Native silver resources in Iberia

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Zusammenfassung

Vorkommen gediegen Silbers in Iberien

Die Nutzung von Silber im Südosten der Iberischen Halbinsel ist während der Bronzezeit (ca. 2250–1450 cal BC) besonders in der sogenannten El Argar Kultur auffallend. Die Analyse der Materialzusammensetzung (Spurenelemente) zeigt, dass nicht durch Kupellation gewonnenes, sondern gediegen Silber oder Silberchlorid (hauptsächlich Cerargyrit) als Rohstoffe genutzt wurden.

Der folgende Beitrag stellt alle Vorkommen gediegen Silbers und Silberchlorids auf der Iberischen Halbinsel vor und diskutiert deren Zugänglichkeit in vorgeschichtlicher Zeit sowie die chemische Zusammensetzung ermittelt durch energiedispersive Röntgenfluoreszenzanalyse (EDRFA) und energiedispersive Röntgenspektroskopie im Rasterelektonenmikroskop (REM-EDX). Des Weiteren werden erste Ergebnisse der Bleiisotopenanalyse vorgestellt. Diese wurde mittels induktiv gekoppelter Plasma-Multikollektor Massenspektrometrie (ICP-MC-MS) durchgeführt.

Summary

The use of silver in south-eastern Iberia during the Bronze Age (c. 2250–1450 cal BC) is conspicuous in the so-called El Argar Culture. Trace elements detected in the compositional analyses of the objects coupled with the absence of cupellation residue reveal that native silver or silver chlorides (mainly cerargyrite) were used as resources.

In this paper we present all the Iberian deposits of native silver or silver chlorides and discuss their accessibility in prehistoric times as well as their compositional characterisation by energy dispersive X-ray fluorescence (EDXRF) analyses and a scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDX). A first approach towards the definition of their isotopic fields by lead isotope analyses (LIA) is also presented. LIA were conducted using an inductively coupled plasma multi-collector mass spectrometer (ICP-MC-MS).

Introduction

The first evidence for the use of silver date back to the 4th millennium BC, recorded in the Middle East and represented by two rings from Beycesultan, Anatolia, and Sialk, Iran (Ghirshman 1938, 16 f.; Wertime 1973, 883; Kohlmeyer 1994). Since then, the use of silver is documented in Central Europe, Italy, and the Aegean during the 3rd millennium BC (Makkay 1991; Primas 1995; Renfrew 1972) and the first silver ingots were excavated by H. Schmidt at Troy II–III (Avilova/Terejova 2007, 186). During the 2nd millennium BC, silver reached Western Europe where its use is documented for Brittany and Iberia (Fig. 1; Montero Ruiz et al. 1995). However, silver finds on prehistoric sites are usually rare apart from some exceptions. One of these is the necropolis of Byblos with 233 objects. 10 % of its burials date to 3880–3200 BC and contained silver objects, while gold only appears occasionally[1]. Another exception is the so-called El Argar Culture of south-eastern Iberia, having so far yielded a total of 826 silver objects (792 Ag and 34 AgCu) with most of these found on the site of El Argar, Almería, containing c. 300 objects (Fig. 2). This amount of silver objects contrasts with just 25 gold objects found until now (Murillo-Barroso 2013, 233). These silver items are mostly ornaments, usually small rings or spirals – but also some massive bracelets –, beads, and sheets or rivets on copper-based tools or weapons. Complex decorations or silver vessels such as those from Brittany or the Middle East are completely absent. A few diadems represent the most complex objects of this group (Fig. 3).

Secure evidence of cupellation (i. e. litharge and cupellation hearth materials) is known in the Middle East from the sites of Habuba Kabira in Syria (Pernicka et al. 1998) or Fatmalı-Kalecik in Anatolia (Hess et al. 1998) both dating to the 4th millennium BC.

However, despite the abundance of silver objects in Iberia during the 2nd millennium BC, cupellation debris is not clearly documented until the 1st millennium BC when the Phoenician presence and wider Mediterranean contacts were well established (Hunt Ortiz 2003; Bartelheim 2007). This absence of cupellation by-products and the significant quantities of volatile elements in the Argaric silver objects (up to 0.3 % Hg) – which would have evaporated if cupellation had been carried out – led us to argue that the Argaric silver objects were produced by melting native silver or silver chlorides (Bartelheim et al. 2012; Murillo-Barroso 2013).

Nonetheless, native silver is a rare element in nature and it has been argued to occur only below the phreatic zone,

1 Dunand 1973, 214–216; Prag 1978; Kohlmeyer 1994; Primas 1995.

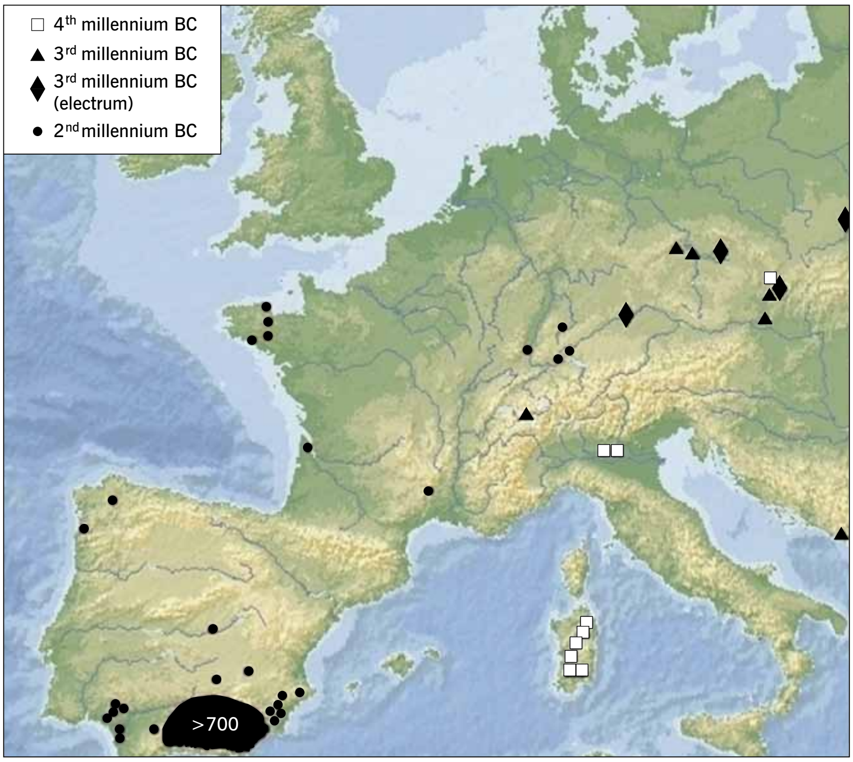
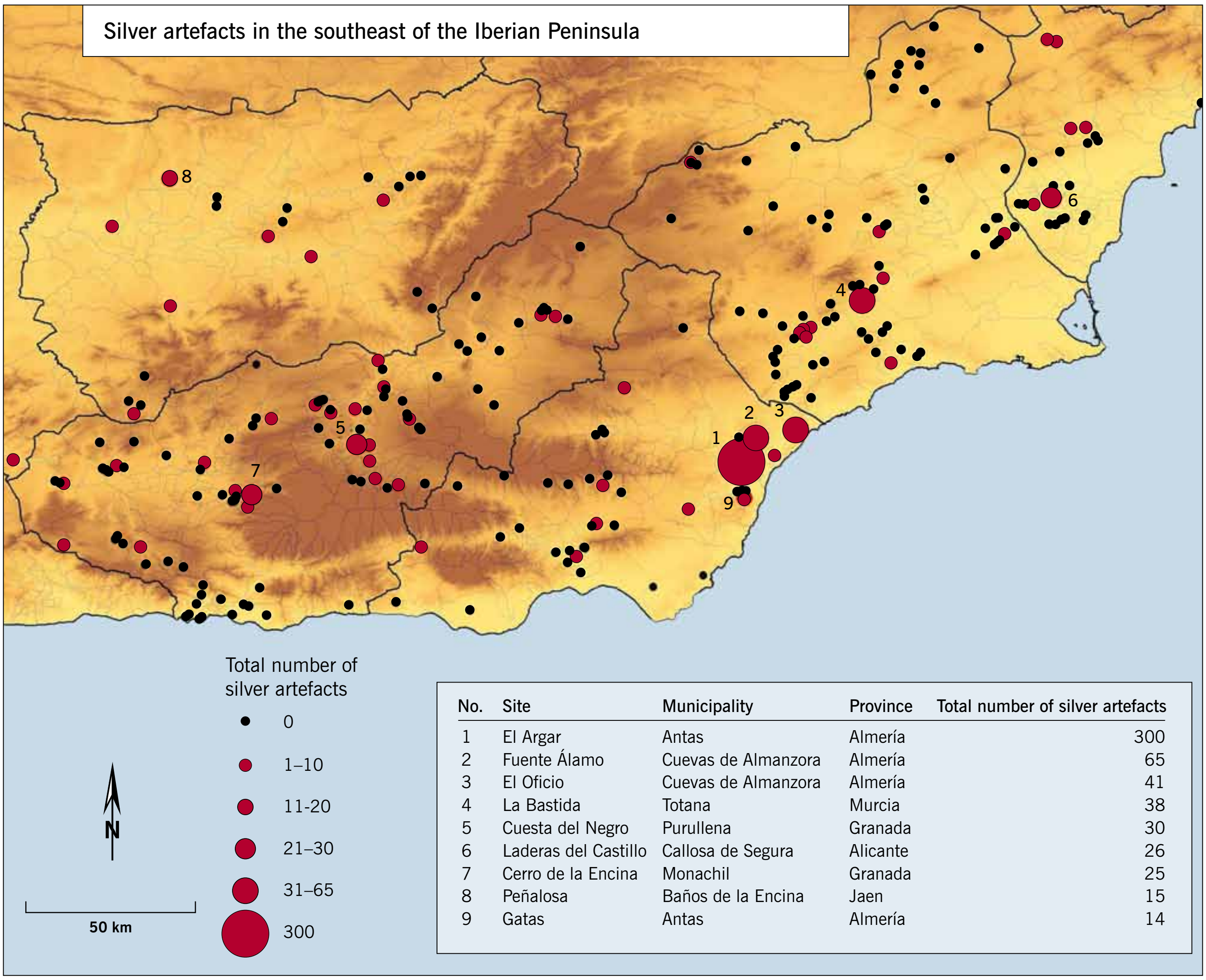


Fig. 1 Distribution of prehistoric (4th–2nd millennium BC) silver finds in Western and Central Europe. The black area in southern Iberia marks the 2nd millennium BC find concentration.

Abb. 1 *Verbreitung der prähistorischen Silberfunde (4.–2. Jt. v. Chr.) in West- und Mitteleuropa. Die schwarz markierte Zone im Süden der iberischen Halbinsel zeigt die Fundkonzentration des 2. Jts. v. Chr. an.*



No.	Site	Municipality	Province	Total number of silver artefacts
1	El Argar	Antas	Almería	300
2	Fuente Álamo	Cuevas de Almanzora	Almería	65
3	El Oficio	Cuevas de Almanzora	Almería	41
4	La Bastida	Totana	Murcia	38
5	Cuesta del Negro	Purullena	Granada	30
6	Laderas del Castillo	Callosa de Segura	Alicante	26
7	Cerro de la Encina	Monachil	Granada	25
8	Peñalosa	Baños de la Encina	Jaen	15
9	Gatas	Antas	Almería	14

Fig. 2 Distribution of silver objects in the southeastern Iberian Argaric society.

Abb. 2 *Verteilung der Silberobjekte der El Argar Kultur im Südosten der Iberischen Halbinsel.*

Fig. 3 Selection of Argaric silver objects. a Massive bracelet from grave 35 of Cuesta del Negro; b Bracelet from grave 292 of El Argar; c Spiral ornament from grave 21 of Cerro de la Encina; d Bracelet from El Oficio; e Ornament from grave 14 of Fuente Álamo; f Ornament from grave 678 of El Argar; g Bracelet from grave 21 of Cerro de la Encina; h Gravegoods fom grave 7 of Fuente Álamo (all objects except for the blade are made of silver); i Diadem from grave 9 of Fuente Álamo; j Handle of a burin from grave 2 of Gatas; k Diadem from grave 2 of Gatas; l Diadem from grave 6 of El Oficio; m Diadem from grave 398 of El Argar; n Diadem from grave 51 of El Argar; o Diadem from grave 454 of El Argar; p Diadem from grave 62 of El Argar.

***Abb. 3** Auswahl von Silberobjekten der El Argar Kultur. a Massiv gearbeiteter Armreif aus Grab 35 von Cuesta del Negro; b Armring aus Grab 292 von El Argar; c Spiralförmiger Schmuck aus Grab 21 von Cerro de la Encina; d Armring von El Oficio; e Schmuck aus Grab 14 von Fuente Álamo; f Schmuck aus Grab 678 von El Argar; g Armring aus Grab 21 von Cerro de la Encina; h Beigaben aus Grab 7 von Fuente Álamo (alle Objekte außer der Klinge sind aus Silber gefertigt); i Diadem aus Grab 9 von Fuente Álamo; j Griff eines Stichels aus Grab 2 von Gatas; k Diadem aus Grab 2 von Gatas; l Diadem aus Grab 6 von El Oficio; m Diadem aus Grab 398 von El Argar; n Diadem aus Grab 51 von El Argar; o Diadem aus Grab 454 von El Argar; p Diadem aus Grab 62 von El Argar.*

because it reacts easily with water (Tylecote 1987). Therefore, some authors propose the pre-eminence of the use of silver-lead minerals as opposed to native silver in early metallurgy (Meyers 1993; Harrison 1983; Kassianidou 1992). Others even suggest that »at least in the Old World, silver metallurgy is automatically connected to lead metallurgy« (Bachmann 1993, 487) due to the fact that it would have been difficult for prehistoric metallurgists to reach the native silver resources under the phreatic zone and especially because of the fact that silver is associated with lead which in most deposits acts as the main collector for noble metals.

However, since the exploitation of native silver or silver chlorides is clearly documented for Iberia, in this paper we will discuss the presence of native silver and silver chloride resources in Iberia, their availability to prehistoric societies, and the analytical data known up to now from these deposits.

Iberian native silver resources

Despite native silver being rare in nature, there are important native silver/silver chloride deposits in Iberia, with Herrerías, El Horcajo, and Hiendelaencina being the most important ones (Fig. 4).

Herrerías (No. 1–7 in Fig. 4), where native silver, amalgam, and cerargyrite are widely recorded, lies in the Vera basin, Almería, in the core region of the Argaric society. Because of its location, Herrerías was proposed to have been the main silver source of the Argaric society (Siret/Siret 1890, 284; Cuadrado Ruiz 1947; Montero Ruiz et al. 1995). It presents a deposit of Fe-Mn oxides and hydroxides, base metal sulphides, and native silver, adjacent to the Pb-Sb-Ag sulphide and sulphosalts of the vein-type mineralisation of Sierra Almagrera (Martínez Frías 1991). Both, Herrerías and Sierra Almagrera, have a similar hydrothermal genesis (Martínez Frías 1992), which might be mirrored in an isotopic similarity, although these deposits are geographically separated by the Palomares Fault (Fig. 5).

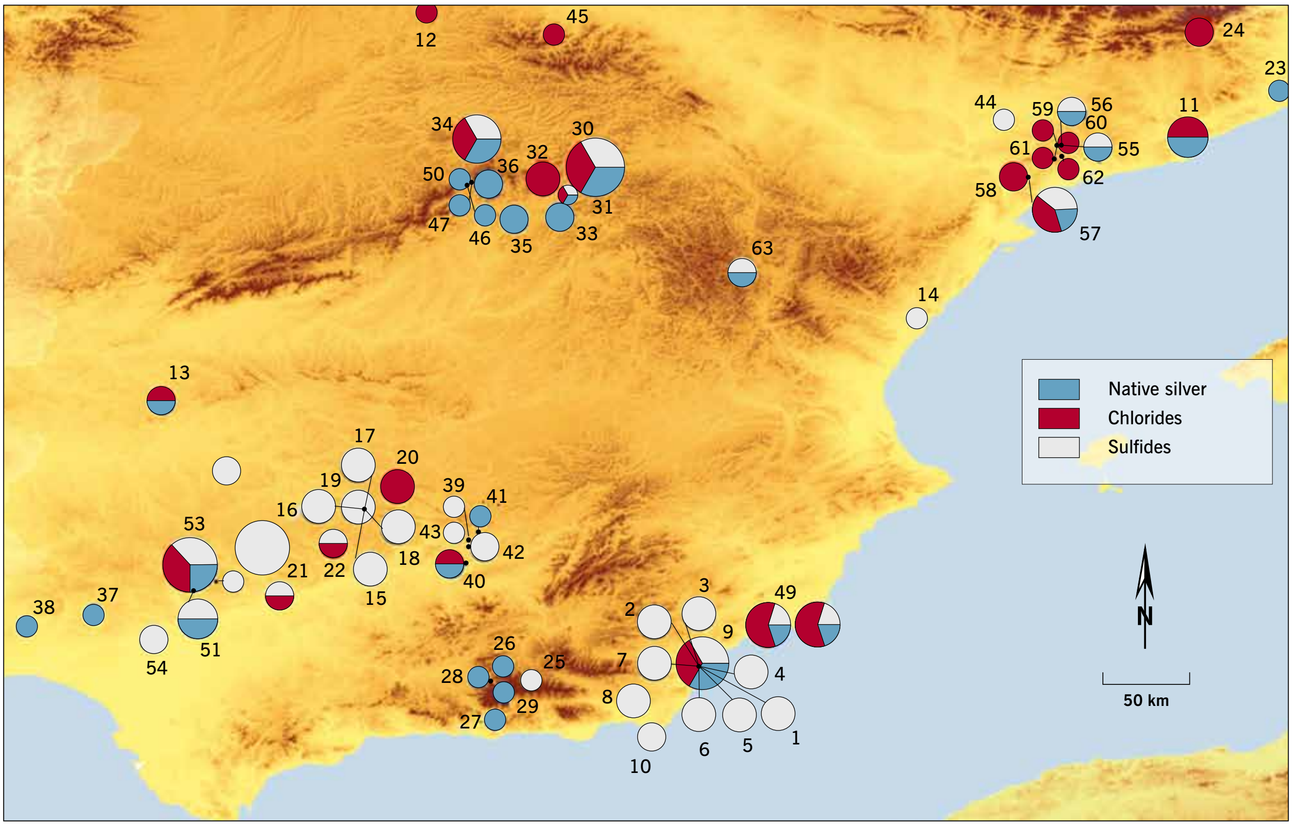


Fig. 4 Location of silver mines. 1–7 Herrerías, Almería; 8 Sierra de los Filabres, Almería; 9 Barranco del Jaroso, Sierra Almagrera, Almería; 10 Cabo de Gata, Almería; 11 S. Cugat del Vallés, Barcelona; 12 Mansilla, Burgos; 13 Plasenzuela, Cáceres; 14 Mina de la Botalaria, Borriol, Castellón; 15–19 El Horcajo, Valle de Alcudia, Ciudad Real; 20 Almodóvar del Campo, Ciudad Real; 21 Casiano del Prado, Córdoba; 22 La Espuela de San Miguel, Villanueva de Córdoba, Córdoba; 23 Caldes de Malavella, Girona; 24 Vall de Ribes, Girona; 25–29 Sierra Nevada, Granada; 30–32 Hiendelaencina, Guadalajara; 33 Gajanejos, Guadalajara; 34–36 Sierra de Guadarrama, Madrid; 37 Río Tinto, Huelva; 38 Tharsis, Huelva; 39–43 La Carolina-Linares-Santa Elena-El Centenillo, Jaén; 44 Mina Eureka, Torre de Cabdella, Lleida; 45 San Lorenzo, Logroño; 46 Acebeda, Madrid; 47 Robregordo, Madrid; 48 La Unión, Cartagena, Murcia; 49 Dolores Mine I and II, Postrana, Mazarrón, Murcia; 50 Prádena, Segovia; 51 Cazalla de la Sierra, Sevilla; 52 Constantina, Seville; 53 Guadalcanal, Seville; 54 Gerena, Seville; 55 Vimbodí, Tarragona; 56 Espuga de Francolí, Tarragona; 57 Falset, Tarragona; 58 Bellmunt, Tarragona; 59 Farena, Tarragona; 60 Capafonts, Tarragona; 61 Prades, Tarragona; 62 La selva del Camp, Tarragona; 63 Silúrico del Albarracín, Teruel.

Abb. 4 *Lage verschiedener Silberminen. 1–7 Herrerías, Almería; 8 Sierra de los Filabres, Almería; 9 Barranco del Jaroso, Sierra Almagrera, Almería; 10 Cabo de Gata, Almería; 11 S. Cugat del Vallés, Barcelona; 12 Mansilla, Burgos; 13 Plasenzuela, Cáceres; 14 Mina de la Botalaria, Borriol, Castellón; 15–19 El Horcajo, Valle de Alcudia, Ciudad Real; 20 Almodóvar del Campo, Ciudad Real; 21 Casiano del Prado, Córdoba; 22 La Espuela de San Miguel, Villanueva de Córdoba, Córdoba; 23 Caldes de Malavella, Girona; 24 Vall de Ribes, Girona; 25–29 Sierra Nevada, Granada; 30–32 Hiendelaencina, Guadalajara; 33 Gajanejos, Guadalajara; 34–36 Sierra de Guadarrama, Madrid; 37 Río Tinto, Huelva; 38 Tharsis, Huelva; 39–43 La Carolina-Linares-Santa Elena-El Centenillo, Jaén; 44 Mina Eureka, Torre de Cabdella, Lleida; 45 San Lorenzo, Logroño; 46 Acebeda, Madrid; 47 Robregordo, Madrid; 48 La Unión, Cartagena, Murcia; 49 Dolores Mine I und II, Postrana, Mazarrón, Murcia; 50 Prádena, Segovia; 51 Cazalla de la Sierra, Sevilla; 52 Constantina, Seville; 53 Guadalcanal, Seville; 54 Gerena, Seville; 55 Vimbodí, Tarragona; 56 Espuga de Francolí, Tarragona; 57 Falset, Tarragona; 58 Bellmunt, Tarragona; 59 Farena, Tarragona; 60 Capafonts, Tarragona; 61 Prades, Tarragona; 62 La selva del Camp, Tarragona; 63 Silúrico del Albarracín, Teruel.*

There are references to the Herrerías' native silver since the 19th century. The deposit was discovered and first exploited in a modern context in 1869 by F. Soler Flores, president of the society »Unión de Tres«, when specimens of native silver up to 2 kg were found (Variedades 1876, 7). Nonetheless, it is not only the huge amount of native silver recovered what is significant in Herrerías, but the fact that it appeared at surface levels (Molina Sánchez 1991; Calvo Rebollar 2003) and therefore would have been easily available for prehistoric societies. Calvo Rebollar states that native silver specimens »could be initially obtained with no more work than picking them up« (Calvo Rebollar 2003, 75). This superficial concentration of native silver was first stated by Sierra (1926) who explained this phenomenon as a process of secondary dissolution in low-mineralised meteoric water. Silver would be deposited then *per ascensum* in the higher layers of the host rock (Sierra 1926, 45). These mineralised fluids are related to magmatic hydrothermal processes (Arribas Rosado/Arribas Moreno 1995, 40 f.). This deposition of silver has also been described for other hydrothermal areas such as Sierra Alhamilla (Guardiola/Sierra 1926, 346). Modern exploitations were resumed at Herrerías in 1992 to extract barite and new specimens of native silver with high levels of mercury (c. 10 % Hg) were recovered (Navarro et al. 1999).

The **El Horcajo mine** (No. 15–19 in Fig. 4), located in the Alcudia Valley mining district, Ciudad Real, is composed by three main veins whose main component is argentiferous galena which is embedded in a host rock of anchorite and quartz. Native silver is recorded since the 19th century, usually as small specimens up to 5 mm long, although there were some exceptions: strands of native silver up to 6 kg were recovered from a single cavity in 1877 and two specimens of 0.3 m² each were donated to the Natural History

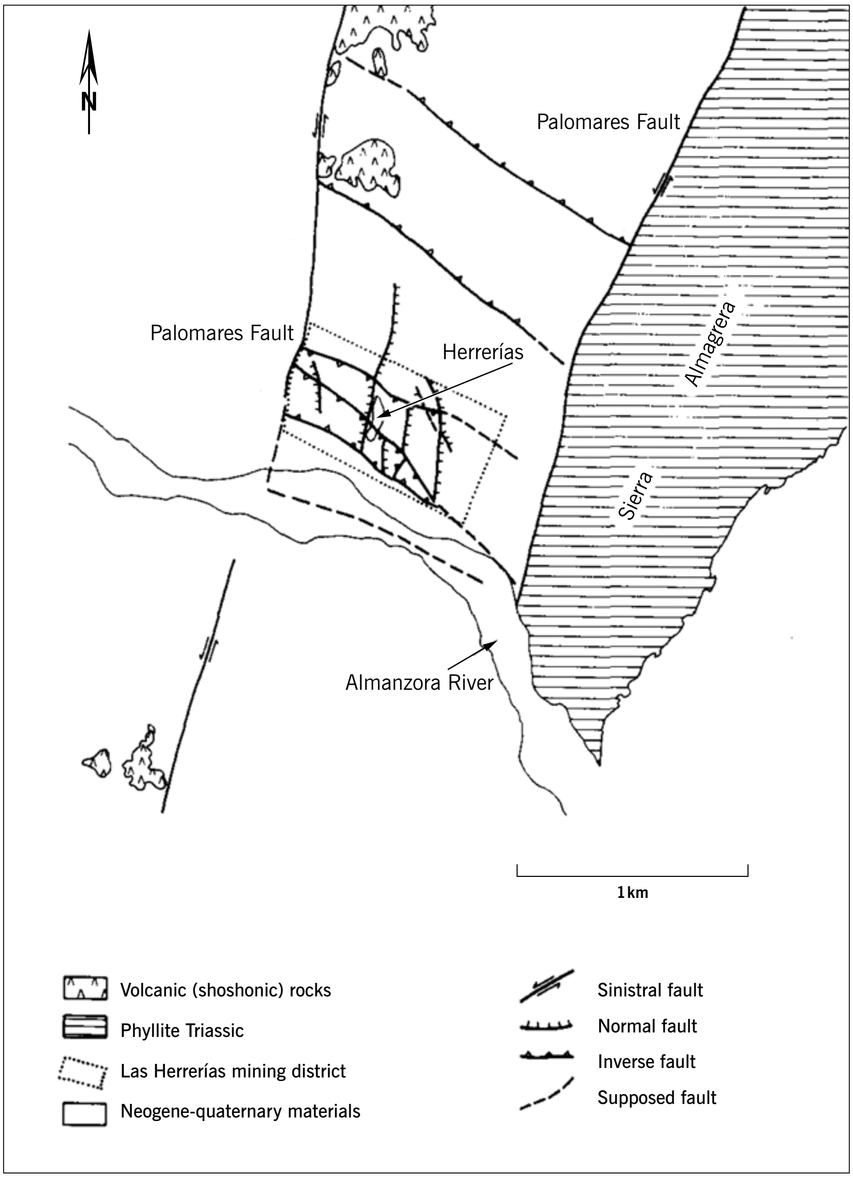


Fig. 5 Location of the Herrerías mining district, separated by the Palomares Fault from the adjacent Sierra Almagrera mining district.

Abb. 5 *Lageplan der Bergbauregion von Herrerías, durch die Palomares Verwerfung getrennt von der angrenzenden Bergbauregion Sierra Almagrera.*

Office and to the School of Mining Engineers (Sáinz de Baranda et al. 2004)[2].

Native copper is also reported to occur intertwined with strands of native silver which for prehistoric metallurgists would have been difficult to isolate and therefore, copper impurities would be expected.

Hiendelaencina (No. 30–32 in Fig. 4) is part of an argentiferous belt in the central system in the province of Guadalajara. It is a vein-type mineralisation where silver is preferentially deposited in vertical faults embedded in a host rock which is rich in quartz and gneiss. In the upper levels, silver occurs in the form of chlorides and bromides, and at greater depth in the form of sulphides (Martínez Frías et al. 1992, 926).

Apart from these main silver deposits, native silver has been documented in small quantities in other areas of Iberia. These sources, which may be of no economic importance today, could have been highly profitable in prehistory.

Southeast (Sierra Almagrera, Sierra Filabres, Cabo de Gata, and Sierra Alhamilla, all Almería; Cabo de Palos and Mazarrón, both Murcia; and Cartagena; No. 8–10, 48–49 in Fig. 4): The significant »Jaroso« vein was discovered in 1840 in Sierra Almagrera. It is rich in native silver and silver chlorides and sulphides, as well as in native copper (Monasterio y Correa 1850; Pellicó 1852). Small specimens, some of them associated with galena, were recovered in Sierra Almagrera (Calderón 1910, 66) and small specimens of native silver were recovered at the surface in Sierra Alhamilla (Guardiola/Sierra 1926, 349). Native silver has also been reported for the Poderoso vein, in Cabo de Palos (Domergue 1987), and – occurring together with cerargyrite – in Mazarrón (Calvo Rebollar 2003).

South (Sierra Nevada and Alpujarras, both Granada; and Níjar, Málaga; No. 25–29 in Fig. 4): Small occurrences of native silver have been stated for Sierra Nevada and Al-

2 This donation was also reported in Correspondencia de España 1877.

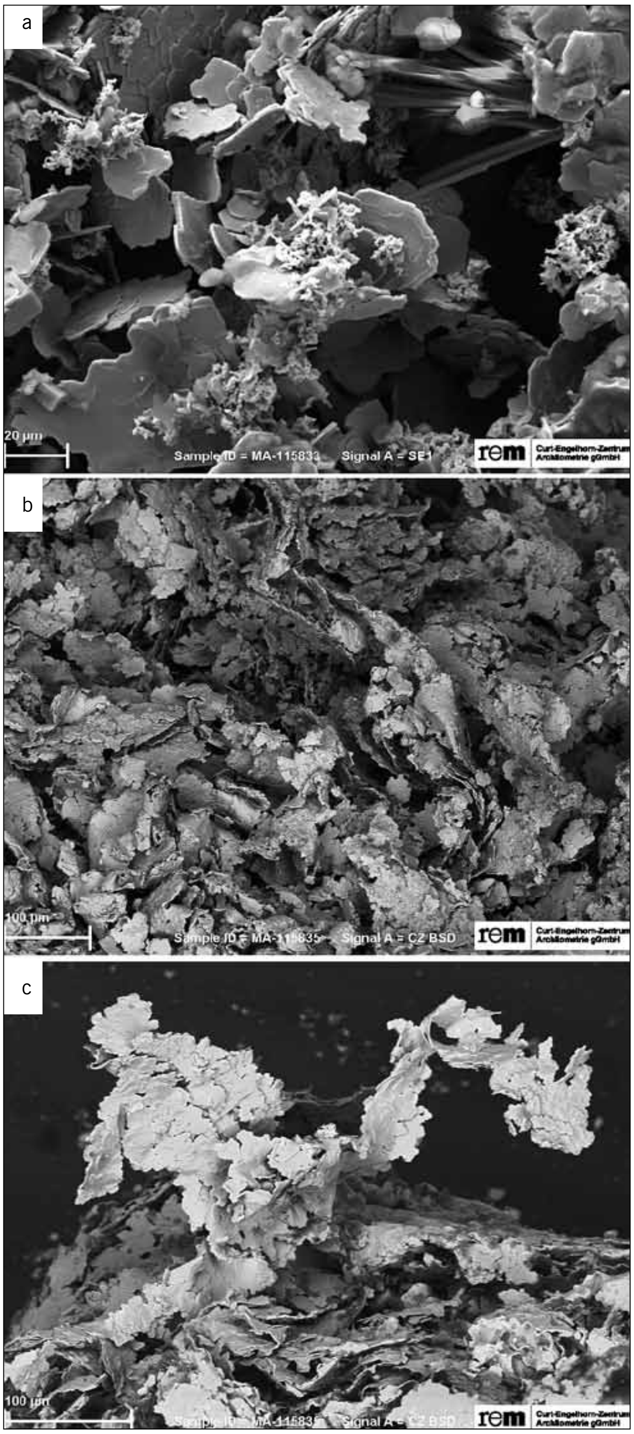


Fig. 6a–c SEM-BSE images of native silver specimens from Herrerías.

Abb. 6a–c *Rückstreuelektronenbild eines Rasterelektronenmikroskops (REM-RE) einer Probe gediegen Silbers von Herrerías.*

pujarra, together with silver sulphides (Calderón 1910, 64; Galán/Mirete 1979).

Southwest (provinces of Córdoba, Huelva, and Seville; No. 21–22, 37–38, 51–54 in Fig. 4): In Córdoba, some small specimens associated with galena and cerargyrite are reported in the area of Posadas (Calderón 1910; Carbonell Trillo-Figueroa 1929), although the biggest specimens come from the San Miguel mine, with examples of reticulated shape up to 4.0 cm in length or strands up to 0.5 cm in diameter (Calvo Rebollar 2003). In Huelva, some specimens of native silver were discovered in Tharsis, Riotinto. However, the richest silver mine in the southwest is Guadalcanar (No. 53 in Fig. 4), in Seville, where some native silver samples were documented (Pérez Domingo 1831).

Central Iberia (Linares-La Carolina, Jaén; Sierra Guadarrama, Madrid; Ciudad Real; No. 20, 33–36, 39–43, 46–47, 50 in Fig. 4): In Linares, some nodules of native silver were recovered on the surface from the Valdeinfierno vein (Mesa y Álvarez 1890, 212; Descubrimiento Importante 1882, 338; Calderón 1910). Nonetheless, galena from Linares is not as rich in silver as those sources in the adjacent mining districts of La Carolina or El Centenillo. It has therefore been suggested that native silver could have also occurred in these latter districts (Arboledas Martínez 2011). In the area of Guadarrama, the occurrence of small specimens of native silver, chlorides, and sulphides has also been noticed as part of the argentiferous band in which Hiendelaencina is located.

North East (Catalonia and Castellón; No. 11, 14, 23–24, 44, 55–63 in Fig. 4): In Catalonia, specimens of native silver have been extensively documented in the Mina Balcoll in Falset, Molar-Bellmunt-Falset (MBF) mining district (Calvo Rebollar 2003; Abella 2008). Acantite (silver sulphide) and cerargyrite are also described for the same mine. Montero Ruiz et al. (2008, 295) provide XRF analyses data of two samples. The main feature is the presence of nickel and the absence of copper in both samples. Some lead and bismuth was also detected in one of them.

For the **north** (Galicia, Asturias, Navarra, Burgos, and Logroño; No. 12, 45 in Fig. 4) as well as for **Cáceres** (No. 13 in Fig. 4; Calvo Rebollar 2003) there are some vague references to the sporadic occurrence of native silver[3].

Nonetheless, despite the abundance of native silver in Iberia, analytical studies of these specimens have not been intensively developed – in part because some of these mines are nowadays exhausted or not economically profitable anymore. In this paper we will present some analytical work carried out for some native silver specimens from Herrerías and will discuss the isotopic characterisation of all mining districts mentioned above.

Compositional analyses of native silver from Herrerías

Three samples of native silver from Herrerías were studied at the laboratories of the Curt-Engelhorn-Centre Archaeometry, Mannheim. Compositional analyses were performed using EDXRF[4] and lead isotopes were quantified using a ICP-MC-MS[5]. Samples were also mounted in resin blocks, polished following the standard procedure, and studied under a SEM Zeiss EVO 60 MA 25 with a silicon drift detector attached.

Samples were observed under the SEM before being cut. Native silver hardly ever forms big crystals; it usually occurs

3 Pérez Domingo 1831, 40; Galán/Mirete 1979, 116; Calderón 1910, 61; Calvo Rebollar 2003.

4 For methodological questions see Lutz/Pernicka 1996.

5 See Niederschlag et al. 2003 for methodology.

Analysis no.	Cu	Ag	Pb	Fe	Se	Co	Cd	Sn	Te	Au	Hg
MA-115835	0.94	85.6	0.05	0.27	< 0.01	0.01	0.02	0.19	< 0.01	0.12	12.8
MA-115834	3.14	86.5	0.03	0.89	0.09	0.01	0.01	0.18	< 0.01	0.11	9.1
MA-115833	0.08	92.1	0.02	0.44	0.03	0.02	0.05	0.16	< 0.01	0.10	7.2

Tab. 1 Results of EDXRF analyses on three samples of native silver from Herrerías. Data are normalised (% wt).

Tab. 1 *Ergebnisse der EDRFA dreier Proben gediegen Silbers von Herrerías. Die Daten wurden auf 100 % normiert (Gew-%).*

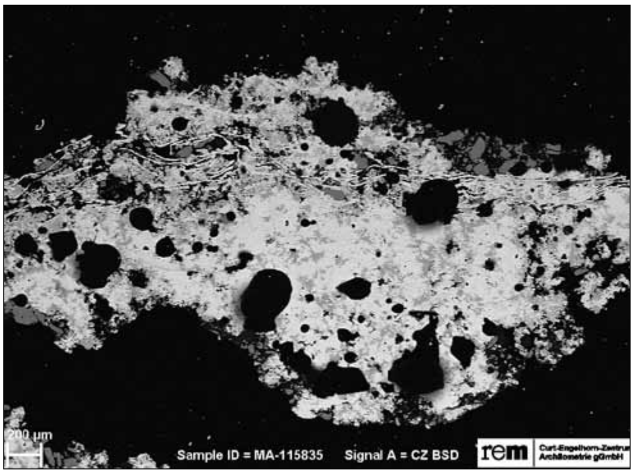


Fig. 7 SEM-BSE image of one native silver specimen.

Abb. 7 *Rückstreuelektronenbild eines Rasterelektronenmikroskops (REM-RE) einer Probe gediegen Silbers.*

forming dendritic, filamentous, flaky, or laminar aggregates although it can also be found as massive lumps filling faults or seams (Klein/Philpotts 2013, 433; Gribble/Hall 1992, 167). SEM analyses of samples from Herrerías showed their flaky shape (Fig. 6); rhomboidal flakes are easily visible, especially in Fig. 6a. EDXRF analyses of the samples revealed high levels of mercury and a significant amount of copper (Tab. 1). Most mercury would volatilise when melting the native silver. However, with a starting point of c. 13 %, some traces of mercury in the objects, as it has been documented (Bartelheim et al. 2012), are to be expected. Siret (1887) also analysed one sample of native silver recovered from Herrerías quantifying traces of copper (0.18 %).

SEM analyses obtained a precise view of the distribution of elements. Native silver appears as thin streams embedded in a matrix of amalgam (white filaments in the upper part of Fig. 7).

Mappings of the three samples were undertaken in detail. One colour is given to each element so their dispersion and alloys can be identified at once. As it had been seen in the SEM image with back-scattered electrons (BSE), silver appears as native silver streams (in dark blue in Fig. 8). Mercury is extensively documented, alloyed with silver and forming an amalgam matrix, distributed quite homogeneous in the entire sample (bright blue in Fig. 8). This is probably a specimen of arquerite (a variety of amalgam containing 13 % Hg).

Cerargyrite appears segregated (purple in Fig. 8). Copper presence is also significant (red in Fig. 8), which is not alloyed with silver but segregated. It is a common inclusion in silver deposits and also appears intertwined with silver in El Horcajo or Hiendelaencina, although it is not documented in native silver from Falset. However, due to the small size of the inclusions, it would probably be alloyed with silver when melted for casting objects. Actually, copper is usually detected over 1 % (up to > 20 %) in Argaric silver objects – but both, their trace elements patterns and lead isotope analyses, show that this variability in copper compositions responds to the variability of copper inclusions in native silver and not to an intentional alloy (Murillo-Barroso 2013). Even some high values (> 20 %) can also be a result of natural alloying.

Crystals of barite were also documented (orange in Fig. 8), being consistent with the recent exploitation of Herrerías.

Isotopic characterisation of native silver deposits

Lead isotope analyses of native silver deposits are rare. Only two samples of native silver from El Falset and three samples from Herrerías have been analysed. From the other two main silver deposits, analyses in El Horcajo were conducted using galena, but there are only two samples analysed from this mine. However, its broader mining district (Alcudia Valley) is well defined with c. 90 samples of galena analysed. From Hiendelaencina, only two samples of lead ores are known, with very different isotopic ratios – therefore, its mining district cannot be established. Herrerías' isotopic field cannot be defined, because only three samples of native silver and one sample of copper ore have been analysed, although its isotopic field seems to overlap with that of Alma-

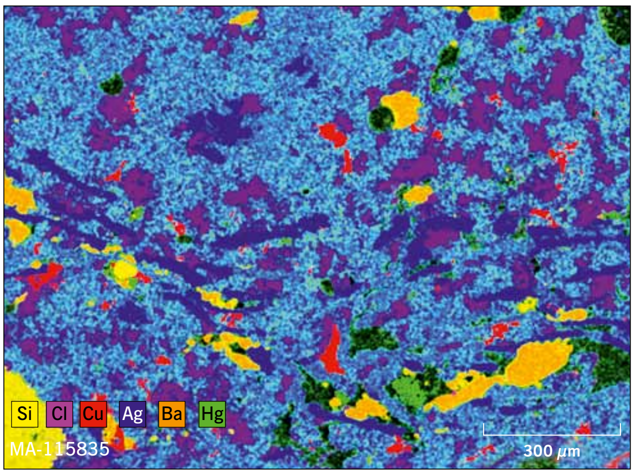


Fig. 8 Element mapping of a native silver specimen.

Abb. 8 *Elementverteilungsmuster einer Probe gediegen Silbers.*

Mine/sample	Id.	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}P/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}P/^{206}Pb$
Falset (Ag)	PA11658	18.358	15.679	38.529	0.85404	2.0986
Falset (Ag)	PA11657	18.358	15.670	38.499	0.85356	2.0971
Herrerías (Ag)	**13230**	**18.738**	**15.660**	**38.887**	**0.83572**	**2.0753**
Herrerías (Ag)	**13232**	**18.758**	**15.666**	**38.900**	**0.83516**	**2.0738**
Herrerías (Ag)	**13229**	**18.555**	**15.645**	**38.672**	**0.8432**	**2.0842**
Herrerías (Cu)	**MO354**	**18.760**	**15.692**	**39.032**	**0.83647**	**2.0806**
Hiendelaencina (Pb)	**PA22108**	**18.185**	**15.707**	**38.468**	**0.86371**	**2.1153**
Hiendelaencina (Pb)	**HIE–1**	**18.456**	**15.650**	**38.698**	**0.84796**	**2.0968**
El Horcajo (Alberto; Pb)	835088	18.185	15.594	38.267	0.8575	2.1043
El Horcajo (María Pilar; Pb)	835088	18.183	15.594	38.261	0.8576	2.1042

Tab. 2 Main silver deposits in Iberia. Lead isotope analyses conducted via a thermal ionisation mass spectrometer (TIMS) or ICP-MC-MS (bold) in different laboratories.

Tab. 2 *Bedeutende Silbervorkommen in Iberien. Bleiisotopenanalyse mittels Thermionen-Massenspektrometer (TIMS) oder ICP-MC-MS (fettgedruckt); Werte aus verschiedenen Laboren.*

grera (which is geographically close to Herrerías) due to the similarity in their geological formation.

Table 2 shows the LIA of ores from Herrerías, Horcajo, Falset, and Hiendelaencina. Native silver samples from Herrerías were conducted using a ICP-MC-MS at the Curt-Engelhorn-Centre Archaeometry. Copper from Herrerías and the unpublished sample from Hiendelaencina were analysed at the Geochronology and Isotopic Geochemistry Service of the Basque Country University (SGiker) also using an ICP-MC-MS.

Other potential catchment areas (such as Sierra Nevada or Sierra Filabres) lack isotopic analyses. The isotopic fields of other mining districts in which native silver has been documented in small quantities such as Sierra Almagrera (9 samples), Cabo de Gata (24 samples), Sierra Alhamilla (5 samples), Cartagena (9 samples), or Mazarrón (8 samples) have been well defined on the basis of galena analyses. The same is true for Linares (33 samples) and the MBF mining district (30 samples). Other even smaller silver occurrences also lack isotopic characterisations. This is the case of the evidence from the north of Iberia or some references from the southwest where the significant silver mine of Guadalcanal is not isotopically characterised.

Although lead isotope analyses of silver samples have not been extensively carried out, we can assume that their isotopic ratios could be similar to the signature of other ores from the same deposit, as it is detected in the samples of Falset and Herrerías, where some copper ores or galenas from the same deposits match with the isotopic ratios of the local native silver. Under this assumption, some preliminary hypothesis can be reached when comparing these geological areas with the isotopic ratios of the Argaric silver objects.

Up to now, 29 Argaric silver objects have been analysed and published. Most of them come from archaeological sites in the provinces of Granada and Jaén, in an area quite peripheral of the Argaric society and c. 200–300 km from Herrerías. Only three rings from archaeological sites close to Herrerías have been analysed (two from El Oficio, at a distance of c. 8 km, and one from El Argar, c. 10 km distant from Herrerías).

Up to now, none of their signatures match the samples from Herrerías (Fig. 9), with the Linares or Alcudia Valley representing the most probable provenance. Only one ring from El Oficio is close to the southeastern districts (Almagrera and Herrerías' samples). However, the exploitation of Herrerías cannot be discarded yet as most of the objects where concentrated in the Vera Basin (see Fig. 2), but the majority of the analyses were undertaken on objects from peripheral sites. Extensive sampling of silver objects from the core of the Argaric society, where Herrerías is located, is still to be undertaken.

Nonetheless, even if their specific provenances cannot be established yet, it seems to be clear that Herrerías was not the only ore deposit exploited in the Argaric period and that different ones were being used. The silver from tomb 255 in El Oficio is the best example: Silver rings were manufactured there using metal both from the southeast and from other mining districts probably somewhere close to the Linares or Alcudia Valley.

Conclusion

Silver studies have not been as intensively developed as copper-based ones and therefore silver mines are not as well characterised as copper or lead ones. Regarding compositional analyses of native silver deposits, ours represents the first approach for Iberia. We have documented the main components which occur together with native silver (mainly amalgam, cerargyrite, and copper), although extensive characterisation of both, Herrerías and other smaller silver deposits, is still needed.

Regarding the isotopic characterisations, there are still some difficulties to be solved: In the same way that the archaeological material is useless without a proper archaeological context, information extracted from minerals is worthless without the study of their geological background – and this is not always considered. The lead isotopic proportions of a given ore deposit depend on four geological aspects: 1. the origin of the metal; 2. the origin of the min-

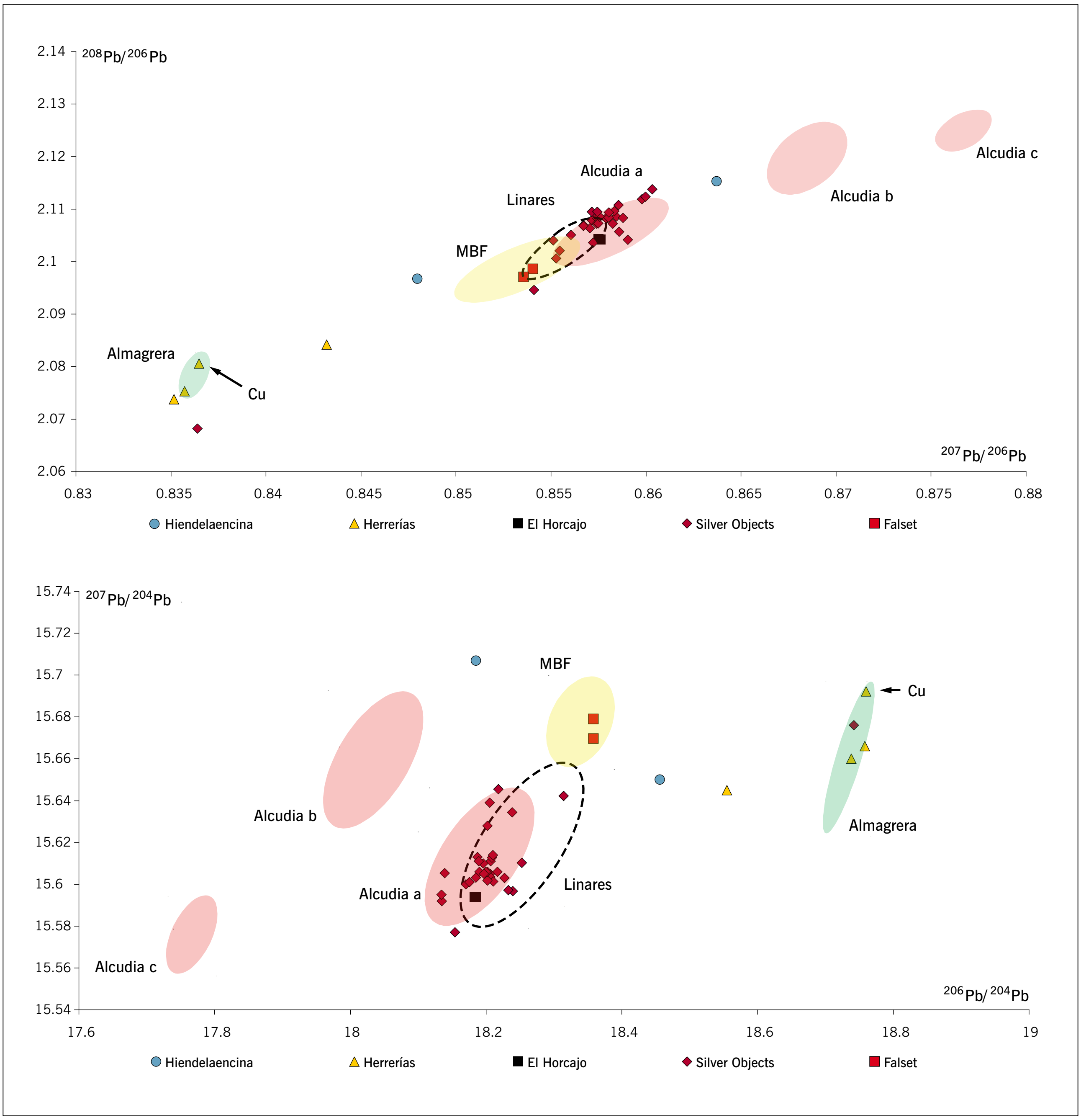


Fig. 9 Isotopic characterisation of the main silver deposits in Iberia and their comparison to the isotopic ratios of silver objects.

Abb. 9 *Isotopenverhältnisse der wichtigsten Silbervorkommen in Iberien im Vergleich mit denen verschiedener Silberobjekte.*

eralised fluids and the fluid/wall-rock interaction; 3. the age of the deposit; and 4. the time span of ore deposition (Baron et al. 2013). Studies of the geological formation of the ore deposit are crucial to understand its homogeneous or heterogeneous isotopic composition: A long period of ore deposition can generate a high isotopic variability. A later superposed geological event can also produce isotopic differences in stratigraphic levels of a given ore district. Understanding the geological background of the samples is essential to better define the isotopic field of ores and in some cases this is an analysis still to be completed.

Another problem that we face is that the isotopic definition of ore bodies has been usually undertaken from a geological perspective. However, when sourcing the provenance of prehistoric metals, the archaeological knowledge must be combined with the geological study in order to trace those mineralisations, which were potentially utilised by prehistoric metallurgists using ancient technology, and those which were actually exploited in prehistory. In this sense, not only the characterisation of the main silver deposits must be considered, but also the small occurrences and outcrops.

Concerning archaeological objects, extensive silver sampling including the whole Argaric area should be undertaken in order to identify possible differences in silver production in the Vera Basin and the peripheral areas. On the whole, after a first advance, we are aware of the potentials (and difficulties) of Argaric silver studies. There are still numerous questions which remain unsolved, but hopefully all these issues will start to resolve in the near future by expanding the sampling and conducting exhaustive geological analyses.

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