Journal of Iberian Geology

A lead isotope database for copper mineralization along the Guadalquivir River Valley and surrounding areas.

--Manuscript Draft--

Manuscript Number:	JIBG-D-20-00057
Full Title:	A lead isotope database for copper mineralization along the Guadalquivir River Valley and surrounding areas.
Article Type:	S.I. : New developments in Geochemistry. A tribute to Carmen Galindo
Funding Information:	Ministerio de Ciencia y Tecnología (CGL2015-63530-P) — Not applicable Ministerio de Ciencia y Tecnología (PIGMALIOM IV HAR-2010-16210, PIGMALIOM V HAR2017-82996) — Dr. Francisco Nocete Universidad del País Vasco (GIU15/05) — Not applicable
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Title:

A lead isotope database for copper mineralization along the Guadalquivir River Valley and surrounding areas.

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Abstract

The Guadalquivir River Valley constitutes the main geographic environment for the earliest development of political structures in the South of the Iberian Peninsula. The inception of Cu-metallurgy over the millennia 4th to 2nd BC in this region coincides with the rise of social complexity as well as the strategic control of the territory based on the command of the supply of mineral resources. One of the main tools in the study of metallurgical processes and goods movement is the analysis of metal provenance by means of Pb isotope composition. This study includes 98 new Pb isotope analyses performed on Cu mineralizations, many of them with archaeological evidence of exploitation by the first metallurgical societies. The results provided here represent a subtantial complement to those presented in published databases and allow for a better discrimination of potential sources for raw material supply of minerals used in the metallurgical processes. The existence of uncertainties introduced by the overlapping of Pb-isotope signatures of Cu-ores obtained from different geological contexts and presence of radiogenic Pb in a number of samples is pointed out.

Keywords: Lead isotopes, ore deposits, Cu-metallurgy, database, Southern Iberian Peninsula, Spain, Portugal

Declarations

Funding: This study was funded by grants from the Spanish Ministry of Science and Technology and the European Regional Development Fund (PIGMALIOM IV HAR-2010-16210, PIGMALIOM V HAR2017-82996, and MINECO/FEDER Project CGL2015-63530-P), and by the UPV/EHU (GIU15/05).

Conflicts of interest/Competing interests: The authors declare that they have no conflict of interest.

1. Introduction

The Guadalquivir River valley (Spain) has been the main axis of communication throughout the history of the SW of the Iberian Peninsula and was crucial at forming the first political structure of regional extension in the prehistory of western Europe between the 4th and 2nd millennia B.C. (Nocete 2001, Nocete et al. 2010). Archaeological information indicates that the generalized production, movement and consumption of copper-based metallurgical products across this area were decisive in the development of a complex, hierarchical network of populated emplacements (Bayona 2008; Nocete 2001; Nocete et al., 2011). This social and geographical system included settlements that received metal products or that had a domestic type of productive activity, such as La Junta de los Ríos and Soto (Huelva) near the Atlantic coast, and La Horca and Úbeda (Jaén) in the upper part of the valley (Nocete, 2008; Nocete et al. 2010, 2011; Bayona, 2015, 2018). Also, large metallurgical centers have been identified in the network. In some cases, they are linked to mining areas, as is the case of Cabezo Juré (Huelva) on the Iberian Pyrite Belt (Nocete 2004, 2006; Sáez et al., 2003). Other metallurgical centers, however, are located far from potential sources of raw material supply, such as Valencina de la Concepción and Carmona (Seville) at the former estuary of the Guadalquivir, and Marroquíes (Jáen) in the upper valley (Nocete et al. 2008, 2011; Bayona, 2015, 2018). The existence of centers of metallurgical production at a distance from potential sources of minerals adds complexity to the process of creation of political structures and calls for the need to evaluate their systems of harnessing resources. A first step to this purpose requires identifying the potential sources of metal ores by means of a reliable system.

The PIGMALIOM Project was a regional archaeological study conducted to evaluate copper metallurgy and its role in the emergence and development of social complexity in the Guadalquivir river valley (Nocete, 2000, 2001, Nocete et al., 2005 a, b; 2008, 2010, 2011).

Systematic archaeological prospects and excavations in the Guadalquivir Basin during the PIGMALION and related projects have revealed the recurring presence of copper artefacts in all of the hundreds of settlements of the Third millennium BC investigated. Moreover, the finding of copper ores, slags and crucibles in nearly thirty of the studied settlements indicate a spread of copper metallurgy along the Guadalquivir Basin between the 4th and 2nd millennia B.C. (Nocete, 2001, 2004, 2008; Nocete et al., 2008, 2010, 2011)

The sites of La Junta, Cabezo Juré and Soto in Huelva, Valencina de la Concepción and Carmona in Seville, and Marroquíes, La Horca and Úbeda in Jaén (Fig. 1) are representative of the different settlements along the axis of the most fertile soils and primary copper mining areas. They cover the observed variations in population, economic (settlements dedicated to mining, agriculture, etc.) and territorial variability (from 0.25 to 300 hectares of surface area). In these sites we developed a systematic program of archaeological extensive documentation and radiocarbon dating of the direct contexts of copper production (Nocete et al., 2011). From this program it was concluded that metallurgical activity was generalized across the whole of the Guadalquivir Basin at the beginning of the Third millennium BC. A complete understanding of this Chalcolithic society needs, however, additional information about the supply areas and catchment systems of copper ores resources, and about the circulation of copper ores and artefacts. Appropriate correlations to determine the source areas and the transportation networks require of good databases on the mineralizations located around the Guadalquivir Basin (Le Guen et al. 1991; Stos-Gale et al. 1995; Klein et al. 2009; Stos-Gale and Gale 2009). Several studies are available that report isotopic Pb data on metal mineralizations in the SW of the Iberian Peninsula, basically conducted to understand the origin of the mineralizations and their geodynamic framework (Marcoux 1998; Pomiès et al. 1998; García de Madinabeitia 2002; García de Madinabeitia et al. 2002; 2003, Tornos and Chiaradia 2004; Mateus et al. 2006). Furthermore, two interesting databases have been published to assist in the surveys for the origin of archaeological ores (Santos Zalduegui et al. 2004; Klein et al. 2009). These publications cover parts of the geographic field considered in our study (see Figures 1 and 2). In the aim to complete this information, we present 98 new analyses of Pb isotope composition on selected samples of Cu mineralizations from the areas surrounding the Guadalquivir Valley and its prolongation into south Portugal (Figure 2, Tables 1 and 2). A summary of the type of work carried out in the field and of the investigated materials can be seen in Figure 3.

2. Sampling and methods

Ore samples were obtained from mineralizations exposed on surface and from waste piles after systematic prospection using the 1:50.000 geological maps of the Spanish Geological Survey MAGNA series and their equivalents for south Portugal. Geographical location of samples and mine names are indicated in Tables 1 and 2. Also, a kmz file from Google Earth is provided as supplementary information for an easy tracking of the studied sample locations.

The analytical results presented below have been obtained in the SGIker-Geochronology and Isotope Geochemistry Facility of the University of the Basque Country (Spain). Samples of copper ores were crushed in an agate mortar and dissolved with concentrated nitric acid, and Pb was isolated from the Cu-rich matrix by conventional ion-exchange chromatography in HBr-HCl media. All employed reagents were triple-distilled at sub-boiling temperature before use. Lead isotopic ratios of samples labelled 'B', 'MRB', 'EAT' and “MIDAS 154” to “MIDAS 250” have been measured with a Finnigan MAT 262 thermal ionization mass spectrometer (TIMS). The measured ratios, given as an average of 10 blocks of 10 scans, were obtained in static collection mode using Faraday cups. The data were corrected off-line for mass fractionation by comparison with replicate analyses of the

NBS-981 Pb standard. Individual errors in Cu ore analyses are similar to those obtained for individual analysis of the NBS-981 standard (further details on the methodology are provided in Santos Zalduegui *et al.* 2004). Lead isotope ratios for samples labelled 'MIDAS 359' to “MIDAS 489” have been obtained at the same facility using a Neptune multi collector inductively coupled plasma mass spectrometer (MC-ICP-MS) with procedures described in Rodríguez et al. (2020). All Pb isotopic data are presented in Table 2.

3. Geological context of studied mineralizations

During its upper and medium course, the Guadalquivir River flows along the limit between a Variscan – pre-Variscan realm, and the Alpine Betic ranges of the southern Iberian Peninsula. This stretch is occupied by the geological units that conform the Guadalquivir foreland basin, bearing a triangular shape open to the Gulf of Cádiz (Figs. 1 and 2). This is an ENE-WSW-trending 400 km long foreland basin developed during the late Miocene in relation to tied flexural subsidence and stacking of thrust units of the external Betic Cordillera (Barnolas et al., 2019). The sedimentary infill is exposed along a topographic gradient from the Sierra de Cazorla uplands to the Atlantic Ocean, where sedimentation continues offshore in the abyssal plains of the Gulf of Cádiz. Along its northern boundary, a rectilinear unconformable contact may be delineated over mostly Palaeozoic basement rocks of the Iberian Massif. The Alpine orogenic domain to the South of the basin comprises detritic and carbonate materials ranging in age from the Triassic to the Quaternary. Small occurrences of mafic volcanic and subvolcanic rocks appear collated in the sedimentary sequences. In the basement along the domain to the North of the foreland basin, a Variscan and pre-Variscan orogenic region comprises rocks of Upper Proterozoic to Permian age that belong to the South Portuguese (SPZ), Ossa-Morena (OMZ) and Central Iberian (CIZ) zones of the Iberian Massif (Julivert *et al.* 1972; Quesada and Oliveira, 2019, 2020) (Fig. 2). The lithologies are highly diverse although with a marked predominance of magmatic and metamorphic types over those of a purely sedimentary origin. The regional structure corresponds to a series of bands running in a WNW-ESE direction and essentially parallel to the dominant directions arising from the Variscan orogeny. In many cases, these bands represent units with differentiated geological characteristics. From the geographical standpoint, it comprises a fairly homogenous morphological unit known as Sierra Morena. Its overall relief is of the Appalachian valley and ridge type, with a marked Alpine rejuvenation in the proximities of the river.

The main sources of supply of raw mineral materials used in the extractive metallurgy of Cu would be related to various types of mineralizations associated with the Variscan – pre-Variscan domain and, in the case of the Alpine domain, with Permo-Triassic formations of red sandstones (New Red Sandstone), the development of which is limited to the upper course of the Guadalquivir in Spain and to the so-called Mesozoic Orla in the Algarve, Portugal.

3.1. *Mineralizations associated with the Variscan – pre-Variscan domain*

As noted earlier, this domain in the proximities of the Guadalquivir Valley has considerable geological complexity, a fact that is also expressed in a great diversity of mineralizations susceptible to have been sources of supply for ancient metallurgical activities.

The trait of the Valley from the NE to the SW successively traverses the southern concealed prolongation of the three geological zones referred to above: CIZ, OMZ and SPZ (see Fig. 2). The limits between zones have been established in terms of tectonic and stratigraphic criteria (Julivert *et al.* 1972; Vera, 2004; Quesada et al., 2019, 2020). Although the precise location of these limits does not appear as being definitively closed, for the purposes of this work, it is assumed that the limit between CIZ and OMZ is located in the area known as Badajoz-Cordoba shear band (Burg *et al.* 1981; Ábalos et al. 1991a; Azor *et al.* 1994) for the Variscan events and north of it, along the so-called Obejo-Valsequillo-Puebla de la Reina domain, i.e. close to the Los Pedroches batholith, for the pre-Variscan evolution (e.g. Eguíluz et al. 2000; Bandrés et al. 2004).

The limit between the OMZ and SPZ zones is better established and is considered to be located in the South Iberian Shear Zone (Crespo-Blanc and Orozco 1988; Ábalos et al. 1991b; Simancas 2004; Ribeiro *et al*. 2010).

3.1.1. *The Central-Iberian Zone (CIZ)*

This zone is represented in the area studied by the Los Pedroches batholith and its surroundings, and by the south-eastern foothills of the Alcudia Valley. The overall direction of structures is WNW-ESE, caving obliquely with respect to the course of the Guadalquivir at an approximate angle of 30°. In the proximities of the Guadalquivir River there are rock outcrops with ages ranging from the Upper Proterozoic to the Carboniferous. Different types of variably metamorphosed metasediments and magmatic rocks predominate. Igneous rocks comprise an important part of the geological record of the region and have an important effect on the metallogenic activity. Roughly speaking, two magmatic cycles are distinguished: (i) a pre-Variscan one represented by volcanic and sub-volcanic rocks interbedded in the Palaeozoic series (e.g. Palero 1991); and (ii) a late-Variscan cycle represented in the study area by the Los Pedroches batholith and associated plutons (Defalque *et al.* 1992; Larrea *et al.* 2004). The latter accounts for a complex magmatic alignment that includes rocks with ages ranging from ca. 314 to 295 Ma (Bea 2004; Carracedo et al. 2009). Associated mineralizations within the batholith and in adjacent areas appear in fractures with different orientations. Mineralizations slotted into lengthwise fractures and transversal to the predominant direction of the batholith correspond to the vein type. Mineralizations of Cu and of Cu-U prevail within the batholith, whereas towards the edges and in the peri-batholithic surrounding, mineralizations of Sn-W, Pb-Zn and of Bi are more common. Towards the SE, the batholith dismembers into several individualized granitic plutons (Cardeña, Linares, Guadalén/Arquillos) and the Santa Elena stock which contain outstanding mineralizations of Pb-Zn-Ag and, to a lesser extent, Cu (Linares-La Carolina mining areas). Towards the N of the batholith and outside its area of influence, lie the mining districts of Almadén (Hg) and Valle de Alcudia (Pb-Zn ±Cu), that are not included in this article as there are relatively recent works on the isotopic composition of Pb for most of the sites already published (García de Madinabeitia 2002; Santos Zalduegui *et al.* 2004; Higueras *et al.* 2005) and because they are quite distant from the area covered by this study.

In this work two sampling areas have been considered, one directly related with different types of igneous rocks of the Los Pedroches batholith and associated plutons, cited in Table 2 as “Los Pedroches batholith”, and other related to mineralizations in the nearby host rocks, North of the batholith except sample MIDAS 233 to the South, and cited in Table 2 as “Culm Pedroches”.

3.1.2. *The Ossa-Morena Zone (OMZ)*

The Ossa-Morena Zone is part of the southern branch of the Variscan orogen in the Iberian Peninsula and was sutured to the Central Iberian and South Portuguese zones during Cadomian and Variscan orogenic cycles (Eguíluz *et al.* 2000) (Fig.2). The dominant structures trend NW-SE and, as for the CIZ, collide obliquely into the structural alignment that sets the limit with the Alpine domain (*cif.*: Guadalquivir Fault). On a large scale, it represents a mobile strike-slip zone with considerable tectonic, stratigraphic and metallogenetic complexity (Tornos *et al.* 2002; 2004). Outcropping materials include diverse types of Precambrian and Palaeozoic series, as well as a great variety of magmatic and low- to high-grade metamorphic rocks.

Due to the high geological complexity of the OMZ, different subzones, domains or terranes have been proposed (e.g. more than 20 in Dallmeyer and Martínez García, 1990). In this work, we have adopted a simplified scheme following more recent studies (e.g., Eguiluz et al., 2000; Ábalos et al., 2002), which is as follows: (i) northern Ossa-Morena, related to a Cadomian suture zone reactivated during Variscan times, it is bounded by the Peraleda fault to the north and the Malcocinado fault to the south and includes the Obejo-Valsequillo sector and the Blastomylonitic shear band; (ii) central Ossa-Morena, this is the largest sector comprising most of the 'domains' of the literature (Olivenza-Monesterio, Barrancos-Hinojales, etc.), with abundant rocks of the Ediacaran Serie Negra (Black Series), and metamorphic areas and intrusives of Cadomian and Variscan ages, it goes from the Malcocinado fault to the north up to the a series of minor faults to the south that separate it from, (iii) southern Ossa-Morena, an area related to a Variscan suture that comprises the metabasites of the Aracena-Acebuches metamorphic belt and a number of mafic to felsic Variscan intrusives. For additional information and equivalence of domain names of the literature with the simplified scheme adopted here, the reader is referred to the works mentioned above.

Unlike the surrounding areas (CIZ and SPZ), magmatism in the OMZ is characterized by the abundance of basic rocks and by a continuity over time (Galindo and Casquet 2004; Casquet and Galindo 2004) with peaks of high activity during the Upper Proterozoic, Cambrian, Ordovician and Carboniferous. From the metallogenetic viewpoint, the OMZ is characterized by the abundance of deposits associated with the Cadomian and Variscan cycles (Tornos et al. 2004). The deposits associated with the Cadomian cycle show general features typical of magmatic arcs along plate edges, whereas those from the Variscan cycle cover a wide range of mineralization types, from magmatic to hydrothermal and sedimentary. Interpretation of a section of the middle crust imaged in seismic profiles as a large body of mafic rocks related to the Variscan cycle (i.e., IRB: Iberseis Reflective Body, Simancas et al. 2003) might support a link between the magmatic and metallogenetic evolution of the OMZ during this orogenic cycle, though other interpretations also exist (Pous et al., 2004; Puelles et al., 2014).

The distribution and diversity of mineralizations in the OMZ is remarkable. In their synthesis on the metallogeny of the OMZ, Tornos et al. (2004) proposed the existence of a series of metallogenetic belts which, roughly speaking, follow the same structural pattern as the tectonostratigraphic domains proposed by Apalategui *et al.* (1990), although some of the alignments proposed in fact overlap with the CIZ. Isotopic data for Pb from 26 different types of mineralization by Tornos and Chiaradia (2004) show a broad range of compositions and indicate two main metallogenetic events, associated with the Cadomian and Variscan orogenic cycles. Most of the values presented by these authors fall below the growth curve by Stacey and Kramers (1975), which suggests a mixture between crustal Pb and mantle sources. This mixture appears to be more evident in the case of mineralizations associated with the Variscan cycle (Tornos and Chiaradia, 2004).

3.1.3. *The South Portuguese Zone (SPZ)*

The South Portuguese Zone occupies the SW part of the Iberian massif. The northern boundary of the zone is marked by a band of metamorphosed mafic rocks, the Beja-Acebuches amphibolites (Simancas 2004 and refs. included). Along the south side, it borders with sediments of Alpine coverage in the Guadalquivir basin and its extension into the Mesozoic sediments of the Portuguese Algarve (Barnolas et al., 2019). In the SPZ, outcropping rocks show ages ranging from the Middle Devonian to the Permian.

Traditionally, three domains with different stratigraphic features have been distinguished within the SPZ. The northernmost, defined as the Pulo do Lobo Group (Schermerhorn 1971; Carvalho *et al.* 1971; Quesada, 1998) is made up of several predominantly detritic formations that include mafic subvolcanic rocks with MORB affinity (Giese and Bühn 1993) and whose ages have been established as Devonian (Oliveira 1990).

The central band of the SPZ is made up of the Iberian Pyrite Belt (IPB), which is considered one of the metallogenetic provinces with the highest concentration of massive sulphides in the world. The stratigraphic record of the IPB includes sedimentary and magmatic rocks with ages ranging from the Upper Devonian to the Carboniferous. Its evolution during Devonian times is marked by the sedimentation on a relatively shallow siliciclastic platform (Moreno and Sáez 1990), giving rise to thick predominantly shale sequences with sporadic intercalations of sandstones (quartz-arenites and quartz-rich wackes of the so-called basal Phyllite-Quartzite Group or PQG). During the uppermost Devonian and up to the Middle Visean, an extensional episode occurred the consequences of which are recorded in the fragmentation of the Devonian platform (Moreno *et al.* 1996), intense bimodal magmatic activity (Sáez *et al.* 1996) and an important metallogenetic event of massive sulphides that brought up the formation of the deposits of the IPB (Leistel *et al.* 1998; Sáez *et al*. 1999). This stage corresponds to the stratigraphic unit regionally known as the Volcano Sedimentary Complex (VSC), which hosts the mineralizations of massive sulphides characteristic of the region. Turbiditic synorogenic deposits of Culm facies overlie the VSC in the region (Moreno 1993). During late- and post-Variscan times, a bimodal intrusive event occurred in the SPZ. The most extensive outcroppings of these magmatic rocks appear in the NE part of the Pyrite Belt comprising the batholith of the Sierra Norte of Seville (De la Rosa and Castro 2004).

The southernmost domain of the SPZ is known as the Carrapateira Group or SW Portuguese Domain. Its outcrops are circumscribed by the Aljezur and Bordeira antiforms.

The stratigraphic record covers a belt with ages similar to the IPB but, unlike this, there is no magmatic activity associated with its evolution during the Devonian and the Carboniferous periods. Data pointing to existence of metal mineralizations in this domain are lacking so far.

As noted earlier, the mineralizations in the SPZ are concentrated in the Iberian Pyrite Belt. There are two large groups of mineralizations in this domain: (a) pre-Variscan mineralizations of Mn and massive sulphides related to volcanic-sedimentary processes, and (b) vein-type mineralizations associated with the late- and post-Variscan evolution of the region. The latter have received scarce coverage in the research studies probably due to its small size and minor economic relevance. Nevertheless, like in the case of the massive sulphides, many of them show evidence of exploitation in remote periods of history (Blanco and Rothenberg 1981). The massive sulphides are syngenetic and occur associated with volcanic and sedimentary rocks of the VSC. Isotopic data on Pb published to date for this type of mineralization and related stockwork mineralizations (Marcoux 1998) highlight a considerable degree of homogeneity at regional scale and also at the scale of the site (Pomiès *et al.* 1998). Late- and post-Variscan hydrothermal mineralizations appear as vein and small replacement masses after the sedimentary and volcanic rocks of the three main lithological groups or units of the Belt (i.e., PQG, VSC and Culm), and also in veins of the late-Variscan plutonic rocks. Generally, they show more radiogenic isotopic values of Pb than those common for the massive sulphides (Marcoux and Sáez 1994).

3.2. *Mineralizations associated with the Betic domain*

In inland zones of the Betic mountain ranges, there exist several ore deposits of widely diverse substances. However, as regards the influences on the area studied, the only recognized mineralizations of interest are found in the upper course of the Guadalquivir and in the Mesozoic Orla of the Algarve (Portugal). This entails “roller front” type mineralizations of Cu associated with red sandstones dating from the Permian and Triassic periods. They comprise small mineralized bodies with associations of minerals typical of the oxidized zones of Cu sites, including malachite, azurite and cuprite as characteristic minerals. The most important deposits are located in the surroundings of Navas de San Juan, Jaén (Torres and Fernández 1983). Similar mineral associations have been identified as related to red sandstones near Silves in the Algarve (Portugal).

4. **Pb isotope results**

The results of the isotopic analyses of Pb ores conducted for this study and the geographic location by means of UTM coordinates of the sampled sites, together with their host-rock environment, are shown in the Tables 1 and 2. Their location in the geological context of the Iberian southwest is shown in Figure 2. The data obtained are presented in the diagrams commonly used in the analysis of metal provenance as applied in archaeometallurgical studies. These diagrams are ^{207}Pb/^{206}Pb *versus* ^{208}Pb^{206}Pb and ^{207}Pb/^{206}Pb *versus* ^{206}Pb^{204}Pb. The general representation of the data (Fig. 4) highlights a wide range of values, out of which three main groups, hereafter referred to as Groups 1, 2 and 3, have been established. One of these groups, the Group 2, is in turn subdivided in a number of more detailed subgroups. Their composition from less radiogenic to more radiogenic is as follows:

Group 1: It is represented by just two samples from the La Preciosa mine (Peñaflor, Seville), whose mineralization, pyrite and chalcopyrite principally, is associated to Upper Proterozoic rocks of the high-grade metamorphic core of Lora del Río (central OMZ). Similar values have been reported for mineralizations elsewhere within old metamorphic or sedimentary domains of the the Ossa-Morena Zone and also of the Alcudia Valley in the Central Iberian Zone (Santos Zalduegui et al., 2004; Tornos and Chiaradia, 2004).

Group 2: This is the main group comprising 79 samples. It forms a compact cluster covering mineralizations of almost all the geological contexts considered in this study. A close inspection expanding the scale of the axes highlights the existence of 4 main subgroups: 2A, 2B, 2C and 2D, while an additional enlargement of the diagram allows to subdivide further 2A and 2B into 2A1, 2A2, 2B1 and 2B2 subgroups (Figure 4).

Subgroup 2A1: It includes 17 samples, out of which 16 are from the Iberian Pyrite Belt in the SW of the investigated area (SPZ) that correspond to: (i) 12 samples of massive sulphides, specially pyrite, chalcopyrite ± galena, and associated gossans (with goethite and hematite as representative minerals) related to the Carboniferous VSC; and, (ii) 4 samples with more complex parageneses from veins related to the Devonian materials of the PQG. The one exception within this group is sample MIDAS 437 from Posadas, within the Cadomian Olivenza-Monesterio antiform in central OMZ.

Subgroup 2A2: It forms the largest cluster within Group 2, with 35 points that correspond essentially to 28 samples from the Linares-La Carolina mining area (Jaén) and nearby localities (Guarromán, Carboneros, Baños de la Encina, Villanueva de la Reina, Andújar, Vilches, Cardeña and Montoro). In this case, the main mineral is galena with associated pyrite and chalcopyrite, while secondary phases are cerussite and malachite, among others. All of them are associated to Variscan granodiorites-monzogranites of the Los Pedroches batholith and the metamorphic rocks of the contact aureole or their sedimentary precursors, that is, the Carboniferous Culm of Los Pedroches in the Central Iberian Zone. This subgroup also includes a few scattered mines toward the West of this area, namely three samples related to metamorphic rocks of Cambrian age from the Cerro Muriano area in northern Ossa-Morena, one rare sample (MIDAS 248) close to the Cala ore district (La Vicaría mine) in central Ossa-Morena, which departs from the composition of other Cala samples analyzed in this work (see below). Finally, three samples are from veins in the Iberian Pyrite Belt, two of them (MRB158, MIDAS 448) from the Portuguese section of the IPB.

Subgroup 2B1: It corresponds to samples from 8 mines; 4 from the Cardeña area within igneous rocks (granite porphyries) of the Los Pedroches batholith in the CIZ, 3 from scattered outcrops in the Cheles-Barrancos sector of central Ossa-Morena, also associated to igneous rocks, and one from a vein in the Iberian Pyrite Belt. In this case the parageneses are more complex. In general, galena is very abundant with secondary minerals as malachite, cerussite, chrysocolla and goethite.

Subgroup 2B2: It includes 11 mines and is the most heterogeneous subgroup in terms of sample provenance. Four samples are from veins in the Iberian Pyrite Belt. Other 4 are from mine shafts at Hornachuelos in Central Ossa-Morena, geographically to the SW and close to the sampling area of Group 2B1. Two samples are from host rocks of the Los Pedroches batholith. And, finally, one sample is from the Obejo-Valsequillo domain in Northern Ossa-Morena. As in case of group 2B1, secondary minerals are very frequent, specially malachite.

Subgroup 2C: It comprises samples from 5 mines that are distinctly more radiogenic than those of the previous sets. The subgroup is also heterogeneous in terms of areal distribution. Three samples are associated to the Permo-Triassic sedimentary materials of the New Red Sandstone in the Betic domain, one sample is from the Obejo-Valsequillo area of northern Ossa-Morena and another one is from a vein in the Iberian Pyrite Belt. As in the case of subgroups 2B1 and 2B2, secondary minerals (malachite, azurite) are notorious.

Subgroup 2D: It is made of samples from 3 mines geographically scattered that, in the $^{207}Pb/^{206}Pb$ *versus* $^{208}Pb^{206}Pb$ and $^{207}Pb/^{206}Pb$ *versus* $^{206}Pb^{204}Pb$ diagrams, are related to the samples of subgroup 2A but without a clear relationship with the previously defined clusters. It includes sample MIDAS 441, from El Centenillo, the only sample in this work collected in Ordovician materials from the Alcudia Anticline (CIZ).

Group 3: This group is characterized by highly radiogenic lead (Table 2 and Fig. 4), and comprises ten samples from different localities (Andújar, Baños de la Encina and Villanueva de la Reina) in the Los Pedroches batholith of the Central Iberian Zone. Three more samples are from the Cheles-Barrancos sector and two are from the Cala skarn, all in central Ossa-Morena. Finally, another three samples are associated with IPB veins from Portugal. At the Los Pedroches batholith, the samples correspond to Cu-U mineralizations, sometimes with presence of torbernite and autunite. In fact, the presence of exploitable U ores in this sector of the batholith has been known for long (e.g., Arribas Moreno, 1963, Ministerio de industria, 1971). Similar large dispersion of analytical data in Pb/Pb diagrams has been related to the presence of U-bearing minerals elsewhere within the Iberian massif (e.g., Huelga-Suárez, 2014).

5. **Conclusions**

The 98 new Pb isotope analyses on Cu mineralizations, many of them with archaeological evidence of exploitation by the first metallurgical societies, presented in Tables 1 and 2 and commented in previous sections of this study represent a substantial complement to those already availabale in published databases. These new data will allow for a better discrimination of potential sources for raw material supply of minerals used in the metallurgical processes. Our results, that concern principally the Pb isotope composition of Cu mineralizations from the areas surrounding the Guadalquivir Valley and its prolongation into south Portugal, clearly show that those samples from the groups where the primary mineralization predominates, like those of subgroup 2A1 (sulfides or directly related gossans from the Iberian Pyrite Belt) or subgroup 2A2 (galenas from the Los Pedroches batholith area), present a restricted range of isotope values and plot on well-defined fields of the Pb/Pb diagrams. A note of caution is however imposed since there exist some uncertainties due to the overlapping of Pb-isotope signatures of Cu-ores in provenance of different geological contexts. Thus, the isotopic compositions of samples from groups in which the secondary mineralization appears to have been extensive (subgroups 2B1 and 2B2), present a greater dispersion regardless of the geological domain or context to which they are associated. Finally, the deposits of the so-termed Group 3, in all probability associated with minor U mineralizations, constitute a special case. Samples of this group show a large dispersion of isotope values albeit following a linear tendency, a fact that in principle is to be linked to their U content and the radioactive disintegration of this element. The identification of U-bearing copper ores that could have been exploited in ancient times in the south of the Iberian peninsula may give a successful provenance interpretation to rare copper and bronze artifacts from the region that have highly-radiogenic lead isotope ratios. In our experience, it is not uncommon that one or some of these artifacts are analyzed together with a larger number of isotopically-conventional (i.e., less radiogenic) archaeological samples. Their oddity make them prone to be discarded in provenance interpretations and their isotopic data are eventually not published.

Acknowledgements

Financial support for this work has been provided by grants from the Spanish Ministry of Science and Technology and the European Regional Development Fund (PIGMALIOM IV HAR-2010-16210, PIGMALIOM V HAR2017-82996, and MINECO/FEDER Project CGL2015-63530-P), and by the UPV/EHU (GIU15/05). We also thank technical and human support provided by the Geochronology and Isotope Geochemistry SGIker facility (UPV/EHU, MINECO, GV/EJ, ERDF and ESF). Improvements to the English text were done by Ian Emmet.

References

Ábalos, B., Gil-Ibarguchi, J.I., Eguíluz, L., 1991a. Cadomian Subduction/Collision and Variscan Transpression the Badajoz-Córdoba Shear Belt (SW Spain). *Tectonophysics,* 199, 51-72

Ábalos, B., Gil Ibarguchi, J.I., Eguíluz, L., 1991b. Structural and metamorphic evolution of the Almadén de la Plata Core (Seville, Spain) in relation to syn-metamorphic shear between the Ossa-Morena and South-Portuguese zones of the Iberian Variscan Fold Belt. Tectonophysics 191, 365-387. Doi:10.1016/0040-1951(91)90068-4.

Ábalos, B., Carreras, J., Druguet, E., Escuder Viruete, J., Gómez Pugnaire, M.T., Lorenzo Alvarez, S., Quesada, C., Rodríguez Fernández, L.R., Gil Ibarguchi, J.I., (co-ordinator) 2002. Variscan and pre-Variscan Tectonics. In: The Geology of Spain (Gibbons, W., Moreno, T., eds.), The Geological Society of London, Ch. 9, pp. 155-183, ISBN: 1-86239-110-6

Apalategui, O., Eguiluz, L., and Quesada, C., 1990, Structure of the Ossa Morena Zone, in *Pre-Mesozoic Geology of Iberia* (ed. R.D. Dallmeyer and E. Martínez García), 280-91, Springer Verlag Berlin.

Arribas Moreno, A., 1963, Mineralogía y metalogenia de los yacimientos españoles de uranio: La Virgen. Andújar (Jaén). *Estudios Geológicos*, T- XIX, 15-33

Azor, A., González-Lodeiro, F., and Simancas, J.F., 1994, Tectonic evolution of the boundary between the Central Iberian and Ossa Morena zones (Variscan Belt, southwest Spain), *Tectonics,* 13, 45-61

Bandrés, A., Eguíluz, L., Pin, C., Paquette, J.L., Ordóñez, B., Le Fèvre, B., Ortega, L.A., Gil-Ibarguchi, J.I., 2004. The northern Ossa-Morena Cadomian batholith (Iberian

Massif): magmatic arc origin and early evolution. *International Journal of Earth Sciences (Geologische Rundschau)*, 93, 860-885

Barnolas, A., J.C. Larrasoaña, V. Pujalte, B. Schmitz, F.J. Sierro, M.P. Mata, B.C. J. van den Berg, J.N. Pérez-Asensio, Á. Salazar, J.M. Salvany, S. Ledesma, D. García-Castellanos, J. Civis, and P.P. Cunha, 2019. Alpine Foreland Basins 2. In: Quesada, C. and Oliveira, J.T. (Eds): *The Geology of Iberia: a Geodynamic Approach*. Volume 4: Cenozoic Basins, 7-59. Doi: 10.1007/978-3-030-11190-8.

Bayona, M.R., 2008. La investigación de la actividad metalúrgica durante el III Milenio A.N.E. en el suroeste de la Península Ibérica. La Arqueometalurgia y la aplicación de análisis metalográficos y composicionales en el estudio de la producción de objetos de metal. *BAR International Series*, no. 1769, Archaeopress, Oxford.

Bayona, M.R. , 2015. Investigación de la primera metalurgia atlántica en la Península Ibérica: el SW y la provincia de Huelva como marcos de referencia (3.100-2.200 B.C.). Fase 1 de Investigación. *Universidad de Huelva y Fundación Atlantic Copper*. Huelva. 294 pp.

Bayona, M.R., 2018. Procesos técnicos y sociales de la actividad metalúrgica en el sur de la Península Ibérica: IV-II milenio A.N.E. Segunda fase de investigación de la primera metalurgia atlántica en la Península Ibérica: el SW y la provincia de Huelva como marcos de referencia (3.100-2.200 B.C.). *Universidad de Huelva y Fundación Atlantic Copper*. 357 pp.

Bea, F., 2004, La naturaleza del magmatismo de la Zona Centroibérica: consideraciones generales y ensayo de correlación, in *Geología de España* (ed. J.A. Vera), 128-33, SGE-IGME, Madrid

Blanco, A., and Rothenberg, B., 1981, *Exploración arqueometalúrgica de Huelva (EAH),* Labor, S.A. Barcelona

Burg, J. P., Iglesias, M., Laurent, P., Matte, P., and Ribeiro, A., 1981, Variscan intracontinental deformation: the Coimbra – Badajoz Shear zone (SW Iberian Peninsula), *Tectonophysics*, 78, 161-77

Carvalho, D., Goinhas, J., Oliveira, V., and Ribeiro, A., 1971, Observaçoes sobre a geologia do sul de Portugal e cosequencias metalogenéticas. *Estudos Notas e Trabalhos do Servicio de Fomento Mineiro*, 20, 153-99

Carracedo, M., Paquette, J.L., Alonso Olazabal, A., Santos Zalduegui, J.F., García de Madinabeitia, S., Tiepolo, M., Gil Ibarguchi, J.I., 2009. U-Pb dating of granodiorite and granite units of the Los Pedroches batholith. Implications for geodynamic models of the southern Central Iberian Zone (Iberian Massif). *International Journal of Earth Sciences*, 98, 1609-1624

Casquet, C., and Galindo, C., 2004, El magmatismo varisco y postvarisco en la Zona de Ossa Morena, in *Geología de España* (ed. J.A. Vera), 194-99, SGE-IGME, Madrid

Chernyshev, I.V., Chugaev, A.V. and Shatagin, K.N., 2007. High-precision Pb isotope analysis by multicollector-ICP-mass-spectrometry using ^{205}Tl/^{203}Tl normalization: optimization and calibration of the method for the studies of Pb isotope variations. *Geochemistry International*, 45, 1065-1076.

Crespo-Blanc, A., Orozco, M., 1988. The Southern Iberian Shear Zone: a major boundary in the Hercynian folded belt. *Tectonophysics*, 148, 221-227.

De la Rosa, J., and Castro, A., 2004, Magmatismo de la Zona Sudportuguesa, in *Geología de España* (ed. J.A. Vera), 215-22, SGE-IGME, Madrid

Dallmeyer, R.D. and Martínez García, E. (eds), 1990, Pre-Mesozoic Geology of Iberia. Springer-Verlag, Berlin, 415 pp

Defalque, G., Denaiffe, D., Dumont, P., and Lalieux, P., 1992, Le Batolite de los Pedroches (Sierra Morena). Études cartographique, pétrographique, géochimique, géochronologique et métallogénique, *Annales Societe Géologique Belgique*, 115, 77-89

Eguiluz, L., Gil Ibarguchi, J.I., Ábalos, B., Apráiz, A., 2000, Superposed Hercynian and Cadomian orogenic cycles in the Ossa-Morena zone and related areas of the Iberian Massif. *Bulletin of the Geological Society of America* 112, 1.398-1.413

Galindo, C., and Casquet, C., 2004, El magmatismo prevarisco de la Zona de Ossa Morena, in *Geología de España* (ed. J.A. Vera), 190-94, SGE-IGME, Madrid

García de Madinabeitia, S., 2002, *Implementación y aplicación de los análisis isotópicos de Pb al estudio de las mineralizaciones y la geocronología del área de Los Pedroches-Alcudia (Zona Centro-Ibérica)* Ph.D thesis, Universidad del País Vasco, 207 pp

García de Madinabeitia, S., Santos Zalduegui, J. F., Larrea, F. J., Carracedo, M., and Gil Ibarguchi, J. I., 2003, Estudio de la composición isotópica de plomo en galenas del distrito minero de Linares-La Carolina (Jaén, España), *Geogaceta*, 34, 31-34

García de Madinabeitia, S., Santos Zalduegui, J. F., Carracedo, M., Larrea, F. J., and Gil Ibarguchi, J. I., 2002, Variación de la composición isotópica del Pb en galenas del área de Los Pedroches: diferencias entre los filones del Zumajo y Linares-La Carolina, *Geogaceta*, 32, 239-42

Giese, U., and Bühn, B., 1993, Early Paleozoic rifting and bimodal volcanism in the Ossa Morena Zone of Southwest Spain, *Geologische Rundschau*, 83, 143-60

Higueras, P., Munhá, J., Oyarzun, R., Tasinari, C. C. G., and Ruiz, I. R., 2005, First lead isotope data for cinnabar in the Almaden district (Spain): implications for the genesis of the mercury deposits, *Mineralium Deposita*, 40, 115-22

Huelga-Suárez, G., Moldovan, M., Suárez Fernández, M., Ángel De Blas Cortina, M., and García Alonso, J. I., 2014, Isotopic composition of lead in copper ores and a copper artefact from the La Profunda mine (León, Spain). *Archaeometry* 56, 651–664.Doi: 10.1111/arcm.12040.

Inacio, N., Nocete, F. y Bayona, M.R., 2019. Al norte de Santa Rita (Portugal y el río Guadiana A.N.E.). *Universidad de Huelva*. 72 pp.

Julivert, M., Fontboté, J. M., Ribeiro, A., and Conde, L. E., 1972, *Mapa tectónico de la Península Ibérica y Baleares a escala 1:1.000.000 y memoria explicativa*, IGME, Madrid

Klein, S., Domergue, C., Lahaye, Y., Brey, G. P., and Kaenel, H.-M., 2009, The lead and copper isotopic composition of copper ores from the Sierra Morena (Spain), *Journal of Iberian Geology*, 35, 59-68

Larrea, F. J., Carracedo, M., Alonso Olazabal, A., Donaire, T., and Pascual, E., 2004, El Batolito de los Pedroches, in *Geología de España* (ed. J.A. Vera), 122-24, SGE-IGME, Madrid

Le Guen, M., Orgeval, J.-J., and Lancelot, J., 1991, Lead isotope behaviour in a polyphased Pb-Zn ore deposit: Les Malines (Cevennes, France), *Mineral Deposits*, 26, 180-88

Leistel, J. M., Marcoux, E., Thiéblemont, D., Quesada, C., Sánchez, A., Almodóvar, G.R., and Sáez, R., 1998, The volcanic-hosted massive sulphide deposits of the Iberian Pyrite Belt, Review and preface to the Tematic Issue, *Mineralium Deposita*, 33, 2-30

Marcoux, E., and Sáez, R., 1994, Geoquímica isotópica de plomo de las mineralizaciones hidrotermales tardihercínicas de la Faja Pirítica Ibérica, *Boletín de la Sociedad Española de Mineralogía*, 17, 202-3

Marcoux, E., 1998, Lead isotope systematics of the giant massive sulphide deposits in the Iberian Pyrite Belt, *Mineralium Deposita*, 33, 45-58

Mateus, A., Munhá, J., András, P., Matos, J. X., 2006 Geoquímica isotópica do chumbo em mineralizações hidrotermais antimonferas do Sul de Portugal, *Procceding VII Congreso Nacional de Geología*, Sociedade Geologica de Portugal – Universidade de Évora

Ministerio de Industria, 1971, Programa nacional de explotación minera. Minería de minerales radiactivos. *Ministerio de industria-Dirección General de Minas-Junta de Energía Nuclear,* 100 pp

Moreno, C., 1993, Postvolcanic Paleozoic of the Iberian Pyrite Belt: an example of basin morphologic control on sediment distribution in a turbidite basin, *Journal of Sedimentary Petrology,* 63, 1118-28

Moreno, C., and Sáez, R., 1990, Sedimentación marina somera en el Anticlinoirio de Puebla de Guzmán, Geogaceta, 8, 62-64

Moreno, C., Sierra, S., and Sáez, R., 1996, Evidence for catastrophism at the Fammenian-Dinantian boundary in the Iberian Pyrite Belt, in *Recent Advances in Lower Carboniferous Geology* (ed. P. Strogen, D. Somerville and G.L. Gilles) Geological Society Special Publication, 107, 153-62

Nocete, F., 2000. De la cultura de la cultura al mercado del mercado, y viceversa. Los modelos World Systems ante las relaciones y contradicciones centro/periferia de las primeras sociedades de clase. *Revista Atlántica-Mediterránea de Prehistoria y Arqueología Social*, 3, 101-120s

Nocete, F., 2001, *Tercer Milenio antes de nuestra era. Relaciones y contradicciones centro/periferia en el Valle del Guadalquivir*. Bellaterra, Barcelona.

Nocete, F., 2004, *Odiel. Proyecto de investigación arqueológica para el análisis del origen de la desigualdad social en el Suroeste de la Península Ibérica*. Monografías de Arqueología 19. Consejería de Cultura, Junta de Andalucía, Sevilla.

Nocete, F., 2006. The first specialised copper industry in the Iberian Peninsula: Cabezo Juré (2900-2200 BC), *Antiquity,* 80, 646-54

Nocete, F., 2008. *El yacimiento de la Junta de los Ríos.* F. Nocete (coord.), Ed. Consejería de Cultura, Junta de Andalucía, 195 pp. ISBN: 8482668307 ISBN-13.

Nocete, F., 2014. Las sociedades complejas (IV-III Milenio Cal BC) en la Iberia Meridional. En Almagro, M. (Ed.) *Protohistoria de la Península Ibérica. Univ. Burgos-Fundación Atapuerca*, Burgos, pp. 83-94

Nocete, F., Sáez, R., Nieto, J.M., Cruz-Auñón, R., Cabrero, R., Alex, E., Bayona, M.R., 2005a. Circulation of silicified oolitic limestone blades in South-Iberia (Spain and Portugal) during the third millennium B.C.: an expression of a core/periphery framework. *Journal of Anthropological Archaeology* 24, 62-81

Nocete, F., Alex, E., Nieto, J.M., Sáez, R., Bayona, M.R., 2005b. An Archaeological approach to regional environmental pollution in the south-western Iberian Peninsula related to Third millennium BC mining and metallurgy. *Journal of Archaeological Science* 32, 1566-1576

Nocete, F., Queipo, G., Sáez, R., Nieto, J.M., Inacio, N., Bayona, M.R., Peramo, A., Vargas, J.M., Cruz-Auñón, R., 2008, The smelting quarter of Valencina de la Concepción (Seville, Spain): the specialised copper industry in a political centre of the Guadalquivir Valley during the Third millennium BC (2750-2500 BC), *Journal of Archaeological Science*, 35, 717-32.

Nocete, F., Lizcano, R., Peramo, A., Gómez, E., 2010, Emergence, collapse and continuity of the first political system in the Guadalquivir Basin from the fourth to the second millennium BC: the long-term sequence of Úbeda (Spain). *Journal of Anthropological Archaeology,* 29, 219-37.

Nocete, F., Sáez, R., Bayona, M. R., Peramo, A., Inacio, N., and Abril, D., 2011, Direct chronometry (14C AMS) of the earliest copper metallurgy in the Guadalquivir Basin (Spain) during the Third millennium BC: first regional database, *Journal of Archaeological Science*, 38, 3278-95

Oliveira, J. T., 1990, *The South Portuguese Zone. Stratigraphy and Sedimentary Tectonism, en Pre-Mesozoic Geology od Iberia* (eds. R. D. Dallmeyer and E. Martínez-García), Springer-Verlag, Berlin, 334-47

Palero, F., 1991, *Evolución geotectónica y yacimientos minerals de la regióndel valle de Alcusia (Sector Meridional de la Zona Centroibérica)* Ph.D. thesis, University of Salamanca, 827 pp.

Pomiès, C., Cocherie, A., Guerrot, C., Marcoux, E., and Lancelot, J., 1998, Assessment of the precision and accuracy of lead isotope ratios measured by TIMS for geological app: example of massive sulphide deposits (Río Tinto, Spain), *Chemical Geology*, 144, 137-49

Pous, J., Muñoz, G., Heise, W., Melgarejo, J.C., Quesada, C., 2004. Electromagnetic imaging of Variscan crustal structures in SW Iberia: the role of interconnected graphite. Earth and Planetary Science Letters 217, 435-45 (doi:10.1016/S0012-821X(03)00612-5)

Puelles, P., Ábalos, B. and Fernández-Armas, S., 2014. Graphite and quartz petrofabrics: examples from the Ediacaran black quartzites of the Ossa-Morena Zone (SW Iberia). Tectonophysics, 615-616: 53-68. DOI: 10.1016/j.tecto.2013.12.0018.

Quesada, C., 1998. A reappraisal of the structure of the Spanish segment of the Iberian Pyrite Belt. Mineralium Deposita, 33, 31-34

Quesada, C. and Oliveira, J.T. (Eds), 2020. The Geology of Iberia: a Geodynamic Approach. Volume 1: General Introduction and Cadomian Cycle. VIII+380 pp. Doi: 10.1007/978-3-030-10397-2.

Quesada, C. and Oliveira, J.T. (Eds), 2019. The Geology of Iberia: a Geodynamic Approach. Volume 2: The Variscan Cycle. XXII+544 pp. Doi: 10.1007/978-3-030-10518-1.

Ribeiro, A., Munhá, J., Fonseca, P. E., Araujo, A., Pedro, J. C., Mateus, A., Tassinari, C., Machado, G., Jesus, A., 2010, Variscan ophiolite belts in the Ossa-Morena Zone

(Southwest Iberia): Geological characterization and geodynamic significance, *Gondwana Research*, 17, 408–21

Rodríguez, J., Montero-Ruiz, I., Hunt-Ortiz, M., García-Pavón, E., 2020, Cinnabar provenance of Chalcolithic red pigments in the Iberian Peninsula: a lead isotope study. Geoarchaeology; 1-12, DOI: 10.1002/gea.21810

Sáez, R., Almodóvar, G. R., and Pascual, E., 1996, Geological constraints on massive sulphide genesis in the Iberian Pyrite Belt, *Ore Geology Reviews*, 11, 429-51

Sáez, R., Pascual, E., Toscano, M., and Almodóvar, G. R., 1999, The Iberian type of volcano- sedimentary massive sulphide deposits, Mineralium Deposita, 34, 549-70

Sáez, R., Nocete, F., Nieto, J.M., Capitán, M.A., Rovira, S., 2003. The extractive metallurgy of copper from Cabezo Juré, Huelva, Spain: chemical and mineralogical study of slags dated to the Third Millennium BC. *The Canadian Mineralogist,* 41, 627-638

Santos Zalduegui, J. F., García de Madinabeitia, S., and Gil Ibarguchi, J. I., 2004, A lead isotope database: the Los Pedroches–Alcudia area (Spain); implication for archaeometallurgical connections across southwestern and southeastern Iberia, *Archaeometry*, 46, 625-34

Schermerhorn, L. J. G., 1971, An outline stratigraphy of the Iberian Pyrite Belt, *Boletín Geológico y Minero*, 82, 239-68

Simancas, J. F., 2004, La Zona Sudportuguesa, in *Geología de España* (ed. J.A. Vera), 199-201, SGE-IGME, Madrid

Simancas, F., Carbonell, R., González Lodeiro, F., Pérez Estaún, A., Juhlin, C., Ayarza, P., Kashubin, A., Azor, A., Martínez Poyatos, D. J., Almodóvar, G. R., Pascual, E., Sáez, R., Expósito, I., 2003, Crustal structure of the traspressional Variscan orogeny of SW Iberia deep seismic reflection profile IBERSEIS), *Tectonics*, 22, 1062-71

Stacey, J. S., and Kramers, J. D., 1975, Aproximation of terrestrial lead isotope evolution by a two stage model, *Earth and Planetary Science letters*, 26, 207-21

Stos-Gale, Z. A., and Gale, N. H., 2009, Metal provenancing using isotopes and the Oxford archaeological lead isotope database (OXALID), *Archaeological Anthropological Science*, 1, 195–213

Stos-Gale, Z. A.., Gale, N. H., Houghton, J., and Speakman, R., 1995, Lead isotope data from the isotrace laboratory, Oxford: *Archaeometry* data base 1, ores from western Mediterranean, *Archaeometry*, 37, 407-15

Tornos, F., and Chiaradia, M., 2004, Plumbotectonic evolution of the Ossa Morena Zone, Iberian Peninsula: tracing the influence of Mantle-Crust interactions in ore–forming processes, *Economic Geology*, 99, 965-85

Tornos, F., Casquet, C., Relvas, J. M. R. S., Barriga, F. J. A. S., Sáez, R., 2002, The relationships between ore deposits and oblique tectonics: the SW Iberian Variscan Belt, in *The timing and location of major ore deposits in an evolving orogen* (ed. D. J. Blundell, F. Neubauer and A. von Quadt), Geological Society Special Publication, 204, 179-98

Tornos, F., Inverno, C. M. C., Casquet, C., Mateus, A., Ortiz, G., and Oliveira, V., (2004) The metallogenic evolution of the Ossa Morena Zone, *Journal of Iberian Geology*, 30, 143-81

Torres-Ruiz, J., and Fernández, J., 1983, Génesis de las mineralizaciones de cobre en las capas rojas triásicas del sector de Navas de San Juan (provincia de Jaen), *Boletín Geológico y Minero*, 94, 244-58

Vera, J. A. (ed), 2004, *Geología de España*, SGE-IGME, Madrid, 890 pp.

Figure captions

Figure 1. Oblique perspective of the Guadalquivir Valley and its surroundings with its prehistoric estuary and the location of the 8 main settlements mentioned in the text

Figure 2. Geological map of southern Iberia with the principal geological zones and the location of the analyzed ores. Areas covered by previous published lead isotope data bases are shown by dotted or dashed colored lines.

Figure 3. Examples of the mines and materials studied in connection with the PIGMALION Project. A) mine 444. B) mine 450; C) mine 228; D) Stone hammer, mine 450; E) Stone hammer, mine 228; F) Stonne hammer, mine 228; G) Metallurgical furnace IES 14 in Valencina de la Concepción (Seville); H) Copper weapons, cruzible and nozzle from Valencina de la Concepción (Seville).

Figure 4. Pb isotopic composition of analyzed samples. A and B show the groups. B, C, D and F show the subgroups. A: Main groups. B: Enlargement of cluster from group 2 to enhance the difference on the potential provenance for mining districts grouped within subgroups 2A, 2B, 2C and 2D. C: Enlargement of cluster from subgroups 2A and 2B to enhance the difference on the potential provenance for mining districts grouped within subgroups 2A1, 2A2, 2B1 and 2B2. In the first diagram above the analytical error is less than the size of the symbols.

Appendix - Table 1 and Table 2

Table 1: Samples studied with their geographic location, mine name and coordinates. The assignation to different groups/subgroups is done on the basis of their Pb isotopic composition (see text). **(***IPB Ms & Gossan: Iberian Pyrite Belt massive sulphides and gossan).

Table 2: Lead isotope data for the samples studied. The assignation to different groups/subgroups is done on the basis of their isotopic composition (see text).


Guadiana River
La Junta
Juré
Soto
Valencina
Carmona
Guadalquivir River/Valley
Úbeda
La Horca
Marroquíes
Estuary
Gulf of Cádiz

Figure 2

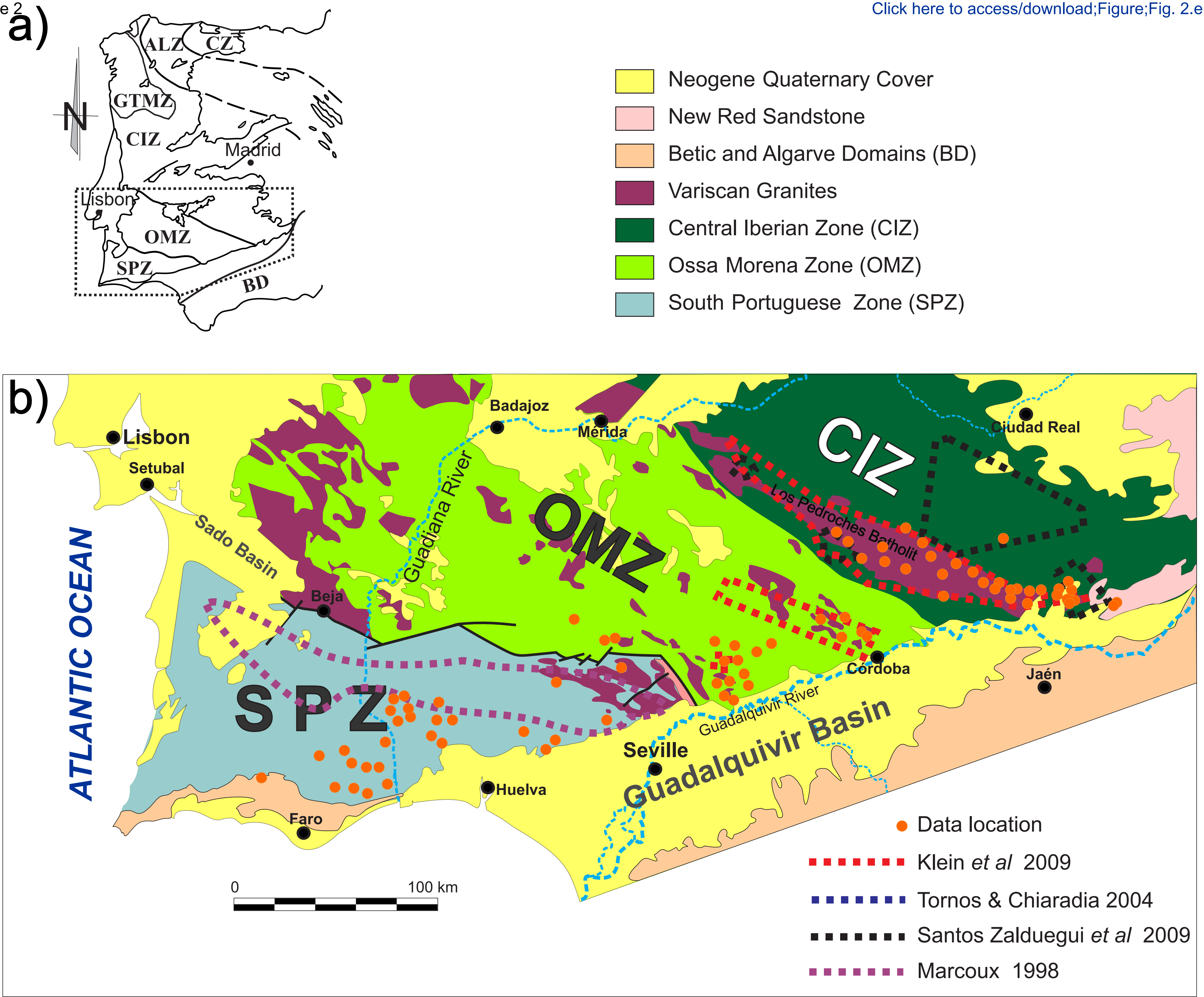

a)
N
ALZ
CZ
GTMZ
CIZ
Madrid
Lisbon
OMZ
SPZ
BD
Neogene Quaternary Cover
New Red Sandstone
Betic and Algarve Domains (BD)
Variscan Granites
Central Iberian Zone (CIZ)
Ossa Morena Zone (OMZ)
South Portuguese Zone (SPZ)
b)
Lisbon
Setubal
Sado Basin
Beja
Badajoz
Mérida
Guadiana River
OMZ
CIZ
Ciudad Real
Los Pedroches Batholit
Córdoba
Jaén
Guadalquivir River
Seville
Guadalquivir Basin
Huelva
Faro
SPZ
ATLANTIC OCEAN
0
100 km
● Data location
Klein *et al* 2009
Tornos & Chiaradia 2004
Santos Zalduegui *et al* 2009
Marcoux 1998

Figure 3

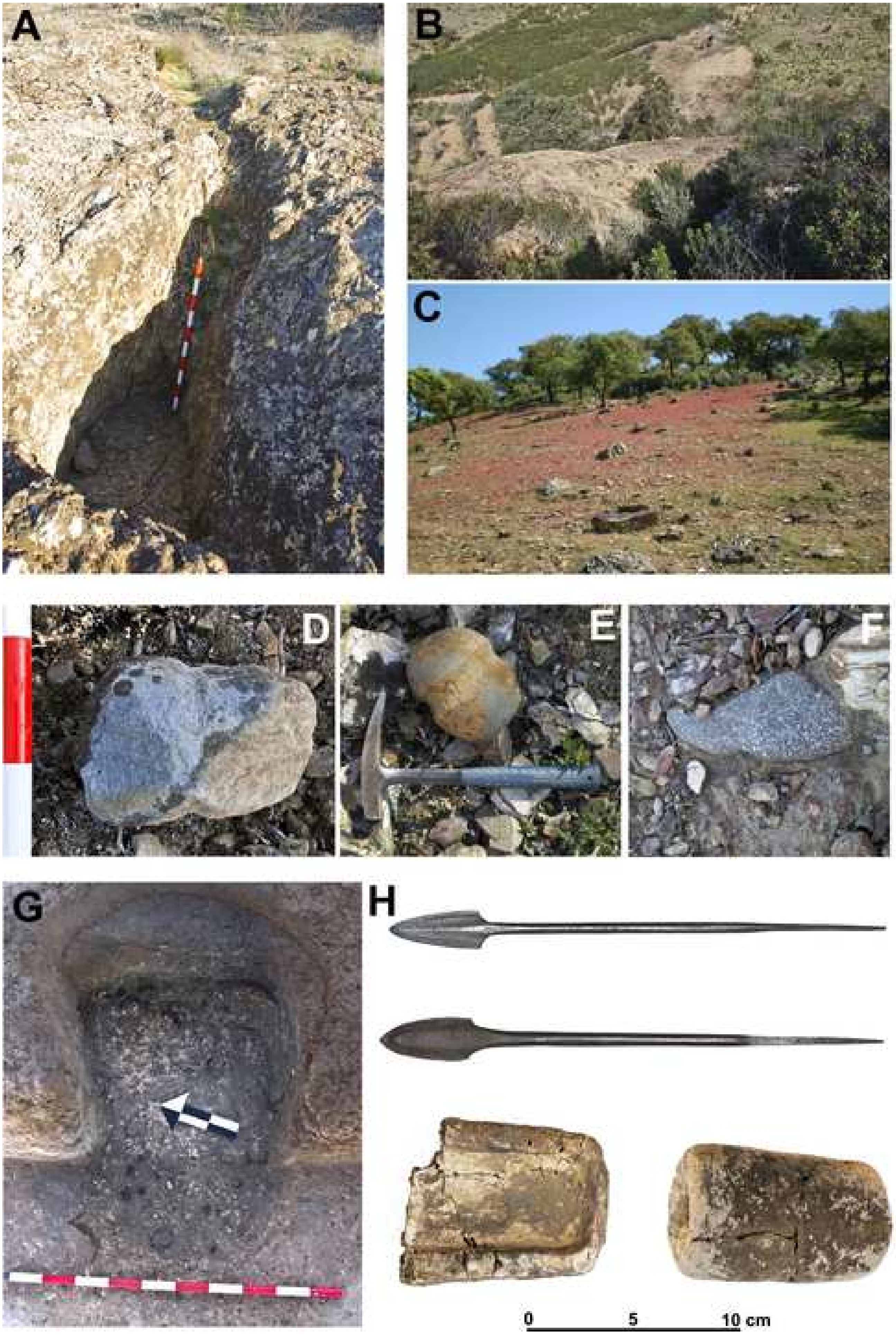
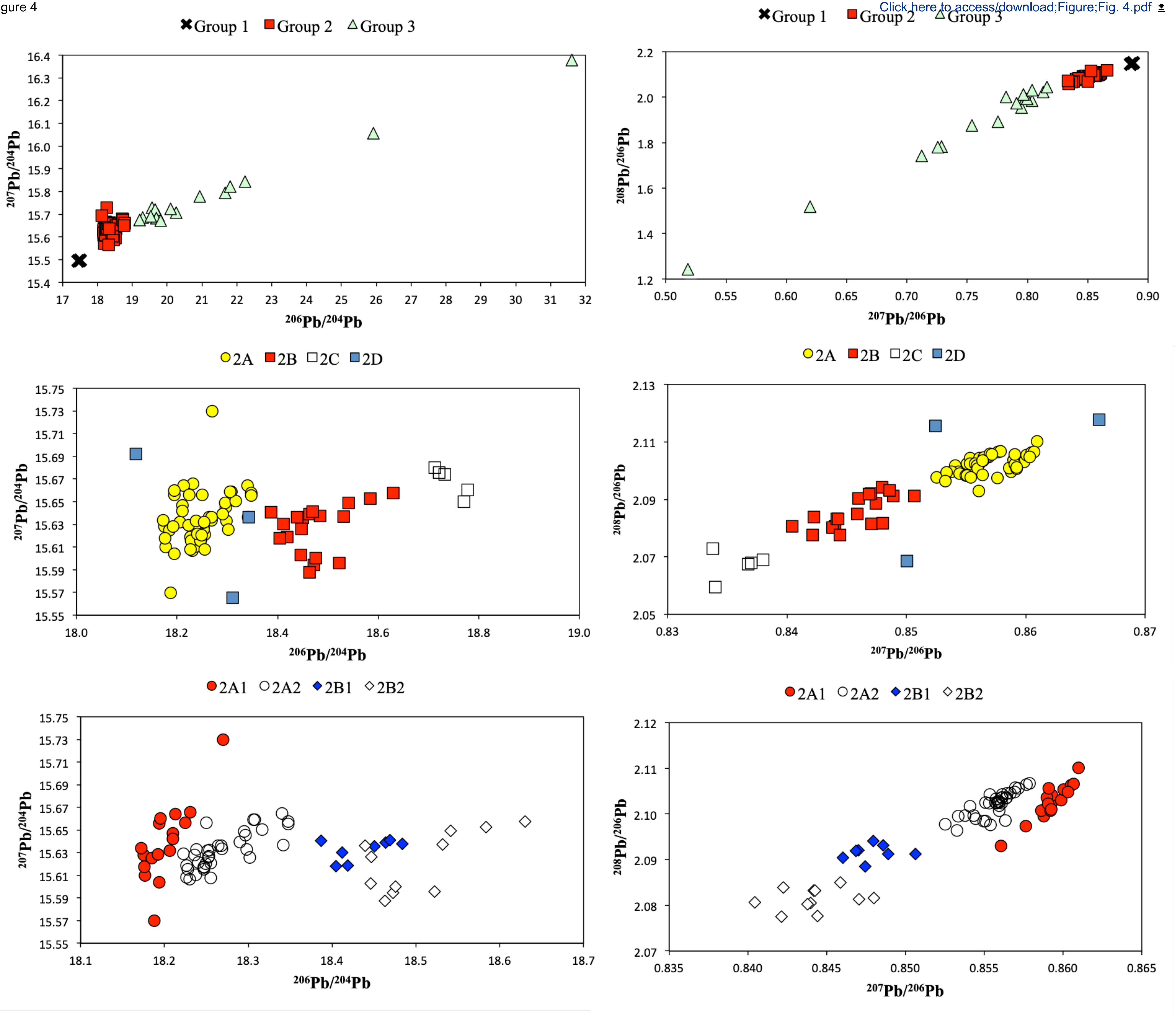


Figure 4



Group 1
Group 2
Group 3
^{207}Pb/^{204}Pb
16.4
16.3
16.2
16.1
16.0
15.9
15.8
15.7
15.6
15.5
15.4
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
^{206}Pb/^{204}Pb
Group 1
Group 2
Group 3
^{208}Pb/^{206}Pb
2.2
2.0
1.8
1.6
1.4
1.2
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
^{207}Pb/^{206}Pb
2A
2B
2C
2D
^{207}Pb/^{204}Pb
15.75
15.73
15.71
15.69
15.67
15.65
15.63
15.61
15.59
15.57
15.55
18.0
18.2
18.4
18.6
18.8
19.0
^{206}Pb/^{204}Pb
2A
2B
2C
2D
^{208}Pb/^{206}Pb
2.13
2.11
2.09
2.07
2.05
0.83
0.84
0.85
0.86
0.87
^{207}Pb/^{206}Pb
2A1
2A2
2B1
2B2
^{207}Pb/^{204}Pb
15.75
15.73
15.71
15.69
15.67
15.65
15.63
15.61
15.59
15.57
15.55
18.1
18.2
18.3
18.4
18.5
18.6
18.7
^{206}Pb/^{204}Pb
2A1
2A2
2B1
2B2
^{208}Pb/^{206}Pb
2.12
2.11
2.10
2.09
2.08
2.07
0.835
0.840
0.845
0.850
0.855
0.860
0.865
^{207}Pb/^{206}Pb

Table 2

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