Silver isotope and volatile trace element systematics in galena samples from the Iberian Peninsula and the quest for silver sources of Roman coinage

Jean Milot, Mariano Ayarzagüena Sanz, Chloé Malod-Dognin, Francis Albarède, Philippe Telouk, Janne Blichert-Toft

▶ **To cite this version:**

Jean Milot, Mariano Ayarzagüena Sanz, Chloé Malod-Dognin, Francis Albarède, Philippe Telouk, et al.. Silver isotope and volatile trace element systematics in galena samples from the Iberian Peninsula and the quest for silver sources of Roman coinage. Geology, 2021, 50 (4), pp.422-426. 10.1130/G49690.1 . hal-03616540

HAL Id: hal-03616540
https://hal.science/hal-03616540v1

Submitted on 22 Mar 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Ag isotope and volatile trace element systematics in galena samples from the Iberian Peninsula and the quest for silver sources of Roman coinage

Jean Milot[1*], Janne Blichert-Toft[1], Mariano Ayarzagüena Sanz[2], Chloé Malod-Dognin[1], Philippe Télouk[1] and Francis Albarède[1]

[1] *ENS Lyon, CNRS, Université de Lyon, France*

[2] *Sociedad Española de Historia de la Arqueología, 28350 Ciempozuelos (Madrid), Spain*

Corresponding author: jean.milot@ens-lyon.fr

Abstract

Silver played a major role in the progressive monetization of antique Mediterranean. Here, we combine Pb and Ag isotopes with volatile trace elements (Bi, Sb, As) to assess whether, during the Roman occupation of Iberia, galena constituted a significant source of silver. We find that Pb and Ag isotopic compositions of 47 samples of galena from eight different Iberian mining provinces, many of them exploited during Roman times, are uncorrelated which indicates that their respective isotopic variabilities depend on different petrogenetic processes. Moreover, the range of Ag isotopic abundances is ~6 times wider than that displayed worldwide by silver coins in general and Roman silver coins in particular. Although galena from the Betics provide the best fit for Pb isotopes with Roman coins, their fit with Ag isotopic compositions is at best sporadic. We suggest that, together with Sb, Bi, and As, silver is primarily derived from fluids boiled off from differentiated mantle-derived magmas. These fluids in turn reacted with pre-existing galena, acting as a silver trap. Lead sulfides with ε^{109}Ag ~0 and unusually rich in Ag, Sb, Bi, and As were the most probable sources of ancient silver, whereas samples with ε^{109}Ag departing significantly from ~0 reflect low-temperature isotopic fractionation processes in the upper crust.

1. Introduction

Considered a luxury commodity, silver has been massively used for coinage from the 7th century BC onwards. It took monetized silver, which first appeared in the Aegean and Anatolian regions, centuries to reach the Occidental Mediterranean. Argentiferous galena (PbS) is considered by some as the main source of silver during ancient times (e.g. Domergue, 2008, 1990) with silver having been extracted from PbS by smelting and subsequent cupellation in the presence of metallic lead (e.g. Pernicka et al., 1998; Tylecote, 1992). Others suggest alternative Ag-rich minerals such as plumbojarosite, tetrahedrite, or chlorargyrite (e.g. Anguilano et al., 2010). In general, whichever the sources of silver for Roman coinage, they have since been used up and whatever is left is so dispersed that it is difficult to assess whether they ever constituted major sources of bullion or were barren PbS.

In contrast to the relative abundances of radiogenic Pb isotopes, which vary with time and the relative proportions of U, Th, and Pb in the ore source, Ag, Cu, and Zn isotopic abundances vary with the nature of fluids and mineral phases contributing to the ore, redox conditions, and the temperature of ore formation. Isotopic variations are related to mass-dependent fractionation and are typically in the range of a fraction of a percent per atomic mass unit for Cu and Zn and one per mil for Ag. Silver isotopic variations are most conveniently reported in epsilon units (ε^{109}Ag; the deviation per 10,000 of a given sample relative to the NIST 978a Ag standard). For the entire body of antique coinage analyzed so far, this range is strikingly narrow within only ±1 ε unit (Albarède et al., 2020, 2016; Desaulty et al., 2011; Desaulty and Albarede, 2013). Since Ag, Cu, and Zn isotopic variations are controlled by thermodynamics rather than geology, they are of marginal interest for provenance studies and rather track ore genesis processes (Arribas et al., 2020).

A trademark of Ag isotopes particularly relevant to archeology is the contrast between the narrow range of ε^{109}Ag (<2 ε units) in silver coins of different origins and age of minting (Ancient Greece and Rome; Medieval Europe; colonial South and Central Americas) (Desaulty et al., 2011; Fujii and Albarède, 2018) and the 12 ε unit range measured in Ag and Ag-bearing base metal (Pb, Zn, Cu) ores (Arribas et al., 2020). Iberia was the major source of silver for the Carthaginian and Roman worlds up until the 2nd century AD and Pb isotope data on potential silver ores are extremely well documented (see García de Madinabeitia et al., 2021 and references therein). We therefore measured Ag isotopes and trace element abundances on the galena sample suite documented for Pb isotopes by Milot et al. (2021a) to

identify which of these Iberian Pb ores may have actually been mined for use of their silver in minting Roman *denarii*.

2. Potential Iberian sources of Roman lead and silver

Geological information on the galena samples analyzed here is summarized in Milot et al. (2021a) and further details can be found in the IBERLID database (García de Madinabeitia et al., 2021). Briefly, most deposits of economic importance are located in the southern part of the Iberian Peninsula (see Supplementary Material). Lead-zinc-rich deposits occur particularly in the Betic Cordillera (southeast Iberia), the Sierra Morena (south-central Iberia), which belongs to the Central Iberian Zone (CIZ), and the Ossa Morena Zone (OMZ, southwest of the Sierra Morena). The South Portuguese Zone (SPZ) counts many world-class giant and supergiant volcanogenic massive sulfide (VMS) deposits all belonging to the Iberian Pyrite Belt that covers the southwest corner of the Iberian Peninsula. Although less common, notable deposits occur in the northern part of the Iberian Peninsula, such as in the Catalonian Coastal Ranges, the Northern Iberian Massif, the Basque-Cantabrian Basin, the Cantabrian Zone, and the West Asturian Leonese Zone (Fig. 1). These mining regions exhibit archeological evidence of ancient exploitation from the Bronze Age to the Roman period.

3. Materials and methods

The Ag isotopic compositions and Ag, Sb, Bi, As, Pb, and Cu concentrations of 47 Iberian galena samples are listed in Table SM1. Table SM2 lists the Pb isotopic compositions for these same samples and samples from the literature. Samples were grouped into eleven distinct regions (Fig. 1), which correspond to the different tectonostratigraphic units that form the Iberian Peninsula (e.g. Vergés et al., 2019). For better readability, the Central Iberian Zone to which the metallogenic province of the Sierra Morena belongs was divided into two distinct mining areas, those of the Linares-La Carolina and Alcudia Valley-Los Pedroches districts.

The Pb and Ag isotopic compositions of Roman silver coins discussed below are from the literature (Albarède et al., 2020, 2016; Desaulty et al., 2011; Westner et al., 2020). The type and age of these coins are reported in Table SM3 and date mainly from the 3rd and 2nd

centuries BC, with a few exceptions dating to the early 1st century BC. We established two groups corresponding to coins minted before and after the Roman 211 BC monetary reform.

The analytical protocols for Ag separation and isotopic measurement are described in Milot et al. (2021b), while the protocols used for measuring the concentrations of Ag, Sb, Bi, As, Pb, and Cu are given in the Supplementary Material.

4. Results

The Ag isotope compositions of the present galena samples span a range of more than 10 ε^{109}Ag units (-8.05 to +2.27), consistent with the findings of Arribas et al. (2020), and vary broadly within each region with significant overlap between regions. In stark contrast, ε^{109}Ag of Roman silver coins fall within a narrow range (-1.05 to +0.37) except for a single outlier with heavier ε^{109}Ag of 1.32±0.08. No noticeable differences in Ag isotopic composition are observed between Roman coins minted before and after the 211 BC monetary reform or for three Carthaginian coins. Iberian galena samples match only sporadically the Ag isotopic compositions of Roman coins: among the 47 samples analyzed, only six galena ores fall within the range of the coins (one from the Eastern Betics, one from the Linares-La Carolina district, two from the Alcudia Valley-Los Pedroches district, one from the Ossa Morena Zone, and one from the South Portuguese Zone).

The extent of Ag isotopic variability displayed by galena samples from the Iberian Peninsula is of the same order as the -4 to +4 ε^{109}Ag range exhibited by hypogene native silver (Arribas et al., 2020; Mathur et al., 2018) but tends to be overall more negative (Fig. 2). ε^{109}Ag < -4 is common in Iberian galena samples, whereas they are rare in other primary or oxidized silver minerals.

With a few exceptions, the log-log (Ag+Cu)/Pb vs Sb/Pb diagram shows a positive correlation between these trace elements (Fig. 3a). Furthermore, both Sb vs ε^{109}Ag (Fig. 3b) and Ag vs ε^{109}Ag (Fig. 3c) show that samples with the highest Sb and Ag contents (>4000 and >3000 ppm, respectively) have ε^{109}Ag values centered around about -1.5, only slightly lighter than the ε^{109}Ag range for silver coins.

5. Discussion

Only few studies so far have investigated the mechanisms of Ag isotope fractionation (Arribas et al., 2020; Fujii and Albarede, 2018; Mathur et al., 2018). Sulfides and sulfosalts play a major role in reduced environments. Pb_2S_2 (galena) can form solid solutions with $AgBiS_2$ (matildite), $AgSbS_2$ (miargyrite), and $AgAsS_2$ (proustite) (Hackbarth and Petersen, 1984; Renock and Becker, 2011) and a strong correlation between Ag and Sb+Bi contents is commonly observed in argentiferous galena (George et al., 2015). These mutually soluble molecules can exsolve from galena upon cooling (Chutas et al., 2008) or, alternatively, upon metamorphic reheating and melting, and recrystallize as interstitial minerals observable in thin sections (Voudouris et al., 2008). Other minerals may contain large concentrations of silver, notably chlorides (chlorargyrite). Under low-temperature, oxidized conditions, jarosite ($KFe_3(SO_4)_2(OH)_6$) and native Ag are important silver-bearing minerals. Arribas et al. (2020) proposed that the oxidation of primary Ag-sulfides under supergene weathering conditions preferentially releases isotopically heavy Ag, which in turn reprecipitates beneath the water table as secondary Ag phases of equally heavy Ag isotopic composition.

As far as silver sources are concerned, the two most crucial questions to emerge from the present work are:

1. Which of the samples analyzed here may have been active sources of monetized Roman silver?
2. Why is the worldwide range of $\varepsilon^{109}Ag$ (–1 to +1; Fujii and Albarede, 2018), including Ancient Greece and Rome, Medieval Europe, and colonial South and Central Americas, so narrow in coins compared to the range of $\varepsilon^{109}Ag$ in potential Ag ores which is nearly two orders of magnitude wider (Arribas et al., 2020; this work)?

The answer to the first question is that, overall, only very few Iberian galena ores fit the Ag isotope compositions of Roman silver coins. Because the sources of Iberian Pb and Ag used in the coinage process may have been disconnected, Pb isotopes unfortunately are of little use to help identify potential silver sources with precision. Answering the second question is more complicated because of two factors: (i) Ag–O bonds tend to concentrate the heavy isotope ^{109}Ag with respect to Ag–S and Ag–Cl bonds; (ii) increasing temperature tends to reduce isotope fractionation with $1/T^2$, where T is the absolute temperature.

The narrow range of $\varepsilon^{109}Ag$ in Roman coins indicates that their silver source was primarily extracted at high temperatures, presumably from the mantle (Fujii and Albarede, 2018). High

temperature will suppress any isotopic fractionation between magmas and crystallizing minerals. The similar ranges of ε^{109}Ag in minted silver extracted by smelting (Greece, Rome) and the patio method (colonial Latin America; Desaulty et al., 2011) do not support the idea that the high temperatures of smelting reduced the range of ε^{109}Ag. Petrologic evidence, however, is inconsistent with Ag-rich sulfides, such as argentiferous galena and sulfosalts, crystallizing at magmatic temperatures. Fluid inclusion studies (e.g. Arribas et al., 1995; Voudouris et al., 2008) point to crystallization and exsolution of $Ag(Bi,Sb,As)S_2$ minerals from galena solid solutions at temperatures of 150-400°C. For tetrahedrite, Hackbarth and Petersen (1984) used strongly curved Cu, Ag, As, and Sb trajectories to suggest that these elements are enriched by fractional crystallization from hydrothermal solutions. These trajectories can, however, be alternatively interpreted as mixing relationships between Ag-poor galena and an $Ag(Sb,As)S_2$ end-member: the Cu+Ag/As+Sb ratios used in Hackbarth and Petersen's (1984) study being highly variable along the trajectories, mixing such end-members results, by definition, in hyperbolae with very strong curvature.

Given the extreme volatility of Ag, As, and Sb, mixing can therefore be used as a model to interpret the Ag isotope compositions in galena: interaction between Ag-poor sulfides, such as galena and sulfosalts, and Ag-Bi-Sb-As-rich fluids boiled off from magmas is expected to be particularly efficient at assimilating Ag from percolating fluids. Chutas et al.'s (2008) data on mineral stability in the system $PbS\text{-}AgSbS_2$ (their Fig. 7) shows that above 200°C, galena behaves as a 'silver sponge' with respect to Sb-rich fluids. George et al.'s (2015) strong correlations (their Table 3) between Ag and Bi in galena makes the extrapolation of this suggestion to Sb- and As-rich fluids relatively straightforward. Argentiferous galena would form in the relatively broad temperature range of PbS stability (150-450°C) upon Ag+Sb uptake from Ag-Sb-Bi-As-rich magmatic and hydrothermal fluids by pre-existing Pb ore deposits. Silver-rich galena could form from either an early phase of the same mineralization event or, alternatively, multi-stage mineralization. Modern magmatic environments with fluids enriched in Ag, As, Sb, and Bi, which can be used as analogs for silver ores, are known, notably from the PACMANUS hydrothermal field situated on Pual Ridge next to Papua New Guinea, and exsolved from felsic volcanic rocks (Binns, 2006; Wohlgemuth-Ueberwasser et al., 2015).

With few exceptions, the Ag and Sb contents of our samples are positively correlated (Fig. 3) (r=0.81), which argues for silver enrichment of galena by coupled substitution of 2 Pb^{2+} by Cu/Ag^{+} and $As/Bi/Sb^{3+}$ leading to the formation of a solid solution between Pb_2S_2 and

$AgSbS_2$ from which each phase may subsequently exsolve upon cooling (Chutas et al., 2008; George et al., 2015; Renock and Becker, 2011) (Fig. 4). Moreover, samples with the highest Ag contents, which may have been of economic interest to Roman smelters, have a narrow range of ε^{109}Ag centered at about -1.5 ε^{109}Ag, which is included in the range of ore-forming fluid compositions determined by Arribas et al. (2020) but slightly lighter than that of silver coins. The lighter ε^{109}Ag values of Ag-rich galena may be explained by leaching of preexisting fractionated Ag-rich deposits by Bi-Sb-As-rich hydrothermal fluids boiled off from mantle-derived magma. Silver isotopic fractionation during partial exsolution of Ag sulfides or sulfosalts from galena solid solutions may also be an explanation. Even slightly fractionated from the mantle value of ε^{109}Ag~0, the Ag isotopic composition of Ag-rich galena is likely to get averaged out in silver bullion during smelting. The Betics, where Neogene magmatism took place (e.g. Arribas and Tosdal, 1994), is a plausible source of such Ag-enriched ores as attested to by archeological evidence (Baron et al., 2017; Domergue, 2008, 1990). Similarly, in other provinces, hydrothermal fluids of magmatic origin most likely are responsible for the Ag enrichment of lead ores, which may have been important sources of silver for ancient miners. Since the Pb isotope compositions of the silver coins considered here range between those of two lead sources from the Eastern Betics (Fig. SM1), we suggest that Pb ore deposits from this province mostly were exploited for Pb in general and cupellation in particular.

In contrast, silver from Ag-poor samples is isotopically fractionated relative to a given reference value which, pending proper isotopic documentation, could be that of the mantle or the crust and hence rather reflects supergene Ag fractionation processes in upper crustal environments. Their ε^{109}Ag values differ markedly from those of Roman silver coins.

6. Acknowledgments

This work is a contribution of Advanced Grant 741454-SILVER-ERC-2016-ADG ‘Silver Isotopes and the Rise of Money’ awarded to FA by the European Research Council. We are grateful to those who contributed samples to the present study and spared time for their careful selection: Eloïse Gaillou (Mineralogy Museum, MINES ParisTech), Ramón Jiménez Martínez (Instituto Geologico y Minero de Espana), and Paul W. Pohwat and Elizabeth Cottrell (Smithsonian Institution). Insightful reviews by Sonia Garcia de Madinabeitia, Antonia Arribas, and an anonymous reviewer are gratefully acknowledged.

7. References cited

Albarède, F., Blichert-Toft, J., Callataÿ, F., Davis, G., Debernardi, P., Gentelli, L., Gitler, H., Kemmers, F., Klein, S., Malod-Dognin, C., Milot, J., Télouk, P., Vaxevanopoulos, M., Westner, K., 2020. From commodity to money: the rise of silver coinage around the ancient Mediterranean (6 th -1 st century BCE). Archaeometry arcm.12615. https://doi.org/10.1111/arcm.12615

Albarède, F., Blichert-Toft, J., Rivoal, M., Telouk, P., 2016. A glimpse into the Roman finances of the Second Punic War through silver isotopes. Geochem. Persp. Let. 127–137. https://doi.org/10.7185/geochemlet.1613

Anguilano, L., Rehren, T., Müller, W., Rothenberg, B., 2010. The importance of lead in the silver production at Riotinto (Spain): L'importance du plomb dans la production d'argent à Riotinto (Espagne). archeosciences 269–276. https://doi.org/10.4000/archeosciences.2833

Arribas, A., Cunningham, C.G., Rytuba, J.J., Rye, R.O., Kelly, W.C., Podwysocki, M.H., McKee, E.H., Tosdal, R.M., 1995. Geology, geochronology, fluid inclusions, and isotope geochemistry of the Rodalquilar gold alunite deposit, Spain. Economic Geology 90, 795–822. https://doi.org/10.2113/gsecongeo.90.4.795

Arribas, A., Mathur, R., Megaw, P., Arribas, I., 2020. The Isotopic Composition of Silver in Ore Minerals. Geochemistry, Geophysics, Geosystems 21, e2020GC009097. https://doi.org/10.1029/2020GC009097

Arribas, A., Tosdal, R.M., 1994. Isotopic composition of Pb in ore-deposits of the Betic Cordillera, Spain - Origin and relationship to other European deposits. Economic Geology 89, 1074–1093. https://doi.org/10.2113/gsecongeo.89.5.1074

Baron, S., Rico, C., Antolinos Marín, J.A., 2017. Le complexe d'ateliers du Cabezo del Pino (Sierra Minera de Cartagena-La Unión, Murcia) et l'organisation de l'activité minière à Carthago Noua à la fin de la République romaine. Apports croisés de l'archéologie et de la géochimie. Arch. esp. arqueol. 90, 147. https://doi.org/10.3989/aespa.090.017.007

Binns, R.A., 2006. Data Report: Geochemistry of Massive and Semimassive Sulfides from Site 1189, Ocean Drilling Program Leg 193, in: Barriga, F.J.A.S., Binns, R.A., Miller, D.J., and Herzig, P.M. (Eds.), Proc. ODP, Sci. Results, 193, 1–22.

Chutas, N.I., Kress, V.C., Ghiorso, M.S., Sack, R.O., 2008. A solution model for high-temperature PbS-AgSbS2-AgBiS2 galena. American Mineralogist 93, 1630–1640. https://doi.org/10.2138/am.2008.2695

Garcia de Madinabeitia, S., Ibarguchi, J. G., & Zalduegui, J. S., 2021. IBERLID: A lead isotope database and tool for metal provenance and ore deposits research. *Ore Geology Reviews*, 104279. https://doi.org/10.1016/j.oregeorev.2021.104279

Desaulty, A.-M., Albarede, F., 2013. Copper, lead, and silver isotopes solve a major economic conundrum of Tudor and early Stuart Europe. Geology 41, 135–138. https://doi.org/10.1130/G33555.1

Desaulty, A.M., Telouk, P., Albalat, E., Albarede, F., 2011. Isotopic Ag-Cu-Pb record of silver circulation through 16th-18th century Spain. Proceedings of the National Academy of Sciences of the United States of America 108, 9002–9007. https://doi.org/10.1073/pnas.1018210108

Domergue, C., 2008. Les Mines Antiques. La Production des Métaux aux Epoques Grecques et Romaines. Picard, Paris.

Domergue, C., 1990. Les mines de la Péninsule Ibérique dans l'antiquité romaine, Publications de l'École française de Rome.

Fujii, T., Albarede, F., 2018. 109Ag–107Ag fractionation in fluids with applications to ore deposits, archeometry, and cosmochemistry. Geochimica et Cosmochimica Acta 234, 37–49. https://doi.org/10.1016/j.gca.2018.05.013

George, L., Cook, N.J., Cristiana, L., Wade, B.P., 2015. Trace and minor elements in galena: A reconnaissance LA-ICP-MS study. American Mineralogist 100, 548–569. https://dx.doi.org/10.2138/am-2015-4862

Hackbarth, C.J., Petersen, U., 1984. A fractional crystallization model for the deposition of argentian tetrahedrite. Economic Geology 79, 448–460. https://doi.org/10.2113/gsecongeo.79.3.448

Mathur, R., Arribas, A., Megaw, P., Wilson, M., Stroup, S., Meyer-Arrivillaga, D., Arribas, I., 2018. Fractionation of silver isotopes in native silver explained by redox reactions. Geochimica et Cosmochimica Acta 224, 313–326. https://doi.org/10.1016/j.gca.2018.01.011

Milot, J., Blichert-Toft, J., Ayarzagüena Sanz, M., Fetter, N., Télouk, P., Albarède, F., 2021a. The significance of galena Pb model ages and the formation of large Pb-Zn sedimentary deposits. Chemical Geology 583, 120444. https://doi.org/10.1016/j.chemgeo.2021.120444

Milot, J., Malod-Dognin, C., Blichert-Toft, J., Télouk, P., Albarède, F., 2021b. Sampling and combined Pb and Ag isotopic analysis of ancient silver coins and ores. Chemical Geology 564, 120028. https://doi.org/10.1016/j.chemgeo.2020.120028

Pernicka, E., Rehren, T., Schmitt-Strecker, S., 1998. Late Uruk silver production by cupellation at Habuba Kabira, Syria. Metallurgica Antiqua, der Anschnitt 8, 123–134.

Renock, D., Becker, U., 2011. A first principles study of coupled substitution in galena. Ore Geology Reviews 42, 71–83. https://doi.org/10.1016/j.oregeorev.2011.04.001

Tylecote, R.F., 1992. A history of metallurgy. Maney Publishing.

Vergés, J., Kullberg, J.C., Casas-Sainz, A., de Vicente, G., Duarte, L.V., Fernàndez, M., Gómez, J.J., Gómez-Pugnaire, M.T., Sánchez, A.J., López-Gómez, J., 2019. An introduction to the Alpine cycle in Iberia, in: The Geology of Iberia: A Geodynamic Approach. Springer, pp. 1–14.

Voudouris, P., Melfos, V., Spry, P., Bonsall, T.A., Tarkian, M., Solomos, C., 2008. Carbonate-replacement Pb–Zn–Ag±Au mineralization in the Kamariza area, Lavrion, Greece: Mineralogy and thermochemical conditions of formation. Mineralogy and Petrology 94, 85–106. https://doi.org/10.1007/s00710-008-0007-4

Westner, K.J., Birch, T., Kemmers, F., Klein, S., Höfer, H.E., Seitz, H. -M., 2020. ROME'S Rise to Power. Geochemical Analysis of Silver Coinage from the Western Mediterranean (Fourth to Second Centuries BCE). Archaeometry 62, 577–592. https://doi.org/10.1111/arcm.12547

Wohlgemuth-Ueberwasser, C.C., Viljoen, F., Petersen, S., Vorster, C., 2015. Distribution and solubility limits of trace elements in hydrothermal black smoker sulfides: An in-situ LA-ICP-MS study. Geochimica et Cosmochimica Acta 159, 16–41. https://doi.org/10.1016/j.gca.2015.03.020

Figure captions

Figure 1. Map of the Iberian mining provinces and galena samples analyzed in this study. Circles: samples from this study (Table SM1); triangles: samples from the literature (Table SM2).

Figure 2. ε^{109}Ag of silver coins (Table SM3) and Iberian galena samples (Table SM1). Dotted lines delimit the range of Ag isotopic variation of silver coins, with the exception of one outlier.

Figure 3. (a) (Ag+Cu)/Pb vs Sb/Pb of Iberian galena samples in atomic concentration. The red line corresponds to a linear regression with a slope of 1. Note the logarithmic scale. (b) Sb vs ε^{109}Ag and (c) Ag vs ε^{109}Ag of Iberian galena samples. Dotted lines delimit the range of Ag isotopic variation of silver coins, with the exception of one outlier. The elemental concentrations are reported in Table SM1.

Figure 4. Solubility relationships in the PbS-$AgSbS_2$ system (after Chutas et al., 2008). gn = galena; gn_{ss} = galena solid solution; fre = freieslebenite; mia = miargyrite. Silver sulfo-antimonides are remarkably soluble in galena over a large range of temperatures. Galena deposits represent an efficient trap for Ag-Sb rich fluids.

Figure 1

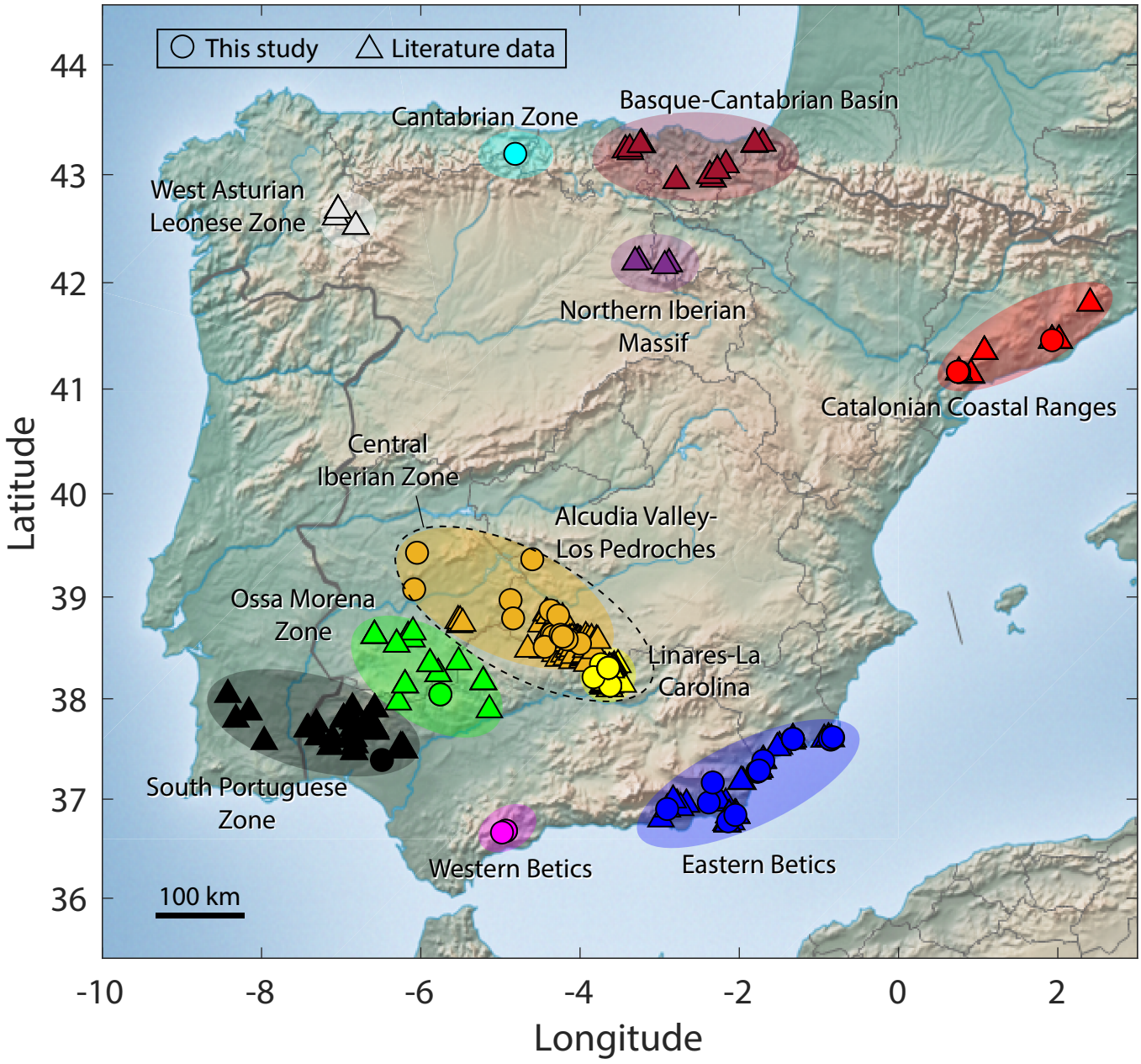

This study
Literature data
Basque-Cantabrian Basin
Cantabrian Zone
West Asturian
Leonese Zone
Northern Iberian
Massif
Catalonian Coastal Ranges
Central
Iberian Zone
Alcudia Valley-
Los Pedroches
Ossa Morena
Zone
Linares-La
Carolina
South Portuguese
Zone
Western Betics
Eastern Betics
100 km
Latitude
Longitude
44
43
42
41
40
39
38
37
36
-10
-8
-6
-4
-2
0
2

Figure 2

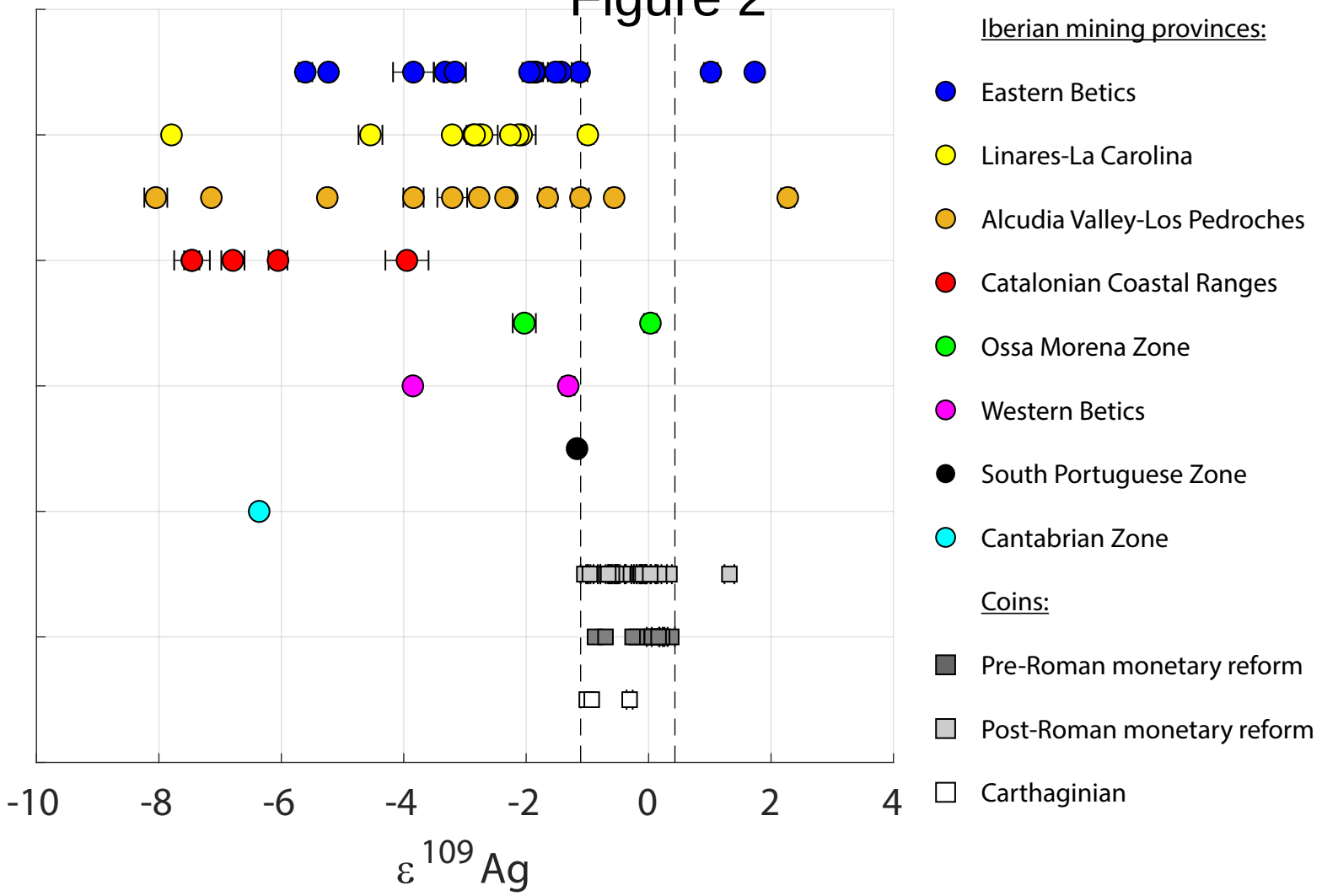

-10
-8
-6
-4
-2
0
2
4
ε 109 Ag
Iberian mining provinces:
Eastern Betics
Linares-La Carolina
Alcudia Valley-Los Pedroches
Catalonian Coastal Ranges
Ossa Morena Zone
Western Betics
South Portuguese Zone
Cantabrian Zone
Coins:
Pre-Roman monetary reform
Post-Roman monetary reform
Carthaginian

Figure 3

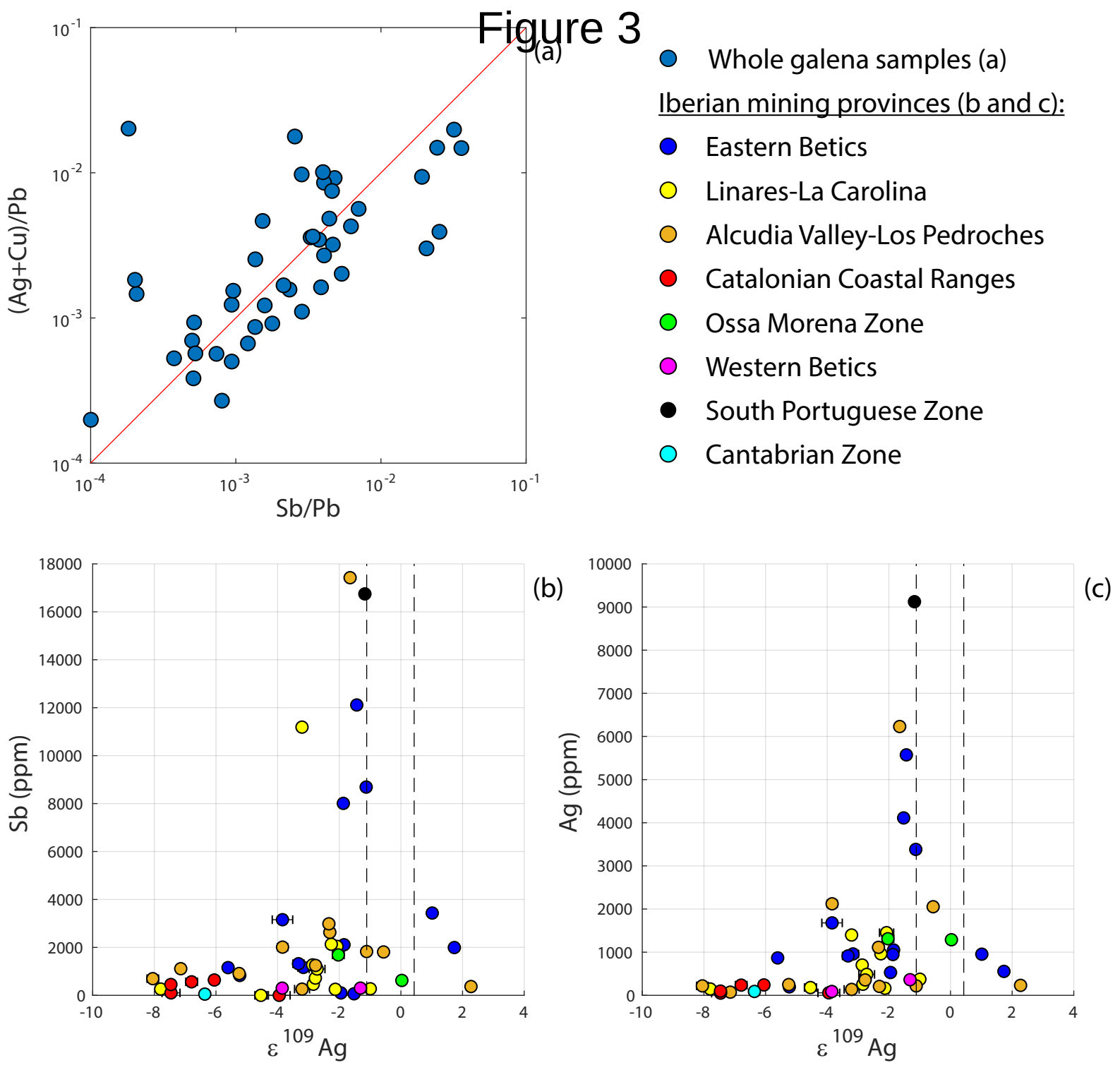
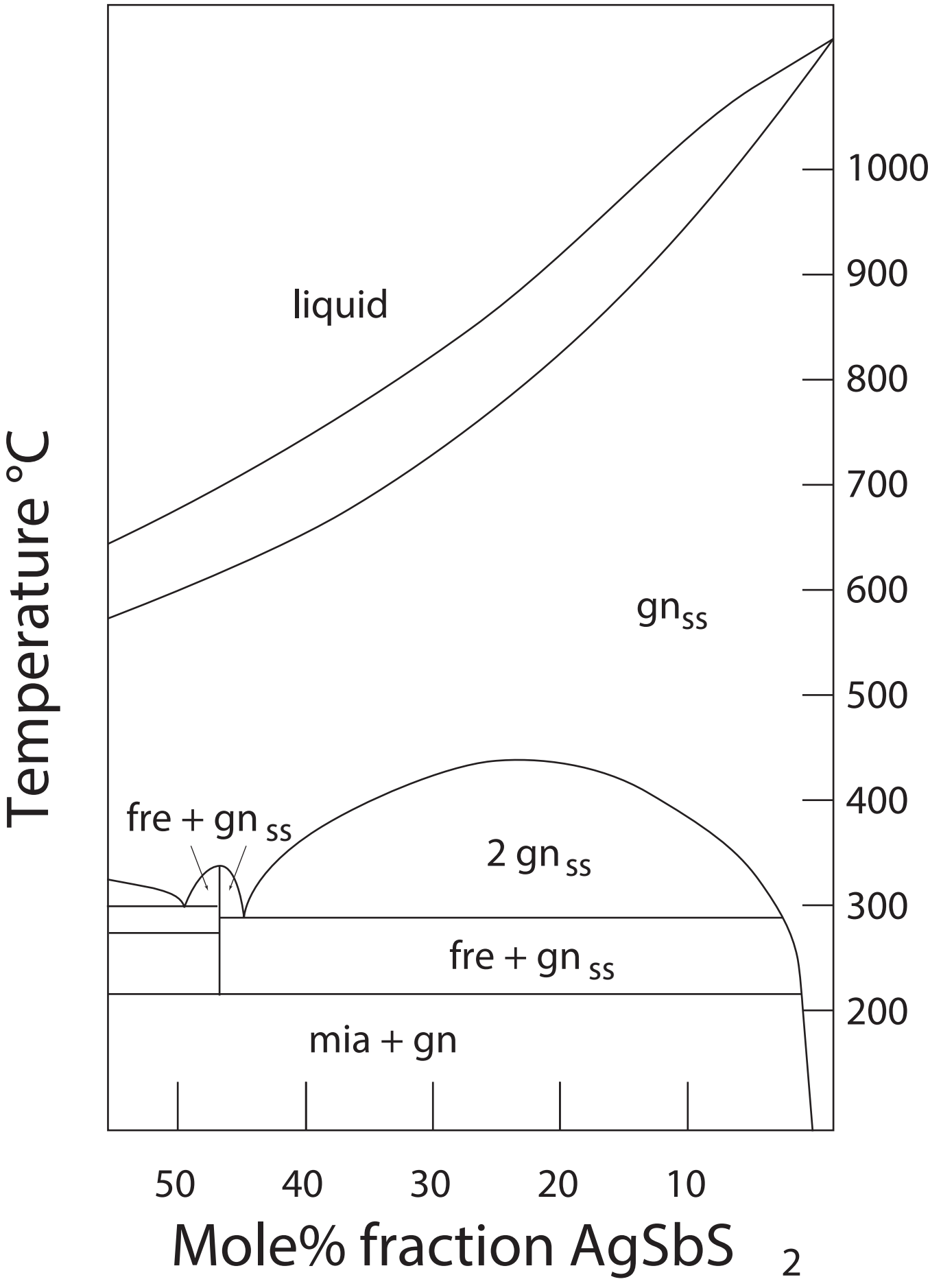

(a)
(Ag+Cu)/Pb
Sb/Pb
Whole galena samples (a)
Iberian mining provinces (b and c):
Eastern Betics
Linares-La Carolina
Alcudia Valley-Los Pedroches
Catalonian Coastal Ranges
Ossa Morena Zone
Western Betics
South Portuguese Zone
Cantabrian Zone
(b)
Sb (ppm)
ε 109 Ag
(c)
Ag (ppm)
ε 109 Ag

Figure 4


liquid
gn ss
fre + gn ss
2 gn ss
fre + gn ss
mia + gn
1000
900
800
700
600
500
400
300
200
Temperature °C
50
40
30
20
10
Mole% fraction AgSbS 2