980, 2011; Reguera-Galan et al., 2019). Moreover, two artefacts from Chalcolithic settlements in Lisbon region, namely a flat axe from Penedo and a Palmela point from Zambujal, show highly radiogenic Pb (Table 6). The Pb isotope signature of Penedo axe is similar to the one of TM-1, thus also pointing to a provenance from La Profunda or El Milagro, while the much higher radiogenic Pb of the Palmela point from Zambujal only matches the signature of La Profunda mine. This correspondence points to a very probable metal trade between the Cantabrian Cornice and the southern Iberian Peninsula during the 3rd millennium BC.

The archaeological evidence of smelting operations in the immediate vicinity of mines has been gradually increasing, together with the scarce record of such operations inside Chalcolithic settlements in southern Portugal. For instance, the numerous metallurgical remains identified at the Chalcolithic settlement of Zambujal (one of the best studied settlements in Portugal of this cultural period) essentially concern casting operations, while smelting debris seem to be almost absent (Gauß, 2016). The metal would probably be transported from mines to settlements in the form of ingots, which are much more easily transportable than big amounts of ores. However, remnants of copper ores have been found in some Chalcolithic settlements perhaps from nearby copper mines, indicating that smelting operations may have taken place there. This is what it may have occurred in the São Pedro settlement (Valério et al., 2020), although no analysis has yet been carried out on the numerous crucibles collected there. Therefore, the Palmela point from Zambujal may have been locally produced using an ingot obtained with copper from La Profunda mine. Nevertheless, the production of the Palmela point in other region cannot be excluded, given the large distribution of such distinctive arrowhead typology during the Bell Beaker period.

Apart from a long-distance metal trade, the supply of copper metal or copper ores to nearby settlements where artefacts are manufactured should be much more common, as we will try to demonstrate next using the ^{206}Pb/^{204}Pb and ^{208}Pb/^{206}Pb versus ^{207}Pb/^{206}Pb ratios, in addition to ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb and ^{208}Pb/^{204}Pb versus ^{207}Pb/^{204}Pb of remaining analysed metals. Therefore, Pb isotope signatures of artefacts (TM-8, SB3-1 and PM-2) and nodules (SP1, SP2, SP3, and SP4) do not completely match the SPZ isotopic field (Fig. 11). Thus it seems obvious that copper must have a different origin and actually Pb isotope ratios of these metals match better the OMZ isotopic field (Fig. 12). Exceptions are SP2 and SP3 nodules, although it could be assumed that the SP2 ratio could result from a mixture of copper from

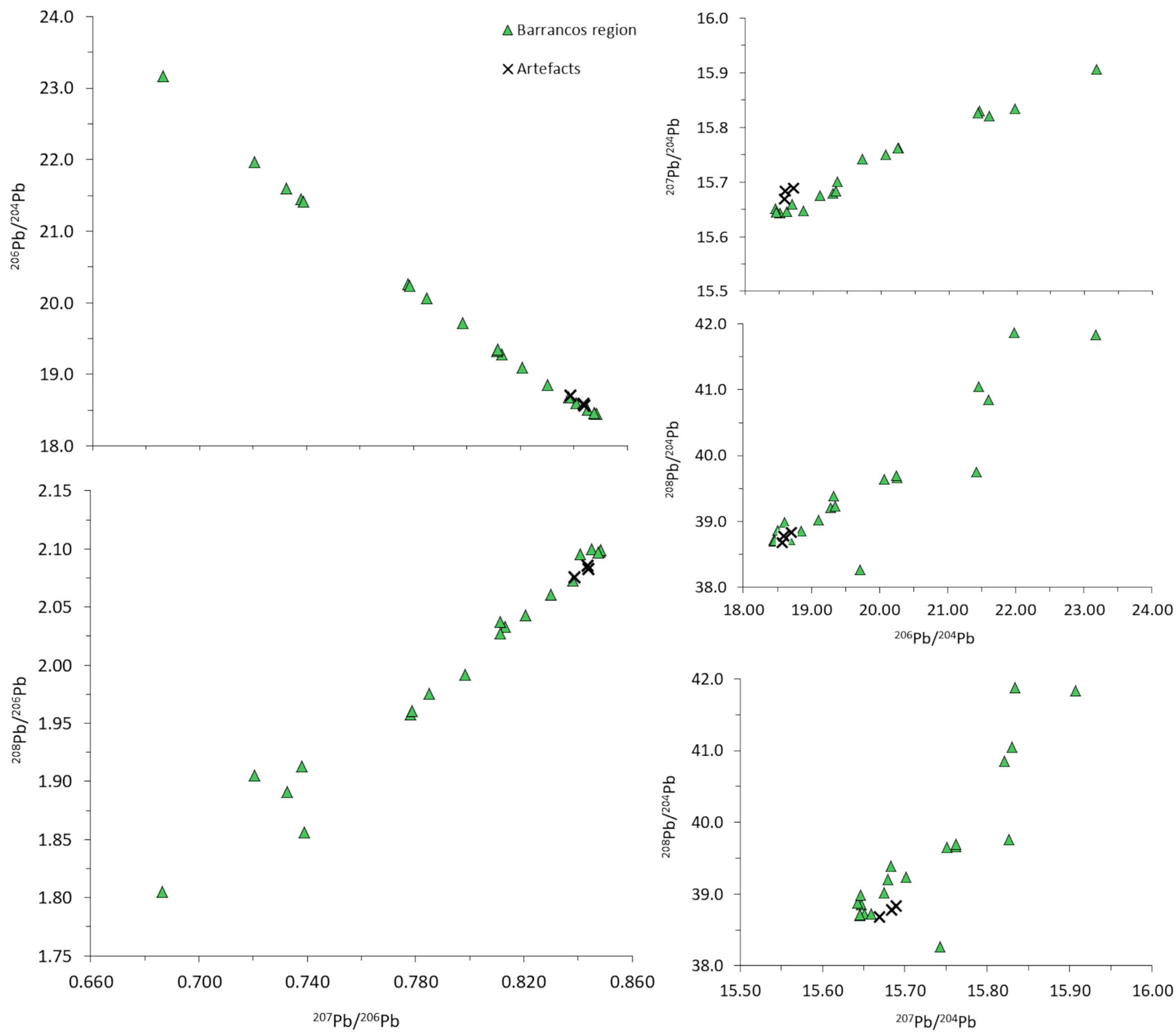

Fig. 14. Pb isotope ratios of artefacts (TM-8, SB3-1 and PM-2) from Chalcolithic settlements in southern Portugal compared with Pb isotope ratios of copper ores from mines located in Barrancos region (see references in text).

two or more OMZ ore bodies. Moreover, we cannot totally exclude this region for the source of copper of SP2 and SP3, given the identified heterogeneity and relatively low number of sampled copper mines. Regarding the CIZ, signatures of most of these copper metals clearly fall outside the Pb isotope field defined for this geologic region, namely when considering the ratios of $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ versus $^{207}Pb/^{204}Pb$ (Fig. 13). To sum up, the LIA suggests that copper of artefacts from Três Moinhos (with the exception of TM-1), São Brás 3, Porto Mourão and São Pedro should have come from the OMZ, although there is some uncertainty concerning two copper nodules from São Pedro settlement. It must be noted that while settlements of São Pedro and Porto Mourão are in the OMZ, the other two sites are in a transition area from OMZ to SPZ and the available data, although few, does not seem to indicate a trade originating in the southern area.

In the prosecution of the analysis of all these data, we tried to go a little further and to see whether it would be possible to determine a more precise origin for the metal artefacts and nodules in question. The mining district of Barrancos is located relatively close to the settlements of Três Moinhos, São Brás 3 and Porto Mourão (< 40 km, see Fig. 3), thus being a promising region for the copper supply. It should be noticed that Porto Mourão is located on the left bank of the Ardila river, which drains the Barrancos mining district. Besides, Três Moinhos and São Brás 3 settlements are located on the right and on the left bank, respectively, of the Guadiana River, downstream from the mouth of the Ardila river. The mining occurrences of Barrancos region are generally constituted by supergene copper ores, some of them showing evidences of prehistoric exploitation, such as the ore bodies of Volta Ferreira and Minancos. The comparison of Pb isotope signatures of abovementioned artefacts with samples from copper ore deposits of Barrancos region shows a possible match (Fig. 14). The small differences may be due to a mixture of copper from different local ore bodies and, thus, it can be argued that the copper of TM-8, SB3-1 and PM-2 artefacts may come from copper mines in Barrancos region.

Regarding the SP1 and SP4 nodules of São Pedro settlement, an additional comparison was made with ores from nearby mines (i.e. located at a distance < 30 km), namely Angerinha, Sobral das Minas, Venda do Duque, Monte Novo, Mostardeira, Vieiros, Mina do Bogalho, Mocissos, Oliveiras, Zambujeira, Mina dos Urmos, Entre Águas, Alcalainha, Souséis, Ganhoteira and Fajoas (Fig. 15). The exercise shows a good match between the Pb isotope ratios of SP1 and SP4 with the Pb isotope field defined by these mines, especially in the case of Souséis, Entre Águas, Zambujeira and Mostardeira. Therefore, these copper mines would be the best candidates for the metal sources of SP1 and SP4 nodules, but none of them shows vestiges of prehistoric works. Nevertheless, it should be emphasised that the archaeological research on ancient copper mining in this region is still very scarce.

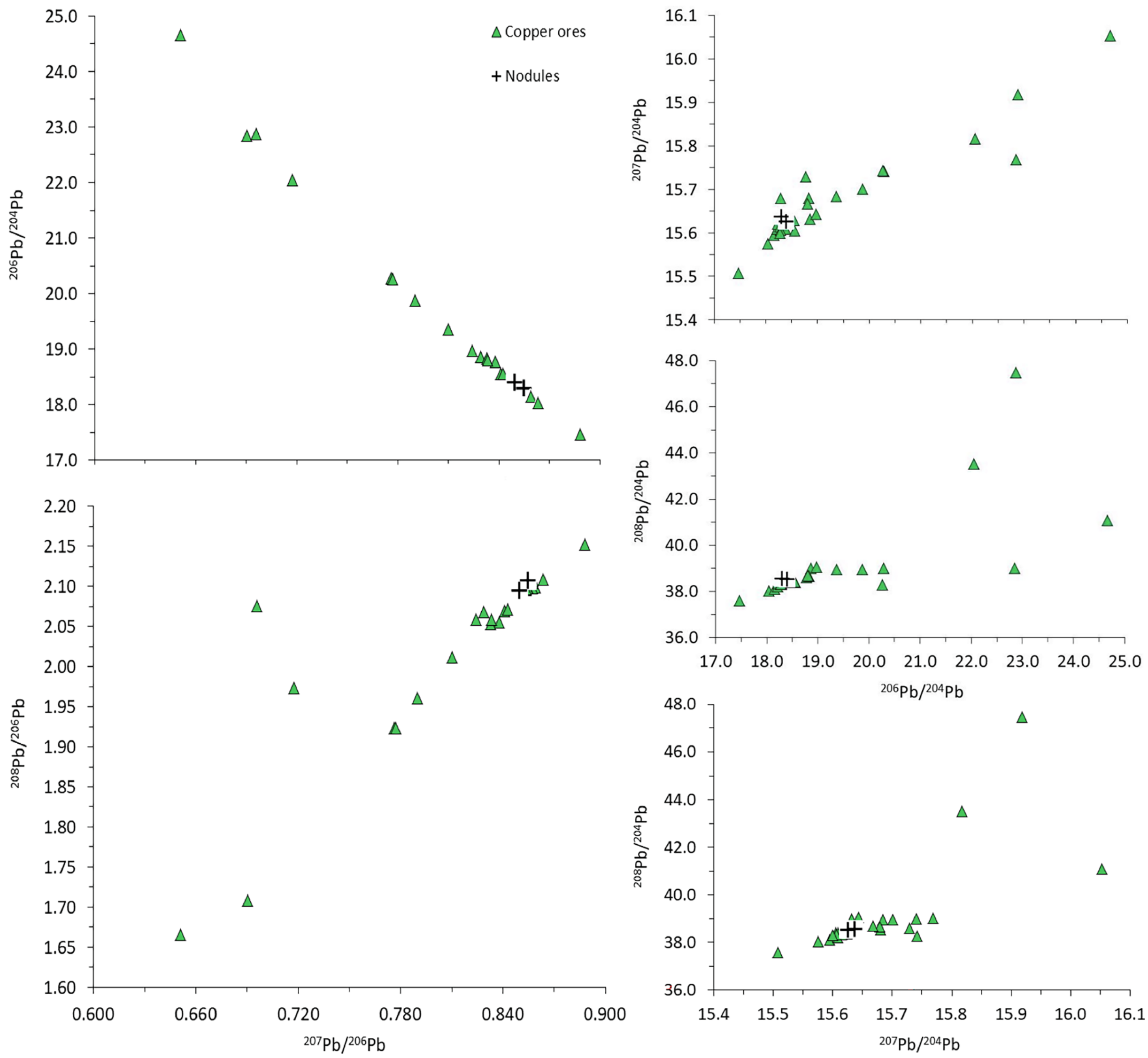

Fig. 15. Pb isotope ratios of nodules (SP1 and SP4) from Chalcolithic settlement of São Pedro compared with Pb isotope ratios of copper ores from nearby mines located in a distance < 30 km (see references in text).

7. Conclusions

Determining Pb isotope ratios of copper artefacts from Chalcolithic settlements in southern Portugal worked as a starting point for the LIA of copper ores from mines located relatively close to those archaeological sites, and, at the same time, revisiting Pb isotope databases of copper ores from geological zones where these sites are located or are close to them. Considering that the primary objective of the study was to identify copper sources of local settlements, it is worth noting that only a limited number of small mines (the ones that actually would be exploited in prehistoric times) have been sampled, and besides that only one or two samples from each mine have been analysed. Additionally, it is often unknown if the sampled ore corresponds to the section of the ore body that was object of ancient exploitation, which is especially important considering the heterogeneous Pb isotope fields of CIZ, OMZ and SPZ, excluding the much more homogenous IPB massive polymetallic sulphide deposits.

The study has shown that highly radiogenic Pb is not as rare as previously thought in southern Portugal, especially in the OMZ, where almost half of sampled small copper mines show such signature, which can provide a more reliable and precise determination of metal provenance. Nevertheless, the usual high heterogeneity of Pb isotopic ratios for the same ore deposit could hinder the assignment. The best sampled copper occurrences of OMZ show a high dispersion of $^{206}Pb/^{204}Pb$ values, for instance Aparis (5 samples: 18.68–19.33), Cala (5 samples: 18.4–19.1), Teuler (4 samples: 18.5–19.6), Minancos (4 samples: 19.72–20.26), Mercês I (4 samples: 21.5–23.2), Fajoas (4 samples: 18.78–20.26, excluding the value of 17.46).

In the Iberian Peninsula, the very high radiogenic Pb of the flat axe from Três Moinhos only has parallels in copper mines of La Profunda and El Milagro. For the first time, evidence is shown of copper trade between the Cantabrian region and the southwestern Iberian Peninsula and pointing to the probable use of copper ingots, at least in this long-distance trade.

The provenance of remaining copper artefacts from settlements in southern Portugal with known Pb isotope ratios (finished artefacts from Três Moinhos, São Brás 3 and Porto Mourão, and copper nodules from São Pedro) can probably be assigned to copper mines in the OMZ, while copper deposits in the SPZ and CIZ can be excluded, although data is still very scarce. More specifically, Pb isotope ratios of artefacts from the first three settlements match the Pb isotope field of Barrancos mining district. Matching is not perfect for two nodules from São Pedro, while the Pb isotope signature of the other two fits the isotopic field of copper occurrences located in a 30 km radius, suggesting, as with

Barrancos copper occurrences, a short-distance trade to nearby Chalcolithic settlements.

Weaknesses detected in Pb isotopic databases can be bridged with additional LIA of copper ores from small mining occurrences, with particular emphasis on copper deposits with traces of prehistoric exploitation. On the other hand, a study using LIA concerning the copper metal used in Chalcolithic settlements located near the Iberian Pyrite Belt or south of this region is needed, since no study of this kind has been carried out to date and, consequently, the precise origin of the copper used in these sites is not fully reliable.

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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