

Narrowing provenance for ancient Greek silver coins using Ag isotopes and Sb contents of potential ores

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ABSTRACT

Variations of $^{109}\text{Ag}/^{107}\text{Ag}$ in silver coins and ores are particularly useful in assessing the provenance of silver bullion. Silver isotope variability results from the temperature-dependent thermodynamic fractionation of Ag isotopes among the solutions and minerals participating in ore formation. They differ from lead isotopic variations which result from the decay of uranium and thorium and reflect the geochemical properties and the tectonic age of the possible ore sources. A remarkable property of Ag isotopes is the very narrow range of isotopic variations in silver bullion used for coinage ($\pm 1 \times 10^{-4}$) with respect to the range of ores ($\pm 1 \times 10^{-3}$). To test the practical usefulness of the technique, we analyzed the Ag isotopic abundances of 29 ore samples from ancient mining districts in the Aegean with major and minor Ag-bearing mineralizations, and of 34 ancient Greek coins minted from the sixth to late fourth centuries BC. We distinguished two groups among the coins: a dominant population (93% of the samples) with $^{109}\text{Ag}/^{107}\text{Ag}$ consistent with literature data ($\epsilon^{109}\text{Ag} = -1$ to $+1$) and an isotopically lighter population ($\epsilon^{109}\text{Ag} = -2$ to -1) which we show originated from Ag-bearing mineralizations in Lavriion (Attica). We further found that sulfur (also analyzed in this study) and silver isotope compositions in Aegean ores do not correlate, a finding that we confirmed on a selection of Iberian galena samples. This shows that the genetic ore type (whether hypo, meso, or epithermal) and silver productivity are not related. Finally, we undertook chemical analysis of the Aegean ore samples and confirmed that Ag-rich ores are also Sb-rich in both Greece and Iberia.

A remarkable outcome of the present Ag isotope studies of galena ores from Iberia and Greece is that silver isotope compositions can exclude, with a high degree of reliability, the majority of mines identified by lead isotope analysis as sources from which coinage silver could plausibly have been extracted and thus significantly narrow down the actual source(s). Silver isotope data on galena ores are thus a useful tool for deciding which Pb isotope data included in ore databases should be included in provenance assessment studies. Contrary to some earlier assessments, subtle silver isotope variations can occasionally help determine ore provenance within a single mining district such as Lavriion.

1. Introduction

Silver coins are useful and abundant artefacts for understanding metal circulation in antiquity. Lead isotopic analysis is the predominant method that has been used by archaeometallurgists over the past fifty years to identify the ore sources of ancient silver coins (Gentner et al., 1978; Gale, 1979; Chamberlain and Gale, 1980; Gale et al., 1980; Wagner et al., 1980; Wagner and Weisgerber, 1988; Stos-Gale and Gale, 2009). Technically, the method has problems related to analytical

accuracy, ore mineralogy, and the extent to which sampling represents a given source (Vaxevanopoulos et al., 2022). The underlying assumptions are that the lead being measured, which usually represents less than 1% of the mass of the coin (Davis et al., 2020), comes from the same source as the silver and that no foreign lead was added during the cupellation process. This assumption is not unreasonable as most silver-bearing ores, notably argentiferous galena, contain sufficient lead for cupellation. Addition of lead was therefore a necessity only for jarosite ores which do not contain it, notably in a number of ore mineralizations found on the

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Iberian Peninsula (Milot et al., 2021a). However, two concerns present formidable problems in reliably identifying an ore source. First, geographically distant mining districts may show similar Pb isotopic compositions, and second, a specific mining district may have a range of Pb isotopic compositions (Vaxevanopoulos et al., 2022). This paper's authors have recently revisited the alternative parameterization of Pb isotopes as model ages, U/Pb, and Th/U to good effect as it takes advantage of the accuracy and precision of multiple-collector inductively-coupled plasma mass spectrometry (MC-ICP-MS) Pb isotope analysis and provides a strong geology-oriented diagnostic (Albarède et al., 2012; Milot et al., 2022; Vaxevanopoulos et al., 2022). Nevertheless, overlap between fields remains a major source of ambiguity.

Silver isotopes offer a potential breakthrough since the realization by Fujii and Albarede (2018) and Milot et al. (2022) that, while the range of $^{109}\text{Ag}/^{107}\text{Ag}$ in silver coins from different periods and places (ancient Greece, ancient Rome, medieval Europe, colonial Spanish Americas) is extremely narrow ($\epsilon^{109}\text{Ag} = -1$ to $+1$; Desauty et al., 2011; Desauty and Albarede, 2013; Albarède et al., 2016, 2021; Hacksilber from the ancient southern Levant: $\epsilon^{109}\text{Ag} = -2$ to $+1$; Eshel et al., 2022), the range is much broader for silver ores (-8 to $+9$; Mathur et al., 2018; Arribas et al., 2020; Wang et al., 2022) and Iberian galena samples ($\epsilon^{109}\text{Ag} = -8$ to $+3$; Milot et al., 2021a). This stark contrast offers the

potential to differentiate Ag-bearing ores that actually may have produced metal used for coinage from other mines which did not contribute to coin production. In addition, the high temperature of metallurgical processes applied to Ag-bearing ores does not cause significant isotopic fractionation (Albarède et al., 2020; Wang et al., 2022). Thus, while Pb isotopes in silver coinage and artefacts allow potential sources to be identified, which are often too many to be of practical use, Ag isotopes allow most of them to be eliminated. It should be noted that the range of values has nothing to do with the resolution. This finding indicates that only certain types of deposit were exploited for Ag production. The possibility that ore sources were mixed for many coins, especially in later periods, cannot always be excluded, but mixing characteristically tends to stretch the range of values along the Pb isotope growth curve (see for example Tell Keisan and Megiddo Hacksilber hoards in Eshel et al., 2021), making it relatively straightforward to identify mixing.

We sampled ores from the major ancient mining areas in Greece as well as other districts with minor Ag-bearing mineralizations from which ore is known to have been extracted in antiquity (Vaxevanopoulos et al., 2022) and analyzed Ag and S isotopic abundances together with the concentrations of diagnostically important trace elements, notably antimony (Sb). Here we present Ag isotopic compositions and select trace element concentrations for 29 galena, cerussite, and

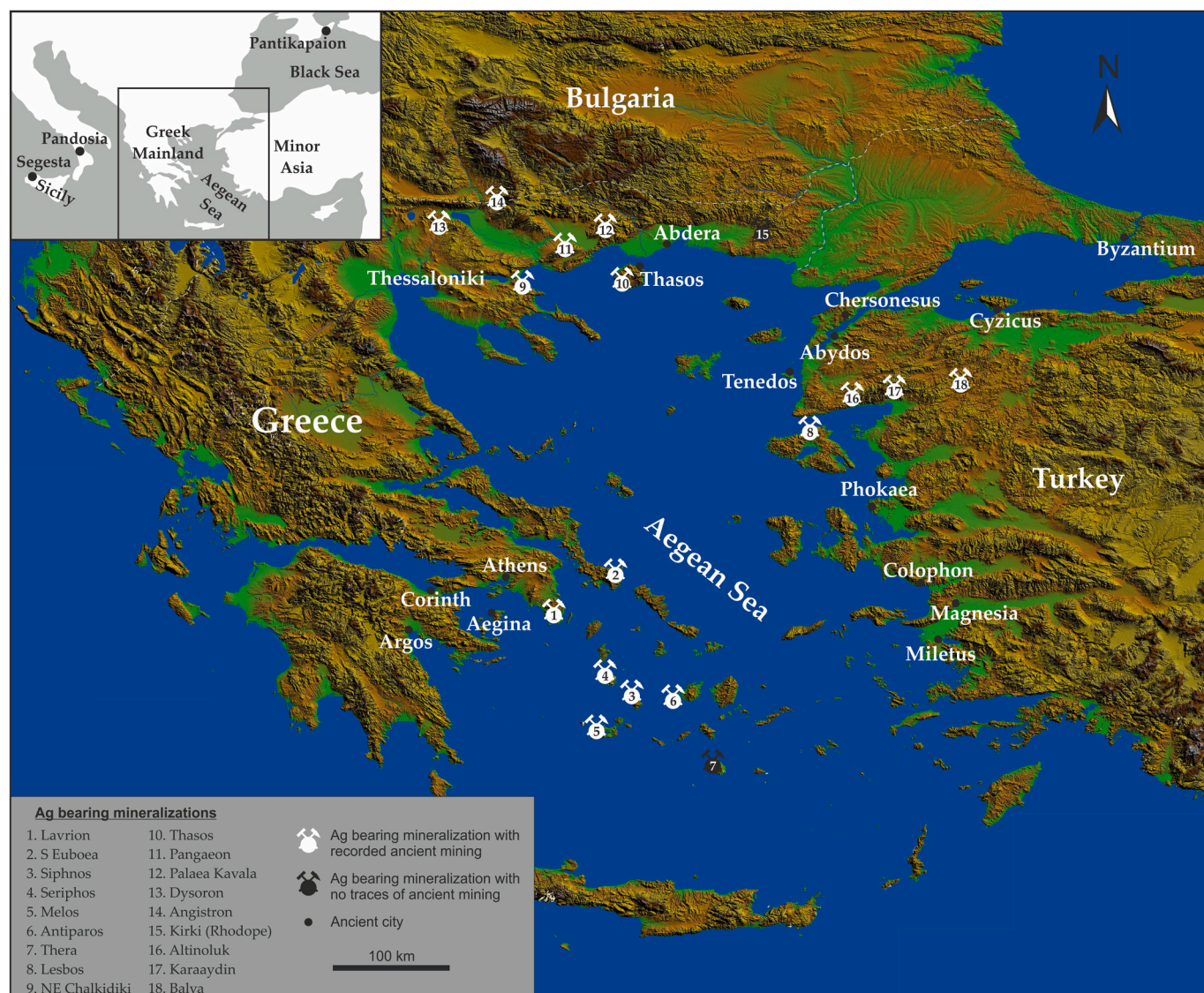


Fig. 1. Map of Greek mining districts and ancient city-states discussed in this work.

pyrrargyrite-proustite samples from Lavrion, Pangaeon, Siphnos, north-eastern Chalkidiki, Euboea, and six other Ag occurrences in Greece for which ancient mining has not so far been clearly attested (Fig. 1). The companion Pb isotopic compositions are published and discussed in Vaxevanopoulos et al. (2022). We also tested whether sulfur isotopes provide a means for ore source discrimination or offer any other insight into the petrological processes of silver ore formation by measuring $\delta^{34}\text{S}$ on a subset of the Aegean ores investigated by Vaxevanopoulos et al. (2022) and the Iberian galena samples for which Ag and Pb isotopes were published by Milot et al. (2021a, 2022). Silver isotope abundances are also reported for coins from across the ancient Greek world. The companion Pb isotope data for these coin samples are published in Blichert-Toft et al. (2022).

2. Materials and methods

Silver separation for high-precision Ag isotope analysis of ores followed the procedure of Milot et al. (2021b), while for silver coins, Ag separation followed the procedure of Desauty et al. (2011) with the modifications of Milot et al. (2021b). Twenty-nine ore samples were collected from 11 different Ag-bearing localities in Greece. After crushing, Ag-rich minerals were separated from gangue minerals (calcite, quartz, fluorite, and feldspars) by handpicking, then powdered by hand in a clean agate mortar. The samples were digested in 10 mL concentrated distilled HNO_3 and dried down at 130 °C. Thirty-four silver coins of low numismatic value were purchased from certified numismatic dealers. Given that the outer layer of the coin sample (the patina) is different from the interior due to interaction with groundwater and other contaminants (Gore and Davis, 2016), which affects the Ag isotopic compositions, each coin was drilled on the edge using a 500 μm diameter drill bit. The surface layer of patina in those cases where patina was observed (Caridi et al., 2013) was discarded, and the rest of the material including only the unoxidized metal was digested in concentrated distilled HNO_3 and evaporated to dryness at 130 °C. The samples were then redissolved in 20 mL 3M distilled HNO_3 . The concentrations of Ag, Pb, Zn, Cu, As, Bi, Sb, Cd, Sn, Ba, La, and Ce in the 29 ore samples of the main Ag-bearing mineralizations in Greece were measured by quadrupole inductively-coupled plasma mass spectrometry (Q-ICP-MS) at the Ecole Normale Supérieure in Lyon (ENS Lyon).

Silver isotopic compositions, as well as Pb isotopic compositions of two ore samples (THE-01 and THE-7/8) not previously published by Vaxevanopoulos et al. (2022), were analyzed by MC-ICP-MS at ENS Lyon. The Pb isotopic compositions of the other ore samples are published in Vaxevanopoulos et al. (2022). Analytical procedures, including precision and accuracy, are described in Milot et al. (2021b).

Sulfur isotope abundances were analyzed commercially at Iso Analytical labs in Crew (UK) by Elemental Analysis-Isotope Ratio Mass Spectrometry (EA-IRMS). The technique consists in placing samples and a reference material in tin capsules loaded into an auto-sampler, which in turn is inserted into a furnace at 1080 °C and combusted in the presence of oxygen. The combusted gases are swept up in a helium stream over combustion catalysts (tungstic oxide/zirconium oxide) and through a reduction stage of high-purity copper wires to produce SO_2 , N_2 , CO_2 , and water. After the removal of water, the resultant SO_2 enters the ion source of the isotope ratio mass spectrometer whereupon it is ionized and accelerated. Gas species of different masses are separated in a magnetic field, then simultaneously measured on a Faraday cup universal collector array. Both the reference material and the samples are converted to SO_2 and analyzed using this method. The analysis proceeds by batch in each of which a reference is analyzed first, then followed by a series of samples, then by another reference. The reference material used for sulfur isotope analysis was IA-R061 (barium sulphate, $\delta^{34}\text{S}\text{-CDT} = +20.33\text{‰}$).

3. Results

The Ag isotopic compositions of the 29 ore samples analyzed here from ancient mining areas in Greece are listed in Table SM1. The corresponding Pb isotopic compositions, Pb model ages (T_{mod}), and μ and κ values published in Vaxevanopoulos et al. (2022) are also included in Table SM1 for convenience to the reader, as are the concentrations of Ag, Pb, Zn, Cu, As, Bi, Sb, Cd, Sn, Ba, La, and Ce and the sulfur isotopic compositions of a subset of the 29 ore samples. The Ag isotopic compositions are reported on carbonate replacement deposits (Lavrion, Siphnos, Seriphos, Chalkidiki), intrusion-related systems (Euboea, Pangaeon), and epithermal mineralizations (Melos, Antiparos, Lesbos, Kirki, Thera) (Table SM1). The $\epsilon^{109}\text{Ag}$ scale used as the x-axis in Figs. 2–4 represents deviations of the measured sample $^{109}\text{Ag}/^{107}\text{Ag}$ ratio from that of the NIST SRM 978a value in parts per 10,000:

$$\left(\frac{^{109}\text{Ag}}{^{107}\text{Ag}}\right)_{\text{sample}} = \left(\frac{^{109}\text{Ag}}{^{107}\text{Ag}}\right)_{978a} \left(1 + \frac{\epsilon^{109}\text{Ag}}{10,000}\right)$$

Confusion may occasionally arise because ore literature often prefers the delta notation $\delta^{109}\text{Ag}$ (parts per 1000). In this work, the epsilon notation (parts per 10,000) is used specifically to deal with the narrow range of isotopic variations in silver coins. The $\epsilon^{109}\text{Ag}$ values of the potential ores vary between -6.1 and $+9.2$ (Table SM1, Figs. 2 and 3). Thirteen samples from the ancient mining district of Lavrion range from -3.7 to $+9.2$ (Fig. 2). A narrow range of $\epsilon^{109}\text{Ag}$ (-0.6 to -1.2) is observed in four samples obtained from the ancient mine in Esperanza-01 (Table SM1). A cerussite sample obtained from the ancient Sykia mine in Lavrion, where supergene alteration is abundant, has an $\epsilon^{109}\text{Ag}$ of -3.7 . Two galena samples from Lavrion with extreme values of $+9.2$ and $+4.6$ (Fig. 2) were collected in a modern mine around the Plaka area from Vein 80, which crosscuts the carbonate replacement bodies. No ancient mining activity has been recorded at this locality. The pyrrargyrite-proustite sample from the same mineralization has a negative $\epsilon^{109}\text{Ag}$ of -1.5 (Table SM1), which makes it a potential source of bullion.

The $\epsilon^{109}\text{Ag}$ values of samples from the ancient mining areas on the Greek islands of Siphnos, Euboea, Melos, Antiparos, Lesbos, and Thera range from -3.3 to $+3.3$ (Fig. 2). A positive value of $+3.3$ was obtained for a cerussite sample from a Siphnos mineralization in the ancient mine of Aghios Silvestros (Fig. 2), which is related to a highly oxidized mineralization of a carbonate replacement deposit in the central part of the island. For the samples collected in Pangaeon, Chalkidiki, and Kirki (northern Greece), the $\epsilon^{109}\text{Ag}$ values range from -6.1 to $+1.7$ (Fig. 2).

Fig. 4 (left-hand-side panel) shows sulfur isotopes ($\delta^{34}\text{S}$) in Greek (Table SM1) and Iberian (Table SM2) galena samples as a function of $\epsilon^{109}\text{Ag}$. No significant correlation is observed between the two isotope systems. Fig. 4 (right-hand-side panel) further shows Sb in Greek (Table SM1) and Iberian (Milot et al., 2022) galena samples as a function of $\epsilon^{109}\text{Ag}$ (Table SM1 and Table SM2). The high Sb concentrations that are so conspicuous in Iberian galena samples with $-1 < \epsilon^{109}\text{Ag} < +1$ (Milot et al., 2022) are also observed in the Greek ore samples of this study for the same $\epsilon^{109}\text{Ag}$ interval (Fig. 4, right-hand-side panel).

Concentrations of a number of trace elements are routinely measured for ore samples together with elements of more manifest interest (Sb, As, Bi, Cu, Zn) and are listed in Table SM1 for potential future scrutiny. Most noticeable are the broad concentration ranges of Cd (2.7 – 4752 $\mu\text{g/g}$) and Sn (up to 3370 $\mu\text{g/g}$). Bismuth is concentrated in Pangaeon samples P-02 (8312.7 $\mu\text{g/g}$) and P-04A (7973.8 $\mu\text{g/g}$) and in Lavrion sample L-25 (1369.7 $\mu\text{g/g}$) indicative of intrusion-related systems (Lang and Baker, 2001).

The Ag isotopic compositions of the 34 ancient Greek silver coins analyzed here dating from the sixth to the fourth centuries BC are listed in Table SM3 and shown in Figs. 2 and 3. Their $\epsilon^{109}\text{Ag}$ values range from -1.9 to $+0.76$. The corresponding Pb isotopic compositions, Pb model ages (T_{mod}), and μ and κ values, reported in Blichert-Toft et al. (2022),

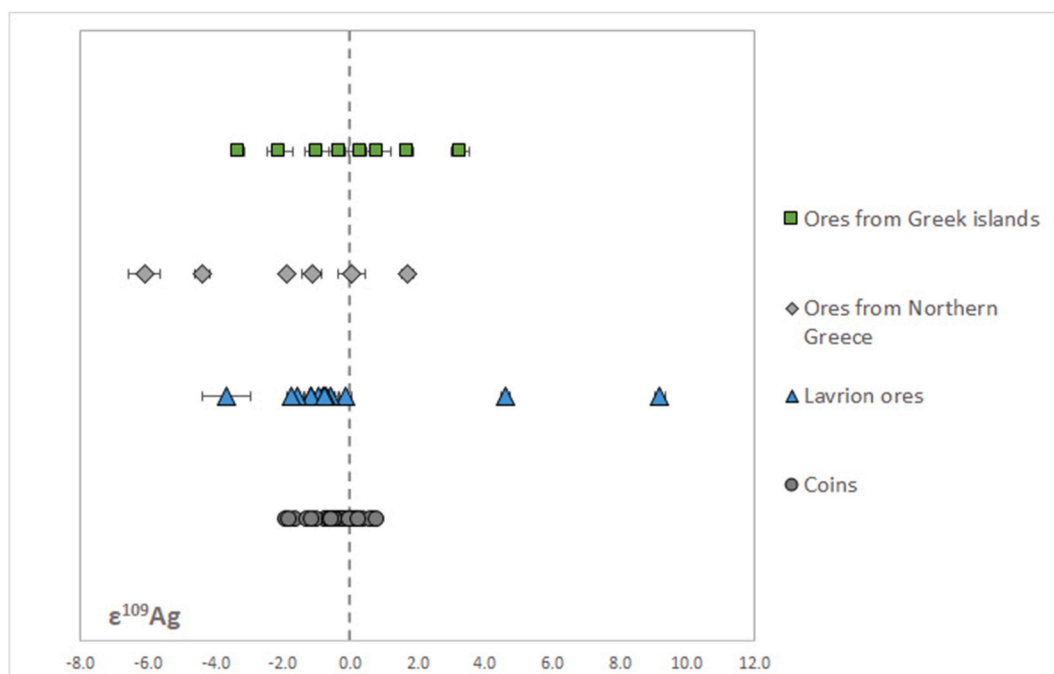


Fig. 2. $\epsilon^{109}\text{Ag}$ of the analyzed ores and coins. The ore data are spatially grouped. Note that the two outliers among Lavrion ores originating from Vein 80 in the Plaka area where no ancient activity is attested have highly positive $\epsilon^{109}\text{Ag}$.

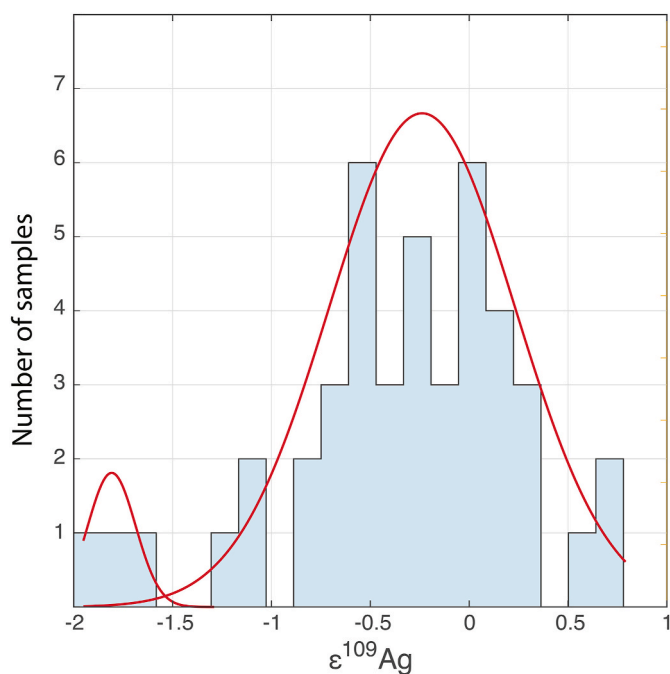


Fig. 3. Histogram of $\epsilon^{109}\text{Ag}$ of the 34 Greek silver coins of this study and 5 coins from Desaulty et al. (2011). The red lines are the two fitted normal distributions discussed below (see scale on the right-hand side). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

are included in Table SM3 for the convenience of the reader.

The Pb isotopic compositions (Blichert-Toft et al., 2022) of 15 of these coins are consistent with an origin of the silver from ores from Lavrion (Fig. 5). Chalkidiki constitutes another major source of silver with five coins having a high potential for Chalkidiki ore provenance. The Pb isotope data for the other coins overlap with the fields of Thasos,

Rhodope, Euboea, Balya, and Kroussia in the Aegean.

4. Discussion

Before suggesting potential provenance and history of the analyzed silver coins, we will first explain the significance of the message conveyed by Ag isotopes. Fujii and Albarede (2018) observed that the $\epsilon^{109}\text{Ag}$ of 132 silver coins of different ages from all around the world cluster tightly between -1 and $+1$ and may be approximated by one, or possibly two, populations. The $\epsilon^{109}\text{Ag}$ of a few coins from the present study, in which we included the five Greek silver coins measured by Desaulty et al. (2011), may be as low as -1.9 , which falls slightly outside the range of Fujii and Albarede's single population. This prompted us to evaluate whether these outliers may reveal a mixture of populations, which is better demonstrated by using the empirical cumulative distribution function (Fig. 6) than the histogram of Fig. 3. Histograms (point density functions) are the derivative of the cumulative distribution functions, and as such, they usually look jagged with their ruggedness being particularly sensitive to bin position and width. For this reason, the cumulative distribution function is normally preferred by statistical software to evaluate underlying mixtures of populations. The two-population hypothesis provides an excellent fit with two populations characterized by the following characteristics:

- % for population 1 (av. $\epsilon^{109}\text{Ag} = -0.24 \pm 0.47$) - 41 samples.
- % for population 2 (av. $\epsilon^{109}\text{Ag} = -1.81 \pm 0.12$) - 3 samples.

Clearly, population 1 tightly overlaps with the range identified by Fujii and Albarede (2018) for worldwide silver coinage. In contrast, population 2 defines a significantly different group with distinctly lower $\epsilon^{109}\text{Ag}$ values. We conclude that the ore sources used for Greek silver coinage span $\epsilon^{109}\text{Ag} > -2$ and $\epsilon^{109}\text{Ag} < 1$ but that the values > -1.2 are by far the majority (93%) and are consistent with Fujii and Albarede's (2018) assessment. The dual character of the population of Ag isotope compositions cannot, at this stage, be uniquely explained. Multiple parameters such as dual sources, temperature, redox conditions, and Rayleigh fractionation (Wang et al., 2022) may, in isolation or in combination, account for the observed dichotomy. Samples are too few and mineralogical and geochemical data on potential ores too fragmentary to support further speculation at this point.

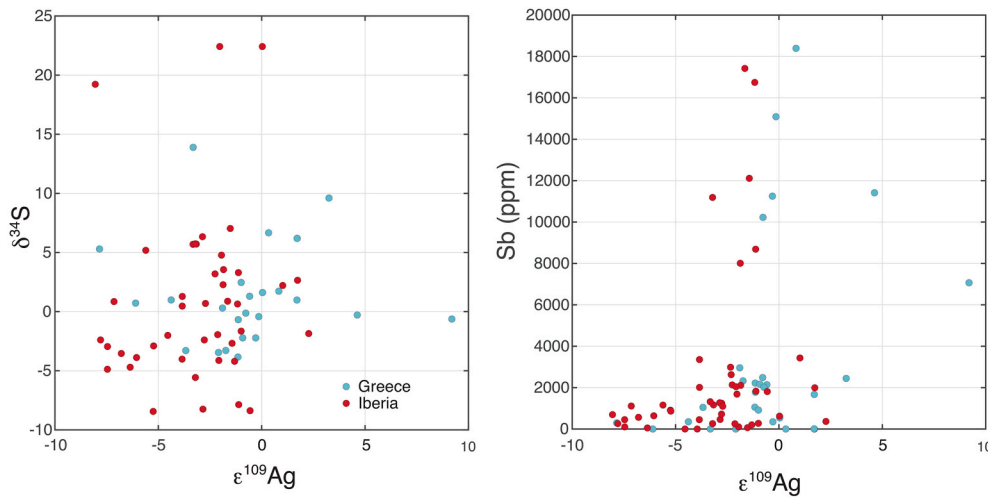


Fig. 4. (Left-hand-side panel) $\delta^{34}\text{S}$ of Greek and Iberian galena samples as a function of $\epsilon^{109}\text{Ag}$. The lack of correlation between $\delta^{34}\text{S}$ and $\epsilon^{109}\text{Ag}$ indicates a lack of fractionation between coexisting species during low- to middle-temperature petrological process. (Right-hand-side panel) Sb concentrations in ppm of Greek and Iberian galena samples as a function of $\epsilon^{109}\text{Ag}$. The peak of Sb concentrations is observed at around $\epsilon^{109}\text{Ag} \sim 0$ in Greek ore samples. A similar Sb peak, also at around $\epsilon^{109}\text{Ag} \sim 0$, was previously identified by Milot et al. (2022) in Iberian galena samples. The high Sb contents of the Lavrion samples with the highest $\epsilon^{109}\text{Ag}$ correspond to Vein 80 (Lavrion), which was not exploited in ancient times.

The present work on Greek mines confirms the suggestion made about Iberian mines (Milot et al., 2021b) that measuring Ag isotopes in galena is important to corroborate the provenance of bullion sources. Lead isotopes show which ore fields are consistent with being bullion sources, and Ag isotopes either confirm or invalidate which of these ore fields are actually suitable bullion sources. We updated the histogram of

$\epsilon^{109}\text{Ag}$ values in silver coinage from different origins (Mediterranean, Europe, Americas) and different ages (from the 6th century BC to the 18th century AD) first published by Fujii and Albarede (2018) by including the results from the present work to reach 237 samples (Fig. 7). $\epsilon^{109}\text{Ag}$ values of galena ores from Iberia and the Aegean world are also plotted to emphasize the small fraction of samples that represents suitable

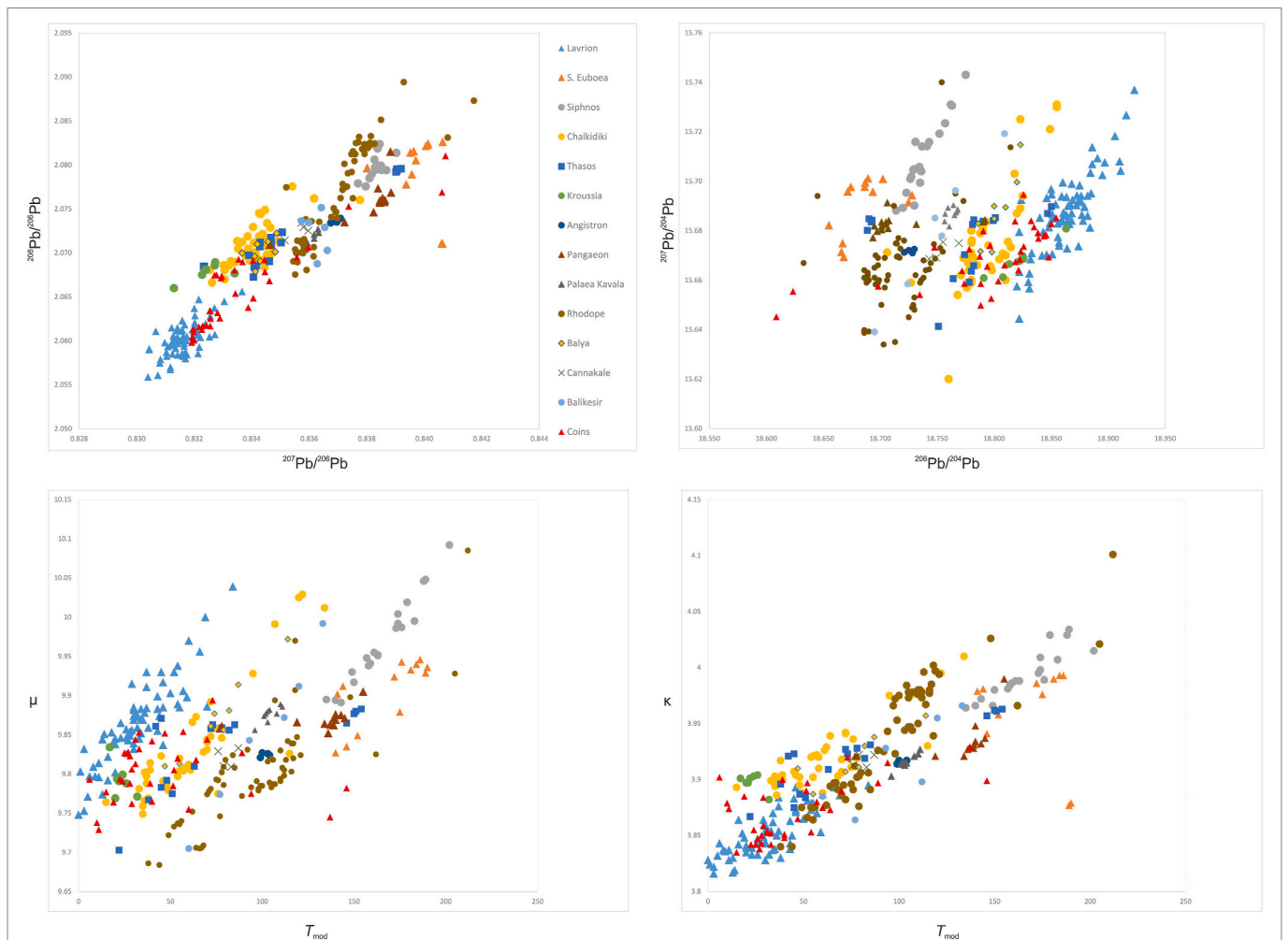


Fig. 5. Lead isotope compositions and Pb model ages, μ , and κ in Greek ore samples (Vaxevanopoulos et al., 2022) and Greek silver coins (red upward-pointing triangles; Blichert-Toft et al., 2022). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

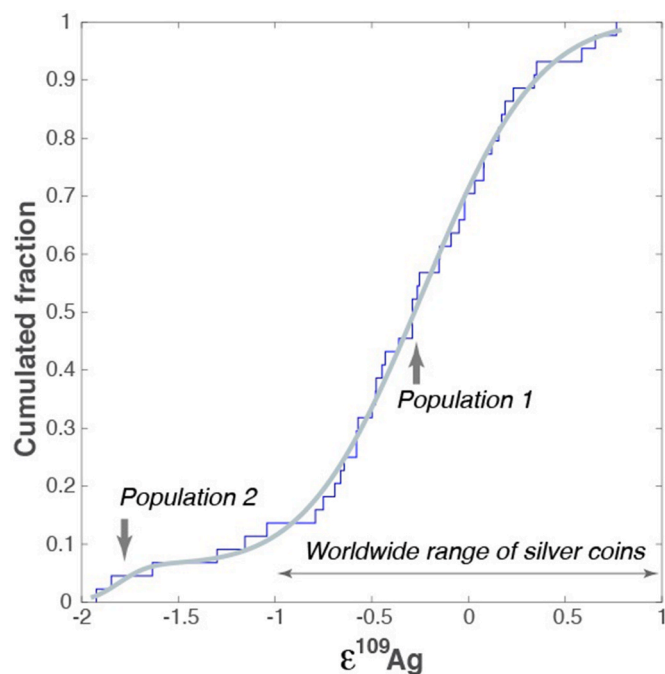


Fig. 6. Fit of the $\epsilon^{109}\text{Ag}$ distribution in silver coins by a cumulative density function formed by the mixing of two distinct populations 1 and 2. The worldwide range ($-1 < \epsilon^{109}\text{Ag} < +1$) is from Fujii and Albarède (2018) and this work.

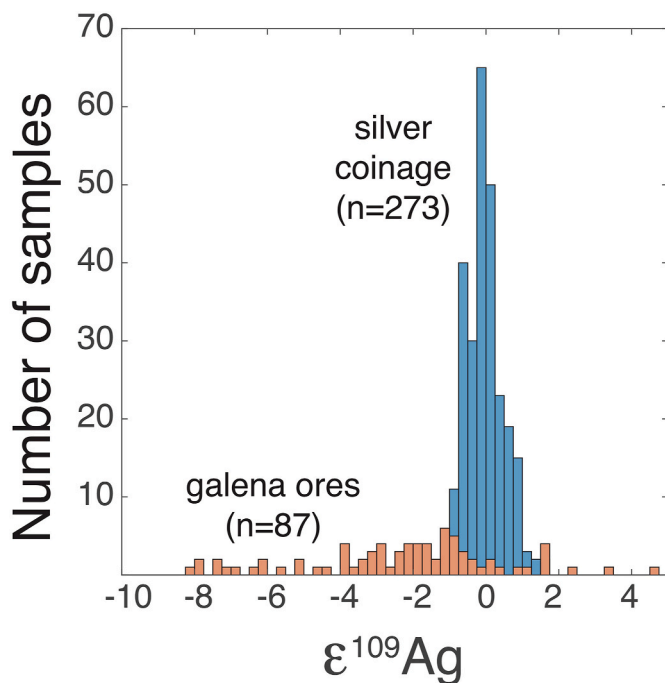


Fig. 7. Histogram of $\epsilon^{109}\text{Ag}$ values in silver coinage (this work, Desauty et al., 2011, 2013; Albarède et al., 2016; 2021). Hacksilver analysis by Eshel et al. (2022) is consistent with this range. The $\epsilon^{109}\text{Ag}$ values of galena ores are from this work and Milot et al. (2022).

bullion sources.

The present work is a caveat that any Pb isotope database used to identify the provenance of coins and other artefacts should ideally be complemented by Ag isotope data. The Ag isotope data on both Iberian and Greek galena samples show that the proportion of galena ores

suitable as bullion sources is small (<5%). It is highly predictable that most of the Pb isotope data on ores compiled in OXALID (Stos-Gale and Gale, 2009), IBERLID (Garcia de Madinabeitia et al., 2021), and the databases used by other groups, including the authors of the present work, contain samples that Ag isotopes would prove could not have been used for bullion production. In addition, keeping in mind that the same silver cannot be hosted in an artefact and in a mine at the same time, implying that the bullion source is by definition missing, and that ancient miners went to great lengths to extract every last bit of silver ore from each mine, provenance should be assigned by using populations of ores and artefacts rather than by comparing isolated objects and poorly characterized ore samples. This is what statistical methods are striving to remediate to some extent, notably the convex hull approach described by Gentili et al. (2021) and Blichert-Toft et al. (2022).

The lack of correlation between $\epsilon^{109}\text{Ag}$ and $\delta^{34}\text{S}$ (Fig. 4, left-hand-side panel) indicates that the petrogenesis of mineralizations is generally of little relevance to the formation of an exploitable mine of silver bullion. As suggested by Fujii and Albarède (2018) and Milot et al. (2021a), the $\epsilon^{109}\text{Ag}$ range (-1 to $+1$ in parts per 10,000) is inherited from the source, most likely from the mantle, with little or no isotope fractionation. The range of Ag isotopic variability in coinage (-1×10^{-4} to $+1 \times 10^{-4}$) is extremely narrow regardless of its origin (Greece, Iberia, Americas) and calls for a high-temperature origin of the bullion because isotope fractionation among minerals and fluids vanishes at temperatures in excess of ~ 300 °C (Fujii and Albarède 2018). With proper attention paid to the units used by Wang et al. (2022) (parts per 1000 instead of parts per 10,000 as used by Fujii and Albarède [2018]), Rayleigh-type fractional crystallization further enhances isotope fractionation in low-to high-temperature environments and reinforces the necessity of a magmatic or, at the very least, a hypogene origin of the silver used as bullion. In contrast, the ~ 15 per mil range of $\delta^{34}\text{S}$ for potential galena sources requiring sulfur isotope fractionation by low-to mid-temperature effects (<300 °C) is in stark contrast to the narrow range of Ag isotope variability. The lack of correlation between Ag and S isotope fractionation therefore requires a strong decoupling of the two systems and that Ag went through the final ore-forming process without visible isotope fractionation.

The two cerussite samples analyzed in the present work (with $\epsilon^{109}\text{Ag}$ of -3.7 and $+3.3$) are well outside the silver coinage range. For common silver coins with $-1 < \epsilon^{109}\text{Ag} < +1$, cerussite deposits cannot have been more than an occasional source of silver for coinage. This is also the case for the values obtained by Arribas et al. (2020) for two tetrahedrite samples. The low $\epsilon^{109}\text{Ag}$ of the cerussite sample from the ancient Sykia mine in Lavrion is not easily explained by the fractionation factors of Fujii and Albarède (2018); oxygen-rich compounds should be isotopically heavy. This is precisely where the Rayleigh distillation effects postulated by Wang et al. (2022) may play a role; the heavy ^{109}Ag isotope is depleted by early precipitation of carbonates or sulfates from low-temperature hydrothermal fluids. This sample can therefore be considered as having formed from well-ventilated residual solutions circulating in the karst.

Sulfosalts are minerals with the general formula $A_xB_yC_z$, where A typically is monovalent (Ag, Cu), B trivalent (Sb, As, Bi), C mostly sulfur, and x,y,z integer numbers. Minerals such as pyrargyrite (Ag_3SbS_3), proustite (Ag_3AsS_3), tetrahedrite ($\text{Cu}_4\text{Ag}_6(\text{Sb,As})_4\text{S}_{13}$), and miargyrite (AgSbS_2) have often been observed in the galena lattice (Voudouris et al., 2008a, 2008b; Bonsal et al., 2011). In general, the values of $\epsilon^{109}\text{Ag}$ found by Arribas et al. (2020) in pyrargyrite and miargyrite scatter significantly (from -3.3 to $+4.9$), leading us to suggest that sulfosalts within the range of $-2 < \epsilon^{109}\text{Ag} < 0$ are predominant in Lavrion mineralizations.

The major Greek silver ore is galena, PbS. The Ag and Sb contents of galena are reasonably well correlated (Fig. 8). Trace element abundances in ores indicate that the $\text{Ag}/(\text{Sb} + \text{As} + \text{Bi})$ atomic ratio is much lower in galena ores than in most common sulfosalts. With one exception from Iberia, galena samples are characterized by $\text{Ag}/(\text{Sb} + \text{As} + \text{Bi}) < 1$,

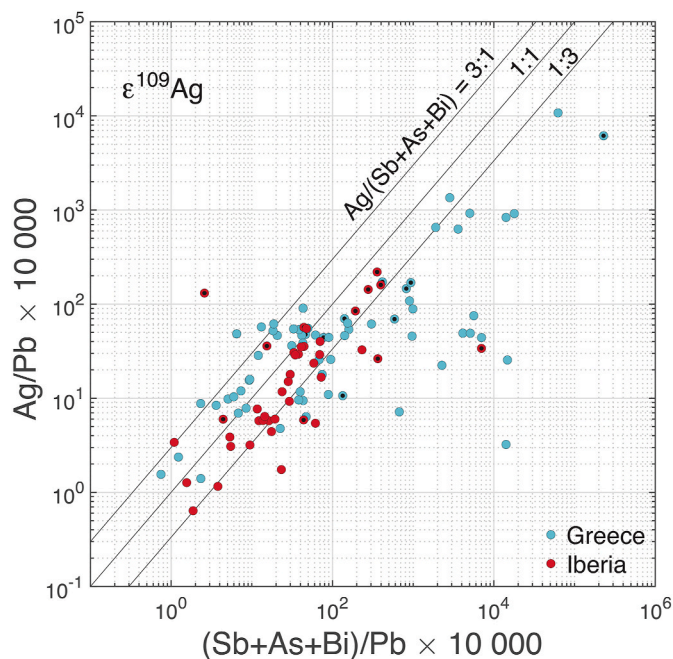


Fig. 8. Correlation between Pb-normalized Ag and Sb + As + Bi concentrations (atomic ratios). The dotted symbols have $\epsilon^{109}\text{Ag}$ values in the interval -1 to $+1.1$, which qualify these samples as potential bullion sources. The $\text{Ag}/(\text{Sb} + \text{As} + \text{Bi})$ is in many cases lower than the ratio in sulfosalts (3:1) which, in contrast, does not support these minerals as bullion sources.

which may be reconciled with the presence of mineralogical end-members or inclusions in galena such as senandorite (a.k.a. andorite VI, $\text{AgPbSb}_3\text{S}_6$) or freieslebenite (AgPbSbS_3). The low $\text{Ag}/(\text{Sb} + \text{As} + \text{Bi})$ ratio of most ores with $-1 < \epsilon^{109}\text{Ag} < +1$ therefore suggests that the main ore used for bullion was galena, not sulfosalt. Lavrion with $-2 < \epsilon^{109}\text{Ag} < -1$ may have been an exception with a larger contribution of minerals other than galena.

Finally, galena samples with high Sb concentrations have $\epsilon^{109}\text{Ag}$ in the same range as the worldwide population of silver coins (-1 to $+1$) and, therefore, present the strongest potential as candidates for Ag sources for coinage (Milot et al., 2022). This correlation is observed in Greek ores as well and potential sources for silver coinage can be proposed as displayed in Fig. 9. Lavrion samples, such as L-08 and L-09 from Vein 80, a probable mineralization with epithermal affinities (Melfos and Voudouris, 2017), nevertheless are exceptions; despite having high Sb contents, their $\epsilon^{109}\text{Ag} \gg +1$ render them ineligible as a source of bullion.

The authors realize that the first-order rules for using Ag isotopes and Sb concentrations to narrow down acceptable sources of silver as advocated by Milot et al. (2022) and the present work may have limits. At the present stage, coins with Ag isotope compositions falling significantly outside the range suggested by Fujii and Albarede (2018) have not been recorded. It is possible that small mining operations associated with sulfosalts and unusual minerals may not conform with the broad landscape of Ag isotopes observed for Iberian and Greek mines. At this point, however, available evidence on Ag isotopes in coins and galena samples, and Sb contents in ores, is strong enough to offer useful guidelines for pruning the mines considered potential candidates on the basis of Pb isotopes alone.



Fig. 9. Geographic distribution of mining districts that can be accepted as potential sources for the silver of the main population 1 (in red). Galena samples are depicted with full circles and other ores with crosses. Lavrion, Melos, Seriphos, Santorini, Euboea, north-eastern Chalkidiki, and Kirki are among the most likely localities. The color bar on the right-hand side shows the $\epsilon^{109}\text{Ag}$ color scale used for the symbols. The red color highlights the range of values (-1 to $+1$) found in silver coinage. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

5. Conclusions

Silver isotope abundances in sulfide mineralizations show a large spread which contrasts with the narrow range of $\epsilon^{109}\text{Ag}$ values characterizing the source of coinage metal. The $\epsilon^{109}\text{Ag}$ values of a selection of Greek Ag coinage define two very unequal groups, a dominant population with values indistinguishable from those obtained from around the world for the last 3000 years, and a small population that may originate from Lavrion galena. The narrow range of Ag isotope compositions of silver coinage predicted by Fujii and Albarède (2018) was confirmed by Albarède et al. (2021) for Roman and Greek coinage, by Eshel et al. (2022) for *Hacksilber*, and now again by the present work on Greek coins. This work demonstrates that although lead isotopes are a powerful provenance tool, companion silver isotope data can be used to exclude mine districts that were not actually used as silver ores even though Pb isotopes allow for it. This observation raises the question of the extent to which databases on Pb isotopes in ores should be used. Finally, Ag-rich sulfides, notably galena, are rich in Sb, leaving open the possibility that this element can be used for paleo-environmental applications and to track ancient ores.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jas.2022.105645>.

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Further reading

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