



HAL
open science

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

Katrin Julia Westner, Markos Vaxevanopoulos, Janne Blichert-Toft, Gillan Davis, Francis Albarède

► To cite this version:

Katrin Julia Westner, Markos Vaxevanopoulos, Janne Blichert-Toft, Gillan Davis, Francis Albarède. Isotope and trace element compositions of silver-bearing ores in the Balkans as possible metal sources in antiquity. *Journal of Archaeological Science*, 2023, 155, pp.105791. 10.1016/j.jas.2023.105791 . hal-04095637

HAL Id: hal-04095637

<https://hal.science/hal-04095637>

Submitted on 12 May 2023

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

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

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

Katrin Julia Westner^{1,§,*}, Markos Vaxevanopoulos¹, Janne Blichert-Toft¹, Gillan Davis², Francis Albarède¹

5

¹ Ecole Normale Supérieure de Lyon, CNRS, and Université de Lyon, 46 Allée d'Italie, 69007 Lyon, France

² Australian Catholic University, 46 Edward Street, North Sydney, Australia 2060

10 § Present address: Forschungsbereich Archäometallurgie, Deutsches Bergbau-Museum Bochum, Am Bergbaumuseum 31, 44791 Bochum, Germany

* Corresponding author: Katrin.Westner@bergbaumuseum.de

15 **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 of 36 mineralizations from the Balkans. Each ore site was selected for its geological characteristics and documented or assumed historical and/or archaeological significance.

20

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.

Keywords: Silver, coinage, ore deposits, Pb isotopes, Ag isotopes, trace elements, 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 their characteristic working traces attest to prehistoric mining activities in some of the districts (e.g. Dimitrov and Stojčev, 2017; Malamidou et al., 2022; Radivojević 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) and this coincides with the spreading use of coinage and, by extension, a general increase of metal extraction.

Coinage issued by inland mints provides more locally resolved indirect 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 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
80 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
85 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
90 centuries BCE. It comprises the coins of Damastion (a city reportedly founded by Greek
settlers near silver mines; Strabo, 7.7.8; Aly, 1931 under the control of the Illyrians) 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 sharing of weight standard
95 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).

100 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
105 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.

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
135 possible importance as ancient silver sources have 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;
140 mostly derived from modern mining sites; cf. Table S2) were purchased from mineral dealers
and obtained from the collection at the Smithsonian Institute, respectively. A total of 128 ore
samples was investigated.

2.2. Sample preparation and analysis

145 The ore samples were prepared for compositional and Pb-Ag isotopic analysis according to
the protocols provided 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
150 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
155 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-
160 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 result 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 lead to obliteration of older remains. Potential dating based on stylistic means can, however, be assigned to some workings. For example, the dimensions and shape of a gallery at Dobrevo (Fig. 2e; Zletovo district) are comparable to Roman workings, for example at Roșia Montană/Romania

(Cauuet, 2014) and Lece/Serbia (Bugarski et al., 2018). Small exploitation chambers within the mineralized porphyry at Tulare (Fig. 2d; Lece district, Fig. 1, #D) are similar to mining remains at Melenicë/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 ($^{238}\text{U}/^{204}\text{Pb} \sim \text{U/Pb}$) and κ ($^{232}\text{Th}/^{238}\text{U} \sim \text{Th/U}$), 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, 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 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; Killis 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),
245 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;
250 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
255 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 mineralisations in the eastern part of Thasos
260 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 Serbomacedonian Massif from northern Greece to North
265 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
270 Serbomacedonian 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
275 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 Serbomacedonian Massif and Rhodopes. Analogous to the SRC, its deposits are hosted
280 within the southern part of 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).

285 3.3. Sulfur isotopes

The S isotope ratios of the four investigated galena samples range from -0.12 to +3.10 $\delta^{34}\text{S}$ (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-
290 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; Velojić 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 mineralisations from the Blagodan-Osogovo district indicate local inhomogeneities. Literature
295 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 Blagodan-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 Kilkis 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 Dobrevo (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

325 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 pyrargyrite [Ag₃SbS₃] and andorite [PbAgSb₃S₆]. The maximum Ag and Sb
contents of the galena specimens (3661 and 3538 µg/g, respectively) are within the solubility
limits (Chutas et al., 2008, their Fig. 7; George et al., 2015), thus suggesting for the
330 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.

335 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 HBK/ABK and
Belloberdë/Belo Brdo (Fig. 1, #7) mining fields. Cadmium contents (maximum 2.15 wt.%),
340 except for two samples with > 0.5 wt.% Cd, are 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
345 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 Albarede,
2018). The effect of weathering was investigated in-situ for sample NB1, which was collected
350 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 analysed 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).

375

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 Bellobërdë/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 Bellobërdë/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.

425

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 Blagodan-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

430

southern Rhodopes core complex (SRC; Pangaeon, Palaea Kavala, Thasos) are associated
435 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.

440 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
445 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
450 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
455 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

460 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 $\epsilon^{109}\text{Ag}$ 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 $\epsilon^{109}\text{Ag}$ 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.

490

The remarkably narrow Ag isotope range of ancient coinage ($\pm 1 \epsilon^{109}\text{Ag}$ for > 90% of the data; Albarède et al., 2021, 2016; Desaulty 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
495 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
500 rather than a theoretical understanding of chemistry and metallurgy (Rihll and Tucker, 2002), it is, however, not self-evident that processes involving silver losses were recognized as such in the first place.

Overlap between $\epsilon^{109}\text{Ag}$ and Pb isotope ratios of ores and semi-reacted galena-rich material sampled from the same district studied here, correlation of Pb and Ag isotope signatures of
505 ores from Lavrion and artifacts consistent with an origin from this district (Vaxevanopoulos et al., 2022b), and similar $\epsilon^{109}\text{Ag}$ ranges for silver extracted by smelting and amalgamation techniques (Desaulty 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
510 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 $\epsilon^{109}\text{Ag} \sim 0$. In the
515 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 $\epsilon^{109}\text{Ag}$ close to 0; and (2) argentiferous tetrahedrite associated with
comparatively Ag-poor galena, producing a bulk $\epsilon^{109}\text{Ag} \sim 0$. Homogenization during
beneficiation, smelting, and subsequent artifact production would successively level Ag
520 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 $\epsilon^{109}\text{Ag}$ close to 0 in
525 most cases exceed the equivalent of 1000 $\mu\text{g/g}$ (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 $-3 < \epsilon^{109}\text{Ag} < -1$ can be
linked to galena-dominant 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
530 period.

Since Ag isotope ratios show a dependence on the Ag content of galena-dominant 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 $\epsilon^{109}\text{Ag}$ values of samples
from modern operations are not necessarily representative of the material extracted in
535 ancient times. Particularly for small sample suites with unclear historical context, 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
540 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 (Albarède 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 545 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 550 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 555 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 560 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 565 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 $\epsilon^{109}\text{Ag}$ range as
570 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 $\mu\text{g/g}$
575 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
580 northern Kopaonik district (Fig. 1, #6, 7, 9) and Srebrenica (Fig. 1, #3) as probable ancient
silver production districts, corroborating evidence for precious metal extraction dating back to
at least the Roman period (Table 1).

5. Concluding remarks

585 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
590 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;
595 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.

Acknowledgements

This work was funded by the European Research Council H2020 Advanced Grant 741454-SILVER-ERC-2016-ADG 'Silver isotopes and the rise of Money' awarded to FA. Paul Pohwat from the Smithsonian Institution of Washington is thanked for providing galena samples from the central Rhodopes. Vasilije Miličić (Šuplja Stijena mine, Gradir Montenegro), Aleksandar Petrić (Gross mine, Mineco), Ilija Goranov, Dimitar Stefanovski, and Aleksandra Naneva (Zletovo mine, Bulmak), Zoran Stojnev (Toranica mine, Bulmak), Ruza Budurova (Zlatograd/Rodopi Eco Projects), and Sergei Atanasov (Gorubso Madan) are gratefully

acknowledged for support during sampling and for supplying ore specimens. Numerous local people are thanked for pointing out historical mining sites. Philippe Télouk and Florent
625 Arnaud-Godet ensured that mass spectrometers worked perfectly. Marine Pinto, Chloé Malod-Dognin, and Jean Milot are thanked for help with the mass spectrometers. Marine Pinto is also thanked for analyzing the samples from the Smithsonian Institute.

References

- Alaj, P., 2019. Les habitats de l'âge de fer sur le territoire de l'actuel Kosovo [Iron Age
630 settlements in the territory of present-day Kosovo; in French] (PhD thesis).
L'Université Lumière Lyon 2, Lyon.
- Albarède, F., Blichert-Toft, J., de Callataÿ, F., Davis, G., Debernardi, P., Gentelli, L., Gitler, H., Kemmers, F., Klein, S., Malod-Dognin, C., Milot, J., Vaxevanopoulos, M., Westner, K., 2021. From commodity to money: the rise of silver exchange around the
635 ancient Mediterranean (6th-1st century BCE). *Archaeometry* 63.
<https://doi.org/10.1111/arcm.12615>
- Albarede, F., Blichert-Toft, J., Gentelli, L., Milot, J., Vaxevanopoulos, M., Klein, S., Westner, K., Birch, T., Davis, G., de Callataÿ, F., 2020. A miner's perspective on Pb isotope provenances in the Western and Central Mediterranean. *Journal of Archaeological
640 Science* 121, 105194. <https://doi.org/10.1016/j.jas.2020.105194>
- Albarède, F., Blichert-Toft, J., Rivoal, M., Telouk, P., 2016. A glimpse into the Roman finances of the Second Punic War through silver isotopes. *Geochemical Perspectives Letters* 2, 127–137. <https://doi.org/10.7185/geochemlet.1613>
- Albarede, F., Juteau, M., 1984. Unscrambling the lead model ages. *Geochimica et
645 Cosmochimica Acta* 48, 207–212. [https://doi.org/10.1016/0016-7037\(84\)90364-8](https://doi.org/10.1016/0016-7037(84)90364-8)
- Aleksandrov, M., 1992. Metalogenetske karakteristike polimetaličnog rudnog polja Sase, Istočna Makedonija [Metallogenetic characteristics of the polymetallic ore field Sase, East Macedonia; in Macedonian] (PhD thesis). Goce Delčev University, Štip.
- Aly, W., 1931. Neue Beiträge zur Strabon-Überlieferung [New contributions to Strabo's
650 tradition; in German]. *Sitzungsberichte der Heidelberger Akademie der*

Wissenschaften, Philosophisch-Historische Klasse 1, 3–32.

<https://doi.org/10.11588/diglit.40159>

Amedoski, D., Petrović, V., 2019. Mining in Dubočica in the 16th century. *TEME* 42, 1125–1140. <https://doi.org/10.22190/TEME1804125A>

655 Amov, B., Arnaudov, V., Pavlova, M., 1990. Lead isotope evolution in the Rhodope Region, Bulgaria. *Freiberger Forschungshefte C 441 Geowissenschaften*, 11–24.

Amov, B., Breskovska, B., Baldzhieva, C.T., Evstatieva, S.S., Mankov, S., 1983. О

результатах масс-спектрального анализа свинца свинцо-во-цинковъх

месторождений Звездельского рудного поля [On the results of mass spectral

660 analysis of the lead-zinc deposits of the Zvezdel ore field]. *Godine na BMGI, C 29*, 79–90.

Amov, B., Kolkovski, B., Dimitrov, R., 1993. Генезис и възраст на хидротермални рудни минерализации в родопската металогенна зона въз основа на изотопния състав на оловото в галенит [Genesis and age of hydrothermal ore mineralization in the Rhodope metallogenic zone on the basis of the isotopic composition of lead in galena; in Bulgarian with English summary]. *Annuaire de l'Université de Sofia "St. Kliment Ohridski" Faculté de Géologie et Géographie* 85, 73–98.

665 Amov, B.G., Breskovska, V.V., Baldjieva, Ts.T., Evstatieva, S.S., 1979. Isotopic composition of lead in ore deposit Madjarovo and some conclusions for the age and the genesis. *Comptes rendus de l'Académie bulgare des science* 32, 1271–1274.

Antić, M.D., Kounov, A., Trivić, B., Wetzel, A., Peytcheva, I., von Quadt, A., 2016. Alpine thermal events in the central Serbo-Macedonian Massif (southeastern Serbia). *Int J Earth Sci (Geol Rundsch)* 105, 1485–1505. <https://doi.org/10.1007/s00531-015-1266-z>

675 Arribas, A., Mathur, R., Megaw, P., Arribas, I., 2020. The Isotopic Composition of Silver in Ore Minerals. *Geochem. Geophys. Geosyst.* 21. <https://doi.org/10.1029/2020GC009097>

- Arvanitidis, N.D., Tsamantouridis, P., Dimou, E., 1996. Gold-bearing sulfide and gossan mineralisation systems of the Myriophyto Region, Northern Macedonia, Greece. *Geologica Balcanica* 26, 25–36.
- 680
- Asch, K., 2005. IGME 5000: 1 : 5 Million International Geological Map of Europe and Adjacent Areas.
- Asvesta, A., Dimitriadis, S., 2010. Facies architecture of a Triassic rift-related Silicic Volcano-Sedimentary succession in the Tethyan realm, Peonias subzone, Vardar (Axios) Zone, northern Greece; Regional implications. *Journal of Volcanology and Geothermal Research* 193, 245–269. <https://doi.org/10.1016/j.jvolgeores.2010.04.005>
- 685
- Babović, M., Cvetković, D., 1976. Osnovna geološka karta SFRJ 1:100000 [Basic geological map of SFRJ 1:100000]: K34-57 Trgovište sa Radmirom. Savezni geološki zavod, Belgrade.
- 690
- Birch, T., Westner, K.J., Kemmers, F., Klein, S., Höfer, H.E., Seitz, H.-M., 2020. Retracing Magna Graecia's silver: coupling lead isotopes with a multi-standard trace element procedure. *Archaeometry* 62, 81–108. <https://doi.org/10.1111/arcm.12499>
- Blichert-Toft, J., Delile, H., Lee, C.-T., Stos-Gale, Z., Billström, K., Andersen, T., Hannu, H., Albarède, F., 2016. Large-scale tectonic cycles in Europe revealed by distinct Pb isotope provinces. *Geochemistry, Geophysics, Geosystems* 17, 3854–3864. <https://doi.org/10.1002/2016GC006524>
- 695
- Borojević Šoštarić, S., Palinkaš, L.A., Topa, D., Spangenberg, J.E., Prochaska, W., 2011. Silver–base metal epithermal vein and listwaenite types of deposit Crnac, Rogozna Mts., Kosovo. Part I: Ore mineral geochemistry and sulfur isotope study. *Ore Geol Rev* 40, 65–80. <https://doi.org/10.1016/j.oregeorev.2011.05.002>
- 700
- Bugarski, I., Dotterweich, M., Ivanišević, V., Maas, A., Röhl, C., Schreg, R., Stamenković, A., Yalçın, Ü., 2018. Rekognosciranje šire okoline Caričinog Grada u 2016. godini [Reconnaissance of the wider surroundings of Caričin Grad in 2016; in Serbian], in: Bugarski, I., Gacrilović Vitas, N., Filipović, V. (Eds.), *Arheologija u Srbiji: projekti Arheološkog instituta u 2016. godini*. Arheološki Institut, Belgrade, pp. 107–115.
- 705

- Bugarski, I., Heinz, G., Ivanišević, V., Maas, A., Röhl, C., Schreg, R., Stamenković, A., Zdravnković, V., 2019. Rekognosciranje šire okoline Caričinog Grada u 2017. godini i snimanje rimskog rudnika u Lecu [Reconnaissance of the wider surroundings of Caričin Grad in 2017 and recording of the Roman mine in Lece], in: Bugarski, I., Filipović, V., Gacrilović Vitas, N. (Eds.), *Arheologija u Srbiji: projekti Arheološkog instituta u 2017. godini*. Arheološki Institut, Belgrade, pp. 159–168.
- Burisch, M., Hartmann, A., Bach, W., Krolop, P., Krause, J., Gutzmer, J., 2019. Genesis of hydrothermal silver-antimony-sulfide veins of the Bräunsdorf sector as part of the classic Freiberg silver mining district, Germany. *Miner Deposita* 54, 263–280.
715 <https://doi.org/10.1007/s00126-018-0842-0>
- Cauuet, B., 2014. Gold and silver extraction in Alburnus Maior mines, Roman Dacia (Rosia Montana, Romania). Dynamics of exploitation and management of the mining space, in: Fontes, L., Martins, C.M.B. (Eds.), *Paisagens Mineiras Antigas Na Europa Ocidental: Investigação e Valorização Cultural: Atas*.
- 720 Ćebić, D., 1990. Konačni izveštaj o geološko-petrološkom i geohemijskom izučavanju tercijarnog magmatskog kompleksa Surduličke oblasti [The final report on geological-petrological and geochemical investigations of the Tertiary magmatic complex of Surdulica area; in Serbian]. Geoinstitut, Belgrade.
- Chutas, N.I., Kress, V.C., Ghiorso, M.S., Sack, R.O., 2008. A solution model for high-temperature PbS-AgSbS₂-AgBiS₂ galena. *American Mineralogist* 93, 1630–1640.
725 <https://doi.org/10.2138/am.2008.2695>
- Cvetkovic, V., Prelević, D., Schmid, S., 2016. Geology of South-Eastern Europe, in: Papic, P. (Ed.), *Mineral and Thermal Waters of Southeastern Europe*, Environmental Earth Sciences. Springer International Publishing, Cham, pp. 1–29.
730 https://doi.org/10.1007/978-3-319-25379-4_1
- Dahmen, K., 2010. The Numismatic Evidence, in: Roisman, J., Worthington, I. (Eds.), *A Companion to Ancient Macedonia*. Wiley-Blackwell, pp. 41–62.
- Davies, O., 1935. *Roman mines in Europe*, reprint from 1979. ed. Arno Press, New York.

- Desaulty, A.-M., Télouk, P., Albalat, E., Albarède, F., 2011. Isotopic Ag–Cu–Pb record of
735 silver circulation through 16th–18th century Spain. *Proceedings of the National
Academy of Sciences* 108, 9002–9007. <https://doi.org/10.1073/pnas.1018210108>
- Diehl, A., Bach, W., 2020. MARHYS (MARine HYdrothermal Solutions) Database: A Global
Compilation of Marine Hydrothermal Vent Fluid, End Member, and Seawater
Compositions. *Geochem. Geophys. Geosyst.* 21.
740 <https://doi.org/10.1029/2020GC009385>
- Dimče, K., 1996. Arheološka karta na Republika Makedonija [Archaeological map of the
Republic of Macedonia; in Macedonian]. Makedonska akademija na naukite i
umetnostite Muzej na Makedonija, Arheološki oddel, Skopje.
- Dimitrov, K., Stojčev, R., 2017. Der Ostbalkanraum als Metall-und Rohstoffquelle von der
745 Vorgeschichte bis zur Antike [The Eastern Balkans as a source of metal and raw
materials from prehistory to antiquity; in German], in: Haag, S., Popov, C., Horejs, B.,
Alexandrov, S., Plattner, G. (Eds.), *Das Erste Gold: Ada Tepe: Das Älteste
Goldbergwerk Europas. Ausstellungskatalog Der Sonderausstellung Im KHM.*
Kunsthistorisches Museum Wien, Vienna, pp. 21–27.
- 750 Dušanić, S., 2004. Roman mining in Illyricum. Historical aspects., in: Urso, G. (Ed.),
Dall'Adriatico al Danubio. L'Ilirico Nell'età Greca e Romana. *Atti Del Convegno
Internazionale Cividale Del Friuli, 25-27 Settembre 2003.* ETS, Pisa, pp. 247–270.
- Eliopoulos, D., Economou, G., Tzifas, I., Pa, C., 2014. The Potential of Rare Earth Elements
In Greece. Presented at the ERES2014: 1st European Rare Earth Resources
755 Conference, Milos, pp. 1–8.
- Eshel, T., Tirosh, O., Yahalom-Mack, N., Gilboa, A., Erel, Y., 2022. Silver Isotopes in Silver
Suggest Phoenician Innovation in Metal Production. *Applied Sciences* 12, 741.
<https://doi.org/10.3390/app12020741>
- Faraguna, M., 1998. Aspetti amministrativi e finanziari della monarchia Macedone tra IV e III
760 secolo A.C. [Administrative and financial aspects of the Macedonian monarchy
between the 4th and 3rd centuries BC; in Italian]. *Athenaeum* 86, 349–395.

- Fontboté, L., Kouzmanov, K., Chiaradia, M., Pokrovski, G.S., 2017. Sulfide Minerals in Hydrothermal Deposits. *Elements* 13, 97–103.
<https://doi.org/10.2113/gselements.13.2.97>
- 765 Frei, R., 1992. Isotope (Pb, Rb-Sr, S, O, C, U-Pb) geochemical investigations on Tertiary intrusives and related mineralizations in the Serbomacedonian Pb-Zn, Sb+Cu-Mo metallogenic province in Northern Greece (PhD thesis). ETH Zürich, Zürich.
- Fujii, T., Albarede, F., 2018. ^{109}Ag – ^{107}Ag fractionation in fluids with applications to ore deposits, archeometry, and cosmochemistry. *Geochimica et Cosmochimica Acta* 234, 770 37–49. <https://doi.org/10.1016/j.gca.2018.05.013>
- Gaebler, H., 1927. Zur Münzkunde Makedoniens. IX. Die Prägung der paionischen Könige. - Die Lage von Damastion und Pelagia [On the numismatics of Macedonia. IX. The Coinage of the Paionian Kings. - The location of Damastion and Pelagia; in German]. *Zeitschrift für Numismatik* 37, 223–253.
- 775 Gale, N.H., Gentner, W., Wagner, G.A., 1980. Mineralogical and geographical silver sources of Archaic Greek coinage, in: Metcalf, D.A., Oddy, W.A. (Eds.), *Metallurgy in Numismatics 1*. The Royal Numismatic Society, London, pp. 3–49.
- Gasparrini, C., Lowell, G.R., 1985. Silver-bearing inclusions in "argentiferous" galena from the Silvermine District in southeastern Missouri. *The Canadian Mineralogist* 23, 99–780 102.
- Gassmann, G., Klein, S., Körlin, G., Matthes, B., Westner, K., 2022. Antiker Silberrausch am Amselfeld [Ancient silver rush in the Kosovo field; in German with English abstract]. *Der Anschnitt* 74, 4–24.
- Gentner, W., Gropengiesser, H., Wagner, G.A., 1980. Blei und Silber im ägäischen Raum. 785 Eine archäometrische Untersuchung und ihr archäologisch-historischer Rahmen [Lead and silver in the Aegean. An archaeometry study and its archaeological-historical framework; in German], in: von Dittfurth, H. (Ed.), *Ein Panorama der Naturwissenschaften*. Mannheim, pp. 143–215.

- George, L., Cook, N., Ciobanu, C., 2017. Minor and Trace Elements in Natural Tetrahedrite-
790 Tennantite: Effects on Element Partitioning among Base Metal Sulphides. *Minerals* 7,
17. <https://doi.org/10.3390/min7020017>
- George, L., Cook, N.J., Ciobanu, C.L., Wade, B.P., 2015. Trace and minor elements in
galena: A reconnaissance LA-ICP-MS study. *American Mineralogist* 100, 548–569.
<https://doi.org/10.2138/am-2015-4862>
- 795 Hammond, N., Griffith, G., 1979. *A History of Macedonia, vol. II: 550-336 BC*. Oxford
University Press.
- Hannington, M.D., 2014. 13.18 - Volcanogenic Massive Sulfide Deposits, in: Holland, H.D.,
Turekian, K.K. (Eds.), *Treatise on Geochemistry (Second Edition)*. Elsevier, Oxford,
pp. 463–488. <https://doi.org/10.1016/B978-0-08-095975-7.01120-7>
- 800 Hatzopoulos, M., 2010. Chapter 18. ΗΕΔΡΟΛΟΣ-ΑΡΡΩΛΟΣ, in: Reger, G., Ryan, F.X.,
Winters, T.F. (Eds.), *Studies in Greek Epigraphy and History in Honor of Stefan
V. Tracy*. Ausonius Éditions, pp. 229–236.
<https://doi.org/10.4000/books.ausonius.2207>
- Haymon, R.M., Kastner, M., 1981. Hot spring deposits on the East Pacific Rise at 21 N:
805 preliminary description of mineralogy and genesis. *Earth and Planetary Science
Letters* 53, 363–381.
- Heinrich, C.A., Candela, P.A., 2014. Fluids and Ore Formation in the Earth's Crust, in:
Treatise on Geochemistry. Elsevier, pp. 1–28. <https://doi.org/10.1016/B978-0-08-095975-7.01101-3>
- 810 Heinrich, C.A., Neubauer, F., 2002. Cu – Au – Pb – Zn – Ag metallogeny of the Alpine –
Balkan – Carpathian – Dinaride geodynamic province. *Mineralium Deposita* 37, 533–
540. <https://doi.org/10.1007/s00126-002-0271-x>
- Hofmann, A.W., 1997. Mantle geochemistry: the message from oceanic volcanism. *Nature*
385, 219–229. <https://doi.org/10.1038/385219a0>
- 815 Hrković, K., Jelenković, R., 1994. Tectonophysical paleoreconstruction of structural shaping
of the Šuplja Stijena deposit. *Geologica Macedonica* 8, 53–58.

- Janković, S., 1997. The Carpatho-Balkanides and adjacent area: A sector of the Tethyan Eurasian metallogenic belt. *Mineralium Deposita* 32, 426–433.
<https://doi.org/10.1007/s001260050110>
- 820 Janković, S., 1982. Yugoslavia, in: Dunning, F.W., Mykura, W., Slater, D. (Eds.), *Mineral Deposits of Europe. Volume 2: Southeast Europe*. The Institution of Mining and Metallurgy and The Mineralogical Society, London, pp. 143–202.
- Janković, S., Serafimovski, T., Aleksandrov, M., 1995. The Besna Kobila-Osogovo Metallogenic Zone. *Geologica Macedonica* 9, 39–50.
- 825 Jelenković, R., 1995. Metallogenic features of the Besna Kobila ore district (SE Serbia). *Geologica Macedonica* 9, 81–88.
- Jelenković, R., Kostić, A., Životić, D., Ercegovac, M., 2008. Mineral resources of Serbia. *Geologica Carpathica* 59, 345–361.
- Kaiser-Rohrmeier, M., Handler, R., Von Quadt, A., Heinrich, C., 2004. Hydrothermal Pb–Zn ore formation in the Central Rhodopian Dome, south Bulgaria: Review and new time constraints from Ar–Ar geochronology. *Schweizerische Mineralogische und Petrographische Mitteilungen* 84, 37–58.
- 830 Kaiser-Rohrmeier, M., Handler, R., Von Quadt, A., Heinrich, C., 2004. Hydrothermal Pb–Zn ore formation in the Central Rhodopian Dome, south Bulgaria: Review and new time constraints from Ar–Ar geochronology. *Schweizerische Mineralogische und Petrographische Mitteilungen* 84, 37–58.
- Kissin, S.A., Mango, H., 2014. 13.16 - Silver Vein Deposits, in: Holland, H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry (Second Edition)*. Elsevier, Oxford, pp. 425–432.
<https://doi.org/10.1016/B978-0-08-095975-7.01118-9>
- 835 <https://doi.org/10.1016/B978-0-08-095975-7.01118-9>
- Kockel, F., Mollat, H., Gundlach, H., 1975. Hydrothermally altered and (copper) mineralized porphyritic intrusions in the Serbo-Macedonian Massif (Greece). *Mineral. Deposita* 10, 195–204. <https://doi.org/10.1007/BF00207136>
- Kołodziejczyk, J., Pršek, J., Asllani, B., Maliqi, F., 2016. The paragenesis of silver minerals in the Pb-Zn Stan Terg deposit, Kosovo - an example of precious metal epithermal mineralization. *Geology, Geophysics & Environment* 42, 19.
<https://doi.org/10.7494/geol.2016.42.1.19>
- 840 <https://doi.org/10.7494/geol.2016.42.1.19>

- Kovacevic, D., 1960. Dans la Serbie et la Bosnie médiévales: Les mines d'or et d'argent [In medieval Serbia and Bosnia: Gold and silver mines; in French]. *Annales. Histoire, Sciences Sociales* 15, 248–258.
- 845
- Kremydi, S., 2011. Coinage and finance, in: Fox, R.J.L. (Ed.), *Brill's Companion to Ancient Macedon*. Brill, pp. 159–178.
- Lang, J., Baker, T., 2001. Intrusion-related gold systems: the present level of understanding. *Mineralium Deposita* 36, 477–489.
- 850
- Lilov, P., Yanev, Y., Marchev, P., 1987. K/Ar dating of the Eastern Rhodope Paleogene magmatism. *Geologica Balcanica* 17.
- Longman, J., Veres, D., Finsinger, W., Ersek, V., 2018. Exceptionally high levels of lead pollution in the Balkans from the Early Bronze Age to the Industrial Revolution. *PNAS* 201721546. <https://doi.org/10.1073/pnas.1721546115>
- 855
- Malamidou, D., Tsirtsoni, Z., Vaxevanopoulos, M., 2022. The Emergence of Metal Use in Greek Eastern Macedonia During the Neolithic Period (Late 6th–5th Millennia BC). *Doc. praeh.* 49, 2–21. <https://doi.org/10.4312/dp.49.6>
- Marchev, P., Kaiser-Rohrmeier, M., Heinrich, C., Ovtcharova, M., von Quadt, A., Raicheva, R., 2005. 2: Hydrothermal ore deposits related to post-orogenic extensional magmatism and core complex formation: The Rhodope Massif of Bulgaria and Greece. *Ore Geology Reviews* 27, 53–89.
- 860
- <https://doi.org/10.1016/j.oregeorev.2005.07.027>
- Marić, M.D., 2019. Late Roman Fortifications of the Eastern Part of the Metalla Dardanica Imperial Domain, in: *Fortifications, Defence Systems, Structures and Features in the Past*. Proceedings of the 4th International Scientific Conference on Medieval Archaeology of the Institute of Archaeology Zagreb, 7th – 9th June 2017. Institut za arheologiju/Institute of Archaeology, Zagreb, pp. 75–90.
- 865
- Márton, I., Dragić, D., Djordjević, B., Fox, P., Tosdal, R.M., van der Toorn, J., Hasson, S., 2013. Intrusion-alteration-mineralization relationships from the porphyry Cu-Au deposit at Kiseljak, Serbia, in: *Proceedings. Volume 2*. Presented at the Mineral
- 870

deposit research for a high-tech world: 12th Biennial SGA Meeting 12–15 August 2013, Uppsala, Sweden, Uppsala, pp. 837–840.

May, J.M.F., 1939. The coinage of Damastion and the lesser coinages of the Illyro-Paeonian region. Scientia, Aalen.

875 McCoyd, R.J., 1995. Isotopic and geochemical studies of the epithermal-mesothermal Pb-Zn deposits of S.E. Bulgaria (PhD thesis). University of Aberdeen.

Mederski, S., Pršek, J., Dimitrova, D., Hyseni, B., 2021. A Combined EPMA and LA-ICP-MS Investigation on Bi-Cu-Au Mineralization from the Kizhnica Ore Field (Vardar Zone, Kosovo). Minerals 11, 1223. <https://doi.org/10.3390/min11111223>

880 Melfos, V., Voudouris, P., 2017. Cenozoic metallogeny of Greece and potential for precious, critical and rare metals exploration. Ore Geology Reviews 89, 1030–1057. <https://doi.org/10.1016/j.oregeorev.2017.05.029>

Milot, J., Blichert-Toft, J., Ayarzagüena Sanz, M., Malod-Dognin, C., 2021a. Silver isotope and volatile trace element systematics in galena samples from the Iberian Peninsula and the quest for silver sources of Roman coinage. Geology 50(4), 422-426. <https://doi.org/10.1130/G49690.1>

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

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

895 Mitrović, D., Gajić, L., Divković-Golić, E., Glavaš, S., Toholj, N., Jolović, B., Leka, K., 2011. Минералне сировине Републике Српске: Mineral resources of the Republic of Srpska. Republic of Srpska, Ministry of Industry, Energy and Mining and Geological Research Institute of Republic of Srpska, Zvornik.

- Moëlo, Y., Makovicky, E., Mozgova, N.N., Jambor, J.L., Cook, N., Pring, A., Paar, W., Nickel, E.H., Graeser, S., Karup-Møller, S., Balic-Žunic, T., Mumme, W.G., Vurro, F., Topa, D., 2008. Sulfosalt systematics: a review. Report of the sulfosalt sub-committee of the IMA Commission on Ore Mineralogy. *ejm* 20, 7–62. <https://doi.org/10.1127/0935-1221/2008/0020-1778>
- Monthel, J., Vadala, P., Leistel, J.M., Cottard, F., 2002. Mineral deposits and mining districts of Serbia: Compilation map and GIS databases (No. BRGM/RC-51448-FR). BRGM.
- 900 Mudrinic, C., Serafimovski, T., 1992. Lead, sulphur, oxygen and carbon isotopes in the Zletovo ore field (Eastern Macedonia). *Geologica Balcanica* 24, 39–48.
- Nielsen, H., 1979. Sulfur isotopes, in: Jäger, E., Hunziker, J.C. (Eds.), *Lectures in Isotope Geology*. Springer, pp. 283–312.
- Olovčić, A., Memić, M., Kevilj-Olovčić, A., Ramić, E., 2017. Medieval Slag from Gornji Potočari (Srebrenica municipality, B&H): a relationship between initial ore and metallurgical processes. *Godišnjak/Jahrbuch* 46, 215–224. <https://doi.org/10.5644/Godisnjak.CBI.ANUBiH-46.95>
- 910 Ono, S., Shanks, W.C., Rouxel, O.J., Rumble, D., 2007. S-33 constraints on the seawater sulfate contribution in modern seafloor hydrothermal vent sulfides. *Geochimica et Cosmochimica Acta* 71, 1170–1182. <https://doi.org/10.1016/j.gca.2006.11.017>
- 915 Palinkaš, L.A., Šoštarčić, S.B., Palinkaš, S.S., 2008. Metallogeny of the Northwestern and Central Dinarides and Southern Tisia. *Ore Geology Reviews* 34, 501–520. <https://doi.org/10.1016/j.oregeorev.2008.05.006>
- Palinkaš, S., Peltekovski, Z., Tasev, G., Serafimovski, T., Šmajgl, D., Rajič, K., Spangenberg, J., Neufeld, K., Palinkaš, L., 2018. The Role of Magmatic and Hydrothermal Fluids in the Formation of the Sasa Pb-Zn-Ag Skarn Deposit, Republic of Macedonia. *Geosciences* 8, 444. <https://doi.org/10.3390/geosciences8120444>
- 920 Pamc, J., Balen, D., 2001. Tertiary magmatism of the Dinarides and the adjoining South Pannonian Basin, an overview. *Acta Vulcanologica* 13, 9–24.

- 925 Pamić, J., Pécskay, Z., Balen, D., 2000. Lower Oligocene K-Ar ages of high-K calc-alkaline and shoshonite rocks from the North Dinarides in Bosnia. *Mineralogy and Petrology* 70, 313–320. <https://doi.org/10.1007/s007100070008>
- Paunov, E.I., 2015. Introduction to the Numismatics of Thrace, ca. 530 BCE–46 CE, in: Valeva, J., Nankov, E., Graninger, D. (Eds.), *A Companion to Ancient Thrace*. Wiley Online Library, pp. 265–292.
- 930 Pavlovska, E., 2008. Monetite na Pajonija od numizmatičkata zbirka na NBRM/The Coins of Paeonia from the Numismatic Collection of the NBRM, Nummi Macedoniae. Narodna banka na Republika Makedonija, Skopje.
- Pe-Piper, G., Christofides, G., Eleftheriadis, G., 1998. Lead and neodymium isotopic composition of Tertiary igneous rocks of northern Greece and their regional significance. *Acta Vulcanologica* 10, 255–264.
- 935 Pernicka, E., 1987. Erzlagerstätten in der Ägäis und ihre Ausbeutung im Altertum. Geochemische Untersuchungen zur Herkunftsbestimmung archäologischer Metallobjekte. [Ore deposits in the Aegean and their exploitation in antiquity. Geochemical studies on the provenance of archaeological metal objects; in German]. *Jahrbuch des Römisch-Germanischen Zentralmuseums* 34, 607–714.
- 940 Pernicka, E., Gentner, W., Wagner, G.A., Vavelidis, M., Gale, N.H., 1981. Ancient lead and silver production on Thasos (Greece), in: *Revue d'Archéométrie*, No. 1. Actes Du XXe Symposium International d'archéométrie Paris 26-29 Mars 1980 Volume III. pp. 227–
- 945 237.
- Petrova, E., 1991. Пajониа и Дамастион [Paeonia and Damastion; in Macedonian with English abstract], in: *Грчко-Римска Антика Во Југославија и На Балканот. Прилози Од V Научен Собир На Сојузот На Друштвата За Антички Студии На Југославија, Одржан Во Скопје, 26–29 Септември 1989 / Greek-Roman Antiquity in Yugoslavia and on the Balkans. Proceedings of the V Yugoslav Congress on Classical Studies, Held in Skopje, Sept. 26–29, 1989.* pp. 188–193.
- 950

- Petrussenko, S., 1991. Minerals of the Madan ore field Bulgaria. *The Mineralogical Record* 22, 439–445.
- 955 Photos, E., Koukouli-Chrysanthaki, C., Tylecote, R.F., Gialoglou, G., 1987. Precious metal extraction in Palaia Kavala, N. E. Greece. An Archaeometallurgical Attempt to Locate Skapte Hyle., in: Hauptmann, A., Pernicka, E., Wagner, G.A. (Eds.), *Old World Archaeometallurgy. Proceedings of the International Symposium "Old World Archaeometallurgy"*, Heidelberg 1987., *Der Anschnitt Beiheft 7. Deutsches Bergbau-Museum Bochum, Bochum*, pp. 179–190.
- 960 Picard, O., 2000. Monnayages en Thrace à l'époque achéménide [Coinages in Thrace during the Achaemenid era; in French], in: *Mécanismes et innovations monétaires dans l'Anatolie achéménide. Numismatique et Histoire. Actes de la Table Ronde d'Istanbul, 22-23 mai 1997. Institut Français d'Études Anatoliennes-Georges Dumézil, Istanbul*, pp. 239–253.
- 965 Popov, H., Jockenhövel, A., Tsintsov, Z., Iliev, S., 2011. Montanarchäologische Forschungen in den Ostrhodopen, Südostbulgarien [Mining-archaeological research in the eastern Rhodopes, southeastern Bulgaria; in German], in: Nikolov, V., Bacvarov, K., Popov, H. (Eds.), *Interdisziplinäre Forschungen zum Kulturerbe auf der Balkanhalbinsel. Sofia*, pp. 253–290.
- 970 Popov, K., Popov, P., 2019. The Alpine late collisional Rila-Rhodope Metallogenic Zone of the Balkan Orogenic System. *Review of the Bulgarian Geological Society* 80, 55–79.
- Psoma, S., 2012. Greece and the Balkans to 360 BC, in: Metcalf, W.E. (Ed.), *The Oxford Handbook of Greek and Roman Coinage. Oxford University Press, Oxford*, pp. 157–174.
- 975 Psoma, S., 2006. The "Lete" Coinage Reconsidered, in: Kroll, J.H., Van Alfen, P.G. (Eds.), *Agoronomia: Studies in Money and Exchange Presented to John H. Kroll. The American Numismatic Society*, pp. 61–86.
- Radimsky, W., 1893. Generalbericht über die bisherigen Ausgrabungen der römischen Stadt Domavia in Gradina bei Srebrenica [General report on the previous excavations of

- 980 the Roman city Domavia in Gradina near Srebrenica; in German], in:
Wissenschaftliche Mittheilungen aus Bosnien und der Hercegovina. 1. Band. Carl
Gerold's Sohn, Vienna, pp. 218–253.
- Radojević, M., Roberts, B.W., 2021. Early Balkan Metallurgy: Origins, Evolution and
Society, 6200–3700 BC. *J World Prehist* 34, 195–278.
- 985 <https://doi.org/10.1007/s10963-021-09155-7>
- Radosavljević, S., Đorđević, D., Stojanović, J., Kašić, V., 2011. Rudno polje Srebrenice,
podrinjska metalogenetska oblast, Istočna Bosna: grajzenizacija i mineralizacija
kalaja, titana i retkih zemalja/Srebrenica orefield, Podrinje Metallogenic District, East
Bosnia: greisenization and mineralization of tin, titanium and REE [in Serbian with
990 English abstract], in: *Zbornik Radova IV. Udruženje / Udruga Geologa Bosne i
Hercegovine and Savjetovanje Geologa Bosne i Hercegovine*, Sarajevo, pp. 117–
126.
- Radosavljević, S.A., Stojanović, J.N., Radosavljević-Mihajlović, A.S., Vuković, N.S., 2016.
(Pb–Sb)-bearing sphalerite from the Čumavići polymetallic ore deposit, Podrinje
995 Metallogenic District, East Bosnia and Herzegovina. *Ore Geology Reviews* 72, 253–
268. <https://doi.org/10.1016/j.oregeorev.2015.07.008>
- Renock, D., Becker, U., 2011. A first principles study of coupled substitution in galena. *Ore
Geology Reviews* 42, 71–83. <https://doi.org/10.1016/j.oregeorev.2011.04.001>
- Rice, C.M., McCoyd, R.J., Boyce, A.J., Marchev, P., 2007. Stable isotope study of the
1000 mineralization and alteration in the Madjarovo Pb–Zn district, south-east Bulgaria.
Mineralium Deposita 42, 691–713. <https://doi.org/10.1007/s00126-007-0130-x>
- Rihll, T.E., Tucker, J.V., 2002. Practice Makes Perfect: Knowledge of Materials in Classical
Athens, in: Tuplin, C.J., Rihll, T.E. (Eds.), *Science and Mathematics in Ancient Greek
Culture*. Oxford University Press, pp. 274–305.
- 1005 <https://doi.org/10.1093/acprof:oso/9780198152484.003.0016>
- Robb, L., 2020. *Introduction to ore-forming processes*. John Wiley & Sons.

- Rücker, A., 1901. Einiges über den Blei- und Silberbergbau bei Srebrenica in Bosnien [About the lead and silver mining at Srebrenica in Bosnia; in German]. Vienna.
- Rudnick, R.L., Gao, S., 2014. 4.1 - Composition of the Continental Crust, in: Holland, H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry (Second Edition)*. Elsevier, Oxford, pp. 1–51. <https://doi.org/10.1016/B978-0-08-095975-7.00301-6>
- 1010
- Savić, M., 1954. Шљакишта на Новом Брду и Качиколу [Slags at Novo Brdo and Kačikol; in Serbian with French summary]. *Starinar* 5–6, 283–294.
- Schmid, S.M., Fügenschuh, B., Kounov, A., Maženco, L., Nievergelt, P., Oberhänsli, R., Pleuger, J., Schefer, S., Schuster, R., Tomljenović, B., Ustaszewski, K., van Hinsbergen, D.J.J., 2020. Tectonic units of the Alpine collision zone between Eastern Alps and western Turkey. *Gondwana Research* 78, 308–374. <https://doi.org/10.1016/j.gr.2019.07.005>
- 1015
- Schumacher, F., 1950. Die Lagerstätte der Trepca und ihre Umgebung [The ore deposit of Trepca and its surroundings; in German]. Belgrade, Izdavacko Preduzece Saveta za Energetiku i Ekstraktivnu Industriju vlade FNRJ.
- 1020
- Seal, R.R., 2006. Sulfur Isotope Geochemistry of Sulfide Minerals. *Reviews in Mineralogy and Geochemistry* 61, 633–677. <https://doi.org/10.2138/rmg.2006.61.12>
- Serafimovski, T., Boev, B., 1996. Metallogeny of the Kratovo-Zletovo volcano-intrusive complex, in: Knezevic, D., Krstic, B.D. (Eds.), *The Formation of the Geologic Framework of Serbia and the Adjacent Regions*. Faculty of Mining and Geology of the University of Belgrade and Committee for Geodynamics of the Serbian Academy of Sciences and Arts, Belgrade.
- 1025
- Serafimovski, T., Dolenc, T., Tasev, G., 2006. New data concerning the major ore minerals and sulphosalts from the Pb-Zn Zletovo Mine, Macedonia. *RMZ - Materials and Geoenvironment* 52, 535–548.
- 1030
- Serafimovski, T., Janković, S., Čifliganec, V., 1997. Principal Metallogenic Features of the Lece-Chalkidiki Zone. *Romanian Journal of Mineral Deposits* 78, 93–105.

- Serafimovski, T., Tasev, G., 2005. Sulfur isotope composition of some polymetallic deposits
1035 in the Republic of Macedonia. *Geologica Macedonica* 19, 1–11.
- Seward, T.M., Barnes, H., 1997. Metal transport by hydrothermal ore fluids. *Geochemistry of hydrothermal ore deposits* 3, 435–486.
- Siddle, R., Bamber, A., Randall, M., Jackson, I., Struthers, S., 2021. Preliminary Economic Assessment and NI 43-101 Technical Report for the Medgold Tlmino Project
1040 Licences, Serbia.
- Simić, M., 2001. Metalogenija zone Mačkatica-Blagodot-Karamanica [Metallogeny of Mačkatica-Blagodot-Karamanica zone; in Serbian with English summary], Posebna izdanja Geoinstituta 28. Geoinstitut, Belgrade.
- Singer, B., Marchev, P., 2000. Temporal evolution of arc magmatism and hydrothermal
1045 activity, including epithermal gold veins, Borovitsa caldera, southern Bulgaria. *Economic Geology* 95, 1155–1164.
- Šoster, A., 2020. Nastanek Zn-Pb-Ag Rudišča Bašibos [Formation of the Zn-Pb-Ag deposit Bašibos; in Slovenian with English abstract] (PhD thesis). University of Ljubljana, Ljubljana.
- 1050 Stacey, J.S., Kramers, J.D., 1975. Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth and Planetary Science Letters* 26, 207–221.
[https://doi.org/10.1016/0012-821X\(75\)90088-6](https://doi.org/10.1016/0012-821X(75)90088-6)
- Stajević, B., 2003. Geochemical haloes of gold in the Lece ore field - southern Serbia. *Geoloski anali Balkanskog poluostrva* 93–99. <https://doi.org/10.2298/GABP0301093S>
- 1055 Stergiou, C.L., Melfos, V., Voudouris, P., Spry, P.G., Papadopoulou, L., Chatzipetros, A., Giouri, K., Mavrogonatos, C., Filippidis, A., 2021. The Geology, Geochemistry, and Origin of the Porphyry Cu-Au-(Mo) System at Vathi, Serbo-Macedonian Massif, Greece. *Applied Sciences* 11, 479. <https://doi.org/10.3390/app11020479>
- Stos-Gale, Z.A., Davis, G., 2020. The Minting/Mining Nexus: New Understandings of Archaic
1060 Greek Silver Coinage from Lead Isotope Analysis, in: Sheedy, K., Davis, G. (Eds.), *Metallurgy in Numismatics* 6. The Royal Numismatic Society, London, pp. 83–96.

- Strmić Palinkaš, S., Palinkaš, L.A., Renac, C., Spangenberg, J.E., Lüders, V., Molnar, F.,
Maliqi, G., 2013. Metallogenic Model of the Trepča Pb-Zn-Ag Skarn Deposit, Kosovo:
Evidence from Fluid Inclusions, Rare Earth Elements, and Stable Isotope Data.
1065 *Economic Geology* 108, 135–162. <https://doi.org/10.2113/econgeo.108.1.135>
- Štrucl, I., 1981. Die schichtgebundenen Pb-Zn Lagerstätten Jugoslawiens [The stratiform Pb-
Zn ore deposits of Jugoslavia; in German with English summary]. *Mitteilungen der
österreichischen geologischen Gesellschaft* 74/75, 307–322.
- Styrt, M.M., Brackmann, A.J., Holland, H.D., Clark, B.C., Pisutha-Arnond, V., Eldridge, C.S.,
1070 Ohmoto, H., 1981. The mineralogy and the isotopic composition of sulfur in
hydrothermal sulfide/sulfate deposits on the East Pacific Rise, 21°N latitude. *Earth
and Planetary Science Letters* 53, 382–390. [https://doi.org/10.1016/0012-
821X\(81\)90042-X](https://doi.org/10.1016/0012-821X(81)90042-X)
- Tasev, G., Serafimovski, T., Dolenc, M., Šmuc, N.R., 2019. Contribution to Understanding
1075 of Ore Fluids in the Zletovo Mine Based on Fluid Inclusion Data. *Materials and
Geoenvironment* 66, 75–86. <https://doi.org/10.2478/rmzmag-2019-0008>
- Tasev, G., Serafimovski, T., Lazarov, P., 2005. New K-Ar, ⁸⁷Sr/⁸⁶Sr, REE, and XRF data for
Tertiary volcanic rocks in the Sasa-Toranica ore district, Macedonia, in: Mao, J.,
Bierlein, F.P. (Eds.), *Proceedings of the Eighth Biennial SGA Meeting Beijing, China,*
1080 *18–21 August 2005. Volume 1. Presented at the Mineral Deposit Research: Meeting
the Global Challenge*, Springer, Berlin, Heidelberg, pp. 837–840.
- Theis, K.J., Schönbächler, M., Benedix, G.K., Rehkämper, M., Andreasen, R., Davies, C.,
2013. Palladium–silver chronology of IAB iron meteorites. *Earth and Planetary
Science Letters* 361, 402–411. <https://doi.org/10.1016/j.epsl.2012.11.004>
- 1085 *Trepca Kosovo under UNMIK administration (Ed.)*, 2005. Summary description of the lead
zinc silver resources and the Trepča mines in Kosovo.
- Tsamantouridis, P., Apostolos, N., 1986. Προδρομη εκθεση για την γεωλογική-
κοιτασματολογική μελετη της ηφαιστειοιζηματογενους σειρας Ακριτα - Μεταλλικο -

- 1090 Κριθία [Preliminary report on the geological and seismological study of the volcanic-sedimentary series at Akrita - Metalliko - Krithia; in Greek]. IGME.
- Tylecote, R.F., 1976. A history of metallurgy. Maney Publishing, London.
- Tzamalis, A.R., 2012. Les ethné de la région « Thraco-Macédonienne ». Etude d'Histoire et de Numismatique. (fin du VIe – Ve siècle) [The ethne of the “Thraco-Macedonian” region. Study of History and Numismatics (end of the 6th - 5th century); in French] 1095 (PhD thesis). Université Paris IV-Sorbonne, Paris.
- Ujes, D., 2002. Recherche sur la localisation de Damastion et ses mines [Research on the location of Damastion and its mines; in French with English abstract]. *Revue Numismatique* 6, 103–129.
- Unger, H.J., 1987. Das Pangaion: Ein altes Bergbauzentrum in Ostmakedonien [The 1100 Pangaion: An ancient mining centre in east Macedonia; in German with English abstract]. *Prähistorische Zeitschrift* 62, 87–112.
- Vassileva, R.D., Atanassova, R., Bonev, I.K., 2009. A review of the morphological varieties of ore bodies in the Madan Pb-Zn deposits, Central Rhodopes, Bulgaria. *Geochemistry, Mineralogy and Petrology* 47, 31–49.
- 1105 Vavelidis, M., Amstutz, G., 1983. Investigations on the gold occurrences in the Kinyra and Thasos (City) area on Thasos Island (Greece), in: Schneider, H.-J. (Ed.), *Mineral Deposits of the Alps and of the Alpine Epoch in Europe: Proceedings of the IV. ISMIDA Berchtesgaden, October 4–10, 1981*. Springer, pp. 385–391.
- Vaxevanopoulos, M., Blichert-Toft, J., Davis, G., Albarède, F., 2022a. New findings of 1110 ancient Greek silver sources. *Journal of Archaeological Science* 137, 105474. <https://doi.org/10.1016/j.jas.2021.105474>
- Vaxevanopoulos, M., Davis, G., Milot, J., Blichert-Toft, J., Malod-Dognin, C., Albarède, F., 2022b. Narrowing provenance for ancient Greek silver coins using Ag isotopes and Sb contents of potential ores. *Journal of Archaeological Science* 145, 105645.
- 1115 Velojić, M., Prelević, D., Jelenković, R., 2018. The origin of lead and sulfur in Tulare ore field, Lece magmatic complex. *GABP* 79, 19–28. <https://doi.org/10.2298/GABP1802019V>

- Veselinović-Williams, M., 2011. Characteristics and origin of polymetallic mineralisation in the Kopaonik region of Serbia and Kosovo, with particular reference to the Belo Brdo Pb-Zn (Ag) deposit (PhD thesis). Kingston University, London.
- 1120 Vgenopoulos, A.G., 1986. Bemerkungen zu mineralogisch-geochemischen und lagerstättenkundlichen Studien an Vererzungen der Gebiete Brskovo/Jugoslawien und Lakonia/Griechenland [Comments on the mineralogical-geochemical and ore deposit geological studies on mineralisations of the areas Brskovo/Jugoslavia and Lakonia/Greece; in German with English abstract], in: Petrascheck, W.E., Janković, S. (Eds.), *Geotectonic Evolution and Metallogeny of the Mediterranean Area and Western Asia*. Springer Vienna, Vienna, pp. 91–101. https://doi.org/10.1007/978-3-7091-5822-7_9
- Von Damm, K., 1990. Seafloor hydrothermal activity: black smoker chemistry and chimneys. *Annual Review of Earth and Planetary Sciences* 18, 173.
- 1130 Voudouris, P., Spry, P., Melfos, V., Haase, K., Klemd, R., Mavrogenatos, C., Repstock, A., Alfieris, D., 2018. Gold deposits in Greece: Hypogene ore mineralogy as a guide for exploration, in: *Proceedings of The 1st International Electronic Conference on Mineral Science*. Presented at the The 1st International Electronic Conference on Mineral Science, MDPI, Sciforum.net, p. 5452. <https://doi.org/10.3390/IECMS2018-05452>
- 1135 Vukmanović, M., Medović, P., 1990. Господари сребра: гвоздено доба на тлу Србије/Masters of silver: the Iron Age in Serbia. Narodni Muzej, Belgrade.
- Wagner, G.A., Pernicka, E., Vavelidis, M., Baranyi, I., Bassiakos, I., 1986. *Archäometallurgische Untersuchungen auf Chalkidiki* [Archaeometallurgical investigations at Chalkidiki; in German]. *Der Anschnitt* 38, 166–186.
- 1140 Wartenberg, U., 2015. Thraco-Macedonian Bullion Coinage in the Fifth Century B.C.: The Case of Ichnai, in: Amandry, M., Wartenberg, U., Demetriadi, B. (Eds.), *Kairos: Contributions to Numismatics in Honor of Basil Demetriadi*. The American Numismatic Society, New York, pp. 347–364.

- Westner, K.J., 2017. Roman mining and metal production near the antique city of ULPIANA
1145 (Kosovo) (PhD thesis). Johann Wolfgang Goethe-Universität, Frankfurt.
- Zartman, R.E., Doe, B.R., 1981. Plumbotectonics—the model. *Tectonophysics* 75, 135–162.
[https://doi.org/10.1016/0040-1951\(81\)90213-4](https://doi.org/10.1016/0040-1951(81)90213-4)
- Živanović, M., 2020. Нова сазнања о средњовјековном Брскову: New data on medieval
Brskovo. *Nova Antička Duklja* XI, 113–130.

1150

Figure captions

- 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)
1155 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. Tab. 1), which also are annotated on the map.
Mining fields located in districts not sampled for this study are shown as blank symbols.
- 1160 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) Kilkis (GR, NMK). Crnook-Osogovo-
1165 Lisets complex: 15) Blagodat (SRB), 16) Karamanica (SRB), 17) Osogovo (NMK, BLG).
Rhodopes: 18) Angistron (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).

1170 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)
Dobrevo, Zletovo: ancient gallery. f) Besna Kobila, Blagodot: ancient gallery (upper left)
1175 exposed by modern mine workings. g) Dobrevo, Zletovo: shaft. h) Vojetin, Bellobërdë/Belo
Brdo: mining depressions surrounded by extensive waste heaps. i) Brskovo: slag heap
transected by modern road construction.

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
1180 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: A) northeast Montenegro, B) Podrinje/Drina, C) Kopaonik, D) Lece, E)
Blagodot-Osogovo, F) Zletovo, G) Kroussia, H) central Rhodopes, I) eastern Rhodopes.
Model parameters were calculated according to Albarede and Juteau (1984). Additional ore
1185 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)
1190 and low-temperature isotopic fractionation (orange) are indicated (cf. Albarede et al., 2020).

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 and Serbomacedonian Massif included.
Note that points are jittered to increase readability. a) Lead model age (T_{mod}), b) μ
1195 ($^{238}\text{U}/^{204}\text{Pb}$), c) κ ($^{232}\text{Th}/^{238}\text{U}$).

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, Velojić 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 Blagodot 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 (gn). 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.

Table captions

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.

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

Supplementary material

S1: Detailed description of preparational and analytical protocols.

1225 S2: Ore mineralogy, compositional data, Pb isotope compositions, and $\delta^{34}\text{S}$ and $\epsilon^{109}\text{Ag}$
values of the investigated samples and Pb-Ag isotope reference data for the study area
(Milot et al., 2021c; Veselinović-Williams, 2011; Westner, 2017). Note that S contents were
not determined and that disseminated ores partially were difficult to separate from the
gangue, resulting in low metal contents and analytical totals. The column “ore mineralogy”
1230 refers to the phases visually observed in the hand samples.

S3: Geographic maps of the distribution of Pb and Ag isotope values in south-eastern
Europe. Symbols in d) are colored according to whether they are in the -1 to +1 $\epsilon^{109}\text{Ag}$ range
of most silver coins or whether they are exceeding or falling below these values. Reference
Pb isotope (MC-ICP-MS analyses only; Milot et al., 2021c; Vaxevanopoulos et al., 2022a;
1235 Veselinović-Williams, 2011; Westner, 2017) and Ag isotope (Milot et al., 2021c) data from the
investigated districts are added to the plots. a) $^{206}\text{Pb}/^{204}\text{Pb}$, b) $^{207}\text{Pb}/^{204}\text{Pb}$, c) $^{208}\text{Pb}/^{204}\text{Pb}$, d)
 $\epsilon^{109}\text{Ag}$.

Abbreviation	Name	Mining fields	T _{mod} (Ma)	μ	κ	Further characteristics
TM	Triassic mineralisations	<ul style="list-style-type: none"> • NE Montenegro, Šuplja Stijena/ Ljubišnja • Kilkis 	<ul style="list-style-type: none"> • 341-379 • 317-360 	<ul style="list-style-type: none"> • 9.80-9.88 • 9.75-9.81 	<ul style="list-style-type: none"> • 3.96-4.00 • 3.93-3.97 	Might be partially remobilised 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

Country	No. on map	Mining field	Mineralisation(s)	Other commodities	Mineralisation style	Mineralisation 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)	Štrucl (1981), Vgenopoulos (1986)
MNE/BiH	2	Šuplja Stijena/Ljubišnja	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; Rucker, 1901)	Radosavljević et al. (2011, 2016)
Kopaonik (C)										
SRB	6	Raška	Kiževak, Sastavči	Pb, Zn, Au	Veins, epithermal (IS)	Oligocene	Andesite-dacite,	-	From antiquity on	Monthel et al. (2002),

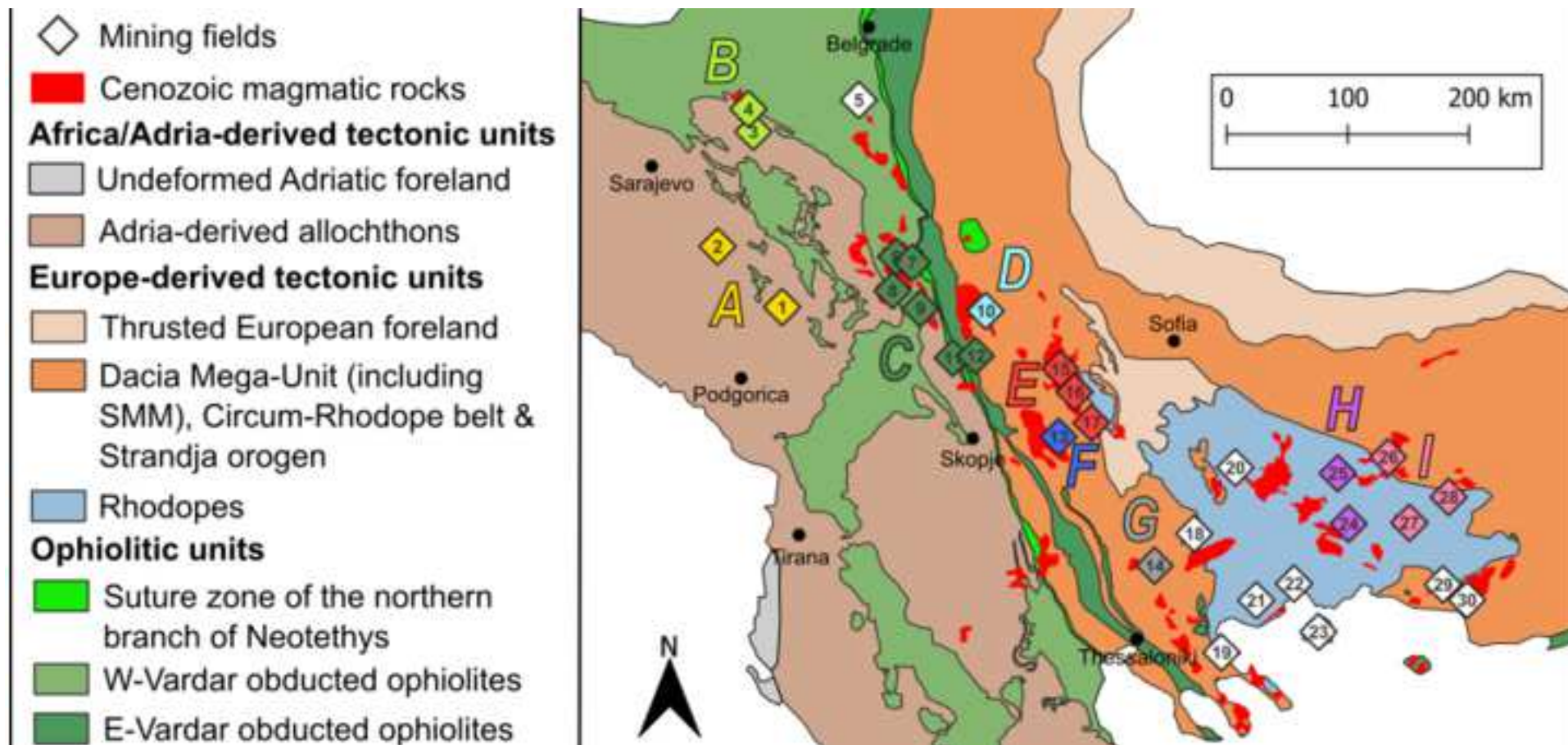
							quartz latite, diorite, pyroclastic rocks		(Marić, 2019)	https://www.adriaticmetals.com/our-projects/srbian-projects/sastavci-prospect/ https://www.adriaticmetals.com/content/?contentID=3163 (last checked 5.4.2023)
SRB/ KS	7	Belloberdë / Belo Brdo	Zaplanina, Vojetin, Belloberdë/Belo Brdo	Pb, Zn, Au	Carbonate replacement, veins	Oligocene	Andesite, serpentinite/listvenite, limestone, flysch	-	Medieval (14 th century), Ottoman (Davies, 1938; 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, 1938; Gassmann et al., 2022; Kovacevic, 1960)	Kołodziejczyk et al. (2016), Schumacher (1950), Strmić Palinkaš et al. (2013)
KS	11	Hajvali-	Kishnicë/Kišnica,	Pb, Zn, Au	Veins	Oligocene	Andesite-	-	Prehistoric,	Janković

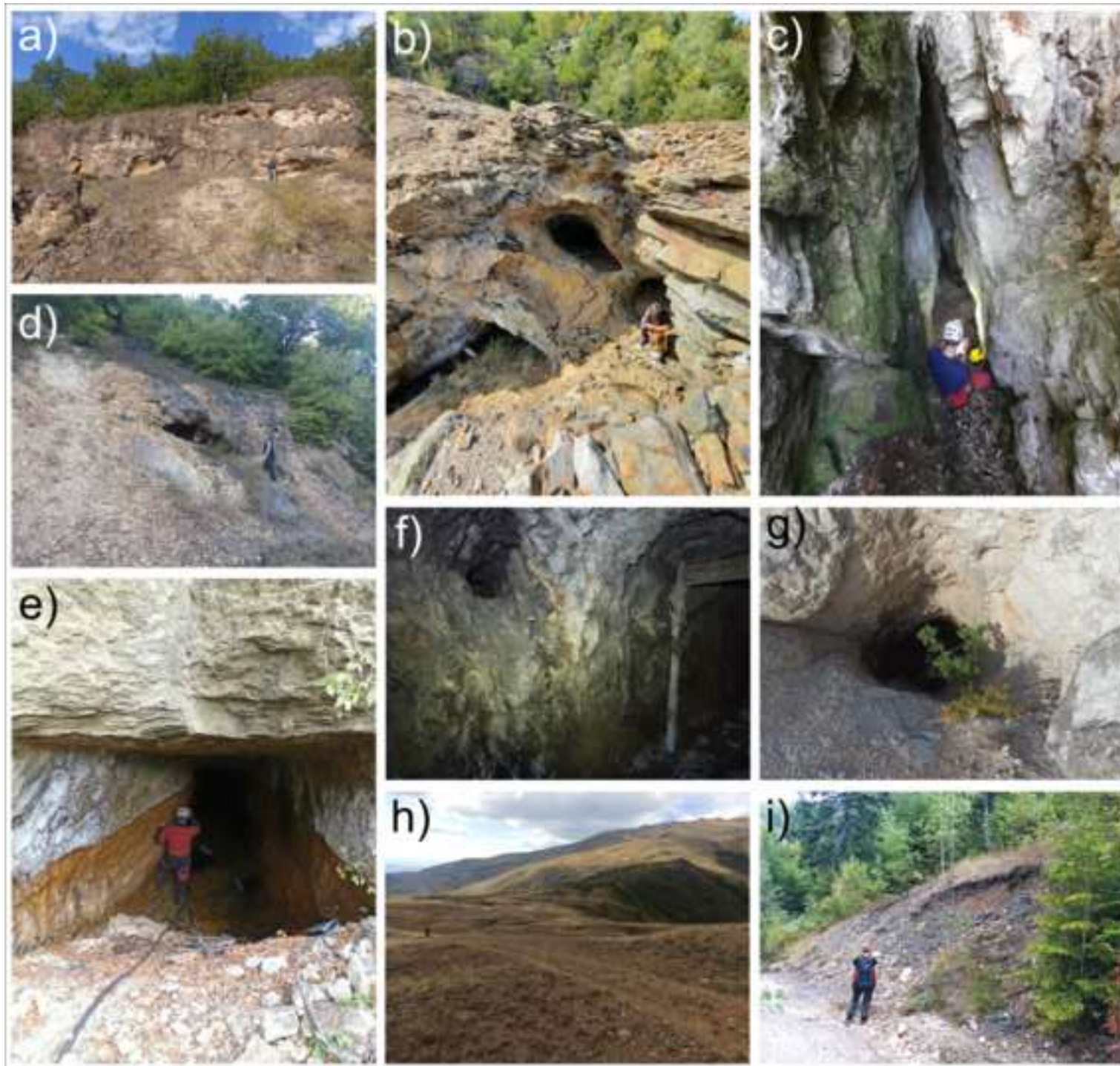
		Badovc-Kishnicë/Ajvalija-Badovac-Kišnica	Janjevë/Janjevo				dacite, serpentinite/listvenite, flysch		Roman-late antique, medieval (1303), Ottoman (Davies, 1938, 1935, p. 223; Gassmann et al., 2022; Kovacevic, 1960; Savić, 1954)	(1982), Mederski et al. (2021)
KS	12	Novobërdë/Novo Brdo	Novobërdë/Novo Brdo	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, 1938, 1935, p. 223; Gassmann et al., 2022; Savić, 1954)	Jankovič (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; Pamic and Balen, 2001; Serafimovski et al., 1997) MA (Tulare): 32.8-33.0 Ma (U/Pb; Márton et al., 2013)	Prehistoric, Roman-late antique, medieval, Ottoman (Amedoski and Petrović, 2019; Bugarski et al., 2019, 2018)	Márton et al. (2013), Stajević (2003), Velojić et al. (2018)

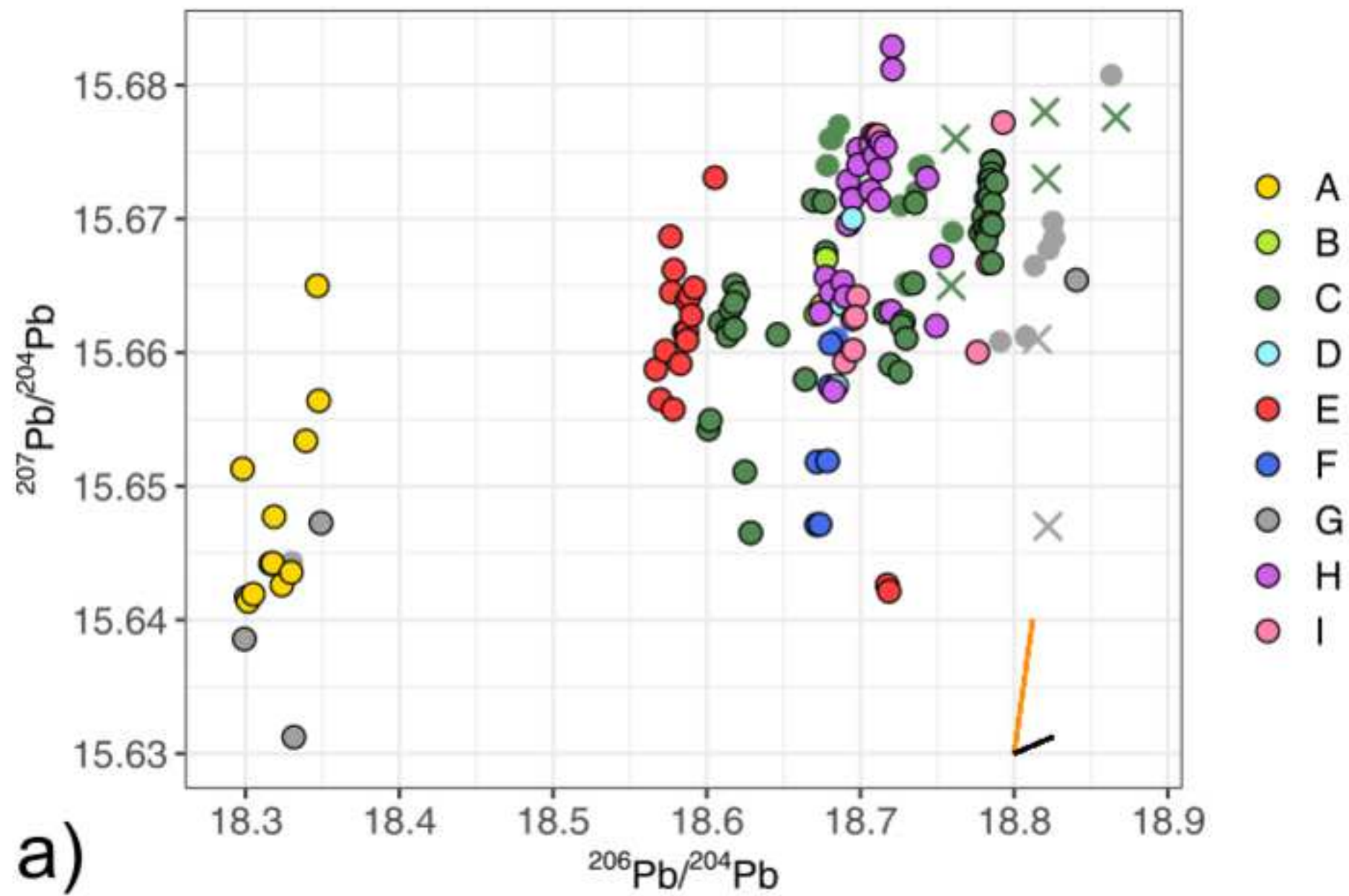
Blagodat-Osogovo (E)										
SRB	15	Blagodat	Grot, Besna Kobilica	Pb, Zn (Cu)	Metamorphosed VMS (primary), carbonate replacement, veins	Oligocene	Dacite, quartz latite, limestone, marble, schist	29.5 Ma (K/Ar; Čebić, 1990)	Presumably Roman (Davies, 1938)	Janković et al. (1995), Jelenković (1995)
SRB	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, 1938, 1935, p. 228; Dimče, 1996)	Janković et al. (1995), Palinkaš 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, 1938, 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,	-	-	Šoster (2020)

							phyllite, schist			
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 (Petrušsenko, 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)

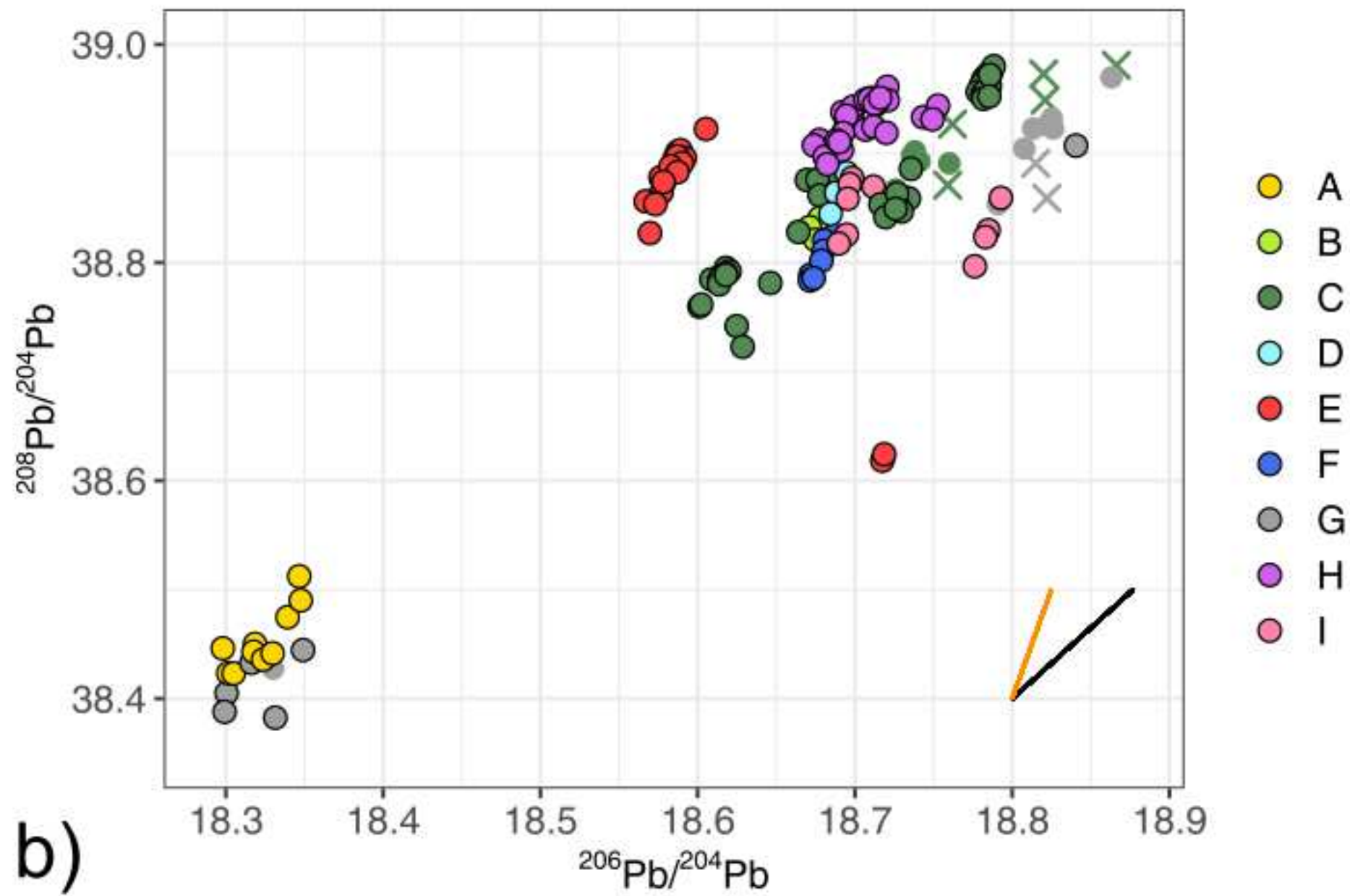
eastern Rhodopes (I)										
BLG	26	Spahievo	Chala	Pb, Zn, Cu (Au)	Epithermal (IS)	Oligocene	Volcanites , plutonites	31.8-32.9 Ma; MA: 32.1 Ma (Ar/Ar; Singer and Marchev, 2000)	-	Amov et al. (1993), Marchev et al. (2005)
BLG	27	Zvezdel-Pcheloyad	Zvezdel	Pb, Zn, Cu (Au)	Epithermal (IS)	Oligocene	Gneiss, 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)

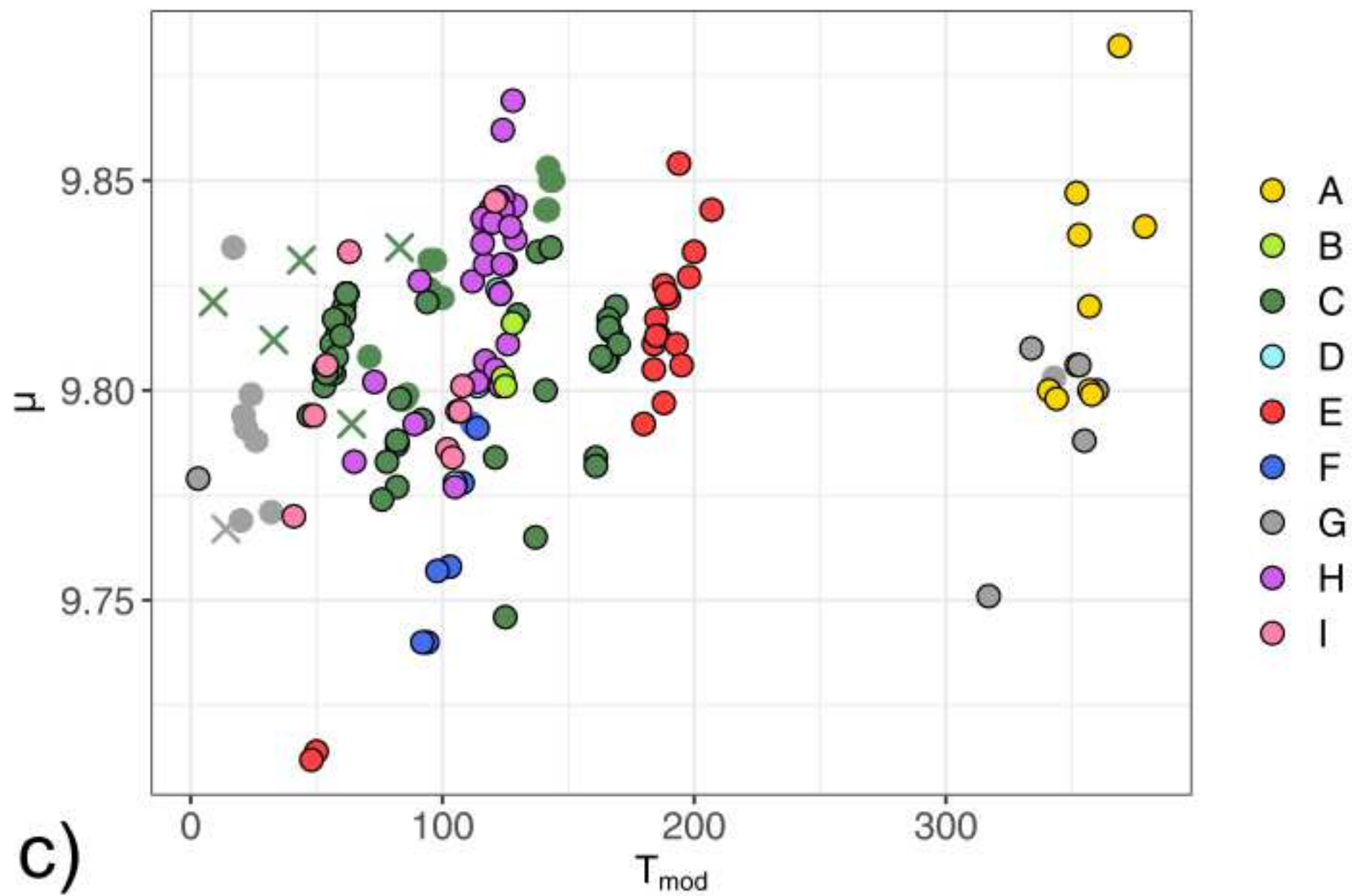


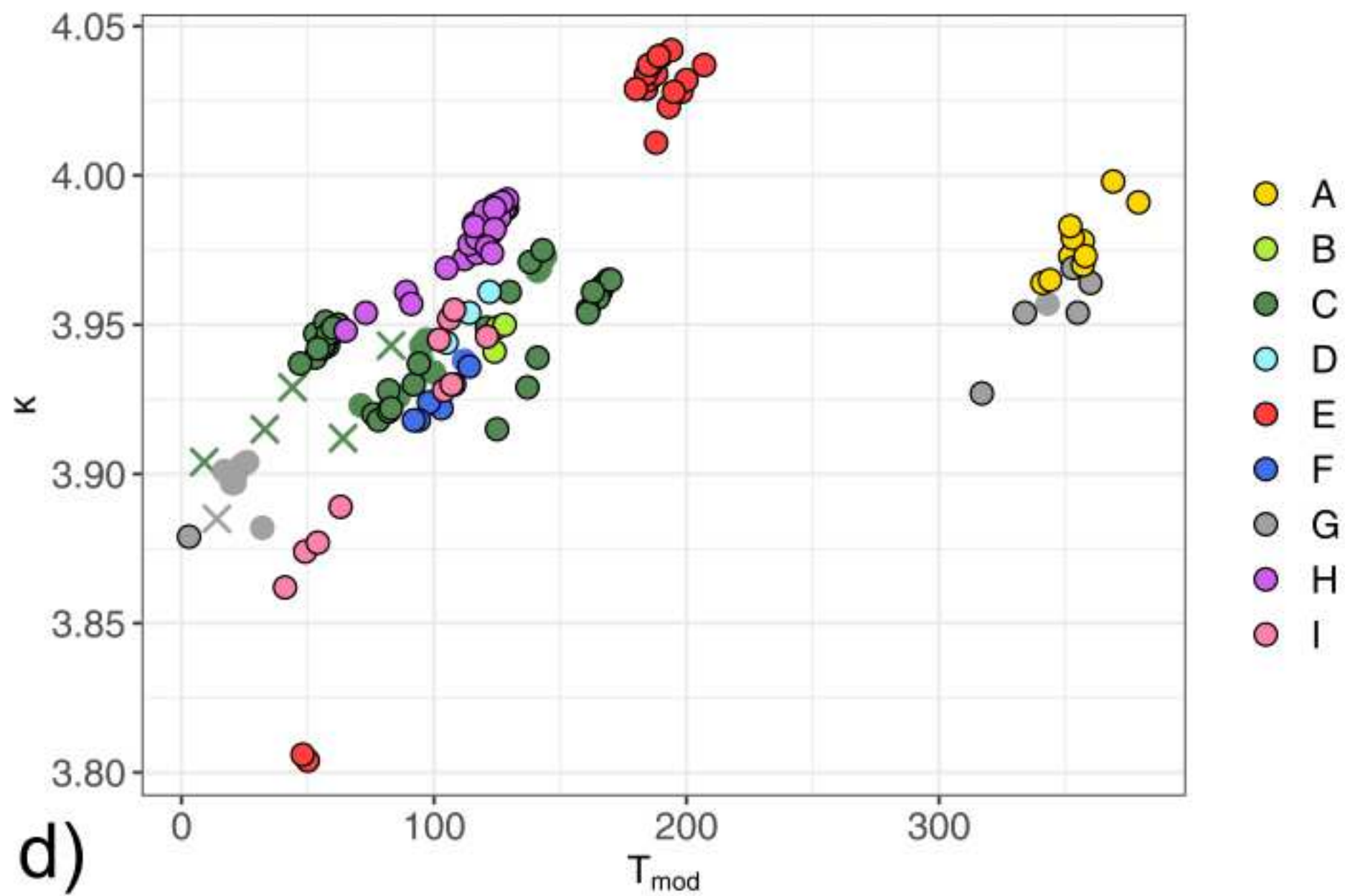


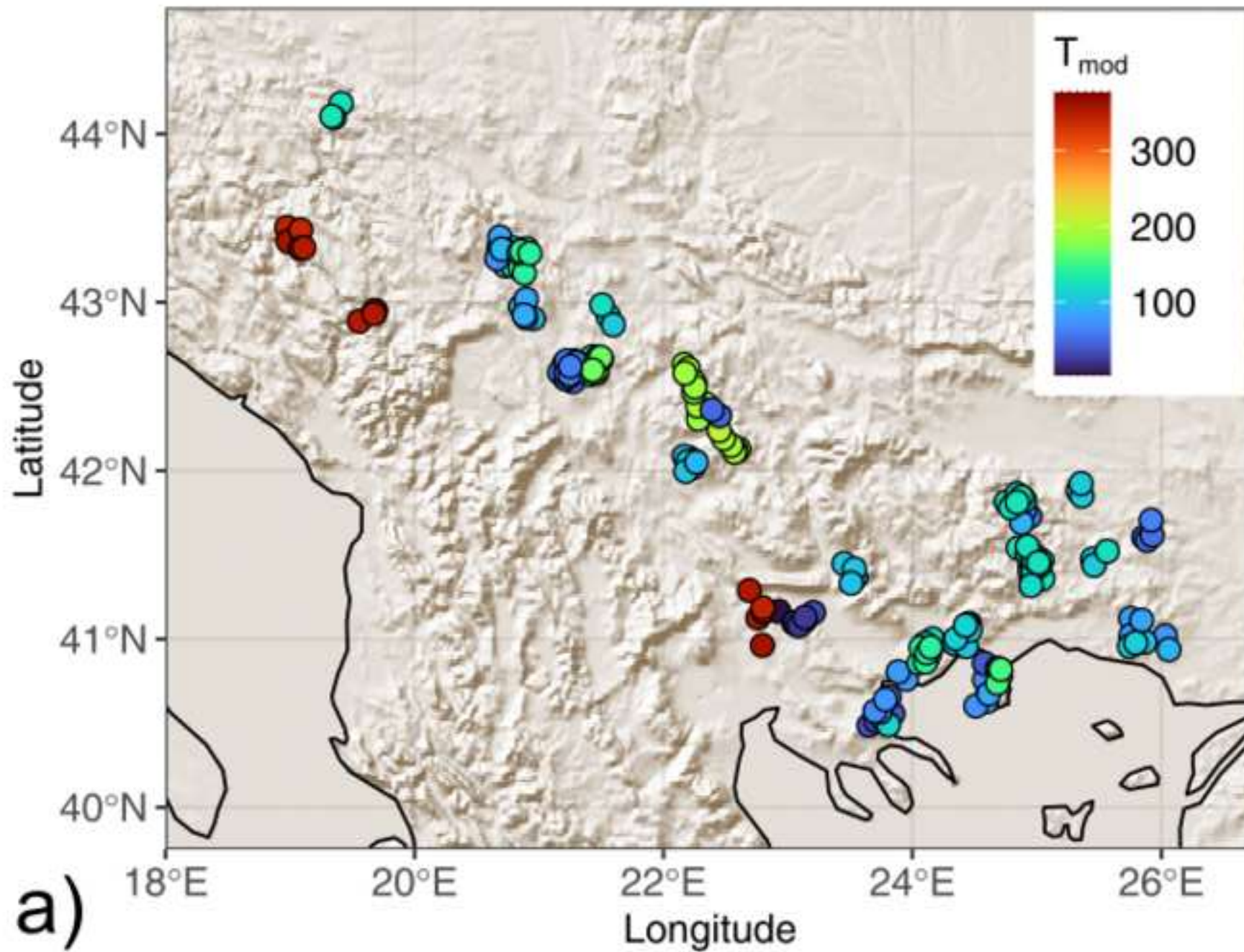


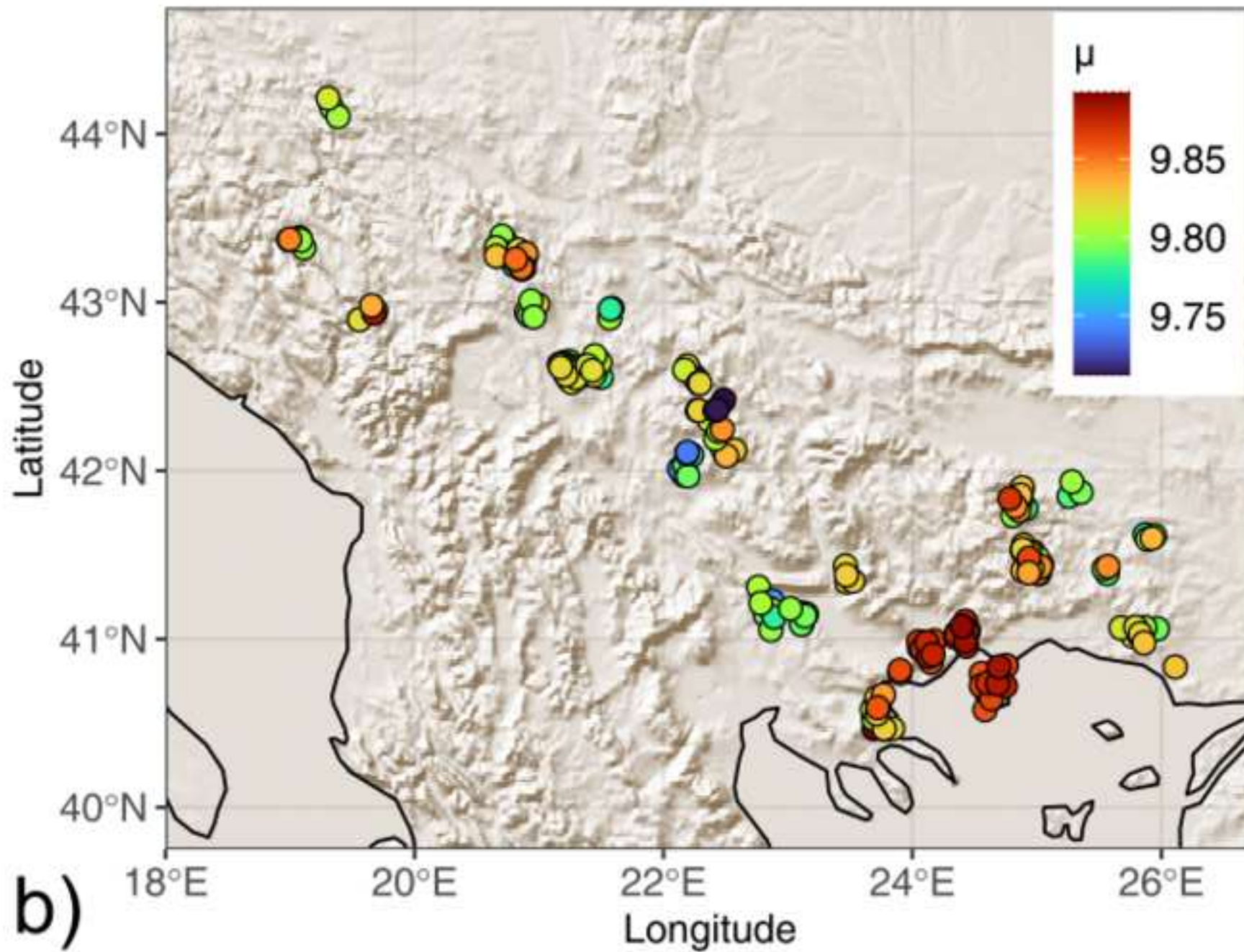
a)











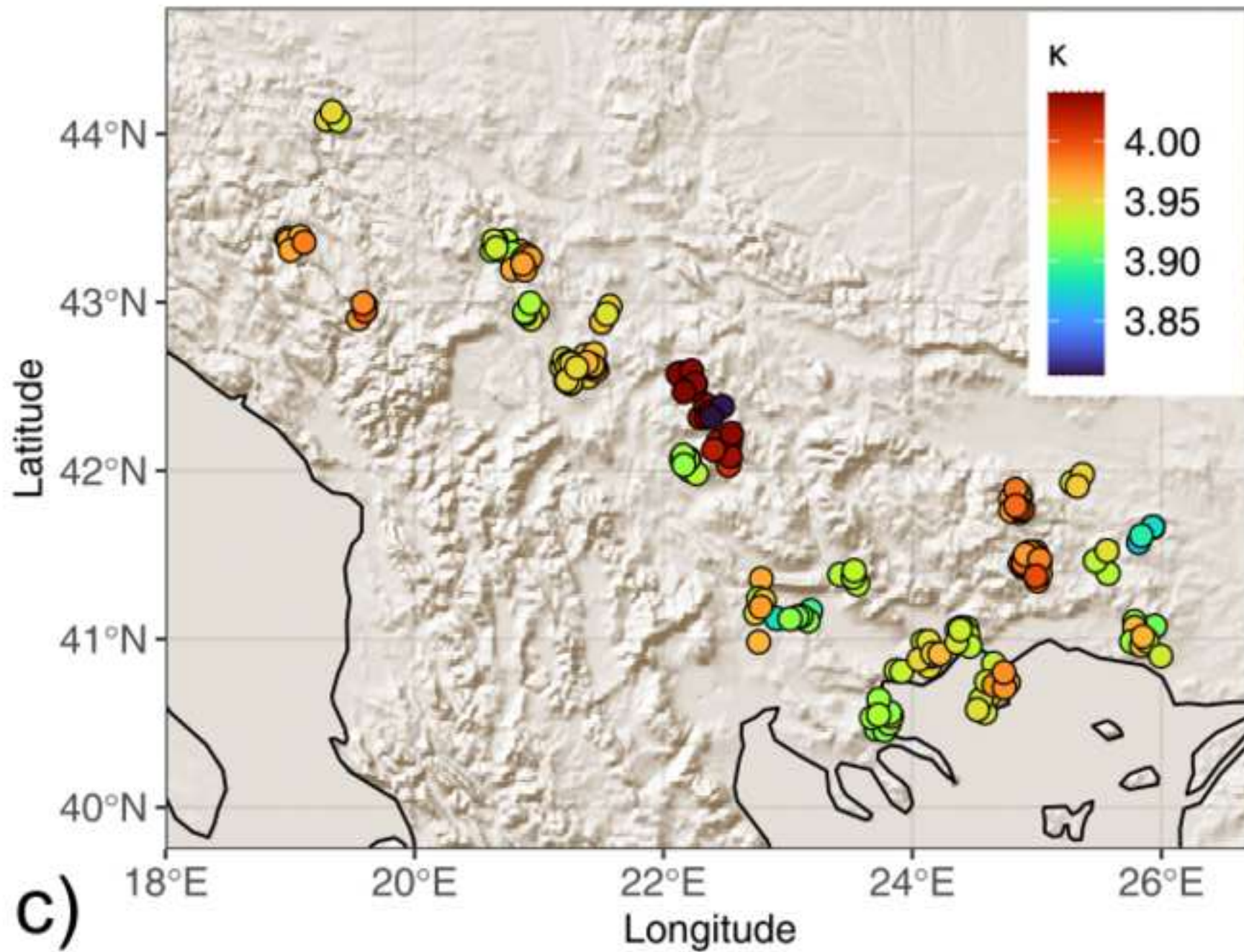
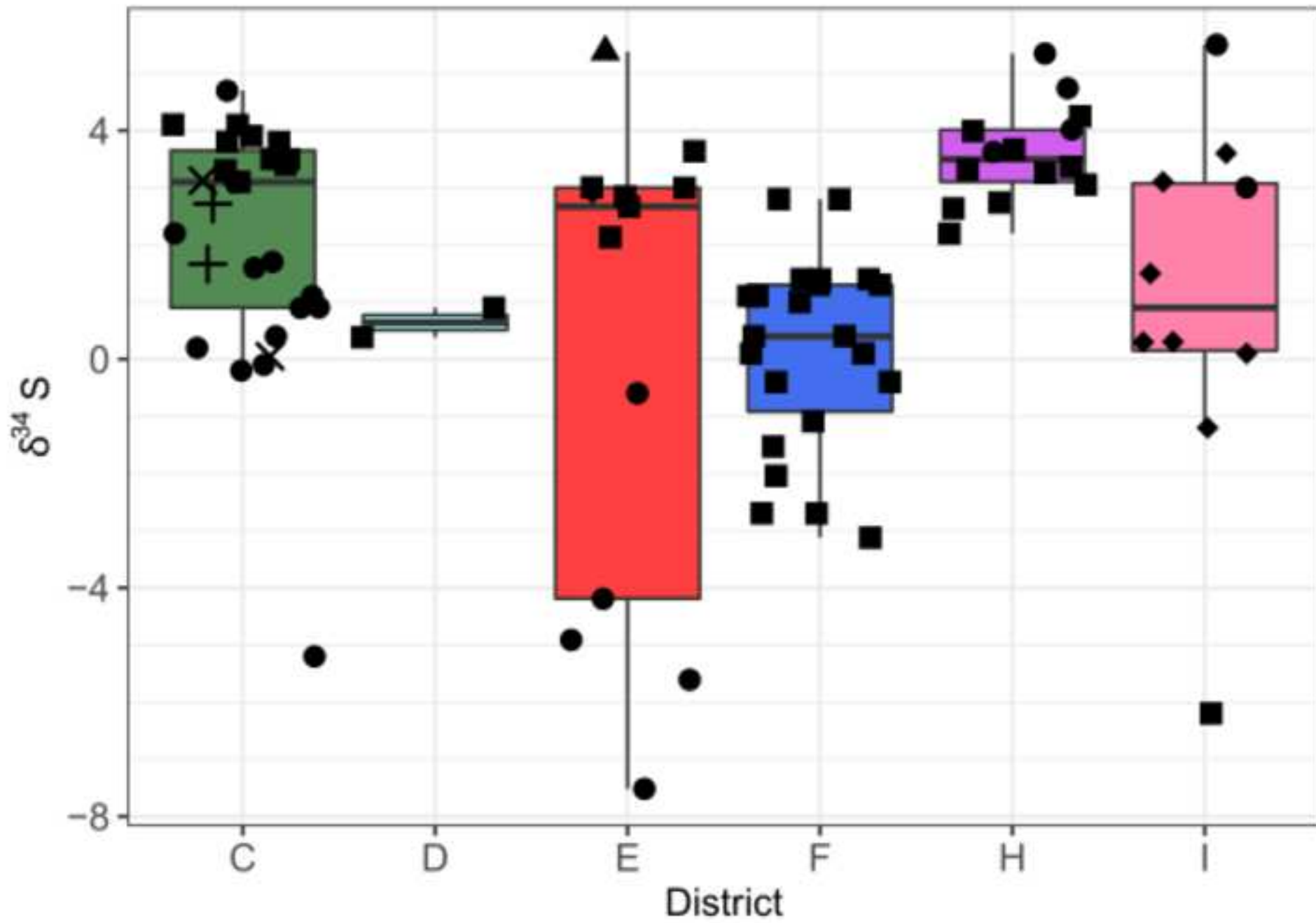
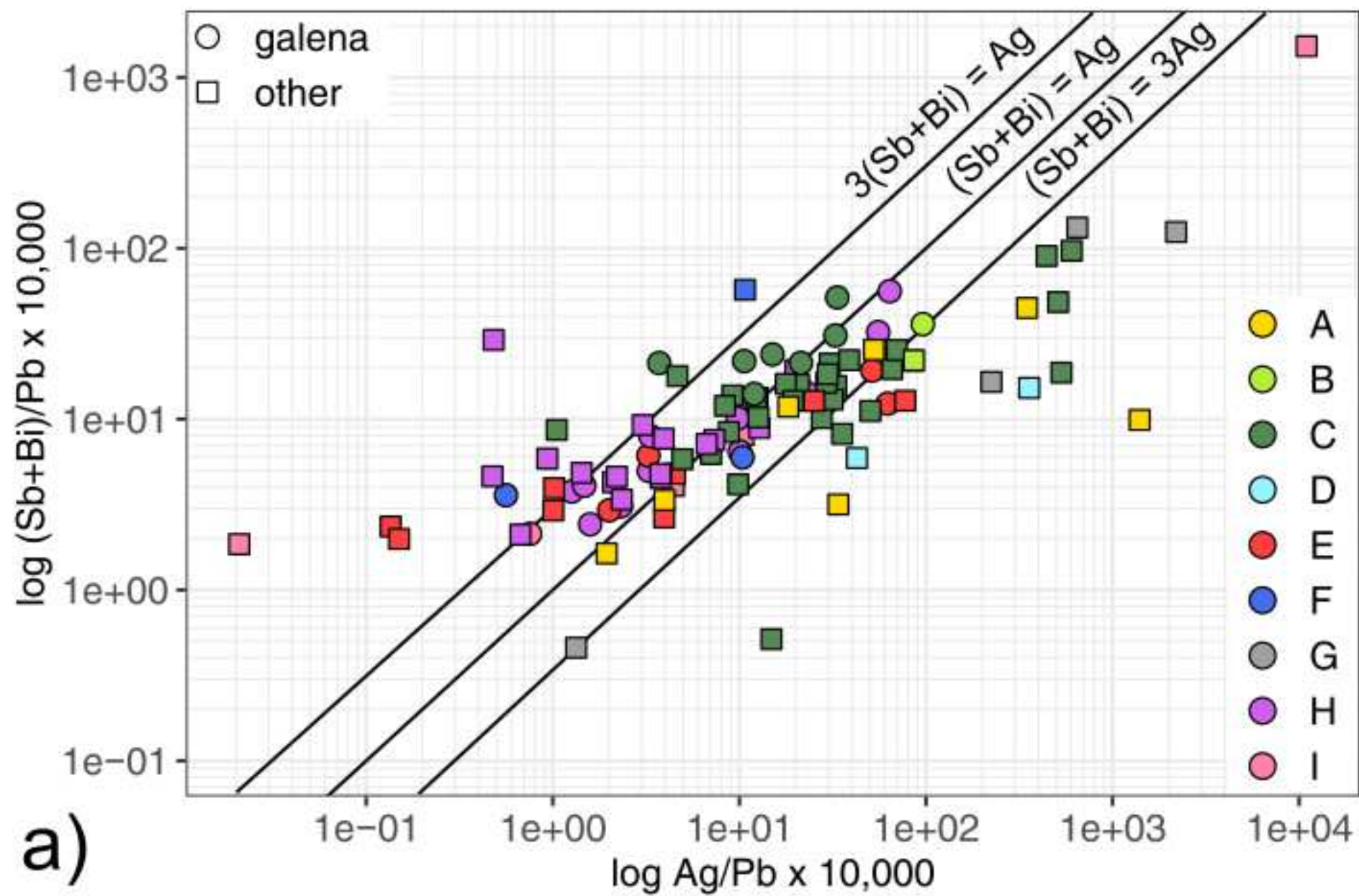
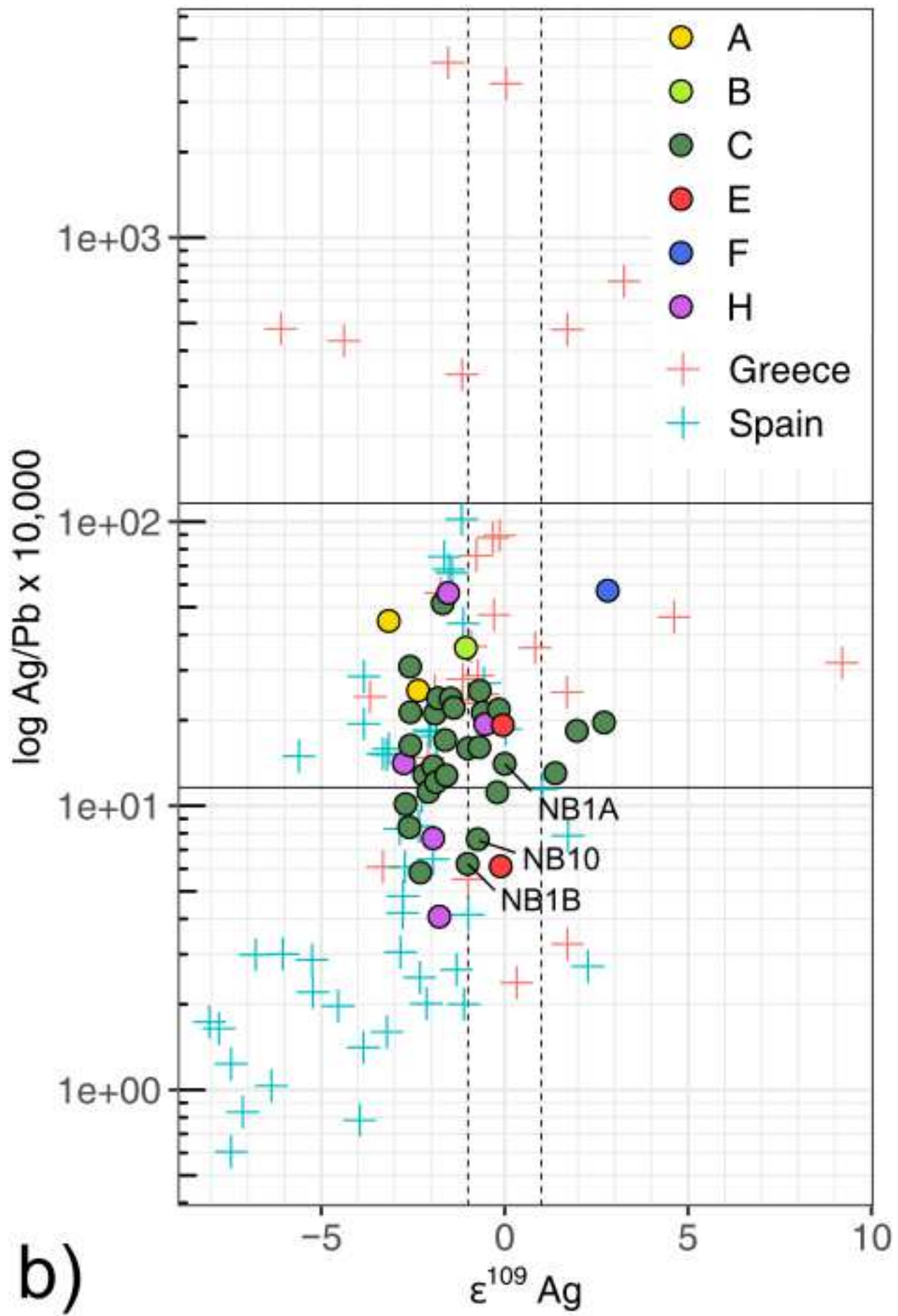


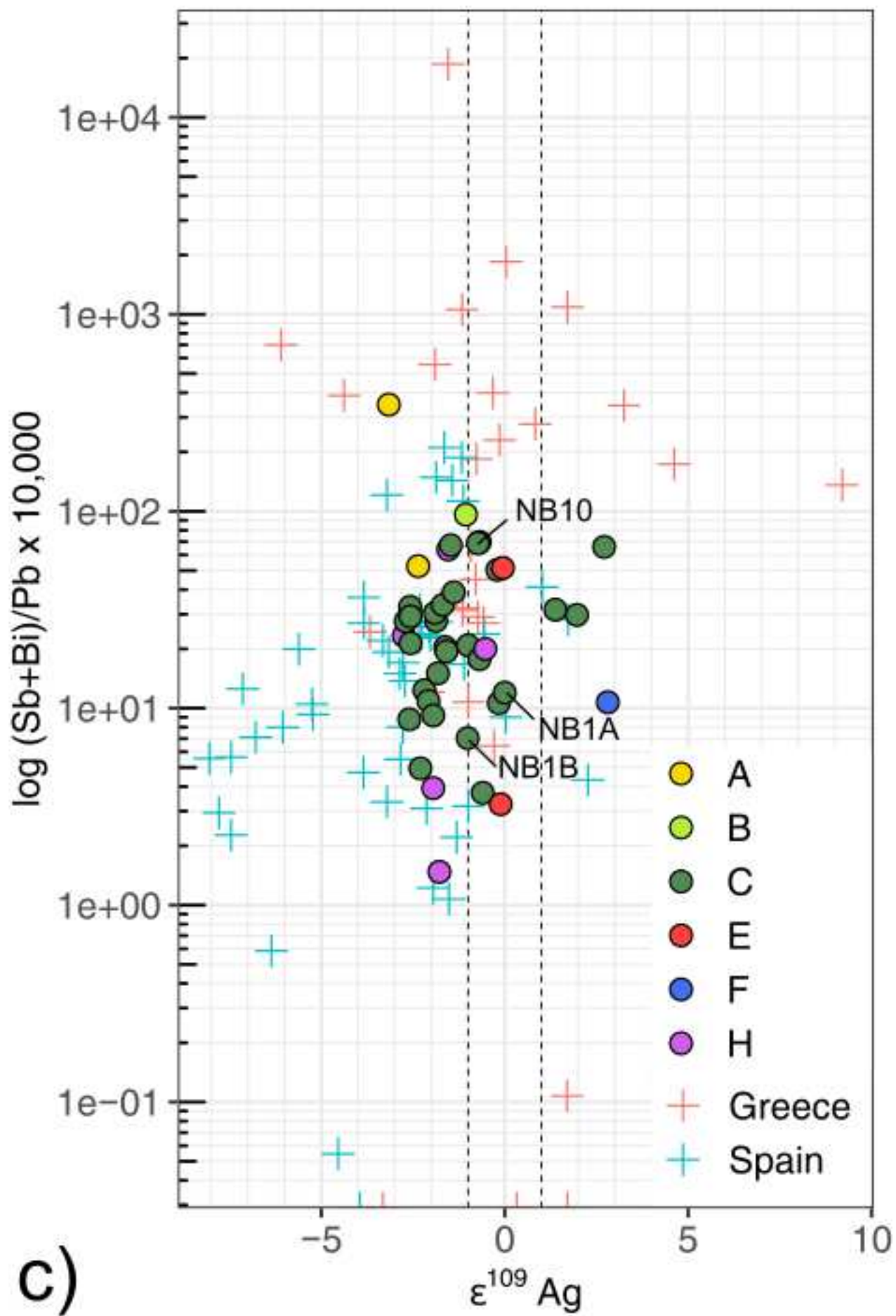
Figure 5







b)



c)