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The lead and copper isotopic composition of copper ores from the Sierra Morena (Spain)

Análisis de los isótopos de plomo y de cobre de los minerales de cobre de Sierra Morena (España)

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Abstract

The paper presents lead and copper isotope analyses of 51 copper ore samples from the Sierra Morena, South of Spain. They are from ancient mines of the Iberian Peninsula collected by Claude Domergue during various field campaigns in the central Sierra Morena from 1965 to 1975. Most samples consist of copper oxide minerals such as malachite, azurite and chrysocolla and stem from the surficial sections of the ore deposits. The aim of the study was to supplement the existing reference data bank on lead isotopic compositions of ancient copper mines from the Iberian Peninsula. This is particularly important for the Sierra Morena for which data exist mostly for lead-zinc but not for copper ores. The lead isotope ratios range from 18.165 to 19.712 ($^{206}Pb/^{204}Pb$), 0.797 to 0.859 ($^{207}Pb/^{206}Pb$) and 1.955 to 2.108 ($^{208}Pb/^{206}Pb$). Two separate fields can be distinguished with a major field intermediate between the ore deposits from SW and SE Spain and a second at higher $^{208}Pb/^{206}Pb$ values. Copper isotopes were analysed additionally to provide further constraints for provenance studies. The copper isotope ratios $\delta^{65}Cu$ of the copper oxide samples are mostly positive and higher on average than those of sulphide minerals. They are a potential tool to distinguish between either sulphide ore or oxide ore deposit derived artefacts.

Keywords: lead isotopes, copper isotopes, mass spectrometry, Spain, Sierra Morena, copper ores, archaeometry

Resumen

En este artículo, presentamos los resultados de los análisis isotópicos (plomo y cobre) llevados a cabo sobre 51 muestras de mineral de cobre de Sierra Morena, Sur de España. Las muestras provienen de minas antiguas de la Península Ibérica, que habían sido recogidas por Claude Domergue en el curso de sus prospecciones en Sierra Morena central, entre 1965 y 1975. La mayoría de las muestras consiste de minerales de óxido de cobre como malaquita, azurita y crisocola que se encuentran en la superficie de los depósitos. El objetivo de este estudio es de contribuir a la base hoy disponible de datos de isótopos de plomo de las antiguas minas de cobre en la Península Ibérica. Este objetivo es particularmente importante puesto que la mayoría de los datos publicados de Sierra Morena se refieren a minerales de plomo-zinc. Las proporciones de isótopos de plomo varían entre 18.165 y 19.713 ^{206}Pb/^{204}Pb, de 0.797 a 0.859 ^{207}Pb/^{206}Pb, y de 1.955 a 2.108 ^{208}Pb/^{206}Pb. Se pueden distinguir dos zonas independientes: una zona principal que se sitúa entre los depósitos de España del sudoeste y sudeste y una segunda zona con las proporciones de isótopos de plomo más altas. Además, los isótopos del cobre fueron analizados para suplir restricciones adicionales en los estudios de proveniencia. Las proporciones de isótopos de cobre, δ^{65}Cu/^{63}Cu, fueron analizadas en los óxidos de cobre y son en la mayor parte positivas y mas altas en medio que las proporciones δ^{65}Cu de los sulfuros de cobre. Los resultados presentan un instrumento eficiente para distinguir los artefactos elaborados de minerales de sulfuros de cobre o de minerales de óxido de cobre.

Palabras clave: isótopos de plomo, isótopos de cobre, espectrometría de masas, España, Sierra Morena, mineral de cobre, arqueometría, .

1. Introduction

Mining in the South of the Iberian Peninsula has been intensive since the Bronze Age. The Romans maintained high mining activities from the end of the second century BC to at least the beginning of the III century AD (Domergue, 1987; Domergue, 1990; Domergue, 1998). Rio Tinto within the Pyrite Belt in the Southwest almost appeared to be the unique centre of copper production in ancient times within the whole of the Iberian Peninsula, but other mines in this pyritic ensemble (i.e. Tharsis, Sotiel-Coronada, São Domingos, Aljustrel) have also produced copper and silver.

It is also known that the numerous copper rich vein deposits of the Sierra Morena in Central South Spain have been exploited reaching back to the beginning of the Bronze Age. The larger copper deposits in this area are Los Escoriales (District of Andujar-Montoro), Cerro Muriano (District de Córdoba), Zumajo (District of Los Pedroches) and are known to have continuously produced copper in Roman times. They are presumably the source of copper for the famous copper production of Córdoba, the *aes Cordubense*, also called *aes Marianum* (Pliny the Elder, *Naturalis Historia,* 34, 4). *Aes Marianum* was named after S. Marius, who was the owner of this mining estate at the beginning of the Roman Empire (Domergue, 1990). The Sierra Morena deposits produced mainly lead, silver and copper. The development of visible gossans on the surface of the copper deposits testifies to their long term exploitation. The remains of ancient mining activities can be observed in situ in the form of tailings, mining tools, ceramics, etc.

In archaeometallurgy, lead isotopes are applied for provenancing the raw materials of metal objects by comparing the lead isotope signatures of ores from known deposits with those of the metal objects. However, prov-

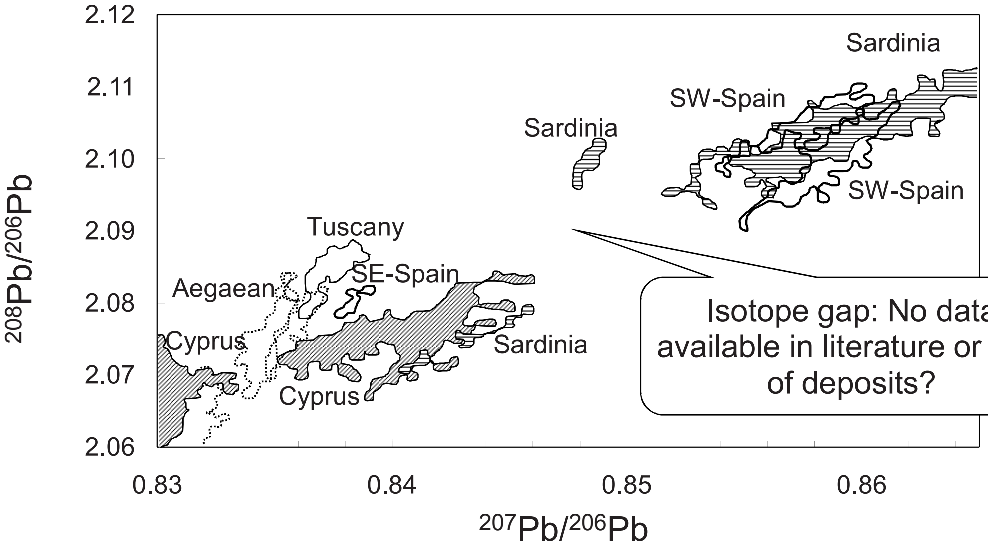

Fig. 1.- Reference lead isotope diagram ^{207}Pb/^{206}Pb *versus* ^{208}Pb/^{206}Pb. Lead isotope fields derived from published lead isotope data of ores from the Mediterranean area.

Fig.1.- Diagrama mostrando las relaciones de los isótopos de cobre Pb^{207}Pb/^{206}Pb *versus* ^{208}Pb/^{206}Pb. Los campos de los isótopos de cobre provienen de aquellos datos publicados de las menas del área mediterránea.

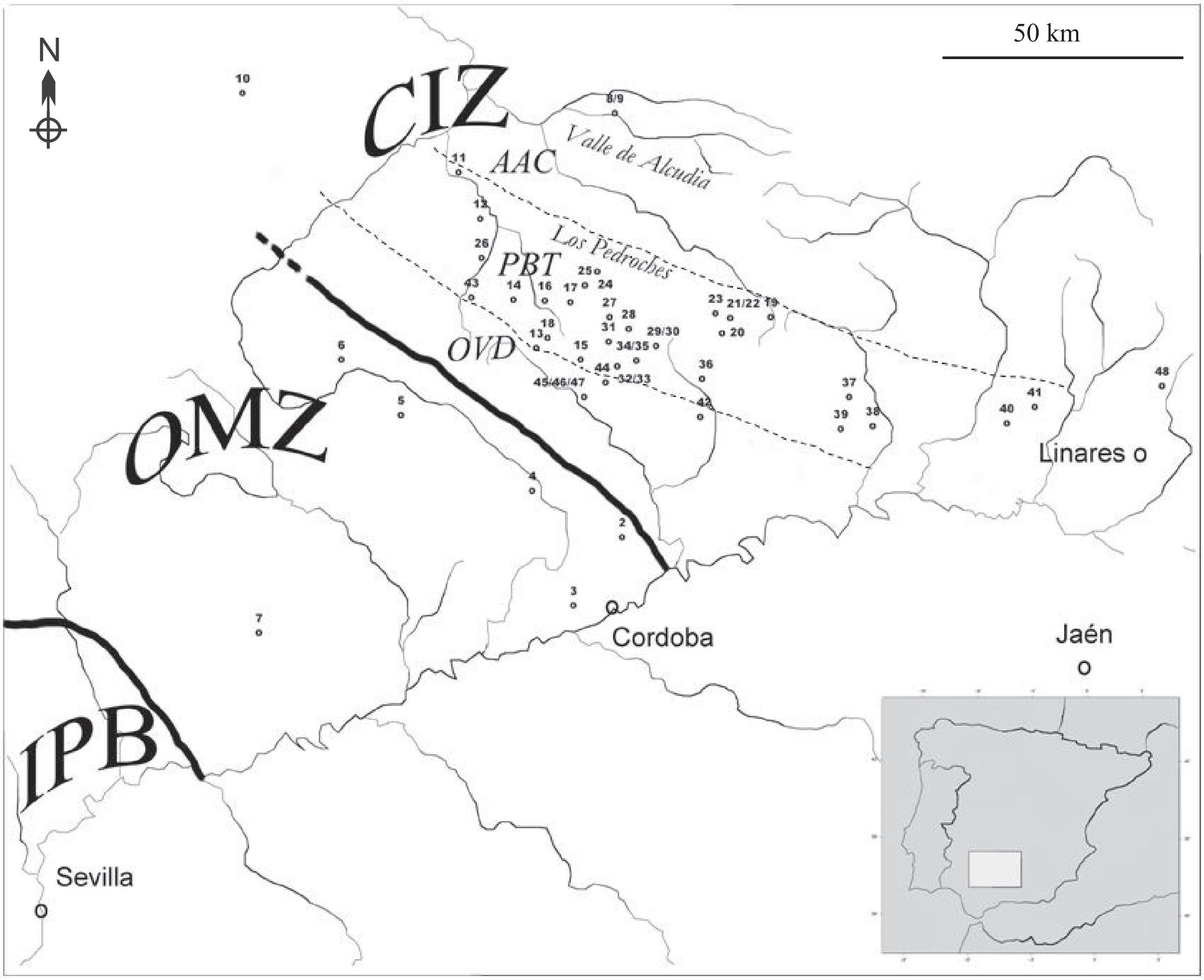

Fig. 2.- Map of Southern Spain indicating the locations of the ore samples. The sample numbers refer to Table I. Map based on C. Domergue's Catalogue des mines et des fonderies antiques de la Péninsule Ibérique. Cartes et plans hors texte (1987). (IPB: Iberian Pyrite Belt, OMZ: Ossa Morena zone, CIZ: Central Iberian zone; OVD: Los Pedroches sector, exocontact batholite, PBT: Los Pedroches sector, inner batholite occurences, AAC: Alcudia-Almadén-Castuera). Not referenced in this map is the LMZ (Lusitan-Marianic zone): this northern limit of the OMZ is still continuously under discussion and modification (de San José *et al.*, 2004).

Fig. 2.- Mapa del sur de España indicando las localizaciones de las menas de las muestras estudiadas. Los números de las muestras están referidos en la Tabla 1. El mapa está basado en "Catalogue des mines et des fonderies antiques de la Péninsule Ibérique. Cartes et plans hors texte (Domergue, 1987). IPB: Cinturón Pirítico Ibérico, OMZ: Zona de Ossa Morena, CIZ: Zona Centro Ibérica, OVD: Sector de Los Pedroches; contacto exterior batolítico

enance studies can only be successful, when the reference data bank is complete. During the accumulation of published lead isotope data of Mediterranean copper ore deposits a significant lack of data for central Iberian deposits became apparent together with a seeming gap in a lead isotope ratio diagram (Fig. 1). Roman copper coins analysed by Klein *et al.* (2004) plotted within this gap of the reference data bank and were interpreted as a mixture of ores from two deposits. Scarce new data from Los Pedroches (cited in Rico *et al.*, 2005-2006), however, provided lead isotope data in the vicinity of these coins. This prompted us to embark on a more comprehensive study of the mines in Central South Spain and especially of Sierra Morena.

2. Geological Setting

The south central Spanish ore deposits are divided east to west into occurrences from the Central Iberian Zone (CIZ), the Ossa Morena Zone (OMZ) and the Iberian Pyrite Belt (IBP) (Fig. 2). Our samples were mostly obtained from the Central Iberian Zone and a few from the Ossa Morena zone. They are the main tectonic units of the Hercynian Iberian Massif (Gibbons and Moreno, 2002). The contact between CIZ and OMZ is a NW-SE trending feature whose nature is not completely understood (e.g. Expósito *et al.*, 1999; San José *et al.*, 2004).

CIZ consists of three major sub-zones: 1. the central Los Pedroches Batholith complex (PBT), 2. the exocontact (peri-)batholith occurrences (OVD), and 3. Alcudia to Linares (Fig. 2). The Los Pedroches Batholith complex is a late-orogenic magmatic alignment mainly with granodiorite and granite (Larrea *et al*., 1999; Pardo Alonso, 1999). The southern part of CIZ is known for its vast number of mineral occurrences and its relative uniformity of metal ore types. The mercury mineralisation of the Almadén district is connected with Silurian-Devonian volcanism and W-Sn-As-Bi ores are related to Hercynian magmatism. The Hercynian magmatism produced the innumerable Pb-Zn-(Ag) vein type occurrences. Copper is always related to the lead bearing veins and is occasionally more abundant than the lead.

The OMZ is located between the Iberian Pyrite Belt (IPB – belongs to the South Portuguese zone) and the CIZ (Tornos and Casquet, 2005; Tornos *et al*., 2006). It extends from the Portuguese Serra de Ossa in the north to the Spanish province of Córdoba. The ore types in the OMZ are the result of two main ore forming events of Cadominan and Variscan age (Tornos and Chiaradia, 2004). They vary from volcanogenic and sediment-hosted massive sulphides to magmatic Ni(-Cu) deposits, Fe-(Cu) calcic skarns, tin replacement bodies, Cu-(Bi-Au) or Cu-Zn-(Pb) veins and W, Sn, Bi, Co, Ni bearing veins. This list continues with gold bearing hydrothermal systems (mesothermal iron oxide-copper-gold mineralisation) and shallower W-Sn and Cu-Pb-Zn veins.

3. The selected copper ores

In total, 51 samples were selected from the Domergue collection. They are predominantly from the vein-type deposits of CIZ and OMZ. Green and blue secondary copper minerals dominate, primary sulphides (chalcopyrite) are subordinate. The Domergue sample numbers are used and given in Table 1. The precise geographic location of each sample can be found in the catalogue and the maps presented in Domergue 1987: Cartes et plans hors texte, no. 71 and 73: Mines antiques de la Sierra Morena. Table 1 also contains our in house numbers which are used in Figure 2. The following is an overview on the number of samples obtained from the different geological units:

Iberian Pyrite Belt:
  -Aljustrel (1 sample).
Central Iberian Zone:
  - Alcudia-Almadén (Santa Eufemia)-Castuera (AAC; 2 samples).
  - Los Pedroches sector, inner batholith occurrences (32 samples).
  - Los Pedroches sector, exocontact batholith (6 samples).
  - Linares (1 sample).
Ossa Morena Zone:
  - Córdoba (3 samples).
  - Azuaga-Fuenteobejuna (2 samples).
  - Sevilla (1 sample).
SE Volcanic province:
  -Cartagena-Mazarron (1 sample).
Internal Betics:
  -Almeria, NE Spain (1 sample).
Cantabrian Zone:
  -Léon, N Spain (1 sample).

4. Methods of sample preparation, chemistry and analysis

The following steps and chemical procedures were carried out in the clean air laboratory of Frankfurt University and with the equipment available in Frankfurt. All chemicals used were of ultra-pure quality.

a) The ore samples were first crushed roughly into small fragments not larger than 0.5 mm in size.

b) Approximately 1 g of the crushed material was treated with 6 mol/l hydrochloric acid (five minutes in an ultrasonic bath and then left overnight for dissolving) to chemically separate the copper mineral fraction from adhering silica-rich gangue. After centrifugation the copper-containing solution was poured and stored. An aliquot of 0.5 ml of this solution was taken and evaporated. The residue was diluted in 1 ml 6 N nitric acid (HNO_3) and kept as our initial solution.

c) An aliquot of 0.1 ml from this initial solution was used for the analysis of the copper and lead contents. The analyses were carried out by using a cyclonic spray chamber, a 50µl PFA MicroFlowTM nebulizer and an Inductively Coupled Plasma Mass Spectrometer (Element2™, Finnigan MAT) at low mass resolution ($\Delta m/m = 400$).

d) For the lead isotope analysis a further aliquot of 0.1 ml from the initial solution was evaporated and the residue was taken up in 0.5 ml HBr. Lead was purified chromatographically in a single-pass 0.6N HBr-based anion resin (Dowex 1*8, 100-200 mesh), subsequently converted to nitrate and diluted adequately in 2% HNO_3 to yield a final concentration of 500 ppb lead. The diluted samples were spiked with 100 ppb of Tl standard NIST SRM-997 of known lead isotope composition and were ready for isotope analysis.

e) A further solution was prepared similarly for copper isotope analysis by taking a 0.1 ml split from the initial solution and dilute it in 2% HNO_3 to yield a final concentration of approximately 500 ppb Cu in the solution. The diluted samples were spiked with 1ppm of the Ni

Geological Unit/District	*Sample*	*Dom. 87*	*Mines*	*Copper Ore Type*	$^{206}Pb/^{204}Pb$	2σ	$^{207}Pb/^{204}Pb$	2σ	$^{208}Pb/^{204}Pb$	2σ	$^{207}Pb/^{206}Pb$	2σ	$^{208}Pb/^{206}Pb$	2σ	$\delta^{65}Cu/^{63}Cu$	2σ
South Portugese Zone																
Iberian Pyritic Belt	1	**POR 2**	Aljustrel	secondary	18.27637	0.00069	15.62711	0.00049	38.30711	0.00067	0.85506	0.00002	2.09605	0.00002	1.91	0.01
Ossa Morena Zone																
District of Córdoba	2	**CO 39**	Cerro Muriano	secondary	18.75073	0.00098	15.62019	0.00076	38.87358	0.00220	0.83305	0.00001	2.07317	0.00002	0.50	0.01
	3	**CO 40**	Casilla Cobre	secondary	18.27266	0.00071	15.61073	0.00055	38.26239	0.00118	0.85430	0.00002	2.09389	0.00005	-0.17	0.01
	4	**CO 114**	Gran Mina	secondary	18.16754	0.00079	15.58193	0.00089	38.22799	0.00291	0.85768	0.00002	2.10416	0.00006	0.98	0.01
District of Azuaga-Fuenteobejuna	5	**CO 25**	La Pastora	secondary	18.71701	0.00019	15.65642	0.00021	38.63111	0.00060	0.83647	0.00001	2.06394	0.00001	-0.15	0.02
	6	**CO 55**	La Loba	primary+secondary	18.17192	0.00006	15.60485	0.00015	38.31083	0.00098	0.85873	0.00001	2.10826	0.00004	-0.42	0.02
District of Sevilla	7	**SE 7**	Gibla	secondary	18.28432	0.00012	15.61644	0.00022	38.33908	0.00028	0.85408	0.00000	2.09680	0.00002	-1.16	0.01
Central Iberian Zone																
ALCUDIA-ALMADÉN (SANTA EUFEMIA)-CASTUERA (AAC)																
District of Alcudia	*8*	**CR 5**	Q. Hierro	secondary	18.18677	0.00056	15.62346	0.00060	38.30571	0.00144	0.85905	0.00001	2.10628	0.00002	0.04	0.01
	9	**CR 5S**	Q. Hierro	primary	18.18419	0.00018	15.62414	0.00006	38.30472	0.00027	0.85921	0.00003	2.10648	0.00001	0.76	0.01
LOS PEDROCHES SECTOR																
Inner batholithe occurences (PBT)																
District of Los Pedroches	11	**CO 19**	Solana	secondary	18.89518	0.00117	15.64594	0.00118	38.36404	0.00243	0.82804	0.00001	2.03036	0.00000	1.96	0.01
	12	**CO 22**	Encinilla	secondary	18.67031	0.00038	15.65303	0.00056	38.70460	0.00099	0.83838	0.00002	2.07305	0.00001	0.61	0.01
	13	**CO 4**	Chap. Barrenado	secondary	18.26094	0.00079	15.61563	0.00068	38.37245	0.00207	0.85514	0.00000	2.10131	0.00001	0.54	0.01
	14	**CO 5**	Cantos Blancos	secondary	18.70590	0.00045	15.65246	0.00057	38.61712	0.00124	0.83675	0.00002	2.06443	0.00002	-0.01	0.01
	15	**CO 13**	Montilla	secondary	19.71266	0.00018	15.71542	0.00021	38.53983	0.00083	0.79722	0.00001	1.95509	0.00004	0.47	0.01
	16	**CO 14**	Medioduro	secondary	19.10664	0.00037	15.67170	0.00024	38.57997	0.00061	0.82022	0.00000	2.01919	0.00001	0.27	0.01
	17	**CO 16**	Requeja	secondary	18.87606	0.00075	15.65761	0.00081	38.65142	0.00225	0.82950	0.00001	2.04763	0.00003	1.38	0.02
	18	**CO 17**	Fontanar	secondary	18.44970	0.00007	15.63289	0.00009	38.51194	0.00107	0.84732	0.00000	2.08742	0.00003	2.00	0.01
	19	**CO 31**	Torrubia	secondary	18.44192	0.00025	15.64109	0.00024	38.59885	0.00066	0.84813	0.00001	2.09300	0.00002	1.63	0.02
	20	**CO 32b**	Zumajo	secondary	18.44796	0.00031	15.64329	0.00046	38.61628	0.00092	0.84797	0.00001	2.09326	0.00001	0.21	0.01
	21	**CO 34**	Quebradillas	secondary	18.56372	0.00076	15.64757	0.00076	38.67078	0.00216	0.84291	0.00001	2.08313	0.00005	0.76	0.01
	22	**CO 34**	Quebradillas	primary	18.58379	0.00092	15.65056	0.00049	38.68268	0.00189	0.84219	0.00001	2.08152	0.00001	-1.04	0.01
	23	**CO 38**	A° Higueruela	secondary	18.53373	0.00027	15.64346	0.00047	38.56774	0.00104	0.84404	0.00001	2.08094	0.00003	0.70	0.02
	24	**CO 48**	La Pililla	secondary	18.46524	0.00026	15.63459	0.00006	38.46971	0.00038	0.84671	0.00001	2.08337	0.00002	2.45	0.02
	25	**CO 49**	Cort. Peralbo	secondary	18.49089	0.00036	15.63458	0.00027	38.55806	0.00044	0.84553	0.00000	2.08525	0.00002	0.51	0.01
	26	**CO 64**	D. Lavera	secondary	18.57234	0.00051	15.64395	0.00063	38.59191	0.00166	0.84232	0.00001	2.07788	0.00003	0.97	0.01
	27	**CO 92**	Tabernero	secondary	18.45616	0.00042	15.63541	0.00042	38.56687	0.00125	0.84716	0.00001	2.08964	0.00003	1.90	0.01
	28	**CO 93**	Romana	secondary	18.72410	0.00045	15.61927	0.00043	38.84482	0.00159	0.83418	0.00000	2.07458	0.00002	0.71	0.01
	29	**CO 94b**	Osi	secondary	18.55484	0.00020	15.64080	0.00032	38.58835	0.00066	0.84295	0.00001	2.07968	0.00002	1.05	0.01
	30	**CO 94b**	Osi	primary	18.36207	0.00048	15.61173	0.00044	38.34769	0.00118	0.85021	0.00001	2.08841	0.00001	-0.70	0.00
	31	**CO 95**	Quiros	secondary	18.45234	0.00012	15.63352	0.00017	38.55485	0.00046	0.84723	0.00000	2.08942	0.00001	0.82	0.01
	32	**CO 96a**	Garabato	secondary	18.49068	0.00031	15.63533	0.00033	38.59809	0.00098	0.84558	0.00001	2.08744	0.00001	0.21	0.01
	33	**CO 96b**	Garabato	secondary	18.53777	0.00045	15.63958	0.00053	38.63741	0.00150	0.84367	0.00001	2.08424	0.00004	0.42	0.01
	34	**CO 97a**	Soberbio	secondary	18.16586	0.00024	15.59850	0.00022	38.29099	0.00074	0.85867	0.00001	2.10786	0.00001	0.56	0.01
	35	**CO 97b**	Soberbio	secondary	18.77077	0.00108	15.64068	0.00106	38.51938	0.00237	0.83326	0.00001	2.05208	0.00005	0.29	0.03
	36	**CO 107**	Posadilla	secondary	18.52617	0.00058	15.64326	0.00049	38.68497	0.00126	0.84439	0.00000	2.08812	0.00000	1.41	0.01
	43	**CO 61**	C° Minillas	secondary	18.42124	0.00029	15.63350	0.00032	38.53152	0.00112	0.84866	0.00001	2.09168	0.00003	-0.04	0.01
District of Andujar-Montoro	37	**CO 28**	A° de la Virgen	primary	18.48508	0.00311	15.64420	0.00311	38.64382	0.00684	0.84633	0.00001	2.09054	0.00002	0.00	0.01
	38	**CO 77**	A° Almadenejos	secondary	19.22474	0.00040	15.68409	0.00029	39.00950	0.00069	0.81582	0.00001	2.02910	0.00000	0.02	0.01
	39	**CO 78**	A° Cuezo	secondary	19.25110	0.00020	15.67989	0.00010	39.00836	0.00027	0.81449	0.00001	2.02628	0.00003	1.10	0.02
	40	**J 8**	Escoriales	secondary	18.38619	0.00063	15.63508	0.00059	38.53145	0.00163	0.85038	0.00001	2.09570	0.00005	1.12	0.01
	41	**J 10**	S. Galiarda	secondary	18.47242	0.00037	15.63851	0.00033	38.52577	0.00058	0.84659	0.00000	2.08554	0.00000	1.91	0.01
Exo contact batholithe (OVD)																
District of Los Pedroches	10	**BA 37**	Antoñita	secondary	18.17681	0.00013	15.60339	0.00013	38.30804	0.00022	0.85842	0.00000	2.10753	0.00000	0.28	0.01
	42	**CO 1**	Los Pobos	secondary	19.12643	0.00037	15.66968	0.00036	38.68986	0.00100	0.81927	0.00001	2.02285	0.00003	0.35	0.02
	44	**CO 98**	A° Tomilloso	secondary	18.32187	0.00007	15.63843	0.00027	38.39026	0.00113	0.85353	0.00001	2.09533	0.00003	2.70	0.01
	45	**CO 99a**	Cuzna	secondary	18.24682	0.00030	15.61348	0.00033	38.36094	0.00096	0.85568	0.00001	2.10232	0.00003	0.22	0.02
	46	**CO 99b**	Cuzna	secondary	18.22039	0.00100	15.60695	0.00099	38.32816	0.00253	0.85656	0.00001	2.10361	0.00004	0.65	0.01
	47	**CO 99c**	Cuzna	secondary	18.19698	0.00030	15.60940	0.00037	38.31693	0.00064	0.85779	0.00001	2.10567	0.00000	1.18	0.01
LINARES																
District of Linares - La Carolina	48	**J 14**	Palazuelos	secondary	18.24194	0.00035	15.61253	0.00034	38.34070	0.00099	0.85586	0.00001	2.10179	0.00002	0.29	0.01
Southeast Volcanic Province																
District of Cartagena-Mazarrón	49	**MU 7**	Cala Reona	secondary	18.75862	0.00046	15.67154	0.00034	39.08204	0.00059	0.83544	0.00001	2.08345	0.00000	-1.49	0.01
Internal Betics																
District of Almeria	50	**AL 5**	Cueva Paloma	secondary	19.30910	0.00033	15.70281	0.00030	38.96495	0.00067	0.81323	0.00001	2.01795	0.00001	-1.59	0.01
Cantabrian Zone																
District of Léon	51	**LE 6**	Profunda	secondary	18.83560	0.00023	15.70031	0.00025	38.53754	0.00085	0.83354	0.00000	2.04600	0.00002	0.51	0.01

Table I.- Lead and copper isotope results of ores from South Spain. Analysis by MC-ICP-MS. (2 σ: standard deviation; CO: Córdoba, CR: Ciudad Real, SE: Sevilla, BA: Badajoz, J: Jaén, MU: Murcia, AL:Almeria, L:Léon).

Tabla I.- Resultados de los isótopos de plomo y cobre obtenidos de las menas del S de España. Los análisis han sido realizados por MC-ICP-MS. (2 σ: desviación standard; CO: Córdoba, CR: Ciudad Real, SE: Sevilla, BA: Badajoz, J: Jaén, MU: Murcia, AL:Almeria, L:Léon).

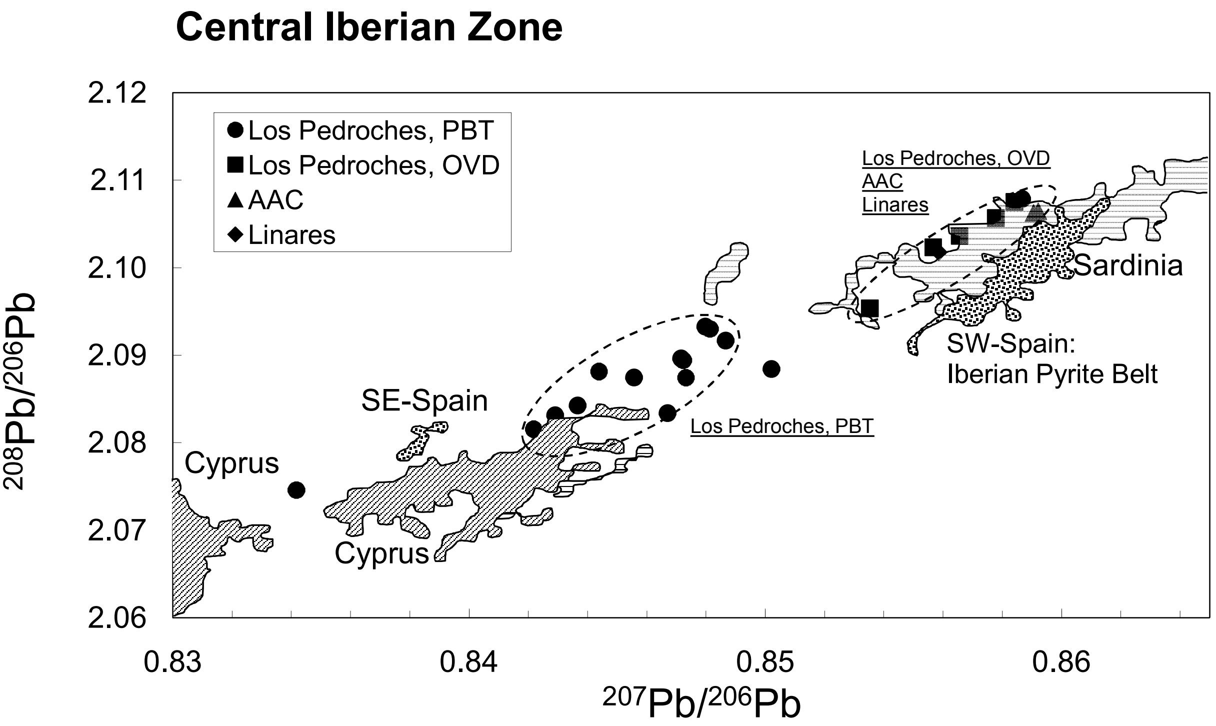

Fig. 3.- Lead isotope results of the copper ores from the Central Iberian zone (CIZ) in a diagram $^{207}Pb/^{206}Pb$ *versus* $^{208}Pb/^{206}Pb$. The analytical errors are smaller than the symbols (compare Table I). Two separate isotope fields result for CIZ. AAC = Alcudia-Almadén-Castuera.

Fig. 3.- Resultados de los isótopos de plomo obtenidos de las menas de cobre de la Zona Central Ibérica (CIZ) en un diagrama $^{207}Pb/^{206}Pb$ *versus* $^{208}Pb/^{206}Pb$. Los errors analíticos son menores que los de los símbolos (ver Tabla I para comparar). Dos campos separados de isótopos han sido obtenidos para CIZ. AAC = Alcudia-Almadén-Castuera.

standard NIST SRM 986 of known copper isotope composition and were ready for isotope analysis

The isotopic measurements were performed with a MC-ICP-MS (Multicollector-Inductively coupled Plasma- Mass spectrometer MC-ICP-MS, Neptune^{TM}, Finnigan MAT) at low resolution ($\Delta m/m = 400$) using 9 blocks of 9 integrations of approximately 8.4 s each for Pb and 5 blocks of 9 integrations for Cu, followed by a 40s baseline measurement. Mercury (^{202}Hg) and Ni (^{60}Ni) interferences on Pb and Cu isotopes respectively were monitored during acquisition.

A standard reference material (NIST 981 and NIST 976) was used to monitor the precision and accuracy of the measurements over the whole period of analysis. The obtained average accuracy is estimated to be below 0.15 ‰ (2σ) for $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ and 1.3 ‰ (2σ) for $^{206}Pb/^{204}Pb$. The average $^{207}Pb/^{206}Pb$ isotopic composition of the last 50 measurements of the NIST981 over the last 4 years is 0.914559 (± 54, 2 σ), which is within error of the certified value of 0.914640 (± 33, 2σ, Catanzaro *et al.*, 1968). External precision for $\delta^{63}Cu$ values is estimated to be 0.4 ‰ (Markl *et al.,* 2006).

5. Results and discussion

5.1. Lead isotopes

The whole range of lead isotope ratios of the ores from CIZ and OMZ is from 18.165 to 19.713 for $^{206}Pb/^{204}Pb$, 0.797 to 0.859 for $^{207}Pb/^{206}Pb$ and 1.955 to 2.108 for $^{208}Pb/^{206}Pb$ (Table I) which encompasses the range between and partly overlaps with the fields for Cyprus and Sardinia (Fig. 1). Our new data together with literature data are shown in figure 3 for CIZ and in figure 4 for OMZ and IPB in comparison with the fields for Cyprus and Sardinia.

As shown in the brief introduction to the geology of the South central ore districts CIZ is subdivided into 1. the central Los Pedroches Batholith complex (PBT), which encompasses the area of Los Pedroches sensu strictu (samples 11 to 36 and 43 in figure 2 and Table 1), and the district of Andujar-Montotro (samples 37 to 41); 2. the exocontact (peri) batholith occurrences (OVD) with samples 10, 42 and 44 to 47, the Alcudia-Almadén (Santa Eufemia)-Castuera (AAC) area (samples 8 and 9) and Linares (sample 48). Our new data (Fig. 3) indicate the

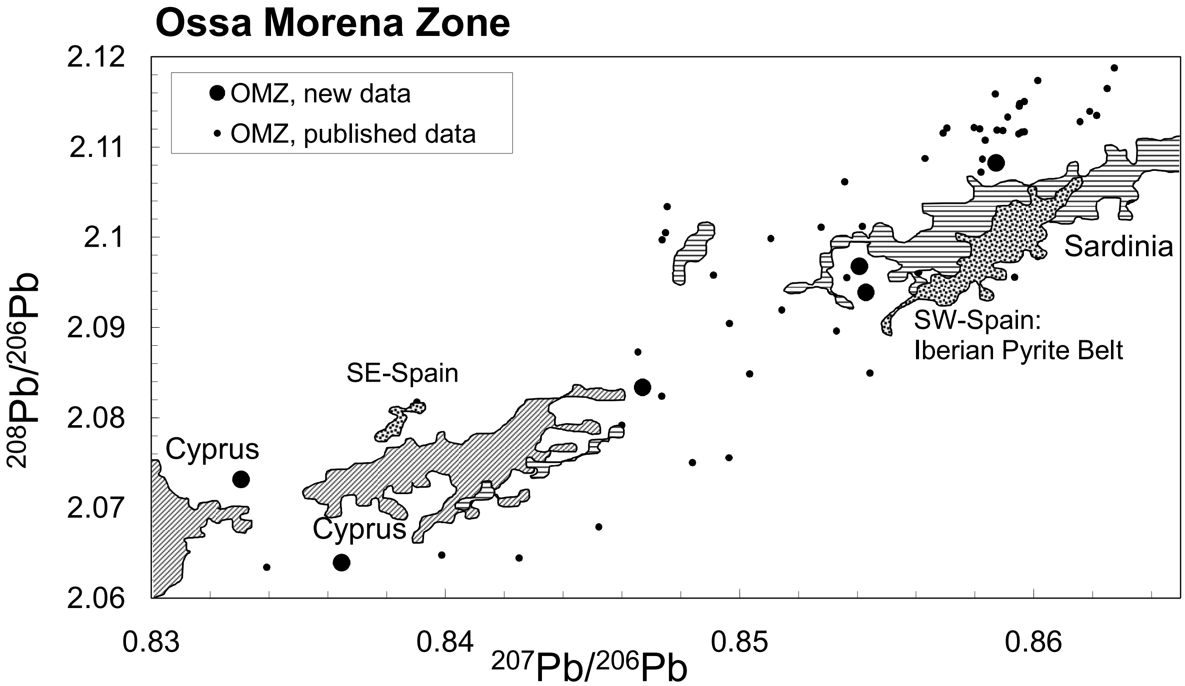

Fig. 4.- Lead isotope results of the copper ores from the Ossa Morena zone in a diagram ^{207}Pb/^{206}Pb versus ^{208}Pb/^{206}Pb. The analytical errors are smaller than the symbols (compare Table I). The OMZ ores cover a large area in the isotope diagram.

Fig. 4.- Resultados de los isótopos de plomo obtenidos de las menas de cobre de la Zona de Ossa Morena (OMZ) en un diagrama ^{207}Pb/^{206}Pb versus ^{208}Pb/^{206}Pb. Los errors analíticos son menores que los de los símbolos (ver Tabla I para comparar). Las menas de OMZ representan una zona importante del diagrama isotópico.

existence of two separate lead isotope fields for CIZ, one consisting exclusively of samples from the inner batholith occurrences (PBT sensu strictu) with comparatively low lead isotope ratios (^{207}Pb/^{206}Pb = 0.842-0.85 and ^{208}Pb/^{206}Pb = 2.078-2.092) and a second with higher lead isotope ratios (^{207}Pb/^{206}Pb = 0.854-0.861 and ^{208}Pb/^{206}Pb = 2.094-2.108) consisting of samples from the exocontact batholith occurrences (OVD), the two AAC samples and the one Linares sample. The consideration of literature data (Santos Zalduegui *et al.*, 2004) clearly establishes Linares, AAC and OVD as a separate, homogeneous, high lead isotope ratio field (Fig. 3). This field is close to one lead isotope field from Sardinia but, on average, at slightly higher ^{208}Pb/^{206}Pb. It is highly unlikely that the similarity will lead to ambiguity in the future since the Sardinian ores are mostly lead deposits and copper mining was subordinate. Highly important is the difference to the occurrences from IPB in SW Spain. Linares, AAC and OVD have significantly higher ^{208}Pb/^{206}Pb which will make a distinction between the two occurrences for artefacts easily possible. The Los Pedroches Batholith complex (PBT) forms a separate isotope ratio group in the vicinity of one field for Cyprus. It fills the missing gap in the general reference data bank and will facilitate provenance studies in the future.

Two samples from PBT (nb. 15 and 16) plot at very low ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratios outside the scale of figure 3. These secondary copper ores may have been formed from U-bearing hydrous solutions soon after the ore formation event which caused the preferential growth of ^{206}Pb. A copper sulphide (nb. 30) plots with the OVD, Linares and AAC ores rather than in the PBT field. We cannot offer an explanation here.

Our three new OMZ data are vastly differing with a range from close to Cyprus up to Sardinia (Fig. 4). This is also the range of the available literature data (Stos-Gale *et al.*, 1995; Marcoux *et al.*, 2002; Hunt Ortiz, 2003; Santos Zalduegui *et al.*, 2004; Tornos and Chiaradia, 2004) as seen in figure 4. A concentration of lead isotope ratios occurs in a high ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb field above Sardinia which gives these ores their own identity. The wide range of lead isotope ratios is an expression of the previously described diversity of the OMZ in ore types, metallogenesis and age of ore deposition. CIZ and IPB have their own identity with distinct ore forming events but OMZ with its geographic position in between them seems to be a mixture of both with repeated ore forming events The field for AAC/Linares/OVD and SW Spain is very tightly constrained and their ore deposits will always be easily identifiable.

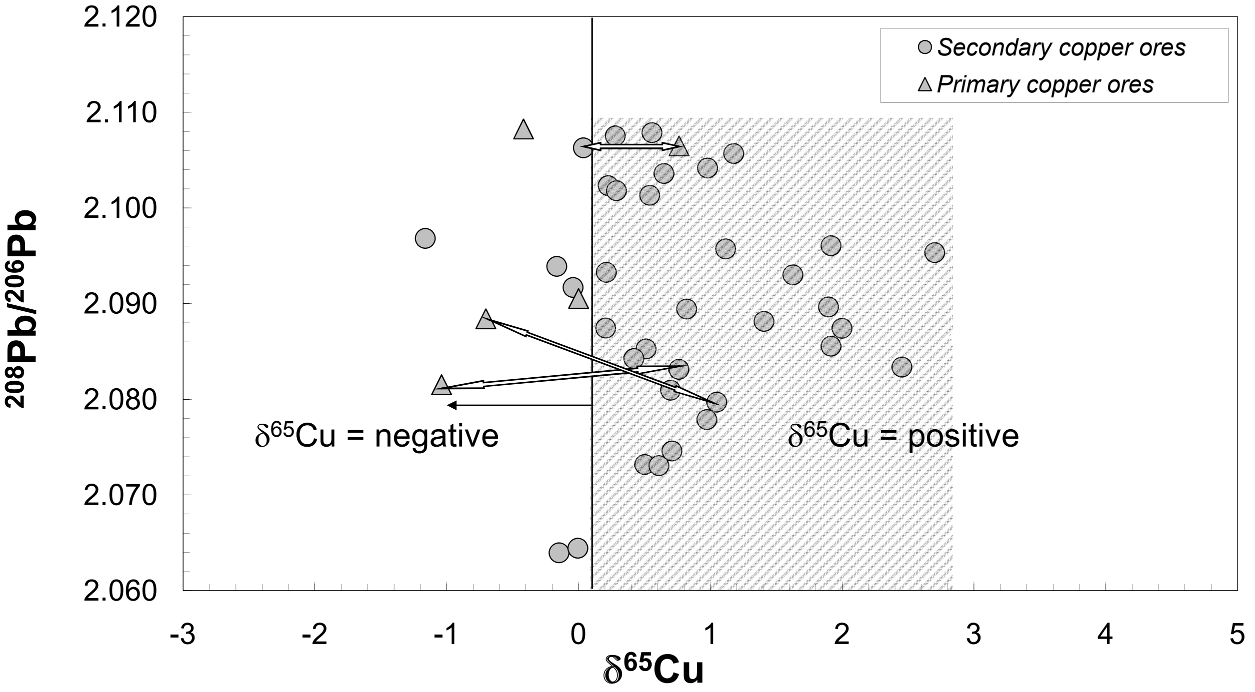

Fig. 5.- δ^{65}Cu isotope diagram. The secondary copper ores of Sierra Morena have positive δ^{65}Cu values but variable lead isotope ratios. The few primary sulphide ores analysed concentrate on negative δ^{65}Cu values. The arrows indicate corresponding primary and secondary ores samples.

Fig. 5.- Diagrama isotópico δ^{65}Cu/^{63}Cu. Las menas secundarias de cobre de Sierra Morena tienen valores positivos de δ^{65}Cu pero relaciones variables del isótopo de plomo. Las escasas menas de azufre analizadas concentran valores negativos de la relación δ^{65}Cu/^{63}Cu. Las flechas indican las muestras de menas primarias y secundarias.

As stated above the lead isotope signature of the Iberian Pyrite Belt (South Portuguese Zone) is well defined by literature data (Pomiés *et al.*, 1998; Lescuyer *et al.*, 1998; Marcoux, 1998; Marcoux *et al.*, 1992; Stos-Gale *et al.*, 1995). IPB ores have extremely homogeneous lead isotope ratios which allow the definition of a tight lead isotope field. Our one analyzed sample plots at the low isotope ratio end of the field. The IPB field does not overlap with that from CIZ, it occurs at significantly lower ^{208}Pb/^{206}Pb ratios (Fig. 4). OMZ ores partly overlap with IPB but at still lower ^{208}Pb/^{206}Pb ratios (Fig. 4).

5.2 Copper isotopes

Natural copper isotope variation have already been found useful as a geochemical tracer in ore geology (Zhu *et al.*, 2000; Larson *et al.*, 2002) and were suggested as a possible tracer in archaeology (Gale *et al.*, 1999; Woodhead *et al.*, 1999). In advance to the present study, Durali-Müller (2005) had analysed copper isotopes of primary and secondary copper ore minerals from individual localities by MC ICP-MS in Frankfurt. She observed that all secondary copper minerals (various malachite and azurite samples from Germany, Tuscany and Namibia) had positive δ^{65}Cu values, whereas δ^{65}Cu values in the corresponding sulphides had negative δ^{65}Cu. The lead isotope ratios were identical in the sulphides and their corresponding secondary minerals. The secondary copper ores from the Sierra Morena are in agreement with these observations: They have positive δ^{65}Cu values from 0 to + 2.7 but encompass a wide range of lead isotope ratios corresponding to their primary mineralisation (Fig. 5). The few primary sulphides analysed in this study support the inferences from the work by Durali-Müller (2005) namely that the primary lead isotope signatures are retained during the oxidation processes in the upper part of an ore deposit or during weathering, but that these processes fractionate the copper isotopes by a preferred partitioning of the lighter copper isotope into a hydrous phase at the low temperature of these processes. Thus, the copper isotopes will become important in detailed studies on the use of primary *versus* secondary ore deposits for the manufacturing of artefacts.

6. Summary and outlook

With this study we provide further and so far lacking data for a lead isotope reference data bank for provenance studies of copper objects. A gap is filled in the knowledge on southern Spain ore deposits which allows the correct interpretation of the origin of the copper ore for antique artefacts. For example, the lack of such data made the ore finger printing very difficult in a study on copper coins from the early Roman emperors (Klein *et al*., 2004). Because the PBT fields were unknown at that time the authors had to resort to an ore deposit mixing model. With the new data it has become clear that mining in the Los Pedroches area was already substantial during the early Roman Empire time. It will be possible in the future to accurately distinguish between the various ore deposit fields in Spain even though the OMZ deposits cover a large area in the lead isotope diagrams. However, the overlap with other ore deposit fields (which are much more tightly constrained) is very small and a distinction should be possible in most cases. Copper isotopes will become useful as tracers of whether oxidized or primary sulphide ores had been used in the production of artefacts.

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