

Isotope and trace element compositions of silver-bearing ores in the Balkans as possible metal sources in antiquity

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ABSTRACT

Ore deposits in the Balkan Peninsula were intensively mined for silver and other metals in the Roman and medieval periods. Coinage mainly issued by tribal groups between the early 5th and the end of the 3rd century BCE provides indirect evidence that silver extraction predates the Roman conquest of the region. However, identification of centers of past metal production and reconstruction of large-scale silver fluxes can only be achieved using a comprehensive geochemical database of potential ores. Here, we present high-precision Pb–Ag–S isotope data and trace element systematics for 128 ore samples from 36 mineralizations from the Balkans as well as one semi-reacted ore from a settlement site (=archaeological sample) and one andesite analyzed as a whole-rock and as a K-feldspar separate. Each ore site was selected for its geological characteristics and documented or assumed historical and/or archaeological significance.

The reported data reconstruct the formation of ore bodies from large pre-existing Pb stocks derived from upper crustal sources, modified by tectonic and metasomatic processes, and eventually remobilized by magmatic activity. Lead isotope maps establish distinct isotopic domains which are linked to geological characteristics and enable an enhanced assessment of potential metal sources in provenance studies. Silver isotopes underscore the importance of hypogene ores of hydrothermal origin comprising galena or sulfosalt minerals as the main silver carrier phases and they can circumscribe ore deposits to those actually used as bullion sources of ancient coinage. We show that the Ag isotope signatures and the silver content of the argentiferous galena-rich ores in the Kopaonik and Zletovo districts (Serbia, Kosovo, and North Macedonia), combined with field evidence for historical metal production and geographical considerations, make them the most likely sources of silver which could have been used for coinage issued by mints in the interior of the Balkans.

1. Introduction

The Balkan Peninsula hosts numerous hydrothermal Pb–Zn–Ag (Cu–Au) deposits (e.g. Heinrich and Neubauer, 2002; Janković, 1997). These occur in the Dinarides, and particularly in the Serbomacedonian Massif which extends from Serbia to the Chalkidiki Peninsula in northern Greece, and the Rhodope Mountain Range located between northern Greece and southeast Bulgaria (Fig. 1; Amov et al., 1990; Janković, 1982; Jelenković et al., 2008; Marchev et al., 2005; Melfos and Voudouris, 2017; Palinkaš et al., 2008; Popov and Popov, 2019). The rich silver and gold deposits located in the southern part of the Balkans corresponding to the ancient regions of Macedonia and Thrace played a

central role in the monetization of the Greek world. Field work and analysis of ores and metallurgical (by-) products (e.g. Pernicka et al., 1981; Photos et al., 1987; Unger, 1987; Vaxevanopoulos et al., 2022a; Wagner et al., 1986) have identified mining districts exploited in antiquity, most of which were mentioned in historical sources (see e.g. Psoma, 2006 for a compilation). Provenance studies of Greek silver coinage (Birch et al., 2020; Stos-Gale and Davis, 2020) document their economic importance. While silver production is well attested for the southern and near-coastal areas of Macedonia and Thrace, it is unclear whether deposits located in the interior of the Balkan Peninsula were mined before the Roman conquest of the region in the 2nd and 1st centuries BCE (e.g. Dušanić, 2004). However, findings of stone tools and

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their characteristic working traces attest to prehistoric mining activities in some of the districts (e.g. Dimitrov and Stojčev, 2017; Malamidou et al., 2022; Radičević and Roberts, 2021; cf. Table 1 and references therein). Significantly rising levels of anthropogenic lead pollution have been recorded in a peat bog from western Serbia c. 600 BCE onward (Longman et al., 2018) which coincides with the spreading use of coinage and, by extension, a general increase of metal extraction.

Coinage issued by inland mints provides indirect local evidence for silver extraction predating the Roman conquest. Mints are located in a broad area comprising Greek Macedonia, Northern Macedonia, and southwestern Bulgaria, and potentially extending north as far as the southern parts of Serbia and Kosovo. Two phases can be distinguished for the coinage issues. Coins were first minted in the region during the first half of the 5th century BCE in the names of tribes living around the rivers Vardar/Axios, Struma/Strymonas, and Mesta/Nestos (e.g. Dahmen, 2010; Paunov, 2015; Psoma, 2012; Tzamalīs, 2012; Wartenberg, 2015). Most of the tribes were located in the southern parts of ancient Macedonia and Thrace and probably accessed ore locally from the areas they controlled in the mining districts of northeast Chalkidiki, Pangaeon, and Palaea Kavala (Picard, 2000, Fig. 1, #19, 21, 22). Some minting authorities, however, seem to have accessed silver deposits located further to the north. Dysoron was a fabulously rich silver mine mentioned by Herodotus (5.17). It is thought to have been originally mined by local tribes and brought under the control of the Macedonian kingdom during expansion of its territory after the retreat of the Persians in 479 BCE (e.g. Kremydi, 2011). It has recently been plausibly identified with the mining district of Kroussia (Vaxevanopoulos et al., 2022a, Fig. 1, #G). An alternative hypothesis based on the discovery of an inscription locates the mine at Menoikio, a mountain range between the Pangaeon and Angistrion (Fig. 1, #18) districts (Faraguna, 1998; Hatzopoulos, 2010), but no Ag-bearing mineralizations are attested there. In another example, based on find spots of small denominations intended for local use dated after 480 BCE, Pavlovska (2008) hypothesized that the tribe of the Derrones lived in eastern North Macedonia and thus

further north than the other tribal groups of Macedonia and Thrace which issued coins in the Archaic period. Hammond and Griffith (1979) connected it with the ore deposits of Zletovo (Fig. 1, #13).

In a second phase, coins were issued between the beginning of the 4th and early 3rd centuries BCE. It comprises the coins of Damastion (a city reportedly founded by Greek settlers near silver mines; Strabo, 7.7.8; Aly, 1931) and issues in the name of small mints based on Damastion's coinage, for example Pelagonia (May, 1939), and the coinage of the Kings of Paeonia (Gaebler, 1927; Pavlovska, 2008) whose lands were located north of the Macedonian kingdom. The shared weight standard and dies point to a close connection between Damastion and the Kings of Paeonia (Gaebler, 1927; Pavlovska, 2008). Based on the circulation pattern of its coinage and abundant silver deposits, it has been suggested that Damastion was located in the vicinity of mining districts in Kosovo and southern Serbia (Petrova, 1991; Ujes, 2002, Fig. 1, around #10, 11, 12, 15 and 16).

To make further progress in identifying centers of ancient metal production and to evaluate silver fluxes from mines to mints, a comprehensive database on ores from potential source regions is essential. Here, we present trace element concentrations and high-precision Pb and Ag isotopic compositions for Ag-bearing ores collected from mineralizations located in the central and western Balkans. A few samples were also analyzed for their S isotopic compositions. Our study (a) locates possible silver sources for ancient coinage, and (b) establishes Pb–Ag isotopic signatures of ores in correlation with their S isotope and trace element data and (c) links them to their geological properties for a generalized application in provenance reconstructions. We emphasize that for many of the ore deposits in the central and western Balkans, the present study provides the first available state-of-the-art data and fills a long-standing gap in the characterization of circum-Mediterranean ore deposits.

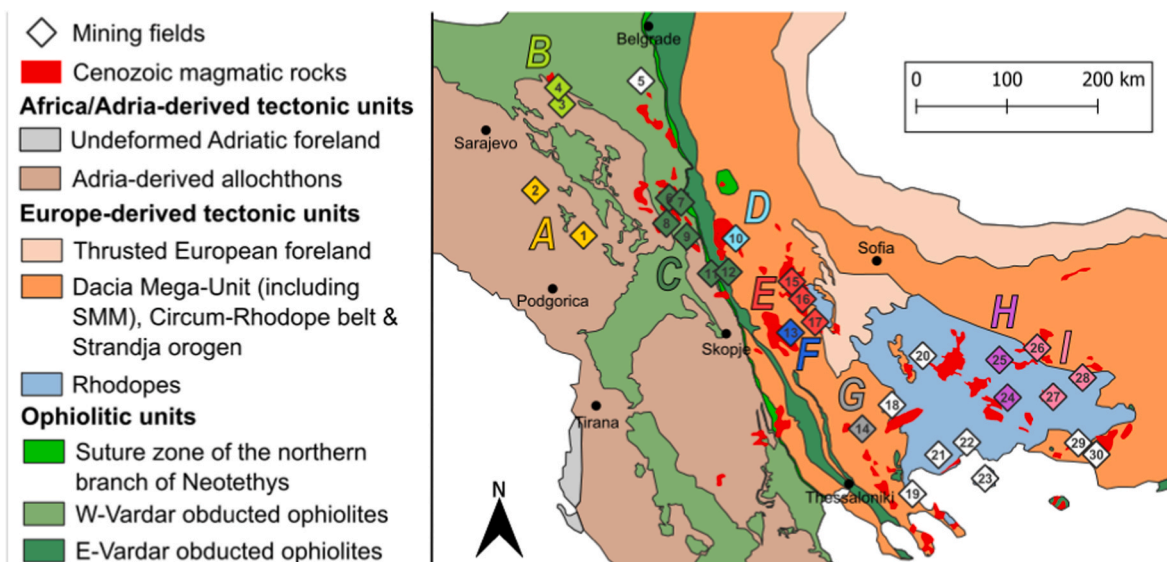


Fig. 1. Geotectonic sketch map of southeastern Europe (modified from Schmid et al., 2020) with Cenozoic magmatic rocks (taken from Asch, 2005) and the most significant Ag (Pb) mining fields (compiled from Janković, 1982; Jelenković et al., 2008; Marchev et al., 2005; Melfos and Voudouris, 2017; Palinkaš et al., 2008; Popov and Popov, 2019; Vaxevanopoulos et al., 2022a). The symbols for the mining fields sampled for this study are colored according to their superordinate mining districts (#A–I; cf. Table 1), which also are annotated on the map. Mining fields located in districts not sampled for this study are shown as blank symbols. Dinarides: 1) Brskovo (MNE), 2) Šuplja Stijena-Ljubišnja (MNE, BiH). Serbomacedonian Massif: 3) Srebrenica (BiH), 4) Boranja (SRB), 5) Šumadija (SRB), 6) Raška (SRB), 7) Belloberdë/Belo Brdo (KS, SRB), 8) Mali i Rogoznës/Rogozna (KS, SRB), 9) Stan Tërg/Stari Trg (KS, SRB), 10) Lece (SRB), 11) Hajvali-Badovc-Kishnicë/Ajvalija-Badovac-Kišnica (KS), 12) Novobërdë/Novo Brdo (KS), 13) Zletovo (NMK), 14) Kilis (GR, NMK). Crnook-Osogovo-Lisets complex: 15) Blagodat (SRB), 16) Karamanica (SRB), 17) Osogovo (NMK, BLG). Rhodopes: 18) Angistrion (GR), 19) northeast Chalkidiki (GR), 20) Rila-western Rhodopes (BLG), 21) Pangaeon (GR), 22) Palaea Kavala (GR), 23) Thasos (GR), 24) Madan-Thermes (BLG, GR), 25) Laki (BLG), 26) Spahievo (BLG), 27) Zvezdel-Pcheloyad (BLG), 28) Madzharovo (BLG), 29) Kirki-Sappes-Kassiteres (GR), 30) Evros (GR).

Table 1

Main characteristics of the investigated Ag-bearing ore deposits. Information on the “dating of genetically associated magmatic rocks” has been included as it provides a time frame for the deposition of the investigated mineralizations of hydrothermal origin. If available, the year in which metal production is first mentioned for the investigated mining fields is given in the column “historical metal production”. Abbreviations are: BIF – banded iron formation, IS – intermediate sulfidation, LS – low sulfidation, MA – mineralization age, SEDEX – sedimentary exhalative deposit, VMS – volcanogenic massive sulfide ore deposit.

Country	No. on map	Mining field	Mineralization(s)	Other commodities	Mineralization style	Mineralization period	Host rocks	Dating of genetically associated magmatic rocks	Historical metal production	References
northeast Montenegro (district A)										
MNE	1	Brskovo	Brskovo	Zn, Pb	VMS, veins	Middle Triassic	Keratophyre, porphyrites, schist	–	Medieval (1254; Kovacevic, 1960; Živanović, 2020)	Štruel (1981), Vgenopoulos (1986)
MNE/BiH	2	Šuplja Stijena/Ljubisnja	Šuplja Stijena, Rajkovići	Pb, Zn, Cu	Veins	Middle Triassic	Keratophyre, andesite	–	Probably medieval (Davies, 1935, pp. 189–191)	Hrković and Jelenković (1994), Mitrović et al. (2011)
Podrinje/Drina (B) BiH	3	Srebrenica	Sase	Pb, Zn, Sb, Sn	Veins	Oligocene	Andesite-dacite, pyroclastic rocks, slate	28.5–30.4 Ma (K/Ar; Pamić et al., 2000)	Roman-late antique, medieval (1352), Ottoman (Davies, 1935, pp. 191–193; Kovacevic, 1960; Olovčić et al., 2017; Radimsky, 1893; Rücker, 1901)	Radosavljević et al. (2011, 2016)
Kopaonik (C) SRB										
	6	Raska	Kiževak, Sastavci	Pb, Zn, Au	Veins, epithermal (IS)	Oligocene	Andesite- dacite, quartz latite, diorite, pyroclastic rocks	–	From antiquity on (Marić, 2019)	Monthel et al. (2002), https://www.adriaticmetals.com/our-projects/serbian-projects/sastavci-prospect/https://www.adriaticmetals.com/content/?contentID=3163 (last checked 5.4.2023)
SRB/KS	7	Bellobërdë/Belo Brdo	Zaplanina, Vojetin, Bellobërdë/Belo Brdo	Pb, Zn, Au	Carbonate replacement, veins	Oligocene	Andesite, serpentinite/ listvenite, limestone, flysch	–	Medieval (14th century), Ottoman (Davies, 1935; Kovacevic, 1960)	Schumacher (1954), Veselinović-Williams (2011)
KS	9	Stan Tërg/Stari Trg	Stan Tërg/Stari Trg, Melenicë/Meljenica	Pb, Zn, Bi, Cd	Skarn	Oligocene	Quartz latite, limestone, schist	23.2–25.1 Ma (K/Ar; Strmić Palinkaš et al., 2016)	Prehistoric (Cu), medieval (1303), Ottoman (Davies, 1935; Gassmann et al., 2022; Kovacevic, 1960)	Kołodziejczyk et al. (2016), Schumacher (1950), Strmić Palinkaš et al. (2013)
KS	11	Hajvali-Badovc-Kishnicë/Ajvalija-Badovac-Kišnica	Kishnicë/Kišnica, Janjevë/Janjevo	Pb, Zn, Au	Veins	Oligocene	Andesite-dacite, serpentinite/ listvenite, flysch	–	Prehistoric, Roman-late antique, medieval (1303), Ottoman (Davies, 1935, p. 223; Gassmann et al., 2022; Kovacevic, 1960; Savić, 1954)	Janković (1982), Mederski et al. (2021)
KS	12	Novobërdë/Novo Brdo	Novobërdë/Novo Brdo	Pb, Zn, Au	Carbonate replacement	Oligocene	Andesite-dacite, marble, schist	25.5–27.5 Ma (K/Ar; Serafimowski, 1999)	Late antique, medieval (1326), Ottoman (Davies, 1935; 1935, p. 223; Gassmann et al., 2022; Savić, 1954)	Janković (1982), Trepca Kosovo under UNMIK administration (2005)
Lece (D) SRB	10	Lece	Lece, Tulare	Pb, Zn, Au, Cu	Epithermal (LS), porphyry copper	Oligocene	Andesite-dacite, andesitic pyroclastics	27.6–32 Ma (K/Ar; Pamić and Balen, 2001; Serafimovski et al., 1997) MA (Tulare):	Prehistoric, Roman-late antique, medieval, Ottoman (Amedoski and Petrović, 2019; Bugarski et al., 2018, 2019)	Márton et al. (2013), Stajević (2003), Velić et al. (2018)

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Table 1 (continued)

Country	No. on map	Mining field	Mineralization(s)	Other commodities	Mineralization style	Mineralization period	Host rocks	Dating of genetically associated magmatic rocks	Historical metal production	References
								32.8–33.0 Ma (U/Pb; Márton et al., 2013)		
Blagodat-Osogovo (E)										
SRB	15	Blagodat	Grot, Besna Kobila	Pb, Zn (Cu)	Metamorphosed VMS (primary), carbonate replacement, veins	Oligocene	Dacite, quartz latite, limestone, marble, schist	29.5 Ma (K/Ar; Čebić, 1990)	Presumed Roman (Davies, 1935)	Janković et al. (1995), Jelenković (1995)
SRB	16	Karamanica	Podvirovi, Karamanica, Liska	Pb, Zn, Cu (Au)	Metamorphosed VMS (primary), veins, carbonate replacement	Oligocene	Quartz latite, limestone, marble, schist, conglomerate	23.0 Ma (K/Ar; Aleksandrov, 1992)	–	Janković et al. (1995), Jelenković (1995), Siddle et al. (2021)
NMK	17	Osogovo	Sasa, Toranica	Pb, Zn	Skarn, veins	Oligocene	Limestone, marble, schist	28.4–31.2 Ma (K/Ar; Tasev et al., 2005)	Medieval, Ottoman (Davies, 1935; 1935, p. 228; Dimče, 1996)	Janković et al. (1995), Palinkas et al. (2018)
Zletovo (F)										
NMK	13	Zletovo	Dobrevo	Pb, Zn, Cu	Veins	Oligocene	Andesites-dacites, dacitic ignimbrites	26.5 Ma (K/Ar; Serafimovski et al., 1997)	Roman-late antique, medieval (1350), Ottoman (Davies, 1935; 1935, pp. 227–228; Dimče, 1996)	Serafimovski and Boev (1996), Serafimovski et al. (2006), Tasev et al. (2019),
Kroussia (G)										
NMK	14	Kilkis	Bashibos	Zn, Pb, Cu	SEDEX (primary), veins	Mid to late Permian (primary), early Cretaceous	Siliciclastic and carbonate sediments (primary), marble, phyllite, schist	–	–	Soster (2020)
GR	14	Kilkis	Myriophyto	Zn, Cu (Pb)	Veins, carbonate replacement	Oligocene-Miocene (?)	Limestone, marble	–	Traces of ancient mining are recorded for the area (Gentner et al., 1980; Pernicka, 1987; Vaxevanopoulos et al., 2022)	Arvanitidis et al. (1996), Stergiou et al. (2021)
GR	14	Kilkis	Metalliko	Pb, Ba, F	Stratiform (VMS?)	Triassic (?)	Tuff	240 Ma (U/Pb; Frei cit. In Asvesta and Dimitriadis (2010))		Tsamantouridis and Apostolos (1986)
GR	14	Kilkis	Mavros Vrachos	Fe (Cu, Zn, Pb)	BIF, stratiform	Triassic	Rhyolite, schist	240 Ma (U/Pb; Frei cit. In Asvesta and Dimitriadis (2010))		Asvesta and Dimitriadis (2010), Tsamantouridis and Apostolos (1986)
GR	14	Kilkis	Divouni	Pb, Cu	Veins, porphyry copper	Oligocene-Miocene (?)	Gneiss, schist	Vathi: 17–18 Ma (U/Pb; Frei, 1992); Gherakario: 22 & 34 Ma (U/Pb; Frei, 1992)		Kockel et al. (1975), Stergiou et al. (2021)
central Rhodopes (H)										
BLG	24	Madan-Thermes	Androvo, Angel Janakiev, Borieva, Deveti Septemvri, Erma Reka, Krushev Dol, Strashimir	Pb, Zn	Carbonate replacement, veins	Oligocene	Marble, gneiss, schist, amphibolite	MA: 30.3–30.8 Ma (Kaiser-Rohrmeier et al., 2004)	Roman-late antique, medieval, Ottoman (Petrusenko, 1991)	Amov et al. (1993), Marchev et al. (2005), Vassileva et al. (2009)
BLG	25	Laki	Chetroka, Djurkovo, Droujba	Pb, Zn	Veins, carbonate replacement	Oligocene	Marble, gneiss, schist, amphibolite	MA: 29.2–29.4 Ma (Kaiser-Rohrmeier et al., 2004)	–	Amov et al. (1993), Marchev et al. (2005)
eastern Rhodopes (I)										
BLG	26	Spahievo	Chala	Pb, Zn, Cu (Au)	Epithermal (IS)	Oligocene	Volcanites, plutonites	31.8–32.9 Ma; MA: 32.1 Ma (Ar/Ar; Singer and Marchev, 2000)	–	Amov et al. (1993), Marchev et al. (2005)

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Table 1 (continued)

Country	No. on map	Mining field	Mineralization(s)	Other commodities	Mineralization style	Mineralization period	Host rocks	Dating of genetically associated magmatic rocks	Historical metal production	References
BLG	27	Zvezdel-Pcheloyad	Zvezdel	Pb, Zn, Cu (Au)	Epithermal (IS)	Oligocene	Gneiss, amphibolite, schists, conglomerates, sandstone, limestone, volcanites, plutonites	31.5–33.0 Ma (K/Ar; Lilov et al., 1987)	Roman-late antique (Popov et al., 2011)	Amov et al. (1983), Marchev et al. (2005)
BLG	28	Madzharovo	Madzharovo	Pb, Zn, Cu (Au)	Epithermal (IS)	Oligocene	Gneiss, amphibolite, marble, volcanites and plutonites (latite, shoshonite, basalt, dacite)	32.1–32.7 Ma; MA: 32.1 Ma (Ar/Ar; Marchev and Singer, 2002) 31.0–33.5 Ma (K/Ar; Lilov et al., 1987)	-	Amov et al. (1979), Marchev et al. (2005), Rice et al. (2007)

2. Materials and methods

2.1. Study area and sampling

Ores were sampled from deposits in Montenegro, Bosnia and Herzegovina, Serbia (including Kosovo), North Macedonia, Bulgaria, and northern Greece (Table 1, Fig. 1). The main formation mechanisms of these mineralizations were extensional tectonics and associated magmatic activity. Ore deposits in the Dinarides and the Serbomacedonian Massif are linked to the Alpine Wilson cycle. Opening and closure of the Neotethys occurred through Permian-Triassic intracontinental rifting (Dinarides) and late Jurassic/early Cretaceous convergence of the European (Eurasian) and African (Gondwana, including the Adria plate, a promontory) continental plates, and subsequent extensional tectonics in the Late Eocene-Miocene periods (Serbomacedonian Massif). Exhumation of the Rhodope mega-core complex in the Middle Cretaceous to Early Tertiary was followed by post-thickening extension in the later phases of orogenic collapse (Cvetkovic et al., 2016; Schmid et al., 2020 for further information on the geological units in south-eastern Europe and their tectonic evolution).

The geographical limits of the study area were set to cover all principal Ag (Pb)-bearing ore districts within the Dinarides and the Serbomacedonian Massif and Rhodopes to establish a comprehensive database of such mineralizations in the Balkan Peninsula. The investigated mining fields were selected on the basis of their geological characteristics and their known or suspected historical and/or archaeological significance. Pre-modern remains are mostly dated to the Roman and later periods (Table 1) but may have followed older workings. Sampling of deposits was concentrated in the southern part of the study area, where the inland mints presumably were located and subsequently brought under control of the Macedonian kingdom. Specific focus was placed on pre-Alpine Ag-bearing ore deposits within the study area for which no state-of-the-art data were hitherto available and thus their possible importance as ancient silver sources has never been evaluated. Samples were also obtained from modern mines and collected from historical workings whenever possible. Some of the Kosovo ores analyzed here were sampled during a previous project of the first author (Gassmann et al., 2022; Westner, 2017). Additionally, galena specimens from the Madan-Thermes and Laki mining fields (Fig. 1, #24, 25) in the central Rhodopes (Fig. 1, #H; mostly derived from modern mining sites; cf. Table S2) were purchased from mineral dealers and obtained from the collection at the Smithsonian Institute, respectively. In total 128 ore samples were investigated.

2.2. Sample preparation and analysis

The ore samples were prepared for compositional and Pb–Ag isotopic analysis according to the protocols in Milot et al. (2021c). A detailed description of the preparational and analytical procedures used in this study is provided in the supplementary material (S1). The Pb isotopic composition of a Tertiary andesite from the Hajvali-Badovc-Kishnicë/Ajvalija-Badovac-Kišnica (HBK/ABK) mining field in Kosovo (Fig. 1, #11 and Table 1) was measured for comparative purposes. From one aliquot of this sample, K-feldspar was handpicked using a binocular microscope. The other sample aliquot was dedicated to whole-rock Pb isotope analysis. Silver contents of the samples were checked after Ag separation by ion chromatography and only samples with Ag yields $\geq 85\%$ were accepted for Ag isotope analysis to avoid results potentially biased due to procedural isotopic fractionation (cf. Theis et al., 2013). Lead was efficiently removed but Zn and Cu, whenever particularly abundant, proved to be difficult to completely separate from Ag by ion chromatography. Some polymetallic ore samples therefore were excluded from Ag isotope analysis. The major and trace element concentrations of the samples were determined by quadrupole ICP-MS (iCAP-Q), and the Pb and Ag isotopic compositions were measured with a Nu Plasma 500 HR MC-ICP-MS, both housed at the Ecole Normale

Supérieure in Lyon (ENS Lyon). Sulfur isotope abundances of two samples from the HBK/ABK and two samples from Novobërdë/Novo Brdo (Fig. 1, #12) mining fields were determined at the Iso-Analytical labs in Crew (England) by Elemental Analysis-Isotope Ratio Mass Spectrometry (EA-IRMS) to obtain a first set of reference data previously not available for these localities. All analytical data are compiled in Table S2.

3. Results

3.1. Historical workings

Pre-modern workings were frequently observed in the investigated districts, particularly in the Zletovo and Kopaonik (Novobërdë/Novo Brdo mining field) districts (Fig. 1, #F, C). Surficial mining followed outcropping mineralizations and left behind exploitation chambers and mined-out veins and fissures (Fig. 2a–c), creating small galleries underground (Fig. 2f). Ore bodies were also accessed through more regularly cut galleries and shafts (Fig. 2e, g). Mining depressions have

resulted from the collapse of workings (Fig. 2h). Metallurgical remains, in particular smelting slags (Fig. 2i), indirectly document mining activities. Previous studies, based on fieldwork and epigraphic and historical evidence, assign Roman to late antique, medieval, or Ottoman dates to most sites (Table 1). Prehistoric mining is hypothesized for the HBK/ABK, Lece (Fig. 1, #10), and Stan Tërg/Stari Trg (Fig. 1, #9) mining fields. The nature of remaining ore at the latter two localities indicates that these activities were related to copper extraction. The dating of workings typically is a challenge as ceramics are rarely found within the mines and their debris heaps, or at beneficiation and smelting sites. Even when found, the sherds may not relate to the mining activity, hence rendering their dating misleading. Furthermore, many districts seem to have been mined at different times (Table 1), which makes it difficult to separate exploitation phases and may have led to obliteration of older remains. Dating based on stylistic means can, however, be assigned to some workings. For example, the dimensions and shape of a gallery at Dobrev (Fig. 2e; Zletovo district) are comparable to Roman workings, such as at Roşia Montană/Romania (Cauuet, 2014) and Lece/Serbia (Bugarski et al., 2018). Small exploitation chambers within

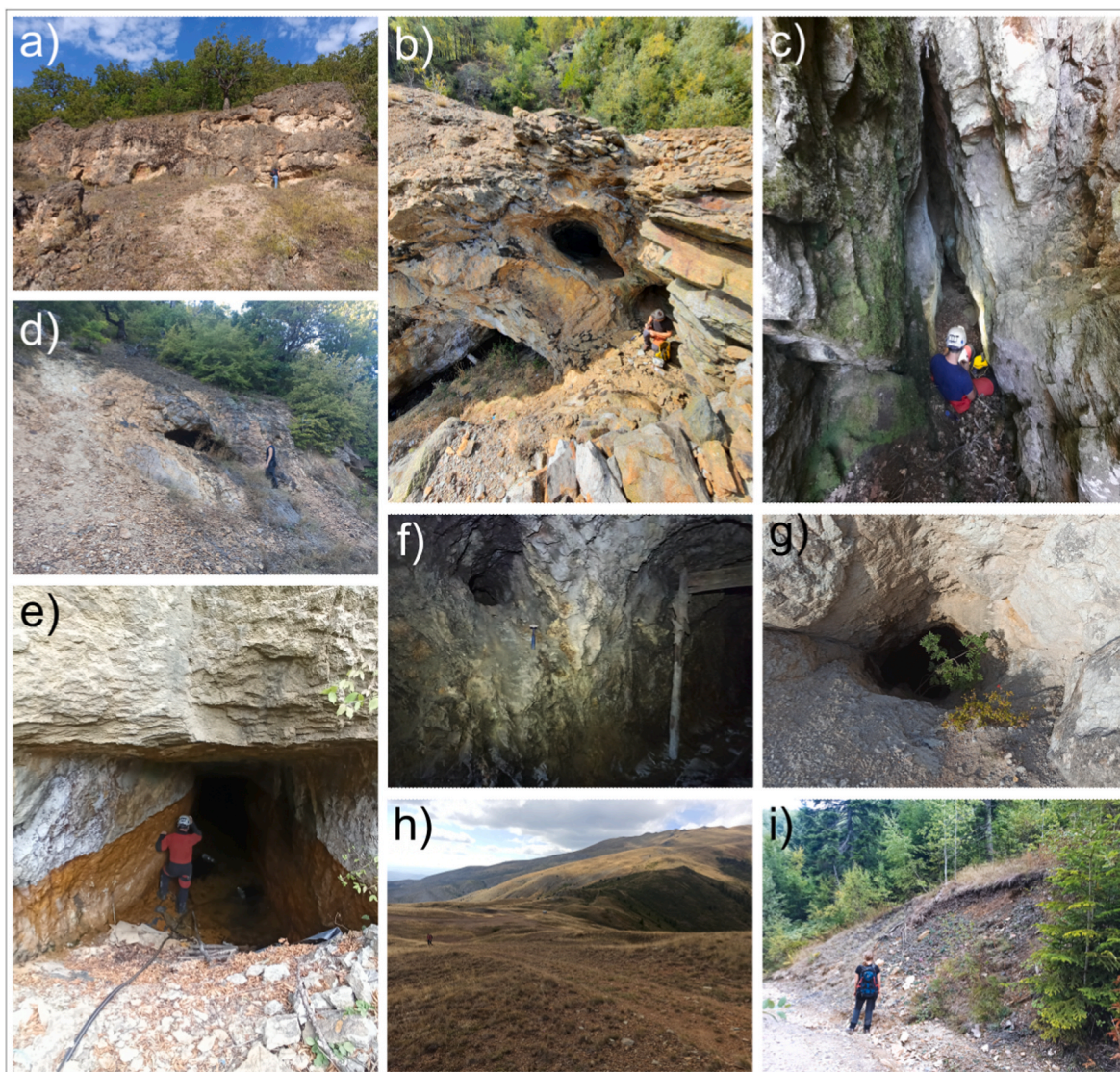


Fig. 2. Photographs of remains from historical metal production at the investigated mining fields. a) Lece: Traces of surface mining within the outcropping andesite. b) Strashimir, Madan-Thermes: mined-out vein (lower left) and transected galleries. c) Lece: mined-out mineralized fissure. d) Tulare, Lece: small mining chamber related to copper extraction. e) Dobrev, Zletovo: ancient gallery. f) Besna Kobila, Blagodot: ancient gallery (upper left) exposed by modern mine workings. g) Dobrev, Zletovo: shaft. h) Vojetin, Bellobërdë/Belo Brdo: mining depressions surrounded by extensive waste heaps. i) Brskovo: slag heap transected by modern road construction.

the mineralized porphyry at Tulare (Fig. 2d; Lece district, Fig. 1, #D) are similar to mining remains at Melenič/Meljenica (Stan Tërg/Stari Trg mining field), which have been related to Bronze Age copper mining (Gassmann et al., 2022). This evidence indicates that the technological know-how relevant for metal production was already existing in part of the present study area before the Archaic period. Silver is thought to have been introduced to the interior of south-eastern Europe in the 1st millennium BCE (e.g. Vukmanović and Medović, 1990) and therefore local extraction of the precious metal might have only commenced with the introduction of coinage.

3.2. Lead isotopes

Lead isotope values are shown in both conventional ^{204}Pb -normalized diagrams and as plots of Pb model ages, T_{mod} , versus μ ($^{238}\text{U}/^{204}\text{Pb} \sim \text{U}/\text{Pb}$) and κ ($^{232}\text{Th}/^{238}\text{U} \sim \text{Th}/\text{U}$), respectively (Fig. 3). Lead model ages and apparent U/Pb and Th/U values were calculated using the parameters of Albarede and Juteau (1984). The Permian to Triassic mineralizations in the Brskovo and Šuplja Stijena-Ljubišnja (Fig. 1, #1, 2) and Kilkis (Fig. 1, #14) mining fields are clearly separated from the Cenozoic ore deposits by their lower $^{206}\text{Pb}/^{204}\text{Pb}$ ratios and older Pb model ages. An exception to this is the Myriophyto occurrence (Kilkis mining field), the Pb isotope ratios of which overlap with those of pre-Alpine deposits despite its assumed Oligocene-Miocene formation age (Stergiou et al., 2021). The model U/Pb and Th/U ratios of Permian/Triassic and Tertiary deposits generally are similar, even though

the geologically older mineralizations are characterized by a narrower Th/U range at rather high values. Several data points form linear arrays with characteristic slopes (cf. Albarede et al., 2020) that are consistent with low-temperature mass-dependent isotope fractionation between Pb (II) and Pb(IV) and different from the slopes produced by radiogenic ingrowth (Fig. 3a and b). Low-temperature fractionation can be induced by alteration of unexposed ore bodies due to circulation of meteoric water at depth, while atmospheric weathering affects specimens collected from debris heaps or exposed gallery walls. Low yields from ion-exchange column procedures and instrumental mass bias may produce similar effects (cf. Albarede et al., 2020) but can be avoided (as done in this study) by measuring yields and running standards. Instrumental mass bias has been brought under control with the advent of MC-ICP-MS and Tl addition to the sample Pb solutions and Pb standard. An additional observation allowing the identification of the effect of low-temperature processes on Pb isotope compositions is that it seems to be restricted to some mining districts while being absent from others (Milot et al., 2021b; Vaxevanopoulos et al., 2022a; this study). There is no systematic difference between the Pb isotope signatures of samples derived from modern contexts and those collected inside pre-historic workings or from their debris heaps. This indicates that Pb isotope signatures are fairly homogeneous within ore bodies and do not simply vary laterally or vertically.

The Pb isotope compositions of Permian/Triassic deposits from the Dinarides and northern Greece overlap widely, which suggests parental Pb sources with nearly contemporaneous fractionation of Pb from U and

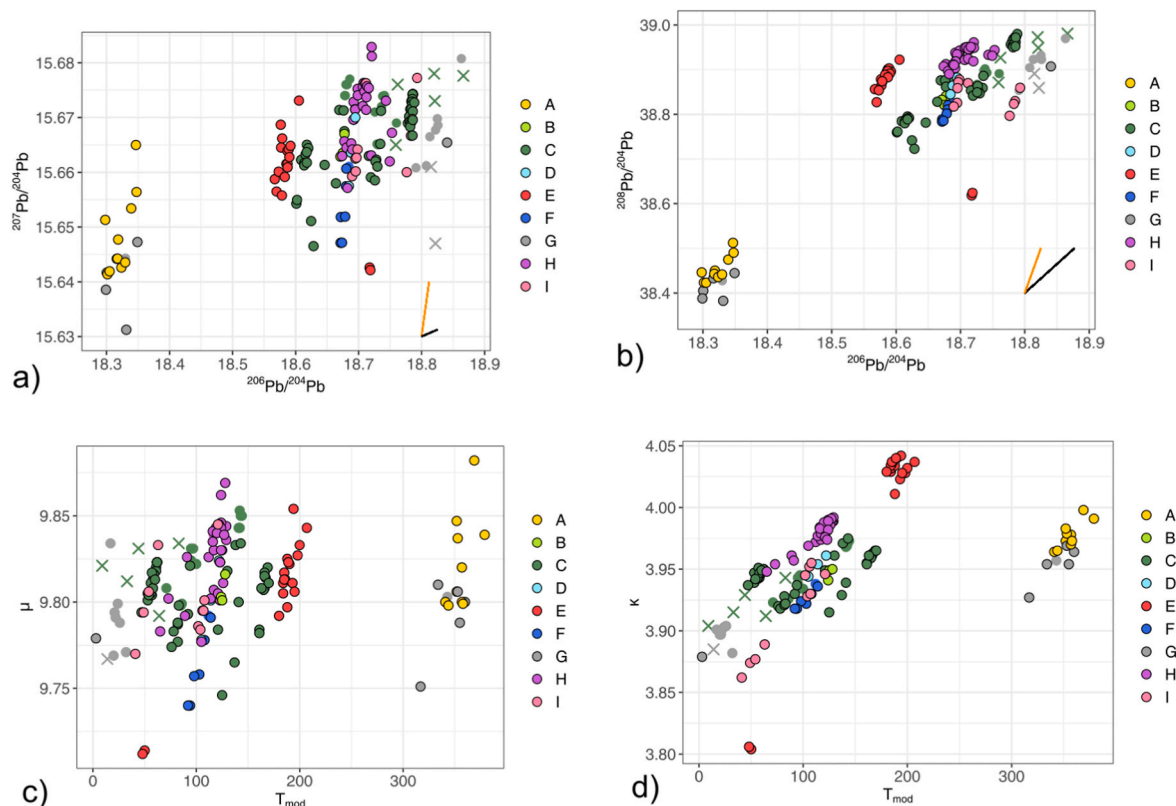


Fig. 3. Diagrams of ^{204}Pb -based Pb isotope ratios (a, b) and Pb model parameters T_{mod} (Pb model age in Ma) versus μ ($^{238}\text{U}/^{204}\text{Pb}$; c) and κ ($^{232}\text{Th}/^{238}\text{U}$; d), respectively, of the investigated samples grouped according to mining districts (Janković, 1982; Marchev et al., 2005; Melfos and Voudouris, 2017; Vaxevanopoulos et al., 2022a) for better readability. Mining districts are (cf. Table 1, Fig. 1): A) northeast Montenegro, B) Podrinje/Drina, C) Kopaonik, D) Lece, E) Blagodat-Osogovo, F) Zletovo, G) Kroussia, H) central Rhodopes, I) eastern Rhodopes. Model parameters were calculated according to Albarede and Juteau (1984). Additional ore reference data from the investigated districts determined by MC-ICP-MS (taken from Milot et al., 2021c; Vaxevanopoulos et al., 2022a; Veselinović-Williams, 2011; Westner, 2017) are shown as open symbols. Legacy whole-rock and K-feldspar Pb isotope data (shown as X) are taken from Frei (1992) and Veselinović-Williams (2011); note that highly radiogenic data plot outside the limits of the diagrams (cf. Table S2). Slopes for radiogenic ingrowth (black) and low-temperature isotopic fractionation (orange) are indicated (cf. Albarede et al., 2020). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Th, and similar formation conditions. The narrow range of Pb model ages (341–379 Ma) significantly exceeds the age of genetically associated Triassic magmatic activity. The Pb isotope signatures of Cenozoic deposits show significant scatter, and considerable overlap exists between mining districts. Utilization of three Pb isotope ratios in single or combined plots enables the partial resolution of this problem as $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios in particular (or calculated Pb model ages and Th/U) offer good discrimination between single mineralizations. Lead model ages range from 3 Ma (Divouni; Kilkis mining field) to 313–343 Ma (Myriophyto) and are ca. 200 Ma for ore samples from the Osogovo-Blagodan district (Fig. 1, #E) and thus in most cases greatly exceed the mainly Oligocene ages of related igneous rocks. Lead model ages and Th/U ratios are correlated with the mineralization style of the deposits and their host rocks. Carbonate replacement/skarn deposits associated with marbles and limestones hosted in metamorphic rocks of the Serbo-Macedonian Massif (Novobërdë/Novo Brdo mining field), the Crnook-Osogovo-Lisets complex (Antić et al., 2016; Blagodan-Osogovo district), and the central Rhodopes have comparatively old Pb model ages, and, in the case of the central Rhodopes and Blagodan-Osogovo districts, elevated apparent Th/U ratios. The U/Pb and Th/U ratios of ores from the Liska outcrop (samples TLA-1, TLA-2; Karamanica mining field, Fig. 1, #16), which are hosted in strongly hydrothermally altered conglomerates, are significantly lower and reminiscent of mantle-derived Pb (Hofmann, 1997). Potassium-feldspar data from the HBK/ABK field contains radiogenic Pb ($T_{\text{mod}} = -708$ Ma), which is most likely derived from U–Th-bearing glass or its devitrified products. The whole-rock datum is overall comparable to literature bulk and K-feldspar Pb isotope data of Tertiary magmatic rocks (Fig. 3; Frei, 1992; Veselinović-Williams, 2011). Varying degrees of similarity between the Pb isotope ratios of ores and Tertiary magmatic rocks indicate variable contribution of magmatic Pb.

Spatially-resolved plots (including data from the Greek part of the Rhodopes; Vaxevanopoulos et al., 2022a) visualize different Pb isotopic domains in south-eastern Europe (Fig. 4; see S3a-c for maps with ^{204}Pb -based isotope ratios). The characteristics of provinces singled out by their Pb model ages and apparent U/Pb and Th/U ratios are identified below (acronyms listed in brackets) and summarized in Table 2. Subtle variations in the model ages of Cenozoic ores distinguish, for example, different mining fields of the Kopaonik district. Furthermore, the auriferous mineralizations in the eastern part of Thasos are discriminated from the Pb–Zn deposits in the west of the island (Vavelidis and Amstutz, 1983, Fig. 1, #23) by their somewhat older model ages. Pre-Cenozoic ore deposits of mostly Triassic age (TM) are readily identified by their notably lower Pb model ages compared to the predominant Oligocene–Miocene ores. There is a trend toward older model ages among the Cenozoic deposits of the Serbo-Macedonian Massif from northern Greece to North Macedonia, Kosovo, and Serbia (cf. Frei, 1992). Apparent U/Pb ratios are comparatively high for samples from the Au-rich mineralizations at Palaea Kavala, Pangaeon, and Thasos in the southern part of the Rhodope core complex (SRC; Voudouris et al., 2018). For some data of ores from northeast Chalkidiki similarly high μ values were calculated as well. The majority of data, however, possesses apparent U/Pb ratios consistent with those of deposits within the Serbo-Macedonian Massif. Pangaeon and Palaea Kavala are classified as intrusion-related gold systems (cf. Lang and Baker, 2001) genetically related to a granodiorite emplaced in the Miocene period. Thasos presumably also hosts polymetallic veins related to an intrusion of Miocene age besides well-attested metasomatic deposits (Melfos and Voudouris, 2017 and references therein). Their metallogeny therefore distinguishes mineralizations of the SRC from the vein and carbonate replacement deposits of the CRC and the epithermal ore bodies of the eastern Rhodopes (Fig. 1, #I), both of Oligocene age, and linked to the detachment fault and plutonic and volcanic rocks, respectively (e.g. Marchev et al., 2005). Northeast Chalkidiki possesses mixed characteristics and is located partially within the Serbo-Macedonian Massif and Rhodopes. Analogous to the SRC, its deposits are hosted within the southern part of

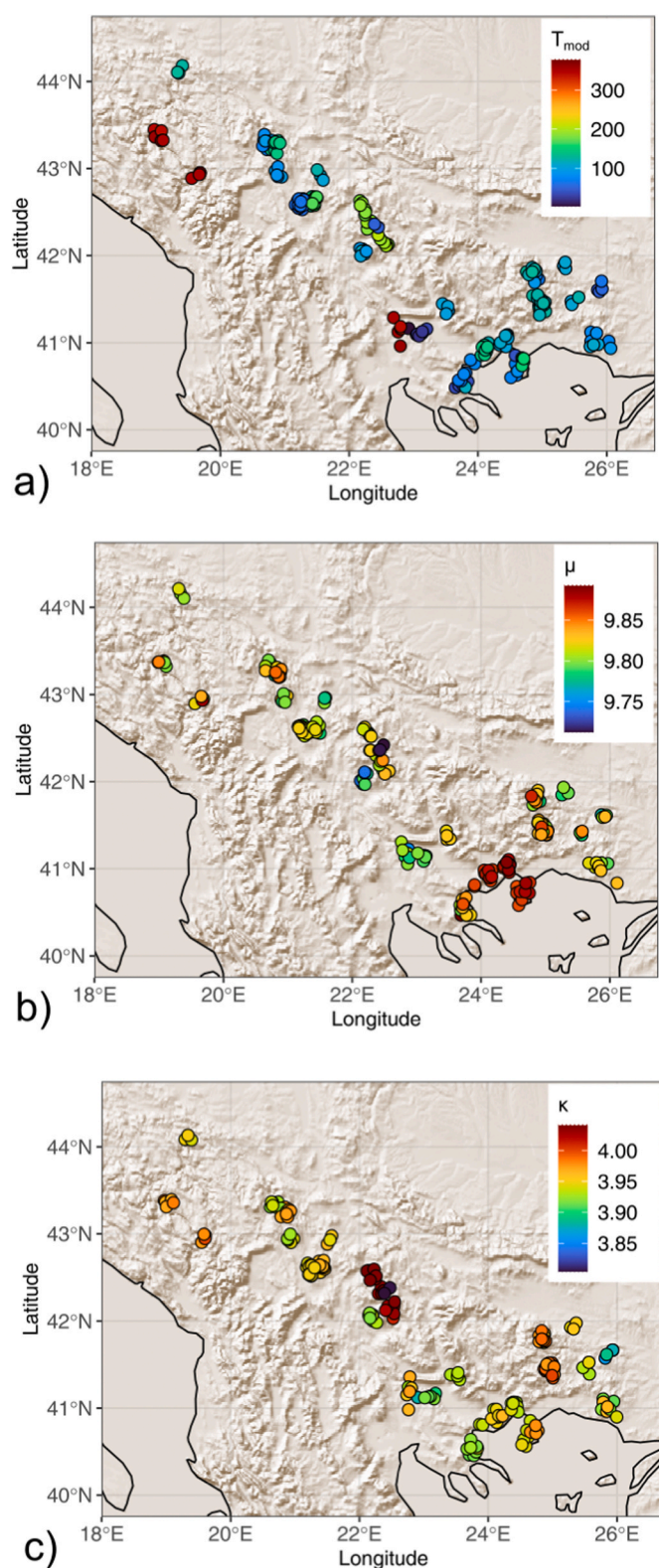


Fig. 4. Geographic maps of the distribution of model parameters derived from Pb isotope ratios of ore samples. Additional ore reference data are as in Fig. 4, with data from other mining districts in the Greek part of the Rhodopes (Vaxevanopoulos et al., 2022a) and Serbo-Macedonian Massif included. Note that points are jittered to increase readability. a) Lead model age (T_{mod}), b) μ ($^{238}\text{U}/^{204}\text{Pb}$), c) κ ($^{232}\text{Th}/^{238}\text{U}$).

Table 2
Characteristics of major Pb isotopic domains in south-eastern Europe.

Abbreviation	Name	Mining fields	T _{mod} (Ma)	μ	κ	Further characteristics
TM	Triassic mineralisations	• NE Montenegro, Šuplja Stijena/Ljubušnja • Kilgis	• 341–379 • 317–360	• 9.80–9.88 • 9.75–9.81	• 3.96–4.00 • 3.93–3.97	Might be partially remobilized by Cenozoic magmatic activity (Kilkis)
SRC	southern Rhodope core complex	Thasos, Palaea Kavala, Pangaeon	42–154	9.85–9.91	3.91–3.98	Ore commonly has a high Au content
COL	Crnook-Osogovo-Lisets complex	Osogovo, Blagodat, Karamanica	180–207 (highest T _{mod} of Cenozoic deposits)	9.79–9.85	4.01–4.04	Ore chemistry is variable and can be enriched in Cu
CRC	central Rhodope core complex	Madan, Laki	65–129	9.78–9.87	3.95–3.99	Ore often is poor in Ag

the Rhodopes and also are intrusion-related but were already formed in the Oligocene (Vaxevanopoulos et al., 2022a and references therein). Ores from the Crnook-Osogovo-Lisets complex (COL) and, to a lesser extent, the central Rhodopes (CRC) are characterized by high apparent Th/U ratios (see above).

3.3. Sulfur isotopes

The S isotope ratios of the four investigated galena samples range from -0.12 to $+3.10$ ‰ ^{34}S (Fig. 5) and hence generally agree with values typical of magmatic-derived sulfur (Nielsen, 1979) and associated hydrothermal vent fluids (Ono et al., 2007; Styr et al., 1981). They fully overlap with literature data of galena specimens from the Kopaonik district and other Pb–Zn–Ag deposits in the study area (McCoyd, 1995; Mudrinic and Serafimovski, 1992; Rice et al., 2007; Serafimovski and Tasev, 2005; Simić, 2001 with references; Strmić Palinkaš et al., 2013; Velić et al., 2018; Veselinović-Williams, 2011). While $\delta^{34}\text{S}$ values typically occupy a comparatively relatively narrow range within single deposits, large variations determined for mineralizations from the Blagodat-Osogovo district indicate local inhomogeneities. Literature S isotope data on other sulfide phases from the study area generally mirror the behavior of galena, but at higher $\delta^{34}\text{S}$ values in agreement with the differing equilibrium fractionation factors (cf. Seal, 2006 and references therein).

Sulfur isotope compositions are correlated with the host rock geology. Deposits exclusively (or primarily) associated with magmatic rocks

in the Lece, Zletovo, and eastern Rhodope districts have mean $\delta^{34}\text{S}$ values close to 0 (also see Rice et al., 2007). The remaining mineralizations are hosted mainly by metamorphic rocks and have positive or occasionally negative S isotope compositions.

3.4. Trace element systematics

The maximum bulk Ag contents of the investigated ores are in the range of 3000 $\mu\text{g/g}$ with the highest Ag abundances being determined for samples from mining fields with abundant evidence of historical metal production (Table 1, S2). In contrast, most bulk Ag contents of ores from the central Rhodopes (Madan-Thermes and Laki mining fields) and in particular from the Blagodat-Osogovo district are well below 1000 $\mu\text{g/g}$ (Fig. 6a). Samples from Lece also overall are characterized by Ag contents below c. 300 $\mu\text{g/g}$, in agreement with its status as a gold-rather than silver-producing deposit. Ores sampled from occurrences in the Kilgis mining field for comparative purposes are dominated by Fe–Cu–Zn sulfides and Fe oxides and have Pb and Ag abundances ≤ 4.87 wt % and < 100 $\mu\text{g/g}$. The Ag content of a sample collected from the wall of a pre-modern gallery at Dobrovo (sample DOB-7; Ag/Pb = 57.2) is more than ten times higher than that of ores from the active mine there (DOB-4, -5; Ag/Pb = 5.96, 3.59). The Ag abundances of ores derived from modern exploitation and of those sampled from debris heaps associated with historic workings are, however, generally in the same range within single mining fields (e.g. at Novobërdë/Novo Brdo). The metal grades of ores not sampled inside historic mines therefore have to be considered as minimum values.

A positive correlation ($r^2 = 0.86$ for logarithmic values) between Sb + Bi with Ag in the investigated galenas (defined on basis of the analytical data as having Zn/Fe/Cu contents < 1 wt%; Fig. 6a) indicates substitution of Ag+(Sb, Bi) for Pb due to the existence of a high-temperature solid solution (Chutas et al., 2008; Renock and Becker, 2011) or the presence of small sulfosalt inclusions concentrating silver in galena (e.g. Gasparrini and Lowell, 1985). The (Sb + Bi):Ag ratios of most samples vary between 1:3 and 3:1, which are equivalent to the stoichiometry of pyrrargyrite $[\text{Ag}_3\text{SbS}_3]$ and andorite $[\text{PbAgSb}_3\text{S}_6]$. The maximum Ag and Sb contents of the galena specimens (3661 and 3538 $\mu\text{g/g}$, respectively) are within the solubility limits (Chutas et al., 2008, their Fig. 7; George et al., 2015), thus suggesting for the investigated samples that Ag and Sb mainly are hosted in solid solution. Galena-dominant ores, which are made up only of galena or comprising galena besides subordinate base metal sulfides and sulfosalts, are the most relevant Ag-bearing material collected from the investigated mineralizations. Specimens which exclusively or mainly consist of argentiferous sulfosalt minerals or other Ag-rich phases were not observed.

Arsenic contents are uncorrelated with Ag and can reach up to 28.9 wt% due to the presence of arsenopyrite in some of the investigated ores. Nickel (up to 2.59 wt%) is enriched in samples from deposits associated with serpentinites and listvenites (carbonated ultramafic rocks; Halls and Zhao, 1995), i.e., mineralizations of the HKB/ABK and Bellobërdë/Belo Brdo (Fig. 1, #7) mining fields. Cadmium contents (maximum 2.15 wt%), except for two samples with > 0.5 wt% Cd, are

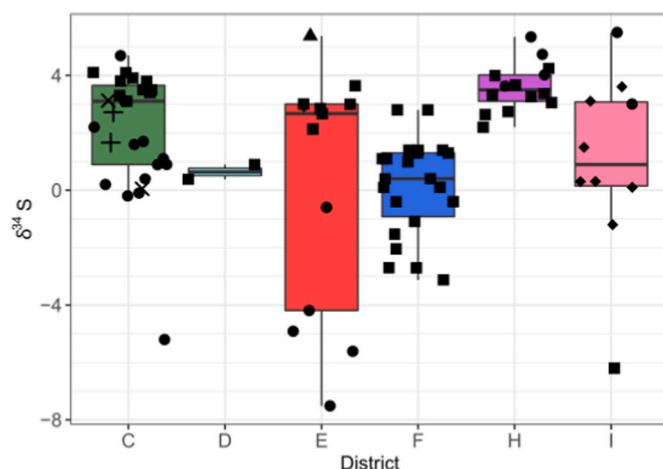


Fig. 5. Boxplot of $\delta^{34}\text{S}$ values of galena samples (reference data from McCoyd (1995), Mudrinic and Serafimovski (1992), Strmić Palinkaš et al. (2013), Rice et al. (2007), Serafimovski and Tasev (2005), Simić (2001) with references, Velić et al. (2018), and Veselinović-Williams (2011)) colored according to the mining districts from which the samples were derived. Single values are displayed as (jittered) data points with different shapes corresponding to individual mines within the districts. Data taken from Simić (2001) are mean $\delta^{34}\text{S}$ values for the Karamanica and Blagodat mining fields as individual data are not given.

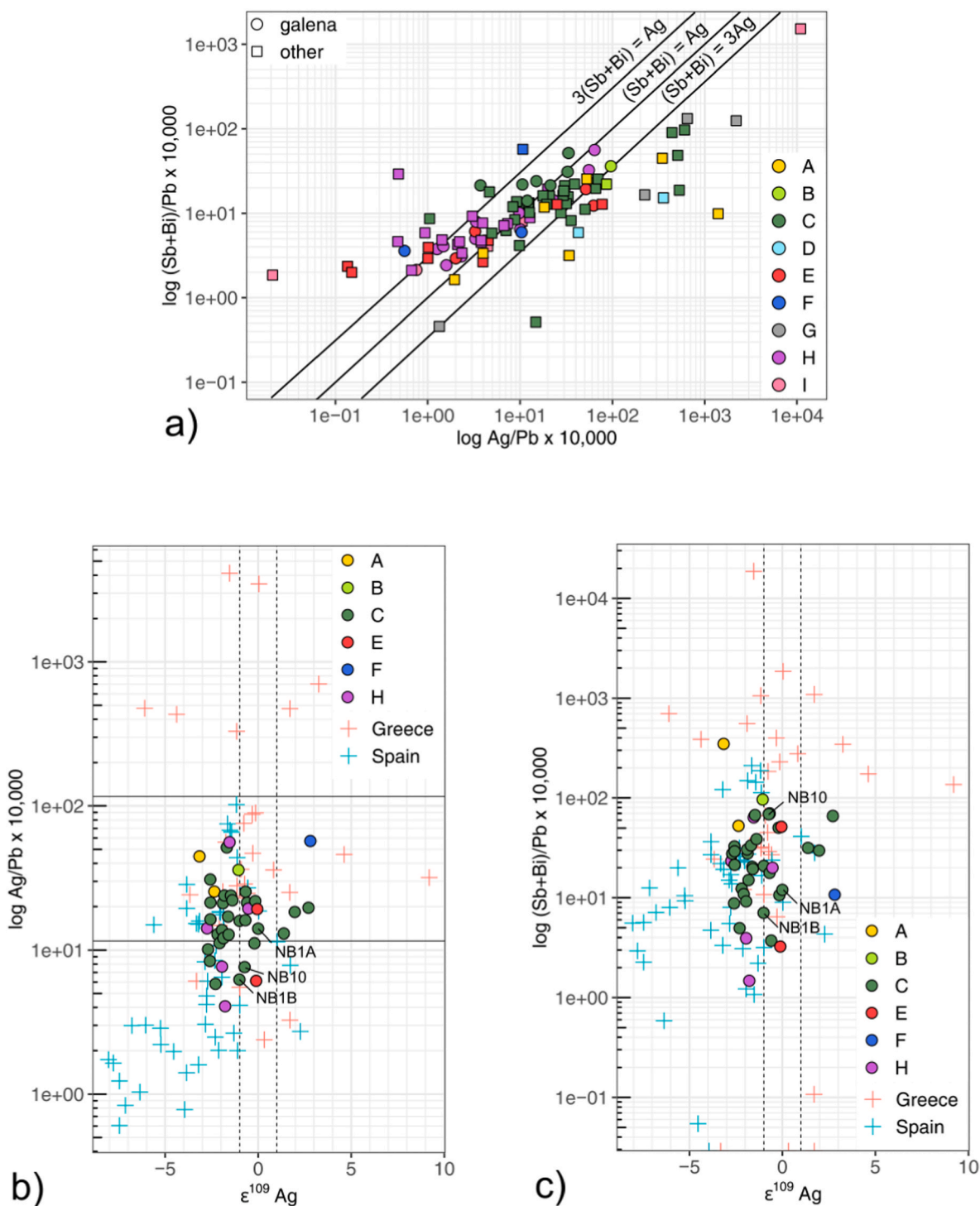


Fig. 6. Diagrams of trace element and Ag isotope systematics with samples colored according to mining districts (see above). Samples mentioned in the text are annotated in Fig. 6b and c. a) Sb + Bi/Pb versus Ag/Pb. Galena ores were defined as having Zn/Fe/Cu contents <1 wt% based on the analytical data and are distinguished from the remaining samples. b) Ag/Pb versus $\epsilon^{109}\text{Ag}$ of the investigated ores in comparison with data from Spain (Milot et al., 2021a) and Greece (Vaxevanopoulos et al., 2022b). The $\epsilon^{109}\text{Ag}$ range (−1 to +1) of most silver coins analyzed so far is indicated, as well as Ag/Pb ratios corresponding to 1 wt% and 0.1 wt% of Ag in pure galena. Note that the presence of other ore and gangue minerals in the samples affects the Ag/Pb ratio. c) Bi + Sb/Pb versus $\epsilon^{109}\text{Ag}$, same data sets as in Fig. 6b.

strongly correlated with Zn ($r^2 = 0.97$) and therefore are mainly hosted by sphalerite, a major phase in the investigated deposits.

3.5. Silver isotopes

The $\epsilon^{109}\text{Ag}$ values of the samples range between −3.2 and + 2.8

(Fig. 6b) but most values are negative. $\epsilon^{109}\text{Ag}$ may scatter from positive to negative values within a single mining field, with no discernible relation to mineralization style or host rock geology. $\epsilon^{109}\text{Ag}$ values > +1 were found in the supergene samples DOB-7 and NB4, in agreement with analytically and theoretically observed Ag isotope fractionation (Arribas et al., 2020; Fujii and Albareda, 2018). The effect of weathering was

investigated in-situ for sample NB1, which was collected from a debris heap of a pre-modern mine, by separately analyzing its core of unaltered galena (NB1A) and the outer layer consisting of oxidized Pb minerals (NB1B). The altered sample part (NB1B) is characterized by lower Ag contents (371 vs. 1051 $\mu\text{g/g}$) and has a lighter Ag isotopic composition ($\epsilon^{109}\text{Ag} = -1.01$ vs. 0.00) which does not overlap with the data for the fresh galena sample part (NB1A) within the analytical uncertainties. A semi-reacted galena-rich ore (NB10) collected from a settlement site of presumably Hellenistic dating (Alaj, 2019) within the same mining field has $\epsilon^{109}\text{Ag}$ of -0.77 and Pb isotope ratios consistent with local ores.

The total range of Ag isotope compositions for the ore samples studied here is much narrower than those observed for Spain and Greece (Milot et al., 2021a; Vaxevanopoulos et al., 2022b), in agreement with the overall similar physico-chemical conditions of magmatic-hydrothermal ore formation throughout the districts in the present study area. Strongly fractionated values with $\epsilon^{109}\text{Ag} \leq -4$ were determined for both non-magmatic and hydrothermal ores from Spain with low Ag contents ($<250 \mu\text{g/g}$). In contrast, the ore samples with Ag isotope compositions between -1 and $+1 \epsilon^{109}\text{Ag}$, i.e., within the range of most investigated silver coins (Fujii and Albarede, 2018), mostly have Ag abundances exceeding the equivalent of 1000 $\mu\text{g/g}$ (0.1 wt%) of Ag in galena (Fig. 6b). Samples from Greece with Ag contents significantly exceeding the level of 1 wt% either possess elevated abundances of Cu ($\pm\text{As} \pm \text{Bi}$) characteristic of sulfosalts (Moëlo et al., 2008) or are oxidized Pb (Zn) species with silver possibly present in its native form. These non-galena ores are clearly separated from the analyzed galena-rich samples by their Ag/Pb ratios, but overall have a comparable range of Ag isotope ratios. Antimony contents of the investigated ores are significantly lower than the range of Spanish and Greek samples and no distinct relationships between Sb + Bi contents and Ag isotope compositions are discernible (Fig. 6c).

4. Discussion

4.1. Lead isotope systematics and their geological relationships

The disparity between Pb model ages of ores and the geological ages of genetically associated magmatic rocks suggests the presence of pre-accumulated reservoirs of geologically older Pb that were re-mobilized by magmatic activity. Lead model ages are calculated from the measured Pb isotope compositions with reference to a model of radiogenic ingrowth (e.g. Albarede and Juteau, 1984; Stacey and Kramers, 1975) and attest to the time that Pb was isolated from U and Th which is not necessarily equivalent to the age of ore formation. The formation of large-scale Pb sulfide protoliths recently has been linked to anoxic events during which Pb in large quantities is flushed into the oceans due to enhanced weathering rates and precipitated there as Pb sulfide after combination with S released from hydrothermal vents (Milot et al., 2021b). Apart from the discrepancy between the age of Pb sulfide precipitation and ore deposit emplacement, several other characteristics of the investigated mineralizations are in agreement with this hypothesis: (a) their upper crustal Pb isotopic signature (cf. Zartman and Doe, 1981); (b) their $\delta^{34}\text{S}$ values mostly $<+7$, which is incompatible with an origin from marine sulfate (with $\delta^{34}\text{S} > +10$; cf. Hannington, 2014) indicating dominant contribution of a magmatic source with $\delta^{34}\text{S} \sim 0$ (e.g. Seal, 2006); and (c) overlap of Pb model age clusters in the sample set with ages of anoxic events (~ 372 Ma for the Kellwasser, ~ 186 Ma for the Late Liassic, and 111–93 Ma for the Cretaceous events). Direct sourcing of Pb and Ag with S is unlikely due to their typically low contents in vent fluids (Diehl and Bach, 2020; Von Damm, 1990), the accessory character of galena in black smokers (Haymon and Kastner, 1981), and the de-coupling of Pb, Ag, and S isotopes observed here. Elevated Cu contents occasionally observed in mineralizations from the Blagodat-Osogovo district (cf. Table 1; Table S2) presumably have been derived from volcano-sedimentary Pb–Zn–Cu ores (Simić, 2001) that are hosted within Ordovician sericite-graphite and sericite-chlorite schists

which originally formed in an oceanic environment and are associated with the deposits (Babović and Cvetković, 1976).

Subsequent tectonic and metasomatic processes during metallogenesis eventually generated the Pb isotope systematics of the investigated ores. The higher κ values calculated for ores hosted in the central Rhodopes (CRC in Table 2) and Crnook-Osogovo-Lisets complexes (COL), which consist of exhumed deep crustal segments, can be related to Th–U fractionation during intra-crustal differentiation (Blichert-Toft et al., 2016; Rudnick and Gao, 2014) upon interaction between percolating magmas, fluids, and wall rocks with the ore stock. Contribution of magmatic Pb and S to the ore bodies depends on the associated rocks and generates notable variation. For example, in the Belloberdë/Belo Brdo deposit, ores from veins hosted by Cenozoic magmatic rocks are characterized by younger Pb model ages and lower apparent U/Pb and Th/U ratios than ores from carbonate replacement bodies of the mineralization (cf. Table S2; Veselinović-Williams, 2011) documenting a greater contribution of magmatic Pb to the vein ores. Sulfur isotope ratios analogously testify to the influence of endogenous S derived from the mantle because deposits exclusively or mainly hosted by magmatic rocks have mean $\delta^{34}\text{S}$ values close to 0 (Fig. 5). The somewhat more positive $\delta^{34}\text{S}$ ratios of most remaining mineralizations (with $\delta^{34}\text{S} > 1$) possibly record contribution of S from deep-sea sediments, matching the theory on the formation of Pb stocks by Milot et al. (2021b). Interaction of mineralizing fluids with wall rocks is indicated by enriched Ni abundances in ores from the Belloberdë/Belo Brdo and HBK/ABK ore fields which presumably are derived from the associated altered ultramafic rocks, i.e., serpentinite and listvenite. Fluid/rock interaction might also have influenced the Pb isotopic composition of the ores, as hypothesized by Marchev et al. (2005) for the deposits of the Rhodopes.

Regional variations of Pb isotope signatures partially correlate with elemental patterns. The mantle-like ore Pb isotope systematics ($T_{\text{mod}} \leq 50$ Ma, $\mu \leq 9.71$, $\kappa \leq 3.81$) of samples from the Liska outcrop (Karamanica mining field) contrast with the older Pb model ages and higher U/Pb and Th/U ratios ($T_{\text{mod}} \geq 180$ Ma, $\mu \geq 9.79$, $\kappa \geq 4.01$) akin to lower crustal rocks as determined for the remaining Pb–Zn (Ag) deposits in the Blagodat-Osogovo district. This indicates a different formation process and parental metal source possibly linked to a neighboring Au-rich base metal mineralization (Barje, 1.5 km northeast of Liska; Siddle et al., 2021). Ores with elevated U/Pb ratios from particularly Au-rich Pb–Zn–Ag deposits in the southern Rhodopes core complex (SRC; Pangaeon, Palaea Kavala, Thasos) are associated with fertile Miocene magmatic rocks comprising elevated REE abundances (Eliopoulos et al., 2014). They are assumed to have been derived from melting of enriched subcontinental lithospheric mantle (Pe-Piper et al., 1998), emphasizing the role of regional heterogeneities for metal enrichment processes.

4.2. Silver isotopes and silver sources of coinage

Since Ag is a redox-sensitive element ($\text{Ag}^0\text{--Ag}^+$), its isotopes may have been affected by low-temperature processes, as suggested by the characteristic slopes observed for some of the Pb isotope data presented here (cf. section 3.1). While detailed mineralogical studies are essential to identify the potential impact of such processes on the investigated samples, the narrow distribution of the ores' Ag isotope values within the $\epsilon^{109}\text{Ag}$ range of ore-forming hydrothermal fluids (Arribas et al., 2020) per se does not indicate that such mechanisms acted on the samples analyzed here.

Since fractionation of Ag isotopes already occurs during primary metallogenesis, it is necessary to review potential mechanisms controlling Ag isotope abundances. The investigated mineralizations all were precipitated from hydrothermal fluids (cf. Table 1 and references therein). Several parameters generally control their metal solubility, i.e., temperature, pH, oxygen/sulfur fugacity, and the availability of complexing ligands (Fontboté et al., 2017; Heinrich and Candela, 2014), of which chloride and bisulfide are the most important (Robb, 2020; Seward and Barnes, 1997). Electroneutrality requires that, after binding

with ligands is taken into account, the higher the chloride content of the fluids, the more elevated their cation concentrations. The pH of the hydrothermal fluids is buffered by fluid-rock reactions which tie up the concentrations of protons and cations, for example H^+ and Ag^+ . Decreasing chlorinity therefore tends to increase the pH and reduces cation solubility. Boiling of the hydrothermal fluid can significantly increase the pH of the fluid due to partitioning of solutes within the segregated vapor phase and thus is an effective precipitation mechanism.

Modelling of mineralization pathways in a base metal-poor epithermal system depending on pH and temperature (Burisch et al., 2019) shows that the atomic proportion of Ag in the precipitated minerals increases within the paragenetic sequence and that Ag–Sb sulfides are generated before Sb sulfides due to their lower stability. Applying this model to the formation of argentiferous galena suggests that galena formed with beginning Ag–Sb precipitation has low Ag/Sb ratios and is poor in both Ag and Sb. Upon cooling of the parent hydrothermal fluid, the solubility of Sb and particularly Ag further decreases, and ores tend to become significantly enriched in both Ag and Sb but with much higher Ag/Sb ratios, which suggests that Ag-rich ores are associated with residual fluids.

Assuming that primary ore-forming fluids on average have an Ag isotope value ~ 0 , i.e., equivalent to the proposed mantle value (Fujii and Albarede, 2018), the comparatively unfractionated $\epsilon^{109}Ag$ of Ag (Sb–Bi)-rich galena-rich ore reflects the isotope composition of the parent fluid if most of the silver precipitates at a late stage. The host galena is therefore dominated by an Ag-rich, low-Sb/Ag sulfosalt component deposited by residual fluids. In the actual ore deposit, this component may be present in solid solution within galena (which seems to be the case here; see above) or may have been exsolved during cooling. Galena samples with (highly) fractionated Ag isotope ratios and low Ag contents may represent relatively hot or low-chlorinity fluids or late, low-temperature incongruent reaction of early sulfosalt components with percolating fluids.

Tetrahedrite-group minerals typically form contemporaneously with galena in the main mineralization stages of Pb–Zn–Ag carbonate replacement and vein ores (e.g. Borojević Šoštarić et al., 2011; Serafimovski et al., 2006; Veselinović-Williams, 2011 for the present study area) and thus at higher temperatures than modelled for Ag–Sb sulfosalts (Burisch et al., 2019). They are the principal silver carrier phases in such deposits (George et al., 2017; Kissin and Mango, 2014). If they concentrate most of the Ag content of the ore fluid, the ore bulk $\epsilon^{109}Ag$ should be comparatively unfractionated. Due to their simultaneous precipitation during ore deposit formation, argentiferous tetrahedrites would have been mined and smelted together with volumetrically dominant galena.

The remarkably narrow Ag isotope range of ancient coinage ($\pm 1 \epsilon^{109}Ag$ for >90% of the data; Albarède et al., 2021, 2016; Desautly et al., 2011; Vaxevanopoulos et al., 2022b) and Hacksilber objects, the dating of which spans from the middle Bronze Age to the Iron Age (Eshel et al., 2022), starkly contrasts with the one-order-of-magnitude larger variation determined for ore minerals (this study; Arribas et al., 2020; Milot et al., 2021a; Vaxevanopoulos et al., 2022b). Metallurgical processes are not considered a factor in isotope fractionation due to the high temperatures employed in primary ore smelting, which suppress isotope fractionation $\sim 1/T^2$, and the assumption that silver losses were kept at a minimum as far as was feasible. Since mining and smelting relied on practical experience rather than a theoretical understanding of chemistry and metallurgy (Rihl and Tucker, 2002), it is, however, not self-evident that processes involving silver losses were recognized as such in the first place.

Overlap between $\epsilon^{109}Ag$ and Pb isotope ratios of ores and semi-processed galena-rich material sampled from the same district studied here, correlation of Pb and Ag isotope signatures of ores from Lavrion and artifacts consistent with an origin from this district (Vaxevanopoulos et al., 2022b), and similar $\epsilon^{109}Ag$ ranges for silver extracted

by smelting and amalgamation techniques (Desautly et al., 2011) all suggest as a first-order conclusion that metallurgical processes did not have a significant impact on Ag isotope signatures. Future experimental studies that target systematic examination of potential Ag isotope fractionation during the metallurgical process chain nevertheless are warranted to confirm this conclusion.

The consistently narrow Ag isotope range of artifacts indicates that it was not the result of averaging the scattered Ag isotope ratios of different silver minerals of both hypogene and supergene origin but rather that it originated from primary ores with bulk $\epsilon^{109}Ag \sim 0$. In the hydrothermal Pb–Zn–Ag deposits of the present study area and of the circum-Mediterranean region in general, two mineralogical silver ore types are most relevant: (1) Ag (Sb + Bi)-rich galenas with $\epsilon^{109}Ag$ close to 0; and (2) argentiferous tetrahedrite associated with comparatively Ag-poor galena, producing a bulk $\epsilon^{109}Ag \sim 0$. Homogenization during beneficiation, smelting, and subsequent artifact production would successively level Ag isotope ratios that slightly deviate from 0. Silver isotope data for acanthite [Ag_2S] and hypogene native silver (Arribas et al., 2020) indicate that these minerals have largely unfractionated Ag isotope compositions. They constitute possible, but far less abundant, silver sources for coinage.

The Ag contents in comparatively Ag-rich galena-dominated ores with $\epsilon^{109}Ag$ close to 0 in most cases exceed the equivalent of 1000 $\mu g/g$ (0.1 wt%) Ag in Pb sulfide (Fig. 6b). This value hence likely corresponds to the averaged lower limit of Ag grades of galena ores typically used to mint ancient coinage. Isolated coin populations with $-3 < \epsilon^{109}Ag < -1$ can be linked to galena-dominated ores with a possibly rather low Ag content. This might have been the case, for example, for silver produced as a by-product of Pb ore smelting in the Roman period.

Since Ag isotope ratios show a dependence on the Ag content of galena-dominated ores, i.e. the most negative Ag isotope ratios were determined for samples from Spain which possess the lowest Ag/Pb ratios within the dataset as shown in Fig. 6b, the $\epsilon^{109}Ag$ values of samples from modern operations are not necessarily representative of the material extracted in ancient times. Particularly for small sample suites with unclear historical contexts, Ag isotope ratios therefore should not be used as an exclusion method on their own.

4.3. Significance and application of the data for provenance studies

Widely consistent geology and analytical noise discernible in some older legacy data caused significant overlap in Pb isotope ratios and generated an “Aegean supercluster” which comprises deposits from the central Balkans to northern Greece and north-western Turkey (Albarede et al., 2020). State-of-the-art data presented here and recently published by Vaxevanopoulos et al. (2022a) greatly reduces ambiguities in three-dimensional Pb isotope space. Nevertheless, data for some mineralizations, for example at Lece and Zletovo or at Pangaeon and Thasos, cannot be fully separated due to their similar geological characteristics. Elemental compositions of ores additionally can support the reconstruction of potential ancient silver sources. The coupling of high μ values with elevated Au contents in ores from the SRC (cf. section 3.1) constitutes a powerful provenance marker. These characteristics distinguish them, for example, from ores from Lavrion and Siphnos, relevant to the discussion of the material origins of early Athenian and Aeginetan coinage (Gale et al., 1980; Stos-Gale and Davis, 2020). Low Ag contents (see above; Table S2) typically determined for deposits in the central Rhodopes and Blagodat-Osogovo districts suggest that they were not principally mined for silver but rather for lead. Extraction of silver as a by-product of lead produced as a commodity in its own right was widespread practice in the Roman period and possibly also related to improved metallurgical processing (Tylecote, 1976). Ores collected in Lece and the eastern Rhodopes (Fig. 1, #26–30; also see the data in Vaxevanopoulos et al. (2022a)) presumably were extracted for gold rather than silver.

The great application potential of Ag isotope ratios for provenance

studies is based on the narrow $\pm 1 \text{ } \epsilon^{109}\text{Ag}$ range determined for the vast majority of silver coins and artifacts in which strongly positive or negative values are, in contrast to the variation determined for Ag-bearing minerals, conspicuously absent. While mining districts with argentiferous galena-rich ores, or less commonly, Ag sulfide or hypogene native silver, generally constitute eligible raw material sources for silver coinage as discussed above, not all of them possess Ag isotope ratios within the $\pm 1 \text{ } \epsilon^{109}\text{Ag}$ limit. Silver isotope ratios therefore distinguish ores that actually were used in antiquity as silver sources for artifact production from those that did not, but possibly supplied lead. In combination with Pb isotopes and trace element patterns, Ag isotope signatures provide an essential contribution to provenance studies of silver artifacts by screening existing ore databases.

Geographical filtering of the $\epsilon^{109}\text{Ag}$ values of the ore samples for the -1 to $+1 \text{ } \epsilon^{109}\text{Ag}$ range as proposed by Vaxevanopoulos et al. (2022b), generally identifies the districts of Drina/Podrinje, Kopaonik, Zletovo, Blagodat-Osogovo, and the central Rhodopes as potential raw material sources of ancient coinage. Focusing on districts in the vicinity of the suspected locations of mints, the mining fields of Zletovo and HBK/ABK and Novobërdë/Novo Brdo stand out for notable bulk Ag contents of up to c. 3500 $\mu\text{g/g}$ (equivalent to up to c. 9000 $\mu\text{g/g}$ Ag per ton of Pb) in their argentiferous galena-rich ores, and their abundant remains of historical mining and metal production, observed both during field work for this study and described in the literature. Among the ore deposits in the interior of the Balkans, they constitute the most likely potential sources supplying silver to inland mints of the tribes, Damastion, and the Kings of Paeonia. Our study further determines mining fields in the northern Kopaonik district (Fig. 1, #6, 7, 9) and Srebrenica (Fig. 1, #3) as probable ancient silver production districts, corroborating evidence for previous metal extraction dating back to at least the Roman period (Table 1).

5. Concluding remarks

Historical workings were observed at most of the sampled mineralizations. They provide a direct but difficult-to-date record of local metal production and require detailed archaeological studies, the potential of which has largely gone unnoticed in the present study area. The restitic ores that we sampled from the interior of ancient mines constitute the only truly reliable representation of the material actually being used, which is critical for the estimation of metal grades and the determination of Ag isotope signatures. Whenever possible, samples should therefore be collected from such contexts.

For many of the ore deposits in the central and western Balkans, this study provides the first available state-of-the-art data and fills a gap in the characterization of circum-Mediterranean ore deposits. Distinct Pb isotopic domains in south-eastern Europe (this study; Vaxevanopoulos et al., 2022a) are readily discriminated in three-isotope plots or visualizations of their calculated Pb model ages, and apparent U/Pb and Th/U ratios. Correlation of Pb isotope ratios with geological characteristics not only increases the understanding of metallogenic processes involved in the formation of investigated ore deposits but also enables a general assessment of potential metal source regions based on artifact data. Provenance studies greatly benefit from an in-depth understanding of local Pb isotope systematics as it renders them largely independent of available reference data. This is particularly relevant if only few reference data are available and when the mineralizations actually exploited in a specific period cannot be clearly localized based on field evidence. Given that tangible evidence of possible pre-Roman silver (lead) production sites has not yet been established in the interior of the Balkans, geologically-based evaluation of artifact Pb isotope systematics is crucial for narrowing down potential source regions. Based on the analytical data gathered on the mineralizations investigated here, deposits of the southern part of the Kopaonik and the Zletovo district are most likely to have been mined for silver used to mint regional coinages before the 2nd century BCE.

In the ore deposits investigated here and at least in the broader circum-Aegean region, argentiferous galena of hydrothermal origin or a mixture of sulfosalts and rather Ag-poor galena were the likely principal metal sources for ancient coinage. Bullion derived from such ores consequently has coupled Pb–Ag isotope systematics that can be used for a refined assessment of possible metal sources.

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

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