

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

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ABSTRACT

Silver played a key role in the progressive monetization of early Mediterranean civilizations. We combine Pb and Ag isotopes with volatile trace elements (Bi, Sb, and As) to assess whether, during the Roman occupation of Iberia, galena constituted a significant source of silver. We find that the 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. This indicates that their respective isotopic variabilities depend on different petrogenetic processes. Moreover, the range of Ag isotopic abundances is approximately six times wider than that displayed worldwide by silver coins in general and Roman silver coins in particular. Although galena from the Betics provides 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 preexisting galena and functioned as a silver trap. Lead sulfides with $\epsilon^{109}\text{Ag}$ of ~ 0 and unusually rich in Ag, Sb, Bi, and As were the most probable sources of ancient silver, whereas samples with $\epsilon^{109}\text{Ag}$ departing significantly from ~ 0 reflect low-temperature isotopic fractionation processes in the upper crust.

INTRODUCTION

Silver, considered a luxury commodity, has been widely used for coinage from the 7th century B.C. onward. 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 to be 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., Tylecote, 1992; Pernicka et al., 1998). Others suggest alternative Ag-rich minerals such as plumbogjarosite, tetrahedrite, or chlorargyrite (e.g., Anguilano et al., 2010). In general, whatever the sources of silver for Roman coinage, they have since been used up, and those presumed sources

left are 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 over time and with 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 ($\epsilon^{109}\text{Ag}$; the deviation per 10,000 of a given sample relative to the U.S. National Institute of Standards and Technology [NIST] 978a Ag standard). For the entire body of antique coinage analyzed so far, this range is strikingly narrow and within only $\pm 1 \epsilon$ unit

(Desaulty et al., 2011; Desaulty and Albarede, 2013; Albarède et al., 2016, 2020). Because Ag, Cu, and Zn isotopic variations are controlled by thermodynamics rather than geology, they are of marginal interest for provenance studies, and instead track ore genesis processes (Arribas et al., 2020).

A trademark of Ag isotopes that is particularly relevant to archaeology is the contrast between the narrow range of $\epsilon^{109}\text{Ag}$ ($< 2 \epsilon$ units) in silver coins of different origins and ages of minting (Ancient Greece and Rome, Medieval Europe, and 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, and Cu) ores (Arribas et al., 2020). Iberia was the major source of silver for the Carthaginian and Roman worlds up until the 2nd century A.D., and Pb isotope data on potential silver ores are extremely well documented (see García de Madinabeitia et al., 2021, and references therein). Therefore, we 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*.

POTENTIAL IBERIAN SOURCES OF ROMAN LEAD AND SILVER

Geological information on the galena samples analyzed here is summarized by Milot et al. (2021a), and further details can be found in the IBERLID database (García de Madinabeitia et al., 2021; <http://www.ehu.es/ibercron/iberlid>). Briefly, most deposits of economic importance are located in the southern part of the Iberian Peninsula (see the Supplemental

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Material¹). Lead- and zinc-rich deposits occur particularly in the Betic Cordillera (south-east Iberia); the Sierra Morena (south-central Iberia), which belongs to the Central Iberian Zone; and the Ossa Morena Zone (southwest of the Sierra Morena). The South Portuguese Zone includes many world-class giant and supergiant volcanogenic massive sulfide (VMS) deposits that all belong to the Iberian Pyrite Belt that covers the southwestern corner of the Iberian Peninsula. Although less common, notable deposits occur in the northern part of the Iberian Peninsula, such as in the Catalanian 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 archaeological evidence of ancient exploitation from the Bronze Age to the Roman period.

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 S1 in the Supplemental Material, and Table S2 lists the Pb isotopic compositions for these same samples and samples from the literature. Galena samples were grouped into 11 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 here are from the literature (Desaulty et al., 2011; Albarède et al., 2016, 2020; Westner et al., 2020). The types and ages of these coins are reported in Table S3 and date mainly from the 3rd and 2nd centuries B.C., with a few exceptions dating to the early 1st century B.C. We established two groups, which correspond to coins minted before and after the Roman 211 B.C. monetary reform (when the new Roman *denarius* was introduced into a Mediterranean economy previously dominated by the Greek *drachma*).

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

¹Supplemental Material. Method of elemental analyses, a description of the Iberian galena deposits, Figure S1 (Pb isotope ratios of coins and Iberian galena samples from the various mining provinces), and data Tables S1–S3. Please visit <https://doi.org/10.1130/GEOL.S.17118782> to access the supplemental material, and contact editing@geosociety.org with any questions.

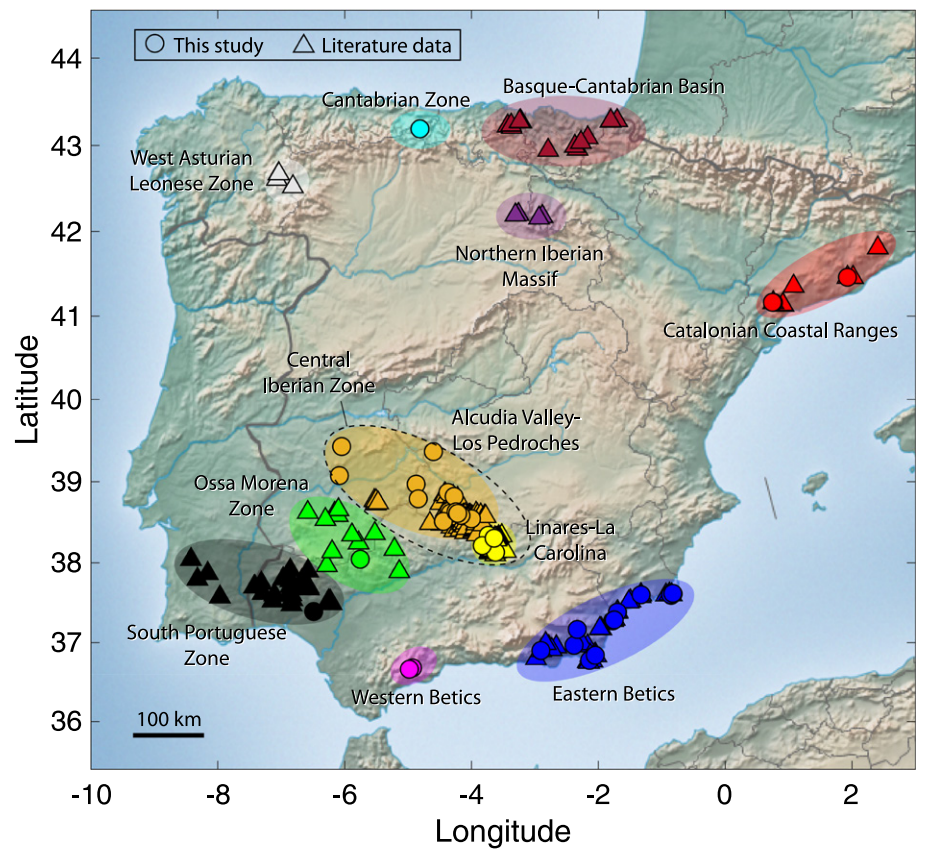


Figure 1. Map of the Iberian mining provinces and galena samples analyzed in this study. Circles indicate samples from this study (Table S1 [see footnote 1]), and triangles indicate samples from the literature (Table S2).

RESULTS

The Ag isotope compositions of the galena samples studied span a range of more than 10 $\epsilon^{109}\text{Ag}$ units (–8.05 to +2.27), which is consis-

tent with the findings of Arribas et al. (2020), and they vary broadly within each region with significant overlap between regions. In stark contrast, the $\epsilon^{109}\text{Ag}$ of Roman silver coins

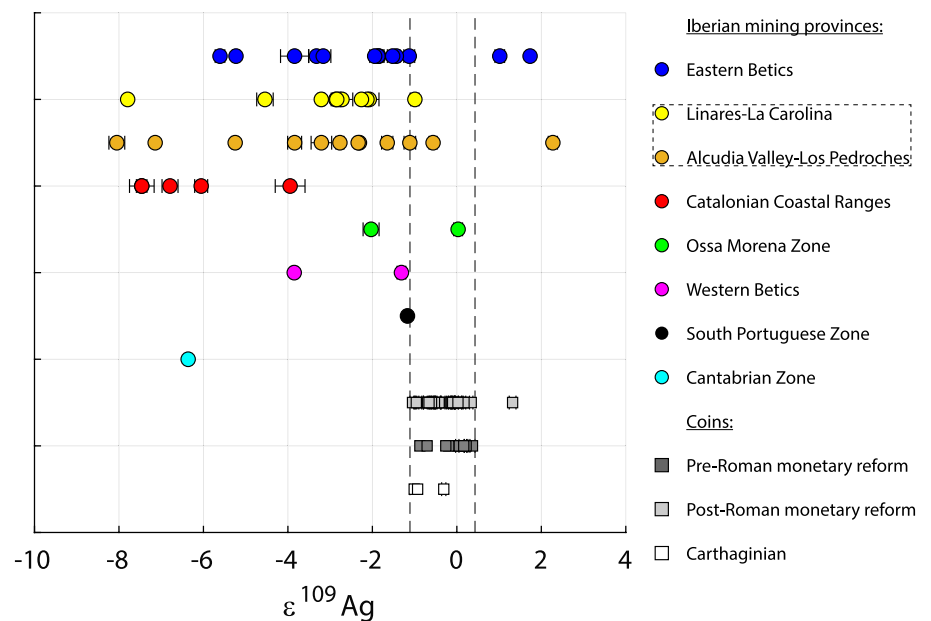


Figure 2. $\epsilon^{109}\text{Ag}$ of silver coins (Table S3 [see footnote 1]) and Iberian galena samples (Table S1). Dashed lines delimit the range of Ag isotopic variation of silver coins; one outlier is an exception. Dashed-line square regroups the Linares–La Carolina and Alcudia Valley–Los Pedroches districts, which both belong to the Central Iberian Zone (see Fig. 1).

falls within a narrow range (-1.05 to $+0.37$) except for a single outlier with heavier $\epsilon^{109}\text{Ag}$ of 1.32 ± 0.08 . No noticeable differences in Ag isotopic composition are observed in Roman coins minted before and after the 211 B.C. monetary reform, or in three Carthaginian coins. The Ag isotopic compositions of Iberian galena samples match only sporadically those of Roman coins: among the 47 samples analyzed, only 6 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 $+4$ $\epsilon^{109}\text{Ag}$ range exhibited by hypogene native silver (Mathur et al., 2018; Arribas et al., 2020) but overall tends to be more negative (Fig. 2). $\epsilon^{109}\text{Ag}$ values < -4 are 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 versus Sb/Pb diagram shows a positive correlation between these trace elements (Fig. 3A). Furthermore, both Sb versus $\epsilon^{109}\text{Ag}$ (Fig. 3B) and Ag versus $\epsilon^{109}\text{Ag}$ (Fig. 3C) show that samples with the highest Sb and Ag contents (>4000 ppm and >3000 ppm, respectively) have $\epsilon^{109}\text{Ag}$ values centered around approximately -1.5 , which

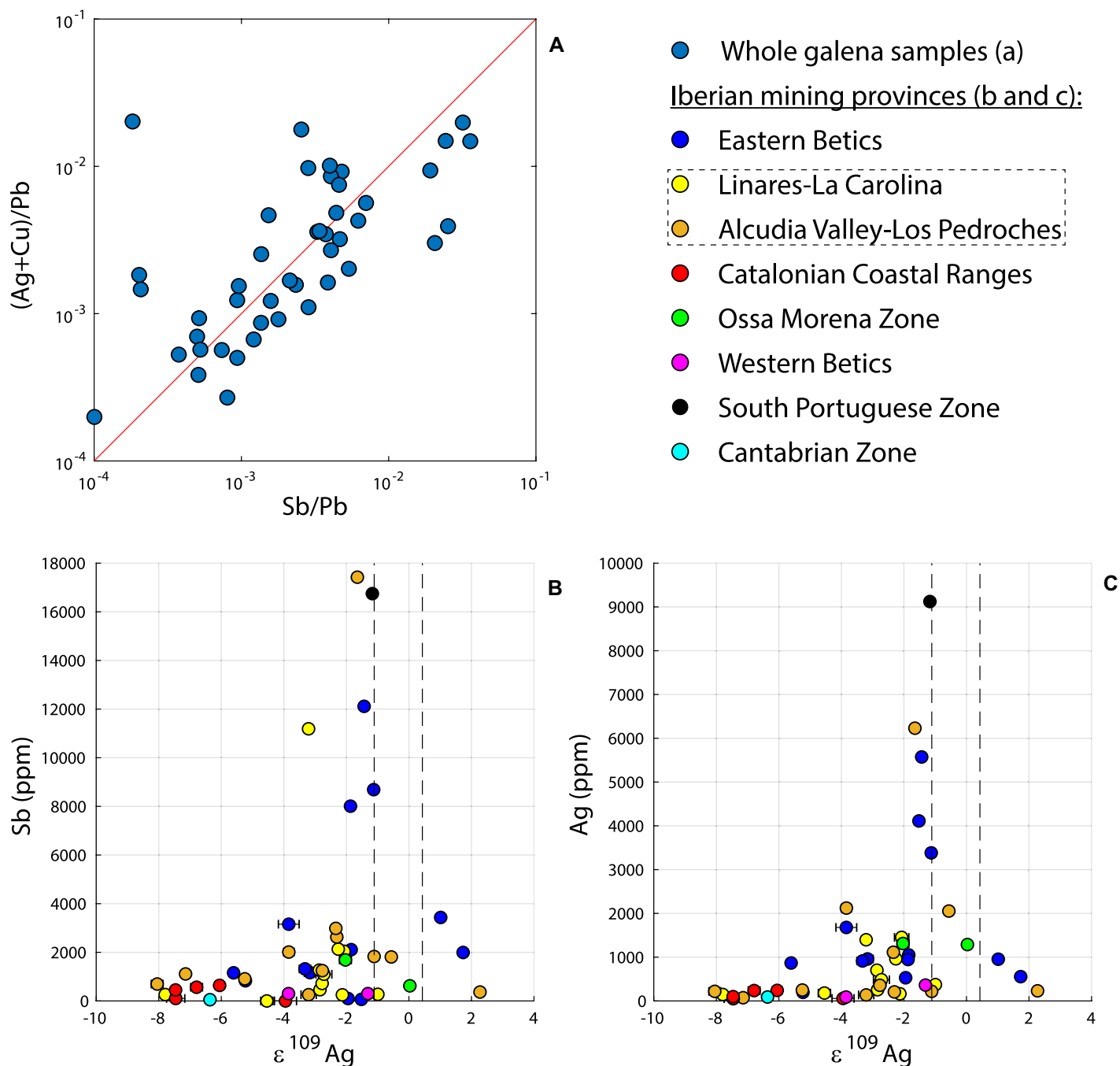


Figure 3. (A) (Ag + Cu)/Pb versus Sb/Pb of Iberian galena samples in atomic concentration. Red line corresponds to a linear regression with a slope of 1. Note the logarithmic scale. (B) Sb versus $\epsilon^{109}\text{Ag}$ and (C) Ag versus $\epsilon^{109}\text{Ag}$ of Iberian galena samples. Dashed lines delimit the range of Ag isotopic variation of silver coins with the exception of one outlier. The elemental concentrations are reported in Table S1 (see footnote 1). Dashed-line square regroups the Linares–La Carolina and Alcudia Valley–Los Pedroches districts, which both belong to the Central Iberian Zone (see Fig. 1).

is only slightly lighter than the $\epsilon^{109}\text{Ag}$ range for silver coins.

DISCUSSION

Few studies to date have investigated the mechanisms of Ag isotope fractionation (Fujii and Albarede, 2018; Mathur et al., 2018; Arribas et al., 2020). Sulfides and sulfosalts play a key 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 (PbS ; 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 $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$ 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 this work are: (1) which of the samples analyzed here may have been active sources of monetized Roman silver?, and (2) why is the worldwide range of $\epsilon^{109}\text{Ag}$ (−1 to +1; Fujii and Albarede, 2018)—which is found in coins from Ancient Greece and Rome, Medieval Europe, and colonial South and Central Americas—so narrow compared to the range of $\epsilon^{109}\text{Ag}$ 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 in helping to identify potential silver sources with precision. Answering the second question is more complicated because of two factors: (1) Ag–O bonds tend to concentrate the heavy isotope ^{109}Ag with respect to Ag–S and Ag–Cl bonds; and (2) increasing temperature tends to reduce isotope fractionation with $1/T^2$, where T is the absolute temperature.

The narrow range of $\epsilon^{109}\text{Ag}$ in Roman coins indicates that their silver source was primarily extracted at high temperatures and presumably from the mantle (Fujii and Albarede, 2018). High temperature will suppress any isotopic fractionation between magmas and crystallizing

minerals. The similar ranges of $\epsilon^{109}\text{Ag}$ in minted silver extracted by smelting (Greece and Rome) and the patio method (colonial Latin America; Desauty et al., 2011) do not support the idea that the high temperatures of smelting reduced the range of $\epsilon^{109}\text{Ag}$. Petrologic evidence, however, is inconsistent with Ag-rich sulfides, such as argentiferous galena and sulfosalts, which crystallize at magmatic temperatures. Fluid inclusion studies (e.g., Arribas et al., 1995; Voudouris et al., 2008) point to crystallization and exsolution of $\text{Ag}(\text{Bi,Sb,As})\text{S}_2$ 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 $\text{Ag}(\text{Sb,As})\text{S}_2$ end-member. The Cu + Ag/As + Sb ratios used in Hackbarth and Petersen's (1984) study are highly variable along the trajectories, and 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, their figure 7) data on mineral stability in the system PbS-AgSbS_2 shows that above 200 °C, galena behaves as a “silver sponge” with respect to Sb-rich fluids. George et al.'s (2015, their table 3) strong correlations between Ag and Bi in galena make 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 preexisting 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 that 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 ($r = 0.81$; Fig. 3), which argues for silver enrichment of galena by coupled substitution of 2Pb^{2+} by Cu/Ag^+ and $\text{As}/\text{Bi}/\text{Sb}^{3+}$. This leads 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; Renock and Becker, 2011; George et al., 2015; Fig. 4). Moreover, samples with

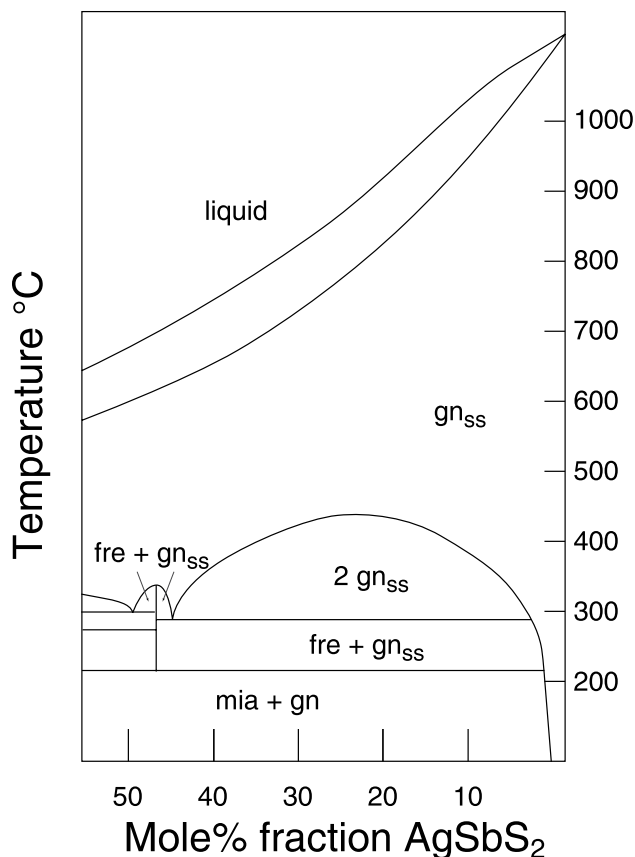


Figure 4. Solubility relationships in the PbS-AgSbS_2 system (after Chutas et al., 2008). gn—galena; gn_{ss}—galena solid solution; fre—freieslebenite; mia—miargyrite. Silver sulfo-antimonides are remarkably soluble in galena over a broad range of temperatures. Galena deposits represent an efficient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

the highest Ag contents, which may have been of economic interest to Roman smelters, have a narrow range of $\epsilon^{109}\text{Ag}$ centered at approximately $-1.5 \epsilon^{109}\text{Ag}$, 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 $\epsilon^{109}\text{Ag}$ values of Ag-rich galena may be explained by the 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 provide an explanation. Even slightly fractionated from the mantle value of $\epsilon^{109}\text{Ag} \sim 0$, 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 archaeological 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. S1), 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 $\epsilon^{109}\text{Ag}$ values differ markedly from those of Roman silver coins.

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